Investigation of postoxidation thermal treatments of Si/SiO₂ interface in relationship to the kinetics of amorphous Si suboxide decomposition


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Interfacial Si suboxides (SiOₓ, x<2) are detrimental to transistor performance and are typically minimized during postoxidation anneals. To study the kinetics of SiOₓ decomposition, thick films (~2000 Å) of amorphous Si:O:H alloys (0.7<x<1.4) were deposited by remote plasma enhanced chemical vapor deposition and subjected to rapid thermal anneals. Films were characterized by Fourier transform infrared spectroscopy, Raman spectroscopy, ellipsometry, photoluminescence (PL), and transmission electron microscopy. At temperatures >500 °C initially there is a rapid segregation into amorphous Si (a-Si) surrounded by a SiO₂ shell which acts as a diffusion barrier decelerating the reaction. Phenomenological modeling of kinetics with a one-dimensional Avrami–Erofe’v treatment gives an upper limit for a-Si lateral growth rates of 1.2 Å/s at 900 °C with an activation energy of 120 kJ/mol. PL, Raman, transmission electron microscopy and ellipsometry confirm this segregation model in the amorphous state. Due to the rapid initial decomposition and relatively large diffusion coefficients, a simple kinetic hindrance explanation for the 4–8 Å of SiOₓ at the SiO₂/Si interface is unlikely. © 1998 American Vacuum Society. [S0734-211X(98)09104-5]

I. INTRODUCTION

Due to its dominating effects in metal–oxide–semiconductor field-effect transistor (MOSFET) performance, the Si/SiO₂ interface is the subject of extensive studies. This interface is well known to be stoichiometric SiO₂ within 4–6 Å of the interface where suboxides, SiOₓ (x<2) are seen.¹² The amount and nature of the suboxides at the interface is highly dependent on surface preparation, annealing temperatures, and growth temperatures.¹ Solid SiO₁₀ is thermodynamically unstable below 1173 °C,³ and decomposes as in Eq. (1). Typically, suboxides in a MOSFET are minimized during a postoxidation anneal. However the quantification of suboxide by x-ray photoelectron spectroscopy (XPS) after this process is extremely difficult due to attenuation of signal from buried interface. If ultrathin oxides are used, the volatilization of SiO gas during anneals becomes significant. It is thus of interest to study the kinetics of Si suboxide disproportionation in bulk samples which can be related to the interface:

\[
\text{SiO}_x \rightarrow \frac{x}{2} \text{SiO}_2 + \left(1 - \frac{x}{2}\right) \text{Si}. \tag{1}
\]

Solid SiO₁₀ grown from evaporation is highly pyrophoric and difficult to study, while H termination stabilized Si suboxides can be synthesized by chemical vapor deposition of semi-insulating polysilicon (SIPOS) or by remote plasma enhanced chemical vapor deposition (RPECVD). Early reports show that SIPOS films decompose into Siₘₓ and amorphous SiO₂ matrix⁴ as expected in Eq. (1) and have been studied further,⁵–⁸ however none of these studies closely examined the temperature region, where ultrathin MOSFET gate dielectric growth is important (700–900 °C). There is one report of SiOₓ decomposition kinetics in SIPOS films which is derived from measurement of Si nanocrystal size.⁹ However, that study measured a crystallization process and is insensitive to reactions in the amorphous state. RPECVD derived films of SiOₓ have been shown to similarly form Siₘₓ in SiO₂ matrix after anneals of 900 °C.¹⁰ Therefore it is of interest to study the SiOₓ decomposition kinetics with a method insensitive to crystallization processes at temperatures less than 1000 °C.

II. EXPERIMENT

A RPECVD reactor previously described¹¹ was employed to grow thin films SiOₓ (0.7<x<1.4). 100 sccm He with 0.05 to 0.2% O₂ was passed through the rf plasma coil tube with 33 W power at 13.56 MHz. 10 sccm of 10% SiH₄/He was introduced through a showerhead ring downstream from the plasma source. Total pressure was maintained at 300 mTorr as well as a substrate temperature of 160 °C. Film thicknesses were typically 2000 Å (16 Å/min). For H₂ plasma treatments, a plasma was generated with 100 sccm of He passing through the plasma coil (50 W power) and 30 sccm of H₂ was introduced downstream with a total pressure of 100 mTorr. The sample was heated to 300 °C and treated for 2 h.

