

Valency changeover in Sm layers on Si(111)7×7 studied with soft-x-ray-absorption spectroscopy

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The valency changeover in Sm overlayers on Si(111)7×7 is probed with high accuracy using x-ray-absorption spectroscopy at the Sm $M_{4,5}$ edges. The valency of Sm has been studied as a function of the layer thickness in the chemisorption regime, and compared with the results obtained for epitaxially grown samarium silicide layers.

I. INTRODUCTION

The valence of rare-earth (RE) ions in the solid state is determined by the competing action between the two energy contributions representing Hund's rules and the cohesive energy term. While the isolated RE ions are generally divalent (in agreement with Hund's rule), in the solid state one nonbonding $4f$ electron is promoted into the $(6s5d)$ band leading to a trivalent ground state for the ion. The reduced coordination number of surface atoms implies a lower cohesive energy with respect to the bulk, and can stabilize the divalent configuration. The existence of distinct bulk and surface valency states for Sm has been well established in spectroscopy experiments^{1,2} and thoroughly investigated in several theoretical works.³ Most surface sensitive experiments are based on photoemission from the $4f$ subshell which gives rise to final-state multiplets separated in energy by (7–10 eV) which correspond to the excitation of the trivalent and divalent initial states.^{1,2} Core-level photoemission of Sm $3d$ electrons gives two well-separated final-state peaks representing the two ionic configurations: their intensity ratio is a measure of the relative weight of the two configurations in the near-surface region of the sample as defined by the electron escape depth. L -edge x-ray-absorption spectroscopy (XAS) is also utilized to yield valency-sensitive spectra, since replicas of the symmetry selected density of final states, just above the Fermi level, are excited for each valence configuration at a few eV energy difference.

We have performed x-ray-absorption measurements at the Sm $M_{4,5}$ edges, which are dominated by $3d \rightarrow 4f$ transitions (the $3d \rightarrow np$ component being comparatively negligible), and hence are extremely sensitive to the $4f$ occupancy. Since the $4f$ orbitals are extremely localized, the $3d \rightarrow 4f$ transitions are correctly described in a purely atomic model, regardless of the specific chemical environment.⁴

The two different ionic ground states for the two valencies of Sm (7F_0 for Sm^{2+} and $^6H_{5/2}$ for Sm^{3+}) give rise to distinct absorption spectra, as shown in XAS studies of bulk compounds.⁵ Moreover, the large cross sections for the $3d \rightarrow 4f$ transitions in RE make XAS in the soft-x-ray range particularly well suited for the investigation of very

low coverages.⁶ We use these facts to study the chemisorption of Sm onto Si(111)7×7 and the solid-state epitaxy of Sm silicide. The equilibrium configuration of the Sm valence is a very sensitive function of the coordination number and bond lengths to neighboring atoms, which is sometimes referred to as a "chemical pressure effect."⁷ The ionic radius of divalent Sm is 12.5% larger than that of trivalent Sm ions. The energy for the promotion of a $4f$ electron into the (sd) valence band is of the order of 100–200 meV in Sm intermetallics.⁸ It was shown, by $L_{2,3}$ XAS on Yb, how the valence of Yb could vary from divalent to trivalent as a function of the chemisorption site on the Si(111), Si(100), or α -Si surfaces.⁹ The surface of Sm appears to be systematically divalent due to charge decompression. Previous studies on Sm/Si interfaces as a function of coverage^{10–12} have shown a first chemisorption regime of mostly divalent Sm at a coverage of about $(4-5) \times 10^{14}$ atoms/cm², a reactive interdiffusion regime for depositions of $(1-3) \times 10^{15}$ atoms/cm², where both valencies are present, and an overlayer growth regime for coverages higher than 5×10^{15} atoms/cm² where spectra identical to those of pure Sm are measured.

II. EXPERIMENT

The experiment was carried out at Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (Orsay) using synchrotron radiation from the 800-MeV positron storage ring SuperACO. The beamline SA-22 is equipped with an UHV double-crystal monochromator mounting, beryl (1,0,1,0) crystals. The radiation within $\pm 15 \mu\text{rad}$ around the plane of the positron orbit was selected using vertical slits. The total beamline divergence on the crystals is in these conditions of about $60 \mu\text{rad}$, and the total instrumental energy resolution $\Delta E/E$ is better than 4×10^{-4} . For this portion of the photon beam the degree of linear polarization (in the orbit plane) is about 95%, and becomes essentially unit after the two Bragg reflections close to 45° for monochromatizing at about 1100 eV. Si(111) substrates were cleaned by Ar-ion sputtering and annealed by resistive heating up to 1100°C. The 7×7 surface reconstruction was checked by

