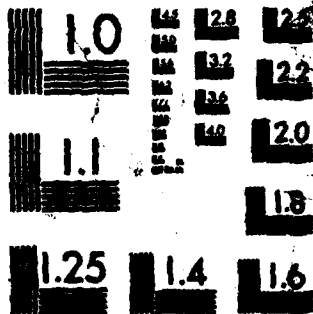END
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surface, on top of a Cr-As subsurface layer that remains largely unaffected
by oxidation.

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OVERLAYER-INDUCED ENHANCED OXIDATION OF GaAs SURFACES

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ABSTRACT

Thin metal overlayers deposited on GaAs (110) cleavage surfaces enhance the surface oxidation rate several orders of magnitude above the clean surface value. The magnitude of this effect depends on the chemistry of the overlayer, on the local morphology of the overlayer-semiconductor interface region and on the nature of the gaseous reactants. We present a synchrotron radiation photo-emission investigation of the GaAs surface interaction with oxygen in the presence of Ag, Au and Cr overlayers, and of the GaAs-H_2O reaction in the presence of Cr overlayers. We find that the promotion effect is maximum in the presence of Cr overlayers, and that the nature of the surface reaction products changes if oxygen or water is employed. In particular, in the case of oxygen, Ga and As-oxide phases are found with high atomic oxidation states present. If water is employed, only Ga oxide/hydroxyl phases are found at the surface, on top of a Cr-As subsurface layer that remains largely unaffected by oxidation.

INTRODUCTION

A number of metal overlayers on silicon yield an increase in silicon oxidation rate when the surface is exposed to an oxidizing atmosphere. Metals as diverse as Au[1,2], Ag[3,4], Cu[5], Pd[5] and Cr[6] have all been shown to give rise to promotion effects, with the production of Si-oxide phases of variable stoichiometry. In the case of Au[1] and Cr[6-7], the Si-oxide appears to nucleate on top of the metal overlayer. To the extent that the metal atoms increase the surface reaction kinetics and do not appear directly involved in the reaction product, i.e. the surface silicon oxide, they play the role of a catalyst. Since the magnitude of the effect depends on the overlayer-silicon interface morphology, in the absence of a more precise denomination we refer to such phenomena as interface catalytic effects.

In this paper we discuss a few examples of interface catalytic effects observed for GaAs. Our interest in GaAs stems from both technological and fundamental reasons. The possible use of practical catalysts to promote the formation of new stable insulating layers on GaAs surfaces would have substantial impact on device technology, if the reacted layers would exhibit inversion and accumulation characteristics suitable for MOS fabrication. From a fundamental point of view, our understanding of the microscopic mechanisms that determine interface catalytic effects could be greatly improved by considering GaAs-metal interfaces, which may exhibit for a given metal different chemistry and different local morphology relative to the silicon case.

The information on GaAs interface catalytic effects is very scarce. We are aware of only one other photoemission study[8], showing that enhanced oxidation effects are produced by submonolayer Cs deposition onto the GaAs(110) surface. We have previously reported[6] that Cr overlayers greatly enhance the GaAs-O_2

reaction at room temperature. Here we compare the effect of Cr overlayers with the effect of Ag and Au overlayers and examine the role of the metal chemistry and the metal-semiconductor interface structure. Ag and Au have similar chemistry, exhibiting relatively low reactivity for oxidizing species, but exhibit different interface morphologies. Several authors[9-10] have indicated a rather sharp GaAs(110)-Ag interface with little or no atomic interdiffusion and possible island formation. For GaAs(110)-Au most authors concur[11-13] in indicating substantial atomic interdiffusion, with the formation of an extended intermixed interface region. Correspondingly, we find evidence of Au-induced oxidation promotion, while no promotion effects are observed for Ag-overlayers. A quantitative comparison with the GaAs:Cr-O_2 case indicates that the promotion effect is greatly enhanced by the use of Cr, a refractory metal exhibiting an extended intermixed interface region with GaAs. Clearly the chemistry of the metal and the interface morphology both play a relevant role. We have also examined the effect of Cr overlayers on the GaAs interaction with H_2O. We have chosen H_2O as a prototype molecular oxidizing species because of its relevent technological role in silicon processing[14]. It has recently been suggested that the chemisorption of H_2O on GaAs shows similarities with GaAs-O_2 interaction[15-17]. We find, however, very dissimilar behavior in the presence of Cr. We do observe enhanced reaction kinetics in both cases, and H_2O chemisorption does not trigger a decomposition of the arsenide-like surface species, but selectively yields oxidation of Ga at the surface. This result appears related to the formation of Ga-oxide or hydroxyl phases where low Ga oxidation states dominate, rather than to the synthesis of Ga_2O_3 at the surface.

