Extended Abstracts of the 20th (1988 International) Conference on Solid State Devices and Materials, Tokyo, 1988, pp. 487-490

In-depth Profiling of SiO₂/Si-Interface Electronic Structure Using Low-Energy Electron Energy Loss Spectroscopy

Nahomi Aoto, Eiji Ikawa, Nobuhiro Endo and Yukinori Kurogi

Microelectronics Research Laboratories, NEC Corporation 1120 Shimokuzawa, Sagamihara, Kanagawa 229, Japan

The SiO₂/Si-interface of thin oxide layer formed thermally in a low O₂ pressure is investigated. The electronic structure and the chemical bondings are analyzed with low-energy electron energy loss spectroscopy and X-ray photoelectron spectroscopy. These results combine to show clearly that either a Si²⁺ suboxide layer or a layer which contains a considerable amount of Si²⁺ is localized at the SiO₂/Si interface region and has a thickness of 1 - 2 monolayers.

I. Introduction

in VLSI Recent progress microfabrication technology and its resulting device-size reduction create the necessity for ultra-thin silicon oxide films. It is important to control SiO₂/Si-interface characteristics because of their strong influence on device properties. Previous studies have attended to learn about interface bondings, structures and electronic states by applying a variety of techniques. in situ analysis In our study here, techniques were used to examine the SiO2/Si interfaces of thin oxide layers, formed thermally in a low O_2 pressure.

For non-destructive in-depth profiling of the SiO2/Si interface, low-energy electron energy loss spectroscopy (LEELS) and X-ray photoelectron spectroscopy (XPS) were employed. LEELS was used to profile the electronic structure in depth by using various primary electron energies. XPS was used to profile the chemical bondings in depth with a coarse angular-resolved analyzing system. New information on the SiO2/Si interface was obtained by combining the results of both.

II. Experiments

The experimental system was constructed of three UHV connected chambers. The background pressures were 2×10^{-8} Pa in the analysis chamber and the oxidation chamber, and 1×10^{-6} Pa in the preparation chamber. The samples were Si(100), of the p-type, with $3 - 6 \Omega$ cm resistivity. Native oxide layers on the Si surfaces were removed with in a HF solution. After mounting the sample, the surfaces were cleaned in the analysis chamber with flashing up to 1100° C by electron backbombardment.

The surfaces were oxidized in the oxidation chamber with an O_2 pressure of 1.3 x 10^{-2} Pa and a substrate temperature of 850°C. The oxidized Si surfaces were analyzed in the analysis chamber by using LEELS, XPS and Auger electron spectroscopy (AES). A double-pass CMA (PHI 15-255 GAR) was used as the electron-energy analyzer.

LEELS probing depth varies with the primary electron energy¹⁾ because the electron mean free path in solids varies

depending upon the electron energy. In our study, the LEELS spectra of the Si(2p)-coreelectron excitation were measured with primary electron beams of 230 - 1600 eV. The approximate probing depths for several electron primary energies reported by Yoshimura et al.¹⁾ are listed in Table I.

For the XPS measurement, the double-pass CMA was modified to be used in the coarse angular-resolved mode. The CMA contained an angle-selecting aperture which reduced the angle of the azimuthal electron-correction. With this aperture, the electron-detecting angle for the sample surface could he coarsely limited. In addition, the sampleangle was also changed. tilting Thus, different electron-detecting angles for the sample surface were employed in the in-depth profiling. The Mg-K $_{\alpha}$ -line was used as the incident X-ray.

Primary electron energy (eV)	Probing depth(Å)
230	~ 3
400	~3.5
600	~5
800	~6
1000	~8
1200	~9
1400	~10
1600	~11

Table I Probing depths on Si(2p)-coreelectron-excitation LEELS spectra for various primary electron energies. (ref.1)



Fig.1 Oxidation time dependence of the O(KLL)/Si(KLL) auger-peak ratio of oxidized Si surfaces. $E_p = 3 \text{ kV}$.

III. Results and Discussion

Figure 1 shows the relative Oconcentration on Si surfaces, evaluated using AES peaks of Si(KLL) at 1622 eV, and O(KLL) at 503 eV. The O-concentration on Si surfaces increased with increase in the oxidation time. The increase saturated for oxidation times greater than 17 min. Tabe et al. have referred to the data of Gelain et al. that a SiO₂ film is formed at thin substrate temperatures lower than 900°C in 1.3 x 10^{-2} Pa 0_2^{2} . Under the oxidation conditions of Fig.1, 850°C and 1.3 x 10⁻² Pa O₂, a thin SiO2 film was formed as was indicated by the O-concentration increase. The saturation of the O-concentration increase indicates the formation of a thin SiO2 film which suppress additional oxidation.

Figure 2 shows the second-derivative LEELS spectra of interband electron transitions on the oxidized Si surfaces. The primary electron energy was 100 eV. The shapes of the spectra changed with the increase in oxidation time. On the spectra of shorter oxidation times, three peaks, at 3.5 eV, 5.0 eV and 7.2 eV, are conspicuous. After longer oxidations, the intensities of these peaks became weaker, while a peak at 10.7 eV appeared with a high intensity.

