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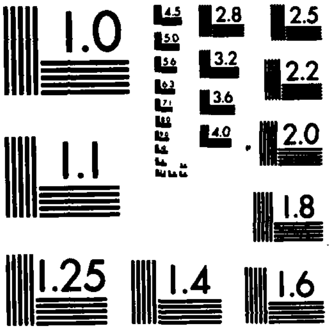

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We examined the effect of ultrathin (0.1-10 Å) on the reactivity with oxygen of Si(111) and GaAs(110) surfaces. Synchrotron radiation photoemission shows that for Cr coverages below a critical threshold coverage the overlayer does not affect substantially the oxygen adsorption rate. For Cr coverage above threshold the overlayer sharply enhances the oxygen adsorption kinetics so that most semiconductor atoms in the surface and near-surface regions appear oxydized at activated oxygen exposures as low as 100L. The critical threshold

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coverage corresponds to the onset of reactive interdiffusion at the Si(111)-Cr and GaAs(110)-Cr interfaces. Threrefore we suggest that ultrathin Si-Cr and As-Cr reacted phases created at the surface act as activation layers for semiconductor oxidation.

MICROSCOPIC CONTROL OF SEMICONDUCTOR SURFACE OXIDATION

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ABSTRACT

The effect of ultrathin (0.1-10Å) chromium overlayers on the reactivity with oxygen of Si(111) and GaAs(110) cleavage surfaces. Synchrotron radiation photoemission shows that for Cr coverages below a critical threshold coverage the overlayer does not affect substantially the oxygen absorption rate. For chromium coverage above threshold the overlayer sharply enhances the oxygen absorption kinetics so that most semiconductor atoms in the surface and near surface region appear oxidized at activated oxygen exposures as low as 100 Langmuirs. The critical threshold coverage corresponds to the onset of reactive interdiffusion at the Si(111)-Cr and GaAs(110)-Cr interfaces. Therefore we suggest that ultrathin Si-Cr and As-Cr reacted phases created at the surface act as activation layers for semiconductor oxidation.

Thin metal overlayers deposited on atomically clean semiconductor surfaces can change dramatically the reactivity of the surface for reactions with gas species[1-4] and metals.[5-6] We have recently shown, for example, that thin Cr overlayers on Si(111) surfaces can act both as passivating layers and as catalysts for Si(111)-Au interface reaction, so that one can control and modulate interdiffusion by varying the thickness of the Cr interlayer.[6] Similar effects have been observed by Brillson and co-workers for Al atoms at the GaAs(110)-Au interface.[5] As far as reactions with gaseous species are concerned, a few pioneering studies have addressed the effect of Ag and Au overlayers[1,3] on the oxidation of Silicon surfaces, while the presence of an Al overlayer has been shown to induce the formation of a potentially stable new oxide phase on Ge(111) surfaces.[2] An understanding of these phenomena requires a search for systematic correlations of the observed "catalytic" trends with. the different local morphology of the metal/semiconductor surface layers. The goal is to establish a connection between the microscopic bonding situation of semiconductor and metal atoms at the surface and the observed specific catalytic activity.

We report here on the interaction of Si(111) and GaAs(110) surfaces with activated oxygen O_2^* in the presence of ultrathin (0.1-10Å) Cr overlayers deposited in situ. We selected the Si-Cr and GaAs-Cr systems because these are within the interfaces best characterized at room temperature.[7-8] Furthermore, chromium compounds show considerable catalytic activity for a number of chemical reactions.[9] Interaction with oxygen was selected as prototype reaction with oxidizing gas phases, and because of extensive literature existing on this subject.[10-13] Our results indicate a qualitatively similar effect of the Cr overlayer on the kinetics of Si and GaAs oxidation. While only limited oxygen adsorption is possible on the clean semiconductor surfaces at the highest activated oxygen exposures explored (10^4 Langmuirs), we see an enhancement of several orders of magnitude in the semiconductor oxidation rate for Cr coverages above a critical threshold coverage (1.3Å for Si). We relate this enhancement to the thin intermixed Si-Cr and As-Cr species that start to form at the surface at the critical threshold coverage. These intermixed species act as catalysts and dramatically increase the semiconductor oxidation kinetics. Most of the silicon, gallium and arsenic atoms in the surface and near surface layers appear oxidized at oxygen exposures as low as 100L. The major reaction product identified at the Si surface is a Si-oxide with average Si-oxygen coordination between 3 and 4. For GaAs, an As oxide similar to As_2O_3 is observed, together with a Ga-oxide phase that involves an effective Ga-oxygen coordination greater than for Ga_2O_3.

