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Physical and chemical effects at rare-earth-metal-SiO_2–Si structures

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Thin rare-earth-metal overlayers (Pr, Eu, Gd, and Yb) have been deposited in an ultrahigh-vacuum environment onto thin SiO_2 layers on Si(111) substrates, and the resulting metal-insulator-semiconductor (MIS) structures have been investigated by photoelectron spectroscopy of core and valence states using synchrotron radiation, Auger electron spectroscopy, and by inverse-photoemission spectroscopy. The spectroscopic data, recorded as a function of metal coverage, clearly reveal the chemical reaction between the SiO_2 and the rare-earth-metal atoms at room temperature for coverages >1 monolayer. The reaction yields metal silicide and metal oxide, thereby reducing the SiO_2. At low metal coverages (<1 monolayer) the Si $2p$ components of the Si substrate and of the SiO_2 layer display different core-level shifts to higher binding energy, which are discussed in terms of changes of band bending in the Si as a result of charge injection, and in terms of changes of the band offset at the buried SiO_2-Si interface; the latter is possibly mediated by rare-earth-atom diffusion through the insulating layer. Annealing of the reacted MIS structures to $\sim 500\,^{\circ}C$ induces an additional solid-state reaction, and the results are consistent with the formation of silicate islands on the Si substrate.

I. INTRODUCTION

Metal-insulator-semiconductor (MIS) elements are widely used in modern electronic-device technology, e.g., in field-effect transistors,[1] as chemical sensors,[2] or in solar-cell devices.[3] Rare-earth metals as gate materials have attracted interest in the development of solar cells and recently in chemical sensors to possibly modify the sensor performance.[4] Besides this direct involvement in technological products, the physics and chemistry of MIS structures remains of fundamental scientific interest. For example, the knowledge of the chemical reactivity of a wide variety of metals on thin insulating layers on semiconductors is of importance in finding suitable metallization schemes, which in turn may then further technological progress in the search for stable contacts.

In this work we have investigated the interfacial reactivity of rare-earth (R) metals deposited onto ultrathin films of SiO_2 on top of Si(111) substrates. Thin layers of Pr, Eu, Gd, and Yb have been evaporated under ultrahigh-vacuum (UHV) conditions onto SiO_2 on Si, and the resulting structures have been characterized spectroscopically by photoelectron spectroscopy with the use of synchrotron radiation, by Auger-electron spectroscopy, inverse photoemission spectroscopy (IPES), and work-function measurements as a function of metal coverage and annealing conditions. The results of this comprehensive spectroscopic study can be divided somewhat arbitrarily into physical and chemical effects. With regard to the physical effects, we will sum up effects which can be related to charge transport across the insulating layer, but also to band-offset alterations at the semiconductor-insulator interface. On the other hand, by chemical effects we can denote the reactive interactions between R-metal atoms and the SiO_2-Si substrate yielding interfacial compounds. Thus, in terms of physical effects we have observed changes of band bending at the Si-SiO_2 interface at small metal coverages and possibly also changes of the band alignment between the Si and SiO_2. Perhaps dominant, however, are the chemical effects, such as the formation of R silicides and oxides and the partial reduction of SiO_2 as a result of metal deposition at room temperature, and the formation of ternary compounds of the silicate type at elevated temperature. These chemical effects prevail in particular at higher metal coverages. The results of Pr will serve as prototypes to illustrate the various effects, whereas only selected data will be presented for the other R systems to highlight similarities and differences between them.

II. EXPERIMENT

The experiments for this study have been performed in a number of different UHV systems and spectrometers. Photoelectron spectroscopy measurements [ultraviolet photoemission spectroscopy and soft-x-ray photoemission

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spectroscopy (SXPS)] have been carried out with use of synchrotron radiation at the synchrotron radiation laboratory BESSY in Berlin at the TGM2, TGM3, and HE-TGM2 beamlines; the spectrometers attached to these beamlines were a modified VG ADES 400 angle-resolving spectrometer[5] and a spectrometer with an ellipsoidal mirror electron analyzer,[6] respectively. The combined resolution monochromator-electron-energy analyzer were 0.3–0.4 eV for valence-band and core-level photoemission spectra on all beamlines and spectrometers. Auger spectra were measured with a concentric hemispherical electron-energy analyzer (Leybold Heraeus LH10), and the IPES spectra in isochromat mode were recorded with a Geiger-Müller-type photon detector with a SrF_2 entrance window using an electrostatically focused electron gun with a BaO cathode. The IPES spectrometer detects photons of $h\nu=9.5$ eV with an overall resolution of ≈ 0.35 eV.[7] The IPES electron gun could also be used for work-function measurements according to the target current spectroscopy method.[8] All systems contained facilities for surface cleaning and preparation, and base pressures of $<1\times10^{-10}$ mbar were routinely achieved. The *R* metals were evaporated from vacuum degased W coils, and metal coverages and mean film thicknesses were measured with quartz film thickness monitors (Inficon). The evaporator-sample-film thickness monitoring geometries were strictly comparable in the different experimental chambers.

