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Cite as: Appl. Phys. Lett. **58**, 1605 (1991); <https://doi.org/10.1063/1.105139>

Submitted: 26 November 1990 • Accepted: 11 February 1991 • Published Online: 04 June 1998

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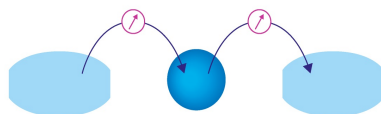
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Reversible $\text{Eu}^{2+} \leftrightarrow \text{Eu}^{3+}$ transitions at Eu-Si interfaces

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(Received 26 November 1990; accepted for publication 11 February 1991)

Valence switching at Eu-Si interfaces is demonstrated by resonant photoemission during repeated oxidation-reduction cycles performed by room-temperature O_2 exposure and mild heating. The $\text{Eu}^{2+} \leftrightarrow \text{Eu}^{3+}$ transitions are accompanied by Fermi level switching associated with changes in the stoichiometry of the surface heterostructure. The ability to cycle between two well-defined magnetic states at a surface may be attractive in technological applications.

Europium is a notable exception among the rare-earth elements in that it is divalent in the atom and in the metal,^{1,2} with a $[\text{Xe}]4f^7 6s^2$ electron configuration and a $^8S_{7/2}$ ground state, whereas most of the other rare-earth elements are trivalent with three $5d 6s$ derived valence electrons in the condensed phase.³ The reason for the divalency of Eu is the particularly high Hund's correlation energy at the half-filled $4f$ shell, which cannot be overcompensated by the gain in cohesive energy in a hypothetical trivalent state of the metal. However, in compounds Eu is known to exist also in the trivalent state, which is created by promotion of an electron from the localized $4f$ shell to the delocalized valence states, where it can take part in the bonding. Thus, a valence change is accompanied by a change of the $4f$ configuration of Eu from $4f^7 \rightarrow 4f^6$ or vice versa. There are compounds in which Eu can adopt both valencies, e.g., in the oxides, where divalent EuO , trivalent Eu_2O_3 , and mixed valent Eu_3O_4 are known. Besides differences in bonding configurations the magnetic properties of Eu^{2+} and Eu^{3+} are very different: Eu^{2+} with its $^8S_{7/2}$ ground state is highly paramagnetic—with an effective magnetic moment $\mu_{\text{eff}} = 7.9\mu_B$ in Eu chalcogenides⁴—whereas Eu^{3+} has a nonmagnetic 7F_0 ground-state configuration and shows only weak Van Vleck-type paramagnetism.⁵

In the present study the valency of Eu at Eu-Si(111) interfaces has been investigated using resonant $4f$ photoemission techniques, and we found that the valency of Eu ions and thus their magnetic moment can be switched reversibly from divalent to trivalent and vice versa by O_2 exposure and mild heat treatments. Thin films of Eu have been evaporated onto clean Si(111) single-crystal surfaces with a (7×7) low-energy electron diffraction (LEED) structure under ultrahigh vacuum conditions, and photoelectron spectra of the *in situ* deposited films have been recorded at the high-energy toroidal grating monochromator (HE-TGM 2) beamline of the synchrotron radiation laboratory Berliner Elektronen-Speicherring-Gesellschaft für Synchrotronstrahlung (BESSY) in Berlin with an ellipsoidal mirror electron analyzer.⁶ As reported elsewhere, Eu forms so-called reactive interfaces with silicon, with silicide-type reaction products.⁷ The stoichiometry of these silicide phases depends on the Eu coverage and on the temperature, but Eu remains divalent through-

out the interaction with silicon.

