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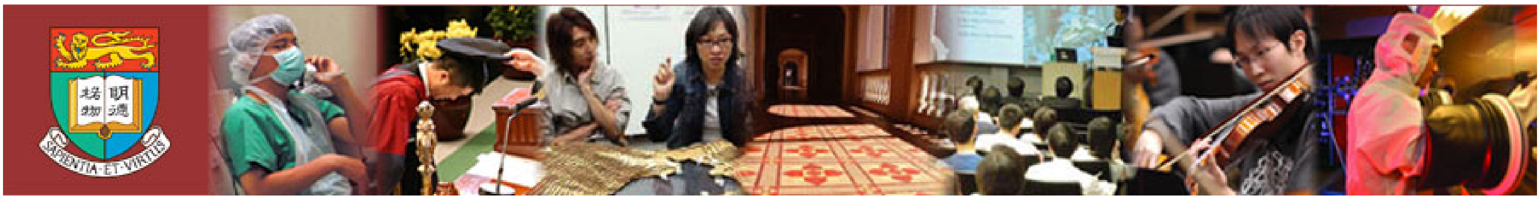

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Author(s)	Banerjee, S; Chakraborty, S; Lai, PT
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Evidence of swelling of SiO_2 upon thermal annealing

S. Banerjee[a] and S. Chakraborty
Surface Physics Division, Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Calcutta 700 064, India

P. T. Lai
Department of Electrical and Electronic Engineering, University of Hong Kong, Pokfulam Road, Hong Kong

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Ultrathin SiO_2 film was thermally grown on Si(001) substrate by dry oxidation and wet oxidation processes. The films were then subjected to thermal annealing (TA) at 1000 °C for 30 min. The structural characterization of the as-grown and the TA samples was carried out using the grazing incidence x-ray reflectivity technique. The analysis of the x-ray reflectivity data was carried out by using a model independent formalism based on the distorted wave Born approximation for obtaining the electron density profile (EDP) of the film as a function of depth. The EDP of both films show a decrease in the electron density as well as an increase in their thickness when the films are subjected to TA. It has also been observed that the total number of electrons is conserved in the oxide film after TA. Our analysis of the x-ray reflectivity data indicates that the SiO_2 film swells and its interface with the substrate modifies upon TA. © *2002 American Institute of Physics.*
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Silicon dioxide films are perhaps one of the most technologically important materials used in high density integrated semiconductor devices. Most often, these films are grown on a silicon substrate by thermal oxidation process. The oxidation is carried out either in a dry or wet oxygen ambient and is termed "dry oxidation" and "wet oxidation" processes, respectively. The time-dependent dielectric breakdown and the interfacial characteristics of the film depend on the oxidation process.[1] It has been observed that the wet oxidized film is more stable to dielectric breakdown and has a smoother interface than the dry oxidized film.[1] The most interesting issue is what happens to these films when they are subjected to thermal annealing (TA) in the absence of oxygen. It has been observed that the thickness and density of the film change during TA.[2–4] From the ellipsometric measurement, it has been observed that the density of the oxide film decreases for the thermally grown oxide upon TA,[2] whereas for the film grown by sputtering technique, the density increases.[5] The density of the film determines the microstructure, which affects the electrical properties of the film.[4] A thickness increase has been observed upon TA of thermally grown oxides from the ellipsometric measurement.[2] If SiO_2 film is deposited using a rf sputtering technique at an elevated substrate temperature, then it was observed that the thickness of the film decreased[3] along with an increase in the density.

The grazing incidence x-ray reflectivity (GIXR) technique has become one of the most powerful techniques for characterizing ultrathin films with Angstrom resolution. The GIXR technique has been successfully used in a nondestructive manner to obtain the structure and chemical profile of a film as a function of its depth.[6–8] GIXR measurements have been carried out recently on such ultrathin SiO_2 films but the issue of the change in thickness and density has not been addressed.[9–12] The main focus of earlier work using GIXR measurement was to study the structure of the SiO_2/Si interface.[9–12] Previous analysis of the GIXR measurements were based on a model dependent recursive formula usually called Parrat's formalism.[13] Here, we analyzed our reflectivity data using distorted wave Born approximation (DWBA) in a model independent way.[6–8] The analysis of x-ray reflectivity data based on DWBA formalism has been recently[14] compared with Parratt's formalism and Fourier inversion technique[15,16] for characterizing the film/substrate interface of an ultrathin oxynitride and TiN films.[14] In this letter, the structure of dry and wet oxidized SiO_2 films for the as-grown and TA films are compared. The behavior of the film density upon TA is also determined by the GIXR technique.

