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Effects of postmetallization annealing on ultrathin SiO_2 layer properties

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Observation of both longitudinal optical and transverse optical phonons of ~1.3 nm ultrathin silicon dioxide (SiO_2) layers formed by immersion in nitric acid shows that the SiO_2 density increases by 16% after postoxidation annealing (POA) at 900 °C. For the SiO_2 layers without POA, postmetalization annealing (PMA) greatly decreases the SiO_2 thickness from 1.3 to 0.2 nm, the effect of which is attributable to the reaction of aluminum with SiO_2 to form a metallic mixture of aluminum oxide and Si. For SiO_2 layers with POA, PMA decreases the SiO_2 thickness to a lesser extent (from 1.4 to 0.9 nm), because of the suppression of aluminum diffusion into SiO_2 due to its dense structure. PMA is found to decrease the interface state density but increase the leakage current density. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1482147]

For fabrication of metal–oxide–semiconductor (MOS) devices, low-temperature postmetallization annealing (PMA) of gate oxide layers is a very important procedure in order to passivate interface states.[1] Aluminum (Al) is often used as an electrode material for PMA.[1–4] According to the model proposed by Deal, Mackenna, and Castro,[5] atomic hydrogen is formed by the reaction of water present in silicon dioxide (SiO_2) layers with active metals such as Al and magnesium, followed by its diffusion to the interface, and then reacts with interface states, resulting in their passivation. It is reported that for a decrease in the interface state density, PMA is more effective than postoxidation annealing (POA),[2,3] and it has been concluded that there exist interface states that can be eliminated by atomic hydrogen but not by molecular hydrogen.[2] In the above studies, SiO_2 layers thicker than 2 nm were employed, without investigating ultrathin SiO_2 layers, which would be important for future ultra-large-scale integration.

In the present work, we investigate the effects of PMA on the chemical structure and electrical characteristics of chemically grown SiO_2 layers with the 1.3–1.4 nm thickness.

Phosphorus-doped *n*-type Si(100) wafers with a ~10 Ω cm resistivity were cleaned using the RCA method and etched with a 5% hydrofluoric acid solution. Next, ultrathin chemical SiO_2 layers were formed by immersion of the wafers in a concentrated nitric acid (HNO_3) solution at 113 °C. POA was performed at 900 °C in nitrogen for 15 min, and then Al dots (~200 nm) with a 0.15 mm diam were formed on the SiO_2 layers, resulting in an ⟨Al/ultrathin SiO_2/Si(100)⟩ MOS structure. Then, PMA was carried out at 400 °C in 5% H_2+95% N_2 for 10 min. This PMA temperature has been reported to reduce the interface state density of thermally grown SiO_2/Si to the lowest value.[1]

Fourier transformed infrared (FTIR) transmission spectra were recorded using a Nicolet Nexus 370S spectrometer in a dry-nitrogen atmosphere with the energy resolution and incident angle set at 4 cm^{-1} and 65°, respectively. Measurements of x-ray photoelectron spectroscopy (XPS) spectra were performed using a VG Scientific ESCALAB 220i-XL spectrometer with a monochromatic Al $K\alpha$ radiation source. Photoelectrons were detected at the surface-normal direction. Capacitance–voltage ($C-V$) measurements were performed with an HP 4192A LF impedance analyzer at 100 k and 1 MHz.

Figure 1 shows the FTIR spectra in the Si–O asymmetric stretching vibrational region for the ultrathin SiO_2/Si(100) structure formed in HNO_3. For the SiO_2 layers without POA, absorption peaks due to longitudinal optical (LO) and transverse optical (TO) phonons were observed at 1219 and 1049 cm^{-1}, respectively. POA at 900 °C greatly shifted the LO peak to 1247 cm^{-1} while the TO peak was only slightly shifted to 1053 cm^{-1}.

