

THE CHEMISTRY OF METALORGANIC CHEMICAL VAPOR DEPOSITION
FROM A COPPER ALKOXIDE PRECURSOR

by

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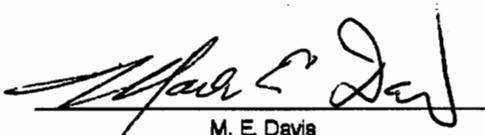
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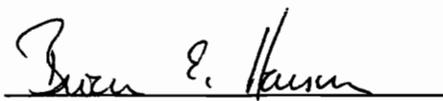
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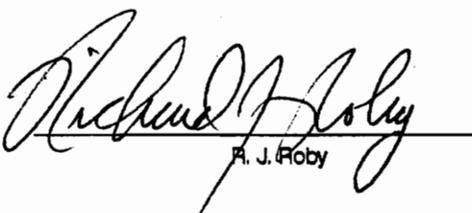
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(ABSTRACT)

The chemistry of chemical vapor deposition from copper (II) dimethylaminoethoxide onto single crystal strontium titanate has been studied by *in situ* infrared analysis of the vapor phase in the reactor, and by simultaneous mass spectrometer analysis of the reactor outlet gas. Species condensed from the reactor outlet gas in a liquid nitrogen trap were analyzed by proton nuclear magnetic resonance. Chemical information was also obtained by Auger electron and X-ray photoelectron spectrometer analysis of the deposited films. Deposition chemistry was studied with respect to deposition temperature, presence of ultraviolet light, and presence of a reactive gas cofeed. The goal was to determine the reaction pathway and relate it to deposited film composition.

In a reduced pressure helium atmosphere, copper dimethylaminoethoxide deposits clean, conductive films of copper metal at 200°C. The ligands are eliminated by two interdependent reactions: β -hydride elimination produces dimethylaminoethanal, while

reductive elimination produces dimethylaminoethanol. The minimum deposition temperature is 150°C. At substrate temperatures near 250°C some ligand fragmentation occurs, in addition to the clean elimination pathway, leading to carbon contamination of the deposited films.

The deposition chemistry of copper dimethylaminoethoxide is not affected by irradiation with ultraviolet light of wavelengths between 360 nm and 600 nm. The ultraviolet light source was a Spectronics B-100 UV lamp. A light source with higher power might affect deposition chemistry.

At a substrate temperature of 200°C in the presence of oxygen, dimethylaminoethanol and dimethylaminoethanal are not detected as products. Decomposition involves extensive ligand fragmentation, producing small amines and carbonyl species, carbon monoxide, and carbon dioxide. Films are free of carbon and nitrogen, because the ligand fragments are volatile and stable. Films are a mixture of copper metal and copper (I) oxide. Optimization of oxygen concentration in the reactor could lead to deposition of a pure copper oxide.

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1. Introduction

1.1 The Value of Copper

Copper has important applications in the electronics industry. The ability to grow pure thin films of copper and copper oxides is of technological value. Methods of growing thin films of many metals and semiconductors are well-established. However, copper presents problems which so far have not been solved by the empirical approaches used for other materials. Research into the chemistry of copper film deposition may help overcome these problems and improve film growth methods for other materials.

Copper metal would be an excellent material for device interconnects on chips. It has a high conductivity and does not exhibit the electromigration problems of aluminum, the material most widely used now. When an aluminum interconnect carries high current density, the aluminum atoms tend to migrate across the surface of the chip. These wayward atoms can cause circuits to break or short. Electromigration will become a severe problem as device sizes shrink and conducting lines must be drawn ever narrower and closer to one another [1]. Apart from copper, the most obvious choices for interconnects are gold and silver, which are highly conductive. Copper has the advantage of being far less expensive than either gold or silver. There is some interest in tungsten, but it has a higher resistivity than copper [2].

Copper (I) and copper (II) oxide are the basis for the current generation of high temperature superconductors. Indeed, it is thought that the sheets of copper (II) ions are responsible for superconductivity in these materials [3]. Copper (I) oxide was used in early solar cells [4].

All of these applications require thin films and control of oxidation state. An ideal film growth system would produce each oxidation state in its pure form on demand. For instance, a change in processing conditions might produce copper metal or copper (II) oxide. In order to be useful, the system must reliably produce pure films of one of the oxidation states. Post-deposition oxidation or reduction could be used to achieve the desired oxidation state.

1.2 Metalorganic Chemical Vapor Deposition for Copper Film Growth

Difficulties in growth and patterning of pure thin films have hindered widespread use of copper in electronics. Thin films of metals and semiconductors are often grown by chemical vapor deposition, CVD [5]. In CVD, a metal-containing molecule (precursor) is transported in the gas phase to the surface to be coated (substrate), then decomposed. When the precursor is a metalorganic, the process is termed metalorganic chemical vapor deposition, or MOCVD. Simple compounds such as silane, SiH_4 [6], tungsten hexacarbonyl, $\text{W}(\text{CO})_6$ [7], and trimethylgallium, $\text{Ga}(\text{CH}_3)_3$ [5a], are volatile and decompose cleanly to leave a metal film.

Unfortunately, simple copper hydrides and carbonyls do not exist [8], and simple copper alkyls are nonvolatile [9]. In fact, few copper compounds exhibit the high volatility and low decomposition temperatures necessary to make MOCVD of copper commercially viable. High temperatures are not compatible with doped semiconductor devices. Dopant diffusion occurs at elevated temperatures. Also, copper is notorious for diffusing into silicon. This diffusion can be significant at 250–300°C [1], so low-temperature deposition is essential for silicon-based applications. Some of the volatile copper metalorganics have ligands that can fragment and contaminate films; these reactions cannot be tolerated.

One solution to the copper film growth problem is to choose another technique, such as sputtering from a pure copper target. However, chemical vapor deposition is already in widespread use in the electronics industry, so copper MOCVD can be integrated with other processing steps. CVD produces conformal films, so steps can be covered and vias filled. In contrast, an uneven surface casts shadows that will not be coated with a line-of-sight technique such as sputtering. With the proper choices of metalorganic precursor, temperature, and atmosphere, CVD produces pure films. The challenge lies in finding the precursor and selecting the processing conditions.

This study was undertaken to study the decomposition chemistry of a precursor for copper MOCVD and the effect of chemistry on film quality. Few studies of copper deposition chemistry have been published, and even fewer involve *in situ* chemical analysis. The emphasis in this work is on obtaining and interpreting chemical information during

deposition. Studies of the deposition chemistry may lead to the design of better precursors and to faster optimization of deposition conditions.

1.2.1 Thermal Metalorganic Chemical Vapor Deposition

Thin films are grown over large areas by thermal MOCVD, in which heat decomposes the precursor. The simplest case is the hot wall reactor, in which the entire deposition reactor is heated above the decomposition temperature of the precursor. The film is deposited on all interior surfaces of the reactor, including the substrate. One refinement is the warm wall reactor, in which the reactor walls are kept only warm enough to prevent condensation of the precursor. The substrate alone is heated above the decomposition temperature of the precursor, and deposition takes place only on or near the substrate.

Variations in deposition temperature can affect film purity. Ideally, for metal deposition, all metal–ligand bonds should be broken, and the whole ligands should leave the reactor in the gas phase. At low temperatures, whole ligands may be left bonded to metal atoms and incorporated into the film. At high temperatures, the ligands may decompose and leave fragments in the film. Temperature control is thus of concern in all MOCVD systems. The precursor must be transported to the deposition region without premature decomposition or condensation in a cold spot. The correct temperature must be maintained in the deposition zone to grow pure films without damage to the substrate. The temperature of outlet lines must also be maintained to prevent them becoming fouled by condensing decomposition products.

1.2.2 Photoassisted Metalorganic Chemical Vapor Deposition

Patterning is usually accomplished by laying down a complete film, then removing the unwanted portions. However, copper is resistant to fluorine etching, a common patterning method. An elegant solution to this problem is to lay down only the desired portions of the film. Several groups are approaching this by searching for precursors and conditions that give selective deposition [10]. If deposition occurs selectively on one type of material and not on another (*ie.* metal *vs.* oxide), a seed pattern could be drawn, then a

patterned film grown on that by CVD. Another possibility is direct-writing of the pattern by photoassisted CVD. The energy required to decompose the precursor is supplied by light and focused only on the desired regions. With photoassisted CVD, a pattern of light produces a pattern of metal [5b].

The term "photoassisted" is used because there are two types of light-induced decomposition processes, pyrolytic and photolytic [5b]. In pyrolytic CVD, the surface upon which the film grows absorbs light and becomes hot. Where it is hot enough, the precursor decomposes, just as in large area thermal deposition. Pyrolytic CVD is usually associated with lasers, which can produce a high intensity of light in a small area. In photolytic CVD, light is absorbed by the precursor itself, rather than by the substrate. Ultraviolet (UV) light of the correct frequency will be absorbed by electronic transitions within the molecule. Some of these transitions involve breaking bonds. The term "photoassisted" accounts for thermal and photolytic processes in the presence of light. It also describes experiments in which light alone or heat alone is insufficient to cause deposition, but a film grows when light shines on a substrate at elevated temperature. Photolytic CVD can be performed with a lower intensity source, such as a lamp.

In theory, the light frequency can be tuned to a particular bond energy, and bonds can be selectively broken [5b]. In practice, absorbed energy is usually redistributed in the molecule quickly, and the bond broken may not be the one expected from $E=h\nu$ and bond energy calculations [11]. Still, light can activate decomposition pathways that are normally seen at higher temperatures. Light can selectively activate one or two decomposition pathways among several. This is because the laser or lamp provides a narrow range of energies, rather than the Maxwell-Boltzmann distribution of heat energy [12].

Copper (II) β -diketonates [13-16] and copper (I) cyclopentadienyl triethylphosphine [17] are the only copper precursors for which photolytic CVD has been demonstrated. Although laser deposition of copper from copper cyclopentadienyl triethylphosphine was shown to have both pyrolytic and photolytic components, the effects were not separated. Photolytic effects were thought to be significant under a 248 nm excimer laser. However, the deposited films are heavily contaminated with carbon. The cyclopentadienyl ligand absorbs strongly at 248 nm. The laser may break up the ligand, and fragments may be incorporated

in the film [17]. This demonstrates the importance of exciting the metal-ligand bond electrons without causing ligand decomposition. The UV absorption spectrum and the electronic transitions which give rise to it are vital considerations in choosing a precursor for photoassisted deposition.

Jones *et al.* [13] showed that copper films deposit from copper (II) hexafluoroacetylacetonate in the presence of ethanol under a low pressure mercury lamp. The lamp emits wavelengths of light which excite charge transfer transitions between the acetylacetonate ligand and the metal center [18]. The films contained about 10 per cent carbon. In the absence of ethanol, copper deposited only under a higher power density UV laser, and the films contained up to 90 per cent carbon. The authors speculated that the mechanism for vapor phase deposition in the presence of ethanol was the same as that in ethanol solution [18]. The β -diketonate ligand abstracts a hydrogen from the ethanol to form the stable β -diketone. The alcohol is oxidized to acetaldehyde in the process. This data indicates that photodeposition may be successful only if there is a stable decomposition product to be formed from the ligand. A reactive gas cofeed may be required.

1.2.3 Reactive Cofeed Metalorganic Chemical Vapor Deposition

Adding other reactive species to the gas phase with the precursor can also change the nature of the deposited film. By cofeeding nitrous oxide, Tsurouka *et al.* deposited superconducting yttrium barium copper oxide at 650°C from β -diketonate precursors [19]. Usually, films must be oxidized for several hours at 800–900°C to achieve superconductivity. Hydrogen and oxygen are other common gases that are cofed to achieve a specific oxidation state or reduce carbon contamination in films. Hydrogen, for example, is cofed with precursors such as trimethylaluminum and trimethylgallium. The methyl radicals formed during decomposition react with hydrogen to form methane. Methane, being stable and volatile, is not included in the growing film [5b].

1.3 Precursors for Copper Metalorganic Chemical Vapor Deposition

Several factors determine the suitability of a metalorganic as a precursor for MOCVD. Its behavior as a function of temperature is most important. The precursor must be volatile below its decomposition temperature. High volatility at low temperatures is ideal. The entire deposition system must be warm enough to avoid condensation in cold spots, and it becomes more difficult to keep a system isothermal with increasing temperature. Another concern is the temperature difference between volatility and decomposition. With a large temperature difference it is easier to avoid premature decomposition in the system.

For thermal or pyrolytic deposition, the decomposition temperature itself is a consideration. A high decomposition temperature means it is easy to transport the complex without decomposing it prematurely. However, if the substrate must be quite hot, damage to the substrate and diffusion of the film into the substrate may become a problem.

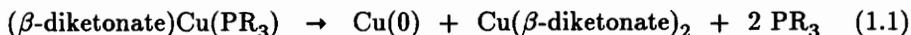
For photolytic deposition, the UV absorption spectrum of the complex is important. The UV absorption spectrum reveals which frequencies of light excite electronic transitions in the CVD precursor molecule. Only frequencies that excite electronic transitions can cause photolytic decomposition, so the light source must emit radiation that will be absorbed by the precursor. However, not all of the absorbed frequencies will cause decomposition. Usually electrons will be excited and return to the ground state without bond scission.

The decomposition products of the precursor are important. Non-volatile products can be incorporated in the growing film as contamination. Coordinatively unsaturated products may bond to the surface and contaminate the growing film.

Because there are no volatile copper hydrides, carbonyls, or alkyls, attention has turned to more complicated copper species. Copper (II) β -diketonates are attractive because they are commercially available, thermally stable, insensitive to water and air. They are the popular choice for attempts to grow yttrium barium copper oxide superconductors. Copper β -diketonates deposit copper metal [20], but require a hydrogen cofeed [21] and substrate temperatures above 250°C [22]. Other reported precursors for copper metal are copper (I) alkoxides [23], copper (I) β -diketonate trialkylphosphines [10b], copper (I) cyclopentadienyl

trialkylphosphines [10a], copper (I) alkoxy trialkylphosphines [10a], copper (I) alkyne β -diketonates [24], fluorinated copper (II) β -ketoimines [25], and copper (I) β -diketonate cycloalkenes [26].

The copper (I) β -diketonate trialkylphosphines deposit copper metal between 100°C and 400°C, with films deposited at 250°C having resistivities near that of bulk copper [10b]. Volatile reaction products include the copper (II) β -diketonate, the β -diketone, and apparent thermal decomposition products of the β -diketonate ligand. Trialkylphosphines are stable to 600°C. A disproportionation mechanism has been proposed for thermal deposition from these compounds:



The decomposition products of fluorinated copper (II) β -ketoimines were also investigated [25]. Deposition with hydrogen cofeed at 270°C to 350°C results in growth of clean metal films and release of the hydrogenated ligand. In the absence of hydrogen, deposited films are highly contaminated with ligand fragments, indicating that there is no pathway available to remove ligands cleanly in the absence of a reactive cofeed.

Volatile products of deposition from cyclopentadienyl copper trimethylphosphine are trimethylphosphine, a small amount of $\text{O}=\text{P}(\text{CH}_3)_3$, some cyclopentadiene, and fulvalenes derived from the cyclopentadienyl ligand [10a]. It is unknown whether the fulvalenes form during deposition or are a product of a later reaction of cyclopentadienyl radicals. These depositions were performed at temperatures in the range of 260°C to 450°C.

The decomposition pathways of copper (I) β -diketonate cycloalkenes were not determined [26]. The authors' observations of condensate on the reactor walls indicate no disproportionation in the presence of hydrogen. If disproportionation were a significant reaction, the blue-green copper (II) β -diketonate would condense on the reactor walls. Copper deposited from copper acetylacetonate cyclooctadiene with a hydrogen cofeed at 200°C.

Little research has been done on MOCVD using copper alkoxides. Few alkoxides are volatile, few are commercially available, and all are extremely water sensitive. Photodecomposition of alkoxides has not been demonstrated. However, alkoxides do have some attractive characteristics. Volatile copper alkoxides decompose at fairly low temper-

atures, desirable for temperature-sensitive substrates. They contain copper bonded to oxygen, and it may be possible to break either the copper–oxygen or oxygen–carbon bond to produce a desired oxidation state. The possibility of deliberately modifying deposition conditions to change the stoichiometry of the deposited film is intriguing.

Volatile products from thermal deposition of copper from copper (I) t-butoxy trimethylphosphine are t-butanol, trimethylphosphine, acetone, isobutene, and trace amounts of $\text{O}=\text{P}(\text{CH}_3)_3$ [10a]. These indicate formation of t-butyl and t-butoxy radicals. The deposited films (deposition at 400°C) contain 10 atomic per cent carbon, oxygen, and phosphorus.

Deposition from copper (I) t-butoxide, $[\text{CuOC}(\text{CH}_3)_3]_4$, was tested by Jeffries and Girolami at 10^{-5} to 10^{-8} Torr and 400°C [23]. Even at these low pressures, copper t-butoxide sublimes very slowly at 100°C. In personal discussion, one author revealed that several days were required to grow the reported 1.5 μm thick films of copper [27]. The exit gas was analyzed by mass spectrometry. The only vapor-phase product was t-butanol. Deposits were copper metal. The authors suggest that the copper–oxygen bond cleaves to yield a t-butoxy radical, which then abstracts hydrogen from hydroxyl groups on the glass reactor walls. In the presence of water (reactive cofeed), copper (I) oxide deposits. Thus, pure films of two different oxidation states can be deposited from the same precursor. However, the deposition temperature is quite high and the compound is not volatile enough for practical use.

1.4 Motivation for Study

The common thread in all of the considerations for MOCVD described here is chemistry. The decomposition chemistry of the precursor determines the chemical characteristics of the deposited film. The strength of bonds between the metal and the ligands, and within the ligands, determines the minimum thermal deposition temperature, determines whether ligand fragments will be incorporated into the film, and determines how the complex will decompose photolytically. The nature of the ligands determines whether the presence of other agents (*ie.* water, hydrogen) in the system will promote clean decomposition. How the complex reacts to changing conditions will determine whether films

of different oxidation states can be grown from the same precursor. Surface chemistry determines whether or not deposition is selective.

In spite of the importance of chemistry in chemical vapor deposition, research into the decomposition chemistry of even simple and widely used compounds like silane is incomplete. Little chemical knowledge was needed to produce gallium arsenide films from trimethylgallium and arsine. These compounds decompose cleanly, and good deposition conditions can be found by trial and error. However, this empirical approach has not resulted in practical processing for copper. In this case, perhaps fundamental knowledge is a necessity rather than a nice addition for optimization.

Recognizing the importance of copper thin film growth, this project was undertaken to study *in situ* the decomposition chemistry of a volatile copper complex. Only a handful of studies address the chemistry of copper deposition. The usual method is to collect products during deposition, then analyze them after deposition is complete. Some products may undergo further reactions between collection and analysis [10a]. The only reported *in situ* study involves the difficult and expensive technique of time-resolved laser fluorescence [28]. Its goal was only to detect copper atoms during photodeposition, and revealed nothing of the organic products. The more general technique of Fourier transform infrared analysis was chosen for this work.

In addition, most precursors studied require deposition temperatures above 250°C, where copper diffusion into silicon becomes a problem. Many of them also require a reactive cofeed in order to produce clean copper films. With the appropriate precursor, it may be possible to eliminate ligands cleanly at lower temperatures. Ideally, even a reactive cofeed would be unnecessary, except perhaps to change the oxidation state of the as-deposited clean film.

From the few known volatile copper metalorganics, copper alkoxides were selected for study. The copper–oxygen bond appears convenient for obtaining different oxidation states, and it has ultraviolet absorption properties of interest for photoassisted deposition studies. The alkoxides have a region of strong UV absorption which is not common to the alcohols, suggesting that UV light may remove the ligands without fragmentation. Published work on copper t-butoxide [23] and copper t-butoxy trimethylphosphine [10a] indicates that there is a

pathway for clean elimination of the ligands to form metals or oxides. Studies of primary alcohols on copper [29] and copper oxide [30] suggest that β -hydride elimination may allow clean removal of primary alkoxy ligands.

Early efforts in this project concentrated on copper (I) t-butoxide, $[\text{CuOC}(\text{CH}_3)_3]_4$. However, transport difficulties with copper t-butoxide proved insurmountable in this experimental system. One chapter, the appendix, is devoted to that work. More valuable results were achieved with copper (II) dimethylaminoethoxide, $\text{Cu}(\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2)_2$. Thermal deposition and reactive cofeed deposition with copper dimethylaminoethoxide were studied. Even with this new aminoalkoxide precursor, attempts at photoassisted deposition were unsuccessful. The situation is discussed fully in Chapter 4.

1.5 Project Goal

The overall aim of this project is the study of the chemistry of film deposition from copper alkoxides. The unique feature of the project is the attempt to gain *in situ* chemical information. The study encompasses conventional thermal as well as photoassisted deposition. It addresses the effect of deposition temperature and atmosphere on film composition. The goal is to learn what effect each change in deposition conditions has on the film produced, and to provide some chemical rationale for these effects where appropriate. While the experiments were designed for scientific study and not for production of device-quality films, it is hoped that the chemistry elucidated will have practical value in designing production systems.

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2. Experimental Equipment and Methods

2.1 Reactor

The deposition reactor (Figure 2.1) is a standard, ultrahigh vacuum (UHV) compatible, stainless steel cube with 2.75 inch nominal diameter conflat flanges. All gaskets are copper. The top window is sapphire, which is transparent to light of wavelengths between 150 and 5000 nm. This window admits ultraviolet light for photoassisted deposition experiments. The side windows are calcium fluoride, which is transparent to light of wavelengths between 150 and 10,000 nm (*i.e.*, these windows pass infrared radiation down to a frequency of 1000 cm^{-1}). Because IR windows mounted in conflat flanges are quite expensive, calcium fluoride was chosen for its resistance to hydrolysis. These infrared-transparent viewports allow analysis of the gas within the reactor by infrared spectrometry. The reactor sits within the optical bench of a Fourier transform infrared spectrometer. A special cover admits ultraviolet light, system tubing, and electrical lines.

The flanges next to each window are fitted with up-to-air valves and connected to a supply of warm gas. The gas flow is directed towards the windows by short lengths of tubing. This purge gas flow reduces deposition and condensation on the windows. The inlet and outlet gas lines are also connected to flanges with up-to-air valves. These flanges are fitted between the calcium fluoride window purge flanges and the cube. Metalorganic precursor and carrier gas enter through the inlet, and all reactor gases leave through one outlet.

The bottom flange is blank. The remaining side flanges are occupied by feedthroughs. One is a rotary feedthrough on which the sample stage is mounted. The opposite feedthrough provides ceramic insulated connectors for a thermocouple and resistance heater inside the reactor. The entire reactor is wrapped and warmed with heating tape to reduce condensation of the precursor on the walls. The temperature of the cube is measured by a thermocouple between the heating tape and the UV window purge flange, and is held at about 115°C . The window purge and inlet gas line temperatures are measured by thermocouples between the heating tape and the tubing, and are held at $95 - 100^{\circ}\text{C}$.

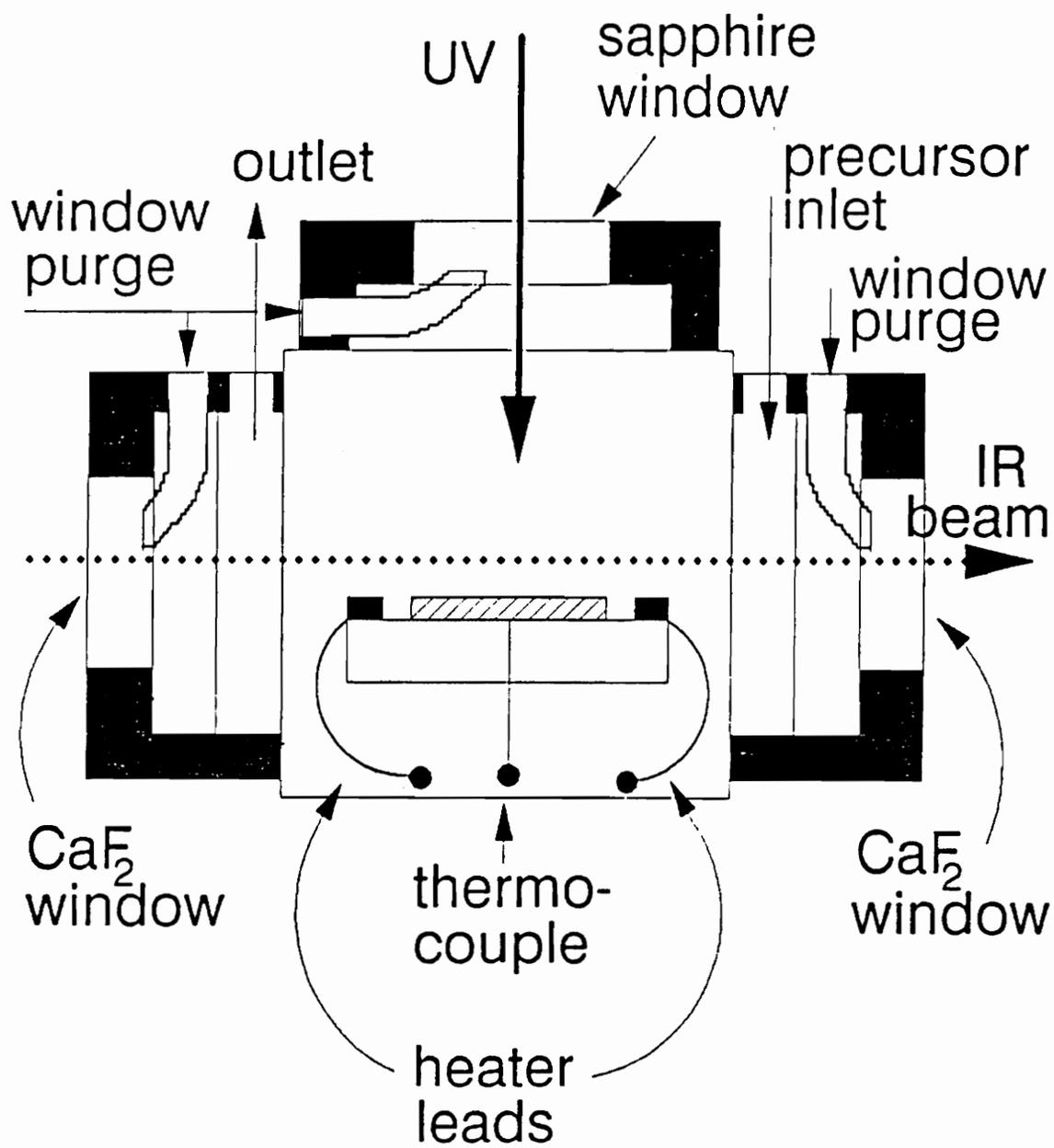


Figure 2.1 Schematic of deposition reactor / Infrared cell

The sample stage is MACOR, a machinable ceramic purchased from Dow Corning. The substrate is clamped to it by titanium shims. A piece of thin platinum foil sandwiched between the substrate and the sample stage serves as a resistance heater. It is connected to the electrical feedthroughs by copper braid insulated with ceramic braid purchased from Omega. The ceramic braid isolates the heater leads from the stainless steel reactor walls. The system was thoroughly tested to ensure that copper deposition was not a result of the copper hardware. The sample stage has a hole through the bottom to admit a thermocouple. This Type-K thermocouple touches the bottom of the substrate and connects to the thermocouple feedthrough. "Substrate temperature" refers to this thermocouple reading.

In order to change the substrate, the reactor must be unwrapped and partially disassembled, then reassembled and rewrapped. If the resistance heater or substrate thermocouple fails, the reactor must be completely disassembled for repair. At such times, each part is cleaned with acetone. Over the course of many experiments, the reactor walls accumulate a thin layer of non-volatile material, some of which can be removed with acetone. Other deposits appear to be metallic copper. The reactor is not cleaned after each run because of the required investment of time and money, and because of the risk of breaking functional electrical connections. After cleaning, the reactor must be heated and purged with helium and evacuated to remove all traces of acetone. Cleaning has no noticeable effect on the experimental results. The calcium fluoride windows are cleaned with acetone after every two to five experiments to maintain infrared spectrum quality.

2.2 Flow System

Figure 2.2 is a schematic of the flow system. Lines and fittings are all stainless steel. They measure 1/8 inch nominal diameter, or 1/4 inch at transitions to the reactor or precursor tube. The carrier gas is helium grade 5.0 (99.999 per cent helium). To insure purity, it passes through a column packed with a copper oxide catalyst which scavenges oxygen. The gas then splits into two lines, one for the carrier gas and one for the window purges. Flow through each line is controlled by a Brooks 5850E mass flow controller. After the flow controllers, the lines are wrapped with heating tape and are maintained at 120°C. This temperature is measured by a sheathed thermocouple placed in the carrier gas flow line *via* the branch of a Swagelock tee. Thermocouples between the heating tape and the tubing on the carrier and purge gas lines read within 5°C of one another. Flow rates are usually low, 2 to 20 sccm for each line.

The line from the reactor outlet is fitted with a metering valve. Samples of the outlet gas can be drawn off for mass spectral analysis. The line between the reactor and the mass selective detector is maintained at 100°C by heating tape. The outlet line is connected to a direct drive mechanical vacuum pump. Thermal and photoassisted deposition experiments are conducted at reduced pressure. Before each experimental run, carrier gas flow rates and deposition temperatures (except for the precursor) are maintained for at least forty-eight hours to reduce water in the system.

For experiments with reactive cofeed, the reactive gas is added into the window purge gas flow to prevent reaction with the precursor before the reactor. Note that the available pump is not explosion-proof and contains hydrocarbon oil. It cannot be used with hydrogen or strong oxidizers. Experiments using hydrogen cofeed are performed at near ambient pressure. The mechanical pump is bypassed and the system outlet is connected to a ventilation duct to insure that hydrogen does not accumulate in the laboratory. A metering valve restricts flow through the system outlet to insure that the system pressure is always slightly higher than ambient pressure, and net flow is out of the system only. Pressure in the system never exceeds 7 psig, the regulator pressure set at the tanks.

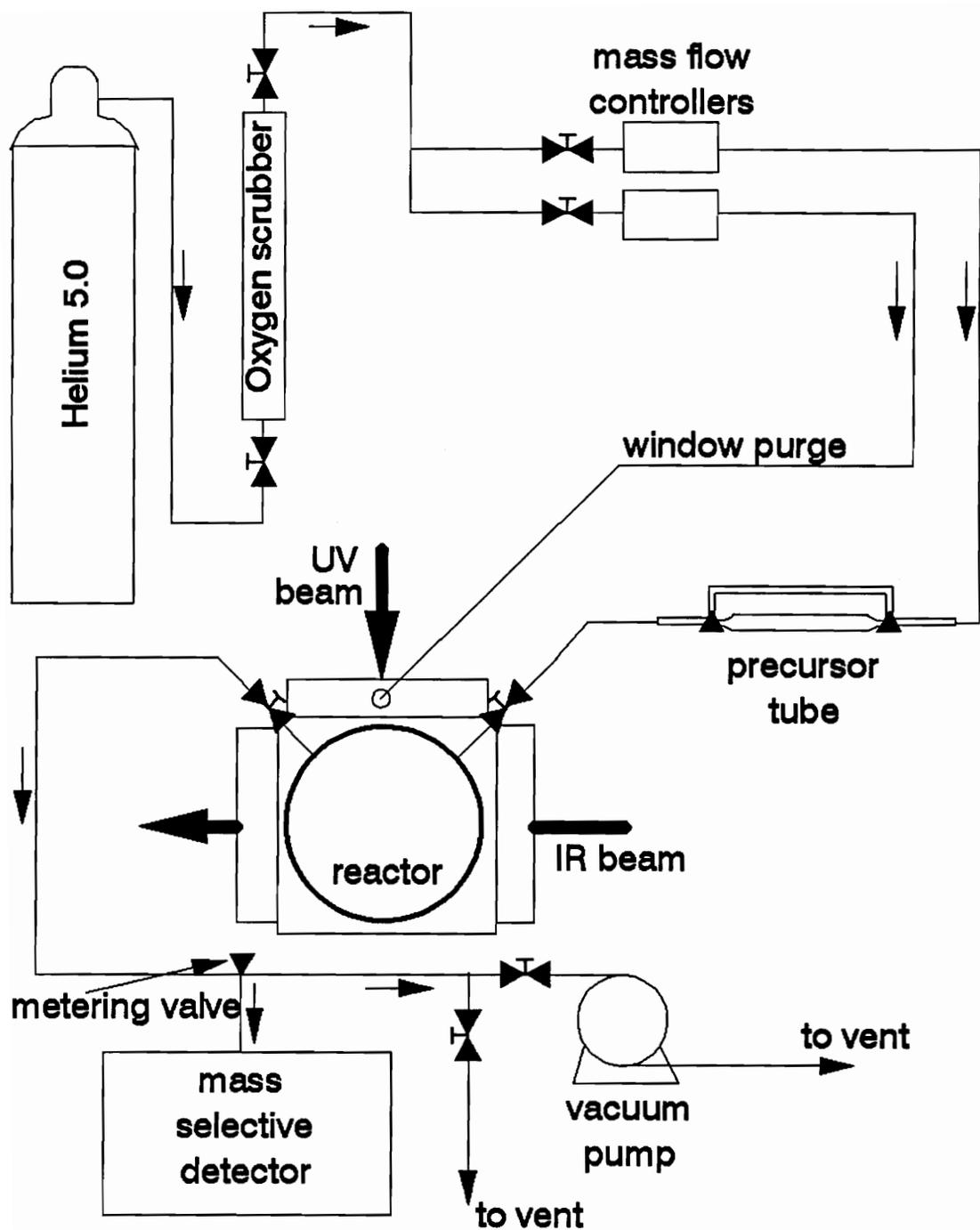


Figure 2.2. Schematic of experimental flow system

2.3 Precursor and Precursor Tube

The precursor is copper (II) dimethylaminoethoxide, $\text{Cu}(\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2)_2$, (Figure 2.3) purchased from Strem Chemicals and used as received. Elemental analysis by Galbraith gave results as expected. Copper dimethylaminoethoxide is water sensitive and must be stored and transferred in a dry box. It is a blue-green powder. Upon exposure to the atmosphere it gradually turns purple.

The precursor is transferred to the glass precursor tube (refer to Figure 2.2) in the dry box and connected to the flow system. The tube's bypass line isolates the precursor while the flow system is flushed before each experiment. The precursor tube is wrapped with heating tape and a thermocouple is sandwiched between the tape and the glass. Copper dimethylaminoethoxide sublimates between 90°C and 98°C at an estimated pressure of $10^{-1} - 10^{-2}$ Torr in this work. Tests with copper (I) t-butoxide show that a water-sensitive compound can be kept safely in the tube for at least ten days. Copper t-butoxide turns instantly from pale yellow to black when hydrolyzed, so it is a useful test compound.

After each run, the precursor tube is washed with aqua regia, acetone, and distilled water. Because it is also a strong oxidizer, aqua regia is one of the few acids that will dissolve copper. Once clean, the tube is treated with dichlorodimethylsilane, $\text{SiCl}_2(\text{CH}_3)_2$, rinsed with distilled water, and baked overnight at 130°C . Dichlorodimethylsilane reacts with the hydroxyl groups on the glass surface. HCl is released and dimethylsilane left bonded to the surface oxygens. This makes the glass hydrophobic and reduces hydrolysis of the precursor by water desorbing from the tube walls during sublimation [1].

Initially, copper (I) t-butoxide was chosen for this study. However, it proved to be impractical. Synthesis, properties, and decomposition studies of copper t-butoxide are described completely in the first appendix, Chapter A1.

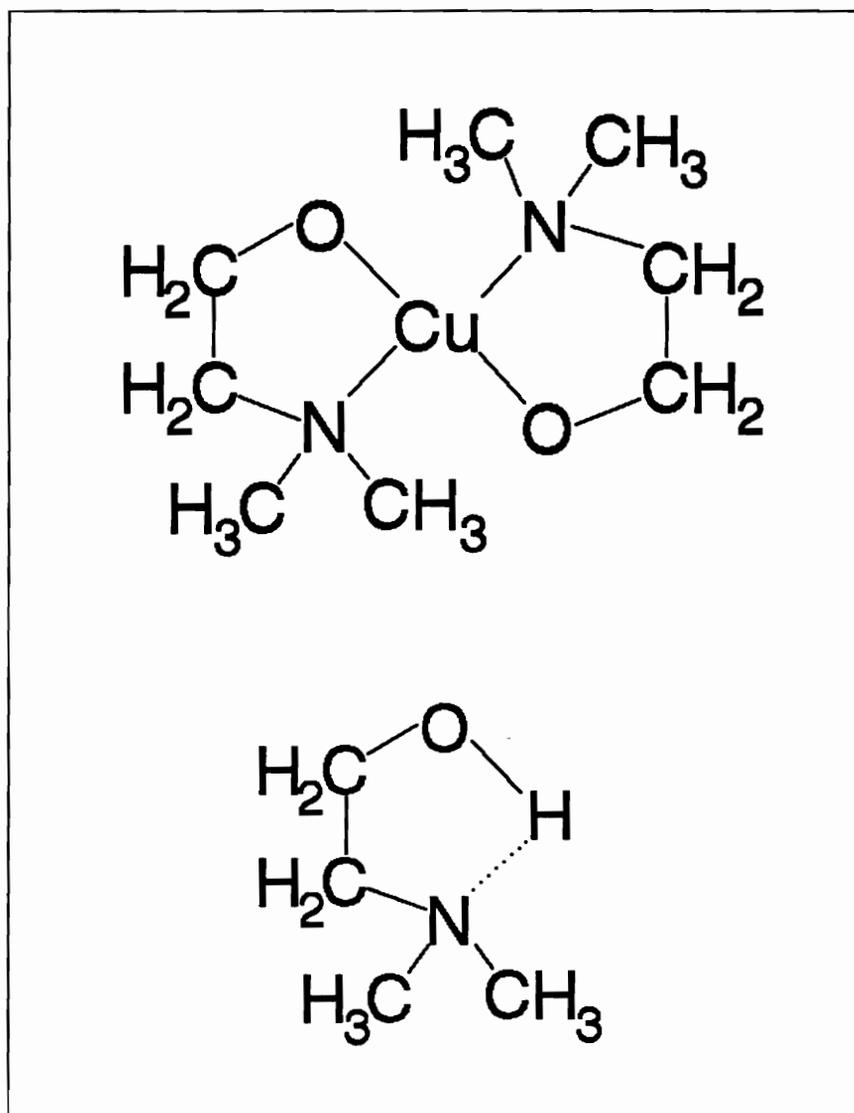


Figure 2.3 Representations of copper (II) dimethylaminoethoxide and dimethylaminoethanol

2.4 Substrate

Single crystal strontium titanate (SrTiO_3) is the substrate used for most of this work. The crystals measure 0.25 x 0.25 x 0.02 inches and are polished on one side. Deposition is performed on the polished side to achieve a more clear delineation between film and substrate for surface analysis. The crystals are oriented in the (100) direction. Strontium titanate has the cubic perovskite structure with unit cell dimension $a=3.905\text{\AA}$. The structure at the surface and in the bulk was confirmed by low energy electron diffraction (LEED) and X-ray diffraction. The crystals were purchased from Commercial Crystal Laboratories, Inc., in Naples, Florida.

Strontium titanate is a semiconductor. When heated in vacuum, it loses oxygen. A small number of oxygen vacancies increases the crystal conductivity. A semiconducting substrate reduces the sample charging which occurs during surface analysis of the film. The color of reduced strontium titanate depends on the number of oxygen vacancies. Oxygen loss of less than 0.1 atomic per cent produces greens, browns, and mustard yellow. Oxygen loss of 0.1 to 1.0 atomic per cent yields a blue crystal. A loss of 2.0 to 3.0 atomic per cent oxygen produces a black crystal, and possibly changes in the crystal lattice parameters [2].