The experiments were performed in part on so-called "native oxide layers" on Si(111) single-crystal wafers (*n* type, ~ 2.5 Ω cm), which are 10–20-Å-thick layers of amorphous SiO_2 on Si substrates formed by a chemical passivation procedure of the manufacturer (Wacker-Chemitronic). The samples were gently degased and heated to 550 °C in vacuum to remove surface contaminants. Auger spectra after pretreatment showed no signals other than those of Si and O. These samples were used only in an experimental evaporation series. The *R* metals were also evaporated onto *in situ* thermally oxidized Si(111) surfaces, which were prepared following the procedure described by Himpsel *et al.*[9] to yield 15-Å-thick SiO_2 layers. The results obtained on the two types of oxides were very similar, and we will therefore not distinguish them explicitly in the following sections.

III. RESULTS

A. Praseodymium

Figure 1 displays the Si 2*p* core-level spectra of SiO_2/Si as a function of PR coverage and after annealing to ~ 500 °C. The spectra have been recorded in normal emission geometry with a photon energy $h\nu\approx 140$ eV and have been normalized to constant photon flux. The pristine SiO_2/Si shows Si 2*p* components due to the underlying Si substrate—its $2p_{3/2}$ component is taken as the zero of the relative binding energy scale—and at ~ 4 eV higher binding energy the Si 2*p* components of the oxide layer. Due to structural inhomogeneity in the amorphous oxide layer the spin-orbit components are unresolved here. Deposition of Pr onto the SiO_2 surface at

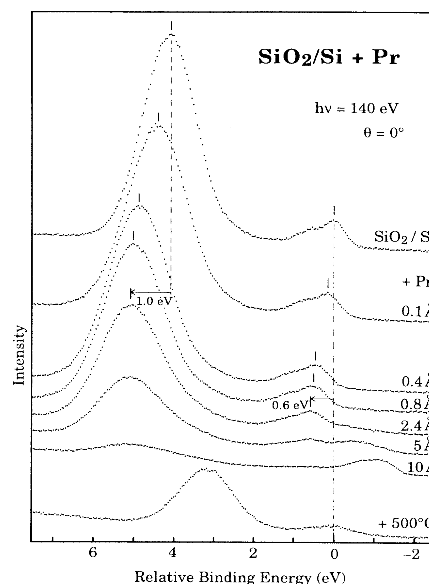


FIG. 1. Si 2*p* core-level spectra of SiO_2/Si as a function of Pr coverage, and after heating the 10-Å Pr surface to ~ 500 °C; photon energy $h\nu\approx 140$ eV, normal emission geometry. The spectra have been normalized with respect to photon flux.

room temperature introduces a number of spectral changes: (i) the Si 2*p* substrate components shift to higher binding energy up to ~ 0.6 eV (at 2.4-Å Pr); (ii) the Si 2*p* oxide peak also shifts to higher binding energy, but by a larger amount (1.0 eV); (iii) the oxide Si 2*p* peak profile broadens with distinct asymmetry to lower binding energy; and (iv) at the lower binding energy side of the Si 2*p* substrate signal new spectral intensity is observed, which is due to Si atoms having reacted with Pr to form a silicide-type compound.[5,10] Increasing the Pr coverage leads to a general reduction of the Si 2*p* intensity, to the relative growth of the reacted component, and to the disappearance of the Si substrate signal. After heating the 10-Å, Pr on SiO_2/Si sample to 500 °C (see bottom curve of Fig. 1), the reacted Si 2*p* peak is replaced by a structure at the position of the original substrate emission, and a new feature is observed at ~ 3 eV relative binding energy. Taken together these data suggest both "physical and chemical" interactions during the formation of this thin MIS structure. The core-level shifts to higher binding energy indicate band bending and band alignment changes, whereas the modifications of the spectral profiles suggest reduction of SiO_2 and the formation of Pr silicide at room temperature; at elevated temperature the formation of a new Pr-Si-O silicate-type compound[11] seems to occur.

