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Low-electronegativity overlayers and enhanced semiconductor oxidation: Sm on Si(111) and GaAs(110) surfaces

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Thin mixed-valence overlayers ($\gtrsim 1$ monolayer) of Sm deposited on Si or GaAs cleavage surfaces prior to oxygen exposure give rise to oxidation promotion effects of unprecedented magnitude. In contrast with this, purely divalent Sm overlayers (thickness <1 monolayer) exhibit negligible oxidation promotion activity on Si(111). On GaAs(110) divalent and trivalent Sm species promote the formation of different reaction products. We examine the role of metal electronegativity and metal-semiconductor interface morphology in determining the specific catalytic activity of the overlayer.

Control of semiconductor surface reactions through a suitable catalyst could have a dramatic impact on semiconductor technology. Pioneering photoemission work has shown that ultrathin metal overlayers can enhance the oxidation rate of Si(111) (Refs. 1–4) and GaAs(110) (Refs. 5–7) surfaces or stabilize new oxide phases on Ge.[8] These studies have mostly focused on noble or near-noble metals, although a few results involve Al (Ref. 8) and Cs (Ref. 5) overlayers.

In this Brief Report we report a photoemission study of the catalytic activity of the low-electronegativity, rare-earth metal Sm in promoting Si(111)-O_2 and GaAs(110)-O_2 reactions. We provide evidence of oxidation promotion effects of unprecedented magnitude for Sm overlayers both on Si(111) and GaAs(110) surfaces. A complete analysis of the coverage dependence of this effect and of the stoichiometry of the reaction products is beyond the scope of this paper. Here we focus on the early stages of reaction and investigate the relationship between the valence of the overlayer and its catalytic activity. In particular, we report that oxidation promotion on Si is associated only with the presence of intermixed trivalent Sm species. On GaAs, divalent and trivalent Sm species both show catalytic activity, but promote the formation of different oxide reaction products.

Samarium was a natural choice for several reasons. First, Sm chemisorption on Si (Ref. 9), Ge (Ref. 9), and GaAs (Ref. 10) seems to follow a two-stage process, with a transition between a "weak chemisorption" stage, where Sm is mainly in divalent form and there is little evidence of metal-semiconductor interdiffusion, to a "reactive" stage, where silicidelike interface species are formed, Sm is mostly trivalent, and large core chemical shifts suggest a relevant ionic contribution to Si-metal bonding. The transition between the two stages occurs at approximately 1 monolayer coverage,[11] although clustering in the submonolayer region may contribute to some uncertainty in the transition coverage.[10] Because of the coverage-dependent interface morphology, Sm overlayers are an ideal test system to investigate the relationship between morphology and catalytic activity. Secondly, rare-earth compounds, and in particular oxides such as Ce_2O_3, have shown catalytic activity in promoting a number of surface reactions of metals.[12] Preliminary work on the Si(111):Ce-O_2 system[13] seems to indicate that they may also exhibit relevant catalytic activity for semicondutor surface reactions.

The low electronegativity of Sm also makes it an interesting system to search for a relationship between metal parameters and overlayer catalytic effects. In the most naive interpretation of catalytic promotion, low-electronegativity elements act as electron "donors," enhancing chemisorption and oxidation processes. Although theoretical studies[14] have demonstrated that the "electron donor" concept is a simplistic description of complex modification of surface or interface states, low-electronegativity overlayers are obviously promising cases in our search for catalysts with maximum specific activity.

The experiments were performed at the Synchrotron Radiation Center of the University of Wisconsin—Madison following the methodology described in Refs. 4, 6, 7, and 9. Angular-integrated photoelectron energy distribution curves (EDC's) of the Si $2p$, Ga $3d$, and As $3d$ core emission are shown after subtraction of a smooth secondary background.