The bottom curve of Fig. 1 shows the valence-band region of 1 Å Eu (≈ 0.25 monolayer) on Si(111) recorded with a photon energy of ≈ 142 eV. At this photon energy the photoionization cross section of the Eu $4f$ levels is greatly enhanced as a result of the giant $4d$ - $4f$ resonance,⁸ and the spectrum is therefore dominated by a single peak at ≈ 2 eV below the Fermi level containing the unresolved multiplets of the 7F_0 photoionized final state of divalent Eu. The Si and Eu derived valence states have very small cross sections at this photon energy as compared to the $4f$ states and are virtually invisible in the display of Fig. 1. Resonant $4f$ photoemission is therefore a unique tool to investigate the valence state of Eu at such interfaces. Exposing the Eu-Si interface to O_2 at room temperature results in a valence change of the Eu atoms to predominantly trivalent as signaled by the appearance of the characteristic multiplet structure of trivalent Eu in the energy range 7.5–11.5 eV below E_F .⁹ Gentle heating of this oxidized interface to $\approx 200^\circ\text{C}$ for about 30 s reverts the valency of Eu back to divalent. The interesting observation of the present study is that this reversible “valence switching” cycle can be performed many times as indicated in Fig. 1. After ten oxidation-reduction cycles, renewed heating of the oxidized surface to 200°C is insufficient to restore the divalency of Eu, but heating to higher temperature (e.g., 500°C) again regenerates the divalent Eu (see the 3 top curves in Fig. 1). The valence changes of Eu are accompanied by reversible binding energy shifts of the divalent Eu spectral components as indicated on the figure, and we will come back to this point further below. The effects described here are not restricted to submonolayer coverages of Eu, but can also be observed for thicker films (e.g., 10–20 Å) as shown in Fig. 3(b).

Experiments have been performed to test the ability of laser irradiation to achieve the temperature-induced part of the valence switching. The oxidized interfaces were irradiated with a defocused 35 mW He-Ne laser beam (illuminated sample area $\sim 5 \text{ mm}^2$), and photoelectron spectra were recorded from illuminated and pristine parts of the sample surface. The spectral results revealed that relatively weak laser irradiation of several minutes was sufficient to reduce the Eu^{3+} component of the interface locally to

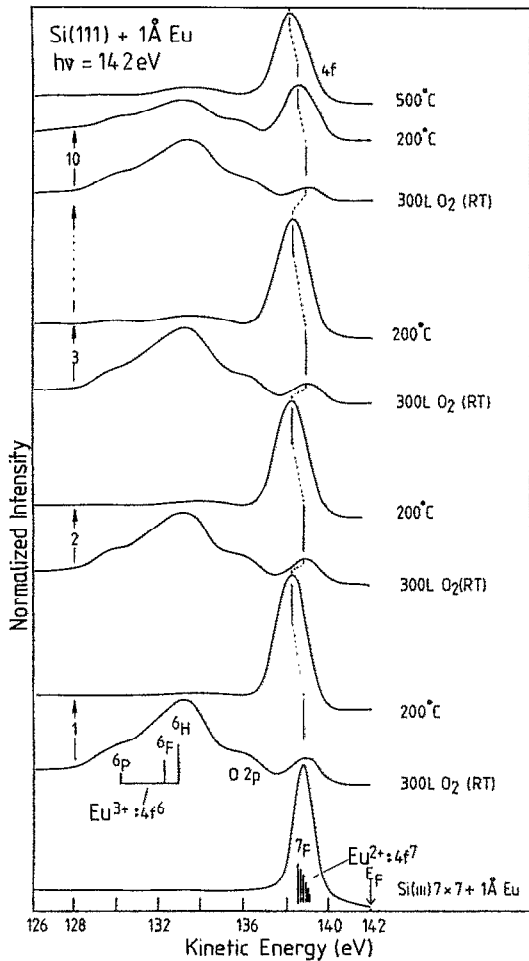


FIG. 1. Resonant photoemission spectra of the $4f$ states of 1 \AA Eu-Si(111) during cycles of valence switching, performed by O_2 exposure and subsequent mild heat treatment. The figures on the left-hand side give the numbers of consecutive switches.

Eu^{2+} . Thus, there is the potential of optical switching of the valence change.

