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X-ray photoelectron spectroscopy study on SiO_2/Si interface structures formed by three kinds of atomic oxygen at 300 °C

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Using the high-brilliant synchrotron radiation at SPring-8 we have studied the SiO_2/Si interface structures, the interface state densities, and the uniformities of ~1-nm-thick oxide films formed by three kinds of atomic oxygen at 300 °C by measuring Si $2p$ photoelectron spectra at the photon energy of 1050 eV and the energy loss spectra of O $1s$ photoelectrons at the photon energy of 714 eV. Among silicon oxide films studied here the abrupt compositional transition at SiO_2/Si interface, the smallest deviation in interface state density, the interface state density comparable to that for thermal oxide formed in dry oxygen at 950 °C, and the highest uniformity was obtained with oxide film formed in krypton-mixed oxygen ($Kr:O_2=97:3$) plasma. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1737793]

The formation of high-quality gate dielectric/Si interfaces at temperatures lower than 400 °C is a key process for fabricating polycrystalline silicon thin film transistors on glass or plastic substrates.[1] While silicon oxide deposited by plasma enhanced chemical vapor deposition (PECVD) from tetraethoxysilane (TEOS) (abbreviated hereafter as TEOS-PECVD film) has been used as a gate dielectric, it is difficult to achieve a sufficiently small deviation in the density of interface states at the interface. To reduce the deviation in the interface state densities, Nakata and his co-workers introduced 4-nm-thick high-quality low-temperature oxides[2,3] formed by atomic, or radical, oxygen beneath the TEOS-PECVD film.[4] In this letter, using the electron energy analyzer ESCA-2002, the chemical structures at the SiO_2/Si interface and uniformities of the ~1-nm-thick SiO_2 structural transition layer,[5–7] which mostly determine the quality of a SiO_2/Si interfacial transition layer, were studied by measuring 1050 eV photons' excited Si $2p$ photoelectron spectra and 714-eV-photons' excited energy loss spectra of O $1s$ photoelectrons with energy resolution of 100 meV at soft-x-ray undulator beam line (BL27SU) of the Super Photon Ring 8 GeV (SPring-8).

The angle of incidence of 1050-eV-photon flux and that of 714-eV-photon flux with respect to the horizontal plane was 70° and 35°, respectively. The electron escape depth of Si $2p$ photoelectrons excited by 1050 eV photoelectrons in Si (1.59 nm) and that in SiO_2 (2.86 nm) was used to determine the oxide film thickness and the amount of suboxides. The former value (1.59 nm) was determined from a value of 2.11 nm for the escape depth of Si $2p$ photoelectrons in Si excited by Al $K\alpha$ radiation[8] by considering the dependence of electron escape depth on kinetic energy of electrons,[9] while the latter (2.86 nm) was obtained in the same way from a value of 3.80 nm.[10]

Approximately 1-nm-thick low-temperature oxide films were formed at 300 °C by using three kinds of atomic oxygen[11] on epitaxially grown Si(100) substrates with a vicinal angle of 0.01°. The atomic oxygen was generated by microwave-excited (2.45 GHz) plasma or by the ultraviolet light. The three films were 1.17-nm-thick film formed by krypton-mixed oxygen ($Kr:O_2=97:3$) plasma (abbreviated hereafter as Kr/O_2 plasma oxide),[12] 1.27-nm-thick-film formed by oxygen plasma (abbreviated hereafter as O_2 plasma oxide),[12] and 1.17-nm-thick film formed using atomic oxygen, which was generated by exciting molecular oxygen with 172-nm-wavelength light from a xenon excimer lamp (hereafter abbreviated as photo oxide). TEOS-PECVD film was formed at 300 °C by VHF (40 MHz)-excited PECVD from O_2 mixed TEOS (0.7%) gases with a pressure of 80 Pa and a VHF power density of 0.33 W/cm^2.