The experiments were performed on a clean Si(111)2x1 and GaAs(110)1x1 surfaces obtained through cleavage of n-type single crystals inside a photoelectron spectrometer, at operating pressure $<5\times10^{-11}$ torr. Cr was deposited from a W coil at pressure $<3\times10^{-10}$ torr, with overlayer thickness measured by a quartz thickness monitor. Since the clean semiconductor surfaces are relatively inert upon oxygen exposure, we elected to use activated oxygen in the pressure range 10^{-5} torr to enhance reaction kinetics.[14-15] A tungsten ionization filament was therefore positioned in line of sight of the substrate during oxygen exposure. The photoemission measurements were performed by positioning the sample at the focus of a synchrotron radiation beam and of a commercial double pass cylindrical mirror analyzer. The radiation from the 240 MeV electron storage ring Tantalus at the Synchrotron Radiation Center of the University of Wisconsin-Madison was monochromatized by means of a 3m toroidal grating monochromator in the 21-130 eV photon energy range. The overall experimental energy resolution (electrons and photons) was typically 0.3-0.4 eV for the valence band and Ga 3d core levels, and of about 0.6-0.8 eV for the As 3d and Si 2p core data.

Photoelectron Energy Distribution curves for the Ga 3d and As 3d core levels are shown in Figs. 1 and 2, respectively, as a function of O_2^* exposure (10-10^4L) of the clean Ga As(110) surface. The zero of the binding energy scale corresponds to initial flat-band core binding energy. Exposures up to 10^4 langmuir yield a rigid shift of the core levels that reflects the change in band bending, and attenuation of the As 3d surface contribution, visible as structure on the low binding energy side of the main As 3d line. These changes reflect the relatively low oxygen adsorption rate observed on cleaved GaAs(110) surfaces.[12-13] Even at the highest exposures explored here, the oxygen coverage is only a fraction of a monolayer.[12] The quasi-saturation value of band bending for 10^3L exposure (0.65 eV) corresponds to the value observed by Lindgren et al[12] at 10^4-10^5L exposure to ground state molecular oxygen, so that the use of activated oxygen in our case yields a 10 to 100-fold enhancement in adsorption.

Results for the Si(111) surface are summarized in Fig. 3. In the top section we show the Si 2p core emission for a clean Si(111)2x1 surface (dashed line) and for the same surface after exposure to 100L of activated oxygen (solid line). Weak oxygen-induced features appear on the high binding energy side of the main line. Vertical bars 0.9, 1.8, 2.6 and 3.5 eV below the main line mark the position of the chemically shifted Si 2p contributions associated by Hollinger and Himpsel[10] with silicon atoms bonded to 1,2,3 and 4 oxygen atoms, respectively. Further exposure to oxygen (10^3L) yields a 3 to 4-fold increase of the oxygen-induced features, that saturate in intensity and show little change[4] upon further oxygen exposure (10^4L), in agreement with the 1-1.5 monolayer oxygen saturation coverage observed in Ref. 10.

The spectra for the oxidation of the clean surface all show[4] the presence of one, two and three-fold silicon-oxygen coordination, as expected in the submonolayer and monolayer oxygen coverage range.[10] The effect of Cr overlayer on the oxygen adsorption kinetics is shown in the middle and bottom sections of Fig. 3. We distinguish two qualitatively different regions as a function of Cr coverage Θ. For Θ below a critical threshold coverage of 1.3±0.3 Å the Cr overlayer affects relatively little the silicon oxidation rate. For example, in the mid-section of Fig. 3 we show EDC's for the Si 2p emission at Θ=0.6 before (dashed line) and after exposure to 100L of activated oxygen (solid line). Deposition of 0.6Å of Cr onto the clean Si(111) cleavage surface[7] attenuates slightly the Si 2p emission with no visible lineshape changes. Exposure to 100L of activates oxygen gives rise to the same oxygen-induced feature observed for oxygen adsorption on the clean Si(111) surface.

