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Reactions at the Gd-Si(111)7×7 interface: Promotion of Si oxidation

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The interactions of various Gd-Si(111) interfaces and surface phases of Gd silicides with oxygen have been investigated by uv and soft-x-ray photoelectron spectroscopy using synchrotron radiation and Auger-electron spectroscopy. At the "reacted" Gd-Si interfaces the room-temperature oxidation of Si is substantially enhanced. In contrast, the epitaxial Gd disilicide–type phases, which are formed after annealing the room-temperature interfaces at elevated temperature, are much less reactive towards O_2; however, reaction can be initiated after an initial induction period. A pronounced dependence of the oxidation rate on Gd coverage is found, which emphasizes the importance of the concentration of Si atoms having reacted with Gd. The Gd component of the interface is also oxidized, and the oxidation product, which is characterized by a Si $2p$ core-level shift of $\simeq 3$–3.3 eV, is insulating with a band gap of several electron volts.

I. INTRODUCTION

The oxidation of silicon and the Si-SiO_2 interface is of fundamental importance in Si-based semiconductor research and technology.[1] A wealth of information is therefore available in the literature on the interaction of oxygen with silicon surfaces.[2] Since it has been established that the room-temperature oxidation of Si with molecular oxygen is a slow process leading to lower oxidation states of Si than SiO_2, a search for oxidation promoters has been initiated to improve the oxidation kinetics. Obvious candidates are thin metal layers present at the semiconductor surface, because it might be expected that the dissociation of molecular O_2 (a possible kinetic bottleneck in the room-temperature oxidation of Si) is promoted by metallic phases. And, indeed, a great number of studies involving noble metals,[3] transition metals,[4] alkali metals,[5] and rare-earth metals[6] have reported as a general tendency the enhanced room-temperature oxidation of Si in the presence of metal layers. In most cases, however, the oxidation product is a lower Si oxide than SiO_2. The metallic components have been found to be oxidized in those cases where thermodynamically stable metal oxides are known. Of particular interest in this context is the report of a rare-earth metal (Ce) as an oxidation promoter,[7] for which a band gap of several electron volts was derived from photoemission experiments, and a ternary reaction product in the form of a silicate has been postulated. In the present paper we will show how Gd, which is an exclusively trivalent rare-earth element, enhances the room-temperature oxidation of Si.

Oxidation reactions at the Gd-Si(111)7×7 interface were investigated in this work as part of a larger program to study reactivity at rare-earth–silicon interfaces. The evolution of this interface at room temperature and its annealing behavior has been reported elsewhere.[8,9] We have employed Auger-electron spectroscopy (AES), uv photoelectron spectroscopy (UPS), and soft-x-ray photoelectron spectroscopy (SXPS) using synchrotron radiation to characterize the interactions of O_2 with various Gd-Si(111) interfaces. We find that the "reacted" room-temperature interface is remarkably active in catalyzing the room-temperature oxidation of Si, but that the chemical shifts of the Si $2p$ core lines in SXPS suggest an oxidation product that is different from SiO_2. The Gd component is also oxidized as revealed by valence-band UPS, and the possible oxidation product of the interface will be discussed. There is a dependence of the oxidation rate on the Gd coverage, which is important in the discussion of the oxidation enhancement mechanism. However, the ordered Gd disilicide phases, which are formed upon annealing of the room-temperature interface,[9] are much less reactive towards molecular oxygen.

II. EXPERIMENT

The experiments were carried out in two different electron spectrometers with base pressures $\leq 1\times10^{-10}$ mbar. One system contained a concentric hemispherical electron analyzer (Leybold EA 10) for Auger and electron-energy-loss spectroscopy, low-energy electron diffraction (LEED) optics for structure monitoring and the usual facilities for controlled evaporations of metal layers. The second system was an angle-resolving electron spectrometer (modified VG ADES 400), which was attached to either of the TGM2 or TGM3 beamlines of the synchrotron radiation laboratory BESSY in Berlin. The energy resolutions of the two monochromators at $h\nu = 140$ eV was $\simeq 0.3$ eV for TGM2 and $\simeq 0.6-0.7$ for TGM3. This latter resolution, which was compensated by a higher photon flux on TGM3, precluded the separation of the two spin-orbit components of the Si 2*p* core line, but since the silicon chemical shifts upon oxidation are comparatively large it still allowed useful investigations of the interface reactions. The Gd films were evaporated onto Si wafers under strictly comparable conditions in both systems, and Gd coverages were measured with quartz film thickness monitors.