EXPERIMENTAL DETAILS

The experiments were performed on GaAs(110) surfaces obtained by cleaving 4 x 4 x 10 mm^3 single crystals of n-type, Te-doped, 10Ω x cm GaAs in-situ in our photoelectron spectrometer at operating pressure < 5 x 10^{-11} torr. Overlayers of Ag, Au and Cr were deposited in-situ from W-coil resistively heated evaporators at pressures below 4 x 10^{-10} torr. Overlayer thickness was monitored with a quartz thickness monitor. Exposure to water or oxygen was performed at pressures in the 10^{-7}-10^{-5} torr range. Ion pumps were isolated from the spectrometer during exposure and the system was pumped down in the 10^{-9} torr range with a cryopump prior to opening to the ion pump. Pressure during exposure was monitored with a low-emission ion gauge that was not directly in line-of-sight of the sample surface. Even with such precautions, we expect a definite contribution of excited molecular species to the gas composition during exposure. For comparison, we also conducted chemisorption studies of the GaAs(110) surface in the same conditions. Promotion effects (or the lack of them) due to the overlayer are defined by comparison with the results for the free surface.

The samples were positioned at the focus of a monochromatic synchrotron radiation beam and an electron energy analyzer. A toroidal grating monochromator or a "grasshopper" grazing incidence monochromator was used to disperse the radiation from the 240 MeV electron storage ring Tantalus at the Synchrotron Radiation Center of the University of Wisconsin-Madison. We used a commercial double pass cylindrical mirror analyzer to energy-analyze the photoelectrons in the GaAs:Ag case, and a hemispherical analyzer for the other studies. Angular-integrated photoelectron energy distribution curves (EDC's) were recorded for 40 < hν < 140eV with an overall energy resolution (electrons & photons) of 0.4 eV for all studies except GaAs:Ag (0.7-0.8eV) and are shown in figs. 1 to 7 after

subtraction of a smooth secondary background estimated with a polynomial fit of the high and low energy spectral range. Here we focus mostly on a systematic comparison of results for the Ga 3d and As 3d core line emission. More complete results concerning the valence states and metal cores from selected interfaces will be presented elsewhere[18-20].

RESULTS AND DISCUSSION

Oxidation

Studies of GaAs oxidation in the presence of Au, Cr and Ag overlayers are summarized in figs. 1-3. We explored overlayer thicknesses in the 0.1 - 15 A range and oxygen exposures in the 10 - 10⁴L range. The spectra have been approximately normalized to the intensity (peak height) of the main emission feature in order to emphasize the lineshape changes and are given in arbitrary units. The zero of the binding energy scale corresponds to the initial core binding energy for the clean surface in flat-band conditions. The metal coverage is given in A or monolayers[21].

In the top section of fig. 1 and 2 we show the lineshape of the As 3d and Ga 3d cores, respectively, for the clean surface (solid line) and after exposure to 1000L of oxygen. Note that the clean spectra (solid line) have been shifted 0.60 eV to lower binding energy to compensate for band bending and emphasize lineshape changes. Except for the band bending variation, very little change is observed in the core lineshape as a result of oxygen exposure. This is in agreement with the results of Landgren et al.[22] who estimate an oxygen coverage on the order of a tenth of a monolayer as a result of exposure to oxygen at room temperature in the 1-10⁴ L range. When Au is predeposited onto the GaAs(110) surface, exposure to oxygen gives rise to a definite core lineshape change

(mid-section of figs. 1-2). The shaded areas emphasize new high binding energy core features that are the result of oxygen chemisorption. For comparison, the vertical bars labeled 1 to 4 in figs. 1-2 indicate the chemically shifted core features observed by Landgren et al.[22] during GaAs oxidation, and associated with As and Ga atoms coordinated with 1, 2, 3 and 4 oxygen atoms. The vertical bar labeled 5 in Fig. 1 shows the binding energy of the As 3d observed by Su et al.[23] during As oxidation and associated by these authors with stoichiometric As_2O_3. Similarly, vertical bar 5 in Fig. 2 was obtained from the results of Su et al.[24] for Ga_2O_3. Figs. 1-2 show that the presence of Au overlayers gives rise to a weak oxidation promotion effect, with the formation of an oxygen chemisorbed layer where low As-O and Ga-O coordination numbers are observed. Correspondingly, little effect is seen on the valence states[19] that mostly reflect a Au-5d derived DOS with only minor modifications following oxygen exposure. The intensity of the core oxidized features in figs. 1 and 2 appears to increase relative to the main line if higher exposures or higher metal coverages are employed. Therefore, we conclude that we did not observe saturation of oxygen chemisorption in the exposure range explored, and that the oxidation promotion effect appears related to the thickness of the Au intermixed species that are formed when Au is deposited onto the clean GaAs surface. There is some disagreement in the literature about the detailed nature and the actual thickness of such species[10-13], but most results seem to indicate an alloyed region of thickness≥ 20 Å.

When Cr is deposited onto the GaAs(110) surface chemically driven interdiffusion takes place[25] with the formation of two main reaction products: a Cr-As arsenide-like phase at the interface and a Cr-Ga intermetallic alloy[25]. This is visible in the core lineshape spectra (solid line) in the bottom-most sections of

figs 1 and 2. The overall As 3d line is the result of the superposition of a bulk As 3d component and of a new low binding energy component some 0.3-0.4 eV below the main line[25]. In Fig. 2, bottom-most section, the Ga 3d line (solid line) shows a broad low binding energy feature centered some 0.6-0.7 eV above the main line that corresponds to Ga atoms in several inequivalent environments in the Cr matrix.

