Enhancement of Si oxidation by cerium overlayers and formation of cerium silicate

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The oxidation of Si(100) surfaces covered with 3 Å Ce was studied by high-resolution photoemission spectroscopy. The oxygen uptake was found to be enhanced by orders of magnitude by the presence of Ce. Because of chemical reaction between Ce and Si, a mixed oxide with a Ce:Si:O composition ratio of 1:1:3 is formed. The sharp photoemission spectra of this oxide indicate the formation of a well-defined compound in which both Ce and Si are in a 3 + oxidation state.

The oxidation of semiconductors is of vital importance in the production of electronic devices to generate insulating layers as well as for masking purposes, and has been studied extensively by numerous experimental techniques.[1] To obtain oxide layers of high quality and sufficient thickness it is often necessary to oxidize under fairly high pressure at high temperature. The oxidation of Si, for example, is normally performed at 1000 °C in O_2 atmosphere. These conditions are required to increase the oxygen uptake and to allow for a high enough mobility of the diffusing species. It is desirable, however, to perform oxidation at temperatures lower than used presently because not only oxygen but also dopants may diffuse at higher temperatures. A way to overcome the low oxygen uptake of Si is to introduce a metal which may act as a catalyst for the oxidation. Some experiments of this kind have been performed by Abbati *et al.*[2] who studied the oxidation of Si—noble-metal interfaces. They found a significant enhancement of the oxygen uptake not only for noble metals, but also for Pd. The chemical shift of the Si core line indicated formation of SiO_2 in the presence of noble metals, but a lower oxide for Pd. Pd reacts with Si at room temperature to form Pd_2Si, whereas the reaction of noble metals is much weaker. It was suggested that the rate of silicide formation is of importance for the oxidation of metal-covered Si. The influence of 0.4–2 Å Al on the oxidation of Ge was investigated by Katnani *et al.*[3] The oxidation rate was found to be increased for high exposures ($\geq 10^6$ L). [1 langmuir (L) $\equiv 10^{-6}$ Torr sec.] The initial oxidation phase showed similarities to the oxidation of metallic Al rather than a Ge/Al oxide.

In this paper we report results of oxidation experiments of Si(100) surfaces covered with Ce overlayers. The experiment was motivated by the finding that the oxidation of Nb is greatly enhanced by the presence of Ce on the surface.[4] This enhancement of oxidation is connected to a valence change between 3 + and 4 + of the oxidized Ce.[5] Rare earths which do not form oxides of different valences do not affect the oxidation of Nb.[6] The results suggest that it may be possible to enhance Si oxidation by the presence of Ce. However, an important difference between the Ce-Nb and Ce-Si interfaces is that Si reacts with Ce,[7-9] whereas Nb does not.[4] Oxidation of Ce compounds always leads to a trivalent oxide, and therefore it is not clear whether the mechanism proposed for the cata-lytic oxidation of Nb will also be effective in enhancing the oxidation of Si.

The interaction of Si and Si-Ce interfaces with O was studied by high-resolution core level and valence photoemission. The experiments were performed at the National Synchrotron Light Source at Brookhaven National Laboratory (Upton, NY) with a $\frac{6}{10}$-m grazing-incidence toroidal grating monochromator[10] in combination with an ellipsoidal mirror analyzer. The combined resolution of monochromator and spectrometer was 0.25 eV. The photon energy was varied between 110 and 150 eV in order to emphasize surface or bulk emission from the Si $2p$ core level. The contribution of Ce states to the valence photoemission was studied by tuning the photon energy to 120 eV (112 eV), where the Ce $4f$ and to some extent also the $5d$ cross sections are resonantly enhanced (suppressed), respectively.[11] The samples were p-type Si(100) wafers which were cleaned by flashing to 900 °C in a base vacuum of 10^{-10} Torr. Surface cleanliness was assessed by the disappearance of oxide emission on the high-binding-energy (BE) side of the Si $2p$ core-level spectrum, and by the presence of the surface core level at a BE reduced by 0.5 eV compared to the bulk. An example is shown in Fig. 1. Ce was evaporated from a W filament at a rate of 1–3 Å per minute in a base vacuum of 10^{-10} Torr, while the film thickness was monitored with a quartz microbalance. Normally the film thickness can also be estimated from the core-level intensities. However, the chemical reaction between Ce and Si makes this difficult. The line shape of the Si $2p$ line is a better indication of the thickness of the Ce overlayer.[7-9,12] While we studied the effect of 2–16-Å-thick cerium overlayers, in this paper we report results only for low coverage.