The situation changes dramatically if Cr coverages above threshold are employed. This is shown in the bottom section of Fig. 3 for Θ=2Å. Exposure of the Cr-activated semiconductor surface to 100L of activated oxygen (solid line) yields a main oxide-induced feature centered 3.0 eV below the main line. Further oxygen exposure[4] increases this feature relative to the Si 2p substrate line, indicating that no saturation of oxygen adsorption is observed in this exposure range ($10-10^4$L). The width of the Si 2p oxide line suggests that several different oxidation states may coexist, and its binding energy, intermediate between those observed for Si-atoms locally bonded to 3 and 4 oxygen atoms,[10] shows that 3-fold and 4-fold coordination are likely to be dominant in the silicon oxidized layer.

The results of Fig. 3 indicate that Cr coverages above the critical threshold coverage change dramatically the reactivity of the semiconductor surface and enhancement of several orders of magnitude, the silicon oxidation rate at room temperature. The observation of enhanced oxygen adsorption kinetics for Ag[3] overlayers on silicon has been related to the disruption of the ordered Si(111) surface upon Ag deposition. The effect of "amorphization" of the Si(111) surface on the Si oxidation rate can be estimated by the results of Riedel et al.[16] who recently studied amorphous Si and Ge layers upon exposure to activated oxygen. The vertical bar in the bottom section of Fig. 3 indicates the position of the dominant Si 2p oxide feature observed by Riedel et al.[16] The similarity with our results suggests that in both cases silicon atoms locally coordinated to 3 and 4 oxygen atoms are likely to coexist and give rise to the broad Si 2p oxide band observed experimentally. Comparison of the intensity of the Si 2p oxide feature relative to the main line, however, indicates that the oxygen adsorption rate on the Cr-activated Si surface is 20 to 30 times higher than on amorphous silicon layers.[4,16] We conclude that while the nature of the surface reaction products appears the same in both cases, the origin of enhanced oxidation has to be found in the Cr-induced modification of surface chemistry rather than in the amorphization of the semiconductor surface layer. In earlier studies of the Si(111)-Cr interface[7] we proposed that for Cr coverages below 1.5 monolayer the Cr atoms participate in weak chemisorption bonds that affect only slightly the stability of the Si-Si bonds in the surface and near surface region. At coverage above 1.5 monolayers a reactive interdiffusion interface formation stage is established, with formation of disordered Si-Cr intermixed species. The onset of reactive interdiffusion coincides within experimental uncertainty with the critical threshold coverage for oxidation determined in this work. The correspondence suggests that the silicide-like surface species formed above threshold act as catalyst for the oxidation of the semiconductor atoms in the surface and near-surface region.

In recent work Cros[17] suggested that the enhanced oxidation of the room temperature grown Si-noble metal interfaces may be explained by the low stability of the intermixed surface phases and on the metallic-like density of states at E_F which may ease the breaking of the oxygen molecule and/or the creation of atomic oxygen excited states. These mechanisms may indeed be active also in the Si-Cr case at chromium coverages above the critical threshold and contribute to the enhanced oxidation effect. However, one word of caution is necessary, since for refractory metals on silicon the stability of the intermixed phase is expected to be higher, as indicated by the trend of the corresponding silicide formation enthalpies, and, as observed by Cros,[17] since the presence of <u>two</u> species (Si and refractory metal) with very strong tendencies to oxidize, changes the nature of the problem with respect to the Si-noble metal case.

