Limiting Si/SiO₂ interface roughness resulting from thermal oxidation

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The changes effected by oxidation on purposely roughened and initially smooth Si surfaces are followed via atomic force microscopy and spectroscopic ellipsometry and a technique called spectroscopic immersion ellipsometry. Initially, rough and smooth Si surfaces yield opposite roughening trends upon thermal oxidation. Rough surfaces become smoother, and smooth surfaces become rougher, ultimately yielding a limiting roughness of about 0.3 nm root-mean square. A consideration of the distribution of surface roughness features plus the thermodynamics of small features are used to explain these trends. It is also reported that the changes of interface roughness are primarily the result of the oxidation reaction and not from the high temperatures. © 1999 American Institute of Physics. [S0021-8979(99)04415-1]

I. INTRODUCTION

The continual downsizing of the metal–oxide–semiconductor (MOS) devices renders the Si/SiO₂ interface a larger fraction of the active device region. Thus, there is reduced tolerance for interfacial defects, such as interface roughness, since such roughness causes carrier scattering and electric-field enhancement effects, which can result in hindered carrier mobility,^{1,2} leakage current, and dielectric breakdown.^{3,4}

It has been shown that both thermal^{5,6} and microwave electron cyclotron resonance (ECR) plasma⁶ oxidation processes smoothen initially rough Si surfaces via a free-energy reduction mechanism according to the Kelvin equation for purely thermal oxidation, and in addition to local electric-field enhancement effects for ECR oxidation. It has also been shown⁶ that these oxidation processes roughen initially smooth Si surfaces but with the underlying reason uncertain. These results suggest that there is a convergence of the smoothening and the roughening effects under oxidation leading to a limiting roughness.

The present study is an investigation into the convergence of smoothening and roughening effects of Si surfaces through thermal oxidation. Specifically, we report on the effects of high-temperature annealing and oxidation on the smoothening and roughening of Si surfaces.

In this study, interface roughness is measured and compared using a nondestructive method, spectroscopic immersion ellipsometry (SIE),^{7–10} and atomic force microscopy (AFM). SIE sensitively measures the changes of the optical properties of the evolving interface roughness of a large area ($\sim 5 \text{ mm}^2$), while AFM gives the local roughness, since it observes a much smaller area ($\sim 9 \mu\text{m}^2$). Two roughness parameters are used together, root-mean-square roughness (rms) and fractal dimension (D_F), which have been shown to provide a reasonably complete surface roughness description.^{5,11,12} Spectroscopic ellipsometry (SE) is also uti-

lized for roughness of the thermally annealed samples which have a negligible SiO₂ overlayer.

II. EXPERIMENTAL PROCEDURE AND DATA ANALYSIS

Commercially available *p*-type Si(100) wafers with a resistivity of about 1–2 $\Omega \text{ cm}$ were used in this study. Some Si samples were purposely roughened using a chemical etching solution of HNO₃:HF:CH₃COOH (3:2:4) at room temperature with ultrasonic agitation. Both rough and smooth (out-of-the-box) samples were cleaned using a slightly modified RCA cleaning procedure,¹³ which consists of dipping the samples in mixtures of NH₄OH:H₂O₂:H₂O and HCl:H₂O₂:H₂O both with ratios of (1:1:5) at 60–70 °C and with ultrasonic agitation and deionized water rinse between each step. The cleaning process is concluded by dipping the cleaned samples in 48% HF for 10 s to remove native oxide followed with a deionized water rinse, and then were blown dry with nitrogen gas. All samples subjected to a 10 s 48% HF dip in this study were rinsed in deionized water before being blown dry with nitrogen gas. It was previously demonstrated that this brief HF dip causes no AFM noticeable changes in rough or smooth Si.¹⁴

The rough and the smooth samples were thermally oxidized using clean dry oxygen (99.98% purity and less than 1 ppmv of water) at 1000 and/or 800 °C in a conventional resistance heated double-wall fused silica lined tube furnace for various lengths of time to oxide thicknesses in the range of 0–200 nm. Some samples were not oxidized continuously, but rather were subjected to a 48% HF dip for 10 s in between oxidation intervals, which removes previously grown SiO₂. The bare Si oxidizes much faster than samples with SiO₂, and thus, this experiment provides a comparison of the interface roughness at high and low oxidation rates.

