Characterization of ultrathin SiO_2/Si interface grown by low temperature plasma oxidation*

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Abstract Ultrathin SiO_2 layers on Si (100) wafers were prepared by plasma oxidation at a low temperature (250 ℃). The analyses of X-ray photoelectron spectroscopy (XPS) and TEM reveal that the chemical composition of the oxide layer is stoichiometric SiO_2 and the SiO_2/Si interface is abrupt. The thickness of the ultrathin oxide layer obtained from XPS, capacitance-voltage (C-V) and ellipsometry measurements indicate a nonlinear time dependence. The high frequency C-V characterization of MOS structure shows that the fixed charge density in SiO_2 film is about 10^{11} cm^{-2}. It is also shown that the strength of breakdown electrical field of SiO_2 film with 6 nm thickness is of the order of 10^6 Vcm^{-1}. These properties of the ultrathin SiO_2 layer ensure its application in silicon quantum devices.

Keywords: **plasma oxidation, X-ray photoelectron spectrum, ultrathin SiO_2 film.**

The ultrathin SiO_2 layer has recently received more attention, owing to the rapid down scaling of silicon devices and the need of thinner gate oxides[1]. The growth of extremely thin gate dielectric films at high temperatures poses several problems: (i) dopant diffusion and redistribution, (ii) thermal material diffusion, and (iii) thermally induced stress which would seriously degrade device performances. Moreover, precise control of the thickness of an ultrathin gate dielectric film at high temperatures is very difficult because of its high initial growth rate. For the low temperature oxidation, the plasma oxidation is one of the powerful techniques. In oxygen plasma, oxygen molecules are ionized by hot electrons (energy >10 eV). On the other hand, the lifetime of oxygen ions at low pressure is much longer than that under the atmospheric pressure, so that plasma oxidation can occur even at low temperatures. The oxidant transport across the growing oxide layer often controls the oxidation rate. Change in plasma parameters such as power, pressure, and frequency can alter the hot electron concentration, thereby varying the oxidant flux to the silicon-silicon dioxide interface to control the oxidation rate. The plasma oxidation at a low temperature below 300 ℃ can reduce dopant diffusion, interdiffusion, and density of defects. In this work a series of ultrathin SiO_2 layers were prepared by using the rf plasma oxidation at the temperature of 250 ℃. In order to investigate the quality of ultrathin SiO_2 layers and SiO_2/Si interfaces, angular-dependence X-ray photoelectron spectroscopy (XPS), TEM, capacitance-voltage (C-V) measurements were used in our study.

1 Experimental

Ultrathin SiO_2 layers were prepared in a capacitively coupled single reaction chamber by the rf plasma oxidation. It is worth pointing out that the temperature of substrates was 250 ℃. The gas source was a mixture of Ar and O_2 mixed at the ratio of 9:1 and the pressure of chamber was controlled at 53.3 Pa. The rf power was 100 W. A series of samples were prepared with different oxidation time from 30 min to 150 min. Before the plasma oxidation process began native oxide layers on the surfaces of substrates were removed by 10% HF. XPS measurement was performed by using a Perkin-Elmer PHI 5300 spectrometer equipped with a concentric hemispherical analyzer. The angular X-ray radiation used for photoelectron emission from the samples was MgK_α ($h\nu = 1253.6$ eV). The acceleration voltage and the emission current used for producing X-rays were 13 kV and 20 mA.

2 Results and discussion

Fig. 1 shows the XPS of samples oxided for 30~150 min. The peaks at 99.3 eV and 103.2~

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104.2 eV correspond respectively to signals of Si-Si binding energy and stoichiometric Si-O binding energy, which agree with the previously published data[2~4]. It can be found from spectrum (30 min) in Fig. 1 that the signals of Si-O are weaker than those of Si-Si in the silicon substrates because the oxide layers are very thin. While for spectra (90 min), (120 min) and (150 min) in Fig. 1, the Si-O signals from oxide layers become larger than those of Si-Si due to the oxide layers getting thicker. This means that at the initial stage of plasma oxidation, silicon atoms have a smaller number of bonded oxygen atoms. As the oxidation prolongs the oxygen atoms appear to have penetrated into the substrates more deeply and the Si atoms are more fully oxidized. Note that the take-off angle is 90°.