The morphology and room-temperature revolution of the Si(111)-Cr and GaAs(110)-Cr interfaces present many similarities. Both interfaces react at room temperature only for coverages above 1.5 Å(Si[7]) and 2 Å (GaAs[8]). Reactive interdiffusion occurs in a limited coverage range of $1.5<\Theta<9$ (Si[7]) and $2<\Theta<20$ (GaAs[8]) and yields silicide-like species on Si and arsenide-like phases on GaAs. Further Cr deposition gives rise to an unreacted metal film on top of the reacted interface.[7,8] The chemical bonding for the main interface reaction products (silicide or arsenide-like) involves in both cases dominant coupling of the metal-d states with anion-p states, with similar modifications of the electronic density of states. These similarities between the two interfaces suggest that an oxidation promotion effect may be found also for GaAs-Cr above a critical threshold coverage value of $\Theta\approx 2$Å. In

Fig. 4 and 5 we summarize, respectively, the effect of exposure to activated oxygen on the As 3d and Ga 3d core level emission. In the top-section of Fig. 4 and 5 we show the clean surface core emission before (dashed line) and after (solid line) oxygen exposure. In the mid-section we show the corresponding results for a Cr overlayer with $\Theta=1$, i.e. below the critical threshold coverage. In the bottom-most sections of Figs. 4 and 5 we present results for $\Theta=10$. Again, the dashed line and solid line indicate, respectively, results before and after oxygen exposure. The zero of the binding energy scale corresponds to the flat-band initial core binding energy, and the spectra have been arbitrarily normalized to emphasize lineshape changes. As indicated in Fig. 1 and 2, and in the topmost section of Fig. 4 and 5, the clean GaAs surface is relatively inert and only low oxygen coverage can be obtained at room temperature. For $\Theta=1$ the Cr overlayer yields only relatively small modifications in the oxygen uptake rate. The spectra at $\Theta=10$, instead, show dramatic modification of the As 3d and Ga 3d lineshape upon oxidation. At $\Theta=10$ the As 3d and Ga 3d lines before oxidation (dashed line) both include two distinct components.[8] For As (tic marks) a low binding energy As Cr reacted 3d line appear above the initial clean surface emission, and a second line shifted to higher binding energy represents segregated arsenic and residual substrate emission.[8] For Ga (dashed line, bottom-most section) the main contribution corresponds to free Gallium atoms that are a byproduct of the As-Cr interface reaction and/or Gallium atoms dispersed in a Cr matrix.[8] Upon exposure to 100L of activated oxygen most of the As and Ga atoms within the experimental sampling depth are oxidized. We find an increase of several orders of magnitude in the overall surface oxygen uptake, and no evidence of saturation in the exposure range explored (10-10^4 L). The character of the oxidation reaction products can be examined by comparing the observed oxide-induced As 3d features with those reported by Landgren et al[12] 0.8, 2.3, 3.2 and 4.2 eV below the initial substrate As 3d line (vertical bars[1-4] in Fig. 4) and related to the presence of As coordinated, respectively, with one, two, three and four oxygen atoms, and with a 3.4-3.5 eV feature reported in Refs. 18 and 19 for As in As_2O_3 (vertical bar 5 in Fig. 4). The broad experimental oxide band suggests that several arsenic-oxygen bonding configurations must coexist in the surface and near surface region, with a dominant contribution coming from high oxidation states that are barely detectable on the oxidized GaAs surface[12] at coverages of 10^{14} L.

For the Ga 3d lines during oxidation of GaAs Landgren et al.[12] observed chemically shifted components 0.45 and 1.0 eV below the main line at low exposure (10^6L molecular oxygen), components at 0.8 and 1.4 eV at high exposure (10^{14}L). These are indicated by vertical bars 1-4 in Fig. 5. While Landgren et al.[12] suggest that the 1.4 eV component may correspond to Ga in Ga_2O_3, Su et al. report[20] a Ga 3d broad oxide feature centered some 2.2 eV below the main Ga $3d_{5/2}$ line for Ga_2O_3. This is marked by vertical bar 5 in Fig. 5. The results in the bottom-most section of Fig. 5 indicate that several non-equivalent oxidation states for Ga coexist within the sampling depth. Furthermore we note that a major spectral contribution derives from Ga 3d oxide features shifted 3 eV below the pinned Ga 3d position (mid-section of Figs. 2 and 5) i.e. from higher oxidation states than previously observed for Ga in Ga_2O_3. The nature of these new oxide species is not clear at present. It may involve mixed Cr-Ga oxide phases, but valence band results are consistent[21] with a main Cr_2O_3 oxidation state for Cr, with no evidence of mixed oxides. In analogy with the present case, we mention that Al overlayers on Ge[2] appear to stabilize a higher oxidation state for Ga atoms upon oxygen exposure at room temperature. Also in this case the morphology of the new potentially stable oxide phase remains unclear.