The clean, well-ordered Si(111)7×7 substrate surfaces were prepared by flashing appropriately cut Si wafers (*n*-type, 1–2.5 Ω cm) to 950–1000 °C in a vacuum better than $(2-3)\times 10^{-10}$ mbar during flashing. Gd was evaporated from W coils after careful outgassing of the starting material. Oxygen dosing was performed from the system ambient via a leak valve.

III. RESULTS

The oxidation enhancement of Si at the Gd-Si(111) interface as compared to the clean Si(111)7×7 surface is demonstrated by the Si 2*p* core-level spectra in Fig. 1. After O_2 exposure of 1000 L [1 langmuir (L) = 1×10^{-6} Torr sec] at room temperature there is only weak emission intensity on the higher-binding-energy side of the bulk Si signal (the relative energy zero) on clean Si(111), but a prominent feature at +2.9 eV is observed for the 12-Å Gd-Si(111) interface. Whereas the clean Si surface is therefore only mildly oxidized, the Gd-Si interface shows signs of pronounced oxidation. For comparison a Si 2*p* spectrum of a thin layer of SiO_2 on top of Si (the "native oxide" layer) is also given in Fig. 1, top curve; the arrows above indicate Si 2*p* positions for Si bonded to one, two, three, or four oxygen atoms, as derived by Hollinger and Himpsel.[10] The oxidation product at the Gd-Si interface is thus different from SiO_2, with a Si 2*p* core-level binding energy suggesting an oxidation state between +3 and +4 on the basis of binary Si oxides.[10] However, a ternary compound of the silicate type may also be possible, as discussed further below.

Figure 2 shows Si 2*p* spectra of Gd-Si interfaces with two different Gd coverages, 4 Å Gd [$\simeq 1.5$ monolayers (ML)] (a) and 12 Å Gd ($\simeq 4.5$ ML) (b), as a function of O_2 exposure. The better resolution of the spectra in Fig. 2(a) allows a shoulder to be distinguished at the lower-binding-energy side of the main structure which is due to Si atoms having reacted with Gd.[8] This shoulder disappears immediately after O_2 exposure, thus indicating that those Si atoms that have reacted with Gd are oxidized first. The evolution of the oxidized Si 2*p* components occurs gradually until a saturation position is reached after about 100 L O_2 with a Si 2*p* shift of $\simeq 3$ eV. Comparing the spectra of Fig. 2(a) with those of Fig. 2(b) reveals significant Gd coverage dependence of the oxidation behavior. The Si 2*p* spectrum of the 12-Å Gd-Si interface—corresponding to the "fully reacted, intermixed" interface, see Ref. 8—is composed by Si 2*p* bulk emission and by a chemically shifted Si component at 0.65 eV lower binding energy due to the Si—Gd bond.[8] The lower resolution of the spectra presented in Fig. 2(b) precludes singling out the reacted components, and a broadened and apparently shifted single peak (−0.6 eV) is obtained. After exposure to O_2 the resultant spectra are sharper and shifted back to the original Si 2*p* bulk position. This is due to the strong reduction in size of the chemically shifted component, indicating the interaction of the "reacted" Si atoms with oxygen. Note that here the oxidized Si 2*p* components are saturated after $\simeq 10$ L O_2. The 12-Å Gd-Si interface is therefore much more reactive towards O_2 than the lower coverage interface. The oxidized Si 2*p* components of the oxygen saturated interfaces shift slightly to higher binding energy upon heating, until a stable reaction product with a Si 2*p* shift of 3.3 eV is reached.

The valence-band photoemission spectra of Fig. 3 demonstrate that the Gd component of the interface is