In Fig. 1 a sequence of Si $2p$ photoemission spectra is shown for a Ce coverage of 3 Å which is close to 1 monolayer (ML). The reaction between Ce and Si shifts part of the Si $2p$ emission to lower binding energy due to the charge transfer from Ce to Si. Annealing at moderate temperatures (600 °C) leads to a sharpening of the spectrum, and an overall shift towards higher BE. The leading peak is at the same BE as the leading peak for larger coverage, so that it can be assigned to $CeSi_2$.[12] Before annealing the threshold is at the same energy; this shows that already for 1 ML coverage the fully reacted species is present. On the (111) surface it was only observed for
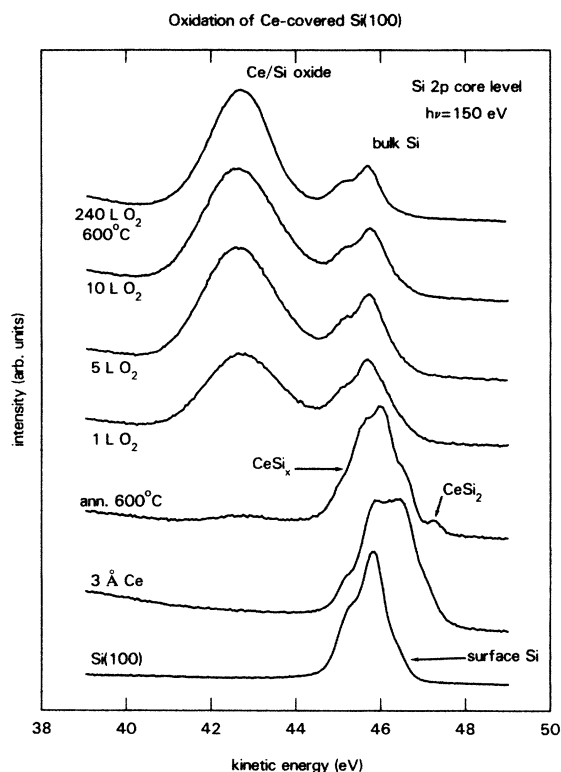
Oxidation of Ce-covered Si(100)

FIG. 1. Si $2p$ core-level spectra taken with 150 eV photons (escape depth 5 Å) after Ce evaporation and subsequent oxygen exposure. The clean surface (bottom) clearly shows spin-orbit splitting and a surface shift. A portion of the Si surface atoms interacts with Ce; this leads to a shift to smaller binding energy and larger width. The annealed surface shows a sharper line at higher average binding energy, indicating a decrease of the average Si-Ce coordination. The leading peak can be assigned to $CeSi_2$. Oxygen exposure immediately yields a Si-Ce oxide with a 3-eV chemical shift of the Si core line.

coverages larger than 4 ML.[8] The average Si:Ce ratio is, however, smaller than 1:2 because the major portion of the Si emission is between clean Si and $CeSi_2$. Exposure to oxygen leads to dramatic changes in the spectrum: a Si-oxide peak appears at 3 eV higher BE, while the emission from the unreacted and reacted Si decreases. For 1 L O_2 the oxidized peak amounts already to 50% of the total intensity. Further exposure leads to a further increase of Si oxide, but at a much smaller rate, as is clear from the relatively small change of the spectrum for 5 and 10 L doses. Finally, thermal oxidation at 600 °C sharpens the oxide peak compared to the room temperature spectra, but does not affect the ratio between oxidized and unoxidized Si any more.