In summary, we have shown that thin Cr overlayers on Si and GaAs surfaces can dramatically enhance the semiconductor oxidation rate if Cr coverages above a critical threshold coverage are employed. This critical coverage corresponds to the onset of reactive interdiffusion of Cr and semiconductor atoms at the interface. The resulting enhancement of several orders of magnitude in the oxygen adsorption kinetics is presumably related to the catalytic activity of ultrathin silicide and arsenide-like overlayers formed for Cr coverages above threshold.[1,4] The end products of oxidation involve semiconductor atoms in several different coexisting oxidation states, with high oxidation states largely dominant. For silicon, for example, dominant 3 and

4-fold oxygen coordination was observed, with compelling analogies to α-Si oxidation processes.

Acknowledgements

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Figure Captions

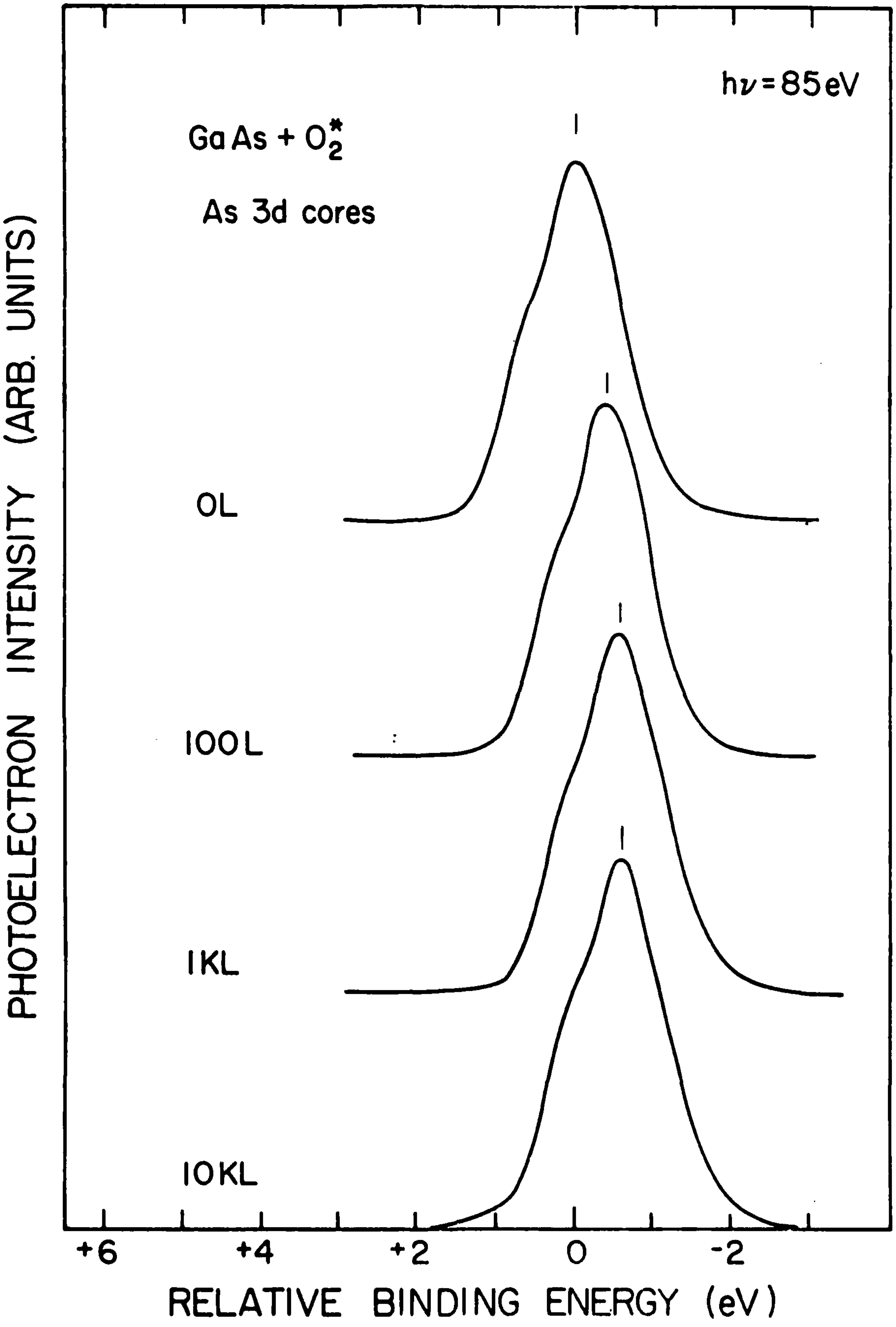
Fig. 1 Photoelectron Energy Distribution Curves (EDC's) for the As 3d core emission from cleaved GaAs(110). Spectra displaced downward show the effect of exposure to increasing amount (100, 10^3, 10^4 L) of activated oxygen. The rigid shift of the core line reflect the variation in band bending from the initial flat-band situation.

