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Silicide formation and valence switching at the Eu–Si interface monitored by electron energy loss spectroscopy in the reflection mode

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Abstract. Electron energy loss spectroscopy in the reflection mode is used to probe changes in the electronic environment and valence changes at Eu–Si interfaces. Reaction of divalent Eu and Si leads to depletion of dipolar electronic excitations at around 4 eV and formation of a divalent silicide with a bulk plasmon energy $\hbar\omega_p = 12$ eV. At primary energies less than 200 eV $4f^n-4f^n$ spin flip excitations are accentuated: modifications in the excitation spectrum on valence change for divalent Eu($n = 7$) to trivalent Eu($n = 6$) on oxidation are demonstrated, and the effect is used in monitoring valence switching during successive oxidation/heating cycles on the silicide.

1. Introduction

Eu has a stable $4f^7 8S_{7/2}$ divalent ground state in the atom and the metal, but also is trivalent in many compounds including the oxide Eu_2O_3 in which promotion of a 4f electron into a delocalized valence band state leads to a reduction in energy. Henle *et al* (1991) recently studied the valency of Eu at Eu–Si(111) interfaces using resonant 4f photoemission and demonstrated reversible switching from divalency to trivalency induced by successive O_2 exposure and heat treatment. In this paper we show that both silicide formation and valence switching can be demonstrated without recourse to synchrotron radiation: electron energy loss spectra (EELS) in the loss energy region $\Delta E = 3\text{--}7$ eV emphasize both distinctive dipolar loss changes and modifications in dipole-forbidden 4f–4f excitations as a result of surface reactions. Valence switching from a $4f^7$ to $4f^6$ Eu ground state can then be readily monitored.

The 4f electrons in the rare earths retain their atomic character and in electron energy loss spectroscopy (EELS) in reflection mode transitions between $4f^n$ multiplet states have been identified by Bauer and Kolaczkiwicz (1985), Modesti *et al* (1985) and Stenborg and Baer (1988). Della Valle and Modesti (1989) demonstrated correspondence with the weak optical spectra of dilute rare earth ion impurities in ionic environments, with the spectral structure of x-ray photoemission of $4f^{n+1}$ systems and with the Bremsstrahlung isochromat of $4f^{n-1}$ systems. The interpretation is further supported by the insensitivity of the phenomena to chemical changes that do not involve valence modification. One surprising feature was the primary

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electron energy (E_p) range within which $4f^n-4f^n$ transitions were prominent, typically $50 < E_p < 200$ eV. For $4f^7 8S_{7/2}$ ground state all $4f^7-4f^7$ excitations involve spin flip transitions whose cross sections fall off approximately as E_p^{-3} (Joachain 1983) rather than the $E_p^{-1} \ln(\gamma E_p/\Delta E)$ variation ($\gamma \sim 1$) which characterizes dipole processes. Matthew *et al* (1991) showed that in Gd the non-dipole signals were mainly due to large-angle inelastic scattering without elastic reflection, in contrast to the dipole contribution which is dominated by small-angle inelastic scattering accompanied by high-angle elastic scattering. When the energy dependence of the elastic scattering cross sections is taken into account, the *ratio* of spin flip to dipole intensity peaks above $E_p \sim 100$ eV before falling rapidly beyond $E_p \sim 200$ eV. In addition resonant enhancement of $4f-4f$ excitation arising from the decay of $4d^{10}4f^n + e \rightarrow 4d^9 4f^{n+1} + e'$ excitations augments the loss signal.

The $4f^7$ and $4f^6$ configurations of divalent and trivalent Eu have distinct multiplet structures and so EELS spectra should show characteristic changes in a valence switch. However, Eu differs from Gd in another way: the shallow filled states in divalent Eu undergo dipolar transitions which may overlap the $4f^7-4f^7$ loss region and are also quite sharp. In this paper we show how changes in the dipole components provide excellent monitors of chemical reactions at the surface without change of valence, while the $4f^n-4f^n$ transitions confirm valence switching during oxidation \leftrightarrow heating cycles.