In order to assess the locus of the chemical reactions the surface sensitivity of the x-ray photoemission spectroscopy (XPS) probe has been modified by varying the electron exit angle from normal to 60° as shown in Fig. 2. The experiments were performed by moving the rotatable analyzer from the normal emission position to 60° emission, keeping all other parameters constant; due to the

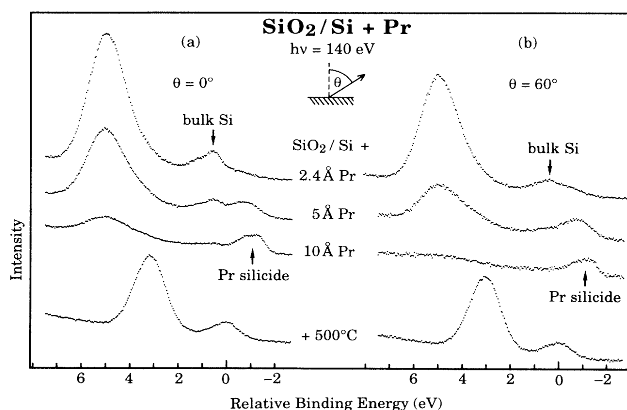


FIG. 2. Si $2p$ XPS spectra ($h\nu \approx 140$ eV) of Pr-SiO_2/Si for (a) normal emission and (b) 60° emission geometry. The Si $2p$ components of bulk Si and Pr silicide are indicated. The spectra are normalized to photon flux, and related to the topmost spectrum of each sequence.

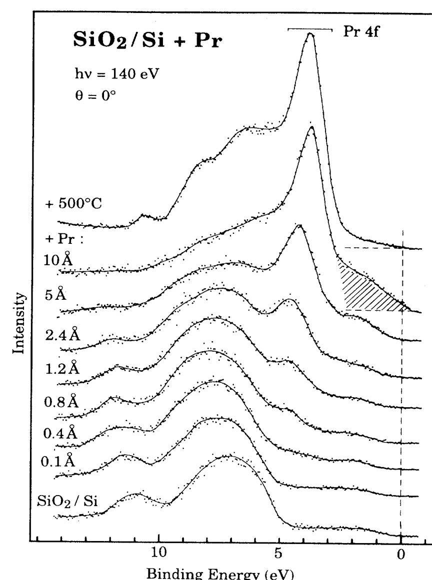


FIG. 3. Valence-band spectra of SiO_2/Si as a function of Pr coverage and after annealing. Photon energy $h\nu \approx 140$ eV, normal emission geometry.

amorphous/polycrystalline nature of the surface phases diffraction effects are not expected and the observed changes are attributed to increased surface sensitivity. The comparison between the two geometries demonstrates that the reacted silicide $2p$ components at the lower binding energy side are enhanced in the 60° emission spectra and that the relative prominence of the oxide components is reduced. This clearly indicates that the reduction of SiO_2 takes place at the outer SiO_2 surface, where the metal layer is evaporated. The 10-Å Pr spectrum in the enhanced surface sensitivity mode shows complete lack of the SiO_2 structure and the presence of only Pr silicide. The oxygen is being transferred to the metal phase to form oxide during the reduction of SiO_2; this is not directly apparent here but can be inferred from the Auger results as discussed below. The annealed surfaces, however, exhibit virtually no changes with the electron take-off angle and show the coexistence of silicate-type Si (Ref. 11) and Si substrate bulk emission. This is interesting and must indicate a total rearrangement of the reacted layer on heating with possibly an island structure of the silicate phase.

