

## CHAPTER 1 INTRODUCTION

### 1.1 Motivation

Metal/semiconductor interfaces are of great technological as well as scientific interest. Silicon is the most widely studied among the semiconducting materials and it also has the most widespread applications in industry. Most metal-semiconductor interfaces used in technological applications are between transition metals and silicon. Such interfaces and others can have complex physical behavior on a microscopic scale such as temperature-dependent intermixing and silicide formation.

On the other hand, alkali-metals such as Na, K, and Cs form simpler interfaces with semiconductors. They form both ordered and disordered ultrathin films on semiconductor substrates without diffusing into the bulk.<sup>1</sup> For these surfaces, saturation at a coverage of a monolayer or less is observed at room temperature where monolayer is defined in general as a layer of substance one atom thick and more specifically as a layer which has the same areal density as the topmost layer of atoms in an ordered substrate. Saturation at a monolayer means that no further growth is observed after one layer of atoms gets deposited on the surface and multilayer formation is also restricted.

Cesium has the most well defined properties, which characterize alkali metals. It has the largest atomic radius and is the most electropositive among them. Thus, cesium and silicon are ideally poised as model systems for the study of surface phenomena and metal-semiconductor interfaces in general. More specifically, a better understanding of

surface metallization and Schottky-barrier formation from an atomic level can be obtained with the study of such interfaces.

In addition to the scientific motivation in studying the cesium/silicon interface as a model system, the system has properties that have industrial and commercial potential. Cesium-coated surfaces are of interest to industry due to the negative electron affinity of its oxide, which makes them ideal low-temperature cathodes. They also have technological applications for the catalytic growth of silicon dioxide coatings for integrated circuits.<sup>2,3,4</sup> In spite of all the interest, the structures of the Cs/Si interfaces are not extensively characterized, with the cesium coverage being a key factor in establishing the structure. As it stands, the properties and structure of the Cs/Si(100)  $2\times 1$  and Cs/Si(111)  $7\times 7$  surfaces are still being debated whereas the Cs/Si(111)  $(\sqrt{3}\times\sqrt{3})R30^\circ$ -B surface has not been widely studied at all.

Of all the techniques used to study the interfaces, Rutherford Backscattering Spectrometry (RBS), is a unique method with which one can make absolute coverage measurements that are independent of any structural model, which can easily distinguish between the cesium overlayer and the substrate. RBS in fact helps in eliminating structural models that are not consistent with the coverage measurements.

For low coverage levels, alkali-metals generally form partially ionic bonds to silicon surfaces, and partially donate their single valence electron to saturate the dangling bonds of the substrate. This leaves a dipole charge distribution at the surface making it

much easier for electrons to be removed from the bulk material. (e.g. the work function of the interface is lower than that of the bare silicon surface, typically by 2.5-3.5 eV.<sup>5</sup> Sometimes, the bulk conduction band can easily be raised above the vacuum energy level creating what is known as a negative-electron-affinity (NEA) state.<sup>6</sup> Cesium is the ideal adsorbate for this application since it is the most electropositive of the stable atoms. In fact, the oxygenated Cs/Si(100) 2×1 interface does form an NEA state.<sup>6</sup> Similarly, cesiated cathodes are highly efficient and operate effectively at high currents and low temperatures.

The cesiated silicon surface has potential as a system for the growth of silicon dioxide as an insulating layer in integrated circuits. Cesium catalyzes the adsorption of oxygen at much lower temperatures than would be possible otherwise. After the oxygen has been adsorbed, the system can be gently annealed to remove the cesium, leaving behind a stoichiometrically pure silicon dioxide layer, which has fewer defects than would be possible using conventional high temperature and high oxygen pressure techniques.<sup>7</sup>

The cesium/silicon interface also is an ideal system for studying the correlations between atomic structure and electronic properties of interfaces. This has been a continuous area of study for many years, and the work of characterizing various faces of silicon crystals has already largely been accomplished. The atomic and electronic structures of Silicon surfaces such as the Si(100) 2×1 and Si(111) 7×7 faces are well-known. This allows comparison between the surfaces, which vary only in structure

but not the elements themselves. Various studies of the electronic structure of the cesiated silicon interfaces<sup>5</sup> have complemented these structural studies to form a picture of how the surface changes between conducting and semiconducting states in unexpected ways. For example, while bulk silicon is a semiconductor, the Si(111) 7×7 surface exhibits a narrow energy band that crosses the Fermi level making it a conductor. The adsorption of submonolayer amounts of cesium changes the surface to a semiconductor – while the cesium-saturated surface is a conductor again.<sup>5, 8</sup> The resolution of structure for this interface would be an excellent test of our theoretical understanding of surface electronic states.