In Fig. 1 we show representative EDC's for the valence-band emission at $h\nu=60$ eV from Sm overlayers on Si(111). The spectra are approximately normalized to the main emission feature and are given in arbitrary units. The bottommost EDC is for clean Si(111), while the spectra at metal coverages (θ) of 1 and 4 Å are representative of two different interface morphologies. In the submonolayer-coverage range most Sm atoms are in a divalent "weakly chemisorbed" state so that $Sm^{2+}4f$ features visible within 4 eV of E_F[10,11] dominate the spectrum. At coverages above a monolayer, trivalent Sm species dominate, giving rise to a characteristic Sm^{3+} multiplet between 4 and 10 eV below E_F. Exposure to 100 L of oxygen (1L $= 10^{-6}$ torr sec) (topmost EDC, $\Theta=4$) yields dramatic modification of the valence EDC which appears dominated by a strong O $2p$ signal with some residual Sm^{3+} emission. In Fig. 2 we show the Si $2p$ core emission before (dashed line) and after (solid line) exposure to 100 L of oxygen. The EDC's have been shifted rigidly when necessary to suppress small band-bending variations and they have been arbitrarily normalized to the Si $2p$ feature at the initial "substrate" position to emphasize line-shape changes. The bottommost EDC shows the effect of oxygen exposure on the Si $2p$ emission when no overlayer is present. Small oxide-induced features 1—3 eV below the main line are consistent with the relatively low oxygen saturation coverage obtainable on the clean Si(111) surface. The vertical bars in Fig. 2 at 0.9, 1.8, 2.6, and 3.5 eV mark the position of the chemically shifted Si $2p$ contributions associated by Hollinger and Himpsel[15] with Si atoms bonded to 1, 2, 3, and 4 oxygen atoms, respectively. Vertical bar α in the top section of Fig. 2 marks the position of the dominant Si $2p$ oxide feature observed by Riedel *et al.*[16] during oxidation of amorphous silicon.

At submonolayer Sm coverage ($\Theta_{\mathrm{Sm}} = 1$) the unoxidized Si $2p$ EDC (dashed line) is very similar to the bottom EDC because of the reduced Si-Sm interaction. Upon oxidation, increased emission is observed on the high-binding-energy side of the Si $2p$ core emission (solid line), suggesting limited oxide formation and low Si oxidation states. For coverages above 1 monolayer (topmost EDC), the unoxidized EDC (dashed line) is broadened by the presence of a low-binding-energy Si $2p$ component that is the result of the formation of a silicidelike reaction product. Upon oxidation, a dominant Si oxide feature appears where high-oxidation states for Si dominate. The magnitude of the oxidation promotion effect at monolayer coverages and at oxygen exposures of only 10—100 L is unprecedented within the series of metal overlayers examined in Refs. 2—5. The residual Si $2p$ emission near the zero for the energy scale appears dominated by a low-binding-energy oxide feature near 0.75 eV and some residual Si $2p$ substrate emission, while relatively little is left

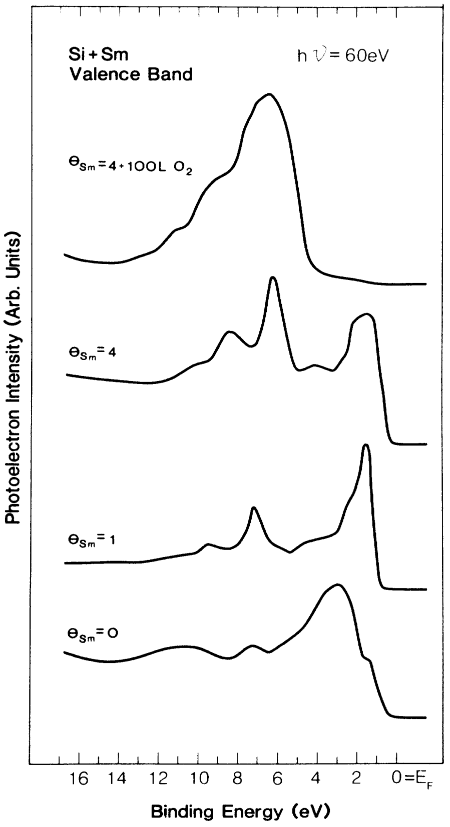

FIG. 1. Valence-band emission at $h\nu = 60\mathrm{eV}$ for Si(111) surfaces with Sm overlayers representative of the submonolayer ($\Theta_{\mathrm{Sm}} = 4$ Å) divalent chemisorption state and of the reactive stage ($\Theta_{\mathrm{Sm}} = 1$ Å) where Si-Sm silicidelike species are formed. Sharp emission features between 5 and 0 eV mostly reflect Sm^{2+} $4f$ final-state multiplets (see Refs. 10 and 11). The trivalent Sm $4f$ final-state multiplet appears between 10 and 5 eV. The topmost spectrum shows the effect of exposure to 100 L of oxygen for the $\Theta_{\mathrm{Sm}} = 4$ overlayer. The final line shape reflects a dominant O $2p$ contribution superimposed with residual Sm^{3+} $4f$ emission.