In Fig. 2 the room-temperature oxidation in the presence of Ce is compared to oxidation of clean Si.[13] If a clean Si(100) surface is exposed to 10 L of nonexcited oxygen, the surface core level on the low-BE side of the $2p$ line is removed, and Si-oxide features appear on the high-BE side with shifts of 1 to 2 eV. The coverage which can be deduced from the intensity ratio is a fraction of a monolayer, with Si bonding to one and two oxygens. In the presence of 1 ML Ce the same oxygen dose makes the
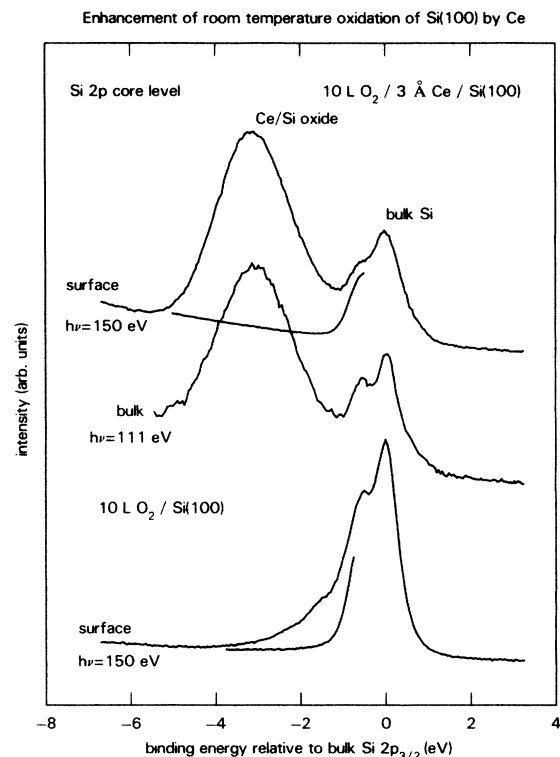
Enhancement of room temperature oxidation of Si(100) by Ce

FIG. 2. Room temperature enhancement of Si oxidation by 1 monolayer of Ce. After exposure to 10 L of O_2 the Ce covered surface exhibits a strong oxide peak shifted by 3 eV to higher binding energy whereas the uncoated Si(100) shows only weak suboxide features near 2 eV. The background curves are for a clean surface.

Si-oxide species the dominant one, with $\simeq 70\%$ of the intensity. Comparing bulk- and surface-sensitive spectra, it is noticeable that the oxide signal is slightly smaller in the bulk-sensitive spectrum. Assuming the electron mean-free path to be similar to that in SiO_2 we estimate that oxidation has penetrated to a depth of about 10 Å.

Figure 3 shows the effect of Ce on the thermal oxidation of Si. Without Ce one obtains an inhomogeneous oxide layer in which the Si atoms have between 1 and 3 (possibly 4) bonds with oxygen.[14] The oxide contribution is larger in the surface-sensitive spectrum, and on the basis of an escape depth of 5 Å the thickness is estimated to 7 Å.[14] The oxide peak obtained after the same oxidation procedure with 1 ML Ce on the surface is first of all much narrower than without Ce being present. It is the dominating feature in the spectrum, containing 70% of the total intensity. This shows that the oxide layer has a larger thickness than the one forming on clean Si. We know from valence-band photoemission that Ce is also reacting with oxygen, therefore the region very close to the surface is a mixed Si-Ce oxide. Note from Fig. 3 that the ratio of the intensities of the oxide peak to the silicon peak is nearly the same for bulk- and surface-sensitive spectra with Ce present. This demonstrates that oxidation has proceeded further into the depth of the crystal than without Ce being present.
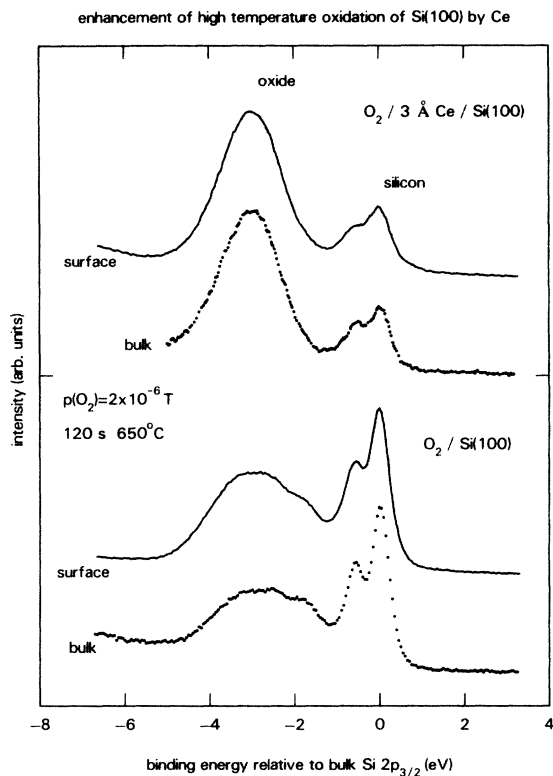
Figure 4 shows a comparison of the valence-band spec-

FIG. 3. High temperature enhancement of Si oxidation in the presence of Ce. The oxide formed on clean Si is much thinner than with Ce as indicated by the smaller intensity ratio oxide/silicon. In order to achieve the same oxide thickness a 10^3 times larger oxygen exposure as well as higher temperature is required (compare with Ref. 14).

