

Overview

Characterization of ferroelectric films by spectroscopic ellipsometry

Data analysis techniques for spectroscopic ellipsometry were developed and used to monitor the quality of ferroelectric $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) thin films. Although this research focused on characterizing SBT, these general methods could be applied to many other insulative materials. In terms of applications, ferroelectric films form the active elements in nonvolatile memory devices and thermal sensory arrays. Therefore this research benefits the semiconductor industry and the energy consuming industries which process large volumes of material at high temperatures.

Summary of research performed

Ellipsometry offers a nondestructive method of estimating film thickness and optical dispersion based on the interaction of polarized light with the sample. Variable angle spectroscopic ellipsometry (VASE) has emerged as a powerful analytical tool which is often under-utilized unless the required data analysis process is performed by an experienced VASE operator. The diagnostic capabilities of VASE were made more accessible by presenting a logical method of modeling the acquired data using commercial software. The structural and optical parameters of VASE models were determined through an interactive process. Structural effects were simulated as combinations of layers and mixtures of components. This multi-layered modeling method was used to characterize surface roughness depths, interior void profiles, secondary phase concentrations, substrate interactions, optical constants, and band gap energies of SBT films. When VASE models were compared with transmission electron microscopy (TEM) cross-sections, the combined results provided a clearer picture of SBT films than either description could alone.

In chapter 1, the multi-layered modeling method was used to separate the effects of material-dependent optical properties from process-dependent microstructures. By estimating the void concentration as a function of depth, VASE characterized the microstructure of SBT films made by pulsed laser deposition, chemical vapor decomposition, and metal-organic deposition. When the microstructure was adequately simulated, the deduced optical properties obtained from SBT films approached those of bulk SBT.

Special VASE techniques provided compositional analysis which helped trace the electrical performance to the processing conditions of SBT films. In chapter 2, VASE was used to estimate the volume fraction of Bi_2O_3 in SBT films made by MOD. Excess Bi_2O_3 is typically added to promote grain growth. However, when the precursor Bi solution was not distilled completely, the excess Bi_2O_3 did not all go into a solid solution with SBT. Instead Bi_2O_3 appeared as a separate phase, which decreased grain size and increased the leakage current by several orders of magnitude.

In chapter 3, VASE characterized the thickness and roughness of an amorphous layer of SiO_2 between Si substrates and SBT films made by MOD. This SiO_2 layer reduced the net capacitance by about 50 %. VASE showed that the refractive index of SBT films did not depend on the substrate. TEM confirmed that nucleation occurred randomly throughout SBT films and was not controlled by substrate interaction.

Digital memory applications

Transistors and capacitors are the basic elements of digital integrated circuits. Numerous designs for new memory devices with ferroelectric transistors or capacitors have been proposed. Designs which flip the internal ferroelectric field produce nonvolatile memory, while designs which change the magnitude but not the direction of the remnant polarization produce volatile memory. Unlike other materials, ferroelectrics exhibit a stable reversible internal electric field which can yield many desirable properties in memory

devices if reliable processing steps for ferroelectric components can be integrated with silicon-based chips.

Traditional metal-oxide-semiconductor (MOS) field-effect transistors use an applied electric field to turn a switch (called the gate) on or off by controlling the conductivity through a shallow layer of silicon near the oxide interface. Nonvolatile memory devices can be made by replacing the oxide with a ferroelectric layer in order to form metal-ferroelectric-semiconductor (MFS) transistors. The stable internal field of the ferroelectric holds the switch on or off without requiring a sustained applied voltage. In these designs, if a ferroelectric film is deposited directly on Si, the chemical and electrical interaction between the ferroelectric film and Si become important issues.

Dynamic random access memory (DRAM) capacitors made of SiO_2 require intermittent recharging, which consumes power and requires additional recharging circuitry. In ferroelectric random access memory (FRAM), the internal field direction (up or down) of a ferroelectric capacitor creates a stable charge concentration (called the remnant polarization) on the electrodes, which stores information as a 1 or 0. In SBT, the internal field direction can be reversed more than 10^{10} times without a significant reduction in polarization strength,¹ which means that SBT has a higher fatigue resistance than most ferroelectrics. Since the stable polarization of a ferroelectric capacitors does not need to be refreshed, the information storage is nonvolatile.

For volatile memory chips, the continual push towards more cost effective manufacturing naturally leads to higher concentrations of smaller devices. Fazan predicts that when DRAMs have features smaller than $0.2 \mu\text{m}$, SiO_2 capacitors will store signals that are too small to be reliably detected by sense amplifiers.² Then the insulator may have to be made out of materials with high relative dielectric constants, ϵ_r . For example, ferroelectrics can store 40 to 20,000 times more charge per unit area than SiO_2 .² Power consumption per unit area must also be minimized, to prevent compact chips from

overheating. This requires capacitors to have low leakage currents. As a quality control tool, VASE was able to detect a conductive phase in SBT films, as discussed in chapter 2.

Infrared detector applications

As much as 80 % of all U.S. industrial energy consumption goes to process aluminum, steel, glass, paper, petroleum, and chemicals.³ To conserve energy and reduce costs, these industries have requested DOE-sponsored research to develop (among other things) cheaper sensitive thermal imaging of high temperature processes.⁴ In response to this need, ferroelectric thin film research could help develop simplified pyroelectric infrared cameras that operate at room temperature.

Much of the cost of traditional infrared cameras, based on narrow-bandgap photoelectric semiconductors, comes from the cryogenic cooling systems required to reduce thermal noise for high detectivity. Even room temperature heat causes a random background current that masks the image current in a long wavelength infrared detector. Although military users prefer long wavelength (8-15 μm) infrared systems to observe people and motors at night, industrial users find that short wavelength (3-5 μm) infrared sensors are more accurate at monitoring higher temperatures inside furnaces, for example.⁵ Infrared detectors that are tuned to these higher energy infrared photons are less sensitive to background thermal noise.

Operating at room temperature, ferroelectric sensors can detect a wide range of infrared wavelengths with higher signal-to-noise ratios than photoelectric sensors.⁶ Depending on design, ferroelectric capacitors produce currents that are proportional to the rate at which the remnant polarization or the capacitance changes with temperature. Therefore constant temperature surroundings do not cause much noise in ferroelectric detectors. Although potentially more affordable, these uncooled pyroelectric cameras are less sensitive than cryogenic photoelectric cameras. One way to potentially improve the sensitivity to cost ratio is to deposit ferroelectric pixels directly on mass-produced, image-

processing chips. Therefore, any reaction layer between Si and a proposed ferroelectric component must be well understood. To address this issue, the structure of an SiO₂ reaction layer between SBT and Si was investigated using VASE in chapter 3.

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