Evolution of Si suboxides into Si nanocrystals during rapid thermal annealing as revealed by XPS and Raman studies

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**Abstract**

Si nanocrystals (nc-Si) were synthesized by rapid thermal annealing of magnetron-sputtered amorphous SiO$_x$ films. X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy were employed to study the evolution of chemical structures and the rapid growth of nc-Si. XPS results reveal five chemical structures of Si in the as-deposited films corresponding to silicon oxidation states: Si$^n$ ($n=0, 1, 2, 3$ and $4$). Their bonding structures are found to be inhomogeneous, and far from that predicted by the random-bonding model. XPS and Raman spectra suggest that the formation of amorphous Si nanoclusters had already taken place in the as-deposited samples. Formation of nc-Si was realized through a combination of thermal decomposition and the diffusion process. Upon thermal annealing, Si suboxides (Si$_2$O, SiO and Si$_2$O$_3$) decompose into Si and SiO$_2$, resulting in the rapid growth of nc-Si.

**1. Introduction**

Recently, there has been considerable research effort into the study of light emission from silicon-based materials, driven by the desire to integrate optical devices with silicon-based integrated circuits. At present, silicon is rarely used in optoelectronics due to its indirect-bandgap nature that hinders its functional integration of optical components. Si nanocrystals (nc-Si) embedded in dielectric matrices, however, have been demonstrated as a potential candidate for Si-based optoelectronic [1–4] and non-volatile memory [5–7] devices produced in a way compatible with the current main-stream complementary metal-oxide-semiconductor process [8,9]. One of the promising techniques to synthesize such a structure is magnetron sputtering of SiO$_x$ ($0 < x < 2$) films followed by annealing to induce formation of nc-Si. It is reported that high annealing temperature (higher than 1050 °C) and long annealing time (more than 30 min) are required to induce the formation of nc-Si due to the low diffusivity (the order of $10^{-16}$ cm$^2$/s at 1000–1150 °C [10]) of Si in SiO$_2$. However, an average of 5 nm nc-Si has been produced very rapidly by us (within 3 min) using rapid thermal annealing (RTA). The evolution of the chemical structures plays a significant role in this rapid growth. Though several investigations have been carried out on formation of nc-Si [11–13], a clear understanding of the chemical structure evolution in nanoscale is still unavailable, neither mechanism of rapid growth of nc-Si during RTA. This paper presents a quantitative study of X-ray photoelectron spectroscopy (XPS) data to reveal the details of the thermal decomposition of Si suboxides during RTA and to address the mechanism of the formation and rapid growth of nc-Si.

**2. Experimental procedure**

A reactive radio-frequency (13.6 MHz) magnetron sputtering system was employed to deposit the SiO$_x$ films from a Si target (99.999% in purity) in a mixed Ar/O$_2$ atmosphere at controlled flow rate. p-Type Si (10 0) wafers were used as substrates. Prior to deposition, the wafers were ultrasonically cleaned consecutively in acetone, ethanol for 20 min each followed by rinsing in de-ionized water. The Si target was placed 80 mm above the substrate. The base pressure of the chamber was better than 1.0 x 10$^{-7}$ Torr. During deposition, the target power and sputtering pressure were fixed at 200 W and 4 mTorr, respectively. The variation of the Ar/O$_2$ flow ratio was achieved by varying the...
oxygen flow rate between 0.8 and 3.0 sccm at fixed Ar flow of 40 sccm. No additional heating was applied during deposition; the substrate temperature was effectively 45 ± 3 °C due to ions bombardment. The target and the substrate were cleaned through pre-sputtering and pre-etching for 15 min, respectively, to remove possible contaminations before the target shutter is opened to allow commencement of deposition. The samples were produced by growing 200–300 nm of SiO2 layer with the composition from SiO0.6 to SiO2. The post-deposition annealing was carried out from 200 to 1100 °C in the rapid thermal annealing system for 3 min. To avoid possible oxidation during annealing, the RTA chamber was first pumped down to 2.0 × 10⁻⁵ Torr, then Ar was introduced as the protection ambient at a flow rate of 2000 sccm. The composition and chemical states of the films were determined through XPS analysis using a Kratos-Atlas spectrometer with monochromatic Al Ka (1486.71 eV) on plane-view samples at a normal take-off angle after removal of surface contamination using Ar ion etching for 10 min at 15 keV. Survey scans and high-resolution spectra were acquired by using pass energies of 160 and 40 eV, respectively. Deconvolution of the XPS curves was conducted by using a fitting procedure based on the summation of Gaussian functions after Shirley background subtraction. The crystallinity of the film was characterized by using Raman spectroscopy (Renishaw 1000 Ramascope system) with 633 nm line excited He–Ne laser. The formation of the nc-Si was confirmed using transmission electron microscope (TEM, JEM 2010).