Photoemission spectra of the valence-band region of samples corresponding to those of Fig. 1 are shown in Fig. 3. The pristine SiO_2/Si (bottom curve) shows emission from the O $2p$ SiO_2 valence band with structures at ~ 11 eV and between 5 and 9 eV, and the weak intensity between E_F and 5 eV is derived from the underlying Si substrate. The SiO_2 structures are modified on Pr evaporation with increasing coverage and the Pr $4f$ emission at ~ 4 eV becomes dominant as a result of the high photoionization cross section of the $4f$ states at the used photon energy of ~ 140 eV. The $4f$ emission peak shifts towards the Fermi level with increasing Pr coverage, an effect which has been generally observed on R-Si interfaces and is attributed to ensemble and photoemission final-state effects.[5,10] Most notable, however, is the development of emission intensity at the Fermi level (see spectrum of the 10-Å Pr sample) and its disappearance on heating. These data are consistent with the reduction of SiO_2 by the R metal and the formation of a metallic silicide with a significant density of states (DOS) at E_F at room temperature, and the formation of an insulating silicate phase at elevated temperature.[11] Note that the O $2p$ related valence-band structure of the silicate in the 5–10-eV region (top curve in Fig. 3) is also very different from that of SiO_2.

In conjunction with the discussion of the valence-band photoemission results we want to add at this point that preliminary measurements in the constant initial state mode were performed on the Pr-SiO_2/Si surfaces during the course of this work using both the valence band and the Pr $4f$ states as initial states. They showed resonating behavior for both types of states in the region of the $4d$-$4f$ resonance,[12,13] thus indicating that the valence bands of the reacted surfaces consist of hybridized O $2p$, Si $3p$, and Pr $5d$ states; this is yet another manifestation of the extensive chemical interactions which take place at these surfaces.

The evolution of the conduction bands of the Pr-SiO_2/Si structures have been investigated by inverse photoemission as presented in Fig. 4. The SiO_2/Si IPES spectrum shows a maximum of the conduction-band DOS of SiO_2 at ~ 8.5 eV above E_F, and the intensity between E_F and the estimated conduction-band minimum of SiO_2 [at ~ 4–4.5 eV (Ref. 14)] is due to the emission from the Si substrate.[15] Deposition of Pr introduces intensity which moves towards E_F with increasing Pr coverage and a structure at around 4–5 eV, whereas the pronounced DOS maximum in the conduction band of SiO_2 disappears. The 10-Å Pr-SiO_2/Si surface shows an IPES spectrum with a metallic Fermi edge which is characteristic of trivalent R silicides.[7] The annealed silicate-

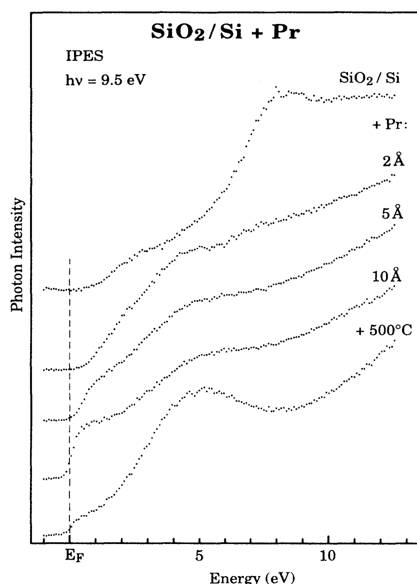


FIG. 4. Inverse photoemission spectra of SiO_2/Si as a function of Pr coverage and after annealing. Isochromat energy $h\nu=9.5$ eV, normal electron incidence.

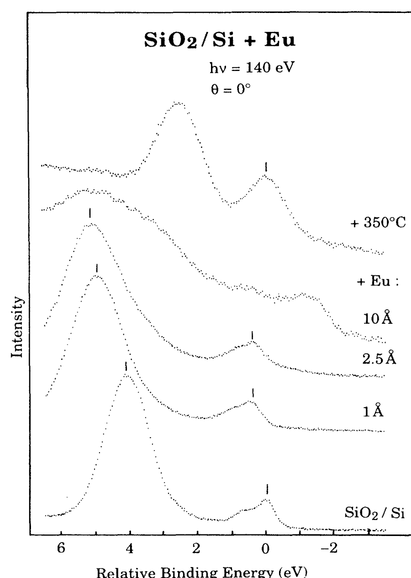


FIG. 5. Si 2p XPS of SiO_2/Si as a function of Eu coverge and after annealing at 350 °C. $h\nu \approx 140$ eV.

type phase (bottom curve in Fig. 4) displays an IPES spectral profile which is distinctly different from that of SiO_2, with a dominant feature at ~5 eV. This remarkable difference in the conduction-band spectra between SiO_2 and the annealed Pr-SiO_2/Si structures gives further credence to the proposition of a separate ternary compound phase on the latter surfaces.