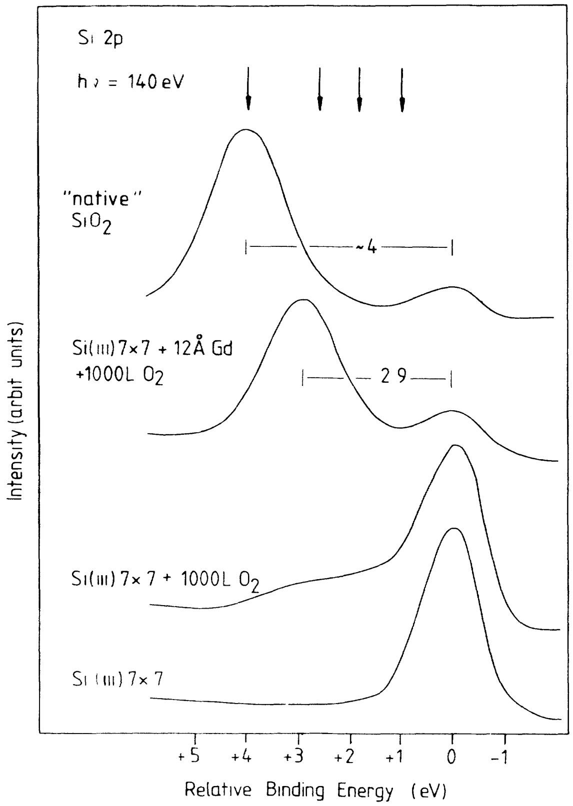

FIG. 1. Si 2*p* core-level spectra of Si(111)7×7 and of the Si(111)7×7+12 Å Gd interface exposed to 1000 L O_2 at room temperature. For comparison, a spectrum of the so-called "native" SiO_2 layer on Si is included, top curve. The arrows indicate Si 2*p* positions of Si atoms coordinated to one, two, three, and four oxygen atoms as derived in Ref. 10. Photon energy $h\nu = 140$ eV.

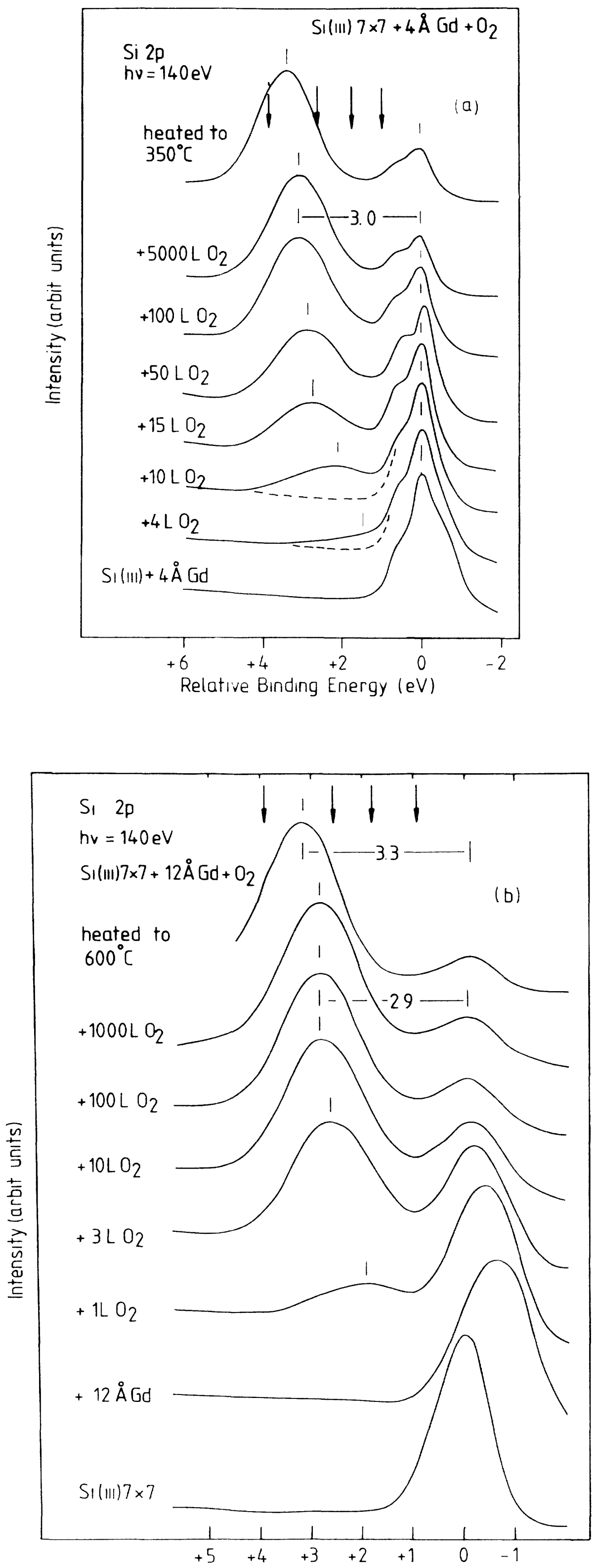

FIG. 2. Si 2p spectra of Si(111)7×7+4 Å Gd (a) and of Si(111)7×7+12 Å Gd (b) exposed to various amounts of O_2. The top curves in both panels show spectra obtained after heating the oxidized interfaces to the indicated temperatures. Arrows as in Fig. 1.