In order to determine the effect of temperature alone, some rough and smooth samples were thermally annealed at 1000 °C in the above furnace with Ar gas for different lengths of time. The rough samples were HF dipped for 10 s in between annealing intervals.

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FIG. 1. Optical models used in SE and SIE data analysis.

SE, SIE, and AFM measurements were performed *ex situ* before and after oxidation or annealing. Conventional SE¹⁵ measures the changes in amplitude (Ψ) and phase (Δ) of elliptically polarized light reflected from all the interfaces of a sample at each wavelength. In our study this measurement is used to obtain the SiO₂ overlayer thickness. Since the light reflected from the sample results from both the air/SiO₂ and the SiO₂/Si interfaces, the sensitivity to the changes of the latter interface is ambiguous. However, SIE obviates this problem because SIE is a SE measurement taken with the sample immersed in a liquid whose optical index matches closely to that of SiO₂, such that the light reflected from the air/SiO₂ interface is minimized. Thus, the SiO₂ overlayer is optically removed, and the measured Ψ and Δ are sensitive to only the SiO₂/Si interface. It has been shown^{7,10} that the sensitivity of SIE to the changes of the interface without physically removing the SiO₂ overlayer is ~ 10 times higher than that of SE. Besides the advantage of higher sensitivity, it is not necessary to remove the film, and thus, SIE eliminates the possibility of changing the interface. Carbon tetrachloride (CCl₄) is chosen to be the optical index matching liquid for our SIE measurements of the SiO₂/Si interface. The refractive index of CCl₄ is calculated using the Cauchy dispersion formula:

$$n(\lambda) = n_{\infty} + \frac{a}{\lambda^2} + \frac{\partial n}{\partial T} \Delta T,$$

where λ is the wavelength of the light, $n_{\infty} = 1.4427$, $a = 5.15 \times 10^5 \text{ \AA}^2$ at $T = 24.8^\circ\text{C}$, and $\partial n / \partial T = 5.5 \times 10^{-4}$ at $T = 20^\circ\text{C}$ for pure CCl₄.¹⁶ The incident angle for SIE measurements is 72° with wavelengths from 315 to 475 nm, and minor differences between the optical indices of CCl₄ are taken care of in the data analysis program. Further details about the SIE technique were previously reported.⁷⁻¹⁰ For SE measurements, the incident angle is 70° and data are taken with wavelengths from 250 to 595 nm.

Data analysis of SE and SIE measurements were performed with one- and two-film models, respectively, as shown in Fig. 1. For SE, the one-film model consists of a SiO₂ overlayer on the single-crystalline silicon (*c*-Si) substrate and is used to measure the SiO₂ overlayer thickness (L_{ox}), which will then be used in the analysis of SIE data. For SIE, the two-film model consists of a SiO₂ overlayer with thickness (L_{ox}) obtained from SE and an interface layer on the *c*-Si substrate. The interface layer is modeled as a uniform mixture of SiO₂ and amorphous silicon (*a*-Si). Demonstrations of the success in using this model for data

analysis of SIE measurements have been reported in several studies⁵⁻¹⁰ and are not repeated here. The Bruggeman effective medium approximation¹⁷ (BEMA) is employed to calculate the pseudodielectric function of this interface layer with the varied volume fraction of each constituent as follows:

$$0 = f_a \frac{\epsilon_a - \epsilon}{\epsilon_a + 2\epsilon} + f_b \frac{\epsilon_b - \epsilon}{\epsilon_b + 2\epsilon},$$

where a and b represent the two different components of the layer, f_a and f_b are the volume fractions, and ϵ_a and ϵ_b are the dielectric functions of pure a and b . The experimental Ψ and Δ are compared with the theoretical values computed using the Fresnel relationships.¹⁵ The unknown parameters (i.e., the interface layer thickness L_{inf} and the volume fraction of each component) of the interface are obtained using a least-square fit such that the following error function is minimized:

$$\chi^2 = \sum_i \{ [\Psi_i^{\text{cal}}(E_i, \mathbf{P}) - \Psi_i^{\text{exp}}]^2 + [\Delta_i^{\text{cal}}(E_i, \mathbf{P}) - \Delta_i^{\text{exp}}]^2 \},$$

where E_i is the photon energy and $\mathbf{P}$ is a vector of unknown parameters. L_{inf} is, therefore, the sum of the suboxide (SiO_{*x*}, with $x < 2$) layer and the roughness layer thicknesses at the interface.

After SE and SIE measurements, all samples were subjected to a 10 s 48% HF dip so as to remove the SiO₂ overlayer, either native or as grown, and expose the Si surface for AFM measurements. Two roughness parameters, root-mean-square roughness and fractal dimension D_F , were used to characterize the topography of the surface obtained with AFM^{5,11,12} with each parameter expressed as a number which enables direct comparison of roughness from sample to sample. Also, each parameter provides a different aspect of roughness. Rms provides vertical height variation information, but provides nothing about the spatial complexity, shape, or density of the roughness features, whereas D_F provides these latter aspects of roughness. However, since D_F is scale independent, it gives no vertical information of roughness. Moreover, D_F can be reliably extracted from AFM measurements using the two-dimensional (2D) variation method proposed by Dubuc *et al.*¹⁸ and adapted to AFM data.¹¹ For a 2D rough surface, D_F varies between 2 and 3. The closer D_F is to 3, the more complex is the rough surface. Further details about the algorithm used and the use of D_F for roughness evaluation can be found in Refs. 11 and 12. AFM measurements were taken at three different spots of each surface, and the averaged values of the extracted roughness parameters are reported here. The statistical standard deviations of all data shown in the following figures are within 10% of the averaged values, so in order to avoid making the multiple plots too difficult to read, the error bars are omitted.

III. RESULTS AND DISCUSSION

A. Smoothing of rough surfaces

Figures 2(a), 2(b), and 2(c) show that for all three roughness characterization parameters: SIE measured interface width L_{inf} , rms, and D_F , respectively, the initially rough

FIG. 2. Roughness parameters: (a) SIE interface region thickness, (b) root-mean-square roughness, and (c) fractal dimension vs accumulated SiO₂ overlayer thickness for initially rough samples smoothed through thermal oxidation at 1000 °C.

surfaces become smoother from thermal oxidation. These results are concordant with those from our previous studies^{5,6} wherein the smoothing effect was explained using the fact that small sharp features oxidize faster with the driving force being the reduction of free energy according to the Kelvin equation:¹⁹

$$\Delta G = 2V\gamma \left(\frac{1}{R_1} - \frac{1}{R_2} \right),$$

FIG. 3. AFM images with a z range of -4 – 4 nm of thermal oxidation at 1000 °C smoothing of initially rough samples.

where V is the molar volume, γ is the surface energy, and R is the radius of curvature. This equation is used to compare the change in free energy from a flat surface ($R_2 \rightarrow \infty$) to a curved surface with R_1 . Therefore, in order for the free energy to decrease, the curvature of the roughness features has to decrease (R_1 increases), and this is accomplished by oxidation at the top of the features such that the features become flatter with the smallest features (R_1 smallest), oxidizing fastest and disappearing. The AFM images in Fig. 3 show that overall the most extensively oxidized sample has the least spatial complexity, and the smallest features (lowest D_F and rms).

In order to determine whether the smoothing effect through thermal oxidation is a result of the high temperature or the oxidation reaction, initially rough samples were annealed in Ar at 1000 °C for different lengths of time. No systematic changes were seen with annealing. This negative result suggests that at least most of the concerted smoothing effect resulting from thermal oxidation can be attributed to the oxidation reaction and not simply the temperature.