Figure 1 shows Si $2p_{3/2}$ photoelectron spectra measured for three kinds of low-temperature oxide films. Here, after removing the extremely small background signal based on Tougaard's method from the observed Si $2p$ spectrum,[13] the spectrum was decomposed into the Si $2p_{1/2}$ and Si $2p_{3/2}$ spin-orbit partner lines. In this deconvolution, it is assumed that the spin-orbit splitting of the Si $2p$ photoelectron spec-

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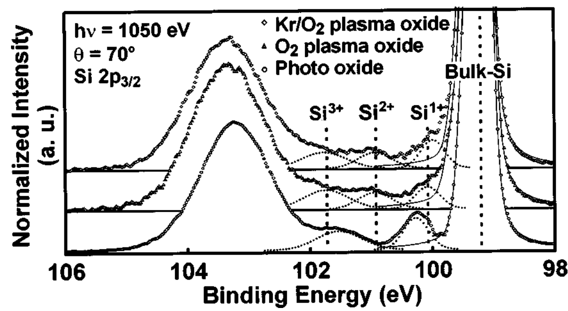

FIG. 1. Si $2p_{3/2}$ photoelectron spectra measured for three kinds of low-temperature oxide films.

trum is 0.602 eV, and the Si $2p_{1/2}$ to Si $2p_{3/2}$ intensity ratio is 0.5.[14] It is also assumed that the intermediate oxidation states (abbreviated hereafter as suboxides) consist only of Si^{1+}, Si^{2+}, and Si^{3+} as defined by Hollinger *et al.*[15]

The chemical shift and the full width at half maximum (FWHM) for the Si $2p_{3/2}$ spectrum originated in the Si^{n+} and the amount of Si^{n+}, which is expressed in one monolayer (ML) of 6.8×10^{14} cm^{-2}, are listed in Table I. Here, it is considered that the normalized intensity (NSi^{n+}/NS) for the Si $2p_{3/2}$ spectrum originated in the Si^{n+} can be approximated as $N_n/(n_s\Lambda_s \sin\theta)$, where NS, N_n, n_s, Λ_s, and θ represent Si $2p_{3/2}$ spectral intensity arising from Si substrate, areal density of Si^{n+}, the density of Si atoms in a Si substrate, the escape depth of Si $2p$ photoelectrons in Si, and the photoelectron takeoff angle, respectively.[16] In these analyses, we used 5×10^{28} m^{-3} for n_s and 1.59 nm for Λ_s. Although the errors in measuring the amount of suboxides were ±5%, the data in Table I show that the total amount of suboxides resulted in the following order for low-temperature oxides: photo oxide<Kr/O_2 plasma oxide<O_2 plasma oxide. Because the amount of suboxides observed for three kinds of oxides is almost equal to 1 ML, an abrupt compositional transition took place in these oxides. However, because the errors in measuring the amount of suboxides were ±5%, we can only discuss the relative abruptness of the compositional transition. We cannot discuss the absolute abruptness in detail, like Lu *et al.*[17] Furthermore, in the case of photo oxide, the SiO_2/Si interface mainly consists of Si^{1+} and Si^{3+}, which means that the SiO_2/Si interface was covered by {111} facets.[18,19]

Figure 2 shows the densities of state at a 2-nm-thick low-temperature oxide/silicon interface covered with 28-nm-thick TEOS-PECVD film as determined by $C-V$ measurement. They resulted in the following order: photo-oxide< Kr/O_2 plasma oxide<O_2 plasma oxide. Therefore, there is a correlation between the amount of suboxides and the density of states at the interface. That is, the larger the amount of suboxides, the higher the density of states at the interface. Because the amount of suboxides is four orders of magnitude larger than the density of states at the interface, a single defect at the interface can be generated by a certain amount of suboxides. Figure 2 also shows the density of states at a 10-nm-thick thermal oxide/silicon interface formed in dry oxygen at 950 °C and at a 30-nm-thick TEOS-PECVD film/ silicon interface. As discovered by Nakata and co-workers[2] the deviation in the density of states at a 2-nm-thick Kr/O_2 plasma oxide/silicon interface covered with 28-nm-thick TEOS-PECVD film is much smaller than that at a 30-nm-thick TEOS-PECVD film/silicon interface and even smaller than that at a 10-nm-thick thermal oxide/silicon interface.

