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Rare earth metal–SiO_2–Si interfaces monitored by Auger spectroscopy

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Abstract. The interfacial reactivity of the rare earth metals Yb and Pr deposited on ultra-thin layers of SiO_2 on Si(111) substrates under UHV conditions is investigated using the Auger spectra of silicon, oxygen and the rare earth metals to monitor chemical changes. At room temperature exposure to ~10 Å of rare earth metal leads to reduction of the SiO_2 to form rare earth oxide and rare earth silicide, while at elevated temperature reaction to form a silicate phase is demonstrated.

1. Introduction

The use of metal–insulator–semiconductor (MIS) devices is well established for example as chemical sensors [1], and rare earth metals have been investigated as potential gate materials in such sensors [2]. However, the use of reactive metals of this type requires a full understanding of the interface chemistry of such structures. In this work we use Auger electron spectroscopy to study the interaction of Pr and Yb overlayers evaporated under UHV conditions at room temperature onto ultra-thin films SiO_2 on Si(111) substrates. It is shown that the environmental dependence of the Auger spectra of Si(LVV), O(KLL) and metal N_{45} (Pr, Yb) are excellent monitors of the chemical species evolving at the surface. The results presented here directly complement photoemission studies on such systems [3], and the strengths and weaknesses of the different techniques are discussed.

2. Experimental details

Auger electron spectra were recorded with a concentric hemispherical electron analyser (Leybold LH10) in a UHV environment with base pressure $< 10^{-10}$ mbar. The spectrometer resolution was in the range 0.5–1 eV, with electron energy referenced to the sample Fermi level. Electron beam exposures were sufficiently low to avoid damage at the surface. Pr and Yb were evaporated from vacuum-degassed W coils at ambient pressures $< 10^{-9}$ mbar onto 'native oxide layers' on Si(111) single-crystal wafers (n-type, $\Omega \sim 2.5\ \Omega$ cm) corresponding to 15–20 Å of amorphous SiO_2 on Si formed by a chemical passivation procedure of the manufacturer (Wacker-Chemitronic). Gentle degassing followed by heating to 550 °C in vacuum yielded clean samples showing no Auger signals other than Si or O. Experiments carried out

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on Si(111), thermally oxidized under conditions controlled to give 15 Å SiO_2 layers [4], yield very similar electron spectroscopic results, so the main studies concentrated on the native oxide samples. Mean metal film thicknesses were measured with a quartz crystal monitor (Inficon).

3. Results

3.1. Ytterbium

Figure 1 shows the Auger emission (energy range 40–220 eV) from SiO_2/Si as a function of Yb coverage (evaporation at room temperature) and a sample covered with 12 Å Yb after annealing at ~500 °C. In addition emission from a thick layer of clean Yb metal is shown and that of the metal exposed to 300 L O_2 (1 Langmuir (L) = 10^6 Torr s) at room temperature. In this case the LVV spectra of Si are well separated from the $N_{45}N_{67}N_{67}$ and $N_{45}N_{67}O_{23}$ spectra of Yb, so the evolution of the contributions of the two atomic species is clear. The clean SiO_2/Si spectrum shows features both due to SiO_2 (63 and 79 eV) and to underlying Si (92 eV). As the Yb thickness grows to 2 Å Yb there is little change in the spectrum, but by 6.4 Å some decrease, particularly in the oxide component, is manifest. At 12 Å Yb the oxide peak is much reduced and shifted in energy, but there is now a slight *increase* in intensity of the higher-energy feature at ~92 eV. On annealing this high-energy peak decreases in intensity and a new broad feature centred at 81 eV becomes prominent.

In parallel with these changes in the Si spectrum a broad rather featureless Yb spectrum rises in intensity approximately linearly with coverage. Annealing at 500 °C leads to the emergence of a new sharp feature at ~157 eV. Comparison with the corresponding metal and metal exposed to 300 L O_2 (i.e. oxidized metal [5]) spectra shows some consistency in overall profile, but suggests that Yb is neither in the pure metallic nor in the pure oxide state, at least at higher coverage levels.