The work function of the SiO_2/Si surfaces decreases continuously with Pr deposition as expected for the absorption of electropositive metals, with a $\Delta\Phi$ saturation value of -2.7 eV at 10-Å metal deposition. This is the result of the combined effects of Fermi-energy movement within the insulating band gap and changes in surface dipole layers as discussed further below. The work function of the Pr-SiO_2/Si surface increases again upon formation of the silicate phase during annealing, i.e., by 0.7–0.8 eV for the 10-Å Pr-SiO_2/Si surface.

B. Europium, ytterbium, and gadolinium

The general pattern of electron spectroscopic results as presented for Pr in the preceding section is qualitatively similar for the other R metals investigated in this study. For example, the Si 2p core-level spectra of Eu-SiO_2/Si samples, as shown in Fig. 5, demonstrate convincingly the different shifts to higher binding energy of the Si and SiO_2 2p components for low Eu coverages and the appearance of a reacted silicide 2p structure at 1.4 eV to lower binding energy for the 10-Å Eu-SiO_2/Si surface. Moreover, the formation of a Eu silicate phase after heat treatment at ~350 °C is also suggested by the corresponding core-level spectrum in Fig. 5.

A summary of Si 2p spectra as obtained after evaporation of 10-Å R metal on SiO_2/Si at room temperature is given in Fig. 6. We note that in all cases R silicides are formed as manifested by the core-level peaks shifted to lower binding energy, and that reduction of SiO_2 takes place. However, there are quantitative differences and it appears that the so-called divalent R metals Eu and Yb are somewhat less effective in reducing SiO_2 as evidenced from the ratio of the silicide intensity to that of the origi-

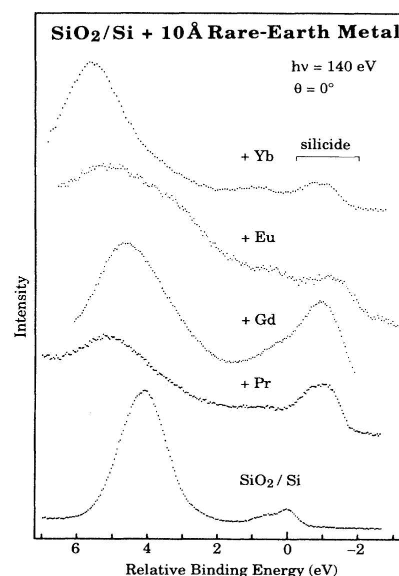


FIG. 6. Si 2p XPS of SiO_2/Si covered with ~10 Å rare-earth metal.

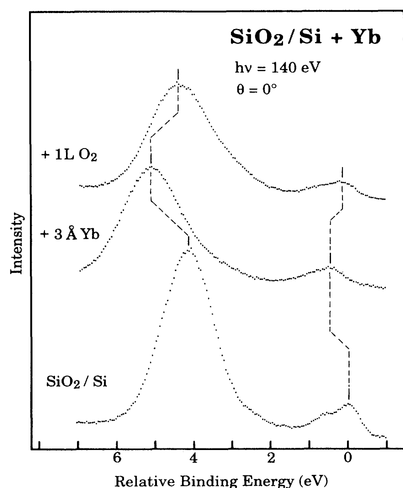


FIG. 7. Si $2p$ XPS of SiO_2/Si, covered with 3 Å Yb, and subsequently exposed to 1 L ($=10^{-6}$ Torr sec) of O_2. $h\nu \approx 140$ eV.

nal SiO_2. This is contrary to the generally observed trend in chemical reactivity, where the divalent R metals are more reactive than the trivalent ones, but it may be the result of the detailed thermodynamic balance of this solid-state reaction as is discussed below.

An interesting effect has been observed after exposure to gaseous oxygen of the R SiO_2/Si structures. This is demonstrated for Yb in Fig. 7, where we show the Si $2p$ level of pristine SiO_2/Si, after deposition of 3-Å Yb, and after subsequent exposure to 1-L O_2 [1 Langmuir (L)$=10^{-6}$ Torr sec]. The different shifts to higher binding energy of the Si $2p$ components after low-coverage Yb evaporation are by now already familiar, but after oxygen exposure both components *shift back,* although the energy positions of the original surface are not quite restored. Thus a fraction of the Si $2p$ shifts to higher binding energy can be reversed by the introduction of electron acceptors such as oxygen into the system, and this will be of relevance in attempting to interpret these effects in the next section.

