

XPS Studies of Silicon Nanoclusters/Nanocrystals Embedded in SiO₂ Matrix

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ABSTRACT

In this study, the analysis of the XPS Si 2p peaks shows the existence of the five chemical structures corresponding to the Si oxidation states Siⁿ⁺ (n = 0, 1, 2, 3, and 4) in Si-implanted SiO₂ films, and the concentration of each oxidation states is determined quantitatively. The evolution of the five Si oxidation states as a function of thermal annealing is studied. On the other hand, Si 2p core levels of Si nanocrystals (corresponding to the Si oxidation state Si⁰) embedded in SiO₂ matrix have been determined also. After the correction of the charging effect, the core level of Si nanocrystals (nc-Si) is found to shift towards a lower binding energy, which is contrary to the prediction of the existing theories that the core level of Si nanocrystals should shift towards a higher binding energy due to the quantum size effect. It is suspected that the core-level shift of the nc-Si towards a lower binding energy is due to the influence of the differential charging between the SiO₂ surface layer and the nc-Si underneath.

Keywords: core level, Si nanocrystal, charging effect.

1 INTRODUCTION

Recently Si nanocrystals embedded in SiO₂ films have attracted much attention because they exhibit new quantum phenomena and have promising applications in optoelectronic devices, memory devices and single electron devices [1-3]. One of promising techniques for the incorporation of Si in SiO₂ films is Si ion implantation into SiO₂ films grown by thermal oxidation of Si substrate, which is fully compatible with the main-stream CMOS process. With this technique, Si nanocrystals can be formed by subsequent thermal annealing in the Si-rich SiO_x (x < 2) films resulting from the ion implantation. There have been many studies on the structural and optical properties of Si nanocrystals embedded in SiO₂

films; however, there are few studies so far on the chemical structures of the SiO_x films containing the Si nanoclusters/nanocrystals. In this work, X-ray photoelectron spectroscopy (XPS) is used to study the annealing effects on the chemical structures, depth profiling of the chemical states and core-level shifts of the Si nanocrystals in the Si-implanted SiO₂ films.

2 EXPERIMENTAL

30 nm SiO₂ thin films were grown on p-type Si wafers with (100) orientation by thermal oxidation in dry oxygen at 950 °C. Then Si ions were implanted into the SiO₂ films at the energy of 1keV with the dose of 8×10¹⁶ cm⁻². Thermal annealing was carried out in N₂ ambient. For the experiment of annealing temperature, the temperature was varied from 500 to 1100°C but the annealing time was fixed at 20 minutes; for the experiment of annealing time, the time was varied from 0 to 100 minutes while the annealing temperature was kept at 1000 °C. XPS analysis was performed by using a Kratos AXIS spectrometer with monochromatic Al K α (1486.71 eV) X-ray radiation. The Si 2p XPS peaks were analyzed by means of a computer program of gaussian peak fitting. From the deconvolution of the Si 2p peaks, the concentrations of various components corresponding to different Si oxidation states Siⁿ⁺ (n = 0, 1, 2, 3, and 4) in the SiO_x films were determined.

3 RESULT AND DISCUSSION

Figure 1 show the XPS Si 2p core level peaks for the as-implanted sample. To extract detailed chemical structure information from the XPS Si 2p peaks it is necessary to establish a suitable peak fitting procedure. As shown in Fig.1, our procedure was based on the use of five Gaussian-shaped peaks of Siⁿ⁺ (n = 0, 1, 2, 3, and 4) to simulate the five silicon oxidation states corresponding to the five chemical structures of Si, Si₂O, SiO, Si₂O₃ and SiO₂, respectively. It has

been reported that the five oxidation states exist in non-stoichiometric SiO_x (0 < x < 2) films prepared by low pressure chemical vapor deposition (LPCVD) or by atmospheric pressure chemical vapor deposition (APCVD), and they are also commonly observed at SiO₂/Si interface. For the Si-rich SiO_x films formed by Si ion implantation into SiO₂ films in this study, it is also reasonable to assume the possible existence of the five silicon oxidation states. As demonstrated in Fig.1, the analysis of the XPS Si 2p peaks shows the existence of the five chemical structures corresponding to the Si oxidation states Siⁿ⁺ (n = 0, 1, 2, 3, and 4) in the Si-implanted SiO₂ films, and the concentration of each oxidation state can be determined quantitatively. For this regard, as a first-order approximation, the relative concentration (in percentage) of each oxidation state is obtained

from the calculation of the ratio of $\frac{I_{Si^{n+}}}{I_{total}}$ (n=0,

1, 2, 3, and 4) where $I_{Si^{n+}}$ is the peak area of the oxidation state Siⁿ⁺ and I_{total} is the total area (=

$$\sum_{i=0}^4 I_{Si^{i+}})$$

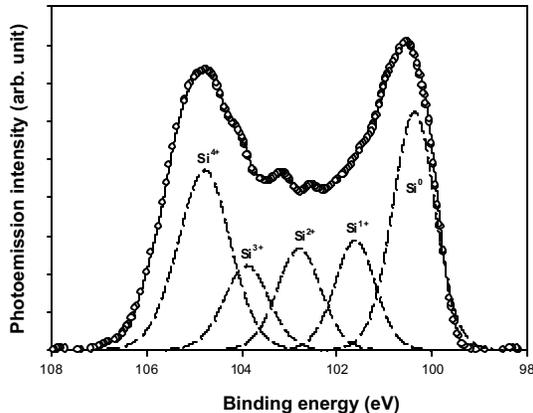


Figure 1: Si 2p peak deconvolution for the as-implanted sample.