The suboxide films were then annealed ex situ in an AG Associates rapid thermal annealing (RTA) furnace under 1 atm of Ar for times of 5 s–3 min (ramp rate 60 °C/s). Fourier transform infrared (FTIR) measurements were performed with a Nicolet 750 spectrometer in transmission mode with a resolution of 4 cm⁻¹. Spectra were subtracted from a reference sample cut from the same Si(100) single side chemically roughened wafer to prevent internal reflection errors. To assure low experimental scatter (from film to film variation), films for each series were annealed sequentially, unless stated otherwise. Photoluminescence (PL) data measurements utilized a capacitance–voltage integrated (CVI) model
III. RESULTS AND DISCUSSION

A. General mechanism of disproportionation

FTIR can be effectively used to monitor the degree of oxygen content \((x)\) in homogeneous SiO\(_x\) films, as the Si–O stretch frequency increases linearly from \(\sim 965\) to \(\sim 1065\, \text{cm}^{-1}\) with oxygen content \(^{12}\) as in Eq. (2). All reported stoichiometries for as-deposited films are calculated using Eq. (2) with observed \(\nu_{\text{Si–O}}\):

\[
x = 0.020(\nu_{\text{Si–O}}) - 19.3.
\]

Figure 1 shows the IR spectra and assigned vibrations for an as-deposited film and the effects of annealing treatments. The most important features due to annealing are the loss of Si–H modes, the increase in Si–O bend and rock modes. The gradual increase in frequency as expected in forming SiO\(_2\). At all temperatures there is a rapid initial rapid segregation of SiO\(_x\) alloy or one with concentration gradients. Two distinct Si–O stretch peaks would form if only SiO\(_2\)+Si were formed, which is not observed:

\[
\text{SiO}_x \rightarrow [x/(x+y)]\text{SiO}_y + [1-x/(x+y)]\text{Si},
\]

\[
\alpha = (\nu_m - \nu_i)/(\nu_f - \nu_i) = y/(2-x).
\]

To quantify the kinetics of reaction (3), the extent of reaction \((\alpha)\) is given in Eq. (4), where reaction completion \((\alpha = 1)\) is when \(x + y = 2\). \(\nu_m\) is the measured \(\nu_{\text{Si–O}}\), \(\nu_i\) is the as-deposited \(\nu_{\text{Si–O}}\), and \(\nu_f\) is the measured \(\nu_{\text{Si–O}}\) at completion (after anneals at 1000 °C with \(\nu_{\text{Si–O}} = 1075\, \text{cm}^{-1}\)). The integrated area of the Si–O stretch peak remains constant indicating no significant parasitic oxidation. With successive anneals the Si–O stretch peak becomes sharper and higher in frequency as expected in forming SiO\(_2\).

Figure 2 shows the extent of reaction \((\alpha)\) of initial SiO\(_{0.93}\) films as a function of time at various annealing temperatures. At all temperatures there is a rapid (<5 s resolution of RTA technique) initial reaction followed by a rate which is highly deceleratory. On this time scale, the reaction proceeds asymptotically to an extent of reaction less than completion. Si suboxide stability can be found through the kinetic hindrance of the disproportionation reaction. We propose a mechanism which is consistent with the observed kinetics. That is, an initial rapid segregation of SiO\(_x\) into a-Si which would by necessity form an SiO\(_2\) shell. This shell acts as a diffusion barrier for continued reaction and explains the observed deceleratory behavior. The higher initial \(\alpha\) with increasing anneal temperature is likely the result of a combination of increased nucleation density and increased growth rates.

To examine the temperature dependence of the kinetics, SiO\(_x\) films of various composition were annealed at successively higher temperatures. Each point of Fig. 3 is for an anneal of 6 min (where the reaction has decelerated appreciably) at the given temperature. For all compositions, the reaction is less hindered with increasing temperature. This suggests that higher temperatures allow for higher diffusion coefficients to negate the deceleratory diffusion barrier. The reaction kinetics are similar for all initial compositions. The notable exception is that the extent of initial reaction (anneal at lowest temperature, 600 °C) is greater for samples with lower oxygen content. This is consistent with an initial segregation into Si regions with the SiO\(_2\) shell. By a simple stoichiometric argument, less oxygen content will by necessity require more SiO\(_x\) to decompose to form an SiO\(_2\) shell at a given nucleation density. Figure 4 shows a cross-sectional transmission electron microscope (TEM) micrograph of SiO\(_{1.0}\) after an anneal at 900 °C. Si nanocrystals are formed.