The LEELS spectra of O-adsorbed and oxidized surfaces have been reported by



Fig.2 Interband -transition LEELS spectra of oxidized Si surfaces for different oxidation times. several researchers. The 3.5 eV, 5.0 eV and transitions were attributed 7.2 eV to)3) electron transitions in SiO_{y} (1 < x < 2and the 10.7 eV transition was thought to be a transition in SiO_2 .⁴⁾ In our study, XPS spectra measured on the same surfaces as are shown in Fig.2 indicated the existence of SiO₂ as well as other suboxides. Thus the Fig.2 are attributed to spectra in the mixture of SiO_x (1 < x < 2) and SiO_2 . The intensity differences in the spectra in Fig.2 are due to the varieties and relative amounts of the species.

3 shows nonderivative LEELS Figure spectra of Si(2p)-core-electron excitation on the oxidized Si surfaces. The oxidation times were (a) 10 s, (b) 3 min, and (c) 45 Figs.3(a), (b), and (c) show the min. primary-electron-energy dependences of the LEELS spectra, i.e. the probing-depth dependence of the spectra. Two conspicuous peaks are shown at about 102 eV and 108 eV. Yoshimura et al. have reported that the 108 eV electron excitation takes place in SiO2, and the 102 eV one takes place in $Si.^{1}$ Thus the gradual changes of spectra from that of the top-surface SiO2 region to that of the bulk Si are shown in Figs.3(a),(b), and (c). On the spectrum which observes principally the SiO₂/Si interface region, both peaks of 102 eV and 108 eV are observed.¹⁾

The appearance of an additional peak at 105 eV was confirmed for the first time in our study. The peak was observed on the spectra of different Si surfaces oxidized over various oxidation times. With increasing thickness in the oxidized layer from Fig.3(a) to (c), the probing depth at which the 105 eV peak appeared became deeper. This peak appeared on the spectra, which show both 102 eV and 108 eV peaks and which were produced by probing the interface region.

The probing depths of the spectra which show the 105 eV peak are about 3.5A, 5A and 8A for Figs.3(a), (b), and (c), these to the corresponding incident electron of 400 eV, 600 eV and 1000 eV. energies respectively. The peak does not appear on the spectra of neighboring incident electron energies in any of the Figs.3(a),(b), and







Fig.4 Detection angle dependence of Si(2p) XPS spectra for a SiO₂/Si structure. (c). Therefore the occurrence of the 105 eV electron excitation is limited to a very thin region, estimated to have a thickness of 1 - 2 monolayers.

These results indicate that the electronic states which relate to the 105eV electron excitation are localized spatially at the SiO_2/Si -interface region. Additionally, it is indicated that this interface region has a thickness of 1-2 monolayers.

existence of suboxides in the The SiO2/Si interface and in the SiO2 layer has been previously determined with another analyzing method, XPS. Suzuki et al. the reported, regarding interface of thermally oxidized films, that the Si²⁺-type suboxides are mostly localized at the SiO2/Si interface. They also reported that Si³⁺-type suboxides are mostly distributed in the oxide film near the interface.5)

Figure 4 shows the Si(2p) XPS spectra for the same surface as Fig.3 (a). The XPS spectra were measured with different 15°, 38°, and 87°. Larger detection angles, angles provide deeper detection probing depth. The spectra for Fig.4(a), (b), and (c) are curve-fitted to chemical shift elements. For the curve-fitting, the chemical-shift al.6) energies reported by Braun et on thin SiO₂ films determined oxidized thermally in low O2 pressure, were used. The chemical shifts originated from the suboxides and oxide, Si¹⁺ (which means Si₂O), Si²⁺ $(SiO), Si^{3+} (Si_2O_3)$ and $Si^{4+} (SiO_2)$. On the spectra of Figs.3(b) and (c), which show deeper regions than (a), the Si^{2+} element has greater intensity than the Si³⁺ element. This shows that Si²⁺ suboxides are distributed closer to the interface than Si³⁺ suboxides, as in the case of thermally oxidized films reported by Suzuki et al.5)

The Si²⁺ existence in the interface region indicates that the 105eV LEELS peak in



Fig.5 Attribution of the Si(2p)core-electron excitation observed in Fig.3.

Fig.3 is caused by Si(2p)-core-electron excitation in the Si^{2+} suboxide layer. As previously noted, the 105 eV LEELS peak occurs at 1 - 2 monolayers in the interface region. Consequently, it would seem that a Si^{2+} layer is localized, with a thickness of 1 - 2 monolayers, at the SiO_2/Si interface region.

Fig.5 shows the attribution of the initial and the final states of the Si(2p)-core-electron excitations observed in Fig.3. For all of Si, SiO_2 and Si^{2+} -suboxide layer, the final states are thought to be in the conduction band.

IV. Conclusion

SiO₂/Si interfaces of thermally oxidized layers which are thinner than 10 Å were analyzed by LEELS and XPS. Results combined to show clearly that Si²⁺ suboxides exist in the interface region at a 1 - 2 monolayer thickness. This new knowledge regarding SiO₂/Si-interfaces provides important information for continued progress in thinoxide-film fabrication techniques.

References

- 1)K.Yoshimura and A.Koma,Extended Abstracts of the 16th Conference on Solid State Devices and Materials,Kobe,1984,p.293
- 2)M.Tabe et al., Phys.Rev.B<u>34</u>(1986)2706
- 3)K.Edamoto, Y.Kubota, H.Kobayashi, M.Onchi and M.Nishijima, J.Chem.Phys.<u>83</u>(1985)428
- 4)H.Ibach and J.E.Rowe, Phys.Rev.B10(1974)710
- 5)T.Suzuki, M.Muto, K.Yamabe and T.Hattori, Jpn.J.Appl.Phys.<u>25</u>(1986)544
- 6)W.Braun et al., Surf.Sci.<u>180</u>(1987)279