3. Results and discussion

3.1. Microstructure of the as-deposited films

Fig. 1. (a) and (b), shows the XPS Si 2p core-level peaks for samples of high and low Si concentration, respectively. The Si 2p core-level spectrum possesses two main peaks separated by a flat region where the intensity does not drop to zero. According to the random-bonding model (RBM) of the atomic structure of amorphous SiOx films [14], the local bonding was statistical in nature, and characterized by five different local-bonding possibilities: Si–Si0.6–Si0.6, where n = 0, 1, 2, 3 and 4. Assuming validity of this bonding model, deconvolution of the XPS curves gives rise to five chemical states, corresponding to Si0, Si1+, Si2+, Si3+ and Si4+ (dotted curves in Fig. 1). The curve fitting was carried out by placing the initial binding energy of Si0 to that of Si reference sample (99.75 eV). These five chemical states were expected to be equally spaced from the binding energy of Si0 to that of Si4+. However, in order to take into account small differences in charging effects on the sample the peak energies were allowed to vary within 0.1 eV during the fitting process. The Si 2p line was decomposed into Si 2p1/2 and Si 2p3/2 lines with intensity ratio 1:2 and a fixed spin–orbit splitting of 0.6 eV as an atomic property (only the sum of the Si 2p1/2 and 2p3/2 partner lines is shown for clearer presentation). The full-width at half-maximum (2σ) was assumed the same for both lines, but allowed to vary from Si0 to Si4+, and the relative weights (W) were allowed to vary without constraint. As shown in Fig. 1, five chemical states were fitted by a superposition of five Gaussian peaks (Si0, Si1+, Si2+, Si3+ and Si4+), corresponding to no Si–Si bond, one Si–Si bond, two Si–Si bonds, three Si–Si bonds, or all four Si–Si bonds had been replaced by Si–O bonds. The relative concentration of each oxidation state can be obtained by calculating the ratio $I_{n+}^0/I_{total}$, where $I_{n+}^0$ is the peak area of the oxidation state $Si^+_{n+}$ and $I_{total}$ is the total area of the Si 2p peaks. Consequently, we obtain the Si relative concentrations of samples with different oxygen content. Fig. 2 shows the changes in concentration of the five Si chemical states in the as-deposited samples with different oxygen concentration. At low oxygen concentration, Si0 was the prominent phase in the films (i.e., minimum replacement of Si–Si bonds with Si–O bonds), and the oxidized Si species were mostly in intermediate chemical states, with very small amount of Si4+. As the oxygen content increases, the concentration of Si2+ and Si3+ species increased, while the amount of the Si0, Si1+ and Si2+ species dramatically decreased as shown in Fig. 2. During reactive sputtering, in the formation of Si–O bond of different Si valence state, the need for oxygen increases progressively from Si0, Si1+, Si2+, Si3+ to Si4+. As such, as more oxygen becomes available (as the oxygen flow rate increases) more Si atoms are oxidized into high chemical states, leading to the concentration of Si1+, Si2+ species to decrease while the high states to increase.

![Fig. 1. Si 2p XPS spectrum of the as-deposited SiO0.65 and SiO1.4.](image)

![Fig. 2. The changes in concentration of the five Si chemical states as function of oxygen content in the as-deposited films.](image)
Table 1 shows a comparison of the chemical structures between the results yielded from XPS and the results calculated according to the idealized RBM. The chemical structures are quite different from those predicted by RBM. The concentration of the Si<sup>0</sup> and Si<sup>4+</sup> from our XPS spectrum is too high compared to the calculated results. This discrepancy illustrates the existence of chemical inhomogeneity on the nanometer scale. Some regions are rich in Si and some contain elemental silicon. Similar chemical structures of SiO<sub>x</sub> films have been found by Rochet et al. [15] after plasma treatments, annealing or laser irradiation. The extra-high concentration of Si<sup>0</sup> in their films was attributed to the formation of Si particles. Here, it is quite likely that amorphous Si clusters are already formed in our as-deposited films. This has been confirmed by our Raman spectra.

