

Interface States for Ultrathin Chemical Oxide Layers on Si(111) and Si(100)

Y. Yamashita¹, Y. Nakato¹, Y. Nishioka², H. Kato³, and H. Kobayashi^{1,4}

¹Department of Chemistry, Faculty of Engineering Science, and Research Center for Photoenergetics of Organic Materials, Osaka University, Toyonaka, Osaka 560, Japan

²Texas Instruments Tsukuba Research and Development Center Ltd., 17, Miyukigaoka, Tsukuba, Ibaraki 305, Japan

³Photon Factory, National Laboratory for High Energy Physics, 1-1, Oho, Tsukuba, Ibaraki 305, Japan

⁴PRESTO, Research Development Corporation of Japan

The energy distribution of interface states for chemical oxide layers 2 ~ 4 nm in thickness formed on Si(111) and Si(100) is obtained from XPS measurements under biases. All the observed interface state spectra have peaked structure. The interface states at the oxide/Si(111) interface are present closer to the midgap than those at the oxide/Si(100) interface. This is attributed to the weaker interaction between the Si dangling bond and atoms in the oxide layer for the Si(111)/oxide interface, resulting from the longer distance between them.

1. Introduction

An increase in the number of component per IC chip requires thinner and thinner gate oxide layers, and for 1 Gbit DRAM, the oxide thickness becomes ~5 nm.¹⁾ For such thin oxide layers, the native oxide layers present before the thermal oxidation play a very important role in determining the electrical characteristics of MOS devices.^{2,3)} Therefore, it may be of importance to observe the energy distribution of interface states present at the native oxide/Si interface. However, for such ultrathin oxide layers, conventional electrical techniques such as capacitance-voltage⁴⁾ and conductance-voltage⁵⁾ measurements cannot be employed because of a tunneling current through the oxide layers. On the other hand, a method recently developed by us, i.e., XPS measurements under biases between the metal overlayer and the semiconductor substrate,⁶⁻¹⁰⁾ can be applied to MOS devices with an ultrathin oxide layer. In the present study, this technique is used to obtain the energy distribution of interface states present at the ultrathin chemical oxide/Si interfaces.

2. Experiments

MOS devices were produced from phosphorus-doped n-type Si(111) and Si(100) wafers with the resistivity of ~1 Ω cm. After chemically cleaning the wafers, thin chemical oxide layers were formed by immersing them in the following solutions: 1) HCl:H₂O₂:H₂O=1:1:5 at 80 °C for 10 min; 2) HNO₃ at 115 °C; or 3) H₂SO₄:H₂O₂=2:1 at 100 °C for 10 min. The oxide layers formed in solutions 1), 2), and 3) are hereafter called HCl oxide, H₂SO₄ oxide, and HCl oxide, respectively. A ~3 nm-thick platinum (Pt) film was deposited on the oxide layers.

XPS measurements were performed with an Ulvac-Phi model 5500 spectrometer. Monochromatized Al K α

radiation was irradiated from the Pt layer side and photoelectrons were collected in the surface-normal direction. During the XPS measurements, the front Pt layer was earthed and a bias voltage was applied to the rear Si surface.

Ultraviolet photoelectron spectroscopic (UPS) spectra for the chemical oxide layers with no Pt layer were measured using BL 3B beam-line of KEK. The incident photon energy was set at 170 eV.

3. Results and discussion

The principle for determination of the energy distribution of interface states by measurements of XPS spectra under biases is briefly explained below.⁶⁻¹⁰⁾ At zero bias, the Si Fermi level, E_F^0 , coincides with the Pt Fermi level and interface states below E_F^0 are occupied by electrons while those above E_F^0 are empty. Under a negative bias applied to Si, the Si Fermi level, E_F , deviates upward from the Pt Fermi level, and consequently, the interface states present between E_F^0 and E_F are newly occupied by electrons. This negative charge induces a potential drop across the oxide layer, and consequently, the substrate Si 2p level at the interface shifts by the same magnitude. Therefore, by analyzing the energy shift of the substrate Si 2p peak measured as a function of the bias voltage, the energy distribution of interface states in the Si band-gap can be obtained.