Before each set of experiments, the strontium titanate is held at 500 to 600°C for two to four hours under reduced pressure and 2.0 to 4.0 sccm helium flow. After cooling, the crystal ranges from colorless, with some black color centers, to mustard yellow. The reduction is carried out in the reactor, and the substrate is isolated from laboratory air until after deposition. Crystals are easily reoxidized by heating in air. In addition to reducing the bulk, this heat treatment cleans the surface of the crystal. Organic surface contaminants combine with surface lattice oxygen at high temperature and are burned off. The heat treatment also reorders the surface, which has been damaged by polishing and chemical cleaning. The influence of heat treatment on surface ordering was confirmed by LEED [3].

Due to the expense of the crystals, they were used in multiple experiments. After a deposited film was analyzed, the crystal was wiped with a cotton swab soaked in aqua regia, then dropped in a 250 ml beaker of distilled water. The crystal was then washed with

acetone, baked in a 600°C oven overnight, and replaced in the cube. No difference in results was observed between crystals used for the first time and cleaned-and-reused crystals.

Strontium titanate has a band gap of 3.2 eV, or 388 nm. This is the energy difference between the valence band maximum and the conduction band minimum. Charge carriers in semiconductors are (1) electrons which were promoted to the conduction band and (2) the holes they left behind in the valence band. Although the valence band and conduction band encompass a range of energy states, charge carriers tend to cluster at the band edges. Neglecting the few defect states within the band gap, electrons must acquire at least 3.2 eV of energy to be promoted across the gap [4].

An electron may absorb one photon, acquiring its energy, and move to a higher energy state. Very few photons of energy less than 3.2 eV are absorbed by strontium titanate, because there are few opportunities for electron-hole pair formation with less than 3.2 eV (*i.e.*, few defect states in the band gap). Many photons of energy greater than 3.2 eV can be absorbed, because there are many valence band electrons available for promotion, and many energy states available in the conduction band [4].

Each photon can promote only one electron, and uses all of its energy to do so. Recall that charge carriers cluster at the band edges. If a photon with higher energy than the band gap is absorbed to create a high energy electron-hole pair, the carriers may relax back to the band edges by emitting phonons, or quanta of lattice vibration. Energy over and above the required 3.2 eV is dissipated in the crystal by these vibrations, that is, as heat [4].

Light of higher energy (shorter wavelength) than the band gap is strongly absorbed, because there are many electrons available for promotion in the valence band, and sufficient energy in each photon to promote an electron to the conduction band. Absorption of high energy photons heats the strontium titanate crystal, as excess energy is dissipated through lattice vibrations. Light of lower energy (longer wavelength) than the band gap is weakly absorbed, if at all, because there are few low energy pathways for electron promotion. There is no excess energy to dissipate as heat. The crystal remains cool [4].

The optical properties of the substrate provide an opportunity to separate pyrolytic and photolytic UV decomposition of the precursor. If wavelengths of light above and below

the band gap of strontium titanate decompose the precursor, results that are due strictly to photolysis can be differentiated from those due to combined photolysis/pyrolysis.

Some preliminary thermal deposition experiments were done on quartz (SiO_2), polished on one side. These substrates measure 10 x 8 x 2 mm. Before each experiment, the substrate was heated to 550°C for several hours under reduced pressure and 2 to 4 sccm helium flow to remove surface contamination. Quartz provides an oxide surface without the expense of strontium titanate, ideal for preliminary work. Quartz is also of more interest than strontium titanate to the semiconductor industry. However, it does not provide a suitable band gap for the envisioned photoassisted deposition studies.

2.5 Ultraviolet Sources

First attempts at photoassisted deposition used a Lumonics TE-860-4 excimer laser. The laser was filled with nitrogen and hydrogen to produce the N_2 (337 nm) and N_2^+ (428 nm) lines. Note that 337 nm photons are of higher energy than the strontium titanate band gap, while 428 nm photons are of lower energy than the strontium titanate band gap. The N_2 line provides 3 to 4 mJ/pulse of energy. The N_2^+ line provides 500 μJ /pulse. The pulse rate was 20 Hz. Both lines proved to be of insufficient power to cause deposition. Later experiments used a Spectronics Corporation B-100 Ultraviolet Lamp. Output from this lamp is shown in Figure 2.4. The lamp sits about one inch from the top of the cover, ten inches from the substrate.

For experiments that take advantage of the band gap of strontium titanate, certain wavelengths were filtered out with Oriol colored glass long pass filters. Filter number 59460 cuts on (reaches fifty per cent transmittance) at 348 nm. At 375 nm, internal transmittance is better than ninety-five per cent. This filter passes some energies above and below the band gap of strontium titanate. Filter number 59472 cuts on at 400 nm. Internal transmittance is essentially zero at 385 nm and reaches ninety per cent at about 425 nm. This filter passes only energies below the band gap of strontium titanate. The cut-on shifts to longer wavelength by 0.07 nm/°C with rising temperature. This shift is reversible up to 90°C. The filters are placed on top of the sample chamber cover, where the temperature has not been observed to exceed 90°C.

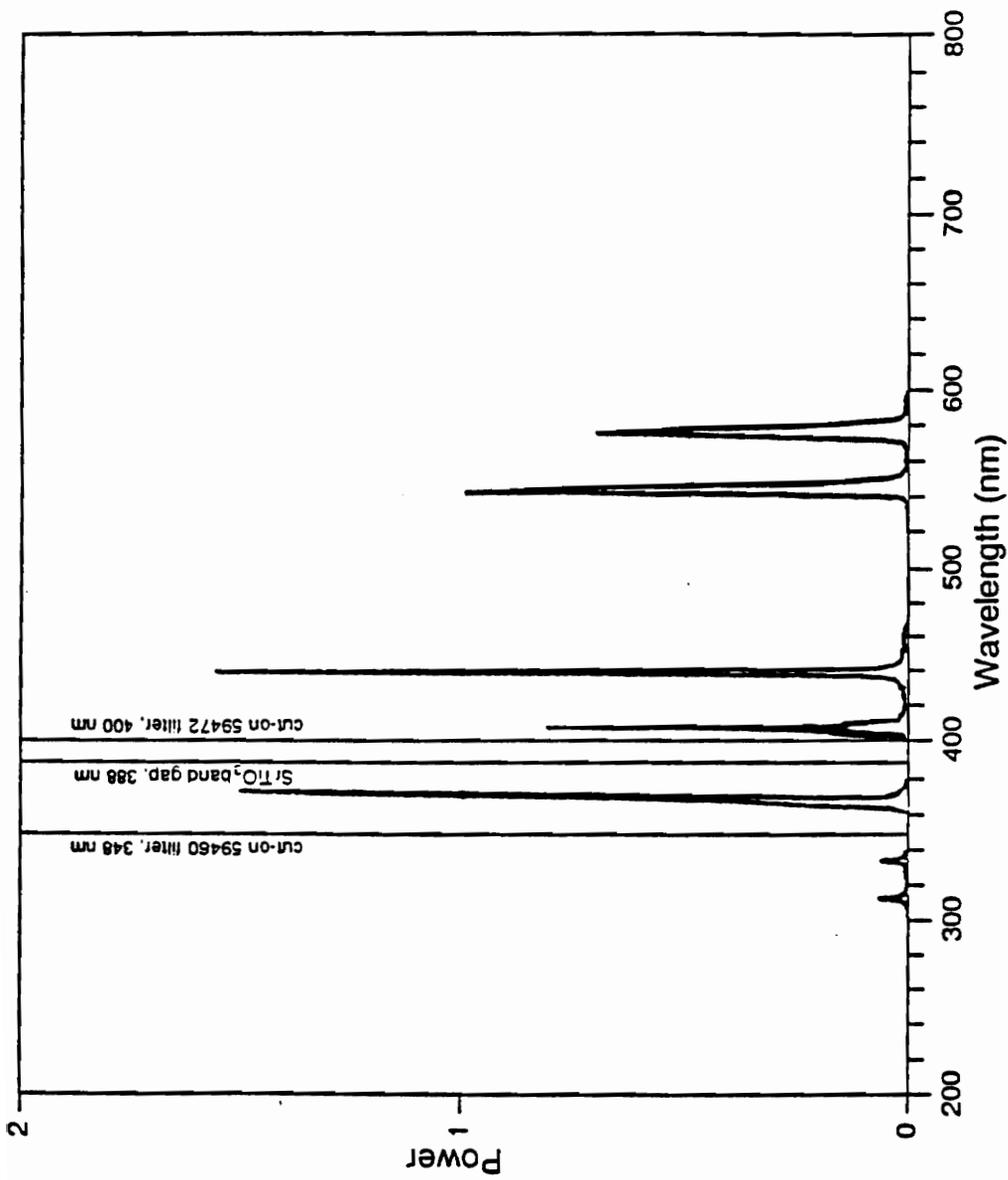


Figure 2.4 Wavelengths emitted by Spectronics B-100 ultraviolet lamp
 Courtesy of Spectronics Corporation, Westbury, NY

2.6 Analytical Instrumentation

The Fourier transform infrared spectrometer is an IBM IR/32 with an IBM 9000 computer for control and data analysis. Apodization is triangular and resolution is 4 cm^{-1} . Experience has shown that peak positions are consistent within 1 cm^{-1} . Mass spectral analysis was performed with a Hewlett-Packard 5970A series mass selective detector (MSD) with a Hewlett-Packard 9825B calculator for control and data analysis. Operating values were set by the built-in autotune program, which uses perfluorotributylamine as a reference. The MSD uses electron impact ionization with an electron energy of 70 eV. It has a detection range of 10 – 800 amu and a resolution of 1 amu.

Ultraviolet absorption spectra were measured on a Shimadzu CS-9000 Dual-Wavelength Flying-Spot Scanner in reflectance mode. The precursor was placed in a special quartz cell sealed with a septum before removing it to the spectrophotometer. When spectra of solutions were desired, the solvent was injected into the cell through the septum.

Atomic composition of the films was determined by Auger and X-ray photoelectron spectroscopy. Auger analysis was performed with a Perkin-Elmer PHI-610 scanning Auger microprobe. Most X-ray photoelectron spectroscopy was performed on a Perkin-Elmer PHI-5400 X-ray photoelectron spectrometer. The exception is data for films on quartz which were analyzed on a Kratos Xsam-800 X-ray photoelectron spectrometer. The scanning electron microscope employed is a Cambridge Instruments Stereoscan 200 [5].

Attempts to measure film thickness with a WYKO TOPO-30 optical interferometer were unsuccessful. The transition observed was between the uncoated area that had been covered by the titanium shim and the coated area. The interferometer showed a marked difference in surface roughness, but no difference in average height. At the time, the transition was suspected to be too gradual. However, after scanning electron microscopy, the conclusion was that the films were so rough that optical interferometry was impracticable. A smooth, reflective surface is required.

Upon removal from the reactor, films are first classified as conductive or nonconductive. Conductivity is tested by touching the leads of a Fluke 75 multimeter to

opposite corners of the film (separation is about 1 cm). The film is defined as conductive if it triggers the continuity signal of the multimeter, indicating the resistance between the leads is less than 150 Ω . Four-point probe measurements of the resistivity of some films were made. The values were corrected for the finite dimensions of the sample [6]. These films were stored in a vacuum dessicator after their initial classification as conductive, and were replaced in the vacuum dessicator after the four-point probe measurements. Resistivity was measured before any other film analysis took place.

2.7 Analytical Techniques

2.7.1 Overview of Infrared Analysis

Bonds between atoms stretch, bend, and otherwise deform. Groups of bonded atoms wag, rock, and twist. All of these motions are periodic, and their frequency lies in the frequency range of infrared radiation. Molecules absorb frequencies of infrared radiation that match the frequencies of their bond deformations. An infrared spectrum is a plot of infrared radiation absorbance (or transmittance) *versus* radiation frequency. Infrared frequencies are commonly reported in wavenumbers (cm^{-1}), where frequency = (wavelength)⁻¹.

The frequency of peak absorbance (peak position) is affected by the type of atoms bonded, the type of bond deformation, the strength and length of the bond, constraints on movement placed by the structure of the molecule (for instance, ring *versus* chain), electron donation or withdrawal by neighboring atoms or groups, and the motion of neighboring atoms or groups. For example, a methylene group (CH_2) has two C–H bonds that can stretch periodically. They may lengthen and shorten simultaneously, a symmetric stretch. The frequency changes if one bond lengthens while the other shortens, an asymmetric stretch. Both symmetric and asymmetric stretching frequencies change if the methylene is attached to an amine or an aryl group instead of a hydrocarbon, or if it is part of a ring or a branched chain instead of a straight chain.

After years of study, the frequencies of radiation absorbed by various types of bonds and bond deformations are generally well established. The presence of a particular functional group in a molecule is indicated by absorption of infrared radiation within a specified range. The peak position within that range gives further clues to the structure of the molecule. Well

known correlations between peak values and molecular structure are published in numerous handbooks and chemistry texts. In theory, every peak in an infrared spectrum can be assigned to a specific deformation of the molecule. In practice, however, for a reasonably complex spectrum, it is seldom possible to assign all peaks based on published correlations.

2.7.2 Vapor Phase Infrared Analysis of Copper Dimethylaminoethoxide and Related Species

Identifying the bands in an infrared spectrum based on published correlations can be a difficult process. In this work, information was drawn from several sources [7-12]. Information was often overlapping and sometimes contradictory. Correlations for condensed phases do not always apply to the vapor phase [13]. In general, peak identifications were made after consulting all the listed sources.

Figure 2.5 shows the infrared spectrum of vapor phase dimethylaminoethanol collected in the deposition reactor. The peak positions are consistent with those read from the standard spectrum in Nyquist's book [14]. The peak shapes are also consistent, although the peaks between 1000 and 1150 cm^{-1} are not as well resolved in the Sadtler spectrum. The alcohol concentration is higher in the Sadtler spectrum, and the peaks may be broadened because they are nearing full-scale.

Figure 2.6 shows the vapor phase infrared spectrum of copper (II) dimethylaminoethoxide. There are striking differences in relative intensities, and a few small shifts in peak position, but overall the spectrum is quite like that of the alcohol. The differences and similarities are more apparent in Figures 2.7 and 2.8, which show the same spectra over narrower frequency ranges. In this text, peaks will be referenced by their experimentally determined positions.

Schematics of the alkoxide and alcohol are shown in Figure 2.3. The aminoethoxy ligands form five-membered chelate rings with the central copper atom [15]. Because of the attraction between the basic tertiary amine group and the acidic proton of the alcohol group, the aminoalcohol also assumes a five-membered ring conformation *via* intramolecular hydrogen bonding [16]. Thus it is not unreasonable for the IR spectra to be similar. There is

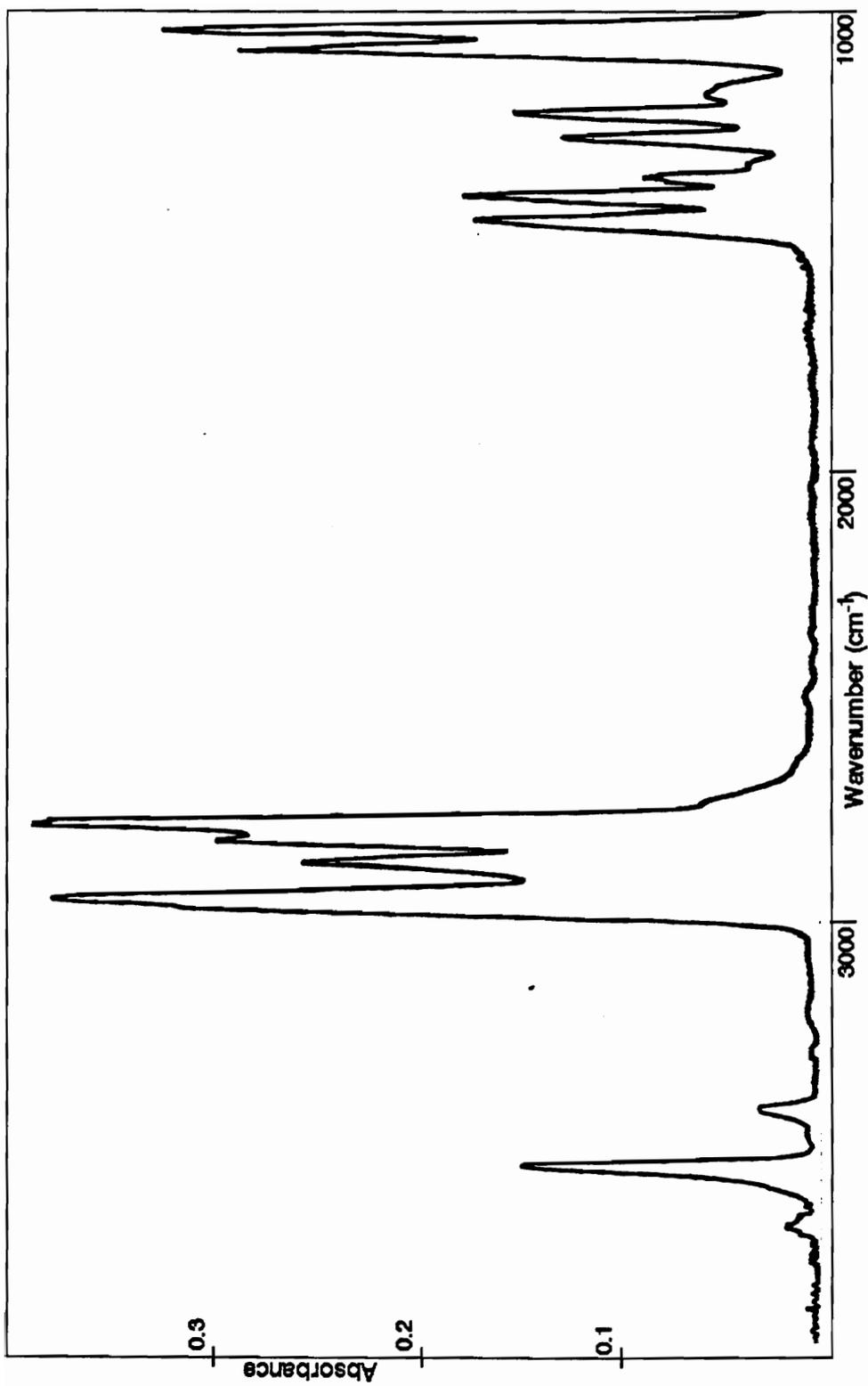


Figure 2.5 Infrared spectrum of vapor phase dimethylaminoethanol

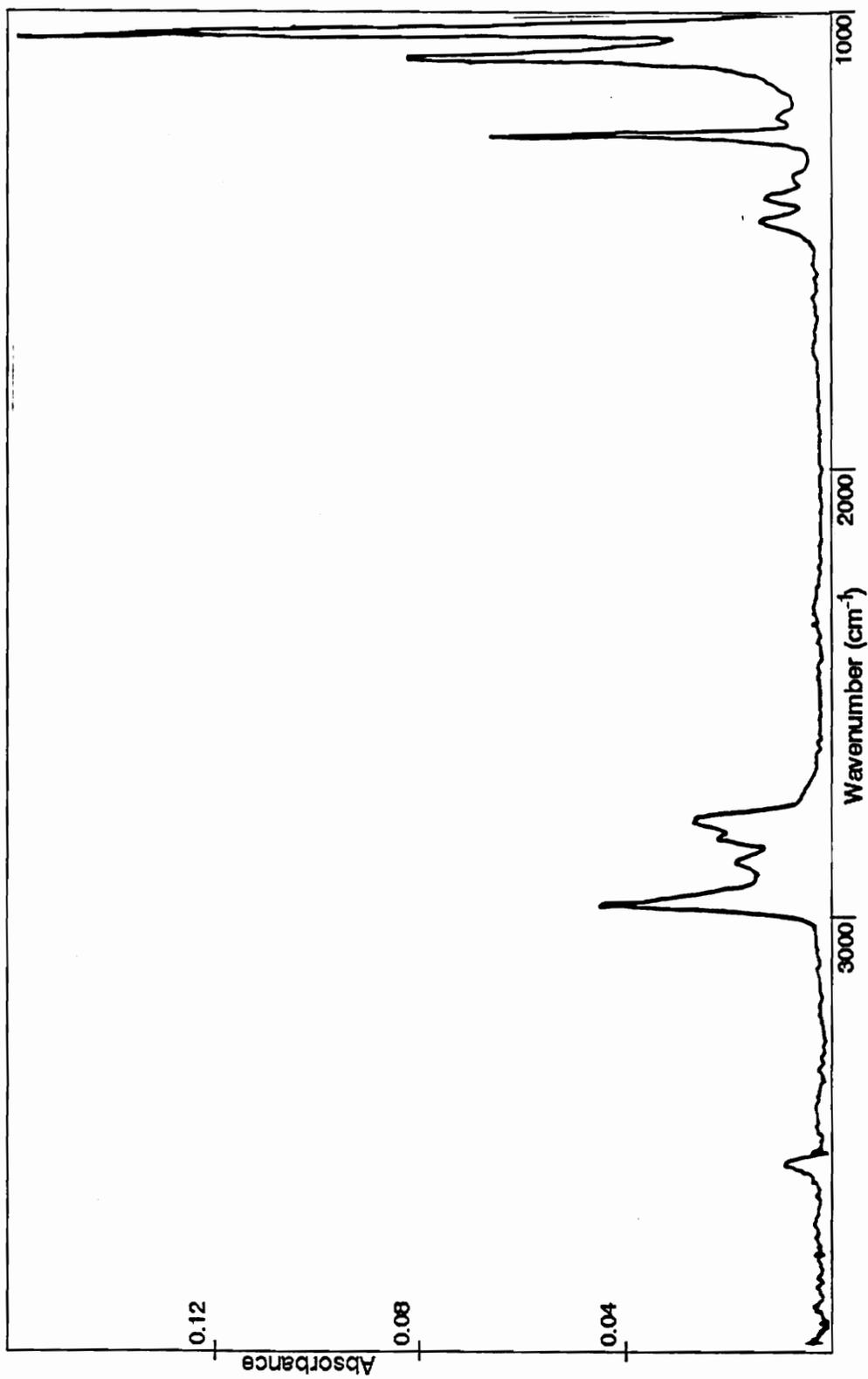


Figure 2.6 Infrared spectrum of vapor phase copper dimethylaminoethoxide

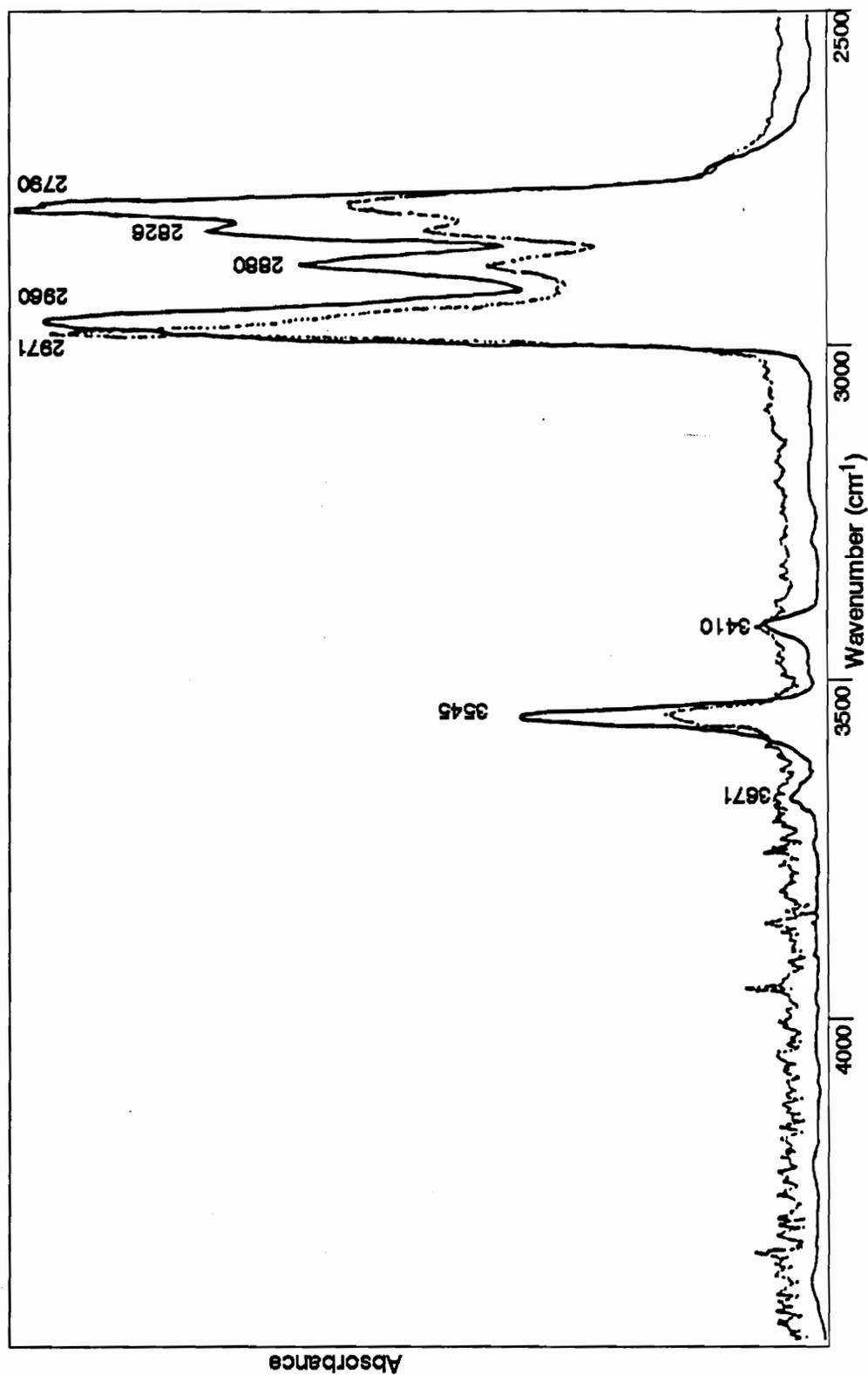


Figure 2.7 Infrared spectra of vapor phase dimethylaminoethanol (solid line) and copper dimethylaminoethoxide (broken line)

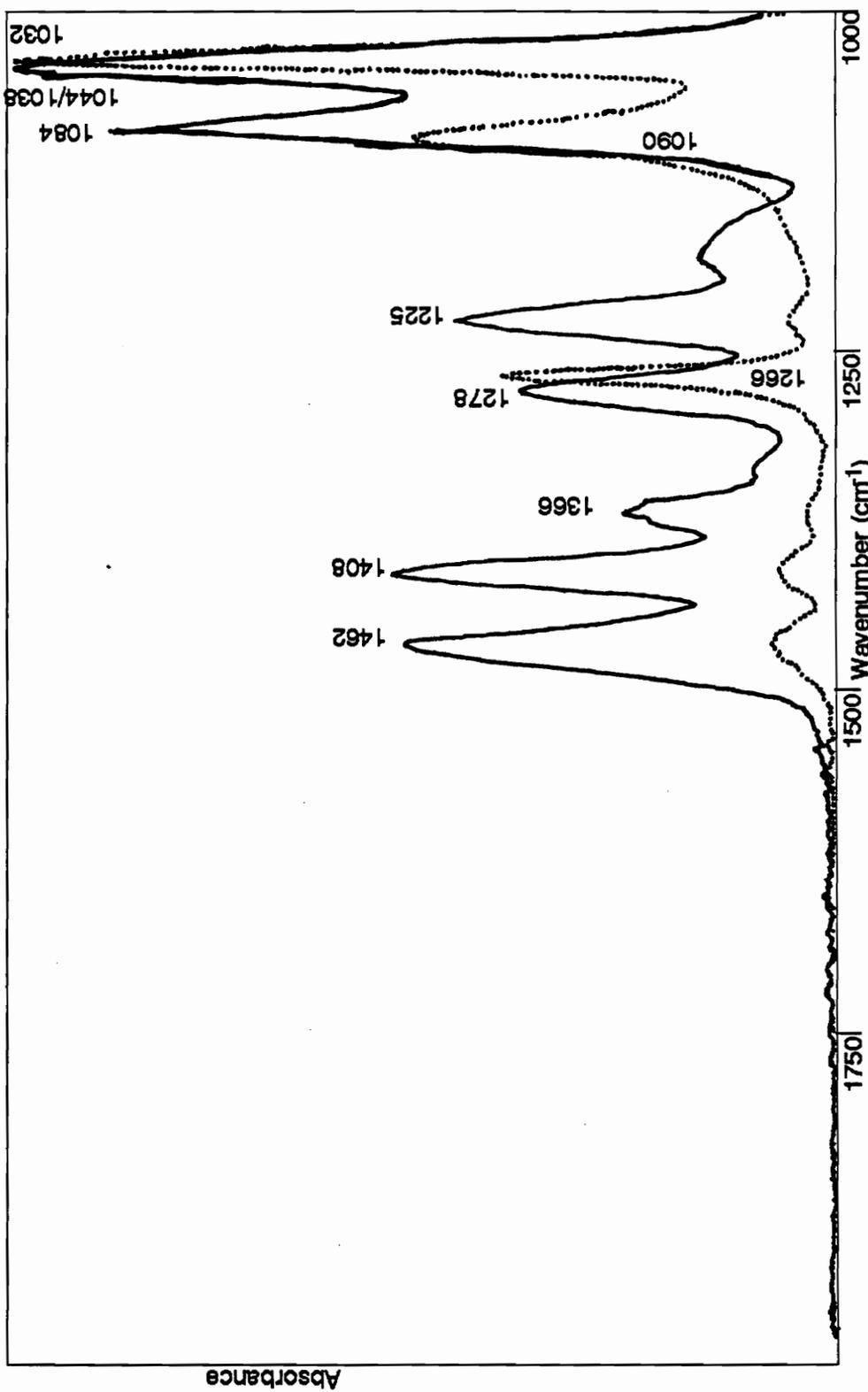


Figure 2.8. Infrared spectra of vapor phase dimethylaminoethanol (solid line) and copper dimethylaminoethoxide (broken line)

an equilibrium between hydrogen-bonded rings and non-hydrogen-bonded chains for the alcohol [16].

Two peaks near 3500 cm^{-1} are related to the O-H stretch, $\nu(\text{O-H})$. The first is at 3671 cm^{-1} , within the range expected for primary alcohols ($3670 - 3680\text{ cm}^{-1}$). This is the stretching frequency for the non-hydrogen-bonded OH group. The O-H stretch at 3545 cm^{-1} is for the hydrogen-bonded aminoalcohol. The peak at 3410 cm^{-1} is identified by Nyquist as an impurity, with no further explanation [14]. It seems odd that the same impurity peak exists whether the dimethylaminoethanol is purchased from Aldrich or obtained from hydrolysis of copper dimethylaminoethoxide.

The complex set of peaks between 2700 and 3000 cm^{-1} are C-H stretches in CH_2 and CH_3 groups. The asymmetric stretch of CH_2 groups in the five-membered ring appears at 2960 cm^{-1} for the alcohol and at 2971 cm^{-1} for the alkoxide. The frequency changes with ring strain and ring chemistry, so the shift upon substituting copper for hydrogen is expected. For comparison, this asymmetric stretch appears at 2970 cm^{-1} for cyclopentane. The asymmetric C-H stretches of any CH_3 or CH_2 groups are expected to produce intense peaks between 2910 cm^{-1} and 2975 cm^{-1} . The symmetric stretch for CH_2 in a five-membered ring appears near 2880 cm^{-1} . It is always less intense than the asymmetric stretch. For cyclopentane, it appears at 2883 cm^{-1} [17].

A doublet near 2800 cm^{-1} is characteristic of the symmetric C-H stretch in $\text{N}(\text{CH}_3)_2$ [18]. There is an additional contribution near 2800 cm^{-1} from C-H stretches in the non-hydrogen-bonded conformation of the alcohol [16]. The asymmetric C-H stretch for a CH_2 on a tertiary nitrogen appears near 2825 cm^{-1} . The symmetric stretch is near 2780 cm^{-1} [18]. Because there are so many overlapping contributions in the C-H stretching region, peaks between 2750 and 2850 cm^{-1} are difficult to assign definitively.

Spectra in this work will often show a positive or negative peak (a doublet with fine structure) near 2300 cm^{-1} . This is absorbance by carbon dioxide [19], primarily in the optical bench. Carbon dioxide is a strong infrared absorber, and slight changes in concentration show up clearly as a change in intensity in the spectrum. With holes in the bench cover to bring in tubes, wires, and ultraviolet light, even purging the bench with liquid nitrogen boiloff

does not prevent fluctuation in carbon dioxide levels. It is difficult to distinguish between fluctuations in bench atmosphere and fluctuations in reactor atmosphere. Unless there is a clear trend in carbon dioxide concentration, this peak is ignored in infrared data analysis.

A broad peak between 1700 and 1750 cm^{-1} is the C=O stretch for aldehydes and ketones [20]. The C=N stretch of imines yields a peak between 1620 and 1680 cm^{-1} [21]. The C=C stretch also appears between 1600 and 1700 cm^{-1} [22]. Peaks in these regions appear in infrared spectra of alcohol and alkoxide decomposition products. One expects a C=C stretch to be accompanied by a medium-to-strong peak for the alkene C-H stretch between 3000 cm^{-1} and 3100 cm^{-1} [22b]. The C-H stretch of the aldehydic proton appears as two weak bands between 2700 cm^{-1} and 2900 cm^{-1} [22b]. It is difficult to detect the aldehydic hydrogen amongst the other C-H stretches present in this region.

If the carbonyl species were a carboxylic acid rather than an aldehyde or ketone, several other features would be present in the spectrum. The carboxylic acid C=O stretch appears between 1755 and 1780 cm^{-1} , notably higher than the aldehyde/ketone peak. Carboxylic acids can also be identified by the C-C-O stretching bands between 1120 and 1178 cm^{-1} and between 1075 and 1108 cm^{-1} . Below 150°C, carboxylic acids are usually dimers rather than monomers. The dimer $\nu(\text{O-H})$ appears between 2800 and 3100 cm^{-1} rather than near 3580 cm^{-1} as in the monomer. The $\nu(\text{C=O})$ for the dimer is at 1680 – 1720 cm^{-1} , and another strong band appears near 1300 cm^{-1} [23].

The alcohol spectrum shows three peaks between 1350 and 1500 cm^{-1} . Close inspection reveals the same peaks in the alkoxide spectrum. These peaks are infrared absorbance by the bending motion of CH_2 and CH_3 groups on tertiary amines [24] and by CH_2 deformations in alkyl chains [17c, 25]. Although they appear weaker in the alkoxide spectrum, their intensities relative to the C-H stretch intensities are comparable. They should not be compared to the peaks between 1100 and 1000 cm^{-1} , whose intensities are strongly affected by the substitution of copper for hydrogen.

The peaks between 1150 and 1300 cm^{-1} are the most difficult to assign. There are contributions in this region from CH_2 deformations [17c]. In addition, tertiary dimethylamines exhibit C-N stretches at about 1270 cm^{-1} and at about 1190 cm^{-1} [24c]. Identification as a C-N stretch is consistent with the shift in frequency and increase in

intensity of the peak near 1270 cm^{-1} between the alcohol and alkoxide. The carbon–nitrogen bond is affected by substitution of copper for hydrogen in the five-membered ring. The infrared spectra of $(\text{CH}_3\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_3)_2$ and $\text{CH}_3\text{CH}_2\text{N}(\text{CH}_3)_2$ are similar to that of dimethylaminoethanol in this region [26].

Note that the peaks between 1100 and 1500 cm^{-1} in the alcohol spectrum are fairly broad and the baseline appears to hump or curve. A broad contribution from O–H bending modes underlies this region. Contrast this with the flatness of the alkoxide baseline in the same region [27].

The strong peaks between 1000 and 1100 cm^{-1} were alluded to earlier. These are the C–O and C–N stretches. As they are so close to the site of substitution, it is reasonable for them to be strongly affected by a change from hydrogen to copper. Nyquist identifies the 1040 cm^{-1} peak ($1044/1038\text{ cm}^{-1}$ doublet) in the alcohol spectrum as $\nu(\text{C–O})$. The C–O stretch often appears as a doublet. Substitute isopropyls for the methyl groups on the nitrogen, and $\nu(\text{C–O})$ appears at 1079 and 1038 cm^{-1} . Substitute normal butyls, and a single C–O stretch appears at 1068 cm^{-1} . It might seem reasonable to assign both peaks below 1100 cm^{-1} as $\nu(\text{C–O})$. However, a C–N stretch is expected between 1030 and 1200 cm^{-1} . C–N stretches are usually less intense than C–O stretches. Thus the higher frequency peak is reasonably assigned to $\nu(\text{C–N})$ [18, 28]. Note that for tertiary dimethylamines, the C–N stretch is expected near 1040 cm^{-1} [24c]. This implies that Nyquist's identification is incorrect, and the higher frequency peak is the C–O stretch. However, correlations for C–N stretches are for aliphatic amines, and a shift due to the ring conformations of the alcohol and the alkoxy ligand is certainly possible.

The frequency range from 600 to 1000 cm^{-1} is called the “fingerprint region” [29]. Few assignments to specific bond deformations are made in this region. It can be used to distinguish between molecules with similar spectra, if standard spectra are available. Unfortunately, it is impossible to collect data in the fingerprint region with this experimental equipment. The infrared-transparent windows are calcium fluoride. They were chosen for their resistance to hydrolysis, but they do not transmit below 1000 cm^{-1} . This also makes it impossible to see Cu–O or Cu–N stretches.

2.7.3 Overview of Mass Spectral Analysis

McLafferty's book [30] is an excellent text for the interpretation of mass spectra, and is the source for the discussion that follows.

In mass spectral analysis, molecules are broken up into charged fragments. The fragments are classified by mass-to-charge ratio, and the abundance of fragments at each mass-to-charge ratio is recorded. From this fragmentation pattern, the structure of the original molecule may be deduced.

The sample to be analyzed is introduced into the ion source, a chamber evacuated to about 10^{-8} Torr. In the ion source, a hot filament produces electrons which travel across the chamber to the anode. These energetic electrons interact with the sample molecules. Some sample molecules lose electrons in the process, becoming positive ions. This process is referred to as electron impact ionization. Other ionization methods exist, but are not relevant to this work. The mass selective detector used in this research uses 70 eV electrons for electron impact ionization.

The positive ions are often unstable and break into positive and neutral fragments. Several standard fragmentation pathways have been studied. The presence of certain atoms or groups favors cleavage of particular bonds in the molecule. The pressure inside the instrument is 10^{-6} Torr or less, so only unimolecular pathways are available. Mass spectral analysis is feasible because fragmentation patterns are somewhat predictable.

The positive ions are guided by electric fields into the analyzer. The instrument used in this work has a quadrupole mass filter, which generates RF and DC fields between the detector and the entrance to the analyzer chamber. The path of an ion in these fields depends on its mass-to-charge ratio. The fields can be adjusted so that only ions of a particular mass-to-charge ratio hit the detector. (For simplicity, most ions are assumed to be singly charged. Occasionally, multiply charged species do appear in a spectrum. They are usually small in abundance and easy to identify.) The fields can be adjusted quickly to monitor the abundance of several ions. A spectrum spanning 800 amu can be scanned in less than one second.

A mass spectrum is usually presented as a graph or a table of the abundance of ions *versus* mass number. The ion of highest abundance is called the base peak. Often, the rest of the spectrum is normalized to this peak, whose abundance is defined as 100. The abundances of other peaks are given relative to the base peak.

To identify a compound from its mass spectrum, the atomic compositions and structures of its major fragments must be identified. Isotopic abundances are the key to deducing a fragment's atomic composition. Consider a fragment of mass M and abundance 100. Each carbon in the fragment contributes an abundance of 1.1 to the peak at mass $M+1$. Each oxygen contributes 0.2 to the peak at $M+2$. Each fragment must also be a logical chemical unit. A peak of mass M may be identified by considering what atoms are required to make up the observed abundances at $M+1$ and $M+2$. Consider a spectrum with the following peaks: 73 amu with a relative abundance of 100, 74 amu with a relative abundance of 4.4, and 75 amu with a relative abundance of 0.2. The isotopic abundances indicate an empirical formula of C_4H_9O .