2. Experimental details

Electron energy loss spectra were recorded with a concentric hemispherical electron analyser (Leybold LH10) in approximately specular reflection geometry. The combined EELS resolution of the spectrometer (electron gun plus analyser) was ~ 0.5 eV. Eu was evaporated onto clean Si(111) surfaces at ambient pressures $< 1 \times 10^{-9}$ mbar during evaporation, and the cleanliness of the deposited films was checked by Auger electron spectroscopy. Mean film thicknesses were measured with a quartz microbalance, and oxygen dosages were performed via a leak valve from the system ambience. The silicon substrates could be heated by calibrated DC currents to give the indicated elevated temperatures necessary for the silicide formation (Henle *et al* 1991b).

3. Theoretical expectations

Low-energy losses in Eu and Eu compounds may be of three basic types, as listed below.

(i) *Bulk and surface plasmon losses*—divalent Eu metal (two quasi-free electrons per atom) has its main bulk plasmon excitation at $\Delta E = 8$ eV, while Eu compounds e.g. oxides have higher mobile densities with plasmon excitations in the energy region 12–14 eV. At lower primary energies there may be significant surface plasmon loss contribution ($\epsilon_1 \sim -1$). Similarly elemental Si has prominent bulk and surface plasmon losses at $\Delta E = 17$ and 10 eV respectively.

(ii) *One electron dipolar transitions*—excitations from filled conduction band states to empty states above the Fermi level in rare earth metals may give rise to one-electron dipolar excitations (peaks in ϵ_2) with $\Delta E \sim 3$ –5 eV. In the case of Eu the

presence of 4f levels of low binding energy (~ 2 eV) and the peaking of d band density at ~ 1.5 eV above the Fermi level (Hofmann and Netzer 1991) leads to the possibility of 4f–5d-like transitions, which will be very sensitive to the chemical environment: marked modification in the loss spectrum will be expected when Eu reacts, e.g. with Si even when there is no valence change.

(iii) $4f^n-4f^n$ transitions—Eu will also be characterized by dipole-forbidden $4f^n-4f^n$ transitions involving spin flip. These are highly localized excitations (the 4f orbital size is less than 1 Å) and will be very insensitive to environment provided there is no valence change. However, Eu may be in the divalent $4f^7\ ^8S_{7/2}$ or in the trivalent $4f^6\ ^7F_0$ ground state, and the spectral distribution of $4f^7-4f^7$ transitions will differ significantly from those of $4f^6-4f^6$. The nature of such differences may be readily estimated from the rare earth Bremsstrahlung isochromat spectra (BIS) of Lang *et al* (1981) and Baer and Schneider (1987): for the case of Sm ($4f^5$ ground state) an electron goes into an empty 4f level so that the experimental results span the manifold of $4f^6$ states (figure 1(a)). Since the sizes of the 4f orbitals in the rare earths vary slowly along the series, the energies observed there should be good indicators of the $4f^6-4f^6$ transition energies in trivalent Eu. The 7F_0 state is around 0.5 eV above E_F with the remaining 5X states, where X denotes the total angular momentum of the multiplet ($X = S, P, D, F, G, H, I$), clustered between 3 and 5 eV. Further insights can be gained from the 5X_J satellites observed by Gerken (1983) in resonant photoemission from Gd. Starting from the $4f^7\ ^8S_{7/2}$ ground state it is not possible to access the $4f^6\ ^5X_J$ states by direct photoemission, but $4d^{10}4f^7 \rightarrow 4d^94f^8$ transitions decaying to $4d^{10}4f^6 + e$ may involve a spin flip to yield the quintet states, which are clustered at binding energies around 4 eV above the 7F_J states, the only feature seen off-resonance. Finally theoretical calculations of weak $4f^6-4f^6$ optical transitions in free Eu^{3+} by Carnall *et al* (1968) also suggest that the transitions should, at the energy resolution of the experiments presented here, be concentrated into a single unresolved loss peak around $\Delta E = 4$ eV.

The BIS of trivalent Eu in EuPd_3 (figure 1(b)) gives a good indication of the likely spectral structure in $4f^7-4f^7$ transitions of divalent Eu. The lowest $^8S_{7/2}$ state lies just above the Fermi level, but the excited 6X states cover a wider range of energy than for $4f^6$ transitions with significant intensity expected around $\Delta E = 6$ eV. This pattern is confirmed by the observations of $4f^7-4f^7$ transitions in Gd (Matthew *et al* 1991), where two distinct groups of losses are found. $4f^n-4f^n$ transitions may be readily distinguished from plasmon losses and one-electron dipole processes by the rapid fall off of their intensity above $E_p = 200$ eV, and their contribution may be enhanced relative to other losses by choice of experimental conditions.