Queeney *et al.*[6] have shown, using the effective medium approximation, that inclusion of foreign species (i.e., pores, SiO, or Si) in SiO_2 with 20% concentration nominally shifts the LO and TO peaks. In the presence of larger concentrations of pores, the LO and TO peaks are shifted toward the lower and higher energies, respectively. These results of the calculations are in disagreement with the present experimental results. Therefore, although POA probably eliminates a low concentration of pores, this is not the main reason for the

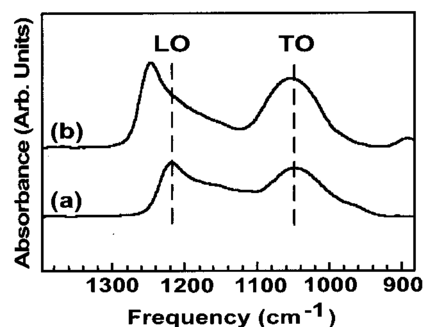

FIG. 1. FTIR spectra in the asymmetric Si–O stretching vibrational region for the ultrathin chemical SiO_2/Si structure: (a) without POA and (b) with POA at 900 °C.

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large shift of the LO peak. Since shifts caused by foreign species in SiO_2 are negligibly small, the SiO_2 layer can be regarded as a homogeneous medium. In this case, using the central and noncentral force approximation, the vibrational frequencies of TO and LO phonos, ν_{TO} and ν_{LO}, are given by[7]

$$\nu_{TO}=\frac{1}{2\pi}\sqrt{2[\alpha\sin^2(\theta/2)+\beta\cos^2(\theta/2)]/m}, \quad (1)$$

$$\nu_{LO}=\frac{1}{2\pi}\sqrt{2[\alpha\sin^2(\theta/2)+\beta\cos^2(\theta/2)+Z^2\rho/\varepsilon_\infty(2m+M)]/m}, \quad (2)$$

where α and β are the central and noncentral force constants, respectively, θ is the Si–O–Si bridging bond angle, m and M are the atomic masses of oxygen and Si atoms, respectively, ε_∞ is the permittivity at the infinite frequency, Z is the electrical charge related to the movement of oxygen atoms, and ρ is the atomic density of SiO_2. Only the slight increase in ν_{TO} by POA shows that the bond angle, θ, is not largely altered. On the other hand, ν_{LO} is greatly increased by POA, and this increase is most probably attributable to an increase in the atomic density of SiO_2, ρ, by $\sim$16%. This increase in ρ may result from a change in the SiO_2 network structure with atomic order size pores to that without it.

From Eqs. (1) and (2) we have

$$\nu_{LO}^2-\nu_{TO}^2=C\rho, \quad (3)$$

where C is a constant. Using the values for thick SiO_2 layers, i.e., ν_{TO} of 1090 cm^{-1}, ν_{LO} of 1256 cm^{-1}, and ρ of 2.28×10^{22} cm^{-3},[8] ρ for the chemical SiO_2 layers without and with POA is estimated to be 2.20×10^{22} and 2.55×10^{22} cm^{-3}, respectively. It is calculated that the geometrical effect slightly increases ν_{TO} with the oxide thickness, d_{ox} (i.e., 2 cm^{-1} between $d_{ox}=2$ nm and $d_{ox}=40$ nm) while ν_{LO} is independent of d_{ox}.[8] In the estimation of ρ, the shift in ν_{TO} caused by the geometrical effect is assumed to be 5 cm^{-1} between the $\sim$1.4 nm SiO_2 layers employed in the present study and bulk SiO_2, whose ν_{LO}, ν_{TO}, and ρ values are used for the calculation of C in Eq. (3).