The substrate Si 2p peak with respect to the Pt 4f_{7/2} peak was shifted in the lower energy direction by applying a negative bias to the Si, while it showed a higher energy shift upon applying a positive bias. These shifts were completely reversible, and attributed to charges accumulated in the interface states by biasing.

Figure 1 shows the interface state spectra for the Si(111)-based (spectra (a)-(c)) and Si(100)-based (spectra (d)-(f)) MOS devices with the ultrathin chemical oxide layer, obtained from the analysis of the energy shift of the

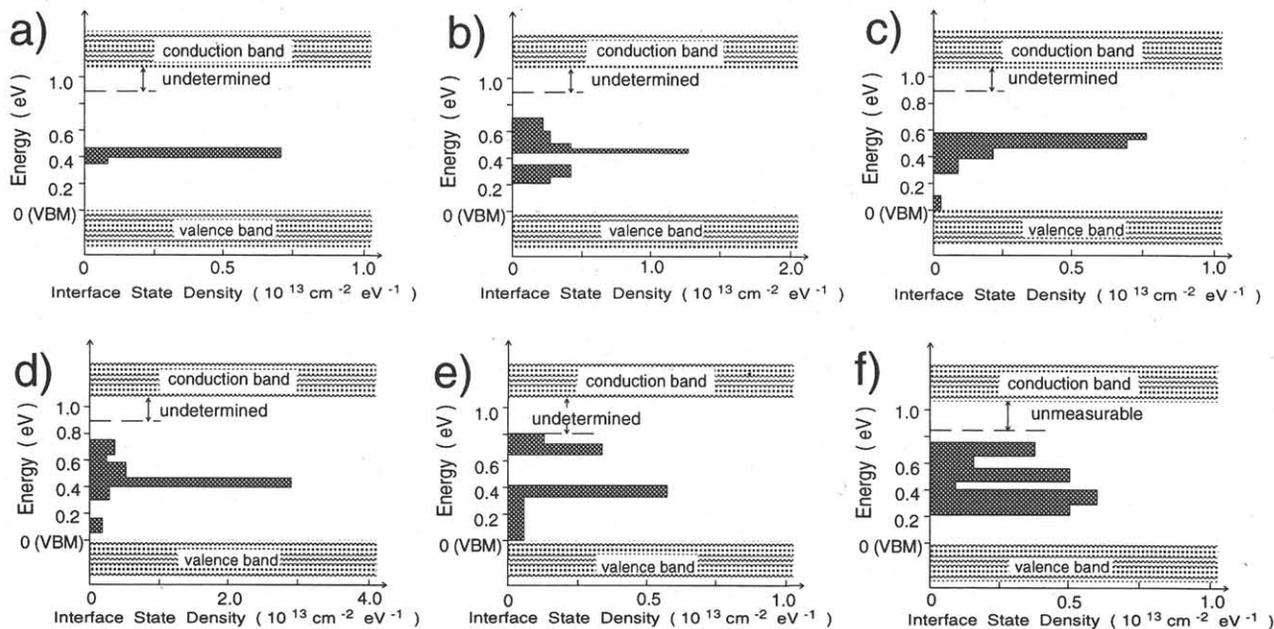


Fig. 1 Interface state spectra for the Si(111)-based (spectra (a)~(c)) and Si(100)-based (spectra (d)~(f)) MOS devices with an ultrathin oxide layer formed in the following solutions: (a) and (d): $\text{HCl}+\text{H}_2\text{O}_2+\text{H}_2\text{O}$; (b) and (e) HNO_3 ; (c) and (f) $\text{H}_2\text{SO}_4+\text{H}_2\text{O}_2$.