### 3.2. Crystallization of the excess Si

Raman scattering provides a nondestructive and fast way to differentiate whether the Si particles are amorphous or crystalline. Information concerning the formation and crystallite size can be obtained from the shape and positions of the optical phonon bands [16–18]. For a typical Raman spectra of thin-layer amorphous SiO<sub>x</sub> film on Si wafer, there is a weak peak at ~300 and a sharp peak at ~520 cm<sup>-1</sup>, corresponding to the crystalline silicon (substrate) lattice vibrations, and two broad peaks at ~160 and ~480 cm<sup>-1</sup> due to scattering from amorphous Si [19–21]. These two broad peaks are usually used to characterize the

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Fig. 3. Raman spectrum of Si wafer and the SiO<sub>1.4</sub> sample before and after annealing at below 400 °C (a), between 600–800 °C (b) and above 900 °C (c). The insets show the Raman spectra from frequency 480 to 560 cm<sup>-1</sup> for a better presentation. The Raman spectrum of Si wafer in the inset (c), which went through the same annealing condition as sample after annealing at 1100 °C, was intended to shift to the same peak position for a better comparison.
formation of small-size (more than 1 nm) amorphous Si phase domain in SiO\textsubscript{2} films [16–22]. The formation of nc-Si can lead to a size-dependent down shift and broadening of the optical phonon peak at \(\sim 520\ \text{cm}^{-1}\) due to the phonon confinement effect in the nc-Si, which can be exploited to characterize the size of nc-Si [16–18].

Fig. 3(a)–(c) shows the Raman spectra of sample SiO\textsubscript{1.4} before and after annealing at different temperatures. The Raman spectrum of Si wafer was also shown for comparison. The Raman peak of the Si substrate centered at 521.8 \text{cm}^{-1} with a full-width-at-half-maximum of 3.8 \text{cm}^{-1}. In the as-deposited sample, the crystalline Si peaks can be seen. By comparing with Si wafer, we could deduce that these crystalline Si signals originated from the silicon substrate. No distinguished amorphous Si peaks at around 160 and 480 \text{cm}^{-1} can be seen when the annealing temperature was below 300 °C. This might be due to the concentration of the amorphous Si being too low, or the size of the initial Si nanoclusters being too small; therefore, separated amorphous Si peaks cannot be detected at this stage [16]. When the temperature reached 400 °C, a broad peak at \(\sim 160\ \text{cm}^{-1}\) appeared as shown in Fig. 3(a). However, separated amorphous Si peak at \(\sim 480\ \text{cm}^{-1}\) still did not present. But, the crystalline Si peak at 520 cm\(^{-1}\) became strongly asymmetric. Quite similar phenomena have been observed by other researchers in nc-Si Raman studies [16,18]. The amorphous Si peak at \(\sim 480\ \text{cm}^{-1}\) is not observable when the amorphous Si concentration is low, but can lead to the strong asymmetry of the crystalline Si peak at \(\sim 520\ \text{cm}^{-1}\). The rise of separated amorphous peaks at around 160 \text{cm}^{-1} and the asymmetry of the peaks at 520 \text{cm}^{-1} showed a phenomenon of formation of amorphous Si nanoclusters. The intensity of the broad peak at \(\sim 160\ \text{cm}^{-1}\) and the asymmetry of the peak at \(\sim 520\ \text{cm}^{-1}\) continually increased with annealing temperature until 700 °C and then decreased when the annealing temperatures were further increased. The availability of the amorphous features on the Raman spectrum when the annealing temperatures are higher than 400 °C is because an increase in amorphous Si concentration resulted from the thermal decomposition (or phase separation) of the Si suboxides (SiO\textsubscript{2}, SiO and Si\textsubscript{2}O\textsubscript{3}) and the growth of the initial amorphous Si nanoclusters. The first increasing intensity indicated a continuity of the thermal decomposition with increasing annealing temperatures. This will be discussed in detail below. The decreasing intensity of the amorphous Si phase after annealing at 800 °C indicated that the amorphous Si has been partially transformed into crystalline Si. This crystalline annealing temperature is slightly lower than Nesbit’s report [10]. Nesbit claimed that minimum annealing temperature of 900 °C and minimum crystal size of 2.5 nm are required to form nc-Si due to the stability (depends on the balance between their volume and surface-free energies) of small crystals [10]. Here, we believe the reduced crystalline temperature is due to the rapid heating and cooling of the RTA process. The stored energy is not released during the heating process because it is too fast. These energies can help the crystallization of Si nanoclusters at relatively lower temperatures, thus certain amorphous Si nanoclusters (even smaller than 2.5 nm) are crystallized during annealing at 800 °C. These crystallized nanoparticles remain at room temperature due to the quenching of the RTA process. The formation of nc-Si can be confirmed from the broadening and down shift of the crystalline Si peak at \(\sim 520\ \text{cm}^{-1}\) when the annealing temperature went up to 900 °C as shown in the inset of Fig. 3(c). By comparing with the Raman spectrum of Si wafer which went through the same annealing condition, the peak position of our sample after annealing at 1100 °C shifted to low frequencies by 3.9 \text{cm}^{-1}. An average size of 5–6 nm can lead to the frequency down shift by 3.9 \text{cm}^{-1}[17], which is consistent with our TEM result (shown later).