4. Results and discussion

The results presented here should be put into the context of previous studies of the Eu–Si system and its oxidation by Henle *et al* (1991a, b) and Hofmann *et al* (1991). The Eu–Si interface is highly reactive at room temperature with a reaction onset at half a monolayer Eu coverage. Heat treatment may give rise to epitaxial silicide phases in which Eu remains divalent as indicated by resonant enhanced photoemission from the Eu 4f levels. O_2 exposure at room temperature then leads to a ternary Eu–Si–O silicate-like phase where the Eu is dominantly trivalent. This paper will show

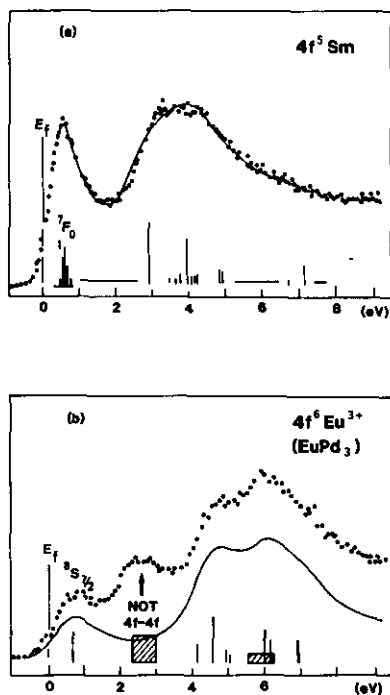


Figure 1. Bremsstrahlung isochromat spectroscopy of (a) Sm metal (ground state $4f^5$): model for $4f^6-4f^6$ transitions in trivalent Eu; and (b) trivalent Eu (ground state $4f^6$) in EuPd_3 : model for $4f^7-4f^7$ transitions in divalent Eu. The spectra are adapted from Lang *et al* (1981) and Baer and Schneider (1987).

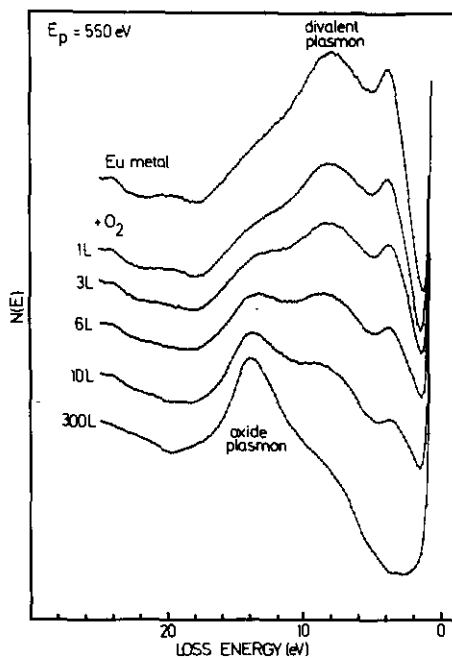


Figure 2. Electron energy loss spectra of a thick clean Eu metal film (85 Å on Si) in $N(E)$ form with primary energy $E_p = 550$ eV exposed to controlled amounts of O_2 . (1 Langmuir (L) = 10^{-6} Torr s.)

how valence switching may be probed without the need for synchrotron radiation tuned to a Eu resonance.

4.1. Thick Eu films

Figure 2 shows the EELS spectra for 85 Å of Eu on Si and those of the sample exposed to varying amounts of O_2 for $E_p = 550$ eV, i.e. at a primary energy at which the conventional dielectric model relating the loss spectrum to $\text{Im}(-1/\epsilon)$ and $\text{Im}(-1/(\epsilon + 1))$ is likely to be valid. Although there is interaction between Eu and Si at the interface, EELS, with its limited sampling depth, here samples only the surface region of clean Eu metal and its oxidation products. The clean metal is characterized by the divalent bulk plasmon ($\Delta E = 8$ eV) and a relatively sharp feature at $\Delta E = 3.5$ eV, a pattern very similar to that found in many rare earth metals. The origin of such low-energy losses remains controversial with possible contributions from allowed $4f-5d$ transitions in this system. Oxidation leads to a steady depletion of the 3.5 eV loss: it is known from the inverse photoemission studies of Hofmann *et al* (1991) that oxidation rapidly removes the empty 5d states, i.e. the likely final states of the loss, from just above the Fermi level to higher energy. At the same time there is a build up of a new loss at $\Delta E = 14$ eV (figure 2)

corresponding to an oxide plasmon, a pattern similar to oxidation of divalent Yb (Bertel *et al* 1982). By 300 L O₂ oxidation in the surface region is substantially complete.