Upon oxygen exposure (dashed line) new oxide-derived features dominate the core spectra so that most As and Ga atoms within the experimental sampling depth are oxidized. We find an increase of several orders of magnitude in the surface oxygen uptake and no evidence of saturation in the exposure range explored[6]. The oxide-derived core features are of two kinds: low oxidation state features appear near the initial flat band position in Fig. 1 for As, together with a broad oxide band centered at 2.4 eV that *reflects several non-equivalent high oxidation states for As within the sampling depth*. In fig. 2 (bottom-most section, dashed line) the two oxide bands are even better defined: a first feature *near the zero of the relative binding energy scale reflects mostly single and double Ga-O local coordination*. A second well-defined feature appears centered some 2 eV below the first one, and corresponds to higher oxidation states than previously observed for Ga. The nature of these new oxide species that appear potentially more stable than Ga_2O_3 is still a subject of investigation.

If the results for $GaAs:Cr-O_2$ are compared with those for $GaAs: Au-O_2$ important differences are found. An obvious difference is in the magnitude of the promotion effect which is several-fold higher for Cr overlayers. A second interesting difference is in the nature of the oxide species. In the case of Au overlayers the oxidized spectra show only low oxidation state features near the

zero of the relative binding energy scale. The high-stability Ga oxide phases observed (bottom-most section of fig. 1-2) are not formed in the presence of Au overlayers. One possible suggestion is that such species involve Cr-arsenate phases, that may exhibit a relatively high oxygen content. However, our metal core and valence band results[1][*] indicate a main Cr_2O_3-like oxidation state for Cr, with no evidence of mixed oxides. Whatever the detailed nature of these high stability oxide phases is, clearly the chemistry of the metal overlayer determines if they form or not.

In examining the GaAs:Ag-O_2 case, we leave aside for a moment the overlayer chemistry and we focus on the importance of the interface morphology in determining interface catalytic effects. In fig. 3 we show the effect of oxidation on the Ga 3d (rightmost section) and As 3d (leftmost section) core lines for two different Ag coverages. The topmost EDC's have been obtained with a 0.1 Å Ag overlayer, the bottom-most ones for a 1 Å Ag overlayer. Relatively small metal coverages were used because of the rather sharp interface morphology reported for GaAs(110)-Ag[9][-10]. The zero of the binding energy scale is referred to the clean surface flat-band position, and the EDC's for the unoxidized surface (solid lines) have been shifted 0.65 eV to lower binding energy to superimpose them on the oxidized spectra (dashed line). Notwithstanding the experimental energy resolution for the series of results above, 0.8 eV, the spectra in fig. 3 clearly show that the Ag overlayers do not give rise to an oxidation promotion effect in the exposure range explored. This fact is confirmed by our valence band results which actually suggest that, if anything, the Ag overlayers passivate the GaAs surface against oxygen adsorption.

As discussed before, Au overlayers give rise to a limited oxidation promotion effect. We have shown that despite the chemical similarity of Ag and Au, Ag

overlayers do not give rise to a promotion effect under the same conditions. We suggest that the different behavior is associated with the different metal-semiconductor interface morphology. It appears that promotion effects occur via a metallic intermixed "activation layer" from which semiconductor atoms are released. Activation effects have indeed been observed only for overlayers that intermix with the semiconductor atoms with the formation of metallic (silicide-like, arsenide-like, etc.) reaction products. Our results for GaAs-Ag vs. GaAs-Au can be compared with those for Si-Au and Si-Ag by Rossi et al.[3,5] and Cros et al.[2,4] Au and Ag overlayers on Si both give rise to oxidation promotion when intermixed phases are formed.

Water Chemisorption

Figs. 4 to 7 summarize studies of H_2O chemisorption on GaAs(110) in the presence of Cr overlayers. Fig. 4 and 6 show the effect of H_2O exposure on the As 3d and Ga 3d lineshape, respectively. The topmost EDC's show the results for the clean cleavage surface, and EDC's displaced downward show the results for increasing Cr coverage prior to oxidation. The spectra have been arbitrarily normalized to emphasize lineshape changes. The zero of the binding energy scale corresponds to the initial core binding energy for the clean surface in flat-band coi...tions.

The effect of H_2O chemisorption on the clean surface is mostly visible in Fig. 4 and 6 in the rigid core binding energy shift due to band bending. In the exposure range explored, the coverage obtainable at room temperature is lower than a monolayer, and our results for the clean surface are in agreement with a number of investigations[15-17] in which molecular water was used.

The effect of Cr overlayers on the oxidation of As is visible in the lower

section of Fig. 4. Apart from the band bending, a relatively small oxide-induced feature is observed between 2 and 3 eV in the spectra at 2 and 4 Å Cr coverage. These modifications appear surprisingly minor when compared to the oxidation promotion effects described in the previous section. In Fig. 5 we compare the As 3d core lineshape during oxidation of the clean surface (topmost curve) and for H_2O and O_2 chemisorption in the presence of Cr overlayers of similar thickness (mid and bottom-most section). The interaction with H_2O does not produce any major oxide feature, indicating that the arsenide-like interface region is essentially stable against water exposure in the exposure range examined.