FIG. 4. Valence-band spectra of a thin film of SiO_2 and oxide grown in the presence of 1 monolayer of Ce. Oxidation at 600 °C leads to a sharpening of the valence-band features and removal of metallic emission at E_F. The bandwidth of the Ce-Si oxide is 40% smaller than that of SiO_2. Neglecting the fully localized $4f$ level one finds the top of the valence band 4 eV below E_F.

tra of a thin SiO_2 film and a thermal oxide of Si(100) covered with 1 ML of Ce. The spectrum of the Ce-covered surface was obtained with 112-eV photon energy where the $4f$ cross section is small. At 120 eV it is resonantly enhanced, and the peak at -2.7 eV increases by a factor of 7 if the spectra are normalized at -6 eV. Apart from this difference the on- and off-resonance valence-band spectra are identical. Therefore we can assign the peak at -2.7 eV to the Ce $4f^1$ initial state, whereas the emission between -4 and -11 eV can be attributed to the valence-band states consisting of O $2p$, Ce $5d$, and Si $3s,p$ states. We note that the valence band shows three structures and is much narrower than the structures found for SiO_2. The dominant feature at -6 eV (-7 eV in SiO_2) is due mainly to O $2p$ states. The lowest feature is at -10 eV in the Si-Ce oxide, and at -13.5 eV in SiO_2. The smaller width of the valence states indicates that Ce $5d$ states are hybridizing with the other states and thereby lead to a narrowing of the band. The sharp lower edge of the valence band rules out any presence of Ce-free SiO_2 within the probing depth.

In SiO_2 the Si atoms have four bonds with oxygen, resulting in a 3.8-eV chemical shift of the Si $2p$ core line. The 3 eV shift for the Si-Ce oxide indicates that Si is in a 3 + oxidation state. The disappearance of all the emis-
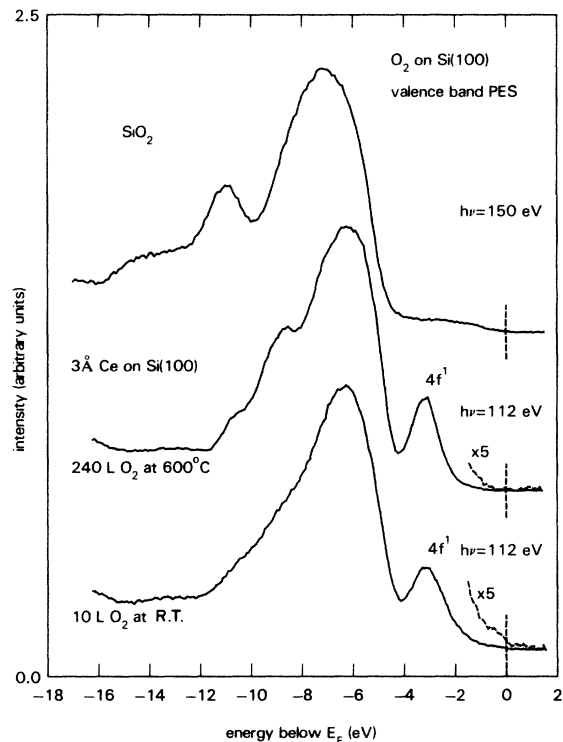
sion from the Ce valence states except the $4f$ state shows that Ce also is in a 3 + oxidation state. The intensities of the Si $2p$ and Ce $4d$ core levels show that the Ce:Si ratio is $\simeq 1$.[12] Thus, to account for the oxidation states of both Si and O the overall Ce:Si:O composition ratio must be 1:1:3. The single cerium silicate known to us is the cerium pyrosilicate with a composition of $Ce_2Si_2O_7$, and it is possible that in our experiments an oxygen-deficient pyrosilicate has formed. $Ce_2Si_2O_7$ is orthorhombic with space group $P2_12_12_1$.[15] The smallest cell dimension of cerium pyrosilicate, 5.400 ± 0.005 Å, deviates only 0.55% from the lattice constant of (100)Si. The sharp features in the Si-Ce oxide valence-band spectrum as well as the sharpening of the Si $2p$ core spectrum are strong evidence showing that a well-defined compound is formed upon annealing. The close similarity of the lattice constants may even facilitate epitaxial growth of the silicate on Si(100). Further experiments are needed to confirm this suggestion.

