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著者	寺本　章伸
journal or publication title	Applied Physics Letters
volume	89
number	15
page range	154103-1-154103-3
year	2006
URL	http://hdl.handle.net/10097/47979

doi: 10.1063/1.2361177

APPLIED PHYSICS LETTERS **89**, 154103 (2006)

X-ray photoelectron spectroscopy study of dielectric constant for Si compounds

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(Received 28 April 2006; accepted 25 August 2006; published online 11 October 2006)

The authors measure the difference of core-level binding energy shifts for Si 1*s* and Si 2*p*, ΔE_{1s}-ΔE_{2p}, for various Si compounds using high-resolution high-energy synchrotron radiation. They find that the ΔE_{1s}-ΔE_{2p} values are in very good correlation with the dielectric constant values of the Si compounds. Using this relation, they deduce the local dielectric constant for each of the Si intermediate oxidation states formed at the SiO_2/Si interface. The results are in good agreement with values predicted by a first-principles calculation. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2361177]

X-ray photoelectron spectroscopy (XPS) has been used to study the SiO_2/Si interface, thanks to its inherent ability to reveal both atomic structures and electronic structures.[1–4] Atomic structures thus revealed were discussed in terms of intermediate oxidation states at the SiO_2/Si interface[1] and strained Si–O–Si bonds near the interface,[2] while electronic structures thus determined were discussed in terms of the valence-band offset at the interface[3] and the dielectric constant near the interface.[4] Most importantly, the dielectric constant near the interface is a major concern in the current Si integrated circuit industry where the device technology demands a dramatic reduction in the gate SiO_2 film thickness to as small as about 1 nm. In a previous letter,[4] we described how we can characterize the dielectric constant of ultrathin SiO_2 films formed on Si(100) substrates by using a photoemission technique, namely, a technique based on the Auger parameter, and clarified that the dielectric constant values of thin SiO_2 films (>0.6 nm) are identical to that of bulk SiO_2. However, it is still an open question as to whether the dielectric constant is also identical for an ultrathin SiO_2 film with a smaller thickness. Recently, several groups have suggested from their electrical measurements that the SiO_2 film formed on a Si substrate has an interfacial region where the dielectric constant is much higher than that of bulk SiO_2.[5–7] Therefore, it is highly necessary to directly reveal the dielectric properties near the SiO_2/Si interface.

The Si 2*p* core level is commonly measured in XPS studies of the SiO_2/Si interface. However, the core-level binding energy shift ΔE_{2p} of Si 2*p* on formation of SiO_2 films largely depends on the distance from the SiO_2/Si interface,[8] which makes it difficult to obtain ΔE_{2p} values intrinsic to the local environment. The effects come from either the Madelung potential contribution to its initial state or the image charge contribution to its final state, both of

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which depend on the distance from the SiO_2/Si interface.[4,9] Therefore we focused on the difference between the core-level binding energy shift ΔE_{1s} for Si 1*s* on formation of SiO_2 and ΔE_{2p} for Si 2*p*, or the relative chemical shift ΔE_{1s}-ΔE_{2p}. The ΔE_{1s}-ΔE_{2p} value is expected to directly relate to the local electronic structures of the photoionized Si atoms in SiO_2 near the interface because the subtraction cancels both the Madelung contribution to its initial state for the Si 1*s* and Si 2*p* and the image charge contribution to its final state for Si 1*s* and Si 2*p*. Recently, a theoretical study revealed that a large relative core-level shift can occur because of different core-valence Slater integrals between two core levels.[10] Furthermore the relative chemical shift has been investigated in greater detail by photoelectron spectroscopy using a synchrotron radiation source with high energy which can excite the deeper Si 1*s* core level as well as the shallower Si 2*p* core level. Eickhoff *et al.* found that the relative chemical shift of SiO_2 films formed on a Si substrate remains constant as the SiO_2 film thickness decreases to as small as about 1 nm.[11] On the other hand, we found that the relative chemical shift decreases as the SiO_2 film thickness decreases below 1 nm.[12] The decrease in the relative chemical shift indicates that the valence charge of Si atoms in the SiO_2 film changes near the interfaces. In this study, we show a new approach for estimating the dielectric constant using the relative chemical shift determined by XPS.