The situation is drastically different for Ga, as can be seen by comparing Figs. 5 and 7 . Before water exposure the result of increasing Cr deposition is the emergence of a broad low binding energy feature some 0.7-0.8 eV below the main line. This feature increases with Cr coverage and has been associated[25] with the formation of Cr-Ga intermetallic alloy. The effect of exposure to 1000 L of H_2O is shown by a dashed line for each Cr coverage. The "alloyed" low binding energy feature is removed in all cases, and new high binding energy features appear between 1 and 3 eV below the main line. Since the intensity of the oxidized feature scales with the initial intensity of the alloyed feature, we suggest that water chemisorption selectively involves the surface Ga atoms possibly through decomposition of the Cr-Ga surface alloy[20]. In fig. 7 we compare the Ga 3d core lineshape during oxidation of the clean surface (topmost EDC) and for H_2O and O_2 chemisorption in the presence of Cr overlayers of similar thickness (mid- and bottom-most section). The vertical bars 1-4 indicate the Ga 3d binding energies observed by Landgren et al.[22] for Ga atoms coordinated to 1, 2, 3 and 4 oxygen atoms. Vertical bar 5 was obtained from the results of Su et al.[24] for Ga_2O_3, vertical bar 6 from the results of Webb and

Lichtensteiger[26] for H_2O chemisorption on GaAs. The authors assigned this feature to Ga-OH bond formation. Fig. 7 shows that during water exposure the new Ga 3d oxidized features indicate relatively low oxidation states. No hint is found of the high stability Ga-oxide feature observed during oxygen exposure. Instead, the relatively broad and structured oxidized feature is qualitatively consistent with Ga-hydroxyl bond formation and/or Ga oxide phases with low Ga-O coordination and lower stability than Ga_2O_3.

The very dissimilar behavior observed in comparing the two bottom-most sections in Fig. 7 is somewhat surprising in view of the suggestion by Childs et al.[15] that water and oxygen chemisorption on GaAs give rise to similar local bonding at the semiconductor surface. Clearly the chemistry of the metal-semiconductor interface yields a drastic asymmetry of the two chemisorption processes. These results argue for a substantially different chemisorption energy in the two cases. The stability of the Cr-As subsurface layer has been effectively compared to the energy gained through the formation of chemisorption bonds, and the layer appears stable only against water chemisorption.

CONCLUSIONS

We have presented what is just the start of a systematic study of overlayer-induced promotion effects for GaAs surface reaction. The chemistry of ternary systems of this kind (semiconductor/overlayer/gaseous species) is both intriguing and complex. Promotion effects are relatively common, but their magnitude depends on the interplay of the chemistry and the morphology of the overlayer-semiconductor interface. Correspondingly, metals with similar chemistry can give rise to quantitatively different promotion effects and so can overlayers with similar morphology and different chemistry.

The large reactivity encountered for these metal-semiconductor interface species is not surprising. In the case of silicon, silicide-like phases are formed at the interface, while for GaAs the reaction products include arsenide-like species. Oxygen chemisorption studies on bulk silicides have shown higher oxygen uptake rates than for elemental silicon, the presence of high silicon oxidation states and a prefential oxygen bonding to silicon atoms that leaves the metal atoms relatively unaffected, at least in the first chemisorption stage[27-28]. It was proposed that the metal atoms are effective in dissociating the O_2 molecule at the silicide surface and consequently promote silicon oxidation[28]. While a detailed understanding of this mechanism is still missing, the similarities in the chemical bonding between arsenides[29] and silicides[30-32] suggest that similar effects can take place at metal-GaAs interfaces.

The oxidation of the interface species results in their decomposition into stable oxide phases. If this process leads to saturation of the chemisorption process, then the technological implications would be minor. However, in all cases we have examined thus far we did not observe saturation at the highest exposures explored at room temperature. This suggests that when the mass-transfer problem is solved by annealing the substrate during reaction, relatively thick oxidized layers can be grown. Even at room temperature thicknesses larger than 20-30 A^{18-20} are easily obtained. The metal atoms that remain relatively unreacted in the first oxidation stage[18,27-28], appear oxidized at high exposure. This, however, may not eliminate catalytic effects, since transition metal mixed oxide phases show considerable catalytic activity for a number of chemical reactions[33], and explain why saturation is not observed.

In this connection, we notice that the metal overlayers examined so far have relatively high electronegativity and varying degrees of d-character at E_F. We

suggest that metals with low electronegativity, relatively high d-character at E_F and intermixed interface morphology may give rise to unprecedented oxidation enhancement effects, since they would play the double role of "catalyst" and electronic "promoter" of the oxidation reaction[33],[34]. Promotion and poisoning effects of catalytic reactions, such as is observed, for example, during co-adsorption of CO with K or S on Ni(001)[34], seems far removed from semiconductor chemistry, but the thought is rather stimulating, and we plan to extend our study to low electronegativity metal overlayers such as Ca and Sm.