Fig. 2 EDC's for the Ga 3d core emission from cleaved GaAs(110). Spectra displaced downward show the effect of exposure to increasing amounts of activated oxygen. The rigid shift of the core line reflect the variation in band bending.

Fig. 3 Si 2p core emission from cleaved Si (111)2x1 surfaces. Top: clean surface emission before (dashed line) and after exposure (solid line) to 100L of activated oxygen. The vertical bars mark the position of Si 2p oxide features associated by Hollinger and Himpsel[10] with silicon atoms coordinated with one, two, three and four oxygen atoms. Mid-secion: A 0.6 Å Cr overlayer was deposited on a freshly cleaved Si(111) surface. The resulting Si 2p core emission is shown before (dashed line) and after (solid line) oxygen exposure. The vertical bars mark Hollinger and Himpsel's Si 2p oxide features. Bottom: Effect of a 2Å Cr overlayer on the Si (111) surface oxidation. The Si 2p core lineshape before oxidation (dashed line) is similar to the initial Si 2p line. After exposure to 100L of activated oxygen (solid line) a major oxide band emerges. The vertical bar marks the position of a major Si 2p oxide features identified by Riedel et al.[16] during oxidation of amorphous silicon.

Fig. 4 Effect of thin Cr overlayers on the oxidation of As at the GaAs(110) surface. Top: Clean surface As 3d emission before (dashed line) and after (solid line) oxygen exposure. Mid-section: A 1Å Cr overlayer was deposited on a freshly cleaved GaAs(110) surface. The resulting As 3d emission is shown before (dashed line) and after (solid line) oxygen exposure. Botton: Effect of a 10Å Cr overlayer on the GaAs(110) surface oxidation. The As 3d core lineshape before oxidation (dashed line) is composed of a low binding energy reacted As 3d feature from Cr-As interface species, and of a high binding energy segregated As/substrate contribution.[8] Upon oxidation (solid line) most of the As atoms appear oxidized. The vertical bars 1-4 mark the position of the oxidized As 3d features observed by Landgren et al.[12] for As coordinated with one to four oxygen atoms. The vertical bar 5 marks the position of the As 3d core level in $As_2 O_3$, from Su et al.[18]