Two ultrathin SiO_2 films were grown on p-type Si(001) substrate by (a) dry oxidation (sample A) and (b) wet oxidation (sample B) processes for 60 min and 15 min, respectively, at a temperature $T=925\,°C$. For TA, the oxides were annealed at 1000 °C for 30 min under an Ar atmosphere and the temperature was raised at the rate of 15 °C/min. For specular x-ray reflectivity measurement, we have used $\Theta-2\Theta$ diffractometer (Microcontrol Inc.). The Cu-$K\alpha$ x ray was obtained from a 18 kW rotating anode x-ray generator (Enraf Nonius Inc.). The details of the GIXR measurement is described elsewhere.[17]

The reflectivity of the film using the DWBA is given by[6,7,18,19]

$$R(k_z)=\left| i r_o(k_z)+\frac{(2\pi r_e)}{k}\left(a^2(k)\Delta\rho(q_z^f) + b^2(k)\Delta\rho^*(q_z^f)\right)\right|^2, \tag{1}$$

where k_z is the scattering wave vector, $q_z=2k_z=4(\pi/\lambda)\sin\theta$, $q_z^f[=\sqrt{q_z^2-(q_c^f)^2}]$ is the wave vector in the film, the subscript c indicates the critical value of the wave

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[a] Electronic mail: sangam@cmp.saha.ernet.in

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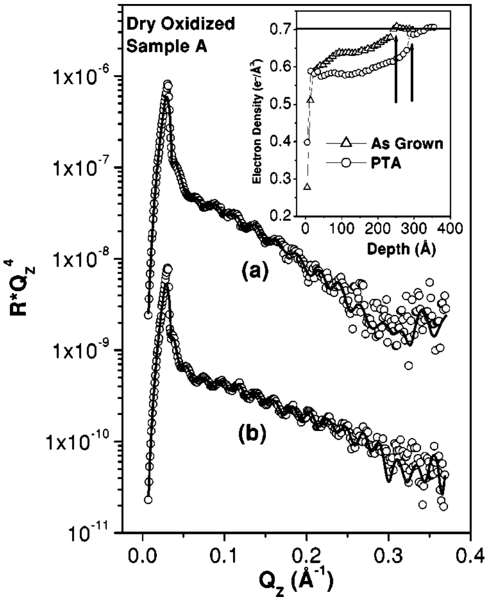

FIG. 1. Dry oxidized SiO_2 film (sample A): x-ray reflectivity data for (a) as-grown and (b) TA sample. Inset: EDP obtained from the analysis based on DWBA formalism.

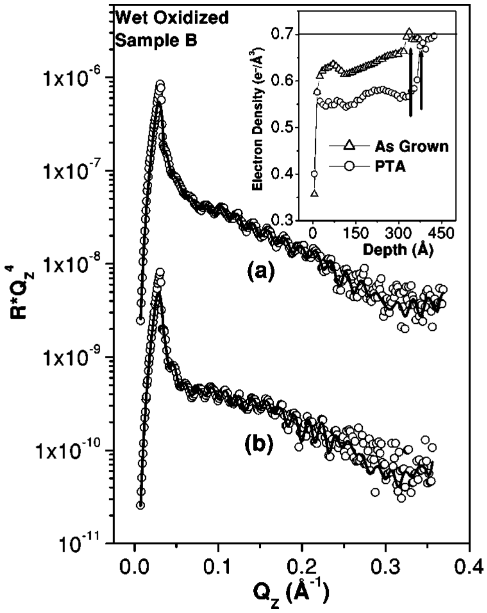

FIG. 2. Wet oxidized SiO_2 film (sample B): x-ray reflectivity data for (a) as-grown and (b) TA sample. Inset: EDP obtained from the analysis based on DWBA formalism.

vector having a critical angle (θ_c) up to which the total external reflection occurs and the superscript f indicates the value of the wave vector in the film. The $r_o(k_z)$ is the specular reflectance coefficient of the film with an average electron density ρ_o, $a(k)$, and $b(k)$ are the transmission and reflection coefficients inside the film, respectively, and r_e is the electron radius. The $\Delta\rho(q_z^f)$ is the Fourier transform of variation of electron density $\Delta\rho(z)=\rho(z)-\rho_o$, where z is the depth of the film. The total thickness of the film can be considered to be composed of a number of thin slices or boxes of electron density ρ_i of the ith box,[6,7,18] $\Delta\rho(q_z^f)$ can be written in terms of $\Delta\rho_i(=\rho_i-\rho_o)$ of thickness d of the ith box as[6,7]

$$\Delta\rho(q_z^f)=\frac{i}{q_z^f}\left[\left(\sum_{j=2}^{j=N}(\Delta\rho_j-\Delta\rho_{j-1})e^{iq_z^f(j-1)d}+\Delta\rho_1-\Delta\rho_N e^{iq_z^f Nd}\right)\right], \qquad (2)$$

where N is the total number of boxes used in the calculation. By selecting the appropriate number of boxes and ρ_o of the film, we fit Eq. (1) with $\Delta\rho_i$ as the fit parameters after convoluting the data with a Gaussian instrumental resolution function. For the present analysis, we have used boxes of size ~9 to 10 Å.