B. Roughening of smooth surfaces

When performing thermal oxidation on initially smooth (out-of-the-box) samples, we observe in Figs. 4(a) and 4(b) that the interface roughness increases for both thermal oxidation at 800 and 1000 °C. Preoxidation cleaning procedures or surface impurities/defects have been speculated to be responsible for the roughening effect.^{1,20} However, the AFM images in Fig. 5 show that the roughness is uniform, which

FIG. 4. Roughness parameters: (a) SIE interface region thickness, (b) root-mean-square roughness, and (c) fractal dimension vs accumulated SiO₂ overlayer thickness for initially smooth samples roughened through thermal oxidation at 800 and 1000 °C.

does not support local impurities/defects as causative. It has also been hypothesized that surface roughness could be the result of an accumulation of a large number of surface defects, such as steps and edges, and the oxidation reaction simply increases the number of these defects on the surface.⁶ One mechanism that could enhance the production of interface defects is the intrinsic stress due to Si oxidation coupled with the production of point defects.^{21–23} Hahn and Henzler¹ reported that defects can be caused by the random diffusion and reaction of oxygen at the Si/SiO₂ interface. Given an initial roughness, by any of the aforementioned mechanisms, the growth of roughness can then be explained using the Kelvin equation¹⁹ as before. The decrease of curvature so as

FIG. 5. AFM images with a z range of -2 – 2 nm for thermal oxidation roughening of an initially smooth sample control (top center) with no oxidation, and oxidation at 1000 °C (left column) and at 800 °C (right column).

to reduce surface free energy can be achieved through oxidation in two ways, as illustrated in Fig. 6. One way is to have oxidation occur on the top of a roughness feature (labeled as 1) such that the width (w) of the feature stays constant, and the height (h) decreases, and another way is to have oxidation occur at the sides of the feature (labeled as 2) such that both h and w of the feature simultaneously increase. The latter provides a mechanism for an overall rough-

FIG. 6. Schematic showing the reduction in surface free energy by decreasing feature curvature in two ways.

ening effect in that the rms will increase while reducing surface free energy. However, this mechanism cannot be applied to an initially rough surface where the roughness features are closely packed. In this case, the width of a feature cannot increase without reducing that of an adjacent feature, hence, surface free energy is only reduced through an overall smoothening effect (i.e., reduction in rms) by decreasing the feature height. From Fig. 4(c), we see that the D_F decreases with oxide thickness which is the same trend as that with initially rough samples. Since D_F represents only the roughness features shape and spatial complexity and not the vertical deviation, this observation can again be explained by the Kelvin equation which predicts that small sharp features oxidize faster. Taken together our results suggest that during thermal oxidation both interface smoothening and roughening occur, and the finally observed surface roughness condition results from the competition between these two effects.

Thermal annealing experiments at 1000 °C in $\text{Ar}_{(g)}$ were also performed on smooth samples to see if interface roughening can be detected, but again, as we observed for rough samples that the interface roughness remains constant over the annealing time. Therefore, we concluded that the smoothening and the roughening effects during thermal oxidation do not arise from the heating alone at temperature up to 1000 °C, but rather from the oxidation reaction.

C. Temperature and oxidation rate effects

Figure 4(a) also shows that the SIE L_{inf} for samples at 800 °C increases faster than those at 1000 °C, which suggests that the higher oxidation rates at 1000 °C suppress the rate of roughening. However, at a SiO_2 overlayer thickness of ~ 50 nm, the two roughening curves become nearly parallel [i.e., roughening rates for the two temperatures become very close, as shown in Fig. 7(a)]. A comparison of the corresponding oxidation rates shown in Fig. 7(b) shows that the rates are different by almost an order of magnitude at the thickness where the roughening rates are nearly equal. Furthermore, Fig. 4(b) does not show much difference in the roughening rates as measured by rms. The larger SIE result for the 800 °C oxidation could be due to the presence of more suboxide (SiO_x with $x < 2$) produced²⁴ at lower temperatures at the interface as compared with the samples oxidized at 1000 °C. This effect would alter the SIE measurement of L_{inf} , but not the AFM measurement. More suboxides are expected at 800 °C because as the oxide layer increases, the diffusion-controlled oxidation reaction provides less oxidant to the Si/ SiO_2 interface, thus moving the reaction

to the right. Now at 800 °C, the diffusivity of the oxygen through the SiO_2 layer is much lower than that at 1000 °C,⁷ so that the deficiency of oxygen is more severe at 800 °C, thereby producing a thicker layer of SiO_x .

In order to further examine the effect of the oxidation rate on roughening, initially smooth samples were first oxidized, then HF dipped to remove the oxide and then reoxi-

FIG. 7. (a) Rate of roughening, which is the change of SIE interface region thickness with respect to the change of SiO_2 overlayer thickness, and (b) rate of oxidation, which is the change of SiO_2 overlayer thickness with respect to the change of oxidation time vs accumulated SiO_2 overlayer thickness.

dized, and this sequence was repeated a number of times. Effectively, the fresh Si surfaces resulting from the HF dip yielded the highest initial oxidation rates. In Fig. 8, we see that the interface roughness changes are small and erratic where the largest changes for SIE L_{inf} and rms are ~ 0.2 and ~ 0.07 nm, respectively. These changes are negligible when compared to Figs. 2 and 4, thus there are no changes in the height variation of interface roughness during oxidation cycles. The change in D_F is ~ 0.09 , which is too large to be disregarded, and the reason for such scatter is not understood, yet we find no systematic changes in spatial complexity (D_F) of the interface roughness with the accumulated SiO_2 overlayer thickness.

Even though no systematic roughness changes are observed for the oxidation cycles, the resulting interface is rougher after oxidation than the smooth (out-of-the-box) samples, due to the roughness introduced through oxidation as suggested by Hahn and Henzler.¹ This unchanging roughness is apparently the result of a steady state in smoothening and roughening effects reaching a local limiting roughness.

D. Limiting roughness

From our results summarized in Figs. 2 and 4, where it is observed that upon oxidation initially rough samples become smoother, and initially smooth samples become rougher, one may expect that these effects will converge at a limiting roughness. Figure 9 combines our results. The SIE results in Fig. 9(a) show that smoothening of the rough samples and

FIG. 8. Roughness parameters: (a) SIE interface region thickness, (b) root-mean-square roughness, and (c) fractal dimension vs accumulated SiO₂ overlayer thickness for both initially smooth samples which have undergone thermal oxidation cycles at 800 or 1000 °C.

the roughening of the smooth samples curves cross. This is untenable and indicates a measurement difficulty, again likely due to the formation of suboxide which is included in the optical response. The AFM/rms results in Fig. 9(b) do not show a crossing, and the rate of roughening of smooth surfaces is slower than that of the smoothening of rough surfaces. This can be understood by considering the competition between the two effects and that for initially rough samples, there is more to be gained energetically from decreasing roughness than producing it. Also, this could be the reason why smooth and rough surfaces do not continue to become infinitely rough or smooth, respectively, during ther-

FIG. 9. Roughness parameters: (a) SIE interface region thickness, (b) root-mean-square roughness, and (c) fractal dimension vs accumulated SiO₂ overlayer thickness for both initially rough and initially smooth samples smoothened and roughened, respectively, through thermal oxidation at 800 or 1000 °C.

mal oxidation, and the two effects converge to a limit of ~ 0.3 nm rms. For both initially smooth and rough samples, oxidation simplifies the interface roughness complexity.

IV. CONCLUSIONS

During thermal oxidation, both smoothening and roughening processes are occurring and affecting the resultant interface roughness. Reduction of surface free energy as described by the Kelvin equation¹⁹ together with the distribution of surface roughness features can be used to ex-

plain both effects. Surface roughness complexity is simplified during oxidation regardless of its initial status, and this is also driven by the reduction of surface free energy. The smoothening and roughening effects are primarily attributes of the oxidation reaction. The smoothening and roughening processes converge to a limiting roughness of about 0.3 nm rms after extensive oxidation.

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