XPS Studies of Silicon Nanoclusters/Nanocrystals Embedded in SiO2 Matrix

T. P. Chen and Y. Liu
School of Electrical and Electronics Engineering, Nanyang Technological University, Singapore 639798
Echentp@ntu.edu.sg

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 Si\textsuperscript{n+} (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 Si\textsuperscript{0}) 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 SiOx (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 SiOx 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\times10\textsuperscript{16} cm\textsuperscript{-2}. Thermal annealing was carried out in N\textsubscript{2} 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\textalpha (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 Si\textsuperscript{n+} (n = 0, 1, 2, 3, and 4) in the SiOx 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 Si\textsuperscript{n+} (n = 0, 1, 2, 3, and 4) to simulate the five silicon oxidation states corresponding to the five chemical structures of Si, Si\textsubscript{2}O, SiO, Si\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2}, respectively. It has
been reported that the five oxidation states exist in non-stoichiometric SiOx (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 SiOx 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 Si n+ (n =0, 1, 2, 3, and 4) in the Si-implanted SiO2 films, and the concentration of each oxidation states 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 Si n+ and \( I_{total} \) is the total area (= \( \sum_{n=0}^{4} I_{Si^{n+}} \)) of the Si 2p peaks.

![Figure 1: Si 2p peak deconvolution for the as-implanted sample.](image)

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 Si1+ (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 Si n+ (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 for a fixed annealing time of 20 minutes.](image)

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 Si n+ (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 SiO$_2$/Si nanocrystals, similarly at the conventional SiO$_2$/Si interface.

![Graph](image1.png)

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 Si$_2$O, SiO and Si$_2$O$_3$ corresponding to the oxidation states Si$^{1+}$, Si$^{2+}$, and Si$^{3+}$, respectively, occurs during annealing to form more stable stoichiometric SiO$_2$ and Si nanocrystals, and the thermal decomposition can be described by

$$\text{SiO}_x \rightarrow \frac{x}{2} \text{SiO}_2 + (1 - \frac{x}{2}) \text{Si}$$  \hspace{1cm} (1)

where $x = 1/2, 1, 3/2$ for Si$_2$O, SiO and Si$_2$O$_3$, respectively. Obviously, the thermal decomposition of the suboxides reduces the concentrations of the oxidation states Si$^{1+}$, Si$^{2+}$ and Si$^{3+}$, and it also leads to the growth of SiO$_2$ 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 SiO$_2$ but the reduction of the Si$^0$ concentration. The thermal decomposition and the oxidation explain the increase of the Si$^{4+}$ concentration with annealing. However, although the thermal decomposition increases the Si$^3$ concentration, the thermal oxidation reduces the concentration.

![Graph](image2.png)

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

![Graph](image3.png)

Figure 5: Si$^{4+}$ shifts relative to the Si 2p core level in pure SiO$_2$ 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 Si$^0$) embedded in SiO$_2$ 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 SiO$_2$/nanocrystal interfaces as the major mechanism. After the correction for the charging effect by using C 1s binding energy due to contamination on the SiO$_2$ surface, the core level of oxidation state Si$^{3+}$ (corresponding to SiO$_2$) is the same as that of pure SiO$_2$ (Fig.5), while the core level of the isolated Si nanocrystal (i.e., Si$^0$) 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 SiOx films. The XPS results clearly show the evolution of the oxidation states Si\(^{n+}\) (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.

REFERENCES


1 T. P. Chen, School of Electrical and Electronics Engineering, Nanyang technological University, Singapore 639798, Ph.: (65) 67904238, email: echentp@ntu.edu.sg.