Another consideration for these studies is that the classical theory of Schottky-barriers takes no account of the structure of the interface and calculates barrier height based only on bulk properties of the metal and the semiconductor. Recent work has shown that varying the atomic structure at the interface can dramatically change the Schottky-barrier height.<sup>9</sup> Unfortunately, not many systems have been analyzed in sufficient detail to provide detailed checks of atomic structure based theory of Schottky-barriers. It is possible to measure the Schottky-barrier height for an atomic Cs/Si interface with a known structure by cooling the surface down below room temperature till there is multi-layer formation and a probe can effectively be used to measure it.

There are several reasons why the cesium/silicon interface is such a good model system for these studies. First, the cesium atom has a single valence electron around a

closed shell and is therefore easier to model than the transition metals. Second, the cesium like other alkali metals adsorbs on Si to form a saturated layer at room temperature. If more cesium is deposited after saturation then it either does not stick to the surface or desorbs rapidly.<sup>10,11,12</sup> Third, cesium, like other alkali-metals, does not penetrate into the bulk or form silicides, so the interfaces are abrupt down to the atomic scale. It is also possible that on some surfaces, particularly the Si(111)( $\sqrt{3} \times \sqrt{3}$ )R30°-B surface, ordered growth of cesium is expected which makes it even more straightforward to characterize the surface by theoretical techniques and describe surface phenomenon. These factors simplify both experimental analysis and theoretical understanding of these interfaces

In spite of all these advantages, there are various difficulties involved with studying the cesium/silicon interface. Scanning Tunneling Microscopy (STM) is a very useful characterization technique, which yields not only the coverage but also structural data. In STM a metal tip is moved close to the sample with a small bias which causes a tunneling current between individual surface atoms and the tip yielding topographic data, I-V characteristics and band structure information at atomic resolution. One problem with this technique for Cs/Si surfaces and alkali metals in general, is the high, induced dipole moment and polarization effects near the Cs atom, which modify the scanning tip.<sup>13</sup> Another problem is that there is some confusion as to the connection between the observed electronic structure and the related atomic structure.<sup>14</sup>

As for some other probes, most of them depend upon having a structural model to interpret the results or it is not easy to deconvolve from the experimental data, contributions from the surface and bulk atoms. Examples of these are LEED, X-ray techniques, photoemission and spectroscopy techniques. There are techniques like Auger Electron Spectroscopy (AES) that make more direct measurements of coverage along with elemental analysis, but these measurements yield relative coverage values, which are not very accurate and absolute coverage data, which can be dependent on models with poorly characterizable dynamics.

Rutherford Backscattering Spectrometry (RBS)<sup>15</sup> on the other hand, provides the absolute coverage information desired, without depending upon any structural model for interpretation. RBS data depends strictly on the physical geometry of the apparatus and the (known) cross sections for various collisions. Thus, the absolute coverage can be determined, and this information used to effectively restrict or even rule out proposed structural models. With this consideration in mind we can state that absolute coverage measurements of the amount of cesium on the various saturated surfaces will place a major selection constraint on the possible structural models and this information is necessary for exact structural determinations.

An overview of this thesis is presented as follows. In Chapter 2, we first cover the basic properties and what is already known about the various Si surfaces and their interfaces with alkali metals with particular emphasis on Cesium.

In Chapter 3, the whole experimental set up and the working of the apparatus is discussed along with some experimental pitfalls and complications. Also discussed is the basic RBS theory and method of data analysis and calibration with the help of simulations.

Chapter 4 details all the experimental results for both the main experiment and preliminary tests of sample quality. An analysis of the data and results of the saturation coverage measurements of the three surfaces are presented with discussions of their validity, reproducibility and margins of error. Also presented is a preliminary analysis of desorption phenomenon on one of the surfaces, which was not expected and was outside the original objectives of these studies.

Chapter 5 restates the results and discusses their implications in the context of the results based on experimental studies by other scientists and predictions of various theoretical structural models. We conclude with a brief discussion of further work in this area that might improve our understanding of the initial stages of growth of metal-semiconductor interfaces and related physical phenomena.

During the course of this work, an ultrahigh vacuum chamber was set up in collaboration with another student, William Sherman, on a new ion beamline at the University of Pennsylvania. New instrumentation and operational parts such as the sample transfer mechanism and alkali-metal dosing system were installed. The LEED system was completely repaired and made operational. The studies of saturation

coverage of Cs on Si(100)  $2\times 1$  and Si(111)  $7\times 7$  resulted in two co-authored publications.<sup>16,17</sup> Subsequent studies of saturation coverage of Cs on Si(111)( $\sqrt{3}\times\sqrt{3}$ )R30°-B has led to completely new saturation coverage measurements and the observation of ion beam- induced desorption of Cs that required a modified procedure for simulation and analysis. These latter results will be submitted for publication shortly.



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