ACKNOWLEDGEMENTS

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20. Results for GaAs:Cr-H_2O will be presented by S. Chang, A. Rizzi and A. Franciosi, to be published.

21. Metal coverages are given in Angstroms, or in equivalent monolayers in terms of the GaAs surface atomic density of 8.9×10^{14} at/cm^2. It is 1ML = 1.06 A of Cr, = 1.5 A of Au, = 1.5 A of Ag.

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16

FIGURE CAPTIONS

Figure 1. As 3d core lineshape at hν = 85eV before (solid line) and after (dashed line) exposure to 1000L of oxygen. The spectra have been approximately normalized to the main emission feature (peak height) in order to to emphasize lineshape changes. The zero of the energy scale corresponds to the initial flat-band core binding energy. Top: oxidation of the cleaved GaAs (110) surface. The clean spectrum (solid line) has been shifted 0.6 eV to lower binding energy to compensate for the band bending that follows oxidation. Mid-section: oxidation in the presence of a Au overlayer (2.7 monolayer) gives rise to lineshape changes. The shaded areas emphasize new high binding energy core features that are the result of oxygen chemisorption. The vertical bars 1-4 indicate the chemically shifted core features observed by Landgren et al.[22] and associated with surface As atoms coordinated to 1, 2, 3, and 4 oxygen atoms, respectively. Bottom: oxidation in the presence of a Cr overlayer (2.8 monolayers). The vertical bars 1-4 are still derived from ref. 22. Vertical bar 5 shows the binding energy of the As 3d observed by Su et al.[23] and associated with As_2O_3.

Figure 2. Ga 3d core lineshape at hν = 60eV before (solid line) and after (dashed line) exposure to 1000L of oxygen. The zero of the energy scale corresponds to the initial flat-band core binding energy. Top: oxidation of the cleaved GaAs (110) surface. The clean spectrum (solid line) is shown shifted 0.6 eV to lower binding energy to emphasize line shape changes and compensate for the band bending that follows oxidation. Mid-section: oxidation in the presence of Au overlayer (2.7 ML) gives rise to new high binding energy features (shaded areas). Vertical bars 1-4 indicate the chemically shifted core features observed by Landgren et al.[22] and associated with Ga atoms coordinated to 1, 2, 3 and 4 oxygen atoms, respectively. Bottom: oxidation in the presence of a Cr overlayer (2.8 ML). The vertical bars 1-4 are derived from ref. 22. Vertical bar 5 was obtained from the results of Su et al[24] for Ga_2O_3.

Figure 3. As 3d (left) and Ga 3d (right) core lineshape at hν = 85 eV and 60 eV, respectively, before (solid line) and after (dashed line) exposure to 1000L O_2. The experimental energy resolution for these results is 0.8 eV. The topmost spectra have been obtained with 0.1 A Ag overlayer, the bottom-most ones for 1A overlayer. Relatively small metal coverages were used because of the sharp GaAs-Ag interface morphology[9-10]. The spectra before oxidation (solid line) have been shifted to low binding energy to compensate for the band bending that follows oxidation and emphasize lineshape changes. No oxidation promotion effects are seen within experimental uncertainty.