Fig.2 and Fig.3 shows the evolution of the chemical structures as functions of annealing temperature and annealing time, respectively. The evolution of the concentrations of the five oxidation states with annealing is explained in terms of the thermal decompositions of the suboxides corresponding to the three oxidation states Siⁿ⁺ (n = 1, 2, and 3) and the thermal oxidation of the implanted Si. Fig.2 shows the changes of the concentrations of the five

oxidation states with annealing temperature for a fixed annealing time of 20 minutes. For the low temperature annealing at 500 °C, the concentration of Si⁰ increases significantly while the Si⁴⁺ concentration changes very little and the concentrations of other oxidation states (Si¹⁺, Si²⁺ and Si³⁺) decrease. For higher annealing temperatures, with the increase of annealing temperature, the Si⁴⁺ concentration increases greatly, but the concentrations of all other oxidation states decrease. On the other hand, we have also measured the evolution of the concentrations of the five oxidation states with annealing time for the annealing temperature of 1000 °C, and the result is shown in Fig.3. As can be seen in this figure, the Si⁴⁺ concentration has a very large increase after the first 20-minutes annealing but increases gently after longer annealing, while all other oxidation states Siⁿ⁺ (n = 0, 1, 2 and 3) show a decrease in concentration with annealing time.

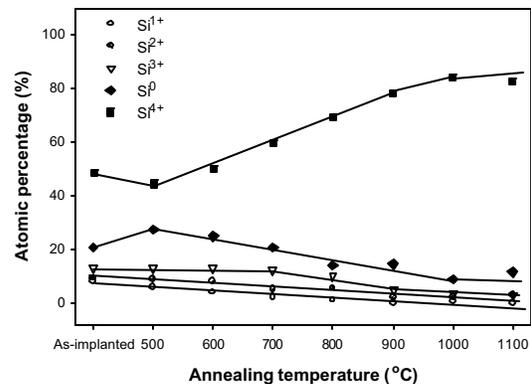


Figure 2: Changes of the concentrations of the five oxidation states with annealing temperature the annealing time is fixed for 20min.

The concentration of each oxidation states at various depths is also determined quantitatively from the XPS analysis, as shown in Fig.4. It can be concluded from Fig. 4 that the depth distributions of both Si⁰, which corresponds to Si nanocrystals formed after annealing, and the suboxides, which correspond to Siⁿ⁺ (n = 1, 2, and 3) are basically the same as that of the implanted Si⁺ ions. Actually, Si⁰ (corresponding to Si atoms or nanoclusters) and all of the suboxides are also observed in the as-implanted sample. This indicates that both the Si⁰ and the suboxides are formed during the ion implantation. Another important observation is the existence of the suboxides at significantly

high concentrations. The suboxides may exist at the interfaces of SiO₂/ Si nanocrystals, similarly at the conventional SiO₂ /Si interface.

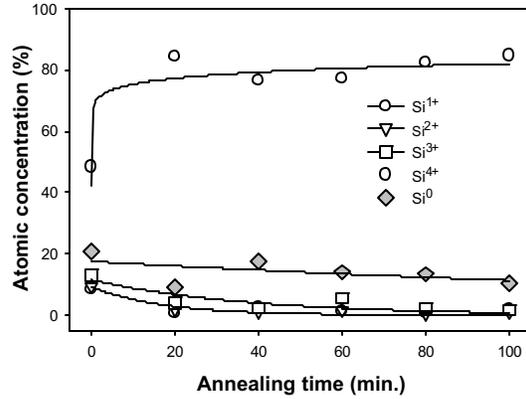
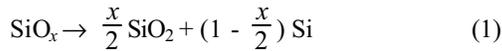


Figure 3: Changes of the concentrations of the five Si oxidation states with annealing time. The annealing temperature is fixed at 1000 °C.

The above results are explained in the following. The thermal decomposition (or phase separation) of the Si suboxides Si₂O, SiO and Si₂O₃ corresponding to the oxidation states Si¹⁺, Si²⁺ and Si³⁺, respectively, occurs during annealing to form more stable stoichiometric SiO₂ and Si nanocrystals, and the thermal decomposition can be described by



where $x = 1/2, 1, 3/2$ for Si₂O, SiO and Si₂O₃, respectively. Obviously, the thermal decomposition of the suboxides reduces the concentrations of the oxidation states Si¹⁺, Si²⁺ and Si³⁺, and it also leads to the growth of SiO₂ and the formation of Si nanocrystals. On the other hand, thermal oxidation of the implanted Si during the annealing due to the presence of residual oxygen in the nitrogen atmosphere may also lead to the growth of SiO₂ but the reduction of the Si⁰ concentration. The thermal decomposition and the oxidation explain the increase of the Si⁴⁺ concentration with annealing. However, although the thermal decomposition increases the Si⁰ concentration, the thermal oxidation reduces the concentration.

