X-ray reflectivity study of SiO₂ on Si

S. M. Heald and J. K. D. Jayanetti
Brookhaven National Laboratory, Upton, New York 11973

A. A. Bright and G. W. Rubloff
IBM T. J. Watson Research Center, Yorktown Heights, New York 10598

(Received 15 September 1989; accepted 27 November 1989)

X-ray reflectivity is a powerful probe of thin film morphology. It can be used to nondestructively determine the interface and surface roughness, thickness, and density of the layers. This paper presents the application of the technique to the case of SiO₂ on Si. Experimental reflectivity results with a dynamic range of 10⁴ have been obtained on a number of oxide layers prepared using processing conditions. The reflectivity oscillations caused by oxide layers could be easily observed over this entire range, and significant differences were observed between samples. In particular, a plasma enhanced chemical vapor deposition grown oxide is found to have an interfacial layer of lower density.

I. INTRODUCTION

X-ray reflectivity techniques have been increasingly applied to the study of thin film structures.¹⁻³ The reflectivity is sensitive to the density distribution of a film normal to the surface. Thus, detailed information can be obtained concerning film thickness, density, and interface roughness. Since the thickness can generally be determined by a number of methods, the main application of the reflectivity method is a detailed determination of the density profile of the film. A key advantage is its nondestructive nature allowing changes in film morphology at a subnanometer level to be monitored in response to outside processing such as thermal annealing. Recently Cowley and Ryan⁴ have shown the usefulness of x-ray reflectivity methods in a study of thin (1–10 nm) SiO₂ layers.

In this paper x-ray reflectivity measurements are used to compare films grown on Si thermally and by plasma enhanced chemical vapor deposition (PECVD). Comparing the two helps to determine to what extent the PECVD process is capable of producing films of thermal quality. The motivation for this is the need in future technologies for a low temperature oxide to reduce the amount of thermal processing in very small device structures.

II. X-RAY REFLECTIVITY

X-ray energies are much higher than typical electronic excitations, except for those associated with deep core electrons. Therefore, for energies away from core electron binding energies, the x-ray reflectivity is insensitive to chemical effects, and is only dependent on the depth dependence of the electron density. The reflectivity can be calculated using the standard Fresnel equations. A recursive formula given by Parratt⁵ is convenient for multilayered systems. These equations have been given by a number of authors¹⁻³ and will not be repeated here.

A number of methods exist for treating interface roughness. An arbitrary distribution can be modeled using a succession of thin layers whose densities follow that of the real distribution. In this work, we have assumed that the localized interface height follows a Gaussian distribution. This gives rise to a complementary error function density profile, and results in a Debye–Waller like term in the reflectivity. We have used the formalism of Vidal and Vincent⁶ to include this roughness term in our calculations.

Figure 1 shows some model calculations for a 50 nm SiO₂ layer on a Si substrate. These are shown to illustrate the sensitivity of the reflectivity to various film parameters (density, surface, and interface roughness). The density of SiO₂ films (2.2–2.3 g/cm³) is quite similar to pure Si (2.33 g/cm³), which means that interference induced oscillations in the reflectivity are small. However, this means that the data are quite sensitive to small changes in density if the oscillations can be detected. Normally, the absolute value of the density would be uncertain by a few percent due to uncertainties in the x-ray optical constants. For the SiO₂/Si system, the accuracies are higher because the experiment is sensitive mainly to differences in density between the oxide film and the well characterized substrate.

In Fig. 1(a) the log of the reflectivity is plotted for four cases. It is clearly seen that the overall slope is determined by the surface roughness only. The other parameters affect the details of the oscillations. For no roughness, the large angle data has a (θ/θr)⁻¹ dependence, where θr is the critical angle of reflection. In Fig. 1(b) this factor has been removed to bring out the details. The interface roughness is seen to damp out the oscillations at large angles, while the density affects the overall amplitude of the oscillations at all angles. Thus, the parameters used in modeling the data are relatively easy to separate if data is obtained to large angles.

III. EXPERIMENTAL

A number of oxides were examined. Since all of the thermal oxides were similar, we will concentrate on a comparison of single thermal oxide with a similar PECVD oxide. The thermal oxide was grown using a conventional dry furnace oxidation process. The PECVD oxide was prepared using a He-diluted PECVD process developed by Batey and Tierney.⁷ This is a silane/nitrous oxide process in which He is added a diluent to suppress gas phase reactions and produce a high quality oxide. The sample was deposited at 1

Torr, 0.07 W/cm², 350 °C, and at a deposition rate of 7.5 nm/min.

The x-ray measurements were made at beamline X-11A at the National Synchrotron Light Source (NSLS). The samples were mounted on a polished Al plate at center of rotation of a precision two circle goniometer. The incident beam size was 0.1 × 5 mm and the exit slit before the detector was 0.2 × 8 mm. The incident beam flux was measured using a N₂ filled ionization chamber, and the reflected beam monitored using a partially transmitting ionization chamber in series with a NaI scintillation detector. This combination allowed us to measure counting rates varying from the direct beam intensity (10⁸) down to a few Hz without changing slits or putting in beam attenuators. A typical scan took 45 min. At large angles the background scattering became significant and was determined by scanning through the specularly reflected beam. The measurements reported here were all made at 8 keV with the monochromator calibration referenced to the first inflection point of the Cu K edge (8.890 keV).