low-energy electron diffraction (LEED). Sm was evaporated by electron bombardment from high-purity metal ingots mounted in tungsten baskets. The deposition rate was monitored using an oscillating quartz. Low coverages were obtained with a rate of $0.2 \text{ \AA}$ per minute, the reproducibility being estimated to be $\pm 10\%$. The base pressure of 1×10^{-10} mbar increased to 1×10^{-9} during the evaporation, due mostly to a partial pressure of hydrogen as monitored by a residual gas analyzer. The Si wafers were mounted on a cryostat ($T_{\min} = 40 \text{ K}$ on the sample) fitted in a differentially pumped rotary feedthrough, in order to allow 360° rotation around the z axis. The measurements were performed in total electron yield mode using a single-channel analyzer. Measuring time was about 7 min per scan. Each spectrum presented here refers to a single acquisition scan on a freshly prepared sample unless otherwise indicated.

III. RESULTS AND DISCUSSION

A. Valency changeover

Figure 1 compares the M_4 and M_5 edges measured for different coverages of Sm on $\text{Si}(111)7 \times 7$. All the samples were measured within 10 min from the deposition on a fresh substrate surface. The coverages indicated by side of each spectrum are in monolayers (ML) referred to the atomic density of the unreconstructed $\text{Si}(111)$ surface ($1 \text{ ML} = 7.8 \times 10^{14} \text{ atoms/cm}^2$). Let us first consider the lowest coverage of 0.2 ML. The line shapes of both edges generally agree with those deduced by Kaindl *et al.*⁵ from deconvolution of trivalent and mixed valent SM spectra, and correspond extremely well to the atomic calculations by Thole *et al.*⁴ for the Sm^{2+} . This confirms that Sm is in the 7F_0 ground state corresponding to $4f^6$ occupancy and $2+$ formal valency. The M_5 part of the spectrum consists of a main peak at about 1079 eV, flanked by two sharp structures at 1082 and 1075 eV. We stress that the 0.2 ML spectra of Fig. 1 were measured in single sweeps: a fairly good signal-to-noise ratio is obtained confirming that XAS at the RE M edges is very suitable for surface studies. Clear spectral changes dependent on the coverage are observable already at 0.5 ML, but it is around 1 ML that a drastic change of the spectra takes place. For higher coverages the main features of the M_5 spectrum are a peak at 1082 eV with side structures at 1085 and 1077 eV, as found in bulk Sm and in the annealed silicide layer, corresponding to the $^6H_{5/2}$ ground state for Sm^{3+} . The thickness range investigated extends up to several tens of layers, but no major change was observed above 2 ML. The same coverage dependence was found in the M_4 edge spectra [Fig. 1(b)]. Our data on the valency changeover versus thickness in the first monolayer are fully consistent with the $3d$ photoemission analysis by Fäldt and Myers.¹¹ They showed that the $2+ \rightarrow 3+$ transition takes place within the first 0.5 ML, with a subsequent tendency to saturation. On the other hand, theoretical models predict for Sm a full divalent layer at the surface, with little dependence on the specific substrate. This apparent discrepancy might simply originate from the definition of monolayer adopt-

ed in this and previous works. In the epitaxial RE disilicides on $\text{Si}(111)$ the RE layer has about half the atomic density of the Si planes.⁸ Rescaling the definition of the Sm monolayer according to this consideration (i.e., $1 \text{ ML} = 4 \times 10^{14} \text{ atoms/cm}^2$) would lead to a simple interpretation of our and previous¹¹ data, with a divalent surface layer and trivalent underlayers. The increase of the trivalent signal with increasing coverage can be related to chemical reaction of Sm with the silicon substrate and interdiffusion. The average local stoichiometry, i.e., the ratio of silicon first neighbors to Sm second neighbors in the growing silicelike interface layer, is a function of the coverage and of the kinetics of the interface reaction. The observed trivalent/divalent ratio of the sample is not strictly linear with the coverage, as seen in Fig. 1. Non-monotonic variations of the $3+/2+$ ratio were previous-