In Figs. 1 and 2, we show x-ray reflectivity data for sample A (dry oxidized) and sample B (wet oxidized) for the as-grown and TA samples. In the insets of Figs. 1 and 2 we show the electron density profiles (EDP) obtained from the scheme mentioned herein and the solid line indicates the electron density value of the Si substrate ($\sim 0.7e^-/\text{Å}^3$). We can distinctly see from both reflectivity measurements that upon TA, the period of oscillation in the reflectivity profile decreases thus indicating an increase of thickness on annealing. From the EDP, one can estimate the thickness of the film as the electron density value approaches the substrate value (see arrows in the insets of Figs. 1 and 2). The thicknesses for as-grown samples A and B are ~260 Å and ~347 Å, respectively and upon TA, the thickness increases to ~289 Å and ~385 Å, respectively. We find that the thickness increase upon TA is ~11%. We have also observed a reduction in the electron density upon TA (insets of Figs. 1 and 2). The reduction in the electron density indicates that the SiO_2 has been relaxed to an open structure after TA thus reducing the mass density of the film. (Note: the mass density of the film is directly proportional to the electron density.[20]) In Fig. 3, we have compared the EDP for the dry

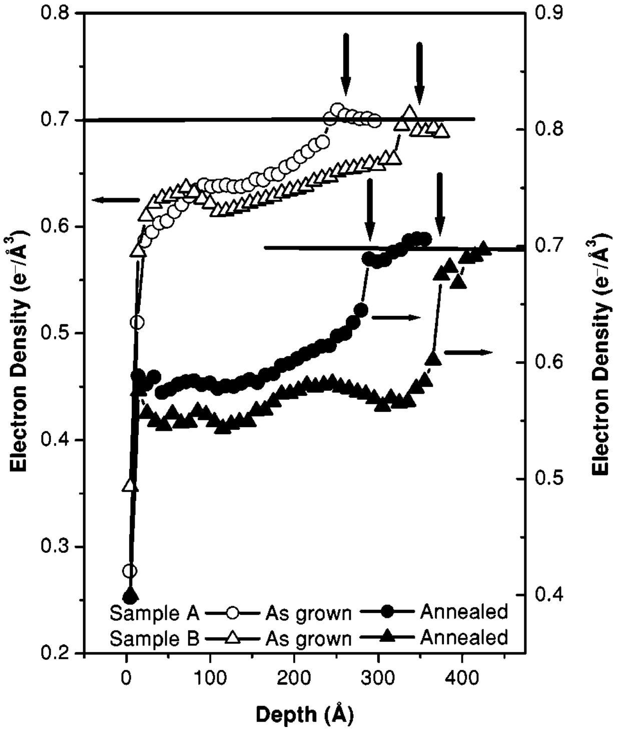

FIG. 3. Comparison of EDP between dry and wet oxidized samples. Open symbols for the as-grown and closed symbols after TA treatment. The arrows indicate the film/substrate interface.

oxidized sample (Sample A) and the wet oxidized sample (Sample B) for the as-grown (open symbols) and for the TA samples (closed symbols). We observe that the wet oxidized as-grown sample, has a lower electron density value than the dry oxidized sample as reported earlier.[1] Similarly for the TA samples, we have observed that the electron density for the wet oxidized sample is lower than the dry oxidized sample. A closer look at the EDP of both the samples reveals a small peak in the EDP at the interfaces of the SiO_2/Si(substrate) for the as-grown oxides and is marked by arrows in Fig. 3. At the interface, an electron density which is higher than the substrate value has also been previously observed.[12] This high electron density can be, as pointed out earlier, due to a quasiepitaxial growth of the oxide at the interface of the SiO_2/Si(substrate) and gives rise to higher density microcrystalline SiO_2 phase.[21,22] On TA, we observe that the peaks have changed to shoulders at the interfacial region as shown by arrows in Fig. 3. From Fig. 3, we also observe a sharp drop in the electron density value at the SiO_2/Si interface (solid lines) thus indicating that upon TA treatment, the interface becomes sharp. The area under the EDP up to the substrate (marked by arrows in Fig. 3) gives the total number of electrons N for a column of length equal to the thickness of the film and having a cross sectional area of 1 Å^2 (i.e., the cross section of the column having a unit area). The value of N for the as-grown and annealed sample A is 162 and 168, respectively, and for sample B is 217 and 216, respectively. This indicates that the electron number N is more or less conserved for both the samples along the column having a unit area and hence no oxygen has been introduced during TA for increasing the thickness of the oxide film.

To summarize, we observe that the wet oxidized sample has an electron density which is lower than the dry oxidized sample. Upon TA, the thickness of the thermally grown SiO_2 film is found to increase along with the reduction of the electron density of the film. The reduction of the electron density of the film indicates a reduction in the mass density of the film. The total number of electrons remains the same upon TA indicating that no oxygen has been introduced to increase the thickness. These observations lead us to conclude that the SiO_2 films swell upon TA. A peak in the EDP is observed at the interface of the SiO_2/Si(substrate) for the as-grown samples and upon TA, the peak appears as a shoulder at the interface. The electron density shows a sudden jump at the interface indicating that the interface becomes sharper upon TA.

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