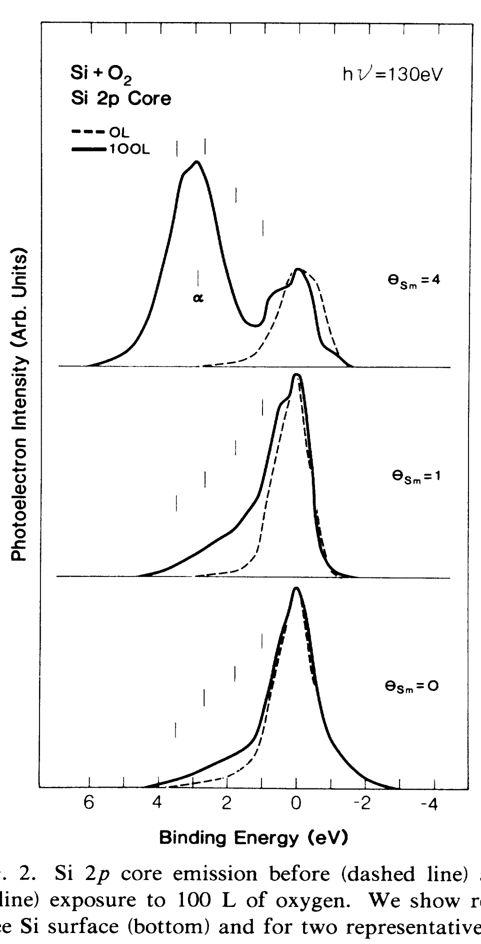

FIG. 2. Si $2p$ core emission before (dashed line) and after (solid line) exposure to 100 L of oxygen. We show results for the free Si surface (bottom) and for two representative Sm coverages. The broad dashed-line spectrum in the topmost section reflects a low-binding-energy Si $2p$ contribution from Si-Sm silicidelike interface species. Upon oxidation, strong promotion effects are observed when trivalent Sm species are present in the interface region. The vertical bars mark the position of Si $2p$ oxide features associated by Hollinger and Himpsel (Ref. 15) with Si atoms coordinates with one, two, three, and four oxygen atoms. Vertical bar α marks the position of a Si $2p$ oxide feature identified by Riedel *et al.* (Ref. 16) during oxidation of amorphous silicon.

of the silicidelike emission feature. If higher oxygen exposures are used, the oxide features are further increased relative to the substrate contribution, and no saturation is observed up to 100 L exposure. The strong promotion effect phenomenologically corresponds to the presence of trivalent Sm in an intermixed Si-Sm interface region. The oxidation promotion effect observed at submonolayer metal coverage ($\Theta_{\mathrm{Sm}}=1$) is relatively minor, and could be explained by the presence of a small Sm^{3+} contribution (see Fig. 1, $\theta_{\mathrm{Sm}}=1$) even at submonolayer coverage, indicating inhomogeneities in the thickness of the Sm overlayer.[11]

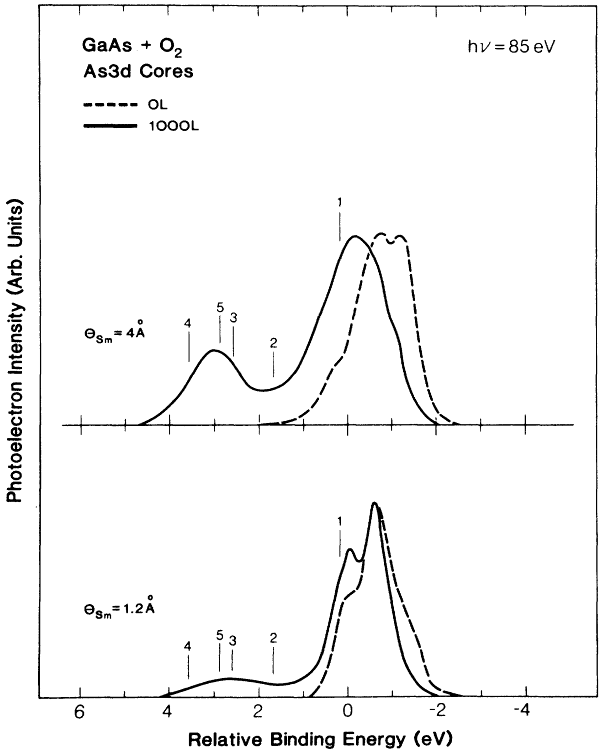

FIG. 3. As 3*d* core emission at $h\nu=85$ eV from GaAs(110) surfaces before (dashed line) and after (solid line) exposure to 1000 L of oxygen. Before oxidation the result of As interaction with mostly trivalent Sm atoms is the emergence of a low-binding-energy 3*d* contribution at about -1.2 eV associated with the formation of arsenidelike interface species. The zero of the binding-energy scale corresponds to the initial flat band As 3*d* binding energy for the free surface. In this exposure range oxidation of the free surface yields only minor modifications of the core line shape, while the presence of Sm overlayers yields oxidation promotion effects. Oxidation gives rise to two distinct oxidized As features, one centered at about 3 eV, and a second one near the zero of the binding-energy scale that involves lower oxidation states and dominates when Sm atoms are mostly in a trivalent state. The vertical bars 1–4 mark the position of the oxidized As 3*d* features observed by Landgren *et al.* (Ref. 18) for As coordinated with one to four oxygen atoms. The vertical bar 5 marks the position of the As 3*d* core level in $\mathrm{As_2O_3}$, from Su *et al.* (Ref. 20).