We used *p*-type Si(100) and three kinds of Si compounds: (i) *n*-type SiC(0001), (ii) 0.75-nm-thick Si_3N_4 formed on *n*-type Si(100), and (iii) 1.96-nm-thick SiO_2 formed on *p*-type Si(100). We paid particular attention to prepare the thin Si_3N_4 film and SiO_2 film and obtained uniform films by the methods described in Refs. 13 and 14, respectively. Briefly, we will mention the method for the SiO_2 film, which is especially important for measuring the intermediate oxidation states formed at the SiO_2/Si interface. First, a 200-nm-thick SiO_2 film was formed on the *n*-type Si(100) substrate. Second, a hydrogen-terminated Si(100) surface was obtained by removing the SiO_2 film in a buffered HF solution. Third, the hydrogen-terminated Si(100) surface was heated in 4 Torr dry oxygen at 300 °C to form preoxide up to a thickness of 0.36 nm without breaking Si–H bonds on the surface. Finally, a 1.96-nm-thick SiO_2 film with an atomically flat interface[14] was obtained by oxidation through the preoxide at 900 °C.

The Si 1*s* and 2*p* photoelectron spectra from the samples were measured using high-resolution high-energy x-ray radiation at SRring-8 (BL47XU and BL27SU), a third-generation synchrotron source.[15] The ΔE_{1s} and ΔE_{2p} values on the formation of the Si compounds were determined with respect to the Si substrate (Si^{0+}). The ΔE_{2p} values were determined for each sample after the spectrum was decomposed, taking into account spin-orbit splitting. In the case of the spectrum decomposition for Si_3N_4 we did not include negligibly small peaks originating from the intermediate nitridation states. On the other hand, in the case of the spectrum decomposition for SiO_2 and intermediate oxidation states we included peaks originating from three intermediate oxidation states (i.e., Si^{1+}, Si^{2+}, and Si^{3+}). The positions of the intermediate oxidation states for Si 2*p* are 0.96 eV for Si^{1+}, 1.75 eV for Si^{2+}, and 2.52 eV for Si^{3+} with respect to that of the Si substrate, while those for Si 1*s* are 1.27 eV for Si^{1+}, 2.19 eV for Si^{2+}, and 3.08 eV for Si^{3+} with respect to that of the Si substrate. These values for Si 2*p* are in agreement with reported date.[16] Because the SiC does not have a Si substrate underneath, the ΔE_{1s} and ΔE_{2p} values were not separately determined: instead, the relative chemical shift ΔE_{1s}-ΔE_{2p} for SiC was determined by comparing the energy difference between Si 1*s* and Si 2*p* for SiC with that for the Si substrate.

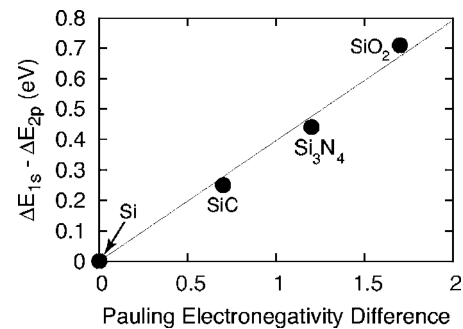

FIG. 1. Correlation between ΔE_{1s}-ΔE_{2p} and Pauling electronegativity difference.

Figure 1 shows a correlation between the relative chemical shift and the Pauling electronegativity for Si and the Si compounds including SiC, Si_3N_4, and SiO_2. It is clearly seen that the relative chemical shift for the Si compounds linearly correlates with the Pauling electronegativity difference between Si and the counter atom in the Si compounds, which corresponds to charge transfer between them. This finding indicates that the relative chemical shift is an excellent indicator for the valence charge of the Si atoms in Si compounds even for the ultrathin Si_3N_4 film and the SiO_2 film formed on Si substrates because it is free from both the Madelung contribution and the image charge contribution.

Furthermore, we have found a correlation between the dielectric constant ε and ΔE_{1s}-ΔE_{2p} values, as shown in Fig. 2. The vertical axis shows the $(\varepsilon-1)/(\varepsilon+2)$ values for the Si compounds obtained from literature[17] ($\varepsilon=12.0$ for Si, 6.7 for SiC, 3.9 for Si_3N_4, and 2.17 for SiO_2), while the horizontal axis shows the ΔE_{1s}-ΔE_{2p} values that we have measured by XPS. It is seen that there is a reasonably good linear relationship between them. Figure 2 shows that the ΔE_{1s}-ΔE_{2p} values give a very good estimation of the dielectric constants for the Si compounds. Recently it has been reported that the polarizability of an atom is associated with the effective charge which reflects covalence, charge transfer, and hybridization for the chemical bonds of the atom.[18] We tentatively speculate that the ΔE_{1s}-ΔE_{2p} values of Si atoms in the Si compounds are good indicators of the effective charge. Thus the ΔE_{1s}-ΔE_{2p} values are expected to have a good correlation with the polarizability of Si bonds in the Si compounds