The KLL oxygen Auger spectrum is shown in figure 2. In SiO_2/Si the main $KL_{23}L_{23}$ and KL_1L_{23} peaks are clearly defined, and again show little change at 2 Å Yb coverage. By 6.4 Å a small peak shift to higher energy is seen, while by 12 Å the shift has increased to about 3 eV to an energy consistent with the position for oxidized Yb (top curve in figure 2). On annealing the spectrum sharpens suggesting a single main feature shifted to higher energy by around 2 eV relative to SiO_2, but still 1 eV below the position in oxidized Yb.

3.2. Praseodymium

The corresponding data for SiO_2/Si exposed to Pr are given in figures 3 and 4. Although the Pr spectrum is well resolved into a number of components [6], there is now overlap with the Si spectrum and so the evolution of Si environment is rather less clear. Changes in the 'Si' profile are already evident at 1.8 Å Pr with contributions from the lowest two components of the Pr spectrum distorting the shape. By 5 Å the strong Pr features dominate, but even at 10 Å the highest-energy Si component (92 eV) remains intense and it is clear that the oxidized Si component is considerably depleted. However, on annealing, this higher-energy Si component declines greatly. The Pr emission following the decay of N_{45} excitation and ionization grows in intensity with increasing coverage: the spectrum consists of four components with energies at 120 eV, 106 eV, 89 eV and 69 eV. On annealing there is a small (~1 eV) shift to

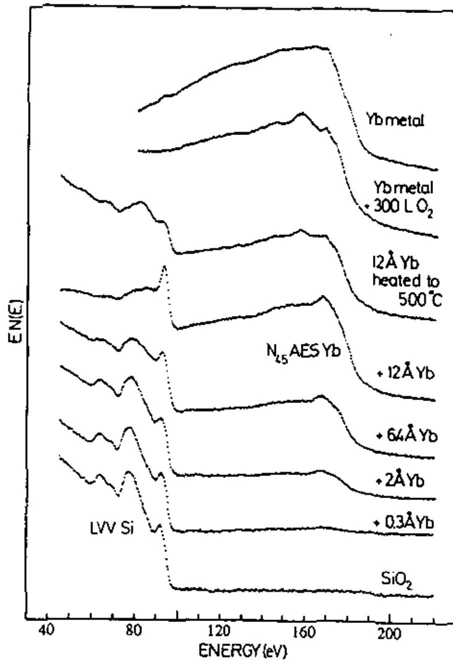


Figure 1. The Si LVV and Yb N_{45} Auger spectra of Yb deposited on Si(111)–SiO_2 at room temperature in $EN(E)$ form. The Yb coverage varies from 0.3 Å to 12 Å. In addition the spectrum of the 12 Å layer heated to ~500 °C is shown, and for reference the $N_{45}N_{67}N_{67}$, $N_{45}N_{67}O_{23}$ etc spectra of Yb metal and oxidized Yb obtained from a thick Yb layer are presented.

lower energy in most components with the 106 eV peak rather more sensitive to the change of environment, but the difference is less marked than between metal and oxide (figure 5).

If the evolution of the (Pr, Si) Auger spectrum is less easy to unscramble than that of the (Yb, Si) spectrum, there is compensation to be found in the O KLL spectrum of Pr on Si/SiO_2 shown in figure 4. The spectrum shows little change between SiO_2 and 1.2 Å Pr coverage, but by 10 Å a 5.5 eV peak shift is observed giving an energy close to that of oxidized Pr (figure 5): the asymmetric profile indicates the survival of some O in an oxidized Si state. Heating leads to a more symmetric $KL_{23}L_{23}$ peak at ~511 eV, 2 eV less than for an oxidized thick metal layer and 2.5 eV less than for 10 Å Pr on Si/SiO_2. There is clear evidence of three distinct oxygen environments.

4. Discussion

The story presented here attempts to use the gross changes of Auger emission profiles with environment to characterize chemical changes at the interfaces of a metal–oxide–semiconductor structure. It is therefore useful to review briefly the environmental changes found in the spectra of the elements involved here.