![FTIR absorbance for SiO\(_x\) film after various sequential anneals for 6 min at each temperature, showing blue shift in \(\nu_{\text{Si–O}}\) as well as loss of Si–H bonds. Spectra are offset by 0.06 abs units for clarity. Integrated area under Si–O stretch remains constant for all anneals.](Image)

![Figure 1](Image) FIG. 1. FTIR absorbance for SiO\(_x\) film after various sequential anneals for 6 min at each temperature, showing blue shift in \(\nu_{\text{Si–O}}\) as well as loss of Si–H bonds. Spectra are offset by 0.06 abs units for clarity. Integrated area under Si–O stretch remains constant for all anneals.

![Extent of reaction (\(\alpha\)) for initial SiO\(_{0.93}\) thin film as a function of time at various annealing temperatures, showing kinetic metastability of Si suboxides. Curve shown is guide to eye. For each temperature the same film is annealed sequentially to reduce experimental scatter.](Image)

![Figure 2](Image) FIG. 2. Extent of reaction (\(\alpha\)) for initial SiO\(_{0.93}\) thin film as a function of time at various annealing temperatures, showing kinetic metastability of Si suboxides. Curve shown is guide to eye. For each temperature the same film is annealed sequentially to reduce experimental scatter.
in an amorphous SiO₂ matrix, consistent with a mechanism of Si segregation with the SiO₂ shell. TEM micrographs of films annealed at 750 °C are completely amorphous; thus the disproportionation reaction proceeds in the amorphous state, not requiring a crystalline growth interface.

SiOₓ and amorphous silicon (a-Si) have well known PL properties and can be readily applied to this system to demonstrate the phase segregation in the amorphous state. Figure 5 shows the characteristic visible PL of as-deposited SiO₁·₃. With modest annealing ≈ 500 °C all PL is lost, due to non-radiative carrier recombination with Si dangling bond defects. Only after treatment of annealed films in H₂ plasma, to passivate Si dangling bonds, is PL restored, similar to results with a-Si after moderate anneals. This PL coincides with the characteristic energy of a-Si (1.3 eV). The inset of Fig. 5 shows the dependence of PL on measurement temperature. The treatment of ln(I₀/I₂) vs T is commonly applied to amorphous Si with the slope being a characteristic temperature (T₀) for carriers to hop from localized states in band tails to conduction band. With higher T₀, PL is more stable to increasing measurement temperature. As-deposited SiO₁·₃ has a T₀ near 63 K while after annealing the temperature stability is markedly reduced to T₀ of 29 K, which is nearly identical to a-Si (T₀; 25 K). Optical absorption measured band gap is also consistent with the segregation forming a-Si, with the E₀ decreasing from 2.2 to 1.8 eV after annealing (1.8 eV is characteristic of a-Si).

Observations in conductivity measurements also support an amorphous state segregation mechanism. Figure 6 shows both the dark- and photocurrent of films of various composition before and after annealing at 650 °C. For as-deposited films, the dark current is very low indicating a low level of Si dangling bond density. With increasing O content, the photocurrent decreases, which is expected for decreased absorption coefficient. After annealing, the dark current increases markedly as expected from the formation of Si dangling bonds. However at high O content, the photocurrent after annealing actually increases because of the increase in absorbance from a-Si regions. Both dark current and photocurrent decrease exponentially with increasing O content, which is consistent with a segregation model in which conduction paths between a-Si regions is reduced. Both PL and conductivity measurements show that Si dangling bond defect density is significant. Therefore it is of importance to determine whether the kinetics of SiOₓ disproportionation are accelerated by defects. Figure 7 shows the extent of reaction as a function of annealing temperature for films of different initial H content. A factor of two difference in initial Si–H
concentration does not effect observed kinetics, thus is not likely to be involved in the dominate mechanism.

B. Kinetic modeling

The previous experimental observations support the general mechanism of an initial rapid segregation of SiO$x$ into a-Si with an SiO$_2$ diffusion barrier which decelerates further reaction. This mechanism would also form a concentration gradient resulting in an oxygen rich SiO$_{(x+y)}$ matrix. To model the kinetics, we can apply the three-dimensional (3D) Avrami–Erofe’v approach [Eqs. (5)–(7)] in which there is an instantaneous nucleation followed by a diffusion limited growth process. $\alpha$ is the extent of reaction, $N_c$ is nucleation density (cm$^{-3}$), $D$ is diffusion coefficient (cm$^2$/s), and $t$ is time of reaction in seconds. In this treatment an alloy of matrix composition $(C_m, SiO_x)$ decomposes into nucleation sites of $\beta$ phase $(C_\beta, a$-Si) and $\alpha$ phase $(C_\alpha, SiO_2)$ which acts as a diffusion barrier for the growth of $\beta$ phase. This geometry is schematically shown in the inset of Fig. 8. With O as the diffusion species, $C_\alpha = (2.27 \times 10^{22} \text{ cm}^{-3}) \cdot x$, $C_\beta = 4.55 \times 10^{22} \text{ cm}^{-3}$, $C_\alpha = 0$, $R_f$ is the final Si nc radius, and $V_f$ is the final Si volume fraction calculated from stoichiometry $(x)$. $N_c$ is $1 \times 10^{19}$/cm$^3$ (from TEM size measurements at $\alpha = 1$):