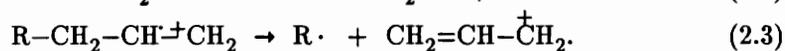
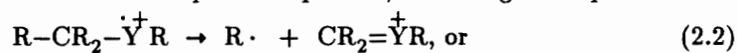
The parent ion is the original molecule, singly charged after having lost one electron. It is also called the molecular ion. If it is present, it will be the major peak at highest-mass in the spectrum of a pure compound. Any higher-mass peaks can be accounted for by the natural abundances of heavier isotopes. All other ion fragments must result from "logical neutral losses" from the parent ion (*i.e.*, loss of CH_3 , H , or $C(CH_3)_3$). The parent ion peak is not necessarily the base peak. Often, the parent ion is not detected.

To identify the parent ion, logical neutral losses, and fragments, it is important to know the common fragmentation pathways. Fragmentation is affected by the structure and composition of an ion. The more stable ions will be more abundant. Where fragmentation involves loss of an alkyl group, the tendency is to lose the largest alkyl group possible by breaking only one bond. The stability of the lost neutral fragment is also important. It should be a whole molecule (CO) or a fairly stable free radical ($CH_2=CH-CH_2\cdot$).

For hydrocarbons, the most common fragmentation pathway is simple σ -bond dissociation:



When π -bonds or atoms with lone pairs are present, α -cleavage is important:



One electron is lost from the lone pair or the π -bond in the initial ionization. The remaining electron is donated to form another bond to an adjacent atom. To complete the bond, another bond to this α -atom is cleaved. This is also called radical-site initiation. An electron donated from the radical site initiates fragmentation. The ability to cause α -cleavage decreases as follows: $\text{N} > \text{S}, \text{O}, \pi, \text{R}\cdot > \text{Cl}, \text{Br} > \text{H}$.

Another common fragmentation pathway is charge-site initiation. It is not important for the species to be analyzed in this work. Several rearrangement pathways are also available which are not important in this work.

2.7.4 Mass Spectral Analysis of Copper Dimethylaminoethoxide and Related Species

A glass tube with a glass-to-metal seal to a Cajon VCR fitting was used to hold standards for mass selective detector (MSD) analysis. The sample tube was mated with another tubing section containing a plug valve. Thus the alkoxide could be loaded into the tube in the dry box and remain isolated from the laboratory atmosphere. The tubing was connected directly to the mass spectrometer inlet. The sample was cooled with ice while the gas in the tube was evacuated. Then the ice was removed. The plug valve was opened briefly to introduce a sample to the mass spectrometer. The vapor pressure of the dimethylaminoethanol was sufficient at room temperature, but the alkoxide required warming with heating tape.

Mass spectral analysis proved less useful than hoped. The alcohol could not be distinguished from the alkoxide. Standard spectra for dimethylaminoethanol and copper dimethylaminoethoxide are shown in Figures 2.9 and 2.10. The base peak for both was 58 amu, $(\text{CH}_3)_2\text{NCH}_2^+$. Other common mass fragments showed no consistent difference in relative abundances. The parent alcohol mass, 89 amu, appeared in small amounts (about 4 per cent of the 58 amu peak) in both alcohol and alkoxide spectra. Alkoxy fragments would be expected from both species, and hydrogen is always present in a vacuum system. It is quite reasonable for fragments to acquire hydrogen atoms in the mass spectrometer.

The base peak at 58 amu is produced by α -cleavage initiated by a radical site on the nitrogen. Both the tertiary amine ion and the methoxy neutral are reasonably stable, so the high abundance of this peak is expected. The tertiary amine ion (58 amu) loses a neutral methyl radical (15 amu) to give a peak at 43 amu. Note that the $\text{CH}_2\text{-CH}_2$ bond is also activated for α -cleavage by the oxygen. There is a major peak at 30 amu, CH_2O^+ .

The peak at 44 amu is a combination of $\text{CH}_2\text{CH}_2\text{O}^+$ and $(\text{CH}_3)_2\text{N}^+$, which are formed by σ -bond dissociation. There may also be a contribution at 44 amu from residual carbon dioxide in the mass spectrometer and the reactor system. This should be constant during an experiment and can be eliminated by background subtraction. The 42 amu peak is probably produced by hydrogen loss from the organic fragments making up the 44 and 43 amu peaks. Methyl ions appear at 15 amu.

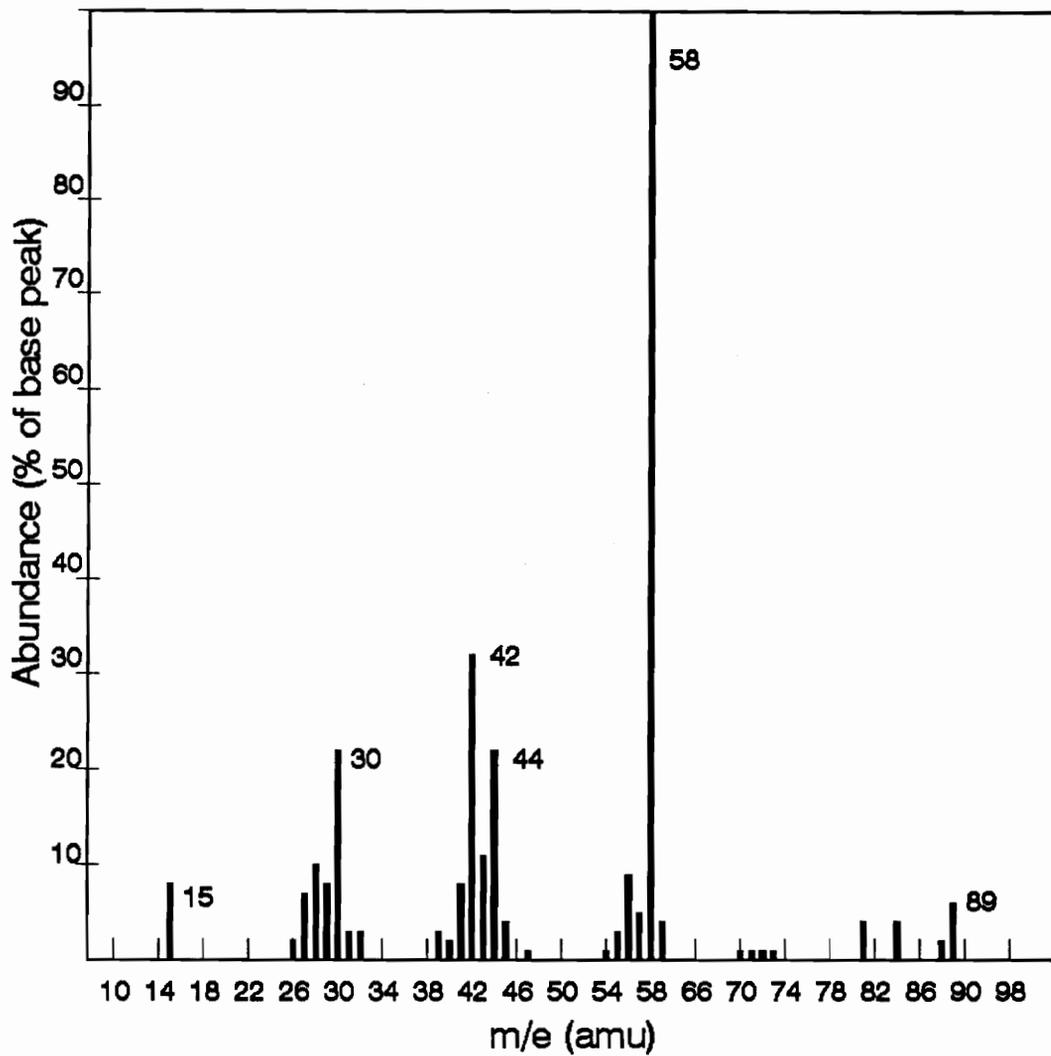


Figure 2.9 Mass spectrum of dimethylaminoethanol

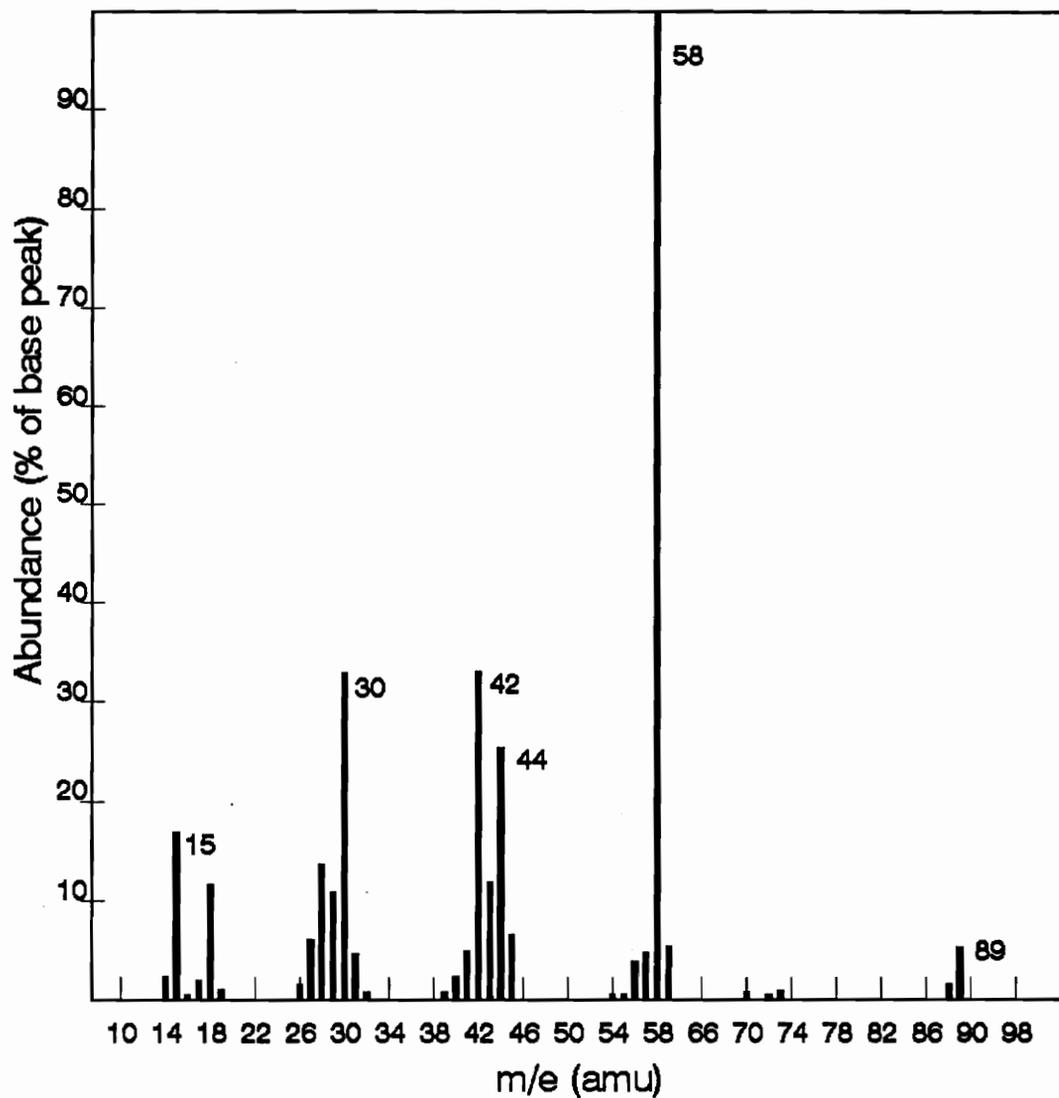


Figure 2.10 Mass spectrum of copper dimethylaminoethoxide

Neither the parent ion nor fragments containing copper atoms were observed in the standard spectra of the alkoxide. Copper-containing fragments are identifiable by the isotopic ratios of ^{63}Cu and ^{65}Cu . A fragment containing copper would have peaks in a ratio of 1.0 to 0.45, the second 2 amu heavier than the first. The ionization method may prevent detection of copper-containing fragments.

Copper atoms or copper-containing fragments may occur primarily as neutrals or negatives, which are not detected. This has been seen in mass spectral analysis of other metalorganics using electron impact ionization [31]. A standard spectrum, collected in the same manner, of copper (II) acetylacetonate also showed no evidence of copper-containing fragments. Copper acetylacetonate can be sublimed without decomposition and is not water-sensitive. These results suggest that premature decomposition of the precursor is not preventing copper-containing fragments from reaching the detector.

Because no copper-containing fragments are detected from the precursor, it is impossible to prove that the alkoxide precursor reaches the ionization chamber. One might argue that all of the precursor decomposes in the sample tube, and the spectra of the alkoxide and alcohol look so similar because they are, in fact, both spectra of the alcohol. However, electron impact ionization is known to be unsuitable for other metalorganics [31]. The available MSD can detect no copper-containing fragments from copper (II) acetylacetonate. The alkoxide transports through a longer and more tortuous path for successful deposition in the reactor than it does to reach the MSD from the sample tube. Thus, it is equally reasonable to argue that the alkoxide precursor does reach the ionization chamber. The alcohol and the alkoxide spectra look so similar because the ionization method, electron impact with 70 eV electrons, is too strong for most metalorganics.

Other ionization methods do exist. For example, chemical ionization generally results in less fragmentation, and might reveal the molecular ion. Although mass spectral analysis with chemical ionization is available on campus, it was decided that use of this technique to obtain a standard spectrum of the alkoxide was of very limited value to this project. Mass spectral analysis with chemical ionization is not available for integration into the

experimental flow system, so it would still be impossible to identify the alkoxide under deposition conditions.

Because of the nitrogen atom, all of the expected organic decomposition products have similar fragmentation patterns. The most abundant peak should be 58 amu for the aminoalkoxide, the aminoalcohol, the aminoaldehyde, dimethylethylamine, and trimethylamine. One must rely on small differences in the relative abundances of fragments to identify products. This identification becomes difficult with a multicomponent sample. Also, the relative ion abundances from a mass spectrometer are unreliable unless the instrument is running near steady state. Usually, pulsed samples were required to avoid flooding the instrument. Even when a low, steady flow was maintained, amine groups posed a problem. They are pumped more slowly than other species and tend to accumulate in the mass spectrometer. Their concentration increased gradually throughout any given experiment.

The mass selective detector proved most useful for identifying very low molecular weight products. For instance, CO or CO₂ in the IR spectrum might be due to a change in the bench atmosphere or the laboratory atmosphere. The mass selective detector samples only the reactor atmosphere.

2.7.5 Proton Nuclear Magnetic Resonance Spectroscopy

On occasion, the reactor outlet gas was passed through a liquid nitrogen trap, located between the mass selective detector sampling valve and the vacuum pump plug valve. After a deposition experiment was finished and the system flushed and cooled, the entire system, including the trap, was brought to atmospheric pressure with helium. The trap was then removed from the system and the inlet and outlet plugged with septa. The trap was placed in an ice bath to melt the condensed species. This required that one septa be removed briefly to release pressure in the trap. The melted condensate collected in the bottom of the trap and could be sampled with a syringe. The hope was that, by keeping the trapped products in an ice bath, secondary reactions between them would be reduced.

Condensed products were dissolved in deuterated chloroform and submitted for proton NMR analysis [32] to confirm infrared and mass spectroscopy analysis. The trap was kept in an ice bath or freezer until the solution was prepared, immediately before analysis, to minimize reactions and evaporation. Standard spectra of dimethylaminoethanol, dimethylamine, and acetaldehyde were collected for comparison.

Because NMR was a secondary technique, it will not be described in detail here. R. S. Macomber's book is a good source of information [33].

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3. Thermal Deposition from Copper (II) Dimethylaminoethoxide

3.1 Introduction

Large area films are commonly deposited by thermal chemical vapor deposition. The gas phase precursor passes over the hot substrate and decomposes. Volatile products leave the system while nonvolatiles deposit a film on the substrate. The chemistry of thermal decomposition affects the purity of the film. To avoid contamination by ligands or ligand fragments, there must be enough energy available as heat to break the desired bonds and to desorb unwanted products from the surface of the growing film.

Intuitively, this indicates that hotter is better, which is not necessarily the case. It might be desirable to leave the metal–ligand bond intact, but break the bond *alpha* to it, and deposit a multicomponent film such as aluminum nitride or copper oxide. High temperatures may break the ligand into less volatile fragments which contaminate the film. Also, the sensitivity of the substrate to high temperature must be considered.

With its high conductivity and resistance to electromigration, copper has potential microelectronics applications, if low-temperature deposition of pure films can be achieved. Copper oxide film growth is potentially important for semiconductor/high temperature superconductor hybrid technology.

The β -diketonates are popular copper MOCVD precursors. Copper (II) hexafluoroacetylacetonate, $\text{Cu}(\text{hfac})_2$, is frequently used because of its high volatility. However, $\text{Cu}(\text{hfac})_2$ is stable to 250°C [1]. At 250°C to 300°C, the diffusion of copper into silicon is significant, which is unacceptable for device manufacture [2]. A change of precursor might allow lower deposition temperatures.

Copper t-butoxide [3], copper β -diketonate trialkylphosphines [4], copper cyclopentadienyl trialkylphosphines [5], copper alkoxy trialkylphosphines [5], copper alkyne β -diketonates [6], fluorinated copper β -ketoimines [7], and copper β -diketonate cycloalkenes [8] have been tested for copper MOCVD. Of these, only copper β -diketonate trialkylphosphines and copper β -diketonate cycloalkenes are reported to deposit copper below 250°C. None are commercially available.

Copper (II) dimethylaminoethoxide, $\text{Cu}(\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2)_2$, is a commercially available, sublimable, water-sensitive solid. Each ligand forms a five-membered chelate ring with the central copper [9], binding to the copper *via* the nitrogen (lone pair association with the central metal ion) and the oxygen (covalent bond with the central metal ion). The alkoxide hydrolyzes to dimethylaminoethanol. This alcohol also has a five-membered ring structure, as the alcoholic proton hydrogen bonds intramolecularly with the lone pair on the nitrogen [10].

The decomposition temperature of copper dimethylaminoethoxide is reported to be either 184°C [9] or 120°C [11]. Thus, this aminoalkoxide may be useful for MOCVD at lower temperatures than $\text{Cu}(\text{hfac})_2$. A previous report suggests that copper dimethylaminoethoxide decomposes to a mixture of copper metal, copper (I) oxide, and copper (II) oxide when heated under nitrogen flow from 25 to 300°C over two hours [9]. This observation suggests that the as-deposited oxidation state of the film may be controlled by adjusting the deposition conditions. However, it leads to questions as to whether single oxidation state films can be deposited.

To investigate the possibility of using copper dimethylaminoethoxide as a low-temperature precursor for copper and/or copper oxides, a study of deposition chemistry as a function of temperature was undertaken. An unusual feature of this study is the use of infrared analysis *in situ* to identify gas phase products of the deposition reaction. Secondary chemical information comes from mass spectrometer analysis of the reactor exit gas and surface analysis of the film.

3.2 Experimental Methods and Procedures

The warm-wall stainless steel deposition reactor was evacuated by a direct-drive mechanical pump. The substrate was mounted on a resistance heater. The deposition reactor was also the infrared cell. The carrier gas and reactor window purge flows were helium at 5 sccm and 2 sccm, respectively. The precursor sublimed at 90 to 98°C. Deposition conditions were maintained for approximately 48 hours. The apparatus and procedures are described fully in Chapter 2. Preliminary deposition experiments were performed on quartz because of financial considerations. Strontium titanate was the substrate used for most of the

subsequent work. Thermal deposition results on strontium titanate were required for comparison to anticipated photoassisted deposition experiments.

Samples for Auger electron spectroscopy and X-ray photoelectron spectroscopy were stored in a vacuum dessicator until the instruments were available. Films stored in the dessicator showed less post-deposition contamination from carbon and oxygen than those held for similar times in air. However, the dessicator was a source of chlorine surface contamination, probably because residue from chemicals previously stored in the dessicator remained in the o-ring seal even after cleaning. This surface chlorine on the films could be removed by ion bombardment. Potassium and sodium were also detectable before ion bombardment, but were more quickly removed by ion bombardment than was chlorine.

3.3 Results of Preliminary Experiments

3.3.1 Spectral Standards

Standard vapor phase infrared and mass spectra of copper dimethylaminoethoxide and dimethylaminoethanol are discussed in detail in Chapter 2. The IR spectra are quite similar, but may be distinguished by differences in peak intensity and position that result from the substitution of copper for hydrogen. It is not possible to distinguish the alkoxide and the alcohol by mass spectral analysis in our experimental apparatus. No copper-containing fragments are detected.

Certain of the possible volatile decomposition products of the alcohol and alkoxide (formaldehyde, acetaldehyde, dimethylethylamine, acetone) can be purchased commercially and handled readily in the experimental system. Standard vapor phase infrared and mass spectra of these compounds were collected to allow their identification in spectra collected during deposition. These standard spectra will not be discussed in detail, but will be referred to in the analysis of experimental results. Collected standards were consistent with published standards [12]. No published standards are available for the alkoxide.

Standard proton nuclear magnetic resonance (NMR) spectra of dimethylaminoethanol, dimethylethylamine, and acetaldehyde in deuterated chloroform were also collected for comparison to spectra of species condensed from the reactor outlet gas during deposition.

3.3.2 Reactions of Dimethylaminoethanol Under Deposition Conditions

Because the alcohol and alkoxide both include the aminoalkoxy group, the behavior of the alcohol under deposition conditions may be related to the alkoxide deposition chemistry. Also, the alcohol is a potential decomposition product of the alkoxide, and may undergo secondary decomposition reactions. This experiment allows identification of products that may be formed by the alcohol alone.

Dimethylaminoethanol was placed in the precursor tube. The precursor tube was unheated, because the alcohol has sufficient vapor pressure at room temperature to maintain a vapor phase concentration in the reactor that was clearly visible by IR. The rest of the reactor system was heated as for a deposition. The substrate was single crystal strontium titanate. The substrate temperature was ramped from 80°C to 355°C. Infrared spectra of volatile species in the reactor were collected at intermediate substrate temperatures. Mass spectral analysis of the reactor outlet gas was performed concurrently.

As expected, no copper deposited in this experiment. This confirmed that successful deposition was due to the presence of the alkoxide. There was some concern initially that the presence of reactive alkoxy species and hot heater leads might lead to some source for copper deposition other than decomposition of the alkoxide originally fed. This experiment shows that copper is not deposited from the reactor hardware under deposition conditions.

At substrate temperatures below 150°C, infrared spectra show gaseous dimethylaminoethanol and no other species. At 150°C, a small peak appears at 1750 cm⁻¹. Aside from this peak, there is no change in the spectrum. Refer to Figure 3.1a. At substrate temperatures near 200°C, the peak at 1750 cm⁻¹ is more intense, as seen in Figure 3.1b. This peak is narrow, nearly symmetric, and centered at 1750 cm⁻¹ for stage temperatures of 150°C to 355°C.

The next new features appear in the IR spectrum at about 350°C. Figure 3.1c shows a small peak near 1640 cm⁻¹, which may be a C=N or C=C stretch. Imines do absorb in this region [13], as do carbon-carbon double bonds [14]. The location of the peak is difficult to pinpoint because it is small and broad, and easily distorted by noise or water in the spectrum.

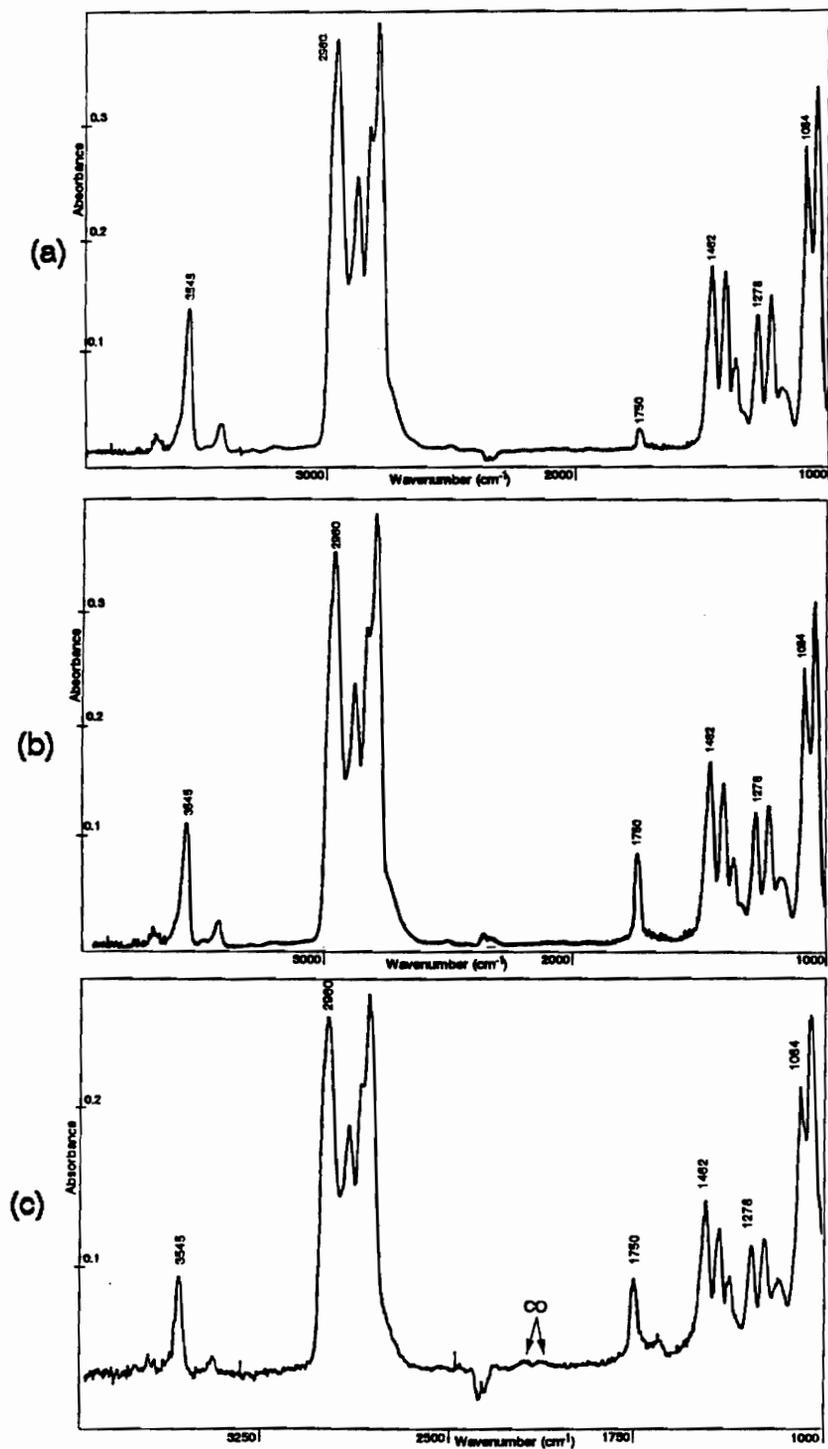


Figure 3.1 Infrared spectra, decomposition of dimethylaminoethanol at (a) 150°C, (b) 200°C, and (c) 355°C

There is no basis for a conclusive identification of this species. There is also a small feature indicative of carbon monoxide just below 2300 cm^{-1} . There are no other changes in the IR spectrum. There is no mass spectral evidence for new species. Again, dimethylaminoethanol is the predominant species in the mass spectrometer trace.

A peak at 1750 cm^{-1} is characteristic of a vapor-phase aldehyde or ketone C=O stretch. Apparently, oxidative dehydrogenation of the alcohol to an aldehyde begins at 150°C . Likely aldehyde products are dimethylaminoaldehyde ($(\text{CH}_3)_2\text{NCH}_2\text{CHO}$), formaldehyde (CH_2O), and acetaldehyde (CH_3CHO). No skeletal rearrangements are necessary to form these aldehydes.

A ketone product is unlikely because its formation involves either migration of the oxygen on the ligand, or formation of a carbon – carbon bond to couple ligand fragments or to couple a ligand fragment and a whole ligand. Production of ketones from primary alkoxy species has not been observed over copper or copper (I) oxide [15-18], titanium oxide (TiO_2) [19], or zinc oxide (ZnO) [20]. Primary alkoxy species on strontium titanate have not been studied, so it is possible that migration or coupling reactions to form ketones do occur on this surface. However, it seems unlikely.

Carbon – oxygen double bond stretching vibrations absorb infrared strongly. Their signals are often the most intense in a single-component spectrum. The carbonyl stretch also occupies a unique region in the infrared spectrum, so it is visible even in a complex or multicomponent system. The identity of the carbonyl-containing compound must be determined from the position of the carbonyl stretch and from other peaks in the spectrum. Note that the position of the carbonyl stretch can change by up to 30 cm^{-1} for the same species in the liquid and the gas phase [21].

The spectrum of the vapor phase alcohol was scaled and subtracted from the spectrum taken of the alcohol over 200°C strontium titanate. The scaling factor was chosen to reduce the peak near 3545 cm^{-1} to the level of noise in the spectrum. This may result in a slight oversubtraction, as an overtone of the carbonyl stretch is expected in this region [22]. However, the overtone intensity is usually about one per cent of the carbonyl stretch intensity

[22], so any oversubtraction should be quite small. The resulting difference spectrum is considered to be the spectrum of the carbonyl-containing product (Figure 3.2).

The difference spectrum was compared to the vapor phase spectra of acetone, formaldehyde, acetaldehyde, and dimethylethylamine which were obtained in this laboratory. The difference spectrum was also compared to published vapor phase spectra for dimethylamine, trimethylamine, propionaldehyde, methyl ethyl ketone, diethyl ketone, and ammonia [23]. None of these species matched the difference spectrum. The peaks in the difference spectrum are consistent with those expected for dimethylaminoethanal. Unfortunately, it was not possible to obtain either dimethylaminoethanal itself or a published standard spectrum.

Although formation of a ketone is unlikely, several ketones were considered for the sake of completeness. The carbonyl stretches of acetone, methyl ethyl ketone, and diethyl ketone are positioned similarly to the carbonyl stretch of the unidentified product. However, the peaks of these ketones between 1000 cm^{-1} and 1500 cm^{-1} are not similar to peaks in the difference spectrum between 1000 cm^{-1} and 1500 cm^{-1} . Acetone is particularly unlikely because its C–H stretches occupy a higher range than the C–H stretches of the difference spectrum. Although the C–H stretches of the other ketones do overlap the high frequency (about 2970 cm^{-1}) C–H stretches of the difference spectrum, they lack the two-pronged appearance seen in the difference spectrum (peaks at about 2970 cm^{-1} and at about 2790 cm^{-1}). Similarly shaped C–H stretches are seen for amines and higher aldehydes [23]. The unidentified product is not a ketone, but an aldehyde.

The vapor phase formaldehyde carbonyl stretch is centered at 1745 cm^{-1} , not far off from the carbonyl stretch of the aldehydic product derived from dimethylaminoethanol. (With a boiling point of -21°C , formaldehyde will not condense in the system.) However, formaldehyde's C–H stretches, $2720 - 2900\text{ cm}^{-1}$, are more intense than the carbonyl stretch. Their absence from the spectrum rules out formaldehyde as a decomposition product. The absence of the formaldehyde C–H bending modes, centered at 1503 cm^{-1} and one-third of the intensity of the carbonyl stretch, confirms this analysis. In addition, the carbonyl stretch of formaldehyde consists of two large lobes at 1775 cm^{-1} and 1715 cm^{-1} , not at all consistent with the shape of the unidentified carbonyl stretch. The product aldehyde is not formaldehyde.

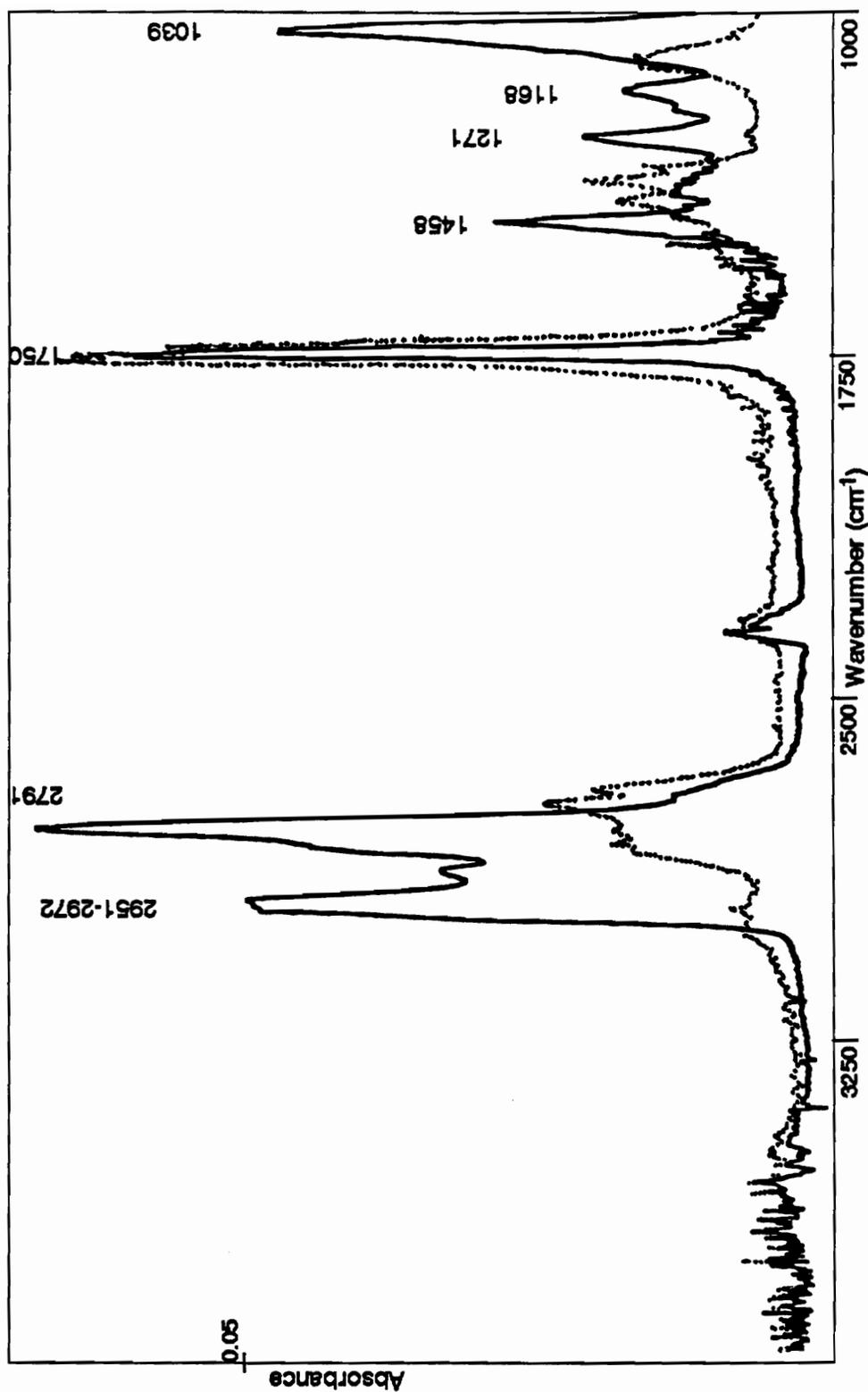


Figure 3.2 Difference spectrum, product of dimethylaminoethanol decomposition at 200°C (solid line), compared to vapor phase acetaldehyde (broken line)

The carbonyl stretch of vapor phase acetaldehyde is centered near 1750 cm^{-1} , consistent with the unidentified aldehyde. (With a boiling point of 21°C [24a], acetaldehyde will not condense in the system.) Acetaldehyde has peaks at 1380 cm^{-1} and 1130 cm^{-1} that are about one third of the intensity of the acetaldehyde C=O stretch. These peaks are not present in the difference spectrum. The C=O stretch of acetaldehyde is broader than the stretch of the unidentified aldehyde (about twice the full width at half maximum). Formation of acetaldehyde suggests formation of an equal amount of dimethylamine. Although some peak positions of dimethylamine match those in the difference spectrum, the peak shapes are drastically different. The aldehyde produced from dimethylaminoethanol above 150°C is not acetaldehyde.

Propionaldehyde has peaks at 2993 cm^{-1} , 1423 cm^{-1} , and 1105 cm^{-1} . These peaks are not similar in position or shape to the difference spectrum peaks at 2970 cm^{-1} , 1458 cm^{-1} , 1270 cm^{-1} , 1167 cm^{-1} , and 1040 cm^{-1} . The difference spectrum is not that of propionaldehyde.

There are no standard spectra of dimethylaminoethanal available. The IR spectrum would probably look quite similar to the dimethylaminoethanol spectrum, although peaks related to C–O stretches should be absent. The carbonyl stretch of dimethylaminoethanal is expected to appear between 1720 cm^{-1} and 1780 cm^{-1} , like other aldehydes. Aldehydic C–H stretches are weak and consist of two lobes, one at 2830 cm^{-1} to 2810 cm^{-1} and one near 2720 cm^{-1} [25]. These aldehydic C–H stretches are easily overlapped by C–H stretches of other structural groups. This is clear in Figure 3.2, which compares the difference spectrum to the spectrum of vapor phase acetaldehyde.

The difference spectrum has one peak between 1000 cm^{-1} and 1100 cm^{-1} . This frequency range is empty for the standard aldehydes and ketones examined. However, the broad and asymmetric peak due to the C–N stretch of trimethylamine, dimethylethylamine, and methyldiethylamine appears between 1040 cm^{-1} and 1060 cm^{-1} . The peak at 1040 cm^{-1} in the difference spectrum can reasonably be assigned to a C–N stretch.

Most of the peaks between 1100 cm^{-1} and 1500 cm^{-1} in the dimethylaminoethanol spectrum have been assigned to wagging and bending modes of methyl and methylene groups. Most wagging and bending motions should be strongly affected by the conformation of the molecule. Dimethylaminoethanol exists primarily as a five-membered ring in the vapor phase. Such a ring configuration is not expected for dimethylaminoethanal. The 1100 cm^{-1} to 1500 cm^{-1} frequency range also includes C-N stretches, which should be affected by the change from ring to chain conformation. Noticeable differences are expected between the alcohol and aldehyde spectra between 1100 cm^{-1} and 1500 cm^{-1} .

Except for the carbonyl stretch, the difference spectrum and the spectrum of dimethylethylamine, $(\text{CH}_3)_2\text{NCH}_2\text{CH}_3$, are very similar, especially between 1000 cm^{-1} and 1500 cm^{-1} . The bending and wagging motions of methyl and methylene groups in this tertiary amine should approximate those in dimethylaminoethanal, $(\text{CH}_3)_2\text{NCH}_2\text{CH}=\text{O}$. A better match would be expected between dimethylethylamine and dimethylaminoethanal in this range than between dimethylaminoethanol and dimethylaminoethanal. It should be noted that the difference spectrum cannot be reproduced by adding the spectra of dimethylethylamine and any of the aldehydes or ketones considered as possible products.

Mass spectral analysis shows no clear evidence for formaldehyde (most abundant fragments 29, 30 amu) or acetaldehyde (most abundant fragments 29, 44 amu). Unfortunately, the fragmentation pattern of the aminoalcohol overlaps the patterns of its potential decomposition products. The base peak of the alcohol, 58 amu, is also the base peak for trimethylamine, dimethylethylamine, and dimethylaminoethanol, and the expected base peak for dimethylaminoethanal. Unique peaks, such as the parent mass of the alcohol, are too small to be used reliably to estimate the appropriate abundance for other fragments and subtract the contributions of dimethylaminoethanol. Mass spectral analysis of the reactor outlet gas is inconclusive, but does not contradict the evidence of infrared analysis.

By comparison with standards, a number of plausible carbonyl species are shown not to be products of dimethylaminoethanol decomposition over strontium titanate at 150°C and above. The infrared spectrum of the product is consistent with that expected for dimethylaminoethanal. Mass spectral analysis offers no contradiction. As will be discussed later, dimethylaminoethanal is also the product most consistent with the known chemistry of

alkoxy species. Thus, the product of dimethylaminoethanal decomposition which gives rise to a peak at 1750 cm^{-1} is identified as dimethylaminoethanal.