IV. DISCUSSION

Although "chemical and physical effects" as mentioned in the Introduction are intimately intertwined in the MIS structures involving R metals, we consider it appropriate here to separate them for clarity of presentation. This somewhat "operational" separation is also not totally without justification since the physical, e.g., band-bending effects are more apparent at low metal coverages, whereas the chemical effects predominate at higher coverages. Thus we begin with the low metal coverage regime and will consider first the "physical effects" in terms of the Si $2p$ core-level shifts to higher binding energy for the Si substrate and for the SiO_2 phase.

Figure 8 gives a summary of the Si $2p$ shifts for the four systems investigated in the form of a schematic energy-level diagram. For the Yb-SiO_2/Si system the corresponding shift of the O $1s$ level of the SiO_2 phase and for the Pr-SiO_2/Si system the work-function change are also indicated; the common energy reference in the diagram is the spectroscopically determined Fermi level. The inset of Fig. 8 illustrates the evolution of the Si $2p$ shifts as a function of Pr coverage along with the work-function changes; the Si $2p$ shifts saturate at approximately one monolayer metal coverage (1 monolayer Pr$=2.8$ Å), whereas the work function reaches saturation at a higher coverage. The Si $2p$ shifts of the Si substrate straddle at approximately 0.5 ± 0.1 eV, but the core-level shifts of the SiO_2 phase display a larger variation with the R metal ranging from 0.6 to 1.4 eV. The shift of the O $1s$ level, which has been determined for the Yb-SiO_2/Si system, amounts to 1.4 eV and is thus consistent with the Si $2p$ shift of the SiO_2.

Three models may be considered to discuss the changes of band bending and band alignment at the Si-SiO_2 interface during low-coverage R metal deposition: (i) an elec-

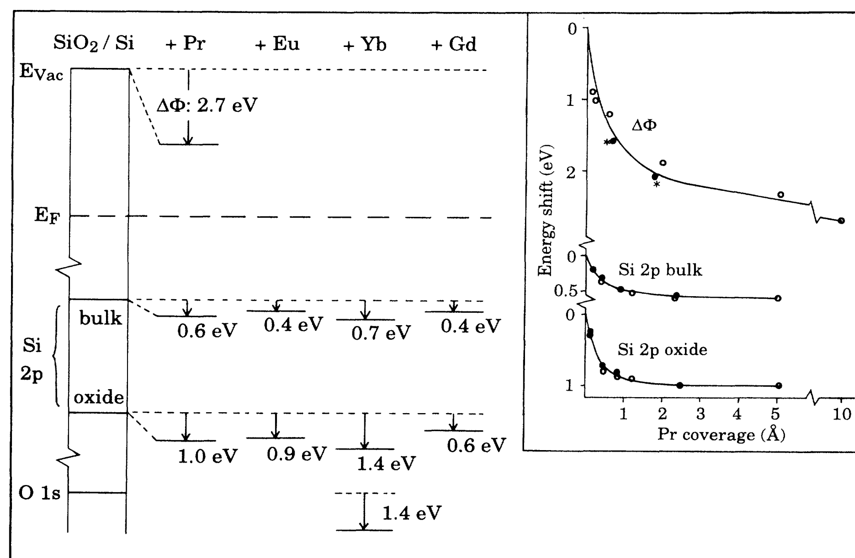


FIG. 8. Schematic diagram of the relative saturation core-level shifts to higher binding energy after evaporation of R metals onto SiO_2/Si. The shifts to lower binding energy due to silicide formation are not included. The inset shows the evolution of the substrate and oxide Si $2p$ shifts with Pr coverage along with the work-function changes.

trostatic charge injection model; (ii) the buildup of an electric field across the SiO_2 layer; and (iii) the diffusion of R atoms through the thin SiO_2 layer to the Si-SiO_2 interface and a resulting change of the band offset.