One suspects that the presence of Si is at the root of this reversible valence switching phenomenon. It has been shown previously that the oxidation of Si at room temperature is greatly enhanced by the presence of thin rare-earth metal layers.¹⁰ Figure 2 displays Si $2p$ core level photoemission spectra, measured using the same photon energy of $h\nu \approx 142 \text{ eV}$, during the valence switching cycles. The bottom spectrum shows that for Si + 1 \AA Eu exposed to 300 L O_2 [$1 \text{ Langmuir (L)} = 1 \times 10^{-6} \text{ Torr s}$] the Si $2p$ signal consists of two structures at ≈ 41 and $\approx 38 \text{ eV}$ kinetic energy, originating from bulk and oxidized Si atoms, respectively. This indicates that Si is oxidized at the interface. During the valence switching cycles Si becomes progressively more oxidized, the distance between bulk and oxidized Si $2p$ components increases in energy,¹¹ and the intensity ratio between the two components decreases; oxygen is therefore pumped into the silicon. A concomitant observation is that the Si $2p$ structures shift forth and back in energy during the valence switching cycles. The shift of

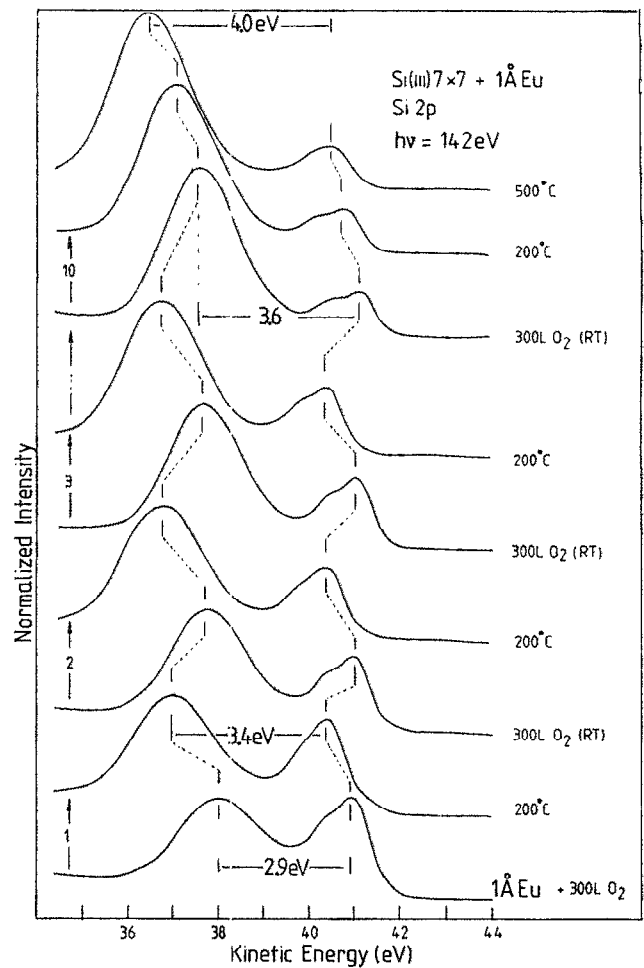


FIG. 2. Si $2p$ core level spectra during cycles of valence switching. The spectral structures at kinetic energies $40\text{--}41 \text{ eV}$ are due to Si atoms in pure Si bulk environment, whereas the peaks at the lower kinetic energies (= higher binding energies) originate from oxidized Si atoms.

the bulk Si $2p$ signal reveals a movement of the position of the Fermi energy of the system in the semiconductor band gap during the oxidation-reduction cycles, and this is also responsible for the reversible $\text{Eu}^{2+} 4f$ shifts noted above in Fig. 1.

The driving force for the $\text{Eu}^{2+} \leftrightarrow \text{Eu}^{3+}$ valence change can be associated with changes in the local oxygen concentration at Eu sites, and the possibility of reversibility is provided by the Si environment. Oxygen exposure increases the oxygen concentration at the surface to a level where Eu^{2+} turns to Eu^{3+} ; note that a minimum O_2 exposure of the interface of $\approx 5\text{--}10 \text{ L}$ is necessary to induce the valence change. Si is the reducing agent in the subsequent reversal step, acting as an oxygen sink when diffusion, promoted by the elevated temperature, allows the O transport from Eu to Si sites. We conjecture that a ternary Eu-Si-O silicate-type surface compound is being formed¹² with the possibility of Eu in different valencies, and the valence switching can then be depicted schematically