Admittedly, this identification is indirect. Positive identification is impossible without standard spectra of dimethylaminoethanal. Dimethylaminoethanal is the product most consistent with all of the experimental evidence and with the known chemistry of alkoxy species. Results of deposition experiments support the identification of the species having an infrared peak at 1750 cm^{-1} as dimethylaminoethanal.

In summary, thermal decomposition of dimethylaminoethanol to an aldehyde begins at a substrate temperature of 150°C over strontium titanate in the deposition reactor. The aldehyde is identified as dimethylaminoethanal. A high temperature product, which may contain a carbon – nitrogen or carbon – carbon double bond, is formed above 350°C . Further identification of the high temperature product was not possible with the on-line analytical instrumentation.

3.3.3 Decomposition of Copper Dimethylaminoethoxide

The purpose of this experiment was to obtain a preliminary idea of the changes in chemistry with temperature in the thermal decomposition of the precursor. It also provides control data for later thermal deposition experiments. Possible catalytic activity of metal surfaces in the reactor was a concern initially. This concern was unfounded, as data obtained during deposition is consistent with this control experiment.

Copper (II) dimethylaminoethoxide was placed in the precursor tube and the system prepared as for deposition. However, the substrate was not heated resistively. Instead, the temperature of the precursor tube was ramped from room temperature to 230°C under vacuum with the usual flow of helium carrier gas. The precursor decomposed in the precursor tube. The volatile species leaving the tube were analyzed as they passed through the reactor. There was no deposition on the substrate.

Below 150°C , infrared analysis shows copper (II) dimethylaminoethoxide. At a precursor tube temperature of 150°C , the spectrum is still typical of the alkoxide, but a small

peak near 1750 cm^{-1} appears (Figure 3.3a). This product is assigned as the dimethylaminoethanal identified in the alcohol decomposition study.

At 180°C , the aldehyde peak is more obvious. Other peaks begin to change in intensity and position, indicating a mixture of the alkoxide and alcohol. For example, peaks at 1090 cm^{-1} and 1032 cm^{-1} , characteristic of the alkoxide, are now at 1087 cm^{-1} and 1034 cm^{-1} . The values for the alcohol are 1084 cm^{-1} and $1044/1038\text{ cm}^{-1}$ (doublet). Refer to Figure 3.3b.

With the precursor tube at 210°C (Figure 3.3c) the spectrum is dominated by the alcohol. The peak at 1750 cm^{-1} is strong, and a new peak is just visible above the background near 1640 cm^{-1} . The 1640 cm^{-1} peak may indicate $\text{C}=\text{N}$ or $\text{C}=\text{C}$, as observed in the alcohol reaction studies described previously. The only change in the infrared spectra as the tube temperature reaches 230°C is a moderate increase in the 1640 cm^{-1} peak intensity. The same product results from decomposition of dimethylaminoethanol at a substrate temperature of 350°C . It is curious that this product appears at a much lower temperature by decomposition of the copper alkoxide.

One explanation for the low-temperature appearance of the 1640 cm^{-1} peak is a concentration effect. In the alcohol decomposition experiment, decomposition takes place only at the hot sample stage, a small fraction of the total volume of the IR cell. The species that absorbs at 1640 cm^{-1} may be produced, but at levels undetectable by the IR. In this alkoxide decomposition experiment, decomposition takes place in the precursor tube itself. A larger fraction of the molecules in the IR cell are decomposition products. The species which absorbs at 1640 cm^{-1} is present in detectable amounts.

Another explanation for the low-temperature appearance of the 1640 cm^{-1} peak is more chemistry related. Studies of propoxy species adsorbed on copper (110) [16], copper (I) oxide (100) [18], titanium oxide (001)-{110} [19], and zinc oxide (0001) [20] in UHV indicate that the propoxy group binds via its oxygen to a metal atom, forming a metal alkoxide on the surface. On each surface, the propoxy group decomposes at a different temperature. ($\text{Cu}\rightarrow 70^\circ\text{C}$. $\text{Cu}_2\text{O}\rightarrow 250^\circ\text{C}$. $\text{TiO}_2\rightarrow 310^\circ\text{C}$. $\text{ZnO}\rightarrow 220^\circ\text{C}$.) This is reasonable, because different metal alkoxides decompose at different temperatures.

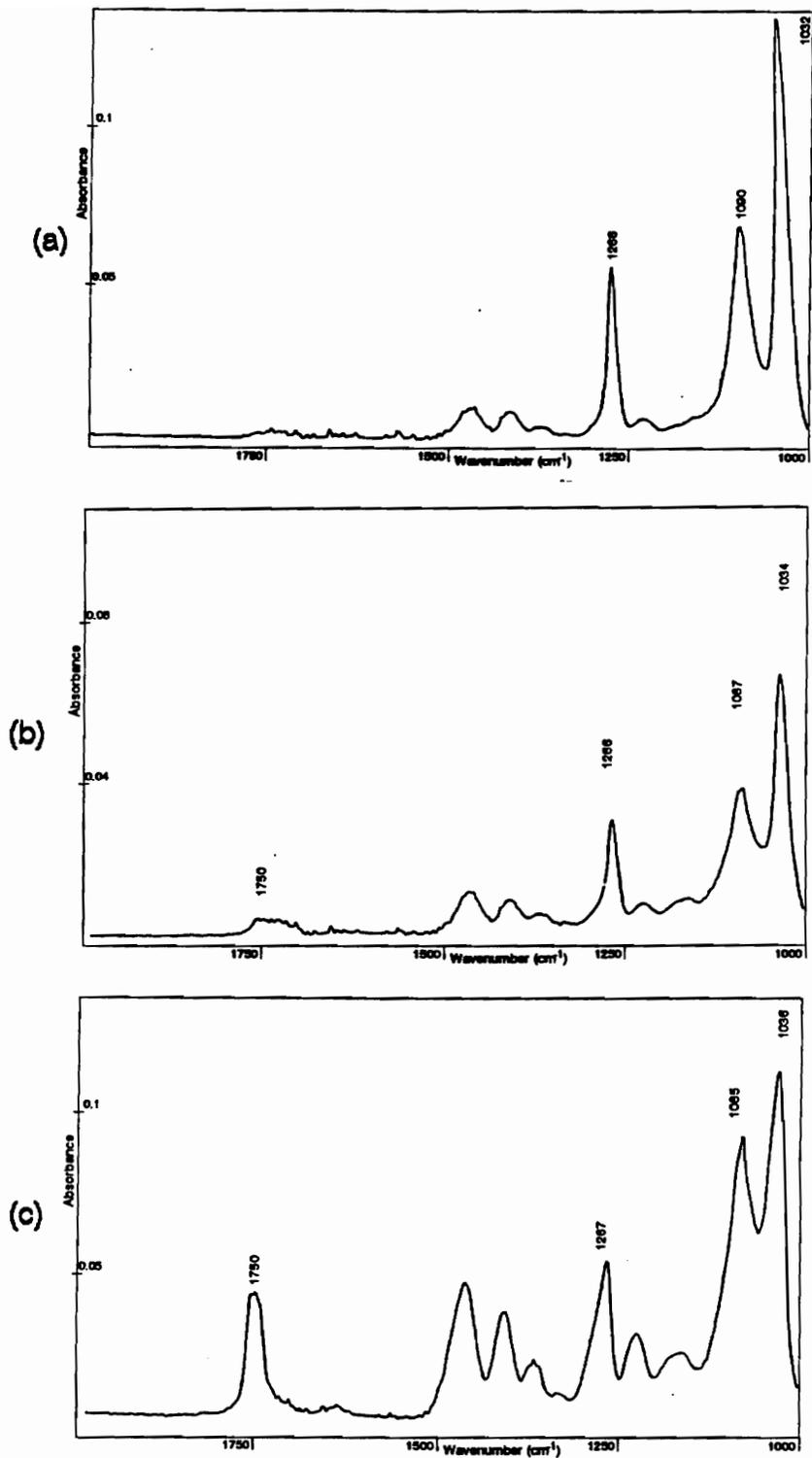


Figure 3.3 Infrared spectra, decomposition of copper dimethylaminoethoxide at (a) 150°C, (b) 180°C, and (c) 210°C

The current experiment involves decomposition of a copper alkoxide. The preliminary experiment with dimethylaminoethanol the same alkoxy species, but with a strontium or titanium metal center. It is not surprising that the product giving rise to a band at 1640 cm^{-1} should appear at different temperatures for copper, strontium, and titanium alkoxides. In fact, it is surprising that the product having a band at 1750 cm^{-1} does appear at nearly the same temperature in the alcohol and aldehyde decompositions.

Examination of the peak near 1750 cm^{-1} reveals that at 180°C (Figure 3.3b), it is not the sharp peak centered at 1750 cm^{-1} that is expected from dimethylaminoethanol decomposition experiments. It is broader and flatter. It looks rather like two peaks, the expected peak at 1750 cm^{-1} and another centered near 1725 cm^{-1} . The low frequency peak is not an artifact of low aldehyde concentration. Carbonyl stretches of similar intensity in the dimethylaminoethanol decomposition experiments are nearly symmetric and centered at 1750 cm^{-1} . There is nothing else in the spectrum to indicate a new product.

The 1725 cm^{-1} peak appears in most experiments involving copper dimethylaminoethoxide, but not in experiments involving only the alcohol. It is in the correct region for a carbonyl stretch. Comparison with standards shows it is not acetaldehyde or formaldehyde. This carbonyl species is discussed in Section 3.5.1.1, after results of all thermal deposition experiments have been detailed.

Spectra collected at precursor tube temperatures below 150°C were subtracted from spectra for precursor tube temperatures above 150°C . Dimethylaminoethanol was then subtracted to obtain the final difference spectrum. This difference spectrum looks substantially like the one obtained for decomposition of the alcohol in section 3.3.2. By the same reasoning employed in section 3.3.2, the product of copper dimethylaminoethoxide decomposition above 150°C is identified as dimethylaminoethanal. Admittedly, the reasoning behind this identification is indirect. However, it is the identification most consistent with all of the experimental data and with the known chemistry of alkoxy species.

In ruling out ketones as potential products, it should be noted that coupling of alkoxy species to form ketones has not been observed on copper or copper (I) oxide surfaces, nor has

migration of the oxygen in a primary alkoxy species [15-20]. Copper (II) oxide surfaces have not been studied, so it is possible that the presence of copper (II) in the precursor allows formation of ketones. However, it seems unlikely, especially since the same product is produced by decomposition of dimethylaminoethanol over strontium titanate.

By the end of the experiment, the precursor tube is coated inside with a deposit ranging in color from yellow to rose-red, suggestive of copper metal and/or copper (I) oxide. The red regions turned black, a color characteristic of copper (II) oxide, shortly after exposure to laboratory air. The deposits dissolved quickly in aqua regia, but appeared untouched by acetone. This suggests the deposits were largely inorganic, not organic. Thus, there is qualitative evidence for deposition of mixed oxidation state copper on the tube walls. Analysis of purity and oxidation state was impossible without breaking the tube. It was decided that analysis of films deposited at constant temperature would be more valuable.

In summary, copper dimethylaminoethoxide begins to decompose at 150°C to dimethylaminoethanal, the same aldehyde produced from dimethylaminoethanol at this temperature. Another carbonyl species is also apparent in the infrared spectrum. As the tube temperature approaches 200°C, significant dimethylaminoethanol is detected as well as dimethylaminoethanal. Above 210°C, a new product appears, which may contain a carbon-nitrogen or carbon-carbon double bond. This is probably the same product formed by the alcohol, and may involve fragmentation of the alkoxide ligand.

3.3.4 Deposition on a Quartz Substrate

This experiment was performed to demonstrate that copper dimethylaminoethoxide could be sublimed, moved through the system, and decomposed in the reactor to deposit a film. An indication of the film properties to be expected was obtained. Deposition was performed on quartz at 270–280°C. Preliminary experiments indicated that copper dimethylaminoethoxide would decompose at this temperature. The resulting films were opaque, red, and non-conductive. Infrared and mass spectral data were obtained during deposition. Figure 3.4 is a typical IR spectrum.

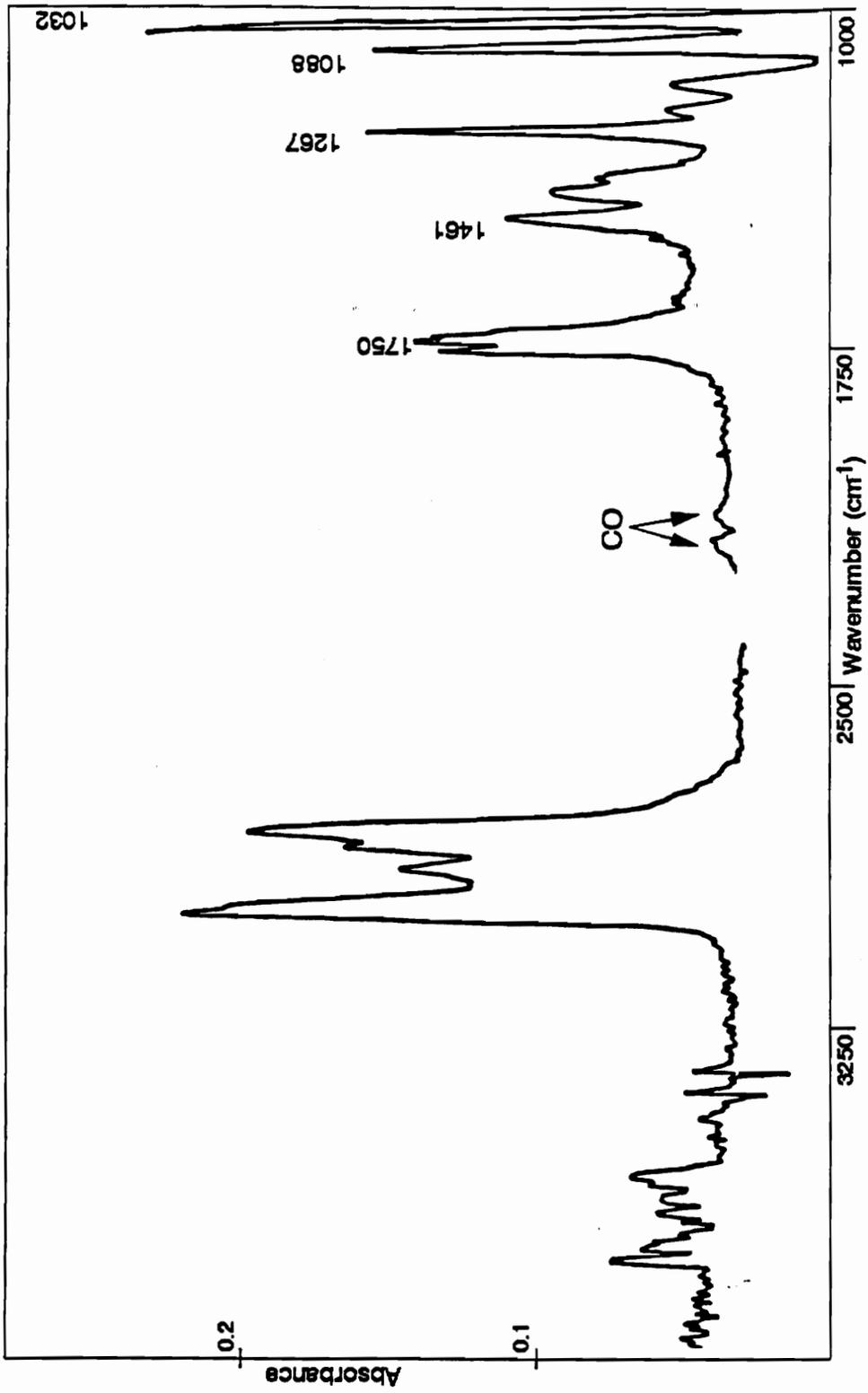


Figure 3.4 Infrared spectrum during deposition on quartz, 280°C

The film compositions were characterized by X-ray photoelectron spectroscopy in conjunction with ion bombardment for depth profiling. The oxidation state of the copper was deduced from the positions and shapes of the copper 2p and copper LVV Auger transition peaks [16]. Collection of spectra was alternated with ion bombardment until no oxygen or copper oxides were detected, which indicates removal of all surface contamination. Silicon was not detected, so the substrate was not yet exposed by ion bombardment. Such a spectrum is considered characteristic of the bulk film.

The carbon-to-copper atomic ratios ranged from 0.5 to 0.7 in the bulk film. No nitrogen was detected. This surface analysis data indicates that dimethylaminoethoxy ligands fragment at 280°C, and carbon fragments are included in the films.

With the substrate at 280°C, an aldehyde species was detected by infrared spectroscopy. This carbonyl stretch is actually two peaks, one at 1750 cm^{-1} and one at 1725 cm^{-1} . The same two species were seen in the preliminary experiments. The 1750 cm^{-1} peak represents dimethylaminoethanal. The other peak is discussed in Section 3.5.1.1, after all of the deposition results have been detailed.

Peaks other than the carbonyl stretch indicate a mixture of dimethylaminoethanol and copper dimethylaminoethoxide in the reactor, as well as carbon monoxide (two lobes near 2150 cm^{-1}). Mass spectral analysis of the reactor exit gas confirms that carbon monoxide is produced at 280°C and shows an accompanying production of carbon dioxide. Signals at 28 amu (CO) and 44 amu (CO₂) are three to four times as intense as the signal at 58 amu (base peak for dimethyl tertiary amines) with the substrate at 280°C. When the substrate is cooled to 100°C, the mass spectrum closely resembles the standard spectra of dimethylaminoethanol and copper dimethylaminoethoxide (Figure 2.9, Figure 2.10). (Infrared analysis is an unreliable indicator of carbon dioxide production, because of interference from carbon dioxide in the bench but outside the reactor.) Production of these small, carbon-containing species is consistent with ligand fragmentation.

It is difficult to tell whether there is a peak at 1640 cm^{-1} . The low frequency baseline is unstable because a constant stage temperature was not maintained during these

experiments. Wide variations in the substrate temperature can affect the reactor temperature. Experience has shown that the baseline tends to curve when the temperature of the reactor changes more than a few degrees.

When the substrate is cooled to 100°C, infrared signals from carbon monoxide and carbonyl species disappear. Other peaks in the spectrum (copper dimethylaminoethoxide, some dimethylaminoethanol) remain. When the substrate returns to 280°C, the carbon monoxide and aldehyde signals also return. Thus decomposition occurs at the hot substrate, not elsewhere in the system.

The alkoxy ligands fragment, but no nitrogen is included in the films, so volatile nitrogen-containing species must be produced. Possibilities are ammonia, methylamine, dimethylamine and dimethylethylamine. None of these are detected by IR or mass spectral analysis.

Ammonia has a distinctive IR spectrum. It should be visible if present in detectable amounts. With its most abundant peak at 17 amu, ammonia should also be detectable by mass spectrometry. Water is the other significant contributor to mass 17, and the ratio of 17 to 18 amu for water is a constant. There is no deviation from this value in the data. The evidence is against ammonia.

Signals from the amines could be hidden amongst the alkoxide and alcohol peaks in the IR spectra. Small amounts of the amines are not detectable by mass spectrometry. Their patterns would be lost among the fragments of the more plentiful dimethylaminoethoxy species as well as carbon dioxide and carbon monoxide. Some amine or amines must be removing nitrogen from the growing film, but they are not detectable with the available analytical instrumentation.

In summary, deposition of copper from copper dimethylaminoethoxide was performed on quartz at 280°C. Films are heavily contaminated with carbon, although complete ligands were not entrapped. Major volatile products at this temperature are dimethylaminoethanol and dimethylaminoethanal. Other volatile products include carbon monoxide, carbon dioxide, and possibly an amine. Ligand fragmentation is a significant problem, resulting in carbon-contaminated films.

3.4 Results of Thermal Deposition on Strontium Titanate

Based on the results of the preliminary experiments, substrate temperatures of 150°C, 200°C and 260°C were selected for study. No deposition is expected below 150°C. Deposition is expected at 260°C, but contamination due to ligand fragmentation is a possibility. At 200°C, deposition is expected, but decomposition is not expected to involve significant ligand fragmentation. Preliminary experiments showed that the major products at 200°C are dimethylaminoethanol and dimethylaminoethanal, formation of which involves only cleavage of copper – oxygen bonds. High film purity is expected at 200°C.

3.4.1 Results at 150°C

As expected, no deposition occurred at substrate temperatures below 150°C. Deposition at 150°C resulted in translucent, non-conductive yellow films. Auger analysis shows the films to contain copper and to be very thin. The titanium signal from the substrate is clearly visible after short ion bombardment. Chlorine and carbon are present and decreasing throughout the films. This suggests that post-deposition contamination persists throughout the films, and no region in the depth profile is identifiable as characteristic of bulk film. Thus, it is impossible to determine the oxidation state of the as-deposited films.

Infrared analysis during deposition shows a small peak near 3545 cm^{-1} , barely visible amongst the water signal and the noise. (Water appears in the spectrum because the overall intensity is low, and small variations in the quantity of water in the bench are noticeable.) This indicates dimethylaminoethanol is formed. The amount is small, because most peaks in the spectrum are characteristic of the pure alkoxide. The 1750 cm^{-1} carbonyl stretch is present only in early spectra. The lower-frequency stretch (1725 cm^{-1}) is quite small but present throughout the two days of an experiment. Figure 3.5 is a typical IR spectrum. Note that the substrate has a yellow cast after twelve hours, and does not change further in color. Thus the 1750 cm^{-1} peak, which has been identified as dimethylaminoethanal, is associated with deposition. The 1725 cm^{-1} peak persists even when there is no apparent deposition occurring. Mass spectral analysis added no information.

In summary, copper (II) dimethylaminoethoxide produces thin, copper-containing films at a minimum deposition temperature of 150°C. The films are non-conductive and so thin that post-deposition contamination makes it impossible to evaluate the purity of the as-deposited film. Organic products of the deposition reaction are dimethylaminoethanal and dimethylaminoethanol.

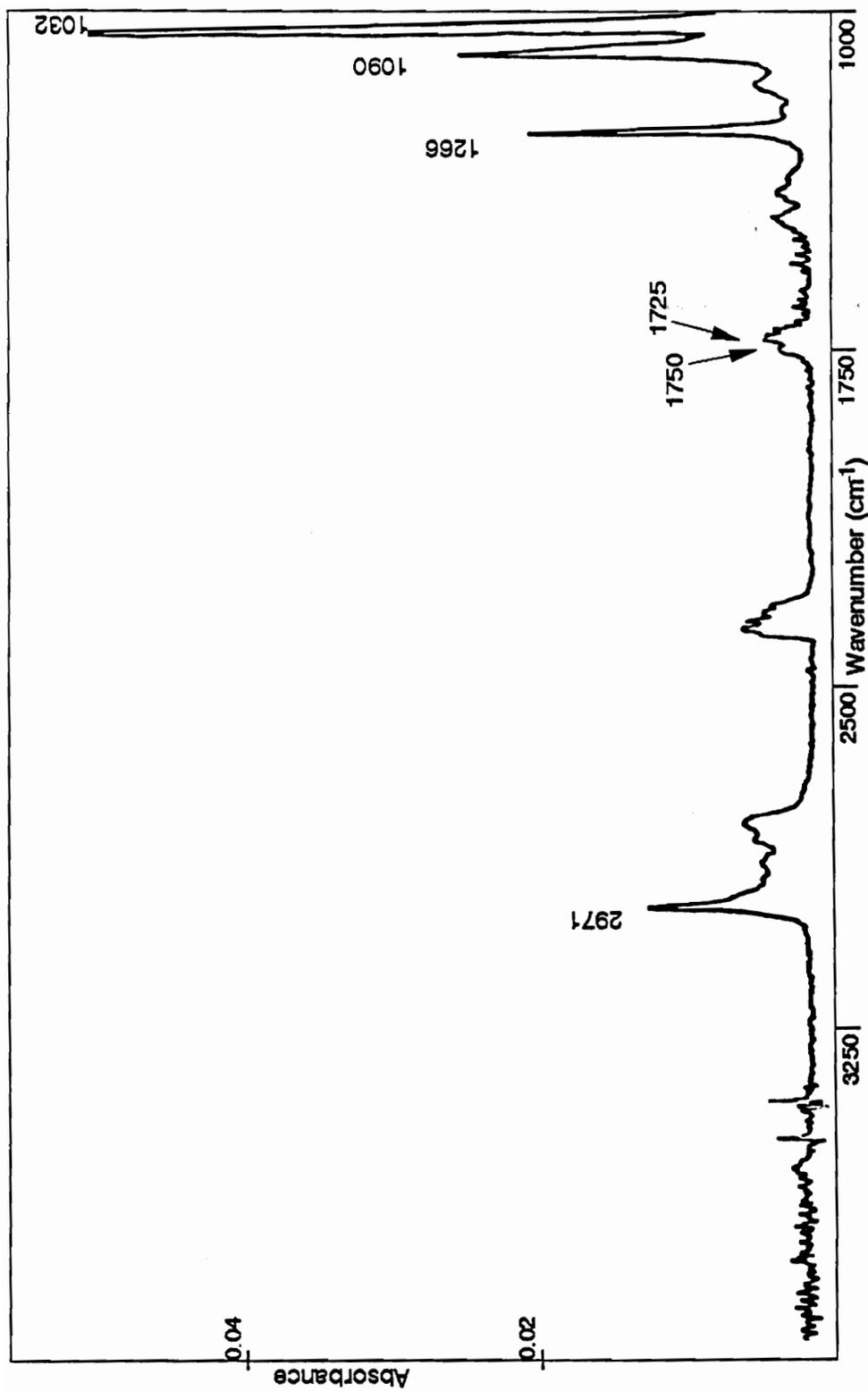


Figure 3.5 Infrared spectrum during deposition on strontium titanate, 150°C

3.4.2 Results at 200°C

Deposition occurs on strontium titanate at substrate temperatures of 200°C to 210°C. The substrate appears to be evenly coated with a pink, opaque, conductive film. Resistivities on the order of $200 \mu\Omega \cdot \text{cm}$ were measured by four-point probe [26]. A film stored in laboratory air darkened to a rose color over three weeks. After ten weeks, the film was nearly black. Surface analysis was performed on this film after one week of exposure to air. Surface analysis results for the bulk film were in agreement with those for a film stored in the vacuum desiccator for one week.

Auger analysis of the films was performed after a short ion bombardment to remove post-deposition contaminants. Figure 3.6 is a typical Auger spectrum. Carbon and nitrogen are below detectable levels (less than 1 atomic per cent). The small amount of oxygen present may be due to recontamination of the surface by oxygen in the vacuum system between ion bombardment and analysis. This phenomenon is common on nickel and aluminum surfaces [27]. Figure 3.7 shows the copper 2p and copper LVV peaks collected during XPS. The absence of shakeup satellites in the copper 2p region and the shape and position of the copper LVV Auger transition peak confirm that copper metal is the only oxidation state present [28].

Scanning electron microscopy (SEM) reveals a film of uniform, spheroid grains, between $0.25 \mu\text{m}$ and $0.5 \mu\text{m}$ in diameter, densely packed on the smooth, strontium titanate surface [29]. The film appears to be about $1 \mu\text{m}$ thick. Adhesion of the film to the substrate is poor. The film is easily scratched.

The IR spectrum (Figure 3.8) shows primarily copper dimethylaminoethoxide. Dimethylaminoethanol is one decomposition product. Both the narrow 1750 cm^{-1} and the broader 1725 cm^{-1} carbonyl stretches are present. At 200°C to 210°C, the 1750 cm^{-1} peak is more intense relative to experiments at 150°C. The 1750 cm^{-1} peak also persists throughout the two days of an experiment. During this time, the film becomes increasingly rich in color. Again, the 1750 cm^{-1} peak is associated with deposition. The 1725 cm^{-1} peak is also present throughout the experiment, at a small but fairly constant intensity.

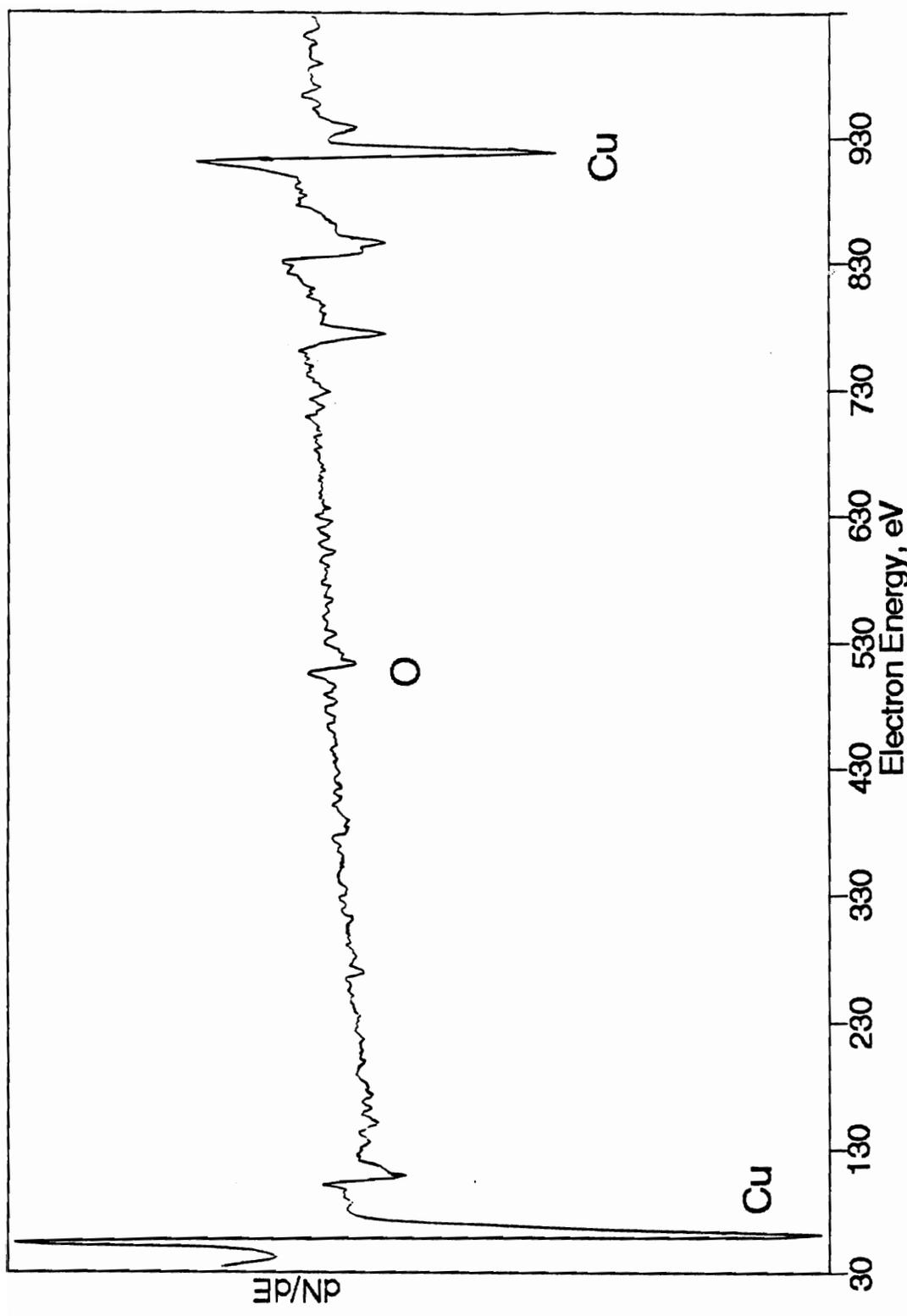


Figure 3.6 Auger spectrum of film grown on strontium titanate at 200°C

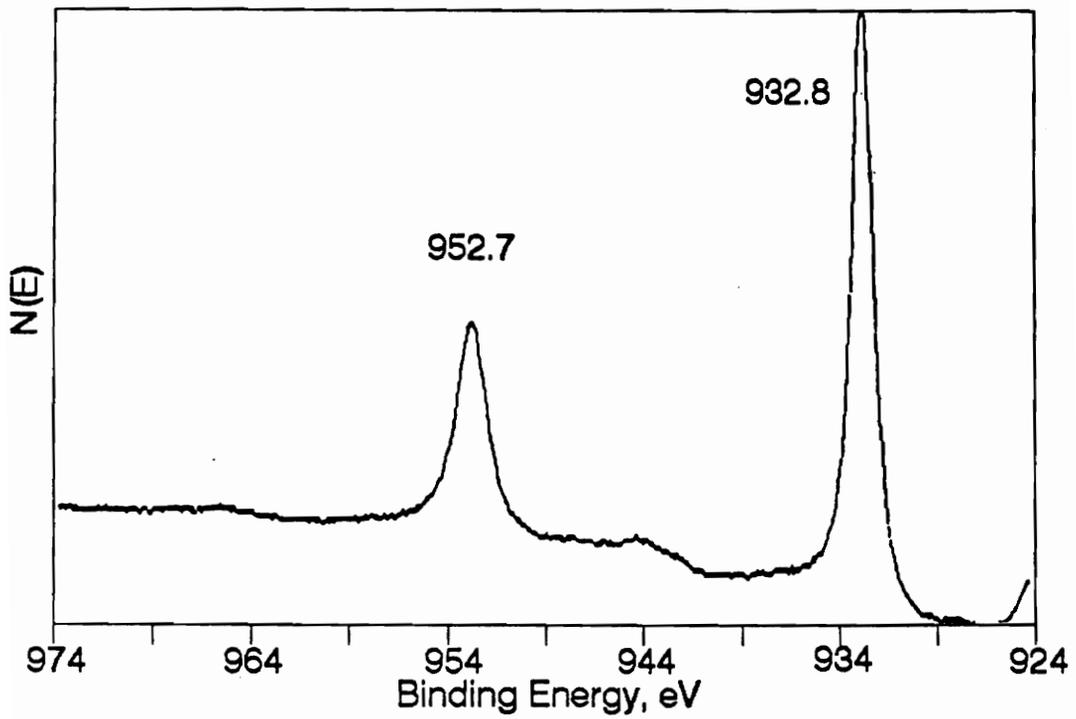
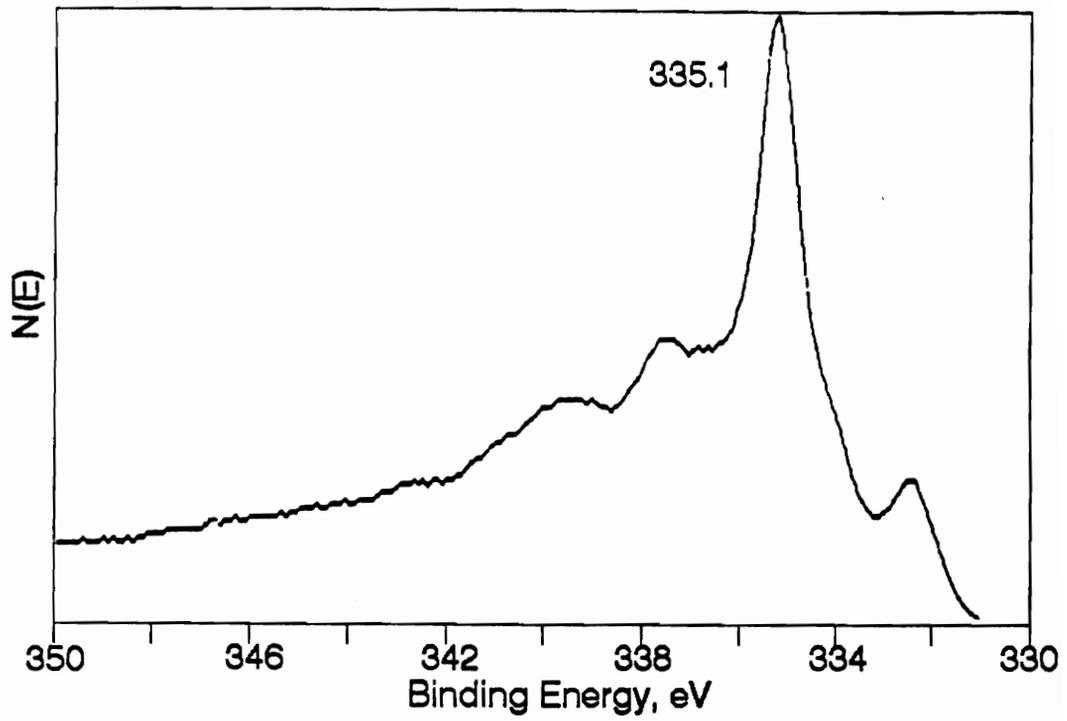


Figure 3.7 XPS spectra, Cu LVV (top) and Cu 2p (bottom) regions, film grown on strontium titanate at 200°C

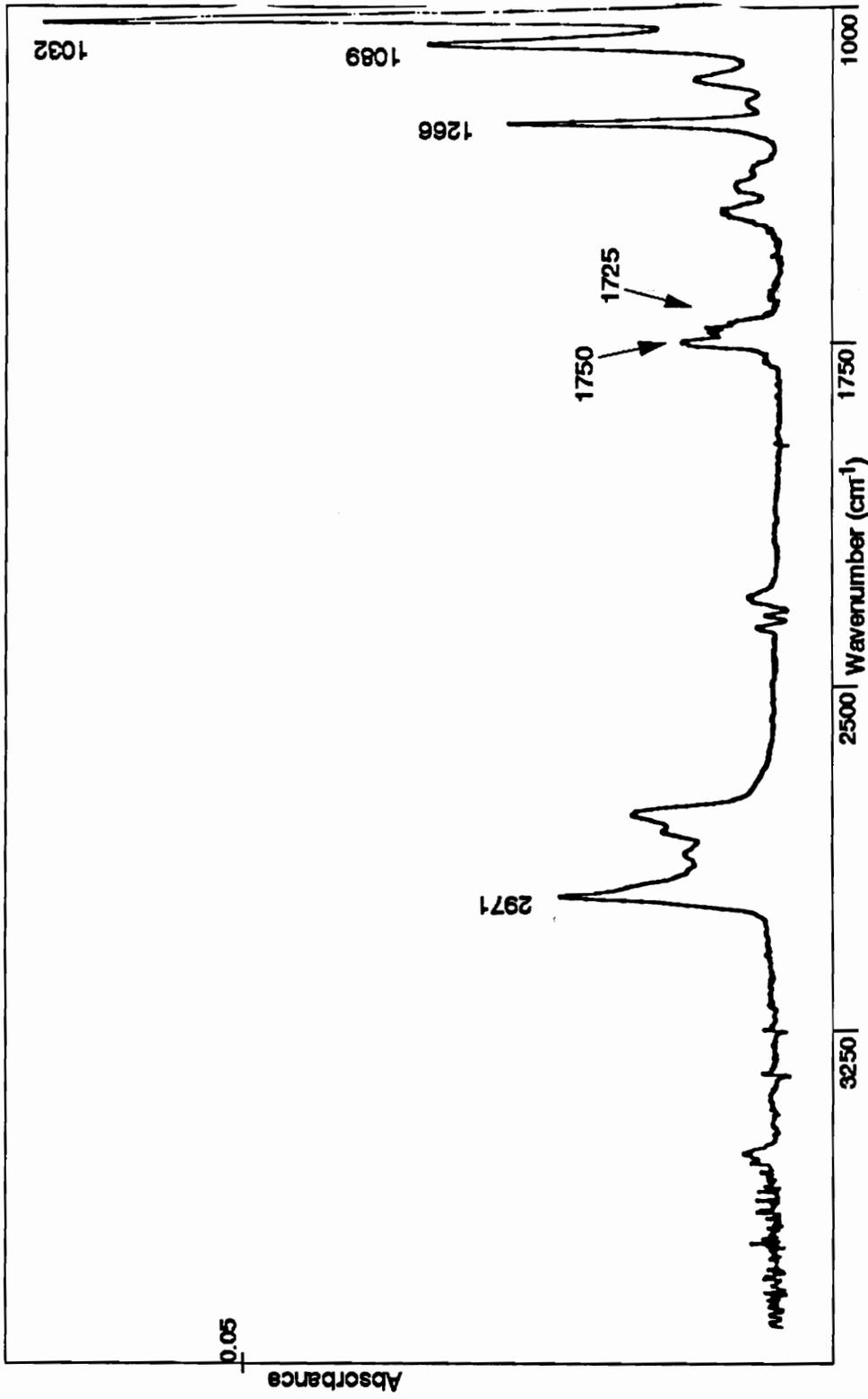


Figure 3.8 Infrared spectrum during deposition on strontium titanate, 200°C

Volatile organics from the reactor outlet gas were condensed in a liquid nitrogen trap and dissolved in deuterated chloroform for proton NMR analysis [30]. Refer to Figure 3.9. Neither aldehydic ($\delta=9 - 11$ ppm) nor alcoholic ($\delta \approx 5$ ppm) protons are visible. However, the alcoholic hydrogen signal is often broad and difficult to detect, so an identification can be made based on other protons in the molecule. The major product detected is dimethylaminoethanol, $\text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$. The large singlet represents the methyl groups on the nitrogen. The triplets near 2.5 ppm and 3.5 ppm represent the two methylene groups between the nitrogen and the oxygen. The methylene group in dimethylaminoethanal, $\text{O}=\text{CHCH}_2\text{N}(\text{CH}_3)_2$, should produce a doublet near 3.5 ppm. This doublet is not apparent. The feature just below 3 ppm remains unidentified.