IV. RESULTS AND DISCUSSION

The results for the thermal and PECVD oxides are shown in Figs. 2 and 3. Distinct differences can be seen. The thermal oxide data looks similar to the model calculations. This data could be well modeled with a single SiO₂ layer. The

Fig. 1. (a) Calculated reflectivity curves for 50 nm SiO₂ on Si. The two upper curves are for no roughness and for SiO₂ densities of 2.26 g/cm³ (---) and 2.22 g/cm³ (—.). The two lower curves are for a density of 2.26 g/cm³ with a surface roughness of 0.5 nm rms and interface roughnesses of 0 (—) and 0.5 nm (——). (b) The same curves as in (a) but with the factor (θ/θ₀)⁴ removed for clarity.

Fig. 2. (a) Comparison of the data (points) with the fitted model (—) for the thermal oxide. (b) Large angle data with the factor (θ/θ₀)⁴ removed for clarity.

Fig. 3. (a) Comparison of the data (points) with the fitted model (—) for the PECVD oxide. (b) Large angle data with the factor (θ/θ₀)⁴ removed for clarity.
results of a least square refinement of this model are given in Table I. These results are quite similar to those determined by x-ray reflectivity on thinner oxide layers in Ref. 4.

The situation is different for the PECVD data shown in Fig. 3. In this case, the interference oscillations are seen to damp out near 20 mrad, and then increase in amplitude at larger angles. This behavior can only be obtained by adding an additional less dense SiO₂ layer near the interface to the model. These fitting results are listed in Table I. For this case, the position and strength of the oscillation minimum uniquely determine the thickness and density difference for the intermediate layer. The two interface roughnesses are strongly correlated with an increase in one being compensated by a decrease in the other. The sum of the roughnesses is well determined to be 0.8–1.0 nm.

The roughness parameters determined by x-ray reflectivity represent the root-mean-square (rms) width of the transition region between layers. The present measurements cannot distinguish between physical roughness or a chemically mixed region. It is known from transmission electron microscopy (TEM) studies that the SiO₂ interface is atomically sharp with the physical roughness mainly in the form of atomic steps. The rms value that we obtain for the thermal oxide seems to agree with TEM results.8–10 An important question is whether a chemical transition layer (often denoted as SiOₓ) exists. X-ray photoelectron spectroscopy (XPS) gives indications of an intermediate layer a few monolayers thick.11,12 This would translate to an rms roughness of a few Å, and is not incompatible with our x-ray results. More extensive measurements on a variety of samples are needed to determine if reflectivity studies can contribute to understanding this important problem. In this regard, detailed studies of the nonspecular scattering can determine the length scale of the roughness and help distinguish between the chemical and physical contributions to the interface roughness.

The density of the PECVD oxide is essentially the same as that of thermal oxide. This is an indication of the high quality of the PECVD oxide produced by this process.7 Conventional PECVD oxides are typically less dense than thermal oxides unless annealed at high temperatures. No anneal was required to produce a dense PECVD oxide film in the present case.

The intermediate layer near the interface of the PECVD oxide is a consequence of the surface preparation technique used prior to the deposition. A full discussion of this layer is beyond the scope of this paper and will be presented else-

<p>| Table I. Parameters used to fit the data in Figs. 2 and 3. Two SiO₂ layers were required for the PECVD oxide. |</p>
<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness (nm)</th>
<th>Density (g/cm³)</th>
<th>Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal oxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>51.7 (0.1)</td>
<td>2.26 (0.01)</td>
<td>0.43 (0.02)</td>
</tr>
<tr>
<td>Si</td>
<td>⋯</td>
<td>2.33</td>
<td>0.1 (0.2)</td>
</tr>
<tr>
<td>PECVD oxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>47.5 (0.2)</td>
<td>2.25 (0.02)</td>
<td>0.62 (0.02)</td>
</tr>
<tr>
<td>SiO₂</td>
<td>4.20 (0.2)</td>
<td>2.21 (0.01)</td>
<td>0.3 (0.2)</td>
</tr>
<tr>
<td>Si</td>
<td>⋯</td>
<td>2.33</td>
<td>0.6 (0.15)</td>
</tr>
</tbody>
</table>

where. PECVD films can be produced with or without the interfacial layer, and we have demonstrated that the x-ray reflectivity is able to distinguish between the two cases.

This paper has shown that x-ray reflectivity can provide useful information about SiO₂ layers. The PECVD results demonstrate that a high sensitivity to density variations can be obtained. The present work used a synchrotron radiation x-ray source, but similar measurements can be obtained using laboratory x-ray sources with some increase in data acquisition time.

ACKNOWLEDGMENTS

We would like to thank Dr. H. Chen for her role in developing the reflectivity fitting programs used in this work. This work was supported in part by the U. S. DOE Office of Basic Energy Sciences under Contract Nos. DE-AS05-80-ER10742 and DE-AC02-76CH00016.