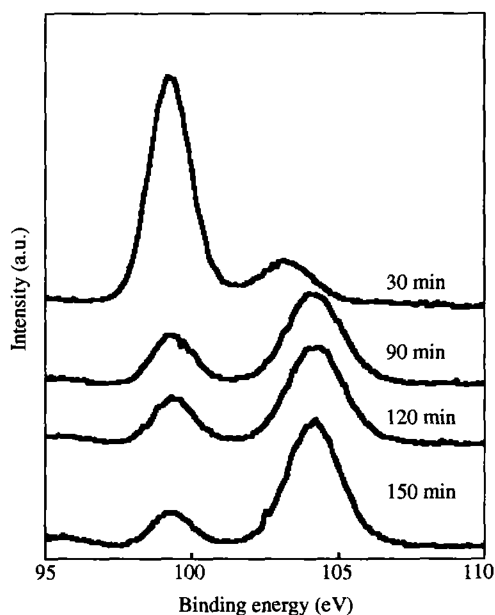

Fig. 1. The XPS of oxide samples with different oxidation time (t_{ox}).

In order to study the structure of the SiO_2/Si interface, it is helpful to get information about the depth distribution of various oxidation states, which can be done by changing the take-off angle α which is defined as the angle between the analyzer and the surface of a sample. Fig. 2 shows the angular-dependence XPS data taken from the same sample oxidized for 30 min at different take-off angles ($\alpha = 30°, 45°, 60°, 75°, 90°$). From these experimental data, we can firstly calculate the thickness and quality of the ultathin SiO_2 layer and SiO_2/Si interface. The binding energy intensity of a SiO_2 layer (I_{SiO_2}) and that of a silicon substrate (I_{Si}) can be calculated from the

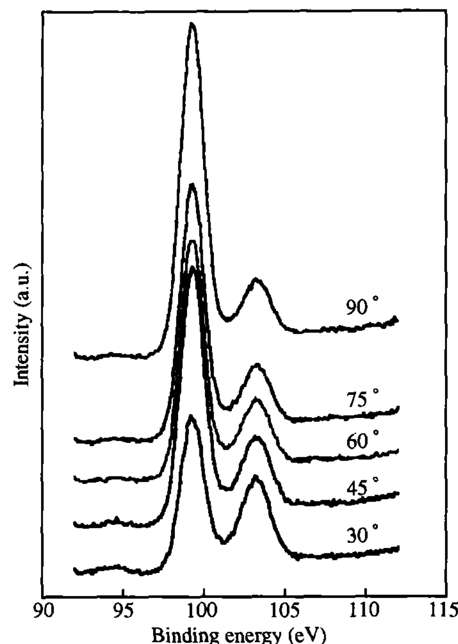

Fig. 2. Angular-dependence XPS for oxide samples (t_{ox} = 30 min).

following equations[5]:

$$I_{SiO_2} = n_{SiO_2}\sigma_{SiO_2}\lambda_{SiO_2}(1 - \exp(-d_{SiO_2}/\lambda_{SiO_2}\sin\alpha)), \quad (1)$$

$$I_{Si} = n_{Si}\sigma_{Si}\lambda_{Si}\exp(-d_{SiO_2}/\lambda_{SiO_2}\sin\alpha), \quad (2)$$

where n_{Si} and n_{SiO_2} are the atomic densities of Si and SiO_2, σ_{SiO_2} and σ_{Si} are the photoionization cross- sections. λ_{SiO_2} and λ_{Si} are the photoelectron paths in SiO_2 and Si, α is the take-off angle.

Combining Eqs. (1) and (2) gives

$$\frac{I_{SiO_2}}{I_{Si}} = \frac{n_{SiO_2}\sigma_{SiO_2}\lambda_{SiO_2}}{n_{Si}\sigma_{Si}\lambda_{Si}}\left[\exp\left(\frac{d_{SiO_2}}{\lambda_{SiO_2}\sin\alpha}\right) - 1\right]. \quad (3)$$

By rewriting Eq. (3), we get

$$d_{SiO_2} = \lambda_{SiO_2}\sin\alpha\ln(1 + (I_{SiO_2}/CI_{Si})), \quad (4)$$

where

$$C = n_{SiO_2}\lambda_{SiO_2}\sigma_{SiO_2}/n_{Si}\lambda_{Si}\sigma_{Si}. \quad (5)$$

The peak intensities ratio (I_{SiO_2}/I_{Si}) is determined from the relationship between α and I_{SiO_2}/I_{Si} by using Eq. (3). Noting that different values of λ_{SiO_2} ranging from 2.1 to 3.5 nm were used[6,7] for the MgKα line in the present calculations, we choose a value of 2.5 nm so that we can use Eq. (4) to calculate the thickness of SiO_2 layers. The thickness as a function of the oxidation time is shown in Fig. 3. For comparison, the thicknesses from C-V and ellipsometry measurements are also shown in Fig. 3. It can be

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seen that there is a deviation in the values of thickness for the same sample because of the thickness dependence of refractive index of the ultrathin SiO_2 layer, which is used in ellipsometry calculation. The time dependence of oxidation rate is nonlinear.