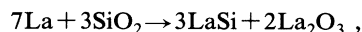
It is tempting to associate the Si $2p$ shifts of the Si substrate with a change in the band-bending conditions at the Si-SiO_2 interface as a result of charge injection through the thin SiO_2 layer. According to this model the R metal atoms deposited at the outer SiO_2 surface would act as electron donors giving off electrons which can tunnel through the SiO_2 layer and be accumulated at the Si-SiO_2 interface. The partial reversibility of the core-level shifts upon application of gaseous O_2 to the low-coverage structures (see Fig. 7) is supportive of these ideas. Oxygen is a well-known electron acceptor and the charge accumulated at the Si-SiO_2 interface may be taken up by the adsorbed oxygen, thereby reversing the direction of the band-bending changes. However, since the SiO_2 is connected to the Si substrate, similar Si $2p$ core-level shifts would be expected in the SiO_2 phase as a result of a simple change of band bending at the Si-SiO_2 interface. This is clearly not the case suggesting that additional effects must be operative at the interface.

An electric field across the thin SiO_2 layer may be thought of as being built up as a result of Fermi-level pinning by interface states at the *inner and outer* SiO_2 *interface.* An electric-field gradient could yield different Si $2p$ core-level positions at the inner Si-SiO_2 interface and at the outer SiO_2 surface. An experimentally observable criterion for an electric-field gradient across the SiO_2 phase would be the broadening of the SiO_2 core levels, and in principle XPS should be able to distinguish between the electric field (ii) and the band offset (iii) option. Unfortunately, however, the reduction of SiO_2, that is, the chemical effects discussed below, is likely to obliterate the experimental possibility of distinction by inducing a similar core-level asymmetry by the chemical reaction.

The influence of metal and semiconductor overlayers on valence-band offsets at buried insulator/Si interfaces has been reported recently by Xu, Voss, and Weaver[16] and Olmstead and Bringans.[17] In both cases a reduction of the valence-band offset up to ~ 1 eV has been observed by core-level photoemission at the CaF_2/Si interface after the deposition of Au or Ge overlayers onto the outer CaF_2 surface. A change of band offset requires a change of the number or nature of interface dipoles, which in turn needs structural or chemical rearrangement at the interface.[18,19] It is unlikely that the room-temperature deposition of R atoms onto the outer SiO_2 surface will induce a structural rearrangement at the buried Si-SiO_2 interface *per se.* However, the facile diffusion of transition metal or R metal atoms through thin SiO_2 layers has been reported in the literature.[20,4] It may therefore be possible that the diffusion of R atoms through the SiO_2 layer to the Si-SiO_2 interface induces a change of the band alignment between the Si substrate and the SiO_2 layer, thus leading to the observed additional core-level shifts in the SiO_2 phase. The modification of heterojunction band offsets by thin interlayers, readily referred to under the umbrella title band-gap engineering,[21] has been described both experimentally and theoretically, and may be considered as a well-established fact.[18,19,21,22] We tend to favor this model of the R atom diffusion-induced band lineup changes at the Si-SiO_2 interface to rationalize the different core-level photoemission shifts of the Si substrate and the SiO_2 layer, but the electric-field option cannot be completely ruled out on the basis of the present experimental results. In fact, the presented data do not permit a definitive distinction between the different models, and experiments involving a system without strong chemical interactions are necessary to clarify the situation; those are presently underway.

A brief comment on the work-function change which has been measured during Pr deposition should be added here. The $\Delta\Phi$ value of 2.7 eV, which is included in Fig. 8, is made up by the change of the electrochemical potential, which initially is caused mainly by the so-called physical effects as discussed above, and by the change in the surface dipole layer. The former amounts to about 1 eV as evidenced by the SXPS shifts, whereas the latter has to account then for the remaining 1.7 eV. The different metal coverages needed for the photoemission core-level shifts and for $\Delta\Phi$ to reach saturation (~ 3 Å versus ~ 10 Å; see Fig. 8) may then reflect the fact that the buildup of the new surface dipole layer is delayed by the diffusion of metal atoms into the SiO_2 layer. However, the chemical reactions at the outer surface again complicate the picture, and studies with nonreactive metals will also be beneficial in this context.