Results for GaAs are shown in Fig. 3. The As 3*d* core emission is shown normalized to the main emission feature after subtraction of the secondary background. The zero of the binding-energy scale corresponds to the initial core binding energy for the clean surface in flat-band conditions. The bottommost EDC is representative of the submonolayer coverage where divalent Sm species dominate. EDC's at $\Theta_{\mathrm{Sm}}=4$ are representative of the coverage range where Sm^{3+} species become dominant. The spectra are shown before (dashed line) and after (solid line) exposure to 1000 L of oxygen.[17,18] If we focus on the unoxidized EDC's, the result of increasing Sm deposition is the emergence of a low-binding-energy component at about -1.2 eV in the As 3*d* line shape, a feature associated with the formation of As-Sm arsenidelike species in the interface region. In the lower section of Fig. 3 we see that at submonolayer coverage, when most Sm atoms are divalent, oxygen exposure gives rise to a broad emission band between 1 and 4 eV and to an oxidized feature that emerges near the zero of the energy scale. For $\Theta=4$, arsenidelike species involving Sm^{3+} atoms are observed[11] as a major emission feature near -1.2 eV, and oxygen exposure gives rise to two well-defined oxidized features: a broad dominant line near the zero of the energy scale, and a high-binding-energy feature near 3 eV, the latter clearly related to the feature observed at submonolayer Sm coverage. Vertical bars 1–4 in Fig. 3 indicate the position of As 3*d* features observed by Landgren *et al.*[18] 0.8, 2.3, 3.2, and 4.2 eV below the initial substrate As 3*d* binding energy, and associated by these authors with the presence of As coordinated with one, two, three, and four oxygen oxygen atoms, respectively. Vertical bar 5 corresponds to the position of the As 3*d* core level observed in $\mathrm{As_2O_3}$ by Su *et al.*[20] The results of Fig. 3 indicate that strong oxidation promotion effects yield the formation of oxidized As species with low-oxidation states and a second phase with higher stability (possibly similar to $\mathrm{As_2O_3}$). The formation of the first oxidized species is related to the presence of Sm^{2+} in the Sm-As interface reaction products, while the second species is related to the catalytic activity of the mixed valent Sm component. No saturation of oxygen uptake is observed up to exposures of 10^3 L.

For the Ga 3*d* line the discussion is complicated by the superposition with the Sm 5*p* core features.[19] We anticipate here that upon exposure to 1000 L of oxygen little oxidation effect is seen at submonolayer Sm coverage, while at $\Theta=4$, most Ga atoms within the experimental sampling depth appear oxidized.[19]

In conclusion, we have shown that thin Sm overlayers act as powerful promoters of the oxidation reaction on both Si(111) and GaAs(110) surfaces. The magnitude of this effect seems to indicate that the naive picture of low-electronegativity overlayers as "electronic promotors" of chemisorption is somewhat relevant. However, the tabulated metal electronegativity is certainly not the single parameter to be used to forecast promotion effects, since our results indicate, for example, that trivalent Sm atoms strongly bonded with Si at least in part ionically exhibit higher specific activity than divalent Sm overlayers.

Two factors that may play an important role are interface morphology and the formation of intermediate reaction products. In the case of Si, since trivalent Sm species are "dispersed" in an intermixed Si-Sm interface region, they may play the role of a dispersed catalyst occuping "active" surface sites that were not available in the submonolayer, divalent chemisorption stage. Alternatively, the oxidation reaction may take place through intermediate Sm compounds where Sm is in a trivalent state, such as a hypothetical Sm_2O_3 surface oxide. In this connection, we note that the formation of a surface Ce_2O_3 intermediate that acts as a medium for ionic transport is a basic element of a theory recently proposed to explain the activity of Ce overlayers during oxidation of Nb.[12] The occurrence of two different kinds of reaction products on GaAs as a result of the activity of divalent versus trivalent Sm species is unprecedented and could indeed be related to the formation of two different kinds of intermediates (oxides or arsenates) during the oxidation process.

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