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# Platinum-Enhanced Oxidation of Silicon: Formation of MOS Structure below 300°C

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We have succeeded in forming a relatively thick silicon oxide layer 4 ~ 5nm in thickness between the metal overlayer and the Si substrate at temperatures below 300℃ using the catalytic activity of the platinum (Pt) layer. A thin chemical oxide layer is formed, a Pt layer is deposited, and then the specimens are heated at temperatures below 300℃. The thin chemical oxide layer effectively prevents the silicide formation and the outdiffusion of Si atoms.

## 1. Introduction

Low temperature catalytic oxidation of Si has been extensively studied using noble metals,[1-3] transition metals,[3,4] and alkali metals.[5-7] When noble metals or transition metals are deposited on clean Si surfaces, outdiffusion of Si atoms through the metal layer occurs because of the interaction of Si atoms with metal atoms, and consequently, a silicon oxide layer is formed on the metal surface even at room temperature.[1-4] The deposition of alkali metals on the Si surface also enables the Si oxidation at room temperature.[5-7] However, moderate temperature heating at ~600℃ is necessary to remove alkali metals,[7] which greatly degrade the electrical characteristics of MOS devices. Moreover, the thickness of the oxide layer formed by sub-monolayer alkali metals is up to ~1nm,[5-7] too thin for the application to MOS devices.

In the present study, we have developed a new method for forming relatively thick oxide layers 4 ~ 5nm in thickness between the Si substrate and the metal layer at temperatures below 300℃ using the catalytic activity of the platinum (Pt) layer.

## 2. Experiments

n-type Si(100) wafers with a resistivity of ~1 Ω cm were cut into 1×1 cm$^2$ pieces, washed chemically, and etched in a 1% HF solution. Then, a thin chemical oxide layer was formed by immersing the Si wafers either in boiled $HNO_3$ or in a mixed solution of HCl : $H_2O_2$ : $H_2O$ = 1 : 1 : 5. The oxide layers formed in these solutions are hereafter called the $HNO_3$ oxide and the HCl oxide, respectively. A ~5nm-thick Pt layer was deposited on the oxide surface by electron beam evaporation. The specimens thus produced were heated in an electrical furnace at temperatures below 300℃ for 1h in oxygen.

X-ray photoelectron spectroscopic (XPS) spectra were measured using an Ulvac-Phi model 5500 spectrometer with a monochromatized Al Kα radiation source or a Shimadzu ESCA 1000 spectrometer with an Mg Kα radiation source. Photoelectrons were collected in the surface-normal direction.

## 3. Results

Figure 1 shows the XPS spectra in the Si 2p region. Doublet peaks were due to Si $2p_{3/2}$ and $2p_{1/2}$ levels of the Si substrate and a broad peak in the higher energy region was due to silicon oxide. For spectrum (a), the Si wafers were immersed in $HNO_3$ and no Pt was deposited. The thickness of the silicon oxide layer was estimated to be 1.2nm from the ratio of the areal intensity of the oxide Si 2p peak to that of the substrate Si 2p peaks. For spectrum (b), the chemical oxide-covered Si surface was heated at 300℃ for 1h in oxygen. The intensity of the oxide peak did not change. For spectrum (c), a Pt layer was deposited on the chemical oxide-covered Si substrate and the specimen was heated at 300℃ in oxygen. The intensity of the oxide peak increased markedly, and the oxide thickness was estimated to be 4.6nm. For spectrum (d), Pt was deposited directly on the HF-etched Si substrate. In this case, additional peaks appeared at 0.7 and 1.5eV, and are attributed to $Si_2Pt$ and SiPt, respectively.[8] These results clearly show that the thin chemical oxide layer effectively prevents the silicide formation.

Figure 2 shows the high resolution cross-sectional TEM micrograph of the specimen with the <Pt/$HNO_3$ chemi-

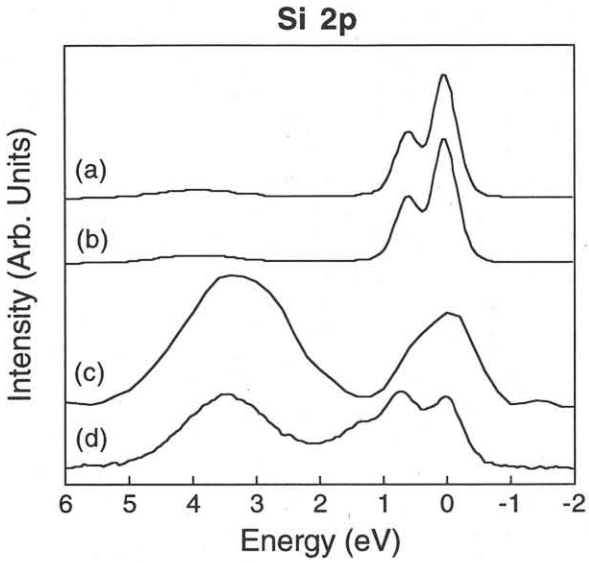


Fig. 1 XPS spectra in the Si 2p region: (a) for the <chemical oxide/Si(100)>; (b) after heating specimen (a) at 300℃; (c) for the <Pt/chemical oxide/Si(100)> after heating at 300 ℃ in oxygen; (d) for the <Pt/Si(100)>