substrate Si $2p_{3/2}$ peak measured as a function of the bias voltage.⁶⁻¹⁰ The thicknesses of the oxide layers are estimated to be 2~3.5 nm from the ratio of the areal intensity of the oxide Si 2p peak to that of the substrate peak.¹¹

All the observed interface states have discrete energy levels, indicating that they are due to defects such as Si dangling bonds. With reference to theoretical calculations,¹² the interface states near the midgap are attributed to isolated Si dangling bonds, while the interface states above and below the midgap are attributed to Si dangling bonds interacting weakly with oxygen and Si atoms in the oxide layer, respectively. For the HNO_3 oxide layers, two peaks are present in the spectra, one above and the other below the midgap. The energy separation of the two interface state peaks for the Si(111)-based MOS device (spectrum (b)) is smaller than that for the Si(100)-based device (spectrum (e)), indicating the weaker interaction between the Si dangling bond and atoms in the oxide layer for the Si(111)-based device. The broad peak for the H_2SO_4 oxide layer of the Si(111)-based MOS device (spectrum (c)) is probably due to the overlap of the interface states of three kinds (cf. spectrum (f)) caused by the small energy separations.

Si dangling bonds present at the oxide/Si(111) interface are located parallel to the Si-O bonds in the first oxide layer. Therefore, the distance between the Si dangling bond and a Si or oxygen atom in the oxide layer is long, resulting in the very weak interaction, which causes small energy shifts of the interface state peaks from the midgap. On the other hand, in the case of the oxide/Si(100) interface, the Si dangling bonds are not parallel to the Si-O bonds, leading to the shorter distance between the Si dangling bonds and atoms in the oxide layer.

Figure 2 shows the Si 2p peaks due to suboxide

species for the chemical oxide layers with no Pt layer on the Si(111) substrate, obtained from deconvolution of synchrotron radiation UPS spectra. The background intensity of the UPS spectra was estimated as follows. The background curve was obtained by measuring the spectra using 10eV lower energy photons. Then, the background curve was subtracted from the corresponding Si 2p spectra. The background intensity due to the inelastic scattering of

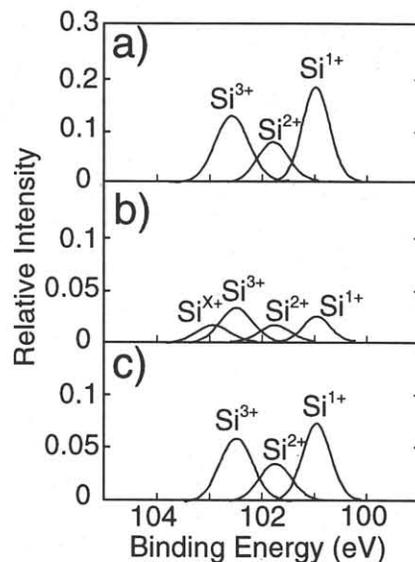


Fig. 2 Si 2p peaks of the suboxide species for the chemical oxide layers on Si(111) formed in the following solutions:(a): $\text{HCl}+\text{H}_2\text{O}_2+\text{H}_2\text{O}$; (b) HNO_3 ; (c) $\text{H}_2\text{SO}_4+\text{H}_2\text{O}_2$. The intensity was normalized by the peak intensity of the Si^{4+} species.

the Si 2p photoelectrons was estimated by use of the method in which the loss intensity at binding energy E was assumed to be proportional to the integral of the Si 2p photoelectron intensity in the energy region lower than E . Then, the Si $2p_{1/2}$ components were mathematically removed.