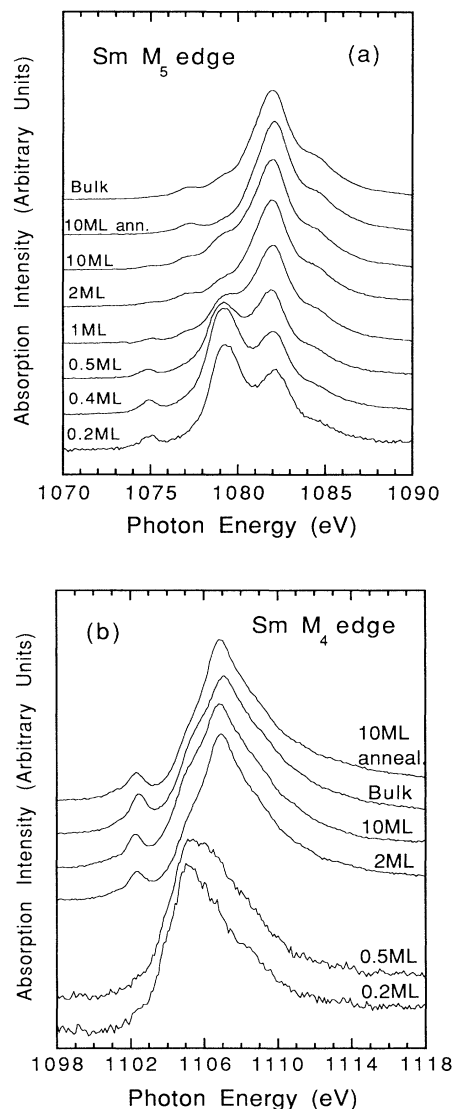


FIG. 1. (a) X-ray-absorption spectra of the samarium M_5 threshold for Sm submonolayer and monolayer coverages on $\text{Si}(111)$ at room temperature. (b) Sm M_4 edge spectra.

ly observed in the interdiffusion regime for Sm on Si(111)2×1 cleaved substrates.¹⁰ XAS-dichroism studies of the isostructural Ho/Si(111)7×7 (Ref. 13) and Dy/Si(111)7×7 (Ref. 14) interfaces show that the silicide ordering is not reached at room temperature (RT). The hindered growth at RT of epitaxial islands probably reduces the rate of valency changeover at the Sm/Si(111) interface. Cluster formation was observed at submonolayer coverages for the Ce/Si(111)2×1 system.¹⁵ The high coordination of the internal atoms of hypothetical Sm clusters would also induce trivalency, but most of the atoms would be divalent surface atoms. About the persistency of divalent samarium in the top layer it is interesting to compare the spectra for the as-deposited 10 ML and for the thick reference layer (Fig. 1). Both spectra present a shoulder at 1079 eV, reminiscent of the 2+ contribution. After annealing for 2 min at 600°C, the sample presented a sharp 1×1 LEED pattern with additional spots corresponding to the $\sqrt{3}\times\sqrt{3}$ reconstruction. Annealing at 500–600°C of thin RE layers (1–10 ML) on Si(111) produces the formation of epitaxial silicides of distorted AlB_2 structure and RESi_{2-x} stoichiometry, with x ranging between 0.2 and 0.3.¹⁶ Sm forms a silicide with formula Sm_3Si_5 and a lattice mismatch on the Si(111) surface of 1.64%. The silicide overlayers of AlB_2 -type structure are made of alternate hexagonal (defective) layers of Si and hexagonal Sm layers of half density along the [111] direction of the substrate. The $\sqrt{3}\times\sqrt{3}$ LEED pattern was attributed to the ordering of the silicon vacancies in the defective silicide layers in YSi_2 surfaces.¹⁷ The surface of the epitaxial RE disilicide layers grown by solid-state epitaxy on Si(111) is terminated by a double layer of Si.^{17,18} All the rare-earth atoms of the epitaxial silicide are in an identical atomic environment of first neighbors (Si) and in-plane second neighbors (Sm). In this situation the valence is homogeneously 3 for all of the Sm atoms of the sample, as measured by XAS (Fig. 1). This result also confirms the surface origin of the weak 2+ component in the 10 ML as-deposited interface and in the thick reference sample.

B. Time evolution of the spectra

Our choice of comparing only results obtained in the first 10 min after sample preparation is dictated by the observation of a relatively fast 2+ → 3+ valency changeover versus time. Figure 2 compares three spectra taken on the same sample [0.2 ML of SM deposited on Si(111) at RT] at different times: just after the evaporation, 2 h later, and 4 h later. The last spectrum corresponds to that of the thick reference layer, indicating that the valency changeover is complete after 4 h. This time evolution is confirmed, with a much slower rate, also for samples deposited and maintained at low temperature (not shown). The observed time dependence of the samarium valency in the submonolayer regime may just be attributed to contamination effects involving a temperature-dependent chemisorption reaction. Previous studies, in similar experimental conditions as ours, did not report such effects.^{10,11,19} A process of lateral diffusion of Sm atoms on the silicon surface, such as that

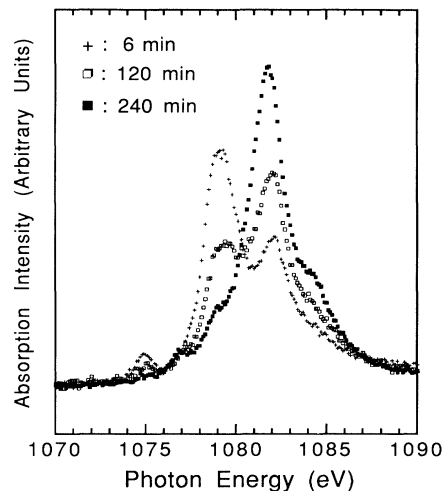


FIG. 2. Time-dependent modifications of the Sm M_5 edge spectrum of 0.2 ML Sm/Si(111) at room temperature.

proposed for the Ce/Si(111)2×1 interface, might be responsible for the formation of clusters with ions in the trivalent state. This has been considered a precursor for the onset of the interfacial reaction between metals and semiconductors²⁰ since the formation energy of the clusters would promote the atomic diffusion from the substrate. Slow interdiffusion of Sm and Si is another possible mechanism for the increase of Sm coordination and valence changeover. Our results alone cannot give a positive answer about this point.