Our experiments show that it is possible to enhance the oxidation of Si by the presence of Ce. In order to achieve the same oxide thickness we achieved at 650 °C, a 10^3 times larger oxygen exposure as well as a higher temperature is needed (compare with Ref. 14) and much more at room temperature. Ce does not act as a genuine catalyst as was found for Nb. This is due to the Ce-Si reaction

which already occurs at room temperature. Oxidation of such a reacted interface leads to a mixed Si-Ce oxide. Analysis of core-line binding energies and intensities shows that both Si and Ce are in 3 + oxidation states, and that the Ce:Si concentration is 1:1. The valence-band narrowing is a sign of Ce $5d$ mixing with the O and Si valence states, and is additional evidence for a mixed Si-Ce oxide. Although oxidation of Si with a Ce overlayer yields a mixed Si-Ce oxide the exposures and temperatures required are much lower than required for Si oxidation without Ce being present. The sharp photoemission features show that a well-defined compound is formed. As the $4f$ state is fully localized and does not contribute to the conductivity one has an effective band gap of 4 eV below E_F. The total band gap is expected to be $\simeq 8$ eV. Analysis of the Si $2p$ core lines shows that the interface to the substrate is much sharper than the Si/SiO$_2$ interface. The dielectric constant of the oxide is expected to be higher than that of SiO$_2$. The results presented here indicate the formation of an ordered cerium silicate, which may grow epitaxially on Si(100). Cerium silicate or silicates containing other rare earths may present an alternative to SiO$_2$ used presently as an insulator in semiconductor devices.

[1]A. Atkinson, Rev. Mod. Phys. 57, 437 (1985).
[2]I. Abbati, G. Rossi, L. Calliari, L. Braicovich, I. Lindau, and W. E. Spicer, J. Vac. Sci. Tech. 21, 409 (1982).
[3]A. D. Katnani, P. Perfetti, Te-Xiu Zhao, and G. Margaritondo, J. Vac. Sci. Techn. A1, 650 (1983).
[4]E.-E. Latta and Maria Ronay, Phys. Rev. Lett. 53, 948 (1984).
[5]Maria Ronay and E.-E. Latta, Phys. Rev. B 32, 5375 (1985).
[6]E.-E. Latta and Maria Ronay, J. Vac. Sci. Tech. A4, 1626 (1986).
[7]M. Grioni, J. Joyce, S. A. Chambers, D. G. O'Neill, M. del Guidice, and J. H. Weaver, Phys. Rev. Lett. 53, 2331 (1984).
[8]M. Grioni, J. Joyce, M. del Guidice, D. G. O'Neill, and J. H. Weaver, Phys. Rev. B 30, 7370 (1984).
[9]A. Fujimori, M. Grioni, J. Joyce, and J. H. Weaver, Phys. Rev. B 31, 8291 (1985).
[10]F. J. Himpsel, Y. Jugnet, D. E. Eastman, J. J. Donelon, D. Grimm, G. Landgren, A. Marx, J. F. Morar, C. Oden, R. A. Pollak, J. Schneir, and C. A. Crider, Nucl. Instrum. Methods 222, 107 (1984).
[11]A. Franciosi, J. H. Weaver, N. Martensson, and M. Croft, Phys. Rev. B 24, 3651 (1981); J. W. Allen, S.-J. Oh, I. Lindau, J. M. Lawrence, L. I. Johansson, and S. B. Hagstrom, Phys. Rev. Lett. 46, 1100 (1981).
[12]F. U. Hillebrecht et al. (unpublished).
[13]G. Hollinger and F. J. Himpsel, J. Vac. Sci. Tech. A1, 640 (1983).
[14]G. Hollinger and F. J. Himpsel, Appl. Phys. Lett. 44, 93 (1984).
[15]Yu. I. Smolin and Yu. F. Shepelev, Acta Cryst. B26, 484 (1970).