(i) Si LVV: in an elemental solid environment or metallic environment the Si spectrum shows a sharp rise near the L_{23} threshold to an asymmetric peak above

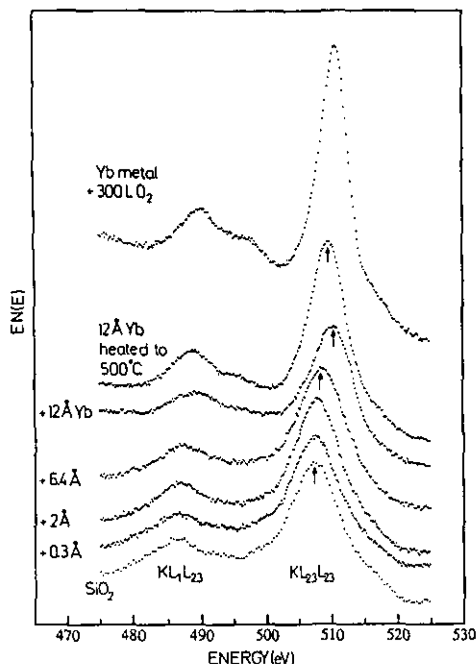


Figure 2. The KLL O Auger spectrum of Si(111)–SiO_2 and of Yb deposited as in figure 1. The spectrum of a 12 Å layer heated to ~500 °C is shown along with that of a thick Yb layer oxidized *in situ*.

90 eV [7]; Si and Si-rich rare earth metal silicides show similar spectra particularly in the main peak region, and the two phases are difficult to distinguish [8]; with increasing metal concentration the main peak becomes more symmetric in the silicide, and in transition metal silicides where the metal has a nearly full d shell, there are larger changes. Si bonded to highly electronegative elements, e.g. O, yield more quasi-atomic spectra with a slow rise from the maximum energy to a peak below 80 eV accompanied by a lower-energy peak above 60 eV. The Si/SiO_2 spectra (figures 1, 3) shows a superposition of these two types of profile.

(ii) O KLL: the oxygen KLL spectrum is generally quasi-atomic or quasi-molecular in character, and shows two main features due to $KL_{23}L_{23}$ and KL_1L_{23} transitions [9]; in some compounds the main $KL_{23}L_{23}$ peak may split due to O 2p hybridization with orbitals of neighbouring metal atoms, but in SiO_2 and metal oxides the single-peak profile prevails. However, marked shifts between different environments are found with the most ionic oxides having the highest Auger energies [9], due both to the initial state environment and the good intra-site screening of negatively charged oxygen species.

(iii) N_{45} direct recombination and Auger emission in the rare earths: rare earth electron emission associated with electron-induced 4d → 4f excitations and 4d ionization leads to a combination of conventional Auger emission, e.g. $N_{45}N_{67}O_{23}$ and direct recombination emission, e.g. $4d^{10}4f^3 \rightarrow 4d^9 4f^4 \rightarrow 4d^{10}4f^2 + e$; the latter arises from a 4d → 4f giant resonance excitation decaying to a single-hole 4f state, which is denoted by DR4d–4f [6]. The main contributions to the Pr spectrum are given in figure 5; the Auger features tend to show greater shifts on oxidation and

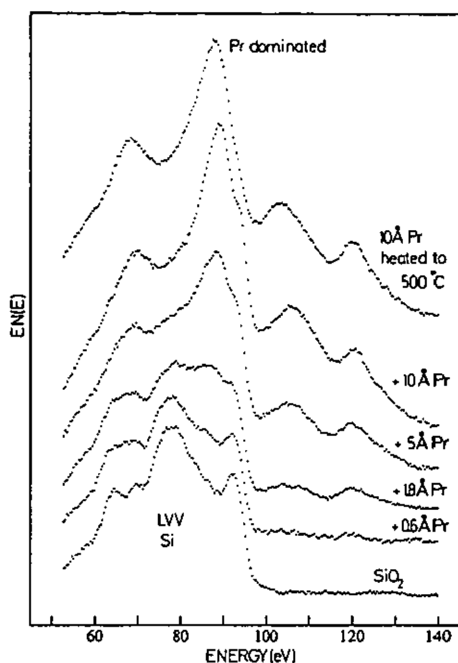


Figure 3. The $EN(E)$ Si LVV and Pr N_{45} Auger spectra of Pr deposited on Si(111)–SiO_2 at room temperature (linear background removed). The Pr coverage varies from 0.6 Å to 10 Å. In addition the spectrum of the 10 Å layer heated to ~500 °C is shown. Note the overlap of the Si and Pr features.

changes in the peak of second-highest energy are particularly marked as it contains a mixture of Auger emission and direct recombination, as in the case of Sm [10]. The Yb spectrum is much broader with less well defined structure due to overlap of the many decay channels [5], but in the oxide more sharp features are resolved.