3.3. Evolution of chemical structures

Fig. 4 demonstrated Si 2p XPS spectra measured on SiO\textsubscript{1.4} after annealing at 400, 700 and 1000 °C. The effect of annealing on the chemical structures is clearly seen by comparing with the as-deposited counterpart. In Fig. 4, with increasing annealing temperatures, two spectral features emerge. Firstly, the concentrations of the various Si chemical states have been changed. The degree of Si suboxides decreased, while the intensity of the Si\textsuperscript{0} and Si\textsuperscript{4+} peaks increased. This occurred because the Si suboxides were unstable and tended to thermally decompose into more stable Si and stoichiometric SiO\textsubscript{2} during annealing [23]. However, there were still strong Si suboxides signals in the spectrum even after annealing at 1000 °C due to the short annealing time. Judging from the light-white edges of the nanocrystals in the TEM images, Si suboxides may exist at the interface of nc-Si and SiO\textsubscript{2} matrix, as also mentioned in Refs. [11,24], and the concentration of which can be further reduced by increasing both the annealing time and temperature [13]. Secondly, the binding-energy difference (chemical shift) between Si\textsuperscript{0} and the Si\textsuperscript{4+} peaks increases, from 3.6 eV (as-deposited) to 4.3 eV (annealed at 1000 °C), most probably due to the better phase separation and, more importantly, enhanced differential charging [25].
To clarify the reaction detail of the decomposition reactions of the Si suboxides in SiOₓ during annealing, the changes of the concentrations of the five oxidation states with annealing have been examined quantitatively. Fig. 5 shows the changes in the concentration of the five oxidation states in the SiO₁.₄ sample with annealing temperature. Upon annealing, the concentration of the Si²⁺ decreased, while both Si⁰ and Si⁴⁺ species increased, whereas the concentration of the Si¹⁺ and Si³⁺ first slightly increased, then decreased. Here, it is reasonable to assume that the SiOₓ films are formed by tetrahedral Si–(O₂,Si₄⁻ₙ) (n=0, 1, 2, 3 and 4) units, where n is the oxidation state of the central Si atom. The decomposition process of the Si suboxides can be described by the following two-step reactions:

\[ \text{Si}^{2+} + \text{Si}^{2+} \rightarrow \text{Si}^{1+} + \text{Si}^{3+} \quad (1) \]

\[ \text{Si}^{1+} + \text{Si}^{3+} \rightarrow \text{Si}^{0} + \text{Si}^{4+} \quad (2) \]