Fig. 5 Effect of thin Cr overlayers on the oxidation of Ga at the GaAs(110) surface. Top: clean surface Ga 3d emission before (dashed line) and after (solid line) oxygen exposure. Mid-section: A 1Å Cr overlayer was deposited on a freshly cleaved GaAs(110) surface. The resulting Ga 3d exposure is shown before (dashed line) and after (solid line) oxygen exposure Bottom: Effect of a 10 Å Cr overlayer. The Ga 3d core line before oxidation (dashed line) includes a main contribution from dissociated Ga atoms or from Ga atoms in a Cr matrix.[8] Upon oxidation (solid line) most of the Ga atoms appear oxidized. The vertical bars 1-4 mark the position of oxidized Ga 3d features observed by Landgren et al.[12] The vertical bar 5 marks the position of the Ga 3d core level in Ga_2O_3, from Su et al.[20]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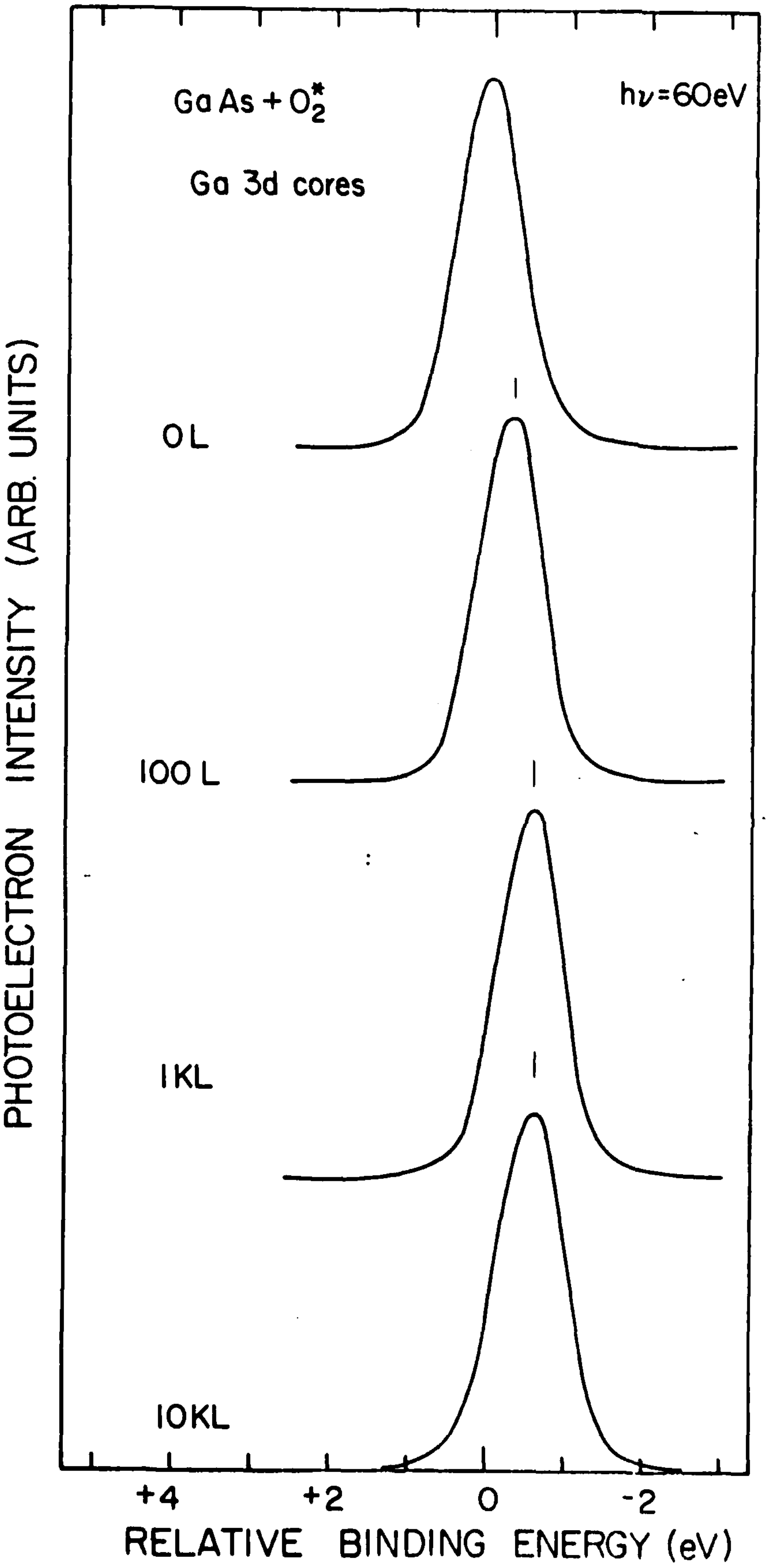
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