There are several explanations for the failure to detect the aldehyde product by NMR. The aldehyde may react in the trap, either during the two days of the experiment or when the condensate is melted for dissolution. However, it is difficult to envision the expected contents of the trap (alcohol and aldehyde) being reactive at 0°C and below.

The aldehyde may be extremely volatile and may evaporate when the trap is moved from liquid nitrogen to the ice bath to melt the condensate. It might, therefore, be absent from the liquid sample for NMR. Dimethylaminoethanal is likely to be more volatile than the corresponding alcohol (normal boiling point 133°C [24b]), because hydrogen bonding decreases the vapor pressure of alcohols. However, dimethylaminoethanal is unlikely to be more volatile than acetaldehyde (normal boiling point 21°C [24a]), which has a lower molecular weight. (Recall that acetaldehyde and the more volatile formaldehyde are proven not to be decomposition products by IR spectroscopy.) Of course, liquids do evaporate below their normal boiling point. Loss of the aldehyde by evaporation is a possible explanation for its absence from the NMR spectrum.

A third explanation is that the aldehyde undergoes an aldol condensation reaction in the hot tubing *en route* to the trap, producing a hydroxyaldehyde product such as $(\text{CH}_3)_2\text{NCH}_2\text{CH}(\text{OH})\text{C}(\text{N}(\text{CH}_3)_2)\text{CHO}$ [31]. Such a product might condense in the reactor outlet line, never reaching the liquid nitrogen trap. Aldol condensation reactions are possible at 100°C in the gas phase, even when the aldehyde concentration is low. For example, aldol

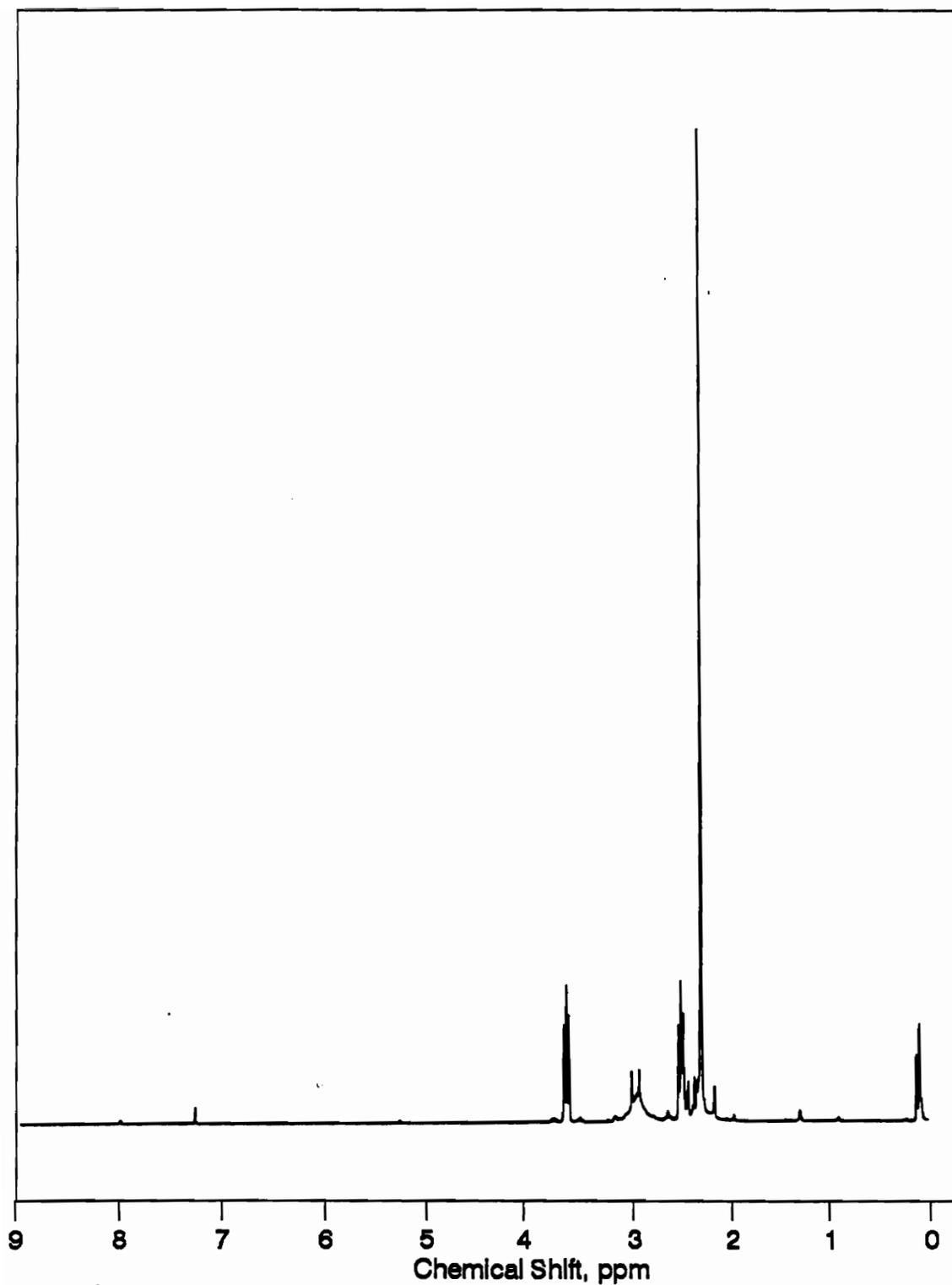


Figure 3.9 - Proton NMR spectrum of reactor outlet gas condensate, 200°C

condensation reactions often interfere with catalytic testing [32]. It is possible that the aldehyde product reacts and condenses before the liquid nitrogen trap.

The NMR results highlight the value of *in situ* studies. IR results clearly indicate an aldehyde product, but it is not revealed by NMR analysis of reactor outlet gas condensate. Without an *in situ* analytical technique, its existence would go undetected.

In summary, conductive films of pure metallic copper are deposited at 200–210°C on strontium titanate. The films consist of small, densely packed, spheroid grains which show poor adhesion to strontium titanate. Dimethylaminoethanol and dimethylaminoethanal are the primary decomposition products.

3.4.3 Results at 260°C

Red, opaque films were deposited on strontium titanate at substrate temperatures of 250°C to 270°C. There was no variability associated with the stage temperature in the IR spectra. Although XPS showed copper present only in the metallic state, films were only 60 to 75 atomic per cent copper. A typical Auger spectrum is shown in Figure 3.10. A small titanium signal from the substrate is visible in this spectrum. Oxygen and carbon contamination persisted throughout the films. The minimum carbon content ranged from 10 to 30 atomic per cent. Nitrogen was absent. The films were conductive, however, the resistivity as measured by four-point-probe was two orders of magnitude greater than for films grown at 200°C. These results are similar to those obtained on quartz at 280°C. Films showed better adhesion to strontium titanate than those grown at 200°C, but were still easily scratched off.

A typical IR spectrum taken during deposition (Figure 3.11) shows mostly peaks characteristic of copper dimethylaminoethoxide. Dimethylaminoethanol and dimethylaminoethanal are present. Again, the carbonyl stretch at 1725 cm^{-1} is present, but tiny. There is also a feature just to the right of the carbonyl stretches, near 1640 cm^{-1} . It appears to be the C=N or C=C stretch seen in the preliminary experiments. IR spectroscopy also shows carbon monoxide as a product. This data is consistent with the thermal decomposition of copper

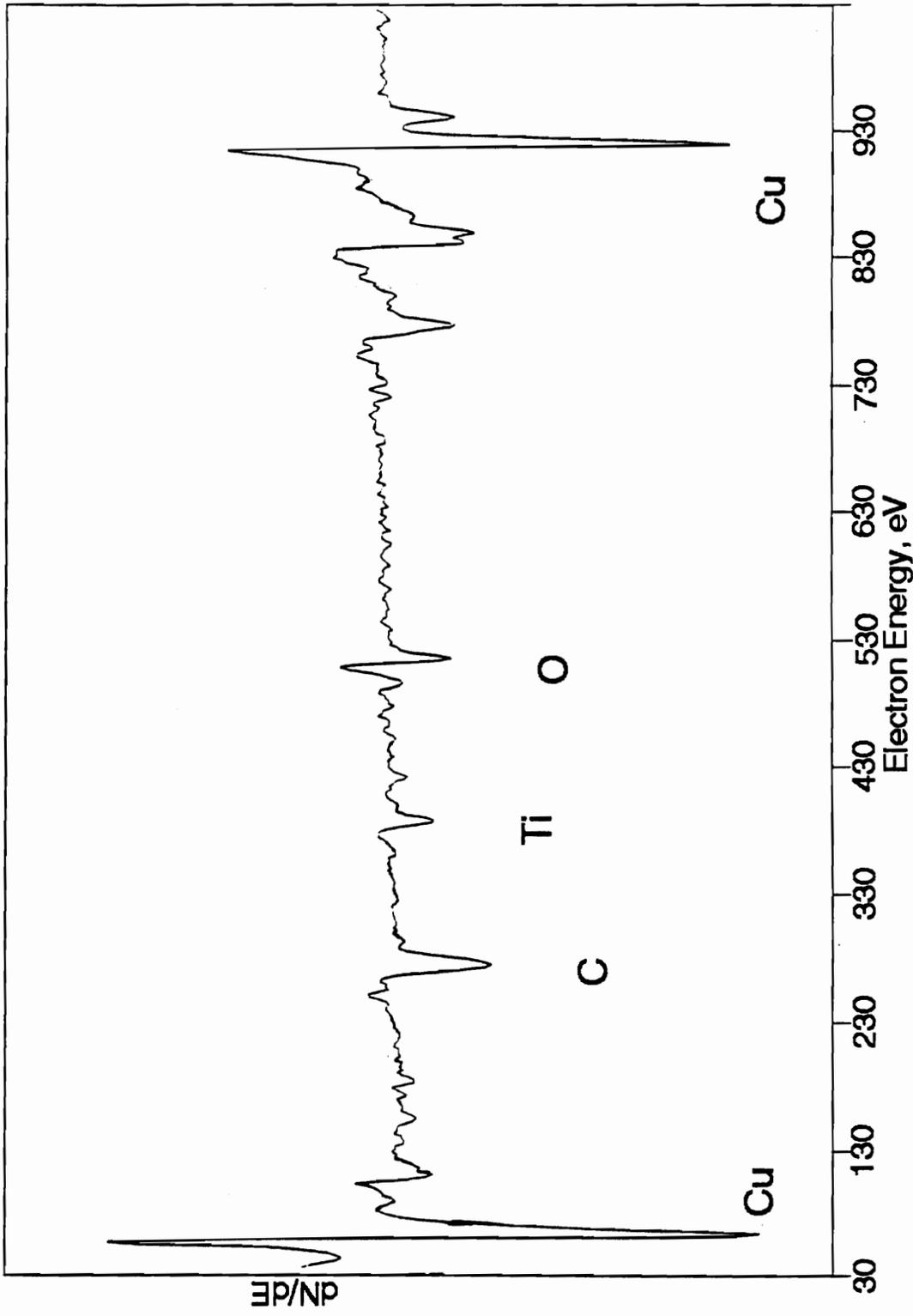


Figure 3.10 Auger spectrum of film grown on strontium titanate at 260°C

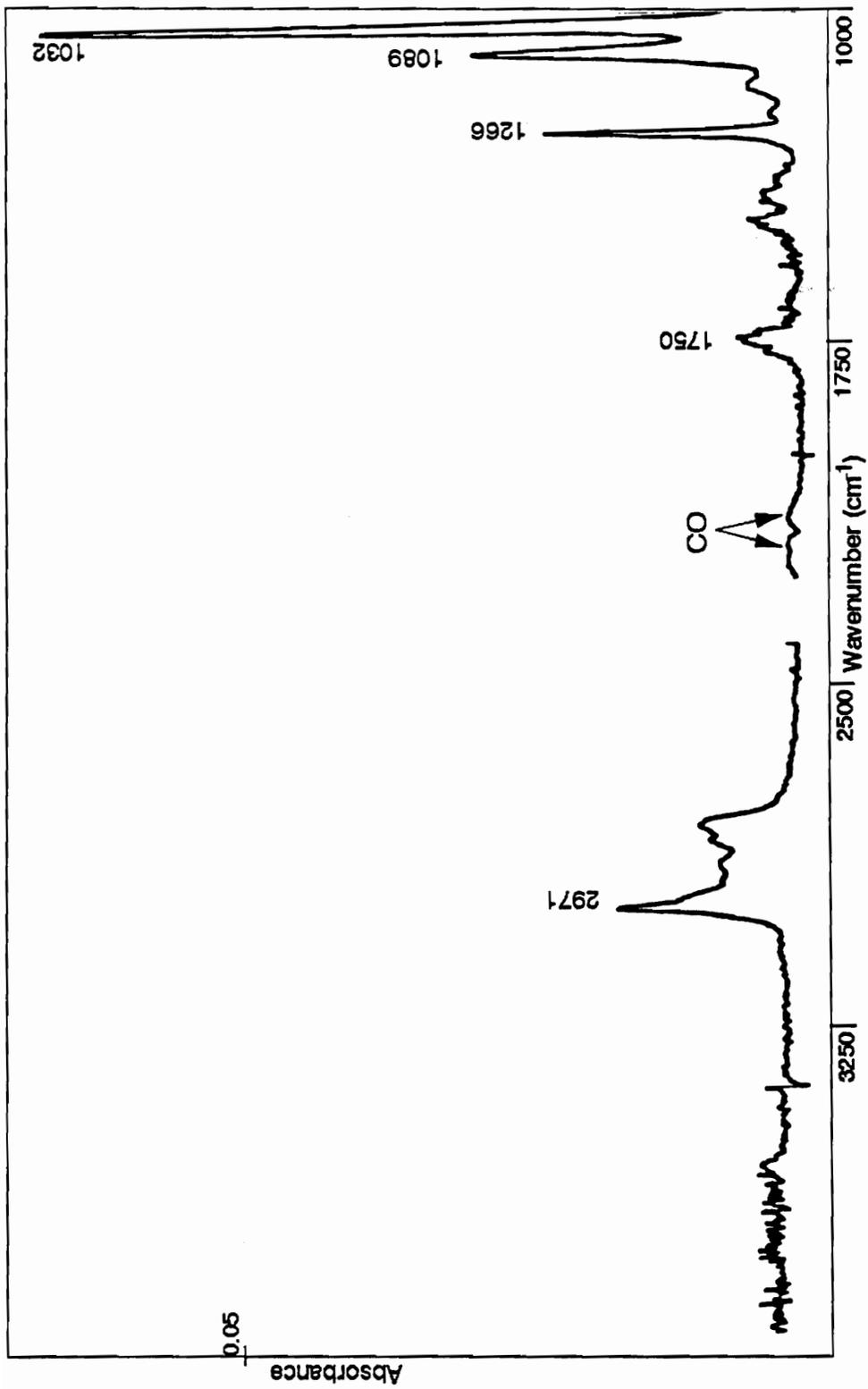


Figure 3.11 Infrared spectrum during deposition on strontium titanate at 260°C

dimethylaminoethoxide as described in section 3.3.3. The formation of CO implies ligand fragmentation, which results in contamination of the growing film.

The reactor outlet gas was again passed through a liquid nitrogen trap and the condensate submitted for NMR analysis. Refer to Figure 3.12. The spectrum is nearly the same as that for the material collected during deposition at 200°C, and is again identified as dimethylaminoethanol. The broad peak at 3.7 is probably the alcoholic proton. Due to hydrogen bonding, the position of this signal can vary widely with temperature and concentration [33]. Failure to detect the aldehyde product by NMR can be explained as in section 3.4.2.

In summary, metallic copper films deposit on strontium titanate at 260°C. Ligand fragmentation results in heavy contamination of the film by carbon and oxygen. The nitrogen-containing fragment(s) must be quite volatile, as they are not included in the film. Major products include dimethylaminoethanol and dimethylaminoethanal.

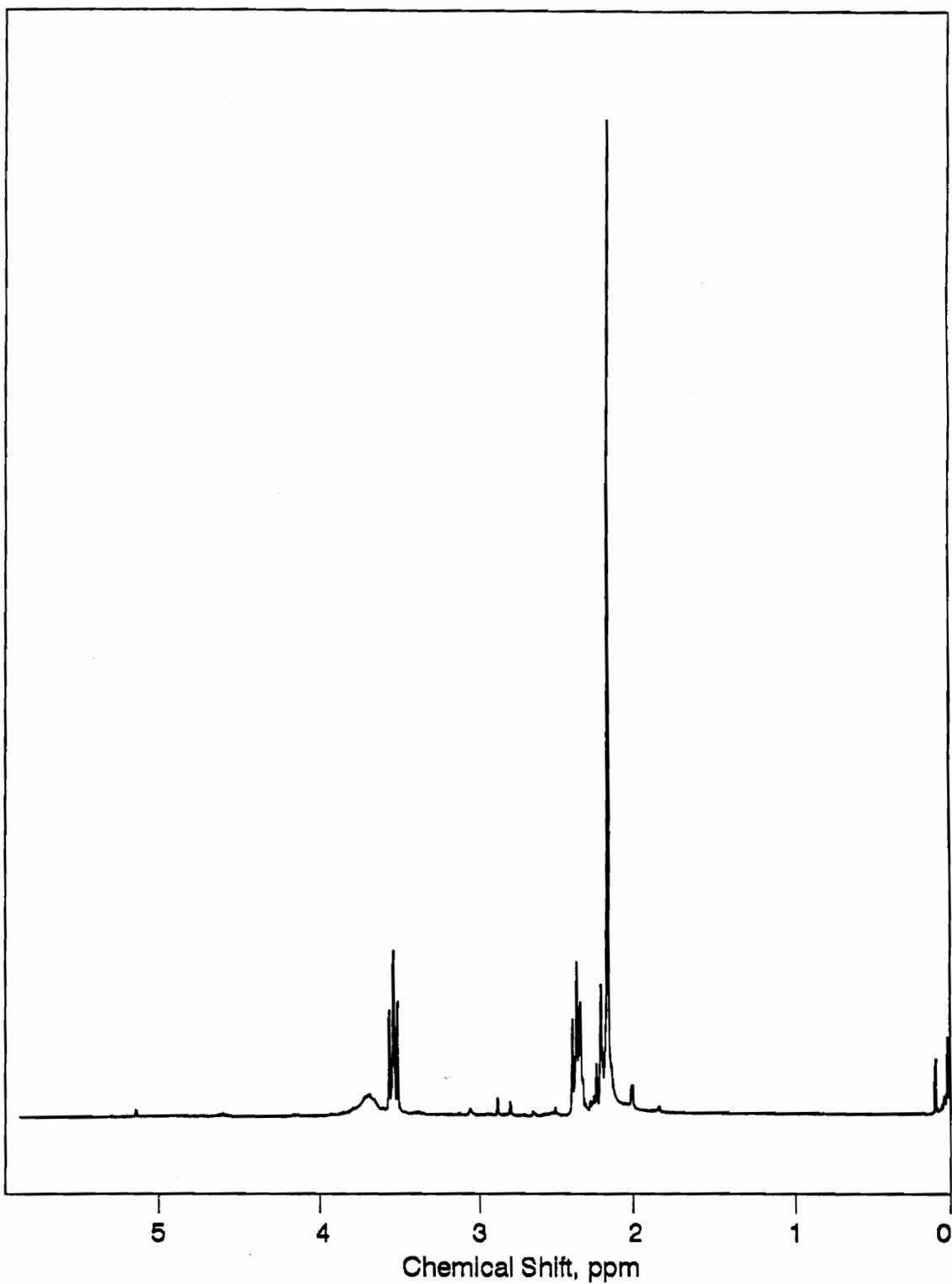


Figure 3.12 Proton NMR of reactor outlet gas condensate, 26°C

3.5 Discussion

3.5.1 The 1725 cm⁻¹ Carbonyl Stretch

Over the course of the project, the 1725 cm⁻¹ peak was almost ubiquitous. Careful examination found it in nearly every spectrum related to copper dimethylaminoethoxide. It was quite prominent immediately after the precursor was placed online if the precursor tube had not been correctly treated to remove surface hydroxyls. On such occasions, the first spectrum showed dimethylaminoethanol and a strong 1725 cm⁻¹ peak. Over about five hours, the spectrum shifted to copper dimethylaminoethoxide, and the 1725 cm⁻¹ was barely visible above the baseline. Once pseudo-steady state was achieved in the reactor system, the intensity of the 1725 cm⁻¹ peak remained fairly constant and small. The intensity of the peak was not affected by the temperature of the substrate. The peak was present even when the substrate was not heated. The 1725 cm⁻¹ peak is not directly related to deposition in the reactor.

The peak at 1725 cm⁻¹ is indicative of a carbonyl species, an aldehyde or ketone. By comparison with standard spectra, it is not vapor phase acetaldehyde, acetone, or formaldehyde. Nor is it formaldehyde or acetaldehyde condensed on the IR windows. The reactor temperature is well above the boiling point of either compound. The liquid phase carbonyl stretch of acetone in solution does appear near 1725 cm⁻¹, although the vapor phase carbonyl stretch is at 1740 cm⁻¹ [21]. Because acetone is used in the system as a cleaning solvent, the system was tested at various times under deposition conditions with an empty precursor tube, and with dimethylaminoethanol in the precursor tube. The peak at 1725 cm⁻¹ is visible when, and only when, copper dimethylaminoethoxide is in the precursor tube. The peak at 1725 cm⁻¹ must be due to a contaminant in the precursor and not in the experimental apparatus.

The aldehyde (or ketone) giving rise to the peak at 1725 cm⁻¹ is not vapor phase dimethylaminoethanal. A peak at 1750 cm⁻¹ has been identified as the carbonyl stretch of vapor phase dimethylaminoethanal. This identification is consistent with IR and mass spectra collected during deposition (which reveal no other nitrogen containing products) and with the production of clean films (which makes ligand fragmentation during thermal

deposition unlikely). The 1725 cm^{-1} peak is not produced by dimethylaminoethanal condensed on the IR windows. If that were the case, the peak would be apparent in spectra of dimethylaminoethanol in the system with the substrate hot.

Because the peak at 1725 cm^{-1} is so small, the carbonyl species cannot be identified from IR spectra alone. The carbonyl species cannot be identified from mass spectra, as the alcohol and alkoxide spectra look the same.

The peak at 1725 cm^{-1} is not associated with deposition from the alkoxide. It is not a peak characteristic of a deposition product, because its intensity does not increase when the substrate is heated. It is not a peak characteristic of a species consumed during deposition, because its intensity does not decrease when the substrate is heated. An exact identification of the trace contaminant in the precursor which gives rise to a peak at 1725 cm^{-1} is not necessary to this work. The contaminant does not participate in the deposition chemistry that is the focus of this work.

3.5.2 Thermal Deposition Chemistry

3.5.2.1 Major Deposition Products

The major products to be included in a proposed reaction pathway are copper (0), dimethylaminoethanol, and dimethylaminoethanal. These products are associated with copper deposition from copper dimethylaminoethoxide at temperatures ranging from 150°C to 270°C . Ultrahigh vacuum studies of primary alcohols adsorbed on metal [15,16] and oxide [17-20] surfaces provide excellent references for proposal of a reaction pathway.

Alcohols adsorbed on surfaces [15-20] may either desorb intact, or may lose the alcoholic hydrogen to form a surface alkoxy species. There are two common reaction pathways available to the surface alkoxy species: β -hydride elimination to form the aldehyde, and hydrogen recombination to form the alcohol.

Hydrogens on the carbon β to the surface (α to the oxygen) are activated by the presence of the oxygen heteroatom [16]. One of these β -hydrogens may be lost to the surface, which triggers formation of a double bond between the oxygen and carbon. The aldehyde formed desorbs. The hydrogen released onto the surface may react with another surface

alkoxy group to form the alcohol, which desorbs. Similar reactions of the alkoxy ligands are expected when copper dimethylaminoethoxide adsorbs on the surface of strontium titanate or the growing film: β -hydride elimination to form dimethylaminoethanal, and reaction with surface hydrogen to form dimethylaminoethanol.

A schematic of the reaction pathway appears in Figure 3.13. Note that the reacting alkoxy ligands, which are normally drawn as bidentate, have been drawn as unidentate for convenience. The available analytical techniques do not allow the orientation and structure of the adsorbed alkoxide to be determined. However, it is reasonable to expect an equilibrium between the unidentate and bidentate forms, especially where the copper center's desire for higher coordination can be met by the surface. A similar equilibrium between intramolecularly hydrogen bonded and non-intramolecularly hydrogen bonded dimethylaminoethanol exists [10].

Figure 3.13 reflects the author's uncertainty about the short-term fate of the eliminated β -hydrogen. It may be bound to the surface of the substrate or the growing film. This is certainly reasonable, based on surface chemistry of alkoxy species derived from adsorbed alcohols. However, it is also possible that the hydrogen remains attached to its own metal center to form a copper hydride. Reductive elimination of the alcohol, leaving the copper metal atom behind, would follow. With the available experimental equipment, it is impossible to tell whether abstracted hydrogens are mobile on the surface and react with neighboring adsorbed species, or whether they remain attached to their metal center and undergo further reaction there.

The surface mobility of abstracted β -hydrogens could be determined in an ultrahigh vacuum system by thermal desorption spectroscopy. A strontium titanate or copper metal substrate could be predosed with atomic deuterium. Then copper dimethylaminoethoxide could be dosed onto the surface. If eliminated hydrogens are not mobile, D_2 should desorb, but not H_2 or HD. Production of the deuterated alcohol, $(CH_3)_2NCH_2CH_2OD$, is not sufficient evidence for mobility of the abstracted β -hydrogens. The surface deuterium is expected to react with alkoxy ligands, and the ratio of alcohol to aldehyde produced should exceed one.

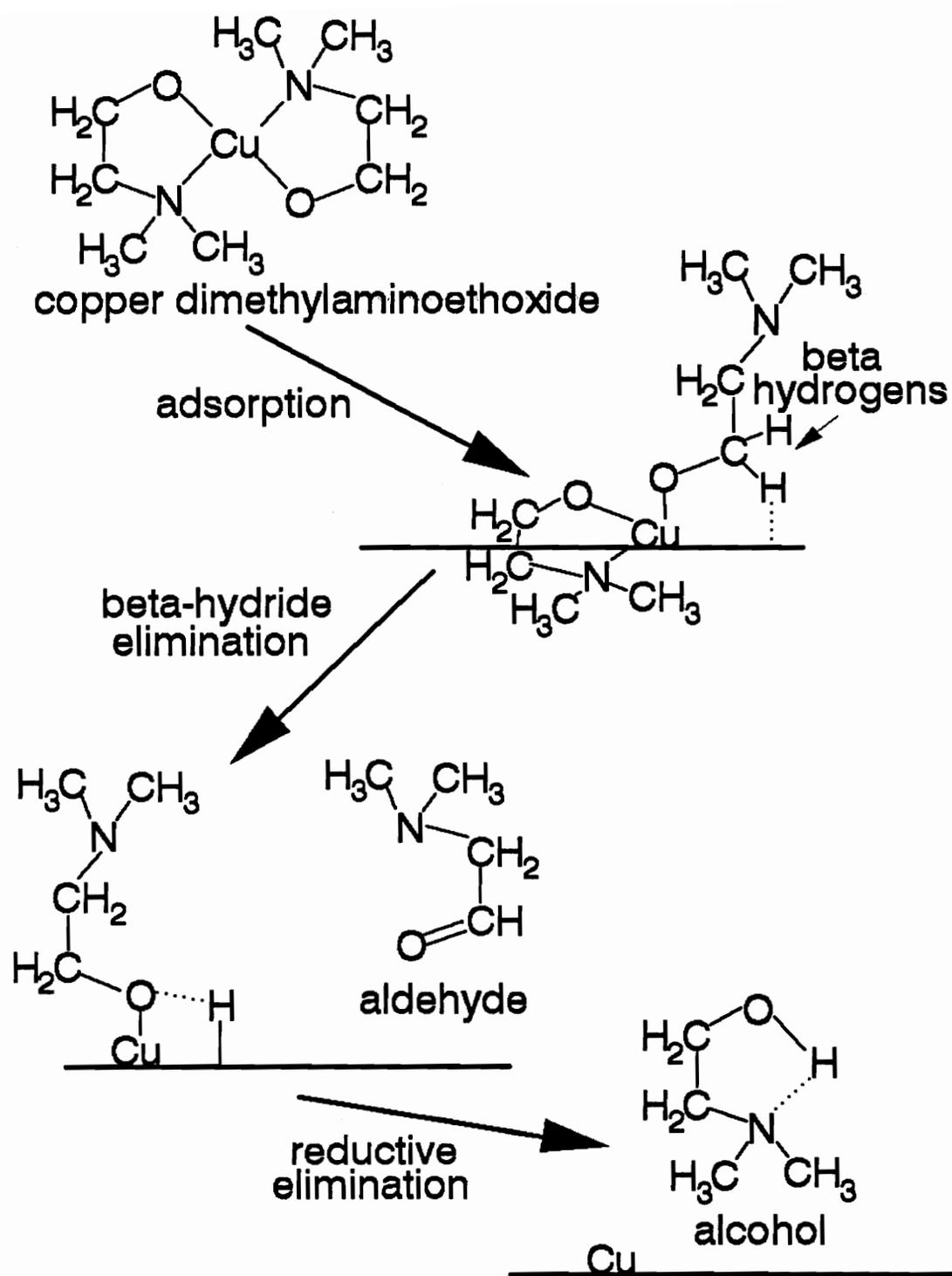


Figure 3.13 Thermal decomposition pathway of copper dimethylaminoethoxide

One might question how a copper species with a formal oxidation state of 2+ can deposit clean copper metal without a coreductant, as is required by copper (II) β -diketonates [34]. The formal change in oxidation state from copper (II) to copper (0), and the difference between the alkoxide and β -diketonate as far as need for reactive cofeed is concerned, are explained as follows.

Each copper (II) atom is accompanied by two dimethylaminoethoxy ligands. The β -hydride elimination of one alkoxy ligand to form dimethylaminoethanal leaves one dimethylaminoethoxy ligand and a hydride. The hydridic hydrogen then reacts with the remaining alkoxy ligand and undergoes reductive elimination to form dimethylaminoethanol and copper metal. This is the pathway in Figure 3.13. Thus the formation of the two organic products results formally in reduction of the surface. Similarly, reductive elimination from a metal hydride results in formal reduction of the metal center [35]. Production of copper metal, dimethylaminoethanol, and dimethylaminoethanal is consistent with known surface chemistry and metalorganic chemistry. Reductive elimination of the alcohol and β -hydride elimination of the aldehyde are interdependent. The fact that both pathways are available to an alkoxy species allows the copper (II) alkoxide to decompose cleanly without a reactive cofeed.

A similar hydride elimination pathway is not available to β -diketonate ligands. The β -diketone is the only stable decomposition product not involving ligand fragmentation. An external hydrogen source is required to form the ketone from the ketonate. Without a reactive cofeed, β -diketonate fragments remain bound to the metal center. Thus clean films of copper metal cannot be deposited from copper (II) β -diketonates without a reactive cofeed to provide hydrogen.

In the absence of hydrogen sources other than β -hydride elimination (such as adsorbed hydroxyl groups or hydrogen from the stainless steel walls of the reactor), the ratio of dimethylaminoethanol to dimethylaminoethanal produced by thermal decomposition of copper dimethylaminoethoxide should be one-to-one. The ratio of alcohol to aldehyde collected in this system over the course of a deposition run might be somewhat higher, because sources of hydrogen other than ligand decomposition cannot be eliminated. However,

it would be interesting to know how closely the ratio of alcohol to aldehyde approaches one. Unfortunately, standards of dimethylaminoethanal are not available, so IR spectra cannot be quantified. It was hoped that NMR analysis of products condensed in the liquid nitrogen trap would reveal the ratio of alcohol to aldehyde. Unfortunately, no aldehyde was detected by NMR.

3.5.2.2 High-Temperature Deposition Products

At a substrate temperature of 260°C, a new product is detected by a peak at 1640 cm⁻¹ in the IR spectrum. This peak suggests the presence of a C=C or C=N bond. Formation of the new species is related to ligand fragmentation, since its appearance is accompanied by the production of CO and CO₂ and by inclusion of carbon and oxygen in the film. Without a more specific identification, the proposed reaction pathway is necessarily speculative. The peak is too small to allow further identification by IR, and neither mass spectral or NMR analysis of species that left the reactor were revealing.

Recall that the dimethylaminoethoxy ligand has a heteroatom at each end that may interact with the surface or the metal center. Discussion thus far has emphasized bonding *via* the oxygen, and the resulting activation of β -hydrogens for elimination. The nitrogen may also interact with the surface. A hydrogen from an amine methyl group, or possibly an entire amine methyl group, may be lost to the surface. This can trigger formation of C=N bonds and fragmentation of the dimethylaminoethoxy group.

Another possibility is that multiple hydrogens may be lost to the surface, rather than just one β -hydrogen. Formation of C=C bonds may compete with formation of C=O bonds. Olefin formation might lead to ligand fragmentation and film contamination.

The alkoxy species may undergo deoxygenation, and the resulting hydrocarbon may be dehydrogenated, leaving hydrocarbon fragments and carbon to be incorporated in the film.

In defense of this speculative and nonspecific explanation of contaminant incorporation, the following is offered. Surface chemistry is often studied under the carefully controlled conditions available in ultrahigh vacuum. Even with analysis by X-ray photoelectron spectroscopy and mass spectroscopy, the mechanisms of formation of CO, CO₂,

and nonvolatile carbon-containing species from adsorbed organics are not fully understood. Studies of carboxylates [36], alkoxides [18], and aldehydes [37], over Cu_2O have revealed some of the processes, but not the precise natures of many surface species.

Reduction of surface oxygenate species to surface hydrocarbons on Cu_2O has been observed from 0°C to 325°C . Studies suggest that several different types of hydrocarbons may be formed [37]. These surface hydrocarbons are observed to dehydrogenate on Cu_2O above 225°C [37]. Dehydrogenation of acrolein on the surface even occurs below room temperature [37]. Thus surface oxygen released by reduction of surface alkoxy species would be available for production of CO and CO_2 from surface hydrocarbons and for inclusion in the film. In addition, above 325°C , surface carbon extracts lattice oxygen from Cu_2O to form CO and CO_2 [18,37]. Extraction of lattice oxygen might be important in early stages of film growth on strontium titanate above 250°C , while the oxide surface is exposed, but is not expected to be important once the oxide is covered by copper metal. Extraction of lattice oxygen allows complete burnoff of surface carbon from Cu_2O in ultrahigh vacuum at 525°C to 725°C [18,36,37]. However, at deposition temperatures of 250°C to 270°C , on the growing metal film, carbonaceous species are expected to remain.

Thus there is precedent for surface reduction (deoxygenation), dehydrogenation, and fragmentation of oxygen containing species on oxide surfaces. Such processes may lead to formation of $\text{C}=\text{C}$ and $\text{C}=\text{N}$ containing species, as well as to other nonvolatile carbonaceous species that may be included in the growing film. Specific organic products of this set of reactions cannot be identified with the available instrumentation.

Although contamination above 250°C is described as "severe", the ligand fragmentation reaction is actually a minor one. There is one carbon atom for every two or three copper atoms in the films. The precursor contains eight carbon atoms for each copper atom. Most of the ligands are probably eliminated virtually intact, gaining or losing only hydrogen. This highlights the sensitivity of film quality to deposition chemistry. Even a minor reaction can have a large effect on film purity.

3.5.2.3 Alternative Reaction Pathways

The β -hydride/reductive elimination pathway explains the available data in a satisfactory manner. It is reasonable based on the chemistry of alkoxy species on surfaces in ultrahigh vacuum. It explains how clean metal films deposit from a copper (II) precursor. However, some small doubt must remain, because dimethylaminoethanal was not positively identified as a product by comparison with IR spectral standards or by NMR.

Perhaps another carbonyl-containing species has been incorrectly identified. This seems unlikely, because dimethylaminoethanal fits the evidence so well, and because so many other potential products have been ruled out by comparison with standard IR spectra. In the author's opinion, there is little doubt that dimethylaminoethanal is a reaction product.

However, it is disturbing that dimethylaminoethanal is not detected by NMR, although it should be present in a one-to-one ratio with the alcohol. This suggests another possibility, that the aldehyde is actually a minor deposition product, and the alcohol is the major organic product of deposition. If this is the case, some source of hydrogen other than β -hydride elimination from the ligand must exist.

A leak in the system is one possibility. This is very unlikely. The system was thoroughly tested for leaks. The system was evacuated, then the valves to the helium tank and the vacuum pump shut. The metering valve to the MSD was opened. No change in the system pressure was observed over the course of an hour by MSD. The system can also hold 7 psig of helium overnight without losing pressure. Aside from leak tests, reasoning rules out leaks as a source of hydrogen.

If the system leaks, water will be admitted. Water is a ready source of hydrogen and will lead to production of alcohol from an alkoxide. However, alkoxides are water-sensitive at any temperature. If hydrolysis were the major reaction producing alcohol, alcohol would be obvious in the infrared spectra below 150°C. Alcohol would be produced all the time, not just during film deposition. A system leak is not the source of hydrogen for alcohol production.

Another possible hydrogen source is complete ligand fragmentation. An occasional ligand may completely decompose on the surface of the growing film. This would release ten

hydrogen atoms, allowing formation of ten alcohols from the decomposition of five alkoxide molecules. In exchange for five copper atoms deposited, four atoms of surface carbon would be deposited. In fact, less than one surface carbon atom deposits for every one hundred alkoxide molecules decomposed at 200°C (based on film analysis by Auger spectroscopy). As discussed in section 3.5.2.2, surface carbons produced by dehydrogenation are expected to remain in the film unless the temperature exceeds 500°C and a source of oxygen is available. It is difficult to visualize a reaction that could release large amounts of hydrogen (to produce alcohol) and produce no other species detectable by vapor phase infrared analysis or by surface analysis of the film.

Still, there must be some explanation for the failure to detect the aldehyde by NMR. The most obvious one is that dimethylaminoethanal may be very volatile. After the trap is moved from the liquid nitrogen bath to an ice bath to melt the condensate, and held there for several hours until the NMR spectrum is collected, perhaps very little of the aldehyde remains in the liquid condensate.

In this experimental system, the reaction pathways cannot be established beyond all doubt. Production of dimethylaminoethanal by β -hydride elimination, and the related production of dimethylaminoethanol by reductive elimination, is the pathway most consistent with the data collected and with the known chemistry of surface alkoxy species.