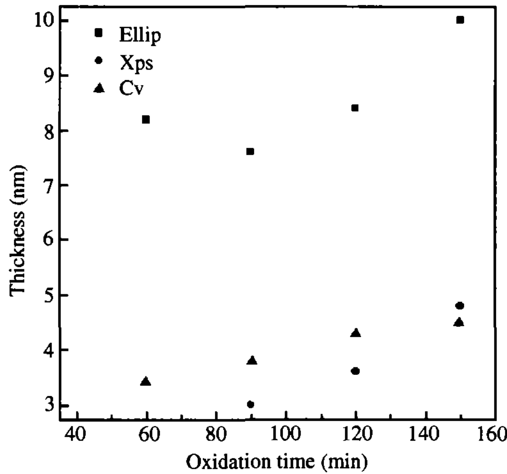

Fig. 3. The thickness dependence on oxidation time obtained from XPS, C-V and ellipsometry.

Secondly we studied the quality of ultrathin SiO_2 layers and SiO_2/Si interfaces. Considering the presence of Si in three intermediate oxidation states, i.e. Si^{1+}, Si^{2+} and Si^{3+} in silicon oxide reported by Grunthaner[8], we fitted the Si_{2p} spectra with three suboxide state peaks by Gaussian function to investigate the configuration of ultrathin SiO_2/Si films. Fig. 4 (a) shows the fitted XPS of the samples oxidized for 30 min with the take-off angle of 90°. The element Si and Si in SiO_2 state are denoted as Si^0, Si^{4+} respectively and the silicon in suboxide states (Si_2O, SiO and Si_2O_3) are denoted as Si^{1+}, Si^{2+} and Si^{3+}. The fitted XPS of other samples oxidized for 90～150 min can also be obtained in the same way. From Eq. (3) we get

$$\frac{I_{SiO_x}}{I_{Si}} = \frac{n_{SiO_x}\sigma_{SiO_x}\lambda_{SiO_x}}{n_{Si}\sigma_{Si}\lambda_{Si}}\left[\exp\left(\frac{d_{SiO_x}}{\lambda_{SiO_x}\sin\alpha}\right) - 1\right]. \quad (6)$$

When $d_{SiO_x} \ll \lambda_{SiO_x}$,

$$\exp\left(\frac{d_{SiO_x}}{\lambda_{SiO_x}\sin\alpha}\right) - 1 = \frac{d_{SiO_x}}{\lambda_{SiO_x}\sin\alpha}. \quad (7)$$

Eq. (6) can be simplified as

$$N_{SiO_x} = n_{SiO_x}d_{SiO_x} = \frac{I_{SiO_x}\sigma_{Si}n_{Si}\lambda_{Si}\sin\alpha}{I_{Si}\sigma_{SiO_x}}. \quad (8)$$

Based on the fitted XPS results we can get the intensity ratio, I_{SiO_x}/I_{Si}. According to $\sigma_{Si}/\sigma_{SiO_x}=1$, $n_{Si}=5\times10^{22}\,cm^{-3}$, and $\lambda_{Si}=1.3$ nm, we calculated the area densities of interfaces of samples oxidized for 30～150 min using Eq. (8), which is shown in Fig. 4 (b). The total suboxide layer area densities of interface ($N_{Si_2O}+N_{SiO}+N_{Si_2O_3}$) ranging from