Si^{1+} , Si^{2+} , and Si^{3+} denote suboxide species in which each Si atom is bound to one, two and three oxygen atoms, respectively. It is clearly shown that the amount of the suboxide species in the HCl oxide layer is the highest. The presence of the high amount of the suboxide species indicates that the HCl oxide layer is not highly oxidized. On the other hand, the small amount of the suboxide species in the HNO_3 oxide layer shows that the HNO_3 oxide layer is in the highly oxidized state. Since the oxidation accompanies the supply of oxygen atoms to the suboxide species forming new Si-O bonds, highly oxidized oxide layers, e.g., the HNO_3 oxide layer, are likely to have a high atomic density. On the other hand, it is likely that the HCl oxide layer which includes a large amount of the suboxide species has a lower atomic density. This expectation is supported by results from X-ray reflectometry that the density of the HNO_3 oxide layer is higher than that of the HCl oxide layer.¹³⁾

The dangling bond at the HCl oxide/Si interface is expected to possess a sufficiently large space because of the low atomic density of the oxide layer, i.e., long distance between the Si dangling bond and atoms in the oxide layer. Therefore, only the isolated Si dangling bond interface states are formed near the midgap (spectra (a) and (d) in Fig. 1). On the other hand, the higher the atomic density of the oxide layer, the shorter the distance between the dangling bond and atoms in the oxide layer, resulting in the weak interaction. The interaction shifts the interface state levels from the midgap (spectra (b) and (e)).

The above argument is supported by the recently observed interface state spectra for the native oxide layers⁷⁾ and the thermal oxide layers,⁸⁾ using the technique employed in the present study. In the case of the native oxide layers formed by leaving Si in air at room temperature, the atomic density is likely to be low. For the native oxide layers, only one interface state peak attributable to isolated Si dangling bonds is observed near the midgap.⁷⁾ On the other hand, the thermal oxide layers are likely to possess a high atomic density. Consequently, the interface state spectra have two-peaked structure, one above and the other below the midgap.⁸⁾

4. Conclusion

The interface states at the ultrathin chemical oxide/Si(111) and Si(100) interfaces have discrete energy levels and attributed to dangling bonds in various environments. The HCl oxide layer contains high amounts of the suboxide species, resulting in the low atomic density. In this case, the Si dangling bond at the interface has a sufficiently large space, and thus, only the isolated Si dangling bond interface states are present near the midgap. On the other hand, the HNO_3 oxide layer includes only small amounts of suboxide, resulting in the higher atomic density. For this oxide layer, an oxygen or Si atom in the oxide layer are located near the Si dangling bonds, shifting the interface state levels upward and downward, respectively, from the midgap. The interaction between the Si dangling bond and atoms in the oxide layer for the Si(111)-based MOS devices is weaker than that for the Si(100)-based MOS devices.

References

- 1) M. Horiguchi et al. Conf. on Int. Solid-State Circuits, Digest of Technical papers, 1995, pp.252.
- 2) F. J. Grunthaler and J. Maserjian, IEEE Trans. Nucl. Sci. **NS-24**, (1977) 2108.
- 3) G. Gould and E. A. Irene, J. Electrochem. Soc. **134** (1987) 1031.
- 4) L. M. Terman, Solid-State Electron. **5** (1962) 285.
- 5) E. H. Nicollian and A. Goetzberger, Bell Syst. Tech. J. **46** (1967) 1055.
- 6) H. Kobayashi, K. Namba, T. Mori, and Y. Nakato, Phys. Rev. B **52** (1995) 5781.
- 7) H. Kobayashi, Y. Yamashita, T. Mori, Y. Nakato, K. H. Park, and Y. Nishioka, Surf. Sci. **326** (1995) 124.
- 8) H. Kobayashi, Y. Yamashita, T. Mori, Y. Nakato, T. Komeda, and Y. Nishioka, Jpn. J. Appl. Phys. **34** (1995) 959.
- 9) H. Kobayashi, T. Mori, K. Namba, and Y. Nakato, Solid State Commun. **92** (1994) 249.
- 10) Y. Yamashita, K. Namba, Y. Nakato, Y. Nishioka, and H. Kobayashi, J. Appl. Phys. **79** (1996) 7051.
- 11) H. Kobayashi, T. Ishida, Y. Nakato, and H. Tsubomura, J. Appl. Phys. **69** (1991) 1736.
- 12) T. Sakurai and T. Sugano, J. Appl. Phys. **52** (1981) 2889.
- 13) 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.