We are now in a position to use this background information in interpreting the chemical evolution of the interfaces. At low coverages little new information other than rare earth coverage data emerges, but beyond 5 Å radical changes in the Si LVV spectrum occur (this is best seen for Yb in figure 1 though the Pr case is consistent). The depletion of the oxide component is accompanied first by maintenance of the 92 eV peak followed by a slight increase in its intensity with a small shift to higher energy. This is a strong indication of reduction of the Si oxide, but what of the elemental Si state? There are two possibilities:

(a) elemental Si remains in the surface region even after 12 Å metal deposition;

(b) a rare earth metal silicide with an Si Auger spectrum very similar to that of the element is formed, as in Si-rich silicides [8].

Inspection of the metal spectrum gives further information. The Yb metal and oxidized Yb spectra show important differences: in the metal only a peak at 170 eV is resolved, while in the oxide there is a distinctive feature at 157 eV. At 12 Å coverage the Yb spectrum resembles a linear combination of a metal-like and oxide-like spectrum. Assuming that metallic silicide will have a spectrum similar to that of the metal this is consistent with the coexistence of silicide and oxide (plus some

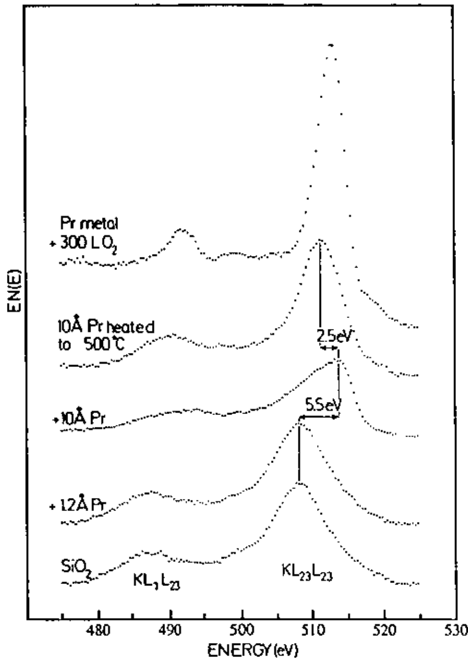
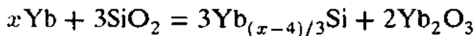


Figure 4. The KLL O Auger spectrum of Si(111)–SiO_2 and of Pr deposited as in figure 3. A polynomial background has been removed from the raw data. The spectrum of a 10 Å layer heated to ~500 °C is also shown along with that of a thick Pr layer oxidized *in situ*.

unreacted metal), simplistically described by the reduction reaction



$$x\mathrm{Yb} + 3\mathrm{SiO_2} = 3\mathrm{Yb}_{(x-4)/3}\mathrm{Si} + 2\mathrm{Yb_2O_3}$$

with a similar equation for Pr. This is a more likely outcome of the reduction process than having Si and Yb_2O_3 as final products, since it is well known that Si and Yb (and other rare earths) react readily to form highly stable silicides [11]. The spectral evidence is consistent with the formation of Si-rich silicide, although there may be some elemental Si exposed in the reaction. The low-energy Pr spectrum is also not decisively metallic or oxidic, and there is again support for silicide formation in the Si Auger spectrum.

The depletion of the silicide Si feature accompanied by a new broad Si peak (figure 1) on heating supports the idea of reaction to form a silicate phase in which the Si has a more electronegative environment than in SiO_2. Such phases have previously been observed in the high-temperature oxidation of clean Si(111) rare earth interfaces [12]. The Yb spectrum changes to a less metallic profile consistent with a new reacted phase. The Pr spectrum is not inconsistent with this view, but the position is clouded by spectral overlap.