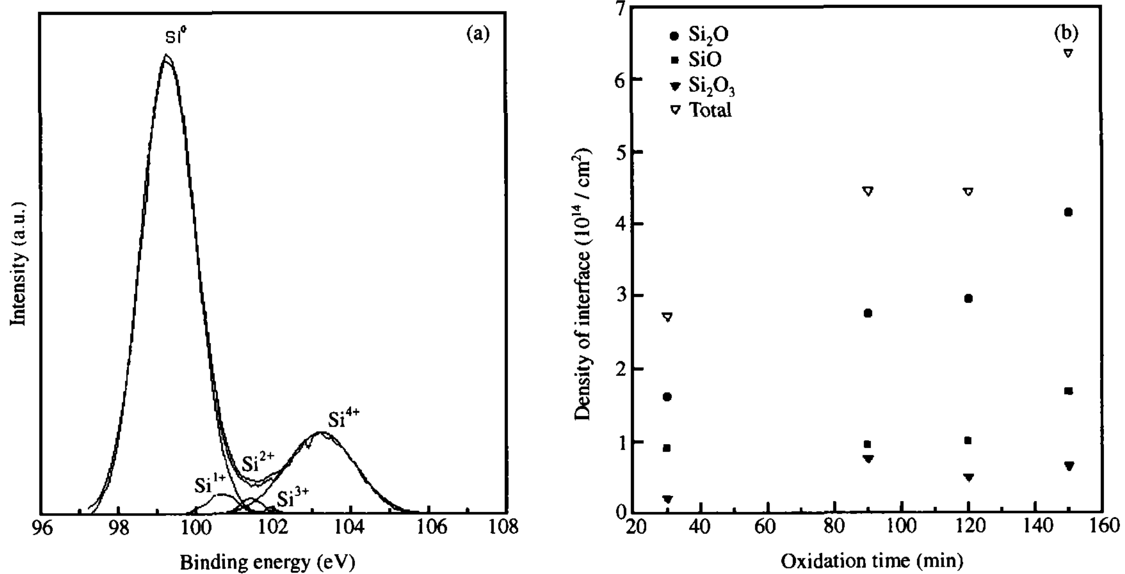

Fig. 4. (a) A fitted XPS at the take-off angle of 90° for oxide sample, $t_{ox}=30$ minutes.
(b) The density of interface states dependence on oxidation time based on fitted XPS.

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2.73×10^{14} to 6.43×10^{14} were shown in Fig. 4(b). With the area density of substrate Si atoms for the (100) interface taken as 6.8×10^{14} atoms/cm^2, the suboxide layer thus ranges within 1 monolayer. Consequently, it can be concluded that the SiO_2/Si interfaces of the samples are abrupt, which are further verified by TEM observations. Fig. 5 shows the TEM image of an a-Si film, 3 nm thick, between SiO_2 layers. It is clear that the interfaces between the substrate and SiO_2 as well as the a-Si are sharp and smooth. The surface of the sample was covered with a SiN layer for protection.

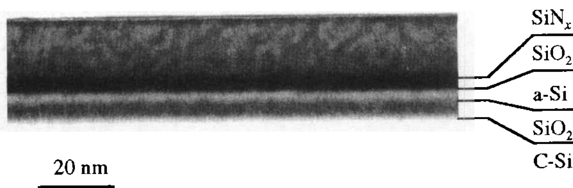

Fig. 5. Cross-section TEM image of Si/SiO_2/a-Si/SiO_2/SiN structure prepared by plasma oxidation method.

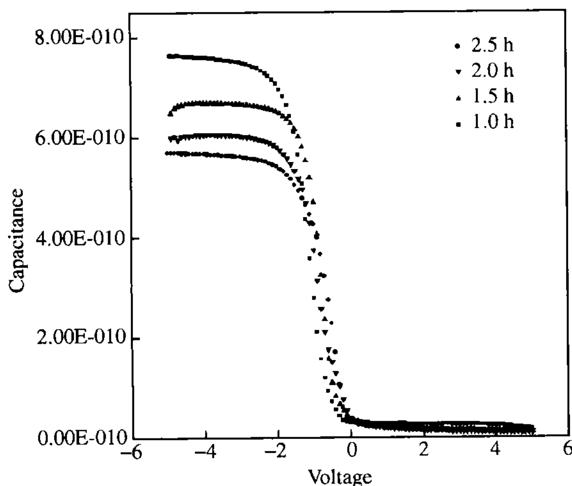

Fig. 6. C-V characteristic of MOS structure with ultrathin SiO_2 gate.

The C-V and I-V characteristics of the oxide films were measured by using an HP4194A impedance analyzer and a ZC36 meter. The gate insulator of Si-MOS used in I-V measurement was 6 nm in thickness. The substantial current for destructive breakdown occurred when the applied voltage reached 0.5 V and the corresponding breakdown electrical field intensity was 2×10^6 Vcm^{-1}. The breakdown fields were similar to those of thermal oxides, which confirms that the oxide films possess good insulating property. Fig. 6 shows the high frequency C-V characteristics of the Si-MOS structure. Using C-V curves, we calculated fixed oxide charge density N_f of the SiO_2 films. For samples with different oxidation time (60 ~150 min), their N_f values are 1.3×10^{11}, 1.7×10^{11}, 1.5×10^{11}, and 3.7×10^{11} cm^{-1} respectively, which can also be compared with the quality of thermally oxidized SiO_2.

3 Conclusion

The ultrathin SiO_2 films (thickness $<$ 5 nm) were successfully fabricated by plasma oxidation at 250 ℃. The chemical composition of the oxide layer is stoichiometric SiO_2 from angular-dependence XPS results. It is proved by XPS and TEM measurements that the interface between SiO_2/Si is abrupt. The electrical characteristics indicate that the quality of SiO_2/Si interface is comparable with that of sample by thermal oxidation.

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