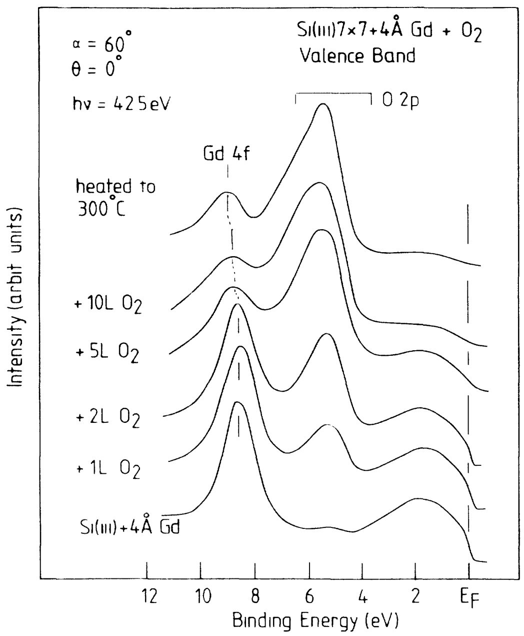

FIG. 3. Valence-band photoemission spectra of Si(111)7×7+4 Å Gd exposed to small doses of O_2. Photon energy $h\nu=42.5$ eV, p-polarized, photon angle of incidence $\alpha=60°$, normal emission $\theta=0°$.

also oxidized. The Gd 4f emission shifts to higher binding energy upon O_2 exposure and the emission near E_f vanishes after 20–30 L O_2. This is a result of the transfer of Gd 5d6s-derived conduction electrons to O 2p valence states, and, as shown previously by oxidation studies on other rare-earth-metal surfaces,[11] indicates conclusively the oxidation of the metal phase. The fully oxidized Gd-Si interface has no emission intensity at E_f and therefore has a band gap of at least 4 eV.

The reactivity of the ordered Gd disilicide phases, which are formed after annealing of the room-temperature Gd-Si systems,[9] is much lower than that of the room-temperature interfaces. This is shown in Fig. 4, where we compare Si 2p spectra of O_2 exposed 4-Å Gd-Si with those of ordered (1×1) Gd disilicide. After 100 L O_2 exposure the (1×1) silicide is barely oxidized, whereas the 4-Å Gd-Si is almost fully reacted. However, oxidation reaction at the ordered silicide surfaces does set in after large O_2 exposures—see spectra after 1000 or 3000 L O_2—but the resulting reaction products appear to be less uniform, as judged from the width of the oxidized Si 2p components. An induction period is therefore necessary to initiate oxidation of the ordered Gd disilicide surfaces.

The quantitative aspects of oxygen uptake of various Gd, Si, and Gd-Si systems, as investigated by AES, are displayed in Fig. 5. The O KLL Auger amplitude as obtained in dN/dE spectra, normalized to the incident electron current, has been plotted versus the O_2 exposure; the Auger signal from the oxidized Gd metal has been set arbitrarily to unity. We note that the O uptake of the clean Si(111)7×7 surface is small, but that Gd metal is rapidly

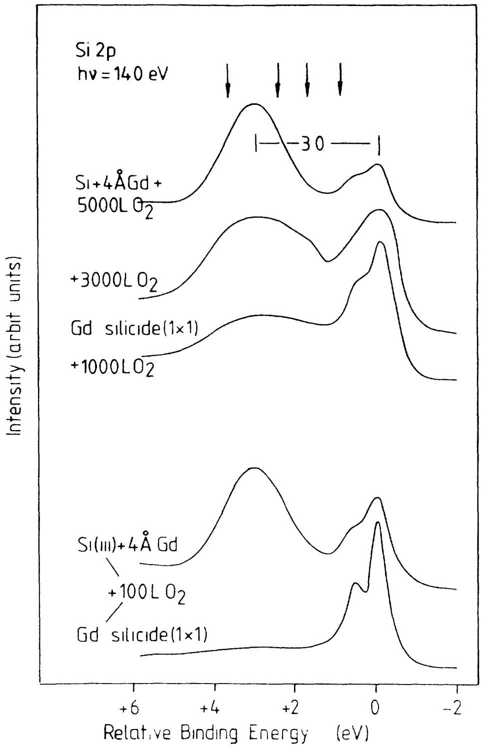

FIG. 4. Comparison of Si $2p$ spectra of Si(111)7×7+4 Å Gd and of an epitaxial Gd disilicide [(1×1) LEED pattern] exposed to O_2. Arrows as in Fig. 1.

oxidized. The initial passivation of the ordered Gd disilicide [data are shown here for the $(\sqrt{3}\times\sqrt{3})$ phase (Ref. 9)] is readily recognized, as is also the Gd coverage effect of the room-temperature interfaces. The Gd-Si systems show no saturation tendencies up to the highest exposures used in this study.