Olsen and Shimura[9] and Boyd and Wilson[10] have observed that the vibrational frequency of TO phonons for thermal SiO_2 layers decreases as the SiO_2 thickness becomes thinner, and attributed the shift to the strain near the interface. In other studies, it is observed that both the vibrational frequencies of LO and TO phonons increase with the SiO_2 thickness or the oxidation temperature, the result of which requires complicated analysis, resulting in the various attributions of the shifts, i.e., stoichiometry changes,[11] inhomogeneity,[6] and roughness near the interface.[12] It should be noted that in the present study, ν_{LO} increases after POA while ν_{TO} is almost unchanged, leading to the clearer conclusion of the densification of the SiO_2 layer by POA.

Figure 2 shows the XPS spectra in the Si $2p$ region for the ultrathin chemical SiO_2/Si(100) structure. For spectra (a), POA was not performed before the Al deposition, while for spectra (b), it was carried out at 900 °C in nitrogen for 15 min. The upper spectra were observed before the Al deposition. For the lower spectra, on the other hand, the Al deposition and PMA were performed and the Al layer was etched away using a HCl:$H_2O=1:3$ solution just before the XPS measurements. The SiO_2 thickness was estimated from the area intensity ratio between the oxide and substrate Si $2p$ peaks using 3.2 and 2.7 nm as the mean-free paths of photoelectrons in the SiO_2 layer and the Si substrate, respectively.

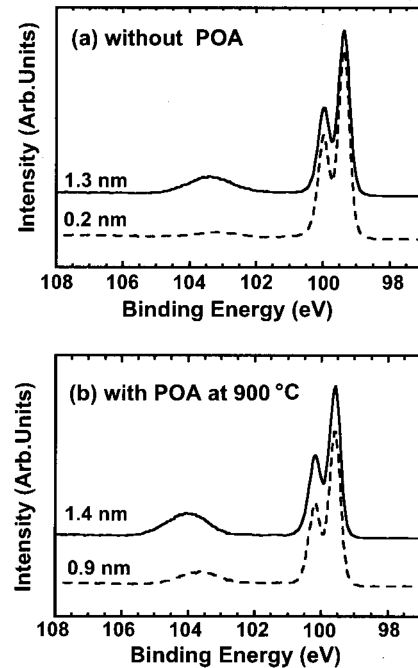

FIG. 2. XPS spectra in the Si $2p$ region for the ultrathin chemical SiO_2/Si structure: (a) without POA and (b) with POA at 900 °C. Solid and dashed lines are for the SiO_2 layers without and with PMA at 400 °C, respectively.

For the SiO_2 layers without POA [spectra (a)], the intensity of the oxide Si $2p$ peak was markedly decreased by PMA, and the SiO_2 thicknesses before and after PMA were estimated to be 1.3 and 0.2 nm, respectively. For the SiO_2 layers with POA [spectra (b)], PMA decreases the SiO_2 thickness only slightly from 1.4 to 0.9 nm. The experimental results show that Al reduces SiO_2 with the following reaction formula:

$$3SiO_2+4Al\rightarrow 2Al_2O_3+3Si. \quad (4)$$

This reaction has a negative Gibbs free-energy change ($\Delta G=-581.9$ kJ mol^{-1}), and thus it proceeds spontaneously. In the previous study, in fact, the formation of Al_2O_3 and Si was observed after PMA by means of XPS.[13] It was also observed that at high temperatures (e.g., 510 °C) Al reacts with thick SiO_2, resulting in the formation of thick (e.g., $\sim$200 nm) Al_2O_3 and Si.[14] XPS measurements in the present study, however, show that Al_2O_3 is not present on Si after the etch off of the Al layer because it is soluble in HCl.