Figure 4. As 3d lineshape before (solid line) and after (dashed line) exposure to 1000 L H_2O. Spectra displaced downward show the
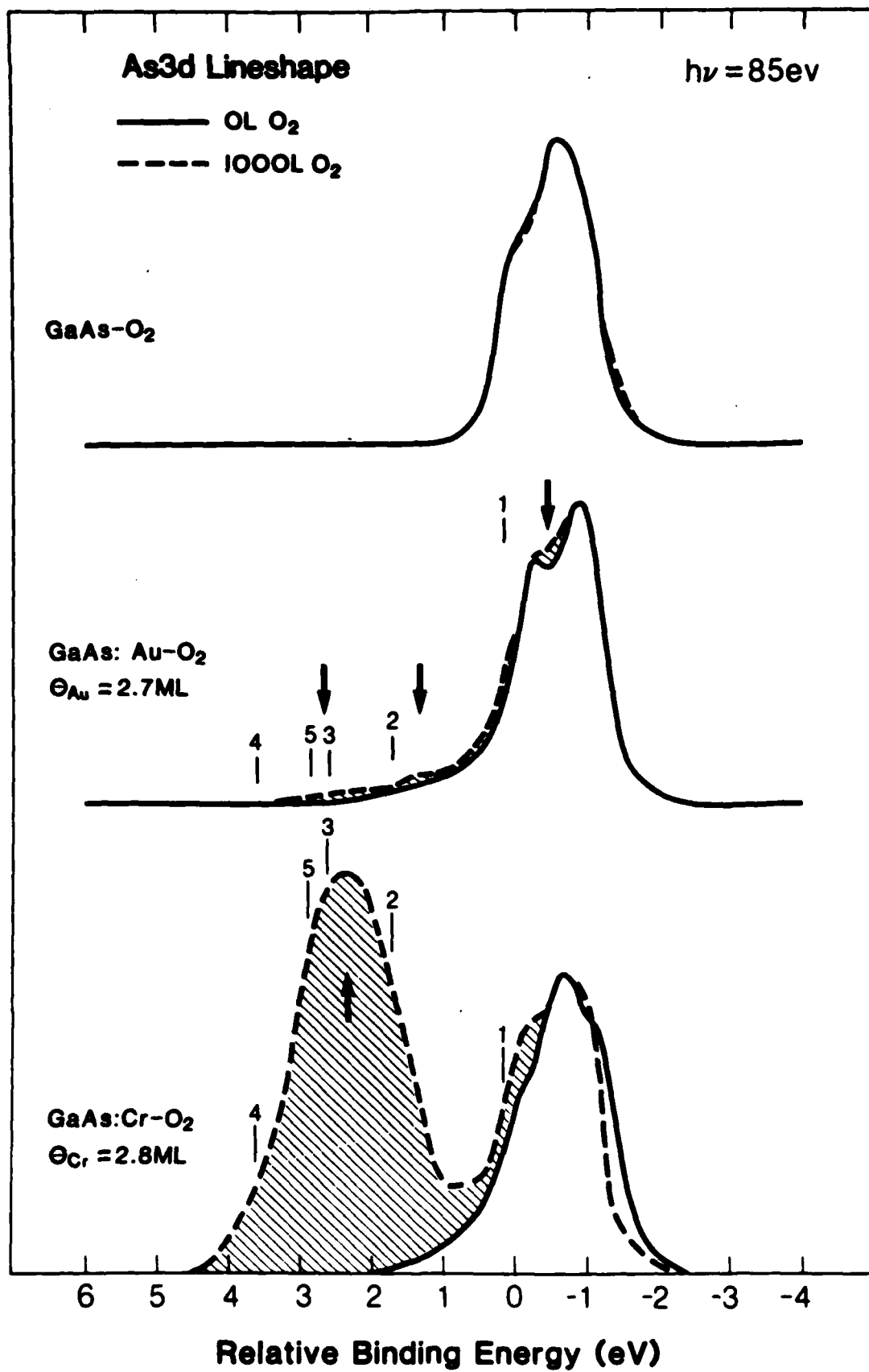
effect of Cr overlayers of increasing thickness during oxidation. Except for the band bending changes, the effect of water chemisorption is seen in the emergence of a relatively small oxidized feature between 2 and 3 eV below the flat-band initial core binding energy. The Cr-As reacted subsurface appears mostly stable against reaction with H_2O.