$$\ln(1 - \alpha) = \frac{8\sqrt{2} \pi}{3} N_c D^{3/2} \left( \frac{C_m - C_\alpha}{C_\beta - C_\alpha} \right)^{1/2} t^{3/2},$$

$$D = D_0 \exp \left( -E_a/kT \right),$$

$$N_c = \frac{4/3 \pi R_f^3}{V_f}, \quad V_f = \frac{1 - x/2}{1 + 0.6x}. \quad (7)$$

In Fig. 8, the solid points are the extent of reaction for initial SiO$_{1.1}$ after successive annealing for 6 min at each temperature. The dashed lines are calculated from Eqs. (5)–(7) using the activation energy ($E_a$) shown and the initial reaction rate at 650 °C. In other words, the rate of reaction at 650 °C (i.e., Δ$\alpha$ 600–650 °C) is used to calculate $D_0$ for a given $E_a$. This $D_0$ and $E_a$ are used to calculate $\alpha$ at successively higher temperatures for the 6 min periods, resulting in the dashed line in Fig. 8. As can be seen in Fig. 8, rather low activation energies of 30 kcal/mol are found to fit experimental data. This treatment predicts significant reaction at 650 °C while isothermal experiments (Fig. 2) show significant deceleration well before reaction completion. This is best seen in Fig. 8, where the calculated extent of reaction at 650 °C ($E_a = 0$) is compared to experimental data (open diamonds) for anneals at 650 °C (in this case the x axis acts as time instead of temperature). The measured kinetics are significantly decelerated compared to those predicted. There is a fundamental inadequacy of the 3D Avrami–Erofe’v treatment. That is while diffusion barrier decelerates the reaction by a factor of $\sqrt{t}$, the volume of a-Si phase grows as the cube of radius. This results in an overall $t^{3/2}$ dependence, which is accelerationary. Significant deceleration would occur only near comple-
tion \((\alpha>0.8)\) from impingement, which is not experimentally observed. Thus the 3D Avrami–Erofe’v’ treatment is not directly applicable to this system.

To account for the highly deceleratory nature of the reaction we can look at the dimensionality of phase growth. Typically the dimensionality of a reaction is found by microstructure of the resultant products, i.e., spherical particles imply 3D growth, platelets 2D, and needles 1D. The observed spherical Si nanocrystals imply 3D growth, however this may not necessarily reflect reactions in the amorphous state. The Si nanocrystals may be nucleated and grown in existing \(a\)-Si regions, representing a different reaction, which is 3D. Crystallization of \(a\)-Si regions in SIPOS has been similarly proposed from Raman experiments. Since the initial segregation in amorphous Si is extensive, it is possible to have volume growth without significantly expanding surface area. Impingement upon itself and regions of decreasing reaction surface area will reduce the dimensionality of the growth reaction. Equation (8) describes the Avrami–Erofe’v’ for the 1D limit:

\[
\ln(1-\alpha) = \frac{A_i}{d_f^2} \left( C_m - C_a \right) \frac{C_m}{C_a} D^{1/2} t^{1/2},
\]

\[A_i = \frac{V_f}{d_f},\]

where \(A_i\) is the initial surface area of the amorphous Si region after initial segregation reaction which is approximated by Eq. (9) and \(d_f\) is the average Si nanocrystal diameter as seen by TEM. Figure 9 shows the fit of Eq. (8) using the same method used in Fig. 8. The reduced dimensionality increases activation energy to 120 kJ/mol. Table I shows calculated parameters for 1D Avrami–Erofe’v’ treatment. The extent of reaction \((\alpha)\) calculated for \(650^\circ\text{C} (E_a=0)\) approaches that observed isothermal data shown in Fig. 9. Thus 1D Avrami–Erofe’v’ is a reasonable limit for the observed kinetics. If we apply the calculated \(D\) to the initial barrier \((\alpha=0.19)\) we find a rapid linear growth rate near 1.2 \(\text{Å/s}\) at 900 °C. This rate is significantly faster and with lower \(E_a\) than the observed by Nesbit’s treatment of \(S_{\text{SiO}}\) growth \((E_a\sim180\ \text{kJ/mol})\), suggesting that those kinetic values are for the crystallization of \(a\)-Si with O impurities. This interpretation is further supported by recent work which has shown that as-deposited SIPOS films have significant segregation into \(a\)-Si regions (~50%).