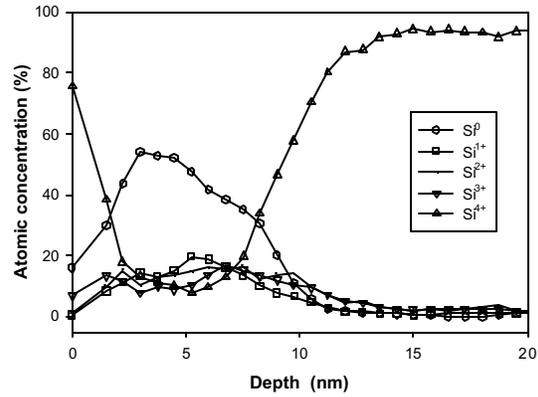


Figure 4: Depth distributions of the concentrations of the five oxidation states for the sample annealed at 1000 °C for 100 min.

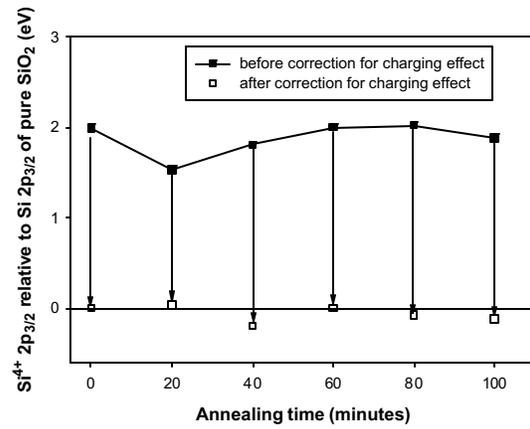


Figure 5: Si⁴⁺ shifts relative to the Si 2p_{3/2} core level in pure SiO₂ thin film. The solid circles represent the uncorrected shifts and the open circles show the values after the correction for the charging effect.

On the other hand, Si 2p core levels of Si nanocrystals (corresponding to the Si oxidation state Si⁰) embedded in SiO₂ matrix have been determined from the XPS experiment also. A large core-level shift is observed, and it is shown that the core-level shift is seriously affected by the charging in the material system with the charging at SiO₂/nanocrystal interfaces as the major mechanism. After the correction for the charging effect by using C 1s binding energy due to contamination on the SiO₂ surface, the core level of oxidation state Si⁴⁺ (corresponding to SiO₂) is the same as that of pure SiO₂ (Fig.5), while the core level of the isolated Si nanocrystal (i.e., Si⁰) with an average size of about 3 nm shifts by ~ 0.6 eV to a lower binding energy as compared to that of bulk crystalline Si as shown

in Fig.6. The core-level shift of the Si nanocrystal towards a lower binding energy is contrary to the prediction of the existing theories that the core level of Si nanocrystals should shift towards a higher binding energy as compared to that of bulk crystalline Si due to the quantum size effect. It is suspected that the core-level shift of the nc-Si towards a lower binding energy is due to the influence of the differential charging between the SiO₂ surface layer and the nc-Si underneath. Further experimental and theoretical studies are required.

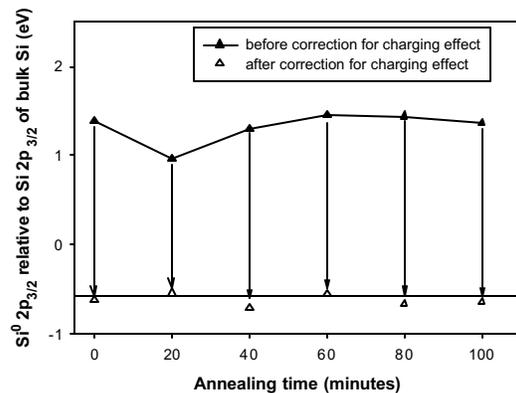


Figure 6: Si⁰ shifts relative to the Si 2p core level in bulk Si for the as-implanted sample (i.e. the annealing time is 0 minute) and the sample annealed at 1000° C for various annealing time. The solid circles represent the uncorrected shifts and the open circles show the values after the correction for the charging effect.

4 CONCLUSIONS

In conclusion, the analysis of the XPS Si 2p peaks is carried out to determine the concentrations of the five Si oxidation states in the SiO_x films. The XPS results clearly show the evolution of the oxidation states Siⁿ⁺ (n = 0, 1, 2, 3, and 4) as functions of annealing temperature and annealing time. The relative concentrations of the five oxidation states at various depths are also determined quantitatively by XPS analysis. On the other hand, it is found the strong positive core level shift of nc-Si is due to the charging effect in the material system. After the correction of the charging effect, the core level of the nc-Si

is found to shift towards a lower binding energy. It is suspected that the core-level shift of the nc-Si towards a lower binding energy is due to the influence of the differential charging between the SiO₂ surface layer and the nc-Si underneath.

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