Shifts in the oxygen KLL spectra give further support to this picture of phase development. The Pr case (figure 4) is particularly clear: the very large 5.5 eV shift in the $KL_{23}L_{23}$ peak at 10 Å coverage relative to SiO_2 is indicative of the presence of rare earth metal oxides, being consistent with what is found for transition metal oxides [9]. Similarly the shift to lower energy on heating is consistent with what is

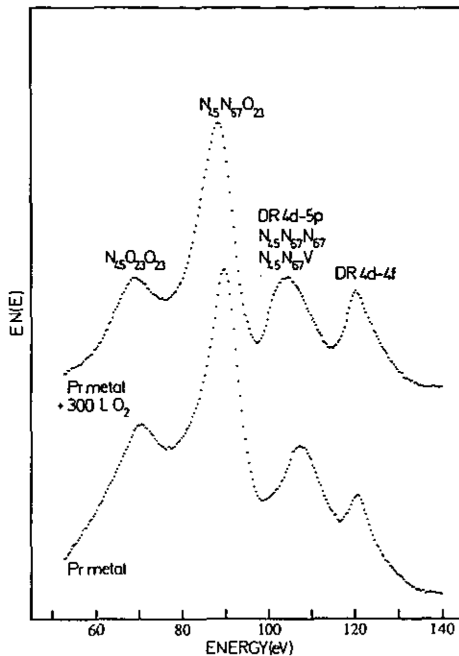
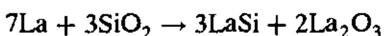


Figure 5. The electron emission spectra of clean Pr and oxidized Pr with main processes contributing to the peaks as given by Rivière *et al* [6]. A linear background has been subtracted.

seen for silicates [9] and what is observed by Carrière *et al* [13] in a quasi-silica layer on FeSi. In the Yb case the oxide shift is smaller (3.5 eV), but the silicate phase accessed on heating gives a lower Auger energy than the oxide as before.

It is useful to compare the information obtained here with complementary photoemission studies using a synchrotron source to optimize sensitivity to the Si 2p level and the rare earth 4f levels (the latter through 4d–4f resonant excitation) [3]. In the photoemission work, shifts due to band realignment in the early stages of evaporation are found: such changes are not clearly parallelled in the Auger studies. However, the behaviour at larger metal coverages and on heating is very consistent: the decline of SiO_2 Auger intensity is mirrored by a corresponding reduction in oxidized Si 2p intensity. In photoemission, the silicide phase is more readily separated from bulk Si (2p binding energy shift ~1 eV), but the silicide Auger peak is more prominent than the corresponding photoemission feature. In photoemission silicide formation is further supported by intensity arising from metallic states close to the Fermi level, but, as in the Auger case, the rare earth 4f peak reflects a superposition of different phases. The O KLL spectrum of Pr shows as clearly as any photoemission study the changes from SiO_2 to Pr_2O_3 to silicate. In the Auger study the evidence for rare earth silicide at 10 Å metal coverage is more circumstantial than in photoemission, but there is additional support for the formation of a silicide phase following the reduction of SiO_2 from thermodynamic considerations. Pretorius *et al* [14] have shown that the reaction



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

is exothermic (ΔH^0_{298} = −9.5 kcal/g atom), and it is anticipated that different

stoichiometry and other rare earths will similarly react to form oxide and silicide.

Overall, although the Auger spectra of the $Si/SiO_2/Yb$ and $Si/SiO_2/Pr$ systems are broader and more complex than corresponding synchrotron-excited photoemission spectra, the distinctive changes in position and shape of the Si, O and rare earth spectra allow a detailed picture of the chemical evolution of the interface to be determined without recourse to specialized (and expensive!) synchrotron-based facilities.

5. Summary

It is shown that Auger emission from the model $Si/SiO_2/M$ (M = Pr, Yb) metal–insulator–semiconductor system is an excellent monitor of the complex junction chemistry. The evolution of the Si LVV and O KLL spectra with increasing coverage at room temperature demonstrates the reduction of SiO_2 to metal oxide and metal silicide. Heating to 500 °C leads to a more homogeneous silicate phase with distinctive Auger fingerprints.

Acknowledgments

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