3.5.2.4 Substrate Effects on Deposition

Films grown from copper dimethylaminoethoxide on strontium titanate are composed of spheroid grains with diameters of 1 μm or less. They adhere poorly to the substrate, and appear poorly connected to one another. Because these small grains have a high surface area, the films are susceptible to oxidation in air. Because the grains are poorly connected, the sheet resistivities are quite high. The resistivity of bulk copper is 1.678 $\mu\Omega\cdot\text{cm}$ [38]. The resistivity of pure (as measured by Auger electron spectroscopy and X-ray photoelectron spectroscopy) copper films deposited at 200°C is about 200 $\mu\Omega\cdot\text{cm}$. Perhaps another substrate would interact favorably with the growing film and yield lower resistivity.

Mention should be made of the fact that deposition at 150°C consistently results in uniform, extremely thin films. This suggests that the substrate has some catalytic effect on the thermal decomposition of the precursor, and deposition ceases when the substrate is completely covered by copper. The initiation of deposition is not simply due to hydrolysis by hydroxyl groups on the substrate surface. If that were the case, deposition of a similar film would result at lower substrate temperatures. Alkoxides are susceptible to hydrolysis at any temperature. The precursor also begins to decompose in the precursor tube at about 150°C, as observed in section 3.3.3. This suggests that the presence of an oxide surface encourages decomposition. Copper dimethylaminoethoxide may deposit selectively on oxides at 150°C. It would be interesting to know whether the minimum deposition temperature is the same on nonoxide substrates, such as silicon.

3.6 Conclusions

Under a reduced pressure helium atmosphere, copper (II) dimethylaminoethoxide is thermally stable to 150°C. At 150°C, a very thin copper-containing film grows on strontium titanate. Apparently there is some catalytic effect of the substrate at 150°C. Volatile by-products of the reaction include dimethylaminoethanol and dimethylaminoethanal. Production of the alcohol and aldehyde occur by reductive elimination and by β -hydride elimination, respectively, of the dimethylaminoethoxy ligands.

The reductive elimination and β -hydride elimination reaction pathways are maintained at 200°C, but are more efficient. Thicker, conductive films of copper metal deposit. The interdependence of the two pathways allows deposition of pure copper metal without a reactive cofeed. The film morphology, which consists of submicron spheroid grains, promotes contamination by the air. This morphology also increases the film resistivity. This is a difficulty with the substrate, not the precursor. The copper films adhere poorly to strontium titanate. Copper dimethylaminoethoxide should be evaluated for deposition on different substrates.

Near 260°C, another thermal decomposition pathway for copper dimethylaminoethoxide becomes available. Ligand fragmentation is a problem. Volatile products include carbon monoxide, carbon dioxide, and a C=N or C=C species, as well as dimethylamino-

ethanal and dimethylaminoethanol. Because of ligand fragmentation, the deposited films are highly contaminated with carbon and oxygen.

Copper dimethylaminoethoxide is potentially useful for deposition of copper metal onto electronic substrates at temperatures near 200°C. Near 200°C, the available reaction pathways lead to elimination of whole ligands and deposition of pure copper metal. Higher temperatures result in ligand fragmentation by additional reaction pathways, which leads to contaminated films. Thus the film quality is clearly related to the chemistry of thermal decomposition. The appropriate temperature range for optimization of deposition can be discovered by observing the vapor phase IR spectra of the precursor as a function of temperature. In the correct temperature range, decomposition occurs, but no products of ligand fragmentation are observed.

The value of an *in situ* chemical analysis technique, such as infrared spectroscopy, should not be underestimated. Dimethylaminoethanal, a major deposition product, was undetected by post-reactor mass spectral and NMR analysis. The formation of dimethylaminoethanol by β -hydride elimination is vital to the deposition of clean copper films from copper dimethylaminoethoxide in inert atmosphere.

It is significant that deposition of pure copper was achieved at 200°C, because diffusion of copper into silicon is less likely to pose a problem at this temperature [2]. Diffusion is a problem at 250°C, the minimum deposition temperature for the widely-used copper (II) β -diketonates. It is also significant that pure copper films are deposited without any reactive cofeed, which is required for clean deposition from copper β -diketonates. In spite of the difficulty of handling water-sensitive compounds, copper (II) dimethylaminoethoxide has these two advantages over the β -diketonates as a precursor for copper MOCVD.

Copper also deposits from copper (I) hexafluoroacetylacetonate cyclooctadiene at 200°C. However, a hydrogen cofeed is required. In the absence of hydrogen, deposition occurs *via* a disproportionation mechanism, and only at higher temperatures. Again, copper dimethylaminoethoxide has the advantage of 200°C deposition without reactive cofeed. In addition, copper dimethylaminoethoxide is commercially available.

However, copper (II) dimethylaminoethoxide is a less promising precursor than the copper (I) β -diketonate trialkylphosphines [4]. Those compounds deposit conductive copper films at temperatures as low as 150°C without reactive cofeed, are apparently more volatile than copper dimethylaminoethoxide, and are less sensitive to air and water.

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4. Photoassisted Deposition from Copper (II) Dimethylaminoethoxide

4.1 Introduction

There is considerable interest in copper as an interconnect material for electronic devices on chips. Copper does not exhibit electromigration, which limits the miniaturization possible with aluminum interconnects [1]. Copper has a high conductivity. However, it is difficult to pattern.

Copper forms no volatile simple halides [2], so it cannot be etched with fluorine. Laser ablation for patterning can cause extreme local heating and substrate damage. Laser ablation may also allow redeposition of copper on other regions of the substrate [3]. Chemical vapor deposition with a photolytically active precursor could solve the patterning problem. A pattern of light could initiate growth of a patterned film. Copper would be deposited only where desired.

Light-induced chemical vapor deposition has two common mechanisms. In photolytic deposition, light absorbed by the precursor provides energy for decomposition. In pyrolytic deposition, light absorbed by the substrate provides heat to decompose the precursor. The term "photoassisted" encompasses both mechanisms. The mechanisms are difficult to separate and often coexist. Even if a nonabsorbing substrate is used, the growing film will often absorb UV light and become hot. However, for a nonabsorbing substrate, initial nucleation of the film must be a photolytic process. For a photolytic process, the question of whether gas phase or surface adsorbed molecules decompose becomes important. Decomposition primarily of adsorbed molecules allows greater pattern definition.

An experimental system was designed to test the feasibility of photoassisted deposition with copper (II) dimethylaminoethoxide. Pyrolytic and photolytic deposition can be separated, at least for the nucleation process, by taking advantage of the band gap of the substrate. Gas phase and surface decomposition can be separated by rotating the substrate out of direct light. The gas phase reaction products are detected *in situ* by infrared spectrometry. Secondary chemical information is provided by surface analysis of the deposited film.

Copper dimethylaminoethoxide has been tested for thermal deposition. No deposition occurs below 150°C. Films deposited near 250°C show significant carbon contamination due to ligand fragmentation reactions. However, films deposited near 200°C are pure copper and conductive. At all three temperatures, copper (0) is the only oxidation state of copper deposited. The major organic thermal decomposition products are dimethylaminoethanol and dimethylaminoethanal. These products are formed by two interdependent pathways: β -hydride elimination to form the aldehyde, and reductive elimination to form the alcohol.

It was hoped that photoassisted deposition would lead to film growth at lower temperatures and/or activate different decomposition pathways from the thermal decomposition process, which could be deduced from the products detected by IR.

4.2 Experimental Methods and Procedures

The warm-wall stainless steel deposition reactor was evacuated by a direct-drive mechanical vacuum pump. The substrate was mounted on a resistance heater. The deposition reactor is also an infrared cell. A sapphire window admits ultraviolet light to the reactor. Carrier gas and reactor window purge flows were helium at 5 sccm and 2 sccm respectively. The precursor sublimed between 90 and 98°C. Deposition conditions were maintained for approximately 48 hours. Conditions for study were selected based on preliminary experiments and on earlier results from thermal deposition.

The UV source was a Spectronics Corporation B-100 lamp. The substrate, strontium titanate, has a band gap at 3.2 eV. Photons of greater energy may heat the substrate, while photons of lower energy will not. A discussion of the process of heating by absorption of photons may be found in Chapter 2.

The UV lamp has a strong line on either side of the band gap. Oriel filter number 59472 passes only energies below the band gap. Oriel filter number 59460 passes those and a limited range of energies above the band gap. Refer to Figure 4.1. With filter 59472 in place, only photolytic nucleation of the film on the substrate is possible. With filter 59460 in place, there is potential for photolytic and pyrolytic deposition.

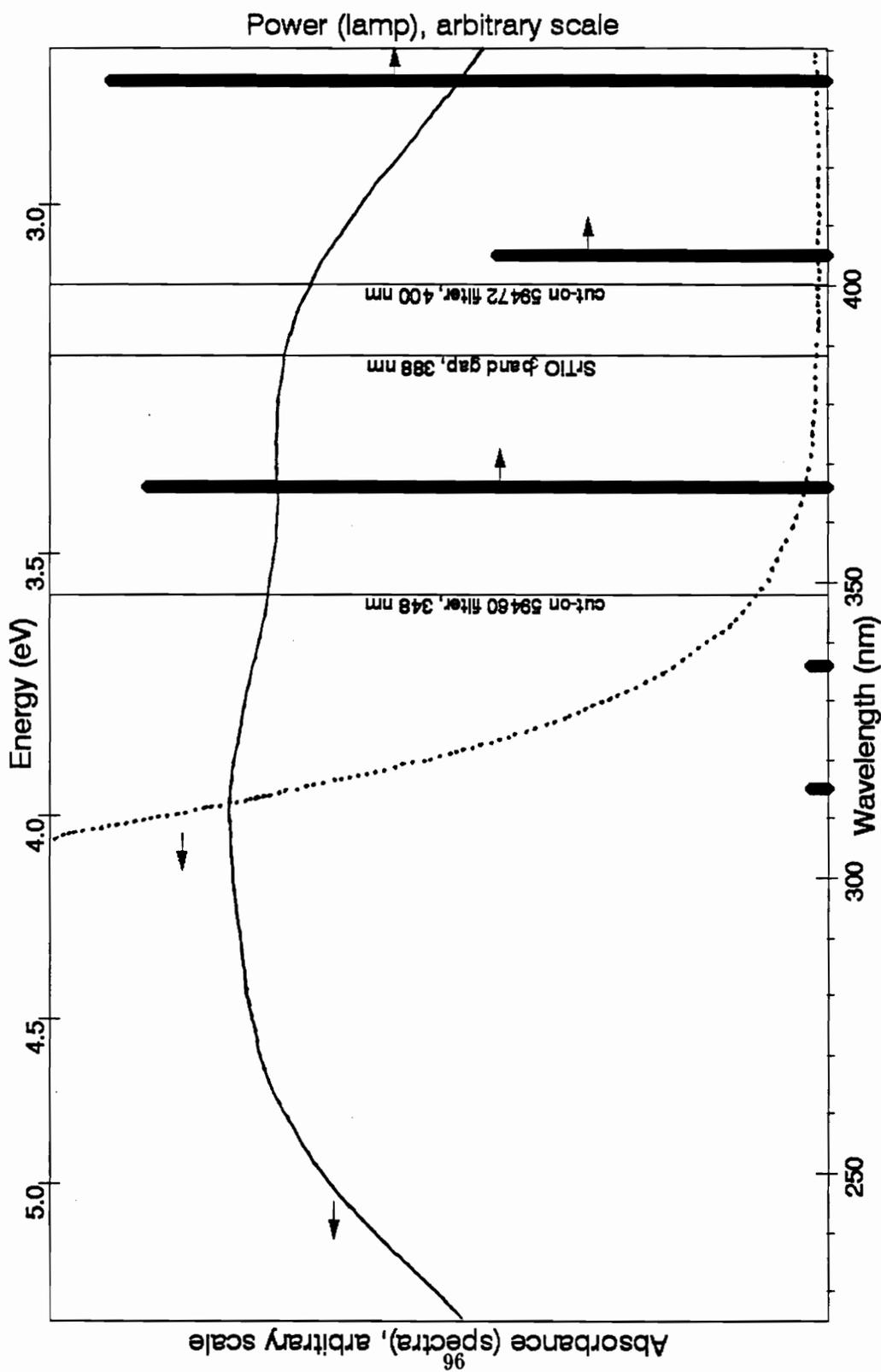


Figure 4.1. UV absorption spectra of copper dimethylaminoethoxide (solid line) and dimethylaminoethanol (broken line) with UV lamp emissions

The substrate holder can be rotated 90°. This shields the substrate from direct incident UV radiation and allows separation of gas phase from surface decomposition.

The apparatus and procedures are described more fully in Chapter 2.

4.3 Results and Discussion

4.3.1 Preliminary Experiments

4.3.1.1 Ultraviolet Absorption Spectra

The ultraviolet absorption spectra of copper dimethylaminoethoxide and dimethylaminoethanol are shown in Figure 4.1. The UV spectrum of the solid alkoxide was measured by reflectance (refer to Chapter 2), so the spectrum cannot be related to the concentration of alkoxide in solution. This technique was used to minimize the chances of decomposition during measurement, because alkoxides are less stable in solution than as solids. Because concentration was not controlled, the spectra cannot be compared quantitatively. However, the qualitative results are important.

Copper dimethylaminoethoxide absorbs in the region near the band gap of strontium titanate, 3.2 eV. The UV lamp also emits strongly in this region. Dimethylaminoethanol does not absorb in this region. The alcohol and the alkoxide have similar five-membered ring structures. They differ chemically in the substitution of copper for the hydroxyl hydrogen. This suggests that absorption near 3.2 eV (388 nm) is related to the copper–oxygen bond in the alkoxide and not to bonds within the alkoxy group. UV light in the region of the substrate band gap may encourage clean separation of the copper from the ligand. UV light near 388 nm should not cause fragmentation of the aminoalkoxy ligand, which would likely result in contaminated films. Filters are used to restrict the UV light incident on the sample to the strontium titanate band gap region.

Copper dimethylaminoethoxide absorbs light energy above and below the band gap of strontium titanate. Light of lower energy than the strontium titanate band gap may cause decomposition of copper dimethylaminoethoxide. Thus, it may be possible to separate

photolytic and pyrolytic effects with the filters. The UV absorption properties of copper dimethylaminoethoxide and dimethylaminoethanol appear promising for this study.

4.3.1.2 Test of Excimer Laser as Ultraviolet Source

Initially, the UV source for this project was to be a Lumonics TE-860-4. This laser is capable of producing two lines near the strontium titanate band gap using only helium and nitrogen, one at 337 nm and one at 428 nm. Several attempts at photodeposition from copper dimethylaminoethoxide onto strontium titanate were made using each line. The substrate was not heated with the resistance heater during the deposition attempts. No deposition resulted.

The power of the 337 nm line is about 3.5 mJ/pulse. The power of the 428 nm line is about 0.5 mJ/pulse. It was speculated that the power of the laser at these lines was insufficient to cause deposition. Only a minuscule fraction of the precursor molecules might be photolyzed, and the power was insufficient to change the temperature of the substrate. The laser can output with more power at other wavelengths, but halogen gases are required. It was not feasible to build a gas handling system for the safe use of halogens. Also, at the more powerful laser wavelengths, the energy of each photon exceeds the energy of the strontium titanate band gap. It would be impossible to conduct purely photolytic deposition on strontium titanate with any of them.

The laser was retired, and further experiments were conducted with the Spectronics B-100 UV lamp.

4.3.1.3 Test for Photodecomposition of Dimethylaminoethanol

In order to confirm that the dimethylaminoethoxy ligand would be unaffected by UV light, dimethylaminoethanol was placed in the precursor tube and the system prepared as usual for deposition. As expected, no copper deposited in this control experiment, again demonstrating that the copper alkoxide is the only source of copper during deposition. The UV lamp shone unfiltered into the reactor. Because the alcohol does not absorb light in the

regions that the lamp emits strongly, the products should depend only on the substrate temperature. Indeed, the results were the same as those obtained without the lamp.

Below substrate temperatures of 150°C, infrared spectra show vapor phase dimethylaminoethanol and no other species. At 150°C, a small peak appears near 1750 cm⁻¹. For substrate temperatures up to 230°C, the IR spectrum does not change except for an increase in intensity of the 1750 cm⁻¹ peak. There are no peaks to indicate amines or ammonia are present.

The peak at 1750 cm⁻¹ is characteristic of a carbonyl stretch. Formaldehyde (H₂C=O), acetaldehyde (CH₃CH=O), dimethylaminoethanal ((CH₃)₂NCH₂CH=O), methyl ethyl ketone ((CH₃)(CH₃CH₂)C=O), acetone ((CH₃)₂C=O), and diethyl ketone (CH₃CH₂)₂C=O are possible decomposition products of the alcohol. Standard spectra of all except dimethylaminoethanal are available. Consultation of standard spectra reveals that the carbonyl stretches in all of the standards are near 1750 cm⁻¹. However, other peaks between 1000 cm⁻¹ and 2000 cm⁻¹ in the standard spectra are not consistent with the product spectrum. Evidence is most consistent with dimethylaminoethanal as the decomposition product. This identification is discussed in detail in Chapter 3.

Note that the temperatures and products of decomposition are the same as those seen for thermal decomposition of dimethylaminoethanol, as described in Chapter 3. There is no evidence for photolytic decomposition of dimethylaminoethanol.

4.3.2 Attempted Photoassisted Deposition at 150°C

In order to determine whether UV light would initiate lower temperature deposition, substrate temperatures from 100°C to 140°C were tested at intervals of 10°C under the UV lamp. Unfiltered light was tested first to maximize the chance of success. No deposition occurs at substrate temperatures below 150°C, the onset temperature of thermal deposition. Ultraviolet light at intensities obtainable from the lamp does not initiate film growth below thermal deposition temperatures, either by direct photolysis of the precursor or by local heating of the substrate surface.

Deposition at 150 – 155°C under UV light results in translucent, nonconductive yellow films. Auger analysis shows the films to contain copper and to be very thin. The titanium signal from the substrate is clearly visible after short ion bombardment. No region in the depth profiles is identifiable as characteristic of the bulk film, so it is impossible to determine the oxidation state of the as-deposited films. Auger spectroscopy shows no difference between these films and those deposited without UV light. UV absorption by the film did not result in sufficient heating of the surface to allow film growth to continue.

IR spectra collected during deposition show a mixture of the alkoxide, dimethylaminoethanol, and dimethylaminoethanal. (The alkoxide and the alcohol were identified by comparison with vapor phase spectra of the pure compounds which were collected previously. Identification of the aldehyde is indirect, but convincing. A complete discussion of the aldehyde identification may be found in Chapter 3.) In all respects, these IR spectra are indistinguishable from those taken during deposition at 150°C without UV exposure. Unfiltered UV irradiation results in no change in the reaction pathway for deposition from copper dimethylaminoethoxide at 150°C. In light of these results, filtered UV radiation was not tested.

4.3.3 Attempted Photoassisted Deposition at 200°C

Infrared, Auger, and X-ray photoelectron spectroscopies indicate no change in the reaction pathway when unfiltered UV light or 59460-filtered (energies above and below the band gap pass) UV light is introduced to deposition at 200°C. Deposited films are red, opaque, and conductive, and consist of pure copper metal. The decomposition products identified by IR are the alcohol and aldehyde, dimethylaminoethanol and dimethylaminoethanal. Proton nuclear magnetic resonance analysis of species trapped by liquid nitrogen from the reactor outlet gas showed dimethylaminoethanol as the only identifiable species. The same results were obtained from Auger, XPS, IR, and NMR analysis for deposition at 200 – 210°C without UV light.

There was only one observable difference between films grown with UV light and films grown without at 200°C. After three days in laboratory air, films deposited in the presence of UV radiation turn black. Films deposited without UV light darken as well, but

are still noticeably red after three weeks. Scanning electron microscopy of a film grown under 59460-filtered UV light shows numerous thin needles as well as the spheroid grains seen previously for pure thermal deposition at 200°C. This change in morphology indicates a less dense film, which facilitates oxidation.

There may be some relationship between the swift oxidation of these films and studies of photoreduction of metal oxides by Fleisch and Mains [4]. Fleisch and Mains found that metal oxides could be reduced by UV photons of energy greater than the metal oxide band gap. The reduced samples were extremely vulnerable to reoxidation. Samples of palladium and platinum made by photoreduction from the oxides, metals which normally do not oxidize under ambient conditions, oxidized swiftly in laboratory air.

Although only one film was viewed by SEM, all of the films grown under UV light at 200°C oxidized swiftly. The phenomenon of low film density is probably general, although no effort at systematic study was made. The purpose of this project is to study deposition chemistry, and deposition under UV radiation of the intensity obtainable from the available lamp offered no unique chemistry for study. The oxidation phenomenon is offered only as an observation.

4.3.4 Possible Causes of Failure of Photoassisted Deposition

UV radiation of the intensity obtainable from the lamp or from the nitrogen lines of the laser does not affect deposition from copper dimethylaminoethoxide as expected. UV radiation from the lamp or the laser does not lower the minimum deposition temperature or change the apparent reaction pathway of copper dimethylaminoethoxide. There are three possible reasons for this: (1) the precursor is not photosensitive, (2) a reactive cofeed is required, or (3) the light source has insufficient power.

Copper dimethylaminoethoxide does absorb UV light near 388 nm. This absorption is probably related to the presence of the metal–oxygen bond, because dimethylaminoethanol does not absorb light near 388 nm. However, excitement of these electronic transitions may not lead to cleavage of the metal–ligand bond. Absorbed energy can be redistributed quickly in the molecule [5]. The excited electrons return to the ground state,

and energy is dissipated in some way other than bond cleavage. For instance, energy may be dissipated *via* molecule – molecule and molecule – wall collisions. Perhaps UV radiation does not cause any observable changes in deposition because the precursor is not photosensitive.

Sometimes, the presence of a reactive cofeed encourages photodeposition. Jones *et al.* showed this effect with copper (II) hexafluoroacetylacetonate [6]. With only the β -diketonate present, photodeposition from copper hexafluoroacetylacetonate required a high power density UV laser and resulted in films that were up to 90 atomic per cent carbon. In the presence of ethanol vapor, photodeposition occurred under a mercury vapor lamp and resulted in films containing only 10 atomic per cent carbon. The authors suggest that photodeposition is enhanced because of the presence of the alcoholic proton, which is abstracted by the β -diketonate ligand to form the stable β -diketone. This suggests that photoassisted deposition from copper dimethylaminoethoxide might also fail in the absence of a reactive cofeed.

However, it has already been demonstrated (in Chapter 3) that copper dimethylaminoethoxide does not require a reactive cofeed to remove the alkoxy ligands cleanly and form stable organic products. The oxygen heteroatom activates C – H bonds α to it for β -hydride elimination. There should be no need for a second source of easily abstracted hydrogens. A reactive cofeed should not be necessary for photoassisted deposition of copper from copper dimethylaminoethoxide to succeed.

Photoassisted deposition might occur with a higher power density light source. The proportion of electronic excitations leading to cleavage of the metal – ligand bond may be small. The absorption cross-section of copper dimethylaminoethoxide for photons with wavelengths near 388 nm may be small. (Recall that the UV absorbance spectra shown in this work are not quantitative.) If the number of available photons is also small, photodecomposition of the precursor would be a very rare occurrence, perhaps not observable over the time frame of the experiment.

Insufficient power density also prevents light induced heating of the substrate, and the resultant pyrolytic deposition. As mentioned previously, heating occurs when excess photon energy is dissipated in the substrate by crystal lattice vibrations [7]. With insufficient photons incident on the substrate, this excess energy can be transferred to the surroundings at

the same rate it is absorbed, with no increase in the substrate temperature. In fact, no temperature increase is measured by the substrate thermocouple. Of course, a temperature rise localized to the upper surface of the substrate would not be measured at the bottom of the substrate. A light source such as a tunable dye laser might result in photoassisted deposition from copper dimethylaminoethoxide on strontium titanate.

4.4 Conclusions

Exposure to UV radiation does not promote lower temperature deposition or different reaction pathways, as compared to thermal deposition from copper dimethylaminoethoxide. It is unknown whether the complex is not susceptible to photolysis by light near 388 nm, or whether the UV source is of insufficient power. This question might be answered with a different light source, such as a tunable dye laser.

The experimental design for separating photolysis from pyrolysis by use of the substrate band gap, and for separating gas phase and surface processes by rotation of the substrate, is believed to be sound. The interplay of the substrate band gap, the light source wavelengths, and the precursor absorption spectrum is important. Perhaps a similar system could be designed for a precursor known to undergo photodecomposition.

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5. Deposition from Copper Dimethylaminoethoxide with Reactive Cofeed

5.1 Introduction

In chemical vapor deposition, an additional reactive gas is often fed to the deposition reactor along with the precursor. The purpose of this additional reactive species is to promote clean elimination of ligands or growth of a different compound. For example, hydrogen gas is cofed with copper (II) β -diketonates to promote clean elimination of the β -diketone [1]. Nitrous oxide may be cofed with yttrium, barium, and copper β -diketonates to grow films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductor [2]. Jeffries and Girolami showed that by predosing their vacuum system with water, they could deposit copper (I) oxide rather than copper metal from copper t-butoxide [3].

Unlike the copper β -diketonates, copper dimethylaminoethoxide does not require a reactive cofeed to deposit pure films of copper metal thermally. The organic ligands are removed by two interdependent reactions: (1) β -hydride elimination and (2) hydride recombination and reductive elimination. The organic products of these reactions are dimethylaminoethanal and dimethylaminoethanol, respectively. However, a reactive cofeed might be used with copper dimethylaminoethoxide to study the reaction chemistry, or to promote deposition of copper oxide rather than copper. Four candidates for reactive cofeeds with copper dimethylaminoethoxide are hydrogen, nitrous oxide, water, and oxygen.

It would be interesting to compare the composition of films grown in the presence of water with this copper (II) alkoxide to those grown with the copper (I) alkoxide studied by Jeffries and Girolami [3]. It is expected that copper oxide can be grown in the presence of water at lower temperatures than the 400°C reported for copper (I) t-butoxide [3], because alkoxides are susceptible to hydrolysis at room temperature and below. The lower limit of deposition temperature should be determined by the need to transport the precursor. In this system, sublimation temperatures near 95°C have been used most successfully. The volatility of the alcohol (the expected organic decomposition product) must also be considered to avoid organic incorporation into the film. As the vapor pressure of dimethylaminoethanol at 90°C is approximately 170 Torr [4], and the system pressure under vacuum is estimated to be 10^{-1} Torr or less, organic incorporation from the alcohol should not be a problem at 95°C.

Unfortunately, it is not practical to test water as a cofeed in the existing experimental apparatus. The introduction of water to the hot reactor would degrade the calcium fluoride IR windows. Calcium fluoride was chosen for its resistance to hydrolysis, but it is not immune to water damage, especially at elevated temperature.

Hydrogen might encourage the production of the alcohol at the expense of the aldehyde, confirming the proposed reaction pathway for thermal deposition of copper. This should be observable by IR spectrometry. IR spectra of dimethylaminoethanal cannot be quantified absolutely, because the aldehyde is not available for calibration spectra. However, there may be an observable decrease in the intensity of the 1750 cm^{-1} C=O stretch with respect to the 3545 cm^{-1} O-H stretch when hydrogen is introduced. This change in relative intensity would indicate a higher proportion of dimethylaminoethanol produced.

Nitrous oxide and oxygen might cause deposition of copper oxide in lieu of copper metal, accompanied by a change in the reaction pathway. If oxide deposition is possible at 200°C , there are potential applications for semiconductor-superconductor hybrid technology. Arita's group deposited the superconducting phase of yttrium barium copper oxide at 600°C [1]. Because diffusion of copper into silicon is significant at 250°C [5], this temperature is too high for hybrid applications.

Because of the opportunity to confirm previous conclusions about the chemistry of thermal deposition from copper dimethylaminoethoxide, and the possible applications for superconductor-semiconductor hybrid electronics, study of the chemistry of chemical vapor deposition with reactive cofeed from copper dimethylaminoethoxide was undertaken.

Because of the limitations of the available vacuum pump, deposition could not be performed under reduced pressure with nitrous oxide or hydrogen. A standard pump lubricated with hydrocarbon oils cannot handle strong oxidizers or explosion hazards. The system was refitted for near ambient pressure experiments, as described in section 2.2. Unfortunately, the precursor could not be transported successfully to the reactor at near ambient pressure. Numerous attempts were made with and without reactive cofeed, at various flow rates of the carrier gas. No deposition resulted. IR spectra of species in the reactor were dominated by peaks from the alcohol. The predeposition purge of the hot system was extended to four days without positive result.

Copper dimethylaminoethoxide is best transported under vacuum. At near ambient pressure, either the small amount of water in the helium carrier gas is sufficient to cause hydrolysis, or water is simply not removed effectively from the system by purging. Kumar *et al.* observed a similar phenomenon with copper cyclopentadienyl trialkylphosphine complexes [6]. These complexes could only be transported by Kumar *et al.* in vacuum. Thus, experimental limitations prevent study of the chemistry of thermal deposition from copper dimethylaminoethoxide in the presence of hydrogen or nitrous oxide.

Oxygen will also degrade the hydrocarbon oil in the vacuum pump. However, it is not so strong an oxidizer as nitrous oxide. It was decided to attempt deposition in the presence of oxygen under the following conditions. The oxygen content of the feed to the reactor should not exceed twenty-five per cent. (This number was chosen as comparable to the twenty-one per cent oxygen content of air.) The pump oil should be changed immediately before and immediately after the experiment. The pump should be monitored for unusual noises or heating during the experiment. The results of a preliminary oxygen cofeed experiment are promising, and this subject is worthy of further study.

5.2 Experimental Methods and Procedures

The warm wall stainless steel deposition reactor was evacuated by a direct-drive mechanical vacuum pump. Pump oil was changed immediately before the experiment, and the pump was monitored for signs of lubricant degradation. The pump did appear to run slightly hotter than normal towards the end of the experiment. After the experiment, the oil was noticeably darker in color.

The substrate, strontium titanate, was mounted on a resistance heater. The substrate temperature was 200°C. The deposition reactor is also an infrared cell. The reactor outlet gas was sampled by a mass selective detector. The carrier gas was 99.999% helium, flow rate 10 sccm. The reactive cofeed was introduced to the reactor through the window purge line to avoid premature reaction with the precursor, at a flow rate of 3 sccm. The precursor sublimates at 95°C. Deposition conditions were maintained for approximately 48 hours.

5.3 Results and Discussion

Deposition from copper dimethylaminoethoxide in the presence of oxygen at 200°C on strontium titanate resulted in an opaque film, orangeish in color, and somewhat iridescent. It was not measurably conductive, even using the available four point probe [7]. Auger analysis shows that the bulk of the film contains no detectable carbon or nitrogen (Figure 5.1), but significant oxygen incorporation. The copper 2p region of the XPS spectrum (Figure 5.2) shows no shakeup satellites characteristic of copper (II) [8]. The copper LVV Auger transition region in the XPS spectrum (Figure 5.3) is characteristic of a mixture of copper (I) and copper (0).

Thus copper (I) oxide has been deposited at the relatively low temperature of 200°C. It is pure with respect to carbon incorporation, but not with respect to oxidation state. It is possible that pure copper (I) oxide was deposited, but has been partially reduced by the argon ion bombardment used to remove surface contamination. Partial reduction of Cu_2O to Cu has been observed after 18 minutes of bombardment with 5 keV argon ions [9]. (Note that total reduction of a copper oxide to copper metal by ion bombardment has not been observed.) This partial reduction was of an oxide overlayer on a copper single crystal.

In an attempt to avoid partial reduction of the films, ion bombardment before XPS was by 3 keV argon ions for only 20 minutes. Although this treatment did not cause observable reduction of an oxide overlayer on a single crystal [9], it may partially reduce a multicrystalline thin film. The as-deposited oxidation state cannot be determined with certainty unless the deposited film is transferred from the deposition reactor to the analysis chamber without exposure to laboratory atmosphere. Such a direct transfer would greatly reduce or eliminate the need for ion bombardment to remove surface contamination. Direct transfer is impossible with the available equipment.

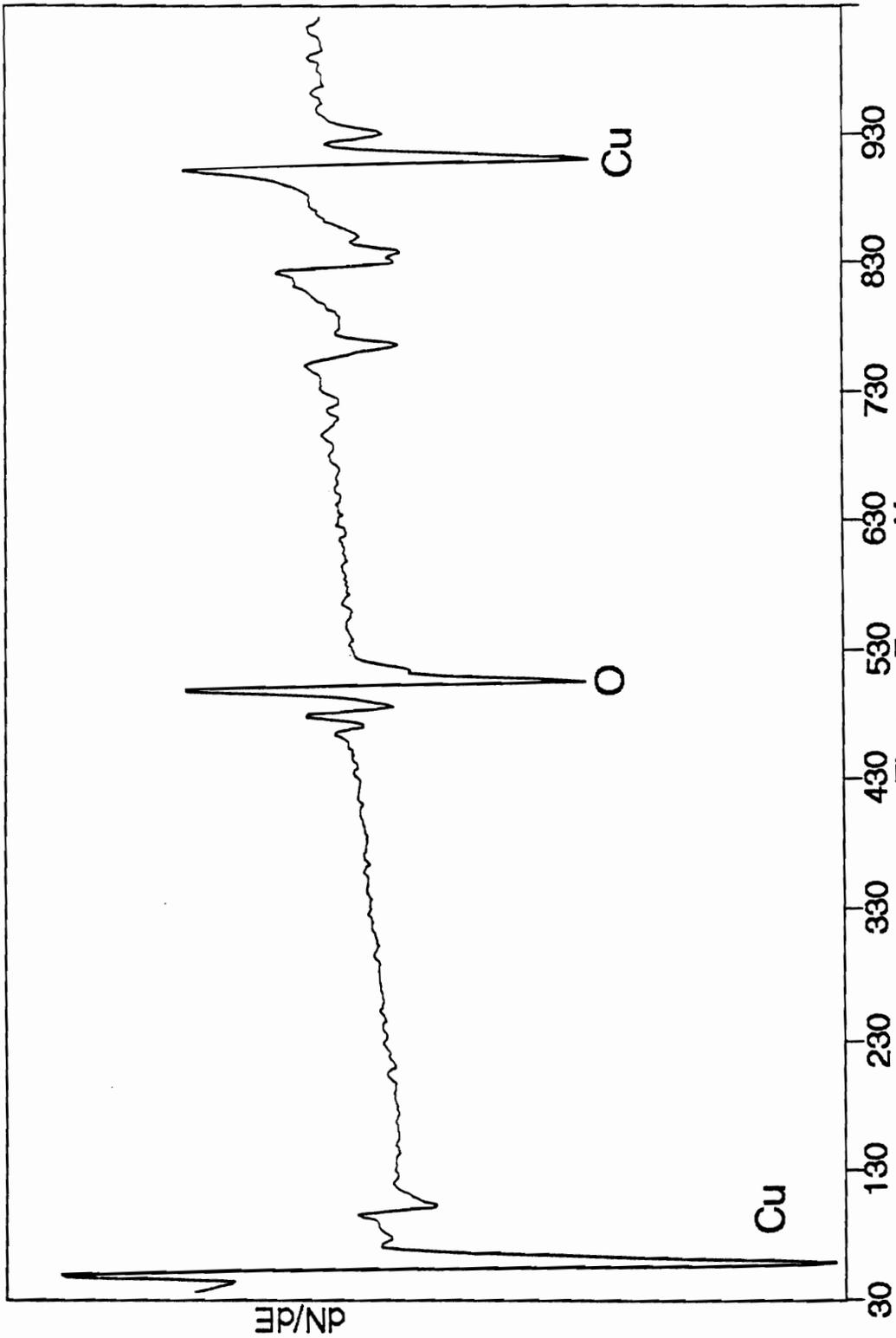


Figure 5.1 Auger spectrum of film grown on strontium titanate at 200°C with oxygen

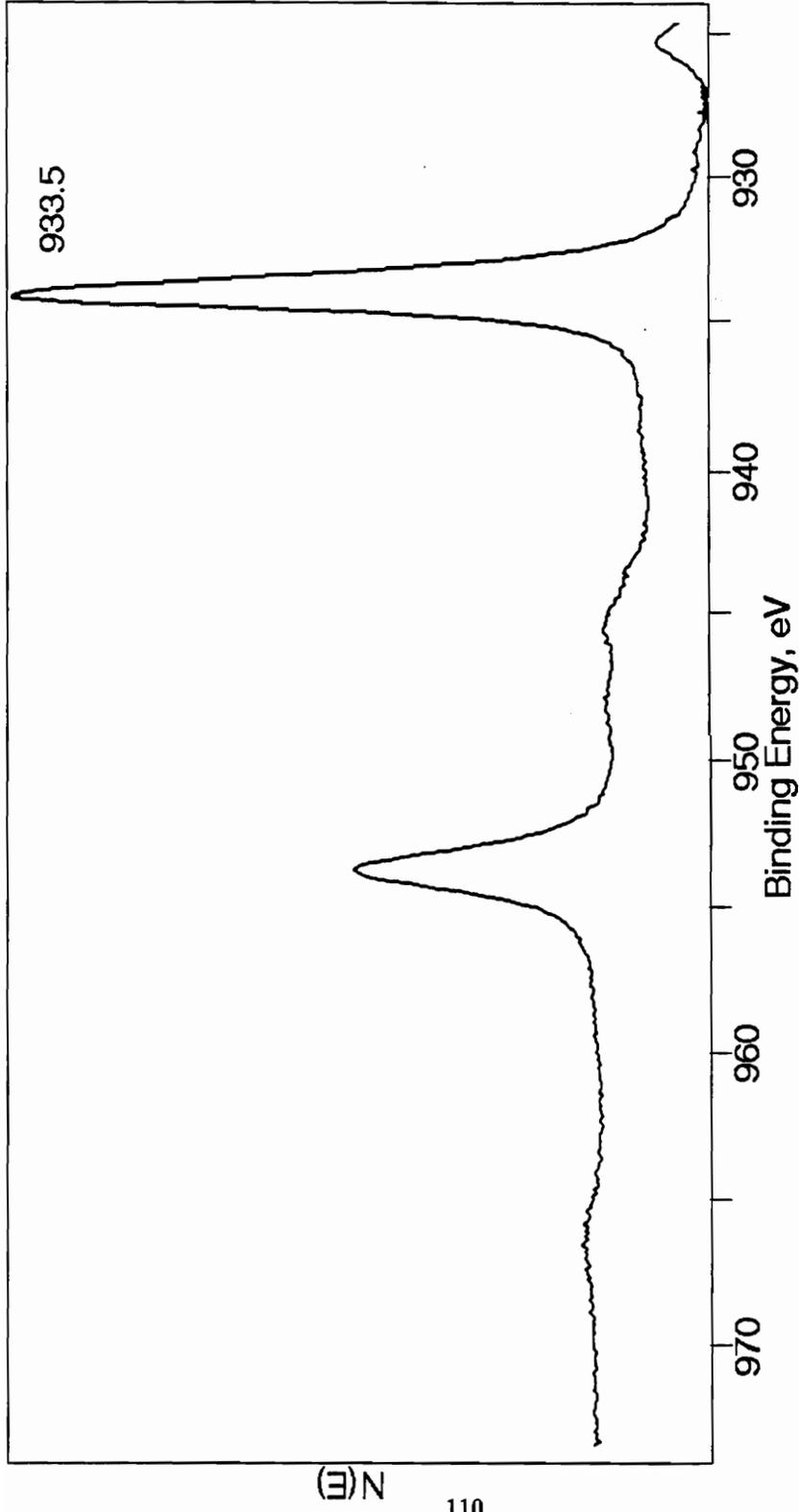


Figure 5.2 XPS spectrum, Cu 2p region, film deposited at 200°C with oxygen

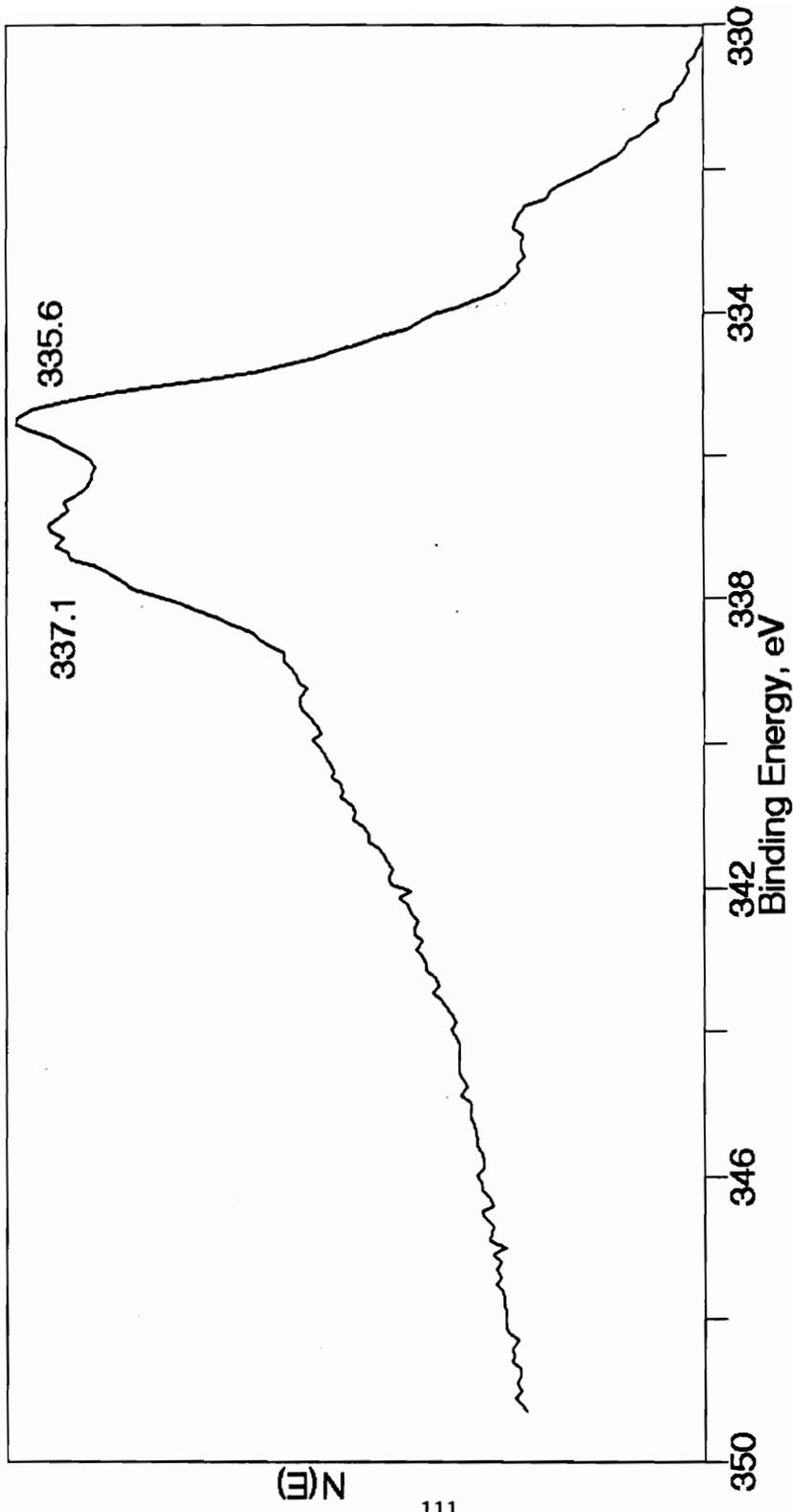


Figure 5.3 XPS spectrum, Cu LW region, film deposited at 200°C with oxygen

Note that the as-deposited film must be at least partially, if not completely, Cu_2O . The oxide cannot result from exposure to the air. Complete oxidation of films deposited under the same conditions, but without an oxygen cofeed, does not occur. The atomic concentrations of copper and oxygen are constant throughout the bulk of the film, as observed by an Auger analysis depth profile. The concentration of oxygen would decrease with depth if oxygen had diffused from the surface. Also, the depth of carbon contamination should indicate the depth of contamination due to air exposure. The oxygen signal in the Auger depth profile remains constant long after all carbon has been removed by ion bombardment.