Figure 3 examines the same oxidation sequence at $E_p = 60$ eV, an energy regime where 4f excitation may be prominent: now the low-energy transition in the metal is more intense than at $E_p = 550$ eV, while the plasmon loss contains a greater surface contribution below 8 eV (figure 3(a)). The EELS spectra evolve with oxygen exposure almost as before, but with one important difference: the main low-energy loss declines in intensity but a sharper loss feature in the same energy range survives. This is confirmed in the d^2N/dE^2 spectrum which suggests the presence of narrow peaks at 3.3, 4.7 and 7.3 eV with greatest prominence at the lowest of these (figure 3(b)). Under such experimental conditions a mixed oxide with trivalent Eu dominant is expected (Strasser *et al* 1982) and the observed peaks will correspond to some mixture of $4f^6-4f^6$ and $4f^7-4f^7$ transitions. Note that spin flip excitations are difficult to observe in the clean metal, but easier to isolate in the oxide because of the depletion of competing dipolar processes.

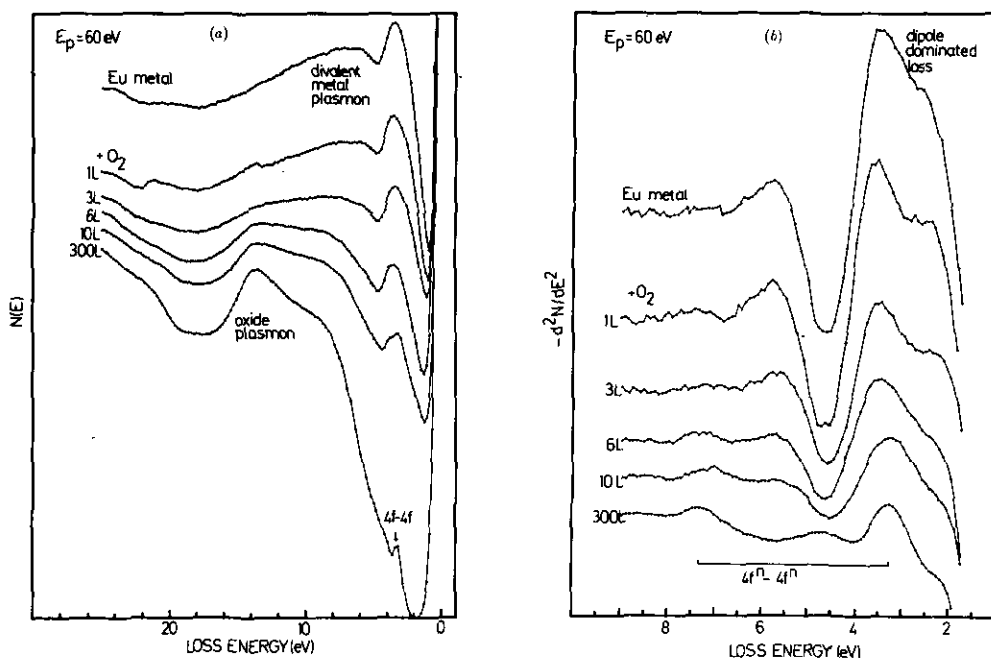


Figure 3. EELS spectra of a thick clean Eu metal film (85 Å) exposed to O₂ for primary energy $E_p = 60$ eV: (a) $N(E)$; (b) d^2N/dE^2 .

4.2. Si + 40 Å Eu

With 40 Å Eu on Si the substrate begins to play a rôle in the observations (figure 4). At $E_p = 550$ eV the clean metal spectrum is similar to before, although the plasmon loss is now broader. Heating to 650°C induces dramatic changes: the low-energy

transition and the divalent metal plasmons are greatly depleted, but two new losses emerge at $\Delta E \sim 17$ eV and $\Delta E = 12$ eV. The former corresponds in energy to that of the bulk plasmon of Si and may correspond either to elemental Si or a highly Si-rich phase, while the 12 eV loss may be that of the divalent silicide observed by Henle *et al.* (1991a, b) using photoemission. Oxidation now leads to a gradual depletion of the silicide peak with the 17 eV loss remaining prominent: this is consistent with enhanced rates of oxidation in the presence of the rare earth.