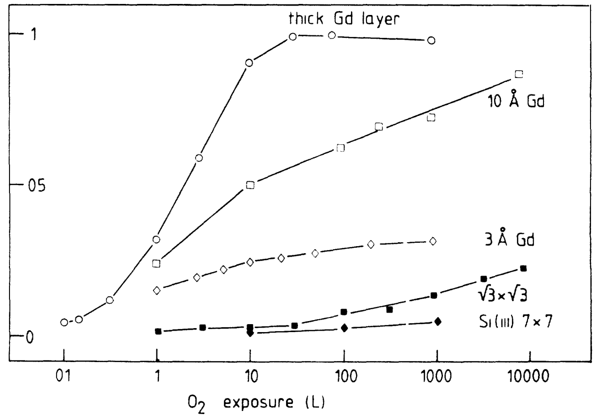

FIG. 5. Oxygen uptake of various surfaces and interfaces as a function of O_2 exposure. The normalized O *KVV* Auger amplitudes are plotted vs O_2 exposure for the clean Si(111)7×7 surface, the $(\sqrt{3}\times\sqrt{3})$ phase of Gd disilicide, the 3- and 10-Å Gd-Si(111) interfaces and for a polycrystalline Gd film surface. The O *KVV* saturation signal of oxidized Gd has been arbitrarily set to unity. Electron primary energy $E_p = 3$ keV.

Some additional Auger observations should be mentioned at this point. The Si *LVV* transition line shapes in $N(E)$ Auger spectra show clearly the oxidation of Si after O_2 exposure of the Gd-Si interfaces, but also reveal the differences from SiO_2.[12] On the "fully reacted" interfaces (Gd coverage $\simeq 8-15$ Å), where the Si *LVV* signal is still about 50–30 % of the clean Si value,[8] exposure to oxygen shows not only the line-shape change towards oxidized Si, but also a decrease of the total amount of Si within the escape depth of the Auger electrons. In addition to being oxidized, it appears that Si atoms are driven away from surface-near regions by the interaction with oxygen. A similar decrease in Auger intensity is not observed for the Gd component of the interface, but the line shape suggests that it is oxidized.

IV. DISCUSSION

The enhanced room-temperature oxidation of silicon in the presence of thin metal layers has been discussed in the literature in terms of two major promoting effects:[3-6] (i) reduced activation energy for the dissociation of O_2 at metal sites and spillover of atomic oxygen to Si , and (ii) disruption of the Si sp^3 lattice by the reaction with metal atoms and easy reaction of the "activated" Si atoms with oxygen. The catalytic aspects of metal atoms in the oxidation process on noble-metal–Si interfaces have been pointed out by several authors,[13-15] but in the systems with strong metal-oxygen affinity it is difficult to speak of a catalytic effect in the classical sense, where the catalyst itself should remain chemically unaltered.