The goal of this project is to study the effect of deposition chemistry on film growth. Since a different film stoichiometry has deposited, different species should be observed in IR spectra collected during deposition. This is the case, as shown in Figure 5.4. The C–H stretching region ($2800 - 3000 \text{ cm}^{-1}$) looks quite different from that seen during deposition under the same conditions without an oxygen cofeed (see Chapter 3). The large, broad peak below 2900 cm^{-1} overlies the usual C–H stretches of the alkoxide, so only the peak at 2970 cm^{-1} is visible. The peaks at 1266 cm^{-1} , 1090 cm^{-1} , and 1032 cm^{-1} are present at their expected intensities for copper dimethylaminoethoxide (see section 2.7.2). The aldehyde peak at 1750 cm^{-1} , which is characteristic of dimethylaminoethanal (see section 3.3.2), is not observed. The carbonyl stretch at 1725 cm^{-1} , which cannot be identified with the available instrumentation (see section 3.5.1), is unusually prominent. Mass spectral analysis of the reactor outlet gas shows production of carbon monoxide and carbon dioxide.

From this data, it is not possible to propose a reaction pathway. There is not enough evidence for a positive identification of the reaction products (aside from the identification of CO and CO_2 by mass spectral analysis). The broad IR peak in the C–H stretching region (just below 3000 cm^{-1}) is similar to that seen for methylamine, which has no other strong peaks above 1000 cm^{-1} . The presence of large amounts of CO and CO_2 suggests extensive ligand fragmentation, and several small amines are probably produced. The broad C–H stretch is probably due to the presence of several decomposition products. Methylamine, dimethylamine, ethylamine, trimethylamine, and dimethylethylamine may all be present. Of these, dimethylethylamine is the least volatile, with a normal boiling point of 36°C . At the

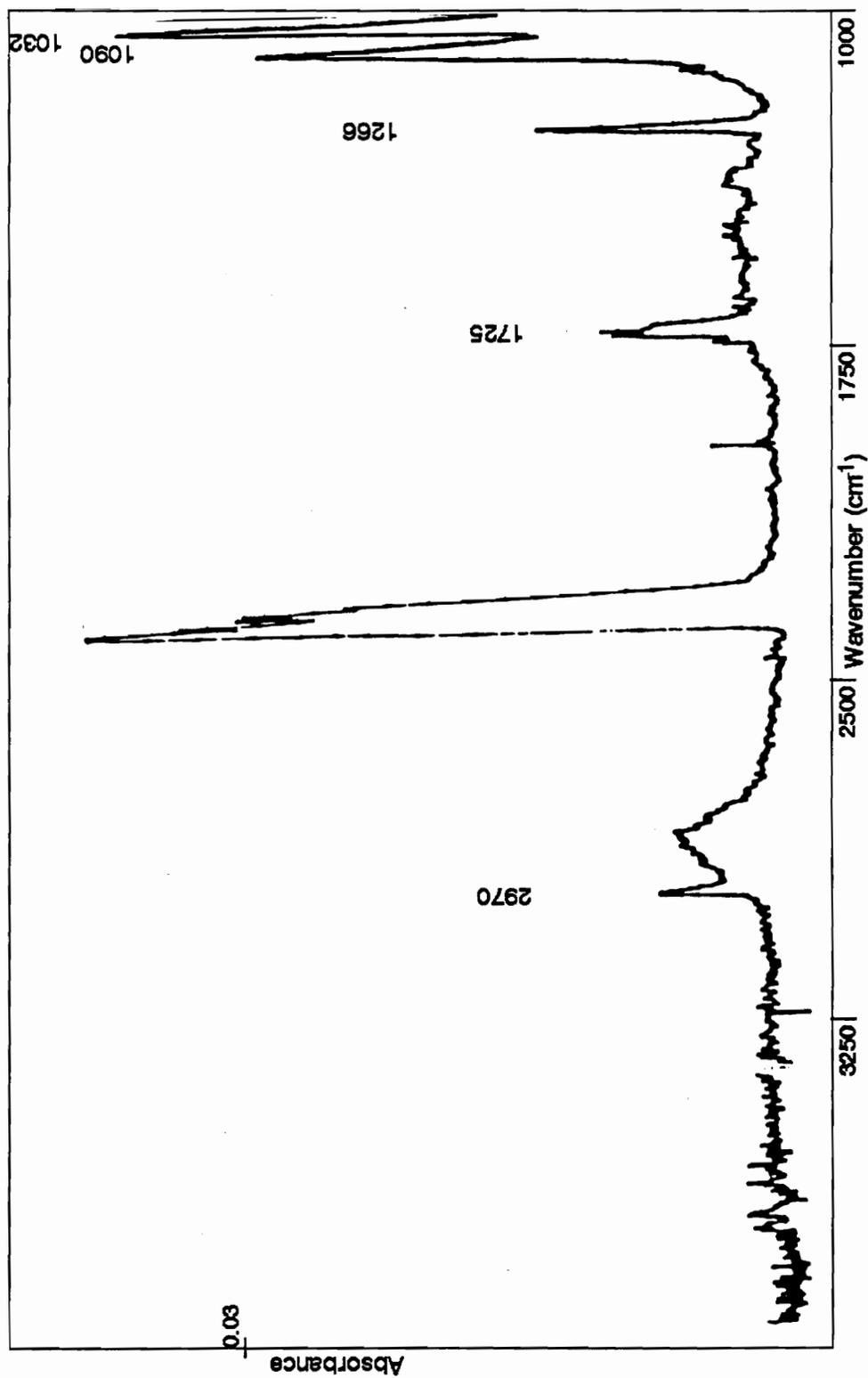


Figure 5.4 Infrared spectrum during deposition on strontium titanate, 200 °C with oxygen

temperature and pressure of this system, all of these amines should be volatile enough to avoid inclusion in the growing film. All the amines except methylamine do have medium or strong peaks between 1000 and 2000 cm^{-1} . However, in a mixture, these might not be apparent.

The peak at 1725 cm^{-1} indicates that an aldehyde or ketone is produced. It must be a volatile and stable species, because Auger analysis shows no organic incorporation in the film. This may be the same carbonyl species that was detected in earlier thermal deposition experiments. In those experiments, a carbonyl species giving rise to a peak at 1725 cm^{-1} was determined to be a trace contaminant in the precursor, and was not observed to participate in the deposition chemistry. The high intensity of the 1725 cm^{-1} peak in spectra collected during this deposition indicates that an unidentified carbonyl species is a reaction product in the presence of oxygen. As discussed in section 3.5.1, positive identification of the carbonyl species is impossible with the available equipment.

In summary, copper (I) oxide deposits from copper dimethylaminoethoxide at 200°C in the presence of oxygen. The oxygen promotes extensive ligand fragmentation, and the fragments are too volatile to be trapped in the film. Only CO and CO₂ can be identified positively, but small amines and an aldehyde or ketone are also present. The film is uncontaminated by carbon or nitrogen.

5.4 Conclusions

Copper (II) dimethylaminoethoxide is potentially useful for hybrid semiconductor-superconductor applications because it deposits uncontaminated copper and copper oxide at the low temperature of 200°C. Deposition of the oxide, mixed with copper metal, occurred with a low flow rate of oxygen as a reactive cofeed. A stronger oxidizer such as nitrous oxide was unnecessary. With optimization of the oxygen concentration, pure copper (I) oxide or copper (II) oxide may be deposited. Such control over oxygen content at low temperatures would be a significant advancement. High temperature oxidation steps which are incompatible with semiconducting materials, may not be required to synthesize thin film high temperature superconductors.

Degradation of the hydrocarbon pump oil was observed after this one experiment. It was decided that an increase in the oxygen concentration in the reactor might result in damage to or failure of the mechanical pump. This experimental system is not appropriate for further experiments with an oxygen cofeed.

Oxide deposition does not occur by the β -hydride/reductive elimination pathway observed for thermal deposition in inert atmosphere. Instead, there is extensive ligand fragmentation. Film contamination does not occur because the fragments are small, volatile and stable. It is not known whether the oxygen in the film originates from the ligands, from the reactive cofeed, or both.

Deposition from copper dimethylaminoethoxide in the presence of oxygen deserves further study to determine the effects of deposition temperature and oxygen concentration on the oxidation state of the as-deposited film. It may also be worthwhile to attempt codeposition with yttrium and barium precursors, to see if superconductivity can be achieved in films deposited at low temperature.

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6. Summary

6.1 Deposition Chemistry of Copper (II) Dimethylaminoethoxide

Thermal deposition from copper dimethylaminoethoxide does not occur on strontium titanate below 150°C. At 150°C, strontium titanate may have a catalytic effect on the precursor, as the films are extremely thin. At substrate temperatures of 200–210°C, conductive films of pure copper metal deposit on strontium titanate. At substrate temperatures of 250–270°C, deposited films are still copper metal, but contain significant oxygen and carbon contamination.

The major organic products of thermal deposition are identified by *in situ* infrared spectroscopy as dimethylaminoethanal and dimethylaminoethanol. Post-deposition NMR spectroscopy supports the identification of the alcohol. The reactions that produce the aldehyde and alcohol are interdependent. The aldehyde is formed by β -hydride elimination, which releases a hydridic hydrogen from the ligand. This hydrogen reacts with another alkoxy ligand. The resulting reductive elimination produces the alcohol and copper metal. These two reactions have been observed for alkoxy species on surfaces studied in UHV [1].

The interdependence of the two reactions leads to deposition of clean metal films without a reactive cofeed. Of the copper precursors reported in the literature, only copper β -diketonate trialkylphosphines deposit clean films without reactive cofeed at similarly low temperatures [2]. Low temperature deposition is important for silicon-based applications [3]. Process optimization is simplified if no reactive cofeed is necessary. The greatest barrier to practical applications of copper dimethylaminoethoxide is its sensitivity to hydrolysis.

The β -hydride/reductive elimination pathway remains important at 250°C. *In situ* infrared spectroscopy shows that dimethylaminoethanol and dimethylaminoethanal are produced. However, additional reactions which produce C=C or C=N species, and ligand fragmentation, also occur. The C=C or C=N species and carbon monoxide are detected by *in situ* infrared spectroscopy. Carbon monoxide and carbon dioxide production are indicated by mass spectral analysis of the reactor outlet gas. Formation of double bonds and production of CO and CO₂ indicates that ligands are fragmenting. This ligand fragmentation leads to carbon contamination of the film.

The nature of the carbon contamination, and the intermediates which lead to its formation, cannot be determined with the equipment available for this project. However, UHV studies of organic oxygenates on copper oxide surfaces have shown that dehydrogenation and deoxygenation of the oxygenates occurs, leaving carbon on the surface [4]. Such reactions may occur during deposition from copper dimethylaminoethoxide on strontium titanate at 250°C. Films deposited near 250°C are less conductive than those deposited at 200°C by two orders of magnitude, because of carbon incorporation.

The sheet resistivity of pure (as measured by Auger spectroscopy) copper films deposited on strontium titanate at 200°C exceeds that of bulk copper by nearly two orders of magnitude. This is probably due to the film morphology, which consists of submicron spheroid grains. Although the substrate is completely covered, the grains are poorly connected. The grains also adhere poorly to the substrate. A change of substrate might alleviate this problem.

This project began with ambitions to study photoassisted deposition from copper dimethylaminoethoxide extensively. The substrate band gap, the precursor UV absorption spectrum, and the output frequencies from the UV sources interact to allow separation of photolytic and pyrolytic processes, at least in the nucleation phase of film growth. Photoassisted deposition studies could lead to direct write techniques for copper patterning. Photoassisted deposition might also lead to film growth at lower substrate temperatures.

Unfortunately, exposure to UV radiation of the intensities obtainable from the Spectronics B-120 lamp or from the nitrogen lines of the Lumonics TE-860-4 laser did not lead to deposition at lower temperatures or to new reaction pathways. All of the observed film growth during UV exposure could be attributed to thermal deposition. A high power light source such as a tunable dye laser might allow studies of photodeposition from copper dimethylaminoethoxide.

The final phase of the MOCVD chemistry study concerned thermal deposition with a reactive cofeed. Experimental considerations limited the reactive species which could be used safely and successfully. It was discovered that copper dimethylaminoethoxide could only be transported in this system under reduced pressure. A preliminary deposition attempt at 200°C on strontium titanate in the presence of oxygen resulted in deposition of a clean (no

carbon or nitrogen detectable by Auger spectroscopy) film of mixed copper (I) oxide and copper metal. Deposition of copper oxide at a similar low temperature is not reported in the literature. This has potential applications for hybrid semiconductor-superconductor technology. Optimization of the oxygen feed might allow deposition of a pure oxide phase.

The reaction products of deposition in the presence of oxygen were quite different than those in inert atmosphere. Extensive ligand fragmentation occurs, yet there is no organic incorporation in the film. The products of fragmentation must be quite volatile and stable species. Volatile products indicated by mass spectral and infrared analysis include carbon monoxide, carbon dioxide, amines, and a carbonyl species (aldehyde or ketone).

The deposition chemistry directly affects the purity of the deposited film. Good precursors have a reaction pathway available that eliminates ligands as stable, volatile species. For copper (II) dimethylaminoethoxide in inert atmosphere, this is the β -hydride/reductive elimination pathway. At higher temperatures, this pathway still operates, but a second pathway involving ligand fragmentation is in competition. The effect of this second pathway is carbon contamination in the film. In the presence of oxygen, the β -hydride/reductive elimination pathway is not observed. However, ligand fragmentation is extensive and the resulting fragments are volatile and stable. This leads to deposition of uncontaminated films.

It is interesting that the effects of varying deposition temperature could be predicted to a great extent from a simple preliminary experiment, in which the precursor decomposed in the precursor tube and the volatile organic products were analyzed by infrared. Onset of decomposition was observed at 150°C. Dimethylaminoethanol and dimethylaminoethanal, whose formation precludes ligand fragmentation, were the only organics observed at 200°C. Deposition of pure films is expected. At 230°C, organic products containing C=C or C=N bonds appeared. The presence of double bonds suggests ligand fragmentation and possible film contamination.

The chemistry of film deposition from copper dimethylaminoethoxide has been studied. *In situ* chemical information was obtained and proved to be valuable. Without *in situ* IR analysis, no aldehyde product would have been identified. The effect of deposition temperature on deposition chemistry and the resulting film composition was addressed.

Clean films deposit in inert atmosphere at temperatures where ligands are eliminated without fragmentation. A lengthy effort was made to study photoassisted deposition chemistry without success. Numerous attempts to study deposition chemistry in reactive atmospheres were frustrated by experimental limitations. However, a successful preliminary experiment, with oxygen, again demonstrated a direct relationship between deposition chemistry and film composition.

6.2 Suggestions for Future Work

6.2.1 Equipment Modifications

If studies of MOCVD chemistry are to continue, the reactor/IR cell should be redesigned. It is time consuming and delicate work to replace the substrate in the current reactor. It is difficult to clean the current reactor, or even to see how dirty it is without disassembling it. It is time consuming and delicate work to disassemble and reassemble the current reactor.

A quartz reactor with IR transparent viewports should be designed. It should be in two pieces, sealed together by an o-ring and clamp assembly. It could be connected to an external flow system by ultratorr fittings. Care would have to be exercised to avoid chipping or breaking the quartz inlet and outlet tubing. However, it would be much easier to replace substrates, clean the reactor, and observe the deposition. This would reduce the minimum time needed for an experiment from seven days to four. A glass-to-metal seal and fitting for a conflat flange would be needed for introduction of a rotatable, heatable sample holder. This would be a warm wall reactor, wrapped in heating tape to prevent condensation of precursors on the walls. Only the substrate would be heated to the deposition temperature.

It would be worthwhile to keep the current stainless steel reactor if the opportunity arose to connect it directly to a UHV system, so samples could be transferred between the two without exposure to the air. However, the quartz reactor would still be useful for conducting preliminary and control deposition experiments.

For either reactor, a new sample holder is required. With the current sample holder, electrical leads come from the opposite flange. When the sample rotates, the leads and

connections are stressed. This leads to frequent electrical failure, especially of the thin substrate thermocouple. It would be better if the thermocouple and heater wires were built into the sample holder, parallel to the rotating shaft. This would be an expensive improvement, but would greatly reduce equipment downtime and researcher frustration.

Use of an existing IR spectrometer was suitable for a first effort to study deposition chemistry *in situ*. However, identification of products was sometimes frustrated by insufficient resolution or insufficient sensitivity. In particular, it is difficult to separate peaks from a mixture of related products. Multipass IR analysis would be preferable. With multipass FT-IR, species present in small concentrations would produce more intense spectra. This would allow spectra of higher resolution to be collected in about the same time. Separation of peaks and quantification would be facilitated by higher resolution. Multipass FT-IR would require careful alignment of mirrors and a method for reproducible placement of the reactor/IR cell.

For studies with reactive cofeeds, an explosion proof pump with a nonhydrocarbon lubricant should be purchased. This would alleviate concerns about safety and equipment failure.

6.2.2 Experimental Opportunities

Several opportunities for further study were mentioned where related experiments were reported.

On the subject of deposition chemistry in inert atmosphere, the question of substrate effects on deposition chemistry could be addressed. Do oxide surfaces have a catalytic effect on the minimum deposition temperature? A substrate of particular interest to the electronics industry is silicon. Would the onset of deposition from copper dimethylaminoethoxide occur at significantly higher temperature on silicon? An oxide surface is probably not necessary for deposition at 200°C, since growth continues after the first layer of copper metal is deposited at 200°C.

Also concerning deposition chemistry in inert atmosphere, the high temperature organic products could be identified and the pathways to their formation studied. This might

best be done in ultrahigh vacuum, using dimethylaminoethoxide adsorbed on copper metal. Mass spectra obtained during thermal desorption experiments might allow identification of the organic products. A more useful technique might be a vibrational spectroscopy. If IR spectra of species adsorbed on the surface at various temperatures were collected, intermediate species might be identified. The use of deuterium labeling to determine the mobility of eliminated β -hydrogens is another study appropriate for ultrahigh vacuum.

Opportunities for study of photoassisted reactions have already been mentioned. One possibility is to retest copper dimethylaminoethoxide with a stronger UV source. Another possibility is to use the same principles of system design to allow separation of photolytic and pyrolytic effects, and separation of surface and gas phase processes, with another precursor.

The most promising opportunity for further study lies in the area of deposition with reactive cofeed. Is it only a question of optimizing the oxygen flow rate to deposit pure Cu_2O at 200°C ? Can high temperature superconductors be deposited under similar mild conditions? These are questions to be answered in a deposition system.

What reactions lead to such extensive fragmentation of the alkoxy ligand? What is the source of the oxygen in the film? These are questions that may be answered *via* UHV studies. For instance, determination of the oxygen source would involve study of adsorbed, ^{18}O -labeled dimethylaminoethanol, and study of dimethylaminoethanol on copper metal, copper oxide, and strontium titanate surfaces predosed with $^{18}\text{O}_2$. The ^{18}O content of oxygen-containing species desorbing would be monitored to see whether C–O bonds in the alkoxy species are broken.

To cofeed $^{18}\text{O}_2$ in a normal deposition experiment would be prohibitively expensive. However, isotopically labeled precursor could be used in a deposition. This would also be expensive, requiring custom synthesis, but probably less expensive than an isotopically labeled reactive cofeed. Secondary ion mass spectrometry (SIMS) could be used to determine the ^{18}O content of the deposited film. The mass selective detector could be used to monitor the ^{18}O content of the volatile products. If the oxygen source is the reactive cofeed, no ^{18}O will be included in the film, but ^{18}O will be included in the volatile reaction products.

In general, these experimental opportunities require equipment that was not available for this work. In the author's opinion, deposition with an oxygen cofeed is the only worthwhile area for further fundamental research with copper dimethylaminoethoxide. The suitability of copper dimethylaminoethoxide as a copper precursor is best evaluated by the microelectronics industry. Further research into the chemistry of deposition from copper dimethylaminoethoxide in inert atmosphere is of little value at this time. The current results discourage further exploration of photoassisted deposition with this precursor. However, similar studies of deposition chemistry with other precursors are encouraged.

6.3 Conclusion

The chemistry of chemical vapor deposition from a copper alkoxide precursor has been studied using *in situ* IR spectroscopy, mass spectroscopy, NMR spectroscopy, Auger spectroscopy, and X-ray photoelectron spectroscopy. Although a major thermal decomposition pathway has been deduced, numerous unanswered questions remain about the reaction pathways available under different deposition conditions. Metalorganic chemical vapor deposition is a chemically complex process. The chemistry directly affects the composition of the deposited film. Information about the reaction pathways for precursor decomposition is useful for evaluating a precursor and choosing deposition conditions appropriate for it. Studies of the deposition chemistry of copper metalorganics should continue if copper is to be useful in the microelectronics industry.

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A1. Appendix 1 - Studies of Copper (I) t-Butoxide

A1.1 Introduction

When Jeffries and Girolami [1] published their study of film deposition from copper (I) t-butoxide, it was the first example of MOCVD from a non- β -diketonate precursor. A key point of their work was the demonstration that clean copper metal or copper (II) oxide could be deposited from the same precursor, simply by varying the amount of water present. This was important because interest in copper MOCVD had recently been stimulated by the desire to grow thin films of the copper oxide high temperature superconductors. The ability to grow thin films of copper oxide at low temperatures is one step towards low temperature growth of multicomponent oxide films that are superconducting as deposited, and do not require a post-deposition anneal in oxygen. Although the deposition temperature Jeffries and Girolami reported (400°C) would be considered high for semiconductor processing, it would be a major improvement over the usual 700 – 800°C anneal to achieve superconductivity.

Jeffries and Girolami deposited films in a high vacuum system (base pressure 10^{-8} Torr). Their chemical investigation of deposition was limited to mass spectral analysis of gases leaving the hot zone of the Pyrex tube reactor. Tertiary butanol was the only product detected in deposition of both copper and copper oxide. However, they proposed a t-butoxy free radical mechanism for deposition of the metal, and hydrolysis as the mechanism for deposition of the oxide. No isobutylene was detected, in contrast to studies of t-butanol adsorbed on copper surfaces [2]. This is strange, because metal alkoxide chemistry is expected to be analogous to the chemistry of alkoxy species adsorbed on metal surfaces.

The chemistry of copper MOCVD is seldom studied. This project was undertaken on the premise that insufficient understanding of deposition chemistry hinders commercial development of copper MOCVD. The goal was an increased understanding of the deposition chemistry of one precursor, which might lead to a more general understanding of requirements for reliable copper MOCVD. Copper t-butoxide was chosen for study rather than one of the β -diketonates for several reasons.

At the inception of this project, a number of established groups were already exploring the possibilities of β -diketonates. The copper β -diketonates and copper t-butoxide

were the only reported copper MOCVD precursors at that time. Copper t-butoxide was a less-tried, but apparently feasible, precursor. There was less likelihood of this project overlapping others. However, there were questions as to whether copper t-butoxide could be used without an ultrahigh vacuum deposition system.

Two decomposition pathways were already proposed for copper t-butoxide. This suggested that a study of chemistry with respect to processing conditions would prove interesting. Could deposition be induced at lower temperatures? Could decomposition to isobutylene be activated, possibly resulting in copper oxide deposition?

Copper t-butoxide contains Cu–O–C single bonds, as opposed to the aromatic structure of the β -diketonates [3]. The β -diketonates always deposit metal in the absence of oxidizers such as N_2O [4], but one might choose to deposit pure metal or pure oxide with an alkoxide. This is confirmed by Jeffries and Girolami's results in the presence of water, but there may be another way to select the bond to be broken. For example, photodecomposition is often selective for one pathway over another [5]. Successful photodeposition is the first step to laser-direct writing, as discussed in Chapter 1.

This chapter summarizes 18 months of effort to study the copper and copper oxide deposition chemistry of copper t-butoxide. When copper (II) dimethylaminoethoxide became available, the copper t-butoxide work was abandoned. Copper t-butoxide could not be transported consistently in the system. However, the results that were obtained are interesting in light of the studies of Jeffries and Girolami [1] and Brainard and Madix [2], and in comparison with the results using copper dimethylaminoethoxide.

A1.2 Experimental Methods and Procedures

A flow system was designed to study the deposition chemistry of copper alkoxides. The components are described fully in Chapter 2. The key component is the stainless steel deposition reactor containing the heated stage upon which the substrate, strontium titanate, is mounted. The reactor is also an infrared (IR) cell and sits within the optical bench of an FT-IR spectrometer. The IR beam passes through calcium fluoride windows to sample the gas phase within the reactor. The carrier gas is 99.999 per cent helium. All lines and the

reactor are warmed by heating tape to within 10°C of the precursor tube temperature, not to exceed 150°C. The precursor tube is heated independently by heating tape. A direct-drive mechanical vacuum pump at the outlet allows evacuation of the system to approximately 10^{-2} Torr.

A1.3 Synthesis and Properties of Copper t-Butoxide

Copper t-butoxide, CuOtBu, was synthesized by the method of Tsuda, *et. al.* [6].



The reactants were stirred for six hours at room temperature under nitrogen. The tetrahydrofuran (THF) was removed by vacuum evaporation. The dry yellow precipitate was purified by sublimation for four to six hours at 160°C under reduced nitrogen pressure. The resulting compound was yellow-white and turned black instantly upon exposure to air. Longer sublimation times resulted in discoloration of the product, likely due to thermal decomposition. Identification of the product as copper t-butoxide was made by nuclear magnetic resonance (NMR) and IR spectroscopy.

The proton NMR spectrum of the synthesized compound shows nine equivalent t-butyl protons [7]. (Chemical shift of t-butyl hydrogens: $\delta(\text{tBuOH})=1.08$ ppm; $\delta(\text{CuOtBu})=1.24$ ppm; $\delta(\text{CuOtBu}+\text{H}_2\text{O})=1.05$ ppm. CuOtBu, CuOtBu+H₂O dissolved in d₆-benzene.) The infrared spectrum is consistent with that reported by Tsuda, *et. al.* [6,8]. Copper t-butoxide can be distinguished from t-butanol by the positions of several peaks between 1000 and 2000 cm⁻¹. See Table A.1. The calcium fluoride windows are not transparent to infrared frequencies below 1000 cm⁻¹.

Copper t-butoxide is extremely sensitive to water and oxygen, hence its rapid conversion to CuO upon exposure to laboratory air. It was stored and handled in a dry box. It was vital to dry all glassware and tightly seal all flasks and the precursor tube.

Copper t-butoxide is a tetramer [9], the oxygen of one molecule bonding to the copper of its neighbor. The oxygens and coppers form a square, with coppers on the edges and oxygens at the corners. This tetrameric structure limits its volatility.

Table A.1 Infrared Peak Positions for t-butanol and copper t-butoxide in wavenumbers

t-BuOH Liquid	t-BuOH Vapor	CuOtBu Vandigrift	CuOtBu Tsuda *
1468	1471	1455	1450
1375	1373	1384	1380
1360	1329	1356	unresolved
1234	1215	1229	1230
1194	1141	1180	1180

* Read from photocopied spectrum

Copper t-butoxide sublimes very slowly at 100°C and 10^{-5} Torr [1,10]. A vapor pressure of at least 0.1 Torr is required for precursors in order to obtain reasonable growth rates [11]. Copper t-butoxide sublimes at 170°C and about 1 Torr [6]. Unfortunately, copper t-butoxide is not stable above 170°C, and its stability is measured in hours at slightly lower temperatures [12]. The thermal properties of the complex proved to be the bane of research with copper t-butoxide.

The UV absorption properties of copper t-butoxide were encouraging for photo-assisted deposition. (Refer to Figure A1.1) Copper t-butoxide absorbs strongly from about 330 nm to 380 nm. Absorption tails off thereafter, but has not reached a minimum at 430 nm. This wavelength region includes the band gap of strontium titanate. Tertiary butanol, which lacks the Cu-O bond, does not absorb UV above 300 nm. This indicates that UV absorption by copper t-butoxide between 330 nm and 430 nm is related to metal-ligand bonding. It was hoped that the metal-ligand bond could be broken by UV light. The ligand itself was not expected to photolyze, since it does not absorb in this region. Since copper t-butoxide absorbs light on either side of the strontium titanate band gap (388 nm), the photolytic component of any photoassisted deposition could be separated from the pyrolytic component.

A1.4 Preliminary Experiment: Batch Thermal Deposition

As a preliminary test of thermal deposition, a batch reactor was designed. Refer to Figure A1.2. The two pieces of the glass reactor are sealed together with a clamp and o-ring, so the precursor and substrate are easily loaded in the drybox. The outlet is at the top of the upper piece. The inlet is at the bottom of the lower piece. The precursor rests on a glass frit in the lower piece, and the carrier gas flows up through the frit and over the precursor. The substrate is mounted on a metal (aluminum and stainless steel) frame and suspended above the precursor. The reactor was baked in a 120°C oven overnight before introduction of the precursor.

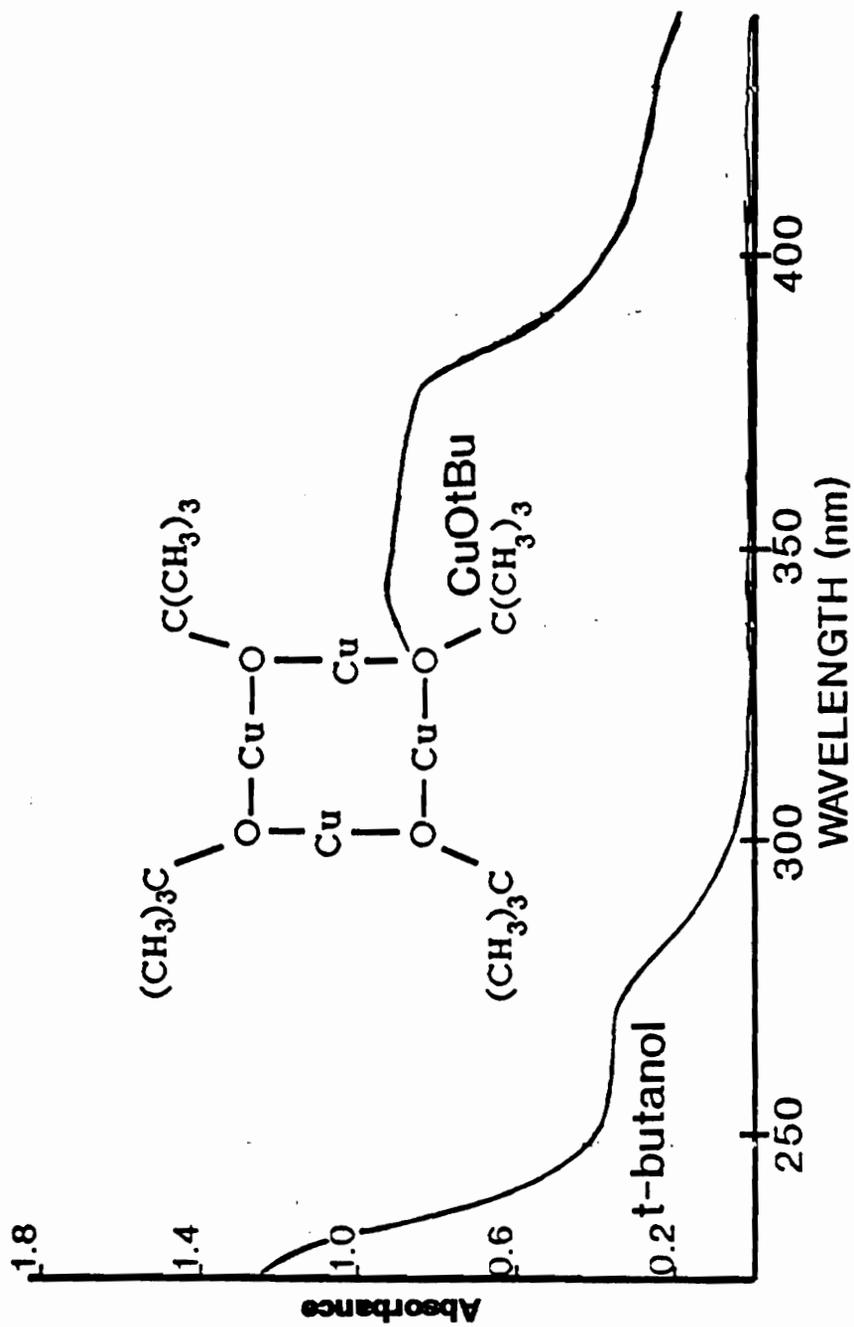


Figure A1.1 UV absorption spectra of copper t-butoxide and t-butanol

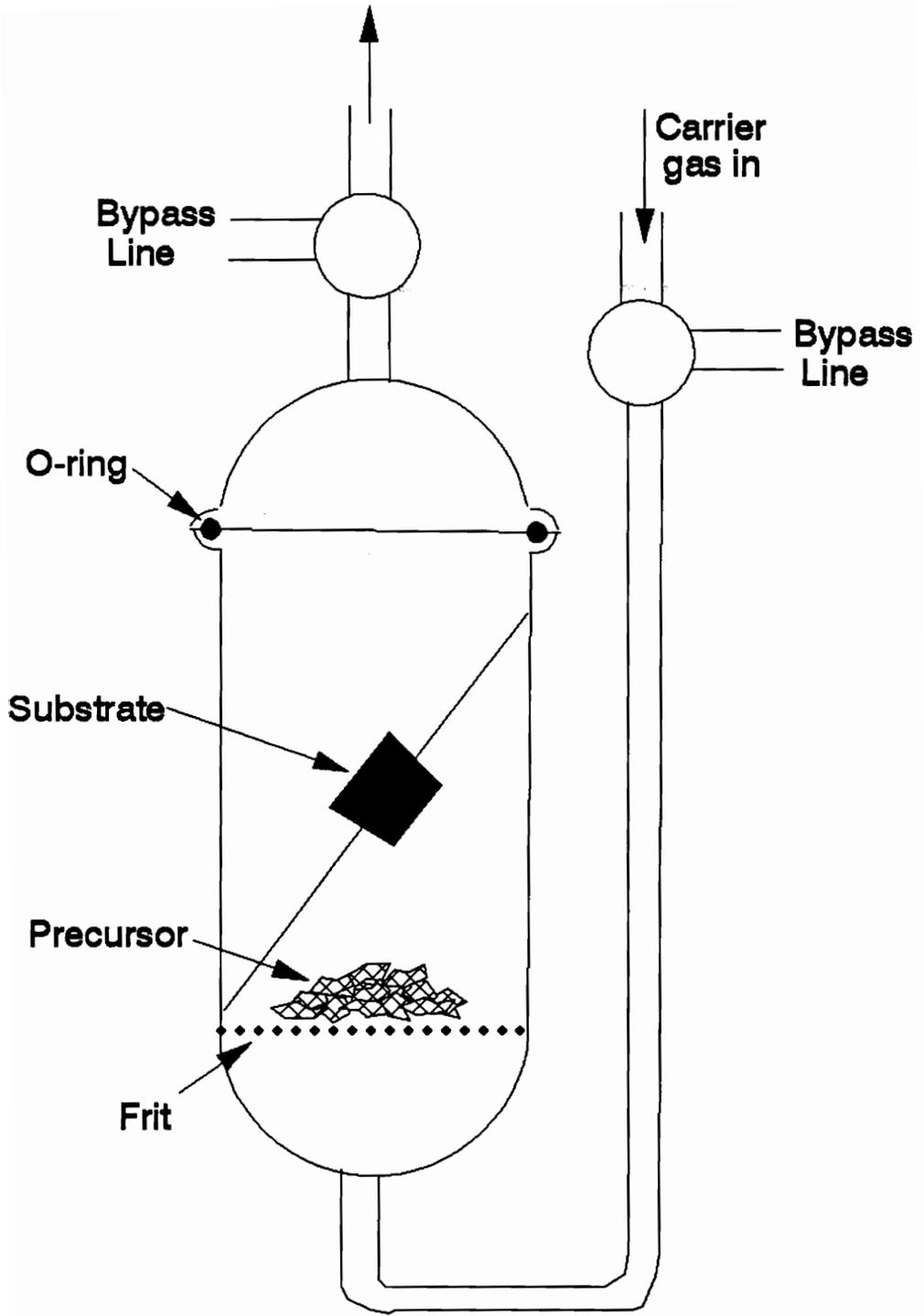


Figure A1.2 Batch deposition reactor

The batch reactor was placed in an oil bath at 91°C and evacuated by a mechanical vacuum pump (pressure estimated at 10^{-2} – 10^{-3} Torr). After four hours, a yellow, non-conductive film was apparent on the substrate and on the walls of the reactor. This film did not change in color upon exposure to air. The precursor remaining on the frit had turned dark brown. Note that the reactor was not treated with dichlorodimethylsilane, so hydroxyl groups are expected on all surfaces and the frit may contain significant adsorbed water in its pores. There was no evidence that copper t-butoxide was carried out of the reactor, although some was condensed on the interior wall of the reactor just above the oil bath level.