C. Probing depth and saturation effects

A monotonic decrease of the Sm^{2+} component of the XAS spectrum originating from the surface atoms is expected as a function of the Sm layer thickness, until a value of the same order of the probing depth (d) of the measurement is reached. The strict similarity of the spectra for the 10 ML and the reference sample suggests that the probing depth of the Sm layer is very short. This observation is not new,²¹ but only recently^{22,23} has received renewed attention: x-ray absorption in total yield mode is intrinsically sensitive to the topmost layers, and particularly for solid RE materials. This prevents the direct interpretation of the XAS data in terms of bulk properties only. In addition to d , also the absorption length of the photons (l) plays an important role at the $M_{4,5}$ edges of rare earths. van der Laan and Thole reported, for instance, saturation effects in the angular dependence of La 3d photoemission.²² We measured the angular dependence of the absorption on thick layers of Sm, as well as of Dy and Ho.¹² Figure 3 displays the spectra measured at normal incidence and at grazing incidence for annealed Sm/Si interfaces together with the spectra of the reference sample. In the case of the thinnest interface (2 ML of Sm) a slight angular change of the intensity of the wing structures with respect to the main peak is observed. This effect is stronger for the annealed 10 ML sample (layered AlB_2 -type structure), and even

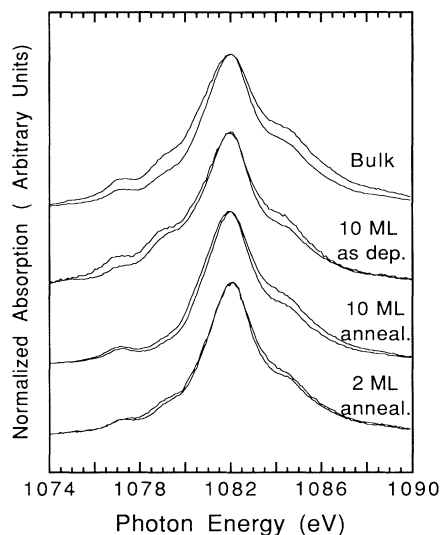


FIG. 3. Comparisons between the Sm M_5 edge of 10 ML (as deposited), 2 ML (annealed), and bulk reference as measured at two difference angles: normal incidence (lower curves) and grazing incidence (upper curves). Saturation effects are evident at grazing incidence. All the spectra are normalized to the central peak for graphical convenience.

more evident in the as-deposited sample. The results for the reference sample are beyond any possible doubt and clearly indicate the occurrence of saturation. When changing the angle α of incidence, d is unchanged, but the effective absorption length (i.e., projected along the normal to the surface) scales as $\sin(\alpha)$. As a consequence, the condition $l \gg d$ at normal incidence (weak absorption in the measured volume) can change to $l \sin(\alpha) \approx d$ at grazing incidence, originating saturation. This angular-dependent saturation in XAS deserves particular care for the study of linear dichroism in thick RE

samples, since the saturation-induced changes might be difficult to distinguish and separate from the true polarization-dependent features of the spectrum. In particular, the data shown in Fig. 3 indicate that saturation is already observed for a layer of about 5 Å (2 ML) at 10° incidence angle: this implies that l is of the order of 30 Å. This value compares fairly well with previous atomic calculations,²² and gives an upper limit for the probing depth of XAS measurement in total electron yield.

IV. CONCLUSIONS

We have shown that XAS at the $M_{4,5}$ edges is very well suited for studying the valency of Sm at surfaces. The $2+ \rightarrow 3+$ changeover has been clearly pointed out in the 0–0.5 ML range. We have discussed the depth sensitivity of XAS in total electron yield mode due to the electron mean free path in RE, as well as the importance of angular-dependent saturation effects. The upper limit for the probing depth of XAS of Sm in electron yield mode is found to be about 30 Å.

The analysis of the Sm/Si(111)7×7 XAS data is understood consistently with the general phenomenology of rare-earth chemisorption on silicon and epitaxy of pseudodisilicides on the (111) silicon surface. The Sm atoms in the ordered sites of the epitaxial silicide are homogeneously trivalent. The surface termination of the silicide with heteroepitaxial silicon eliminates any surface divalent signal from Sm.

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