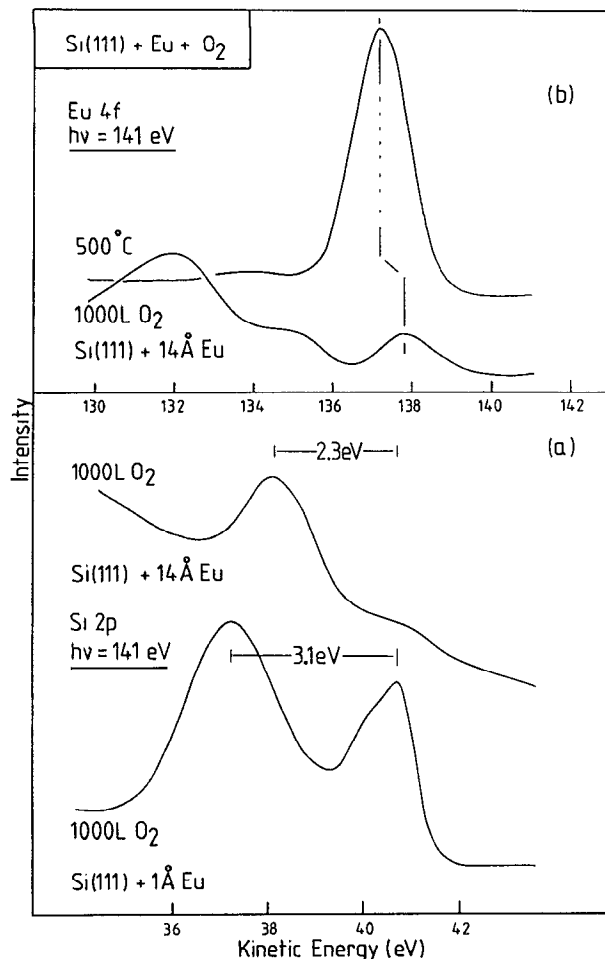
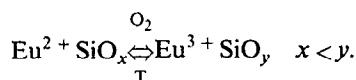


FIG. 3. (a) Si 2p core level spectra of 1 Å Eu-Si and 14 Å Eu-Si exposed to 1000 L of O₂. (b) Resonant 4f photoemission spectra of 14 Å Eu-Si showing the valence change from trivalent (after O₂ exposure) to divalent (after heating to 500 °C).



The notion of a silicate phase is corroborated by the Si 2p core level data of Fig. 3(a). The position of the Si 2p components of the oxidized Eu-Si interfaces is a function of the Eu concentration: whereas a chemical shift of 3.1 eV with respect to the Si bulk signal is observed for the oxidized 1 Å Eu-Si phase, the oxidized Si 2p component of the 14 Å Eu-Si phase shows a shift of only 2.3 eV. We take the dependence of the Si 2p position on the Eu stoichiometry as an indication of ternary compound formation.

These silicate phases may also play a role in the observed movement of the Fermi energy position in the semi-

conductor band gap during valence switching. The silicate compounds are insulators as evidenced by the absence of filled density of states at the Fermi level in UV photoemission and inverse photoemission spectra,¹³ and these surface phases may form heterostructures with the Si substrate. The Fermi energy position in these systems can depend on the stoichiometry and the geometrical structure of the interface,^{14,15} which in turn may depend on the valence state of the Eu and on the oxygen concentration.

In summary, we have observed a reversible switching of the valency of Eu ions and, by implication, of their magnetic state in thin interfacial layers of Eu on silicon. The valence changes in these structures are driven by variations in the local oxygen concentration mediated by O₂ exposures from the gas phase and by mild heat treatments. The latter step can be achieved by laser irradiation: the trivalent Eu³⁺ of the oxidized interface can be switched locally to divalent Eu²⁺ by irradiation with a 35 mW He-Ne laser for several minutes. These structures therefore provide a two-state magnetic system with technological potential.

This experimental program has been supported by the Fonds zur Förderung der Wissenschaftlichen Forschung of Austria. We are grateful to Professor J. A. D. Matthew, University of York, for enlightening discussions during the course of this work.

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