These two reactions take place simultaneously but in different manners. Barranco et al. [23] suggested that reaction (1) takes place by the ligand exchanging of oxygen atom within the Si–(O₂,Si₄⁻ₙ) tetrahedron with an energy barrier of at least 54 kJ/mol. Reaction (2) takes place by inserting oxygen into a Si³⁺–Si¹⁺ bond with an activation energy of 125 kJ/mol. Since the kinetic barrier of reaction (2) is much higher than that of reaction (1), it needs a high annealing temperature. Reaction (1) should be easier to take place than of reaction (2), especially at low annealing temperature. Therefore, reaction (1) should dominate at low annealing temperature, and reaction (2) is more pronounced at higher temperatures. This is consistent with XPS results (Fig. 5), in which Si¹⁺ and Si³⁺ first increase because of reaction (1) and then decrease because of reaction (2) with increasing annealing temperature.

3.4. Growth mechanism of nc-Si

Based on the above discussion, the formation process of the nc-Si can be rationalized as follows. There are two Si⁰ resources available: one is the ‘free’ Si atom initially exist in the SiOₓ films, and the other is the Si⁰ decomposed from the Si suboxides. Since the diffusivity of Si in SiO₂ at annealing temperature below 700 °C is less than the order of 10⁻¹⁹ cm²/s [10], at low annealing temperatures, the long-range diffusion process of the ‘free’ atom can be ignored. However, the initial amorphous Si clusters do grow by short-range diffusion of the Si atoms from the decomposition reactions of the Si suboxides. Since decomposition reaction (1) dominates at this stage, the amount of decomposed Si atoms is very small and the growth of the nanoclusters is not significant at this stage, but size is still enough to be detected by Raman microscopy. As the temperature increases to provide enough diffusion energy and atomic mobility, decomposition reaction (2) becomes pronounced and large amount of Si phase segregate along the boundaries of the amorphous Si nanoclusters, leading to rapid growth of these nanoclusters to form the Si nanoparticles. At higher temperatures, two types of Si diffusions take place. The diffusion of the excess Si atoms towards the nanoparticles together with further decomposition of Si suboxides contributed to their growth; the diffusion of Si atoms inside the clusters transformed them into more compact crystalline Si with well-defined atomic lattices, which lead to the formation of nc-Si in a surrounding of amorphous SiO₂ network. During annealing at 1000–1100 °C, the diffusivity of Si in SiO₂ increases to the order of 10⁻¹⁸ cm²/s [10], even this, for the 3 min treatment (with a diffusion length of 0.5–0.6 nm) is still not sufficient for all the excess Si atoms to diffuse into the crystalline boundaries. However, because of the direct joining in the decomposed Si atoms, nc-Si with an average size of 5 nm still formed (as shown from Raman spectrum and TEM). The main function of the high annealing temperature here is to provide sufficient energy to self-organize the amorphous Si nanoparticles into more compact nc-Si. The formation of nanoscale particles in a network of amorphous SiO₂ matrix by direct formation by TEM as shown in Fig. 6. High density and homogeneously distributed Si nanoparticles with nearly spherical shape in the amorphous matrix of SiO₂ are clearly visible in the TEM micrograph. The corresponding electron diffraction patterns (EDPs) show that these Si nanoparticles have well-defined atomic lattices, indicating the formation of nc-Si. Their size range from 4 to 7 nm resulting in a mean crystal size of 5 nm in diameter.

4. Conclusions

X-ray photoelectron spectroscopy and Raman spectroscopy analyses reveal the formation of amorphous Si nanoclusters in the as-sputtered Si-rich amorphous SiOₓ films. The amorphous Si nanoclusters grow rapidly upon rapid thermal annealing through thermal decomposition of Si suboxides Siⁿ⁺⁺ (n=1, 2 and 3). It is proposed that at low annealing temperature, decomposition
reaction $S^{2+} + S^{2+} \rightarrow S^{1+} + S^{3+}$ dominates; at high annealing temperature, decomposition $S^{1+} + S^{3+} \rightarrow S^{0} + S^{4+}$ becomes pronounced.

Acknowledgements

We are grateful to Ms. Chow Shiaw Kee and Ms. Yong Mei Yoke in the Materials Lab A for their assistance in the XPS and TEM measurement.

References