The data presented in Sec. 3 of this paper are supportive of a combination of the two oxidation promoting effects. The dependence of the rate of Si oxidation on the Gd coverage, that is, on the number of "reacted" Si atoms, is consistent with the picture of activation of Si atoms by reaction with Gd. On the other hand, the fact that Gd is oxidized first (see Figs. 3 and 5) suggests that O_2 is dissociated by Gd and that oxidized Gd acts as an oxidizing agent. A pertinent question, however, concerns the chemical identity of the oxidation product at the interface: Is it a mixed oxide of Gd and Si or a ternary compound of the Gd silicate type? On the Ce-Si(100) system Hillebrecht *et al.*[7] have proposed Ce pyrosilicate as the reaction product of the oxidized interface. Note that the chemical shift of the Si $2p$ core lines of Ce-Si plus oxygen is $\simeq 3$ eV, and thus very similar to the one observed here. Gd pyrosilicate, $Gd_2Si_2O_7$, is orthorhombic and contains six $Si_2O_7{}^{6-}$ entities in the unit cell with 12 Gd^{3+} cations to counterbalance the negative charge.[16] The formal oxidation state of Si in the pyrosilicate unit is 4+ and every Si atom is coordinated to four O atoms as in SiO_2; however, due to the very different structure and bonding in the pyrosilicates as compared to SiO_2,[16] it is difficult to predict Si $2p$ core-level shifts. The correlation between a Si $2p$ core-level shift and Si-O coordination as derived for the binary Si oxides by Hollinger and Himpsel[10] is therefore not applicable to the ternary silicates, and in the absence of Si $2p$ core-level data for pyrosilicates the above-mentioned 3-eV core-level shift is of little diagnostic value. The question of mixed oxide or ternary silicate as an oxidation product is therefore difficult to answer at the present time. Nevertheless, as noted previously at the Ce-Si interface[7] an effective band gap >4 eV, presumably of the order of 8 eV,[17] opens up at the Gd-Si interface upon oxidation, as indicated by the valence-band photoemission results. The interface becomes therefore insulating and may be in itself an interesting dielectric layer.

The initial passivation of the ordered Gd disilicide-type phases towards oxidation may be taken as an indication of the structural effect in the oxidation promotion mechanism. $GdSi_{2-x}$ appears to grow epitaxially on Si(111),[9] and the (1×1) and $(\sqrt{3}\times\sqrt{3})$ structures observed by LEED after annealing Gd-Si room-temperature interfaces need large O_2 exposures until reaction in initiated. The Si atoms are regularly coordinated in $GdSi_{2-x}$ to two or three Si atoms in the Si layers of the AlB_2-type compound, and the Si layers are separated by Gd layers.[18] According to a recent structure determination of epitaxial *Y* disilicide[19] the topmost surface layer consists of an ordered Si layer; a similar arrangement is expected for epitaxial Gd disilicide. Obviously, this regular arrangement of Si atoms renders the silicide surface more resistant towards the attack of oxygen than the disordered environment of the room-temperature interfaces. Similar observations have been reported on Au-Si and Cu-Si surfaces with ordered LEED patterns,[20,21] where the correlation between oxidation properties and local environment of Si atoms has been pointed out.

The Auger results mentioned at the end of Sec. III indicate that Si is driven away from the surface as a result of the oxidation reaction. The intermixing of Gd and Si at the interface is thus reversed and a Gd-rich layer (in oxidized form) is built up at the outer surface. The oxidized Gd-rich layer, however, is still able to promote further oxidation of the system, since no clear indication of oxygen saturation is seen in Fig. 5. This behavior at the Gd-Si interface is in contrast to what has been observed in near-noble-metal silicides or in noble-metal–Si alloys:[22] there, the oxidized Si atoms form a uniform layer at the surface and leave a metal-rich phase underneath.

Finally, we wish to comment briefly on the suggestion of Latta and Ronay[23] of the possibility that multiple valencies of Ce atoms play an important role in the oxidation enhancement of Nb in the Ce-Nb system. The present results on the Gd-Si interface demonstrate that an exclusively trivalent rare-earth metal acts as a promoter for the room-temperature oxidation of Si, and that the valence change of rare-earth atoms in itself is not a necessary condition to stimulate enhanced oxidation of Si. Our results are consistent with those of Chang *et al.*,[24] who found that promotion of oxidation takes place for Sm in the trivalent state, but not in the divalent state. Taken together this suggests that the valency which is present in the corresponding stable rare-earth oxide supports the oxidation enhancement.

V. SUMMARY

Using photoemission techniques with synchrotron radiation and AES we have investigated the room-temperature oxidation of Si at Gd-Si(111) interfaces. The room-temperature oxidation of Si is greatly enhanced at the "reactive" Gd interfaces, and the Gd coverage dependence of the oxidation rate emphasizes the importance of Si atoms having reacted with Gd, that is, with "lifted sp^3 configuration." The Gd component of the interface is also oxidized, and the oxidation reaction product, which is characterized by a Si $2p$ chemical shift of $\simeq 3-3.3$ eV, exhibits a band gap of several electron volts. The detailed chemical nature of the Gd-Si oxidation product, however, is still unclear. In contrast to the very reactive room-temperature Gd-Si interfaces the annealed, ordered Gd disilicide phases are much less reactive towards molecular O_2 and show initially a passivating behavior.

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