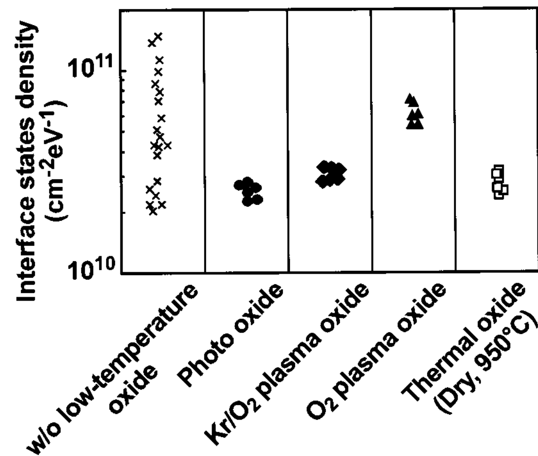

FIG. 2. Density of states at three kinds of 2-nm-thick low-temperature oxide/silicon interfaces covered with 28-nm-thick PECVD film as determined by $C-V$ measurement. Density of states at 10-nm-thick thermal oxide/silicon interface formed in dry oxygen at 950 °C and that at 30-nm-thick PECVD film/silicon interface are also shown.

Figure 3 shows the O $1s$ photoelectron energy loss spectra observed for three kinds of low-temperature oxide films. In addition to the energy loss at a threshold energy[20,21] of about 9 eV, an energy loss at a threshold energy of 3.5 eV was observed for all oxide films. The amount of energy loss at a threshold energy of 3.5 eV resulted in the following order for low-temperature oxides: Kr/O_2 plasma oxide <photo-oxide<O_2 plasma oxide. A value of 3.5 eV corresponds to the minimum energy required for direct interband transition at the Γ point in the energy band structure of Si.[22,23] The O $1s$ photoelectrons lose their energy in Si substrate by exciting the direct interband transition when O $1s$ photoelectrons penetrate into Si substrate before escaping

TABLE I. Chemical shift and full width at half maximum (FWHM) for Si $2p_{3/2}$ spectrum originated in Si^{n+} and amount of Si^{n+} and total amount of suboxides for three kinds of low-temperature oxide films.

	Chemical shift (eV)/FWHM (eV)			Amount of suboxide (ML)			
	Si^{1+}	Si^{2+}	Si^{3+}	Si^{1+}	Si^{2+}	Si^{3+}	Total
Kr/O_2 plasma oxide	0.812	1.761	2.593	0.326	0.259	0.357	0.943
	0.484	0.647	0.867				
O_2 plasma oxide	0.889	1.746	2.550	0.265	0.269	0.420	0.954
	0.484	0.647	0.867				
Photo oxide	1.074		2.334	0.427	0.024	0.459	0.910
	0.484	0.647	0.867				

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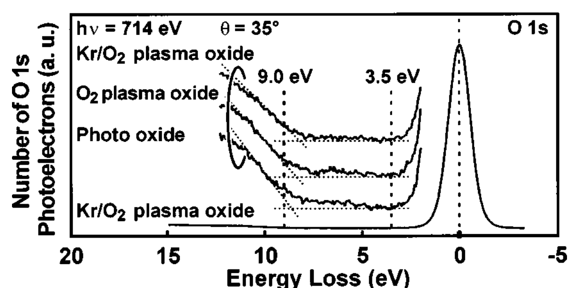

FIG. 3. O 1*s* photoelectron energy loss spectra measured for three kinds of low-temperature oxide films.

into vacuum. The O 1*s* photoelectrons also lose their energy in oxide by exciting the direct interband transition between the electronic states penetrated from Si substrate into oxide.[24] In both cases, the number of O 1*s* photoelectrons escaping into vacuum without inelastic scattering in oxide film decreased as the uniformity of silicon oxide film increased. Therefore, uniformity resulted in the following order for low-temperature oxides: Kr/O_2 plasma oxide$>O_2$ plasma oxide>photo oxide. This implies that the highest uniformity does not necessarily mean the most abrupt compositional transition at the interface.

In conclusion, we studied the SiO_2/Si interface structures, the interface state densities, and the uniformities of three kinds of low-temperature oxide films by measuring Si 2*p* photoelectron spectra and the energy loss spectra of O 1*s* photoelectrons. Measurement of these spectra revealed that uniformity was strongly dependent on the oxidation process, while the total amount of suboxides was weakly dependent on the oxidation process. Among silicon oxide films studied here the abrupt compositional transition at SiO_2/Si interface, the smallest deviation in interface state density, the interface state density comparable to that for thermal oxide formed in dry oxygen at 950 °C, and the highest uniformity was obtained with Kr/O_2 plasma oxide. The photo-oxide/Si interface mainly consists of Si^{1+} and Si^{3+}, which means that the SiO_2/Si interface was covered by {111} facets. The amount of suboxides can be correlated with the density of states at the interface, although the errors in measuring the amount of suboxides were ±5%.

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