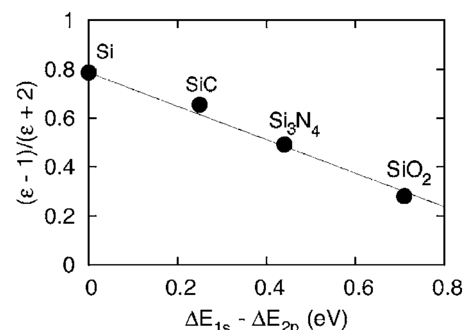

FIG. 2. Correlation between ΔE_{1s}-ΔE_{2p} and dielectric constant ε.

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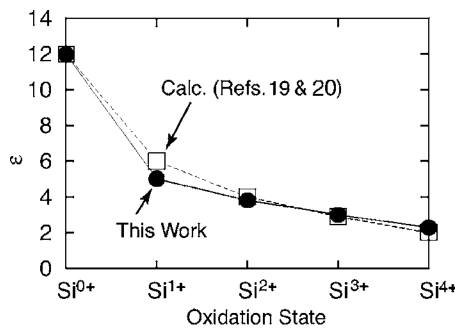

FIG. 3. Dielectric constant deduced from measured ΔE_{1s}-ΔE_{2p} values.

and can give a good estimation of the dielectric constant through the Clausius-Mossoti equation, which describes a relation between the polarizability and the dielectric constant. Since a Dirac-Fock self-consistent field calculation for free atoms and ions showed that the relative chemical shift is small if two core levels concerned have the same principle quantum number,[10] the difference of core-level binding energy shifts for Si 2*s* and Si 2*p*, ΔE_{2s}-ΔE_{2p}, for various Si compounds which are obtained by using XPS with a conventional Al $K\alpha$ x-ray source would have less information about the effective dielectric constant.

Then we applied the above findings to Si intermediate oxidation states formed at the SiO_2/Si interface, namely, Si^{1+}, Si^{2+}, and Si^{3+}, considering them to be included in Si compounds. We measured ΔE_{1s}-ΔE_{2p} values for the intermediate oxidation states and estimated the local dielectric constant for each intermediate oxidation state from the solid line as shown in Fig. 2. Figure 3 shows a plot of the local dielectric constant deduced from the measured ΔE_{1s}-ΔE_{2p} values as a function of the number of oxidation states. It is seen that the local dielectric constant increases with decreasing number of oxidation states. In addition, it can be seen that the local dielectric constant deduced from the present study is in good agreement with the local dielectric constant into which Giustino *et al.*[19] and Giustino and Pasquarello[20] converted the microscopic polarizability obtained by first-principles calculations. Note that this is a direct measurement of the local dielectric constant, which can be compared with a first-principles calculation. We therefore conclude that the present approach for estimating the dielectric constant is reasonably useful for studying a local dielectric constant in thin dielectric films, such as gate stacked dielectric films in advanced Si large-scale integrated circuits.

In summary, we measured the relative chemical shift between Si 1*s* and Si 2*p*, ΔE_{1s}-ΔE_{2p}, for various Si compounds including SiC, Si_3N_4, and SiO_2 using high-resolution high-energy x-ray radiation. We found that the ΔE_{1s}-ΔE_{2p} values were in very good correlation with the dielectric constant values of the Si compounds. Using this relation, we deduced the local dielectric constants for all the Si intermediate oxidation states, which were in good agreement with the values predicted by a first-principles calculation. The present approach for estimating the dielectric constant is quite useful for studying a local dielectric constant in thin dielectric films, such as gate stacked dielectric films in advanced Si large-scale integrated circuits.

The authors express sincere thanks to K. Kobayashi and Y. Tamenori from JASRI/SPring-8 and Y. Takata and S. Shin from RIKEN/SPring-8 for their help in the present study. The synchrotron radiation experiments were performed at SPring-8 with the approval of Japan Synchrotron Radiation Research Institute as a Nanotechnology Support Project of The Ministry of Education, Culture, Sports, Science and Technology. This work was partially supported by the Ministry of Education, Science, Sports and Culture through a Grant-in-Aid for Scientific Research (A) (15206006) and (C) (15560025), (B) (18360026), and partially by the Ministry of Economy, Trade and Industry and the New Energy and Industrial Technology Development.

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