Auger analysis reveals a very thin, copper-containing film. The substrate was not detectable before ion bombardment of the film. However, after only five minutes of ion bombardment, the titanium signal from the substrate was strong. An order-of-magnitude estimate of the film thickness is 50 Å, slightly larger than the 20 to 30 Å sampling depth of Auger electron spectroscopy. Because the substrate was reached so quickly, it was not possible to remove surface contamination by ion bombardment and analyze the bulk film. The oxidation state and purity of the deposited film is unknown. The copper signal was still strong after 5 minutes of ion bombardment, while the carbon signal was barely above the noise. This suggests that little or no carbon was included during deposition. The carbon remaining can be attributed to post-deposition contamination from air exposure.

The thinness of the film, coupled with the low deposition temperature suggests some surface-catalyzed reaction. It is possible that vapor phase copper t-butoxide molecules react with surface hydroxyl groups and decompose. Similar deposition was not observed during sublimation for purification. However, hydroxyl groups on the reactor walls may be constantly replenished by water desorbing from the frit. Solid copper t-butoxide is hydrolyzed simultaneously by water from the frit. When the solid is completely decomposed and the gas-phase copper t-butoxide is exhausted, deposition ceases. The film is thin because the precursor is quickly exhausted by hydrolysis. Raising the reactor temperature is unlikely to be effective. The desorption rate of water from the frit is always in competition with the sublimation rate of the precursor.

The results of Jeffries and Girolami [1] indicate t-butanol and copper (II) oxide as likely products of this deposition, given the presence of water. The actual products in this batch deposition experiment are unknown. The yellow color of the film would seem to rule out copper (II) oxide, which is black. However, color is an unreliable indicator in such a thin film.

This preliminary experiment showed that water in the system would strongly impede the efficient transport of the precursor. Much of the precursor was hydrolyzed before it sublimed. To minimize water in the system, glassware was treated with dichlorodimethylsilane, and the system was heated and purged with helium gas under reduced pressure for two to three days before a deposition attempt.

The preliminary experiment also demonstrated that a copper-containing film could be deposited from copper t-butoxide in the presence of water at lower temperatures than reported by Jeffries and Girolami [1]. However, the introduction of water into the system would have to be carefully balanced with the vapor phase concentration of the precursor to grow thicker films. Water should only contact the precursor in the deposition zone. Unfortunately, it is not practical to test water as a cofeed in the stainless steel deposition reactor because of the likely damage to the calcium fluoride IR windows.

A1.5 Attempted Thermal Deposition in the Flow System

Despite the encouraging results of the preliminary experiment, deposition was never successful in the flow system. In fact, significant amounts of the precursor reached the reactor only twice. On the first occasion, copper t-butoxide condensed on the calcium fluoride windows. (Identification of the condensate was made from the IR spectrum and the fact that it turned black on exposure to air.) To counter this, the temperature of the window purge gas was increased. On a later occasion, concentric rings, metallic in appearance, were deposited on the windows at the window purge gas lines. On both of these occasions, the substrate happened to be unheated.

Numerous other attempts, under the same conditions as far as could be measured, gave no evidence for precursor transport into the reactor. Copper t-butoxide was not detected

by IR spectroscopy. No deposition ever occurred on the hot substrate, as evidenced by the absence of copper peaks in Auger spectra of the surface. Precursor tube temperatures from 90°C to 150°C were tested. Attempts were made at atmospheric and reduced pressure. Carrier gas flow rates of 20 sccm to 100 sccm were tried. Run times as long as 24 hours with the substrate hot showed no deposition. Consistent transport of copper t-butoxide in this experimental system was not achieved.

One source of trouble is the thermal behavior of copper t-butoxide. The sublimation temperature was 150°C on both occasions that copper t-butoxide was transported into the reactor. Unfortunately, copper t-butoxide is not stable at 150°C. A solid sample decomposes completely within a few hours to leave a brownish residue. Gas-phase molecules may decompose on impact with the warm system walls, never reaching the deposition zone.

At lower sublimation temperatures, copper t-butoxide was never detected in the reactor by IR spectroscopy. (It was demonstrated, on the two occasions that copper t-butoxide did reach the reactor, that the alkoxide could be distinguished from the alcohol in the reactor by IR spectroscopy.) The volatility of copper t-butoxide appears to fall off sharply with temperature. It was not unusual, upon unwrapping the heating tape from the precursor tube, to see a metallic-looking film in one region and condensed precursor a short distance away.

Although the metal system conducts heat, uniform heating cannot be achieved with heating tape. Molecules may condense in one section of the system and decompose in another. On occasion, the heating tape is placed just right, and heating is sufficiently even to transport observable amounts of precursor. The system must be unwrapped and disassembled to clean the windows or analyze the substrate for copper. The tape is placed slightly differently on reassembly, and the previous conditions are not reproduced, although the same readings may be obtained from system thermocouples. Thus it was impossible to control the system temperature with enough precision to reliably transport copper t-butoxide.

The other source of difficulty in moving the precursor is adsorbed hydroxyl groups on the interior walls of the system. In general, copper t-butoxide decomposed completely to t-butanol before reaching the deposition reactor/IR cell. t-Butanol is the only gas phase t-butyl species observed by IR spectrometry in the reactor. t-Butanol is produced by reaction

of the copper alkoxide with hydroxyl groups adsorbed on the system walls. In spite of long-term heating and purging of the system, such adsorbed species persist.

Consider results obtained in the same experimental system with copper dimethylaminoethoxide, another precursor subject to hydrolysis. Copper dimethylaminoethoxide is sublimed and transported at 90°C to 100°C. The precursor is brought online after two days of purging the heated system with helium under reduced pressure. In the first four to six hours of the run, the infrared spectra show only dimethylaminoethanol, the alcohol. Over the next two or three hours, the spectrum changes to that characteristic of the alkoxide. This suggests that precursor at first reacts with surface bound groups containing hydrogen (*i.e.* hydroxyls, water) in the system. Precursor transport through the passivated system is then possible. The same pattern is seen after an initial purge of three days, suggesting the hydrogen source is surface-bound and not removable by purging.

After a two day purge of the heated system with helium under reduced pressure, *t*-butanol is the only species observed by IR when copper *t*-butoxide is put online. *t*-Butanol remains the only species detected until the precursor is exhausted (as indicated by detection of no organic-related stretches by IR spectroscopy) about twenty-four hours later. Copper *t*-butoxide appears unable to passivate the system walls. This inability to passivate the system is related to the thermal behavior of copper *t*-butoxide.

Copper *t*-butoxide has a low vapor pressure, even at 150°C, and thermal decomposition competes successfully with sublimation. Apparently, the precursor is simply exhausted before the system walls are passivated. Because sufficient vapor pressure can be achieved with copper dimethylaminoethoxide at temperatures at which it is more stable thermally, copper dimethylaminoethoxide can be successfully studied in this system.

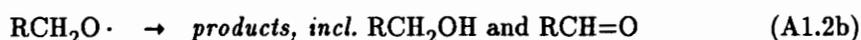
It is appropriate here to address specifically claims made by Jeffries and Girolami in their paper on thermal deposition from copper *t*-butoxide [1]. In their work, deposition occurred in a section of the ultrahigh vacuum system heated to 400°C by a tube furnace. The gaseous products leaving the reaction zone were analyzed by mass spectrometry. *t*-Butanol was the only product detected. Jeffries and Girolami propose that copper *t*-butoxide decomposes via homolytic bond scission to copper metal and *t*-butoxy radicals. These free

radicals then wander through the system until they collide with the system walls, where they react with adsorbed hydroxyl groups to form t-butanol.

This scenario is difficult to credit. Jeffries and Girolami give no direct evidence for the presence of t-butoxy radicals. Under ultrahigh vacuum, some free radicals would be expected to escape the deposition zone without collision and be detected. Alcohols adsorbed on surfaces in ultrahigh vacuum have been studied extensively. [2,13,14,15,16] Upon adsorption, alcohols lose the alcoholic hydrogen to form an adsorbed alkoxy group. This alkoxy group is no different from the alkoxy group of copper t-butoxide. There is no evidence for desorption of free alkoxy radicals in ultrahigh vacuum studies of alcohols on surfaces. There is no reason to expect alkoxy species derived from copper t-butoxide to act differently.

Whitesides, *et. al.* [12] also propose the formation of t-butoxy radicals in the thermal decomposition of copper t-butoxide. They show evidence for alkoxy radical formation in the thermal decomposition of primary copper (I) alkoxides. This evidence was mainly the affect of solvent proton donor strength on the product distribution.

Thermal decomposition of copper (I) alkoxides was observed to produce an alcohol and an aldehyde or ketone. Two thermal decomposition pathways in solution were proposed: (1) homolytic scission of the copper – oxygen bond to form alkoxy radicals, and subsequent reaction of the radicals to form the alcohol and aldehyde products; (2) β -hydride elimination to form the aldehyde/ketone and a copper hydride, and subsequent reaction of the hydride with another alkoxide to form the alcohol. These two pathways are shown below.



The products of thermal decomposition of a number of primary and secondary alkoxides in solution were analyzed. For primary alkoxides, the ratio of alcohol to aldehyde produced was greatly increased in a strong proton donor solvent, such as tetrahydrofuran,

versus a weak proton donor, such as pentane. This would be expected for an alkoxy radical intermediate, which could react with the solvent. Also, small amounts of radical fragmentation and radical-radical combination products were detected for primary copper (I) alkoxide decomposition in solution. Whitesides *et. al.* concluded that primary copper (I) alkoxides decomposed via an alkoxy radical intermediate. The ratio of alcohol to ketone produced was not affected by the solvent for secondary alkoxides, and was consistently near 1.0. The alcohol and ketone were the only products detected. From this evidence, Whitesides *et. al.* concluded that secondary copper (I) alkoxides decompose via a copper hydride intermediate.

Copper t-butoxide does not have β -hydrogens to be eliminated, so formation of the copper hydride intermediate is precluded for this alkoxide. For this reason, Whitesides *et. al.* proposed that it would decompose via formation of the t-butoxy radical. (Note that this decomposition was not actually studied.) More recent studies of t-butoxy species on metal surfaces [2,8] have shown that products such as isobutylene, t-butanol, acetone, and water are formed without a free radical intermediate. It is speculated that the adsorbed t-butoxy species interacts with the surface via a methyl hydrogen as well as through the oxygen. Such studies of tertiary alkoxy species are a better analogy for copper t-butoxide MOCVD chemistry than solution behavior of primary alkoxides.

The following mechanism for the formation of t-butanol from copper t-butoxide is proposed to explain the production of t-butanol in this system and the system of Jeffries and Girolami.

Copper t-butoxide adsorbs on a surface. To simplify visualization, the copper atom may be regarded as part of the surface, leaving an adsorbed alkoxy species. This adsorbed alkoxy species reacts with an adsorbed hydroxyl group or adsorbed hydrogen to form t-butanol, which desorbs. The adsorbed alkoxy species may also react to form isobutylene, $(\text{CH}_3)_2\text{C}=\text{CH}_2$, which then desorbs. This releases more hydrogen onto the surface, and oxygen. (Jeffries and Girolami do report 5 atomic per cent oxygen in their films.) Formation of isobutylene is a minor reaction when adsorbed hydrogen sources are available, as would be expected in a Pyrex vacuum system. Thus the reported decomposition to t-butanol is

actually a bimolecular reaction between surface species, not a unimolecular decomposition resulting in vapor phase free alkoxy radicals.

Although copper t-butoxide proved unsuitable for MOCVD chemistry studies in this system, some aspects of alkoxy species decomposition chemistry were observed with the FTIR. Comparisons can be made with the ultrahigh vacuum studies of t-butanol adsorbed on copper published by Brainard and Madix, [2] which confirms the applicability of chemistry seen under ultrahigh vacuum to less ideal conditions.

A1.6 Decomposition Chemistry of t-Butanol

Because t-butanol was the only species present in the reactor during attempts at deposition from copper t-butoxide, no copper was ever deposited on hot strontium titanate. However, decomposition of t-butanol was observed.

With the substrate (strontium titanate) at 200°C, stretches characteristic of isobutylene, $(\text{CH}_3)_2\text{C}=\text{CH}_2$, were observed by IR spectrometry [17]. A typical spectrum is shown in Figure A1.3. Isobutylene and t-butanol were the only organic gas-phase species detected up to 360°C, the highest substrate temperature tested. Concurrent production of water is expected. However, water production is difficult to track by IR. The water content of the atmosphere in the FTIR bench, outside of the reactor, is too variable. Another likely decomposition product is acetone, $(\text{CH}_3)_2\text{C}=\text{O}$. The strong C=O stretch at 1738 cm^{-1} characteristic of gas-phase acetone [18] was not detected by IR. There was also no indication of isobutylene oxide as a product. This is interesting in light of ultrahigh vacuum studies of t-butanol decomposition on oxygen-predosed copper [2] and on oxygen-predosed silver [13]. There are no published studies of t-butanol decomposition on oxide surfaces.

t-Butanol reacts with the oxygen-predosed surfaces in ultrahigh vacuum to form a t-butoxy intermediate. On silver, reactions at 165°C and 235°C produce isobutylene oxide, isobutylene, and water. Acetone is produced at 315°C [13]. On copper, however, the t-butoxy species decomposes at 325°C to isobutylene and t-butanol [2]. The absence of oxygenated products from copper is explained by copper's higher affinity for oxygen as compared with

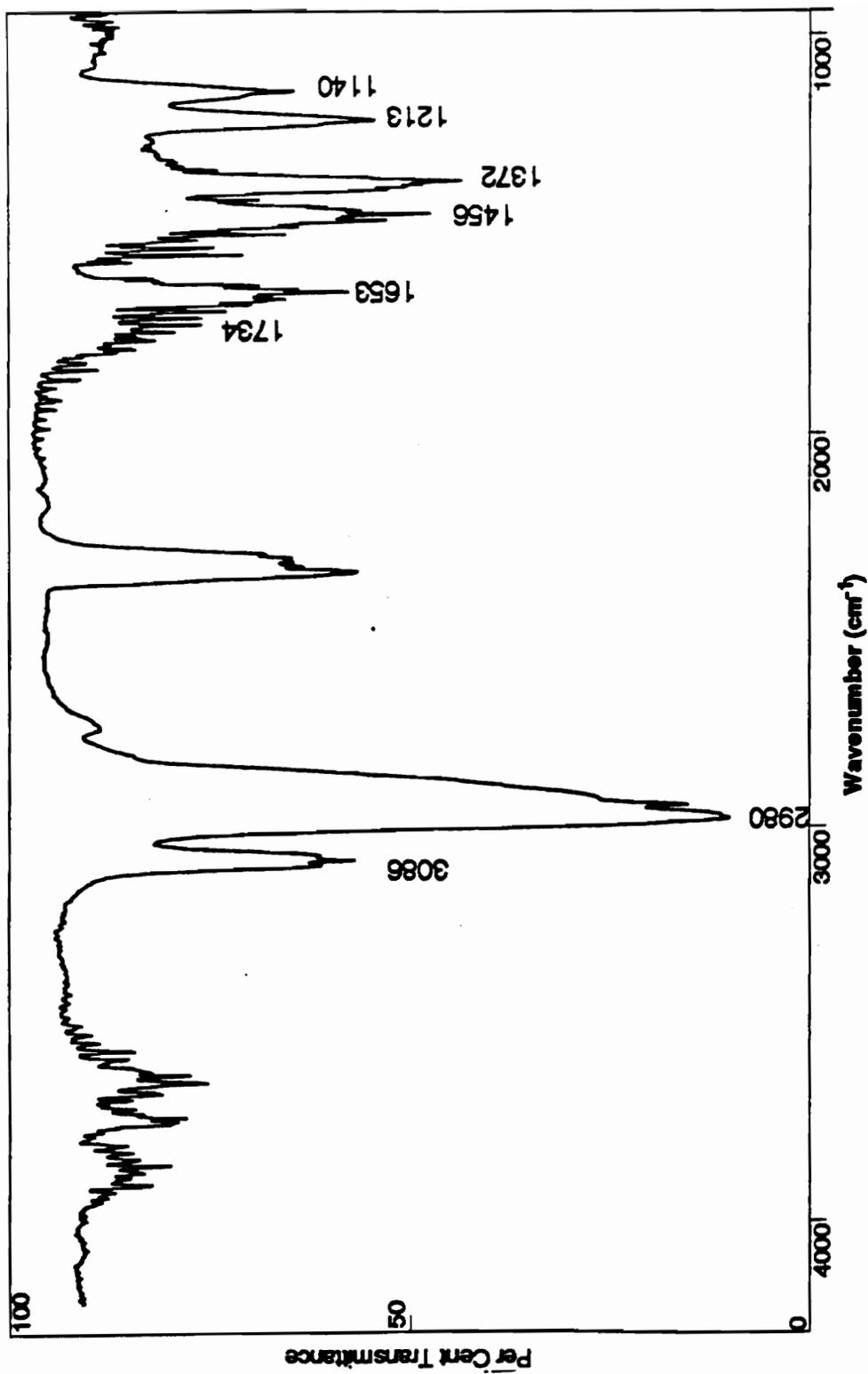
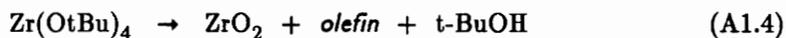


Figure A1.3 IR absorption spectrum, t-butanol reacts to form Isobutylene

silver. A similar argument may be made for the strontium titanate crystal, which is reduced, and therefore would be likely to have a high affinity for oxygen.

Because t-butanol lacks a β -hydride elimination pathway (having no β -hydrogens) there is no low-energy pathway to the formation of carbonyl species. Primary and secondary alcohols form aldehydes and ketones by the elimination of hydrogen. Formation of acetone from a t-butoxy species requires the elimination of methane, which is a high energy process. Note that formation of acetone on silver occurs at a temperature 250°C higher than the formation of isobutylene. This, combined with the affinity of the reduced surface for oxygen, suppresses the production of acetone in this system. However, a t-butyl methyl group may lose a hydrogen to the surface. This triggers formation of a carbon – carbon double bond, and cleavage of the carbon – oxygen bond. Isobutylene desorbs from the surface. A schematic of the process is shown in Figure A1.4.

Bradley and Factor investigated the decomposition of zirconium t-butoxide at about 220°C [19]. The overall reaction was found to be



They theorized that the olefin (not identified, but most likely isobutylene) was not a direct product of the alkoxide decomposition, but rather resulted from dehydration of the alcohol. Trace water in the system hydrolyzed the zirconium alkoxide to zirconium oxide and t-butanol. t-Butanol reacted on the hot reactor walls to form isobutylene and water. The water hydrolyzed more of the alkoxide. Thus Bradley and Faktor were also unable to study the thermal decomposition of an alkoxide separate from its hydrolysis. Their results also indicate that the surface chemistry of alkoxy species reported from ultrahigh vacuum studies is generally applicable.

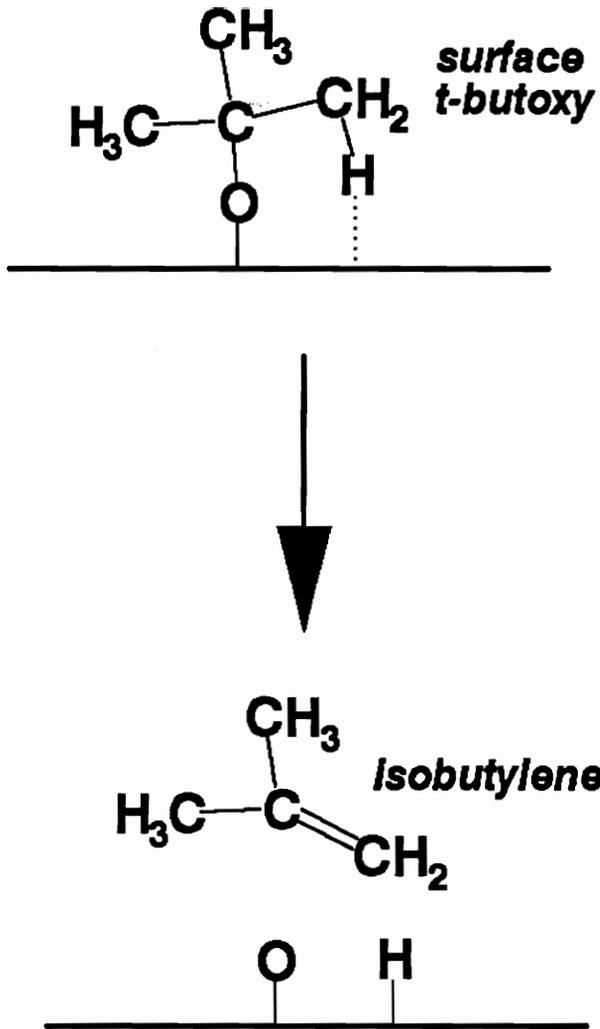


Figure A1.4 Schematic of reaction of surface t-butoxy group to isobutylene

A.7 Conclusions

Dehydration of t-butanol to isobutylene occurs between 200°C and 360°C on strontium titanate. Acetone is not formed, probably because too little energy is available for methane elimination and because the reduced strontium titanate surface has a high affinity for oxygen. Production of isobutylene takes place via a t-butoxy surface intermediate, as has been shown on metal surfaces in ultrahigh vacuum.

It is impossible, in this experimental system, to study the thermal decomposition of copper t-butoxide separate from its hydrolysis. Copper t-butoxide cannot be transported reliably because of its low volatility, thermal instability, and tendency to react with adsorbed hydroxyl groups in the system. This reaction is analogous to the reactions of alkoxy species resulting from the adsorption of alcohols, which have been studied in ultrahigh vacuum. Copper t-butoxide adsorbs on the system wall. The t-butoxy group reacts with an adsorbed hydroxyl group to form t-butanol, which desorbs. Although it has been shown to produce copper-containing films, copper t-butoxide is not suitable for further study in this system. The same difficulties in transport and handling make copper t-butoxide unlikely to find application in the electronics industry.

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A2. Appendix 2 - Standard Spectra

This appendix contains vapor phase infrared spectra of acetone, acetaldehyde, formaldehyde, and dimethylethylamine. The chemicals were purchased from Aldrich Chemical Company and used without further purification. The spectra were collected with the IR/32 FT-IR used in this project. Resolution was 4 cm^{-1} and apodization was triangular, as for all other spectra in this work. The deposition reactor acted as the IR cell, and the samples were evaporated from the precursor tube.

Formaldehyde was obtained by heating solid paraformaldehyde. The other samples were liquids when introduced to the precursor tube. Acetaldehyde presented difficulties because its boiling point is near room temperature. The acetaldehyde, the disposable pipette, and the precursor tube were all placed in the freezer for an hour before attempting to pipette the acetaldehyde into the precursor tube. In addition, the precursor tube was kept in an ice bath during the transfer.

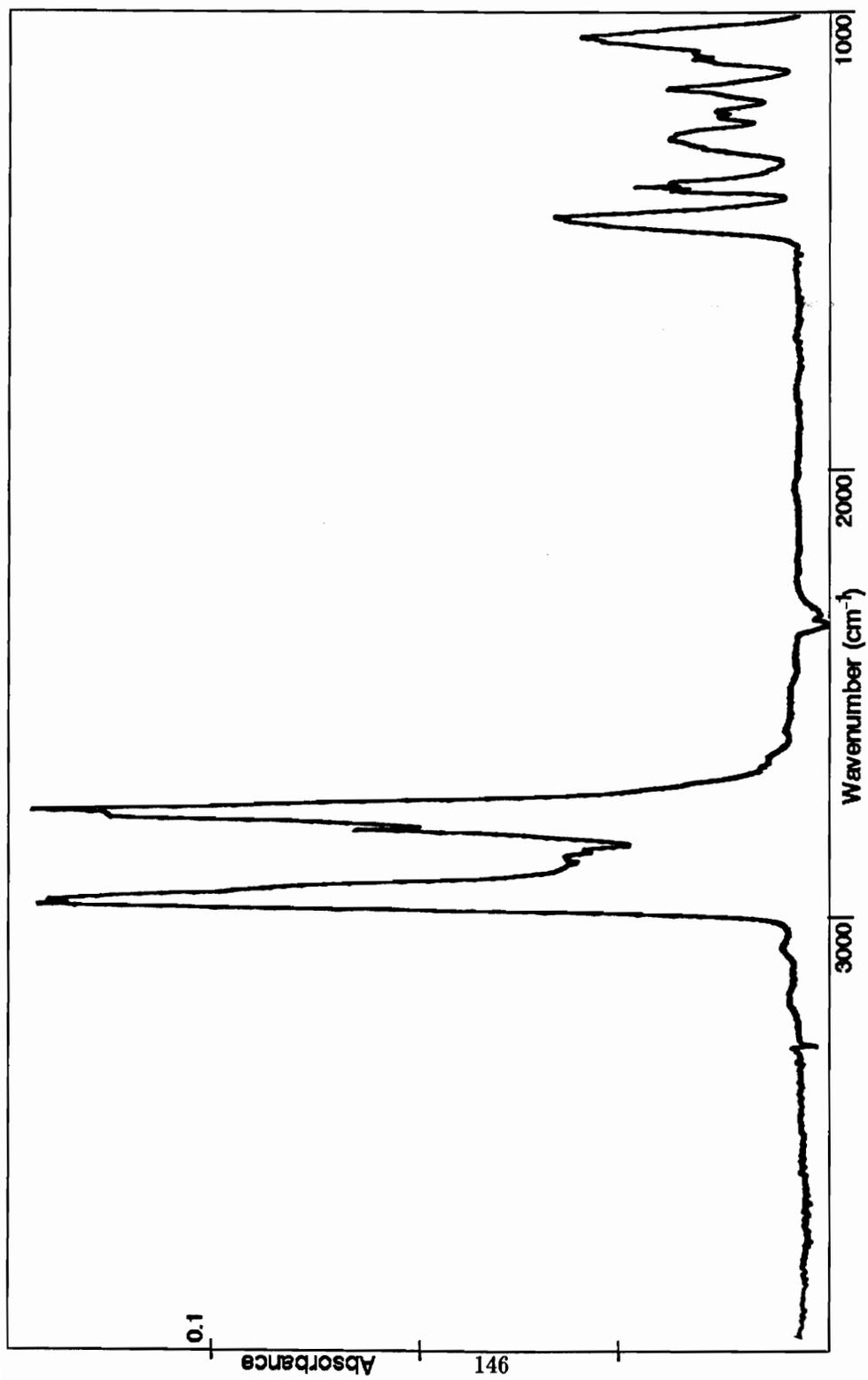


Figure A2.1 Infrared spectrum of vapor phase dimethylethylamine

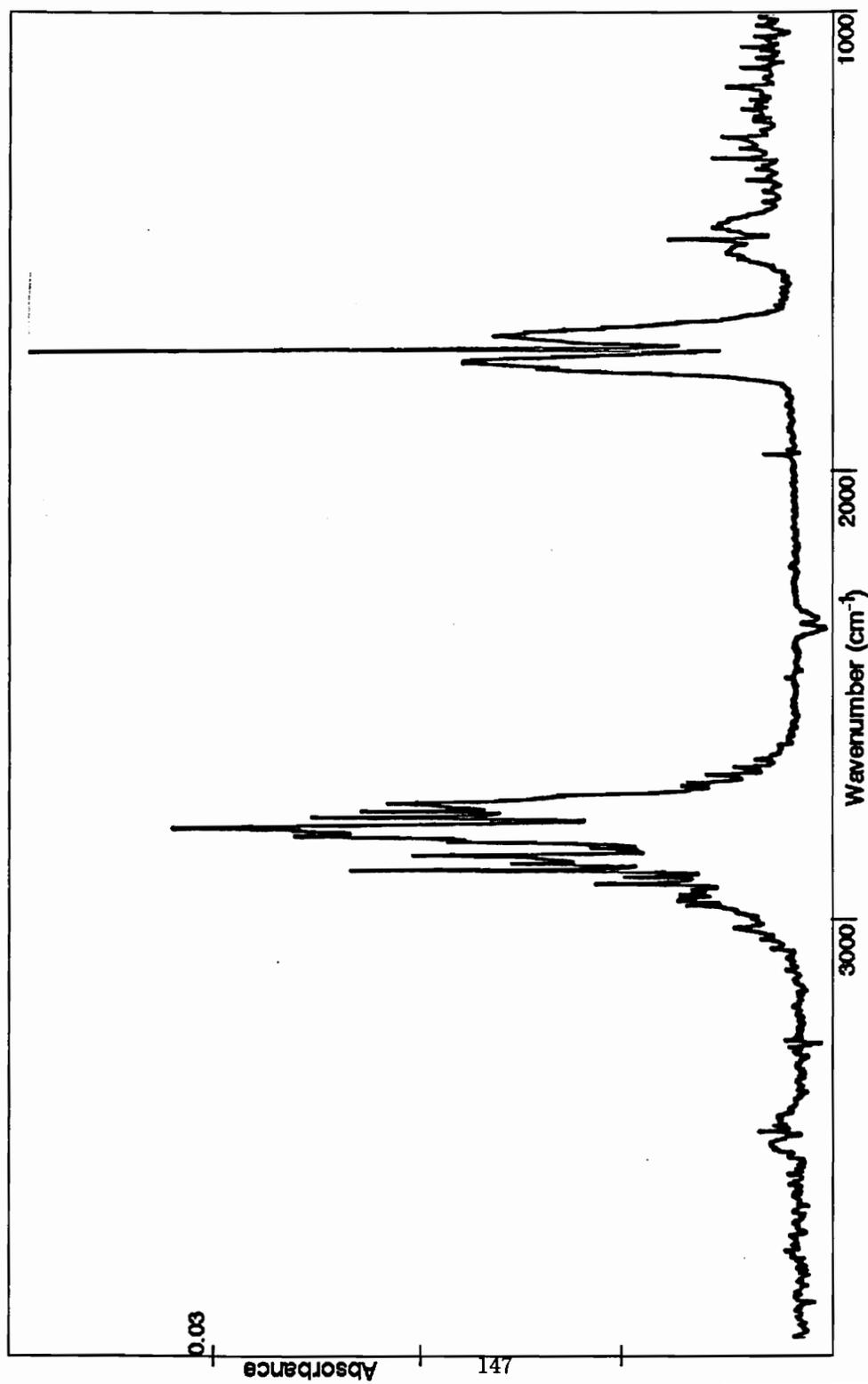


Figure A2.2 Infrared spectrum of vapor phase formaldehyde

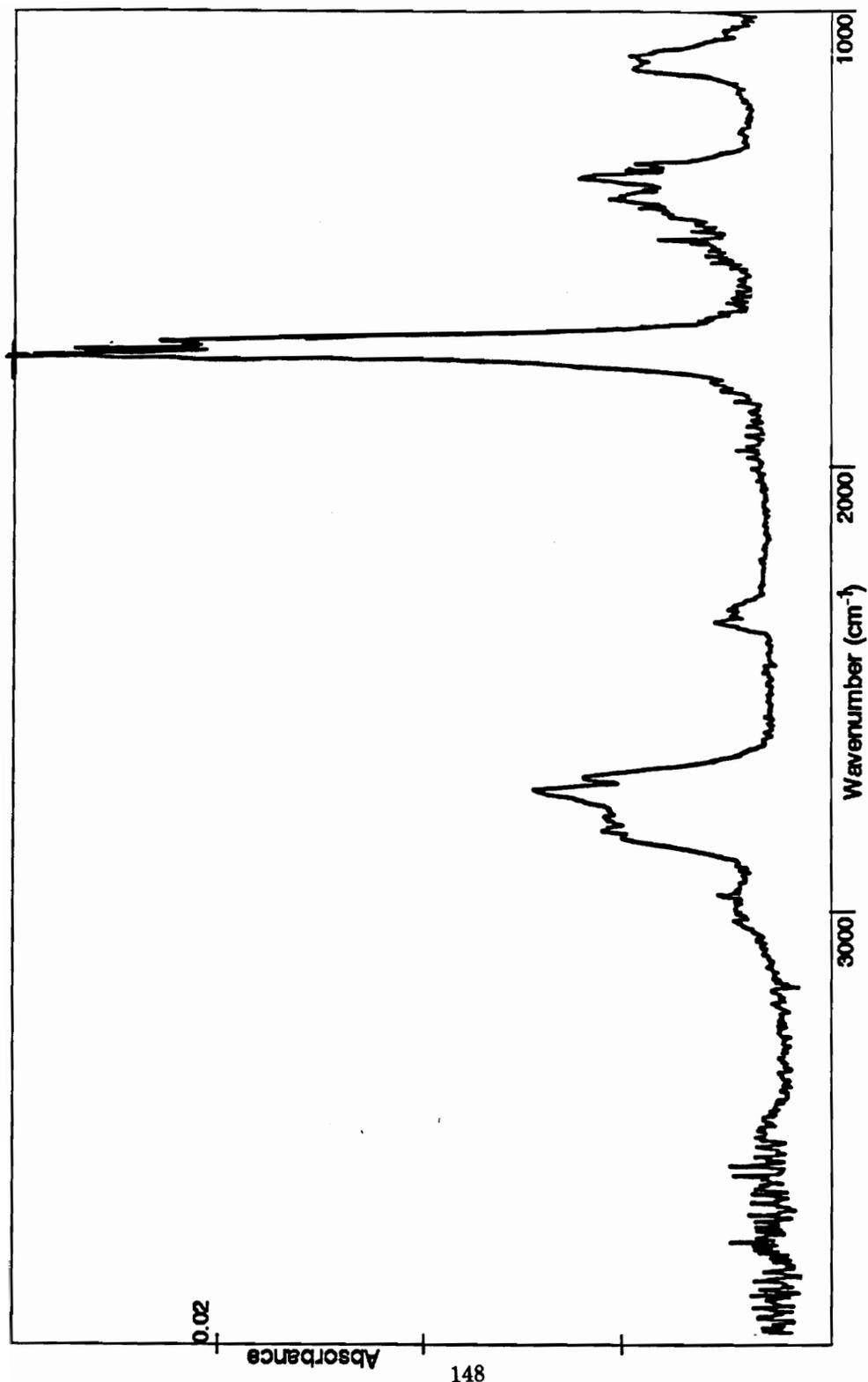


Figure A2.3 Infrared spectrum of vapor phase acetaldehyde

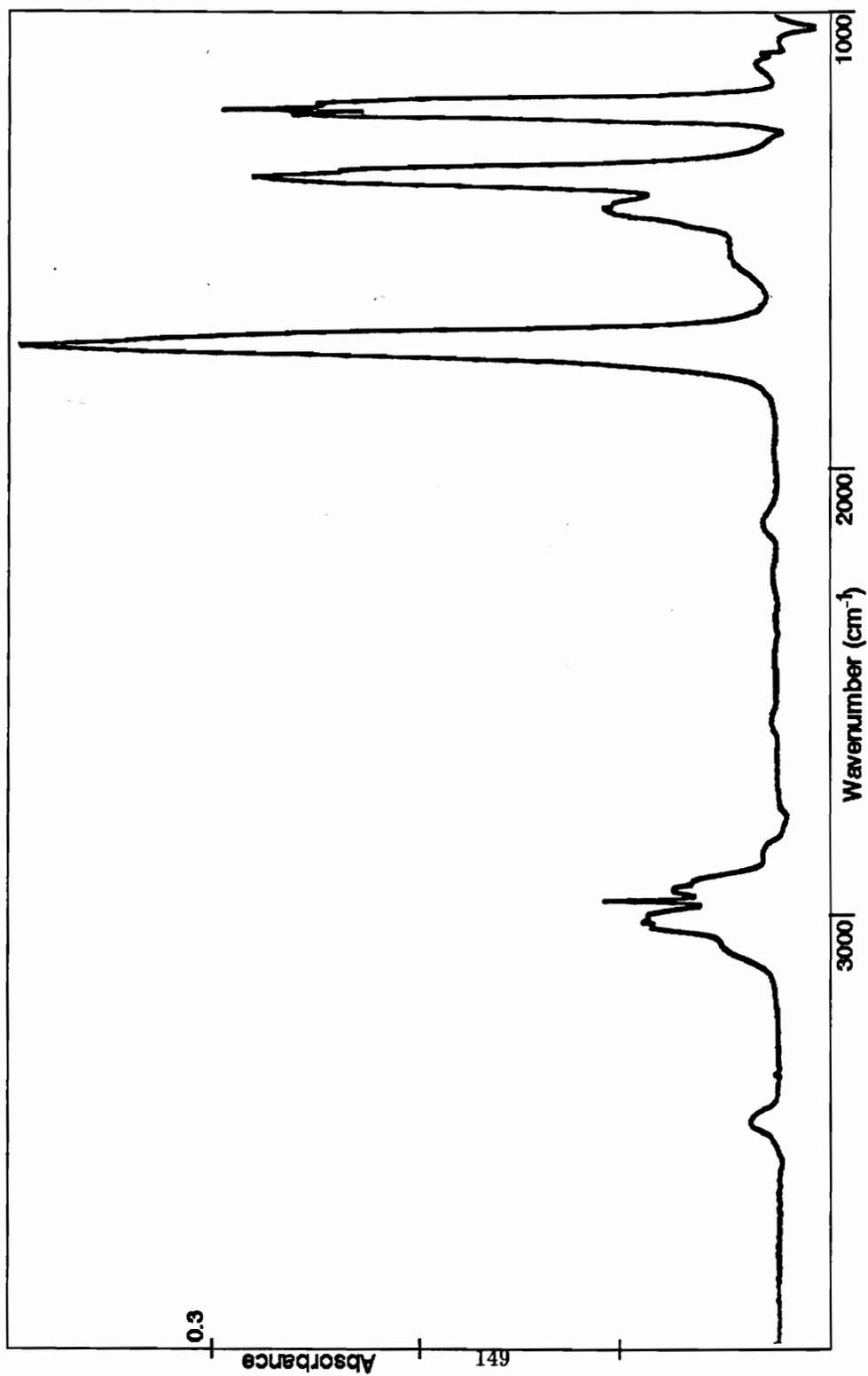


Figure A2.4 Infrared spectrum of vapor phase acetone

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The author was born in Plano, Texas, on October 1, 1965. After short stays in Memphis, Tennessee; Lenexa, Kansas; Yorktown Heights, New York; and Purdys, New York the Vandigrift family settled in Sherman, Connecticut. During her years at New Milford High School, the author decided she would pursue a career in chemical engineering. She graduated as valedictorian in 1984.

The author graduated from Lehigh University (Bethlehem, Pennsylvania) in 1988 with a B.S. in chemical engineering. During her four years there, she earned a place on the varsity field hockey team, coached a children's soccer team, and was elected to membership in Tau Beta Pi. She did undergraduate research supervised by Dr. Harvey Stenger, and dabbled in process simulation and control. This secured her a summer position with Rohm and Haas in 1988. However, she had already determined to pursue a doctorate in chemical engineering.

The author entered the doctoral program at Virginia Polytechnic Institute and State University in August, 1988. While conducting her research, she showed her dog to a championship in conformation, and closed in on an obedience title with him. She enjoyed hiking, camping, and a couple of trips to Europe. She also met a bright and caring post doc from Scotland, whom she married in the summer of 1992.

Following the submission of her dissertation, Valerie Lynne Young left Blacksburg for Toronto, Canada. There she plans to spend a year or two as a post doc in the Centre for Atmospheric Chemistry, York University. Eventually, she hopes to become a professor.