The solid-state reactions between thin metal overlayers and SiO_2 have been investigated by several groups[23–25] and most comprehensively by Pretorius, Harris, and Nicolet[26] who have addressed the thermodynamic aspects in particular. The thermodynamic feasibility of the reduction of SiO_2 by metals, assuming metal silicide and metal oxide as reaction products, have been correlated in this latter study with the electronegativity of the metals: it has been concluded that metals with an average electronegativity of less than 1.5 on the Pauling scale react with the SiO_2 substrate. The relevant thermodynamic quantity that determines the direction of a chemical reaction is the Gibbs free energy ΔG. For a solid-state reaction the change in entropy is usually small, and the reaction enthalpy ΔH may instead be used for a first-order thermodynamic estimate. Pretorious, Harris, and Nicolet[26] have compiled standard heat of formations for a large variety of metal silicides and oxides, but their tabulations include only lanthanum among the R elements. However, since R elements behave chemically in a very similar fashion, La is a good substitute for Pr, and in fact should give reasonable indications for the other R metals. We consider the chemical reaction



$$7La + 3SiO_2 \rightarrow 3LaSi + 2La_2O_3 ,$$

for which $\Delta H^{\circ}_{298} = -9.5$ kcal/g atom is obtained. This reaction is thus largely exothermic and thermodynamically favorable for the reaction of SiO_2. Of course, the exact ΔH value will depend somewhat on the R metal and on the particular stoichiometry of the silicide and oxide which are being formed, but as a general pattern this

type of reaction will always yield strongly exothermic ΔH values for the R elements.

The thermodynamic expectations are fully supported by the present electron spectroscopic results. The Si $2p$ core-level photoemission spectra demonstrate convincingly the formation of silicides after R metal evaporation onto SiO_2 by the appearance of Si $2p$ components shifted to lower binding energy, whereby good quantitative agreement is obtained with previous results of silicide formation on R metal-Si interfaces.[5,10,27] Moreover, the reduction of SiO_2 is also clearly apparent from the core-level spectra. The valence-band and conduction-band spectra (IPES) add supportive evidence for the reduction of SiO_2 and for the formation of a R silicide. The formation of metal oxide during the course of the reaction has been deduced from the O *KLL* and the R *NNN* Auger spectra. The presentation of Auger results and their detailed analysis will, however, be the subject of a separate publication,[28] but it is useful to note the existence of such supporting evidence.

The modification of the surface sensitivity of XPS as obtained by varying the electron takeoff angle (Fig. 2) has revealed that the reduction reaction is initiated at the outer SiO_2 surface. An important question is whether a critical metal coverage is necessary to initiate the reaction, as it has been discussed in some cases of so-called reactive metal-semiconductor interfaces,[29] or whether the reaction starts right with the first metal atoms impinging onto the SiO_2. The experimental core-level data are not totally conclusive in answering this question because sensitivity is an obvious problem at small metal coverages, but it appears that the "physical effects" predominate at low coverages and that a certain induction period in terms of metal coverage is necessary for the chemical reaction to take place (see Fig. 1). This would mean that kinetic effects take over at low metal coverages, with an activation energy that decreases to a reasonable value only when sufficient metal atoms are present at the surface.

Annealing of the reacted R SiO_2/Si structures leads to the formation of phases, which in close correspondence to the results obtained on oxidized R-Si interfaces upon annealing[15,30,31] are associated with ternary compounds of the silicate type. The Si $2p$ core-level positions, which exhibit on average a chemical shift with respect to bulk Si of ~ 3 eV, are compatible with those of other silicates,[32,33] and the valence-band and conduction-band results of Figs. 3 and 4 reveal the insulating character of these phases. The morphologies of the MIS structures also seem to be severely modified by the moderate temperature treatment: the angular XPS effects in Fig. 2 are obliterated, and this may indicate growth of the silicate into an island-type structure on top of the Si substrate.

V. SUMMARY

Thin MIS structures of rare-earth metals on SiO_2/Si substrates have been investigated by electron spectroscopic techniques as a function of metal coverage and annealing treatment. The R metals react readily with the insulating SiO_2 layer at room temperature to form metal silicide and metal oxide thereby reducing the SiO_2, in accord with thermodynamic expectation. It appears, however, that a certain critical R overlayer coverage of about one monolayer is necessary to launch the chemical reaction. At lower metal coverages the observed core-level binding-energy shifts of the Si $2p$ photoemission components of the Si substrate and of the SiO_2 suggest other effects, such as a change of band bending in the Si and a change of band offset at the buried Si-SiO_2 interface. The latter may be induced by diffusion of R-metal atoms across the thin SiO_2 layer to the Si-SiO_2 interface. Annealing of the reacted R MIS structures to moderate temperatures leads to the formation of ternary R-Si-O compounds, presumably of a silicate type, by solid-state reaction. The morphology of the structures is significantly altered by the annealing reaction, exposing silicate and Si substrate regions at the surface, and an island-type silicate phase on top of the Si substrate is suggested.

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