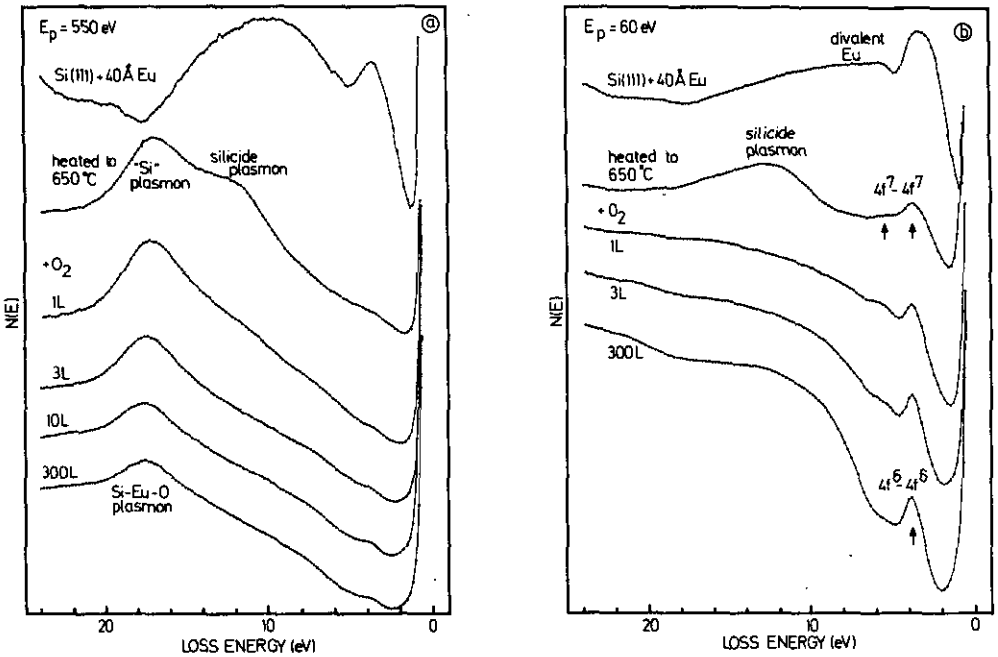


Figure 4. EELS spectra of Si + 40 Å Eu in $N(E)$ for (a) $E_p = 550$ eV, (b) $E_p = 60$ eV. Note changes in the spectra due to silicide formation on heating and on formation of a silicate-like phase on oxidation.

The $E_p = 60$ eV spectrum losses paint a slightly different picture: on heating the silicide plasmon loss is much more prominent than the 'Si', a result that may reflect the differing depth of sampling of the two experiments. In addition the low-energy loss narrows and shifts, reflecting as before modifications of the dipole losses with changing environment to reveal $4f^7-4f^7$ transitions. Before exposure to O_2 and at low exposure two peaks are in evidence at $\Delta E = 3.7$ and 5.5 eV. With oxidation to a mainly trivalent oxide (as discussed by Henle *et al.* 1991a) the higher-energy peak decreases with intensity signalling valence change.

4.3. Si + 20 Å Eu

With 20 Å Eu on Si (figure 5) more modest heating ($\sim 250^\circ\text{C}$) promotes silicide formation at the surface. With a primary energy of $E_p = 150$ eV spin flip transitions are prominent, a result consistent with the previous experiments on Gd. As before, oxidation modifies the spin flip transitions at low loss energy indicating valence

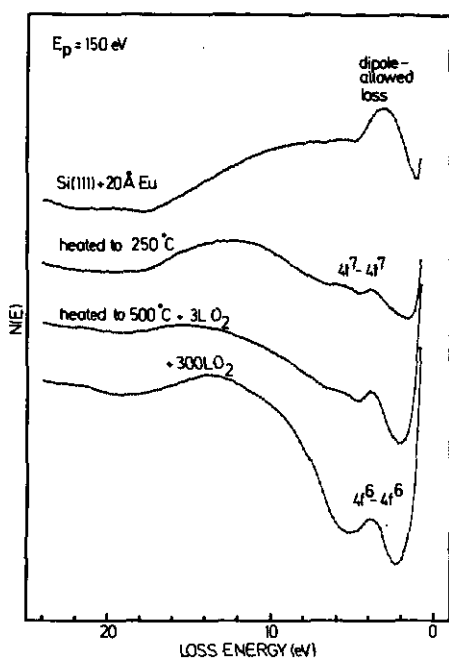


Figure 5. EELS spectra of Si + 20 Å Eu in $N(E)$ form at $E_p \approx 150$ eV emphasizing changes in $4f^n-4f^n$ transitions in the 3–6 eV loss energy range associated with silicide formation on heating (divalent Eu) and on development of a silicate-like phase on O_2 exposure (trivalent Eu).