The different magnitudes of the decrease in the thickness of the SiO_2 layers without and with POA are attributable to the variation in the SiO_2 density. FTIR measurements show that the atomic density increases by $\sim$16% after POA at 900 °C, as described above. It is likely that Al readily diffuses into the SiO_2 layers when the layers are less dense and then reacts with SiO_2. On the other hand, the SiO_2 layers with POA have a dense structure, resulting in the suppression

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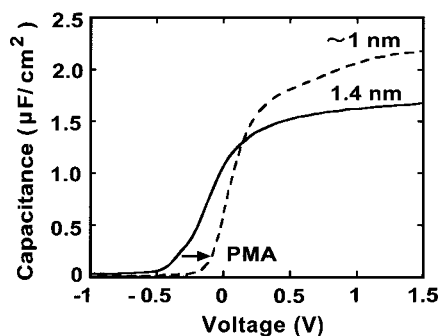
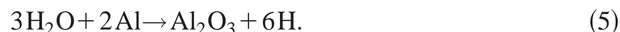


FIG. 3. $C-V$ curves for ⟨Al/ultrathin chemical SiO_2/Si(100)⟩ MOS diodes in which POA was performed at 900 °C. Solid and the dashed lines are for the diodes without and with PMA at 400 °C, respectively.

of the Al diffusion. Consequently, only the surface region of the SiO_2 layers is transformed to Al_2O_3 and Si by PMA.

Figure 3 shows the $C-V$ curves for the ⟨Al/ultrathin SiO_2/n-Si(100)⟩ MOS structure. In order to eliminate the effect of a leakage current on the capacitance measurements, we have adopted the two-frequency method.[15] PMA causes a shrinkage of the bias region in which the capacitance changes greatly. This shrinkage is attributable to a decrease in the interface state density, the result of which is consistent with those obtained for thermal SiO_2 layers.[1–5] It is highly probable that a trace amount of water is present in SiO_2 even after POA.[1] Water reacts with Al to form atomic hydrogen (H):



$$3H_2O + 2Al \rightarrow Al_2O_3 + 6H. \quad (5)$$

The atomic hydrogen produced migrates to the Si/SiO_2 interface, and then reacts with interface states to make them electrically inactive.[5] For this reason, the $C-V$ curve becomes steeper after PMA.

Another change caused by PMA is an increase in the saturation capacitance. This increase is attributable to a reduction in the SiO_2 thickness, as is evident from the XPS result shown in Fig. 2. If we adopt 3.9 (i.e., SiO_2 bulk dielectric constant) as the relative dielectric constant of the ultrathin SiO_2 layers, the effective SiO_2 thicknesses without and with PMA were estimated to be 2.0 and 1.6 nm, respectively, from the saturation capacitances. These values are much larger than those estimated from XPS spectra. Such a discrepancy is often reported[15,16] and may result from the different electronic structure from that of bulk SiO_2, leading to a lower dielectric constant.

The flatband voltages for the $C-V$ curves in Fig. 3 of nearly zero differ from that predicted from the difference in the work function between n-Si and Al (i.e., -0.3 V). This shift possibly results from an increase in the effective work function of the Al layer by oxygen adsorption and/or oxide fixed negative charges in the order of 10^{11} cm^{-2}.

The density of the leakage current was markedly increased by PMA for the MOS diodes even with POA, (i.e., from 0.4 to 6 A cm^{-2} at the gate bias, V_G, of 1.5 V). This increase is attributable to the decrease in the SiO_2 thickness, and indicates that the layer formed by PMA consists of a mixture of Al_2O_3 and Si and that the mixture has a metallic character.

It is well known that Si penetrates into Al layers through the weak points of SiO_2 layers, leading to an increase in the leakage current.[17,18] In the case of such a spiking effect, deep pits were observed in the scanning electron microscopy micrographs after the removal of the Al layers.[18] In the present experiments, no pits were observed in the secondary electron micrographs, indicating that the increase in the leakage current density was not due to the spiking effect but the reaction between Al and SiO_2.

In conclusion, although PMA passivates interface states, the density of the leakage current for the ultrathin SiO_2 layers increases. This increase results from a decrease in the SiO_2 thickness caused by the reaction of Al with SiO_2. The magnitude of the decrease in thickness strongly depends on whether POA is performed or not. This dependence is attributable to the variation in the SiO_2 density, which in turn affects the magnitude of the Al diffusion into SiO_2.

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