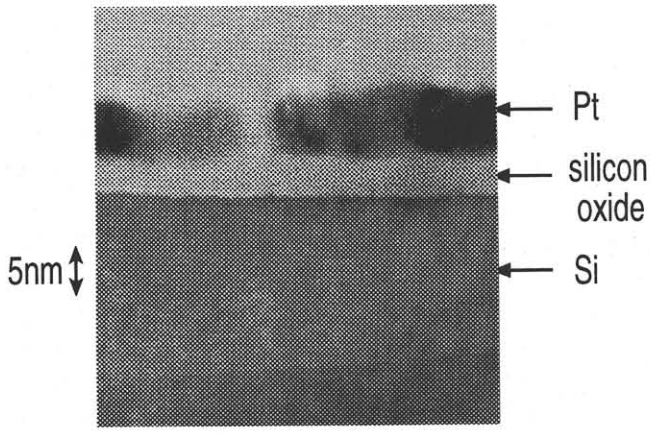


Fig. 2 TEM micrograph for the <Pt/chemical oxide/Si(100)> after heating at 300℃ in oxygen.

cal oxide/Si(100)> structure after the heat treatment at 300℃ in oxygen. It is clearly seen that the oxide layer is present between the Pt film and the Si substrate, and the thickness is 4 ~ 5 nm, in good agreement with that estimated from the XPS spectrum (spectrum (c) in Fig.1).

Figure 3 shows the thickness of the oxide layers for the <Pt/silicon oxide/Si(100)> specimens as a function of the heating temperature. The thickness of the oxide layer formed in $HNO_3$ with no Pt layer is shown by the dashed line for comparison, and it is seen that the oxide thickness was almost unchanged by the heat treatments up to 300℃. In the presence of the Pt overlayer, on the other hand, the oxide thickness was increased markedly by the low temperature heating. The rate of the increase in the thickness of the HCl oxide

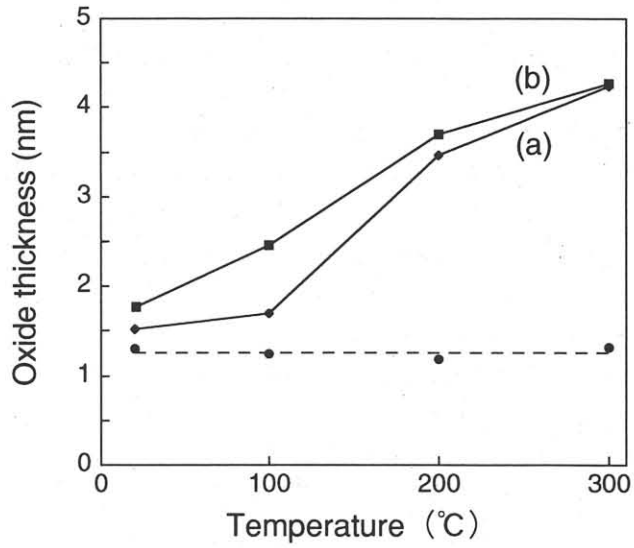


Fig. 3 Thickness of the oxide layers for the <Pt/chemical oxide/Si(100)> vs. the heating temperature. The chemical oxide layers were formed in the following solutions: (a) $HNO_3$; (b) $HCl + H_2O_2 + H_2O$.

layer was larger than that of the $HNO_3$ layer when the heat treatment was carried out below 200℃. Both the oxide thicknesses became almost identical after heating at 300℃.

## 4. Discussion

In the present study, a thin chemical oxide layer is formed before the deposition of the Pt layer. This chemical oxide layer effectively prevents the direct contact of the Pt layer with the Si substrate, and hence no silicide is formed at the interface. In the previous studies on the low temperature oxidation promoted by noble metals[1,2] or transition metals,[3,4] on other hand, the metals are deposited directly on the Si surface. The interaction of metal atoms with the Si substrate forms Si atoms in the metallic state, and these Si atoms diffuse to the metal surface. Therefore, in the presence of oxygen molecules in the atmosphere, oxidation proceeds even at room temperature, resulting in the formation of an oxide layer on the metal surface.[1-4] The thin chemical oxide layer formed before the Pt deposition prevents the interaction between Pt and Si, and hence, no silicon oxide layer is formed on the Pt layer, evident from the TEM micrograph (Fig. 2). The absence of the oxide layer on the Pt surface is also supported by synchrotron radiation UPS measurements using 140eV incident photons, i.e., Si 2p photoelectron kinetic energy of ~40eV, that no Si 2p signal was observed because of the short mean free path of the photoelectrons (~0.4nm[9]). Instead, the thickness of the oxide layer between the Si substrate and the Pt layer increases by the catalytic activity of the Pt overlayer.