Figure 5. As 3d core lineshape during oxidation of the clean surface (topmost spectra) and for H_2O (mid-section) and O_2 chemisorption (bottom-most section) in the presence of Cr overlayers of similar thickness. The core emission is shown before (solid line) and after (dashed line) exposure to 1000L. The interaction with H_2O leaves the arsenide-like interface species relatively unchanged, while high stability oxidized phases are formed during oxygen exposure.
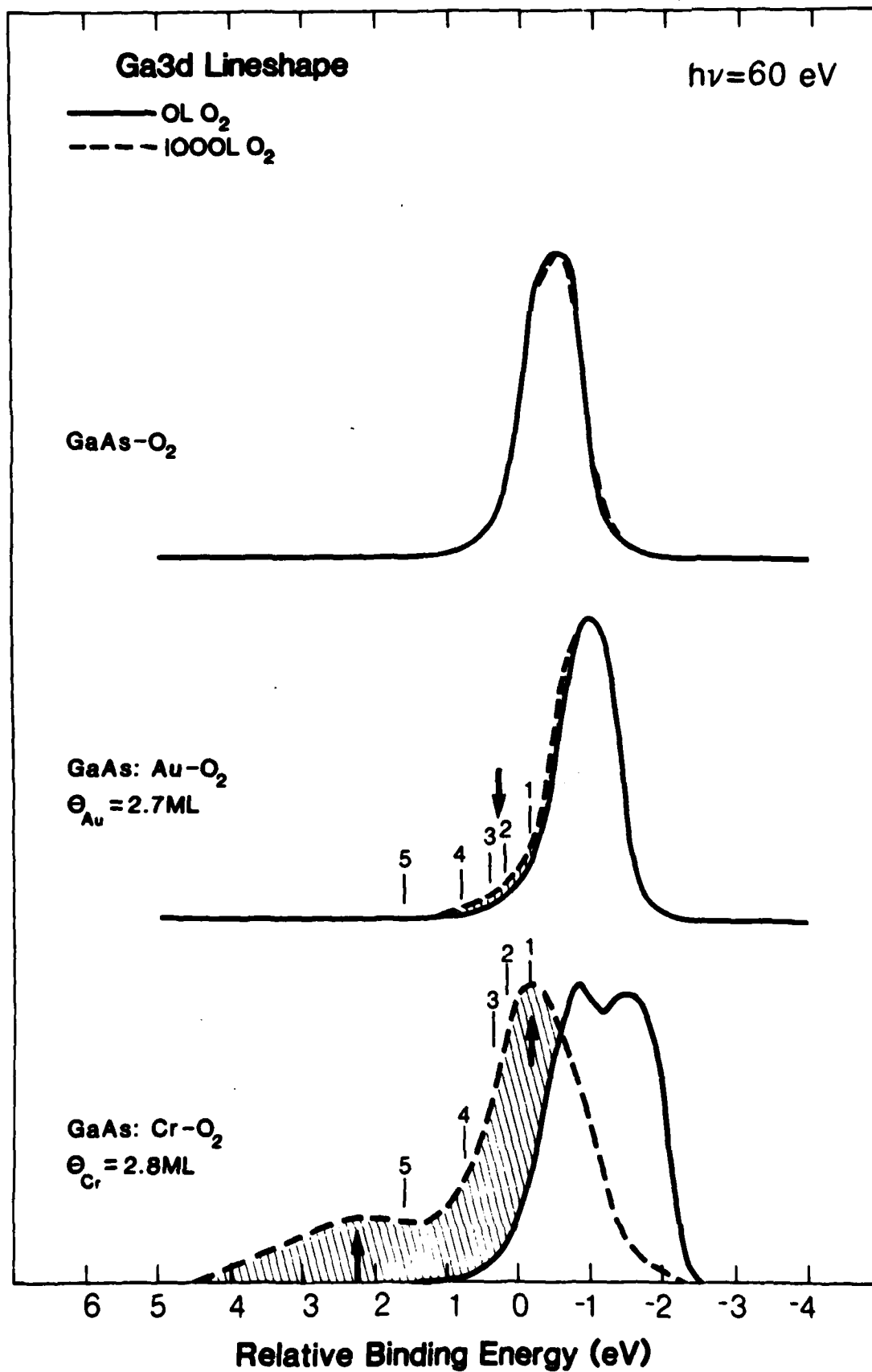
Figure 6. Ga 3d lineshape before (solid line) and after (dashed line) exposure to 1000 L H_2O. Spectra displaced downward show the effect of Cr overlayers of increasing thickness during exposure. Before water exposure increasing Cr deposition yields a low binding energy Cr-Ga alloyed feature 0.7-0.8 eV below the main line (solid line spectra). Upon water chemisorption the alloyed feature is removed and new high binding energy oxidized features appear between 1 and 3 eV below the main line.
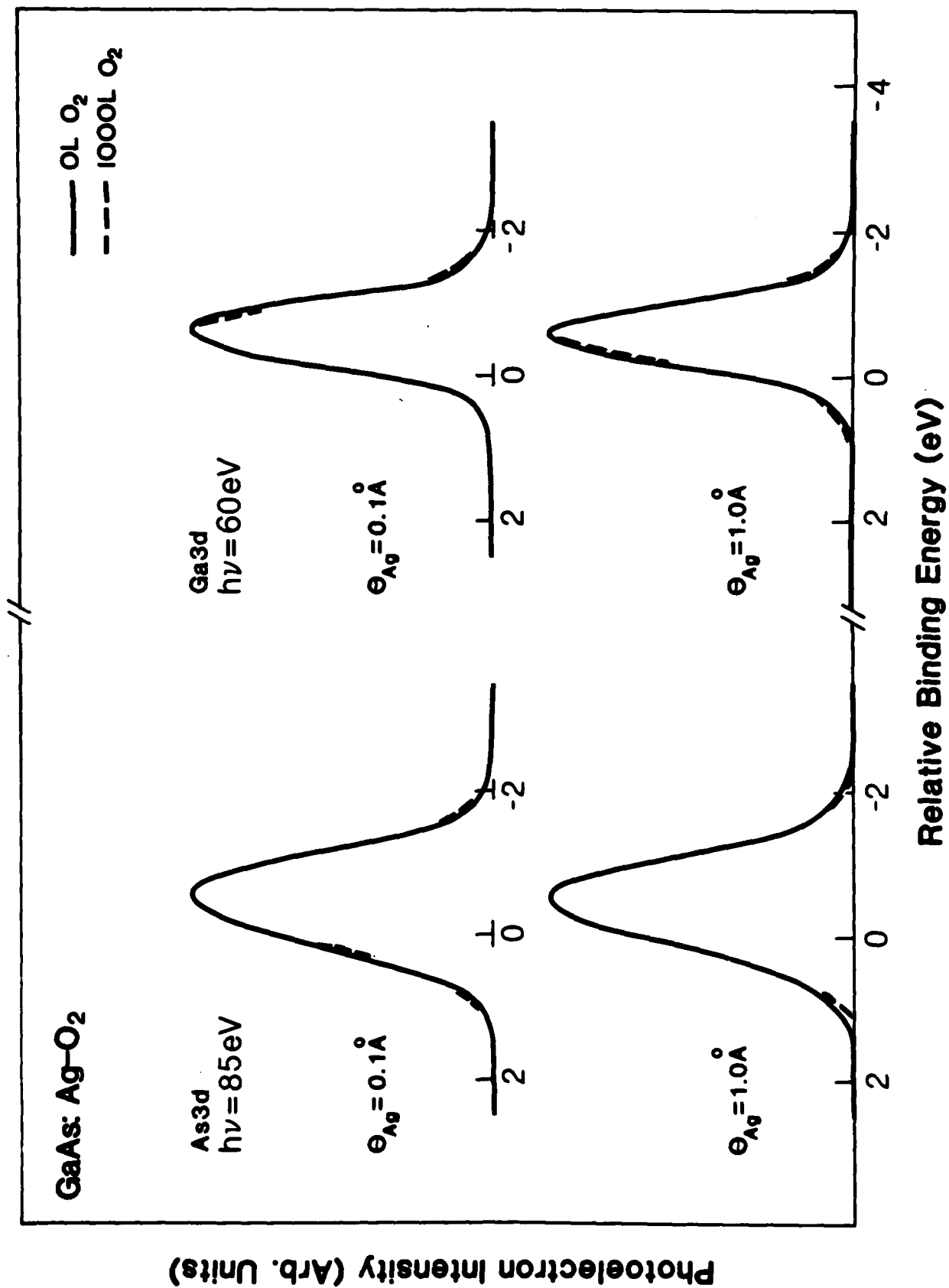
Figure 7. Ga 3d core lineshape during oxidation of the clean surface (topmost spectra) and for H_2O (midsection) and O_2 chemisorption (bottom-most section) in the presence of Cr overlayers of similar thickness. The core emission is shown before (solid line) and after (dashed line) exposure to 1000L. The vertical bars 1-4 indicate the chemically shifted core features observed by Landgren et al.[22] and associated with Ga atoms coordinated to 1, 2, 3, and 4 oxygen atoms, respectively. Vertical bar 5 was obtained from the results of Su et al[24] for Ga_2O_3, vertical bar 6 from the results of Webb and Lichteusteiger[26] reportedly for Ga-OH bond formation. During water exposure no high stability Ga-oxide features (see bottom-most spectrum) are observed. Relatively broad and structured oxidized features are observed instead, suggesting Ga-hydroxyl bond formation and/or Ga oxide phases with low Ga-oxygen coordination and lower stability than Ga_2O_3.