change, while the plasmon losses indicate the presence of a Si-dominated phase and a silicon-rich silicide phase prior to oxidation.

4.4. Si + 5 Å Eu

At 5 Å Eu (1.5–2 monolayers) a reaction with Si at the interface is observed at room temperature and the loss spectra ($E_p \approx 150$ eV) immediately reveal two $4f^7-4f^7$ losses accompanied by a broad silicide plasmon (figure 6(a)). The spin flip losses change as before on oxidation, but it is possible to continue the cycle by analogy with the work of Henle *et al* (1991)—figure 6(b). It is known that heating the oxidized silicate-like phase containing trivalent Eu leads to the diffusion of oxygen into the substrate and reformation of a mainly divalent phase with lower oxygen concentration. Heating to 200 °C changes the intensity of the loss around 4 eV and shows evidence of a higher transition characteristic of a $4f^7$ configuration. Repeating the oxidation reduces the 4 eV loss intensity and the higher loss ceases to be resolved. Heating again to 200 °C revives somewhat the $4f^7-4f^7$ loss pattern, while raising the temperature to 500 °C increases the intensity of the higher 4f spin flip loss consistent with recovery of the divalent phase. Looking at the cycle in d^2N/dE^2 (figure 6(c)) gives further support to valence switching with loss peaks at ~ 4 and ~ 5 eV fluctuating both in absolute and relative intensity.

5. Conclusion

Electron energy loss spectroscopy on the Eu-Si system is shown to be highly sensitive both to environmental changes and valence changes at the surface. At primary energies above 250 eV dipole excitation dominates with the low-energy losses probing empty 5d state density, while at lower primary energies spin flip $4f^n-4f^n$ transitions

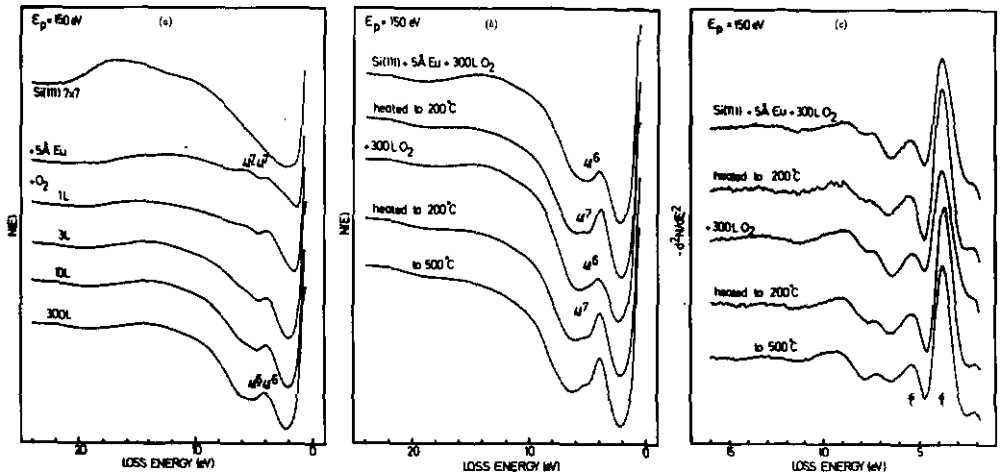


Figure 6. EELS spectra of Si + 5 Å Eu at $E_p = 150$ eV: (a) $N(E)$ spectra showing effects of oxidation at the reacted interface; (b) $N(E)$ spectra under successive heating and oxidation cycles; (c) corresponding d^2N/dE^2 spectra.

become prominent. Differences between the $4f^7-4f^7$ transitions in divalent Eu and the $4f^6-4f^6$ transitions of trivalent Eu are clearly demonstrated, and the effect is used to monitor valence switching in successive heating and oxygen exposure cycles.

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