It is well known that oxygen is adsorbed dissociatively on the Pt surface at room temperature.[10] There probably exists an equilibrium between oxygen molecules in the gas phase, oxygen atoms at the Pt surface, and oxygen atoms in the Pt bulk. Therefore, in the presence of the large amount of oxygen molecules in the gas phase, a considerable amount of oxygen atoms diffuse into the Pt bulk. A part of oxygen atoms in the Pt layer are injected into the silicon oxide layer, diffuse to the oxide/Si interface, and react with the Si substrate there. Namely, the diffusing species through the Pt layer and the silicon oxide layer is oxygen atoms. If the diffusing species in the oxide layer were Si atoms, they would react with Pt at the Pt/oxide interface, forming platinum silicide. XPS measurements for the specimens with the <Pt/chemical oxide/Si(100)> structure exclude the silicide formation, showing that the thin chemical oxide layer prevents the outdiffusion of Si atoms.

The oxidation rate of the specimens with the HCl oxide layer is higher than that with the $HNO_3$ oxide layer (Fig. 3). It is expected that the oxidation rate is affected by the diffusing rate of oxygen atoms in the oxide layer, which is likely to depend on the atomic density and the defect density of the oxide layer. It is reported that the density of the HCl oxide layer is lower than that of the $HNO_3$ oxide layer.[11] Moreover, our recent measurements of synchrotron radiation UPS spectra show that the amounts of the suboxide species, $Si^{+}$, $Si^{2+}$, and $Si^{3+}$, in the HCl oxide layer is much larger than those in the $HNO_3$ oxide layer.[12] The presence of the suboxide species is likely to lower the atomic density. They also may act as defect states. For these reasons, the diffusion of oxygen atoms in the HCl oxide layer is enhanced.

The diffusion rate of oxygen atoms in the chemical oxide layer affects the oxidation rate only when the oxide layer formed by the catalytic activity of the Pt layer is thin. On the other hand, for the thick oxide layer, e.g., the oxide layer formed by the heat treatment above 300℃, the diffusion in the chemical oxide probably present on the newly formed oxide has a nominal effect on the oxidation rate, but the oxide region newly formed during the heat treatment strongly affects the oxidation rate. The nature of the newly formed oxide region is likely to be independent on the kinds of the chemical oxide layers. Therefore, for sufficiently thick oxide layers, the oxide thickness does not depend on the kinds of the chemical oxide layers.

## 5. Conclusion

Pt-enhanced oxidation of Si is studied using XPS and TEM. The thin chemical oxide layer formed before the Pt deposition effectively prevents the silicide formation. After the het treatment of the <Pt/chemical oxide/Si(100)> specimens at 300℃ in oxygen, the thickness of the oxide layer increases to 4 ~ 5nm. The diffusion rate of oxidizing species in the oxide layer depends on the kinds of the chemical oxide layers.

## References


1) A. Hiraki, E. Lugujjo, and J. W. Mayer, J. Appl. Phys. 43 (1972) 3643.
2) A. Cros, J. Derrien, and F. Salvan, Surf. Sci. 110 (1981) 471.
3) I. Abbati, G. Rossi, L. Calliari, L. Braicovich, I. Lindau,and W. E. Spicer, J. Vac. Sci. Technol. 21 (1982) 409.
4) A. Franciosi, S. Chang. P. Philip, C. Caprile, and J. Joyce, J. Vac. Sci. Technol. A3 (1985) 933.
5) F. U. Hillebrecht, M. Ronay, D. Rieger, and F. J. Himpsel, Phys. Rev. B 34 (1986) 5377.
6) H. I. Starnberg, P. Soukiassian, and Z. Hurych, Phys. Rev. B 39 (1989) 12775.
7) P. Soukiassian, M. H. Bakshi, Z. Hurych, and T. M. Gentle, Phys. Rev. B 35 (1987) 4176.
8) P. J. Grunthaner, F. J. Grunthaner, and A. Madhukar, J. Vac. Sci. Technol. 20 (1982) 680.
9) F. J. Himpsel, F. R. McFeely, A. Taleb-Ibrahimi, J.A.Yarmoff, and G. Hollinger, Phys. Rev. B 38 (1988) 6084.
10) H. Steininger, S. Lehwald, and H. Ibach, Surf. Sci. 123 (1982) 1.
11) Y. Sugita, N. Awaji, S. Ohkubo, S. Watanabe, S. Komiya, and T. Ito, Extended Abstract of the 1995 International Conference of Solid State Devices and Materials, pp.836.
12) K. Namba, T. Yuasa, Y. Nakato, K. Yoneda, H. Kato, and H. Kobayashi, submitted to J. Appl. Phys.