As3d Lineshape $h\nu = 85 ev$

——— OL O_2
– – – IOOOL O_2

GaAs–O_2

GaAs: Au–O_2
$\Theta_{Au} = 2.7ML$

GaAs:Cr–O_2
$\Theta_{Cr} = 2.8ML$

Photoelectron Intensity (Arb. Units)

Relative Binding Energy (eV)

Ga3d Lineshape $h\nu = 60$ eV

——— OL O$_2$
- - - - 1000L O$_2$

GaAs-O$_2$

GaAs: Au-O$_2$
$\Theta_{Au} = 2.7$ML

GaAs: Cr-O$_2$
$\Theta_{Cr} = 2.8$ML

Photoelectron Intensity (Arb. Units)

Relative Binding Energy (eV)

GaAs: Ag-O₂

Ga3d
hν=60eV

As3d
hν=85eV

OL O₂
IOOOL O₂

$\Theta_{Ag}=0.1\text{Å}$

$\Theta_{Ag}=1.0\text{Å}$

$\Theta_{Ag}=0.1\text{Å}$

$\Theta_{Ag}=1.0\text{Å}$

Relative Binding Energy (eV)

Photoelectron Intensity (Arb. Units)

GaAs:Cr–H₂O

As3d
—— OL H₂O
– – – – 1000L H₂O

$h\nu = 85$ eV

$\Theta_{Cr} = 0\text{Å}$

$\Theta_{Cr} = 1\text{Å}$

$\Theta_{Cr} = 2\text{Å}$

$\Theta_{Cr} = 4\text{Å}$

Photoelectron Intensity (Arb. Units)

Relative Binding Energy (eV)

GaAs
As 3d

——— OL
– – – IOOL
·········· IOOOL

GaAs-H$_2$O
GaAs-O$_2$

GaAs: Cr-H$_2$O
$\Theta_{Cr} = 4\text{Å}$

GaAs: Cr-O$_2$
$\Theta_{Cr} = 3\text{Å}$

hν=85 eV

Photoelectron Intensity (Arb. Units)

Relative Binding Energy (eV)

GaAs : Cr—H₂O

$h\nu = 60$ eV

Ga3d

—— 0L H₂O

- - - 1000L H₂O

$\Theta_{Cr} = 0\mathring{A}$

$\Theta_{Cr} = 1\mathring{A}$

$\Theta_{Cr} = 2\mathring{A}$

$\Theta_{Cr} = 4\mathring{A}$

Photoelectron Intensity (Arb. Units)

Relative Binding Energy (eV)

Figure: GaAs Ga3d photoelectron spectra. Plot of Photoelectron Intensity (Arb. Units) versus Relative Binding Energy (eV). $h\nu = 60$ eV.

Labels: GaAs, Ga3d; OL, IOOL, IOOOL; GaAs-H_2O, GaAs-O_2; GaAs: Cr-H_2O, $\Theta_{Cr} = 4$Å; GaAs: Cr-O_2, $\Theta_{Cr} = 3$Å.

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