### C. Uncertainty in kinetic parameters

It is important to quantify the uncertainties in the kinetic parameters found in the 1D Avrami–Erofe’v’ treatment. Most significant is the uncertainty of IR measurements. As-deposited films contain significant amounts of \(\text{Si–H}\) which broaden the \(\text{Si–O}\) stretch peak and adds uncertainty to \(n\) in Eq. (4). Uncertainty in \(n\) will shift the position of all measured \(\alpha\). The most extreme case is if the observed shift in \(n\) \((600^\circ\text{C})\) due solely to H loss and not to the reaction in Eq. (4). Using the kinetic treatment as in Fig. 9 on this limiting case would result in a \(E_a\) of 170 kJ/mol. However photoluminescence, ultraviolet visible (UV-vis) absorption, conductivity, and Raman data all show the presence of \(a\)-Si after low temperature anneals, thus there must be a disproportionation reaction at these low temperatures with simultaneous H loss. The data in Fig. 7 also strongly suggest the H content does significantly shift the \(\text{Si–O}\) stretch position. A factor of two reduction in the initial H content did not change \(\alpha\) observed at 600 °C. A 50% error in \(\alpha\) after 600 °C anneal would result in an \(E_a\) of 135 kJ/mol. Viscoelastic relaxation can play a role in shifting \(n\). Using \(\alpha\) at 925 °C as \(\alpha\) the lower limit where viscoelastic effects are known to be minimal, the maximum error in the derived \(E_a\) is +5 kJ/mol. Thus the \(E_a\) value of 120 kJ/mol for the 1D Avrami–Erofe’v’ treatment is a lower limit with an uncertainty of +20 kJ/mol.

Any significant nucleation rate after initial rapid segregation would result in an accelatory reaction rate, which is not observed. A possibility is that there is no growth of existing nuclei and the measured extent of reaction is only due to forming new nuclei. The observed deceleration could be explained as function of a reduction in nucleation rate. An increase in temperature may allow otherwise hindered sites to nucleate. It is difficult to separate this effect from the growth of existing nucleation centers as in the Avrami–Erofe’v’ treatment. This effect can be discounted for several reasons. Generally, impingement effects which decelerate nucleation typically are seen at \(\alpha\sim0.8\). Yet this system of deceleration...
occurs around $\alpha \sim 0.2$–0.4. If only a nucleation mechanism were present, an $\text{SiO}_2$ shell would be formed and the IR measurements would show two peaks corresponding to $\text{SiO}_2$ and $\text{SiO}_x$, not the observed gradient. Thus there must be an $\alpha$-Si phase growth mechanism. Any effects of nucleation at higher temperature would increase observed transformation rates, thus the $E_a$ derived from the 1D Avrami–Erofe’v treatment is a lower limit.

IV. CONCLUSIONS

$\text{SiO}_x$ metastability in thick films can be found through kinetic hindrance. The disproportionation reaction proceeds by (1) rapid ($\leq 5$ s) initial segregation forming $\alpha$-Si and $\text{SiO}_2$ diffusion barrier, (2) highly deceleratory growth of $\alpha$-Si regions form $\text{SiO}(x+y)$ diffusion gradient, (3) crystallization of $\alpha$-Si regions into Si nanocrystals. FTIR, PL, TEM, Raman, and conductivity measurements all support a model with significant disproportionation in the amorphous state. Analysis of the highly deceleratory kinetics shows that the initial $\alpha$-Si regions is extensive and growth is of low dimensionality. The 1D limit of Avrami–Erofe’v treatment gives lateral growth rates of $1.2$ Å/s ($900$ °C) and $0.04$ Å/s ($650$ °C) with an activation energy of $120$ kJ/mol, after initial segregation reaction. Due to the rapid initial segregation and relatively large lateral growth rate, a simple kinetic hindrance explanation for the $4$–$8$ Å of interfacial $\text{SiO}_x$ at the $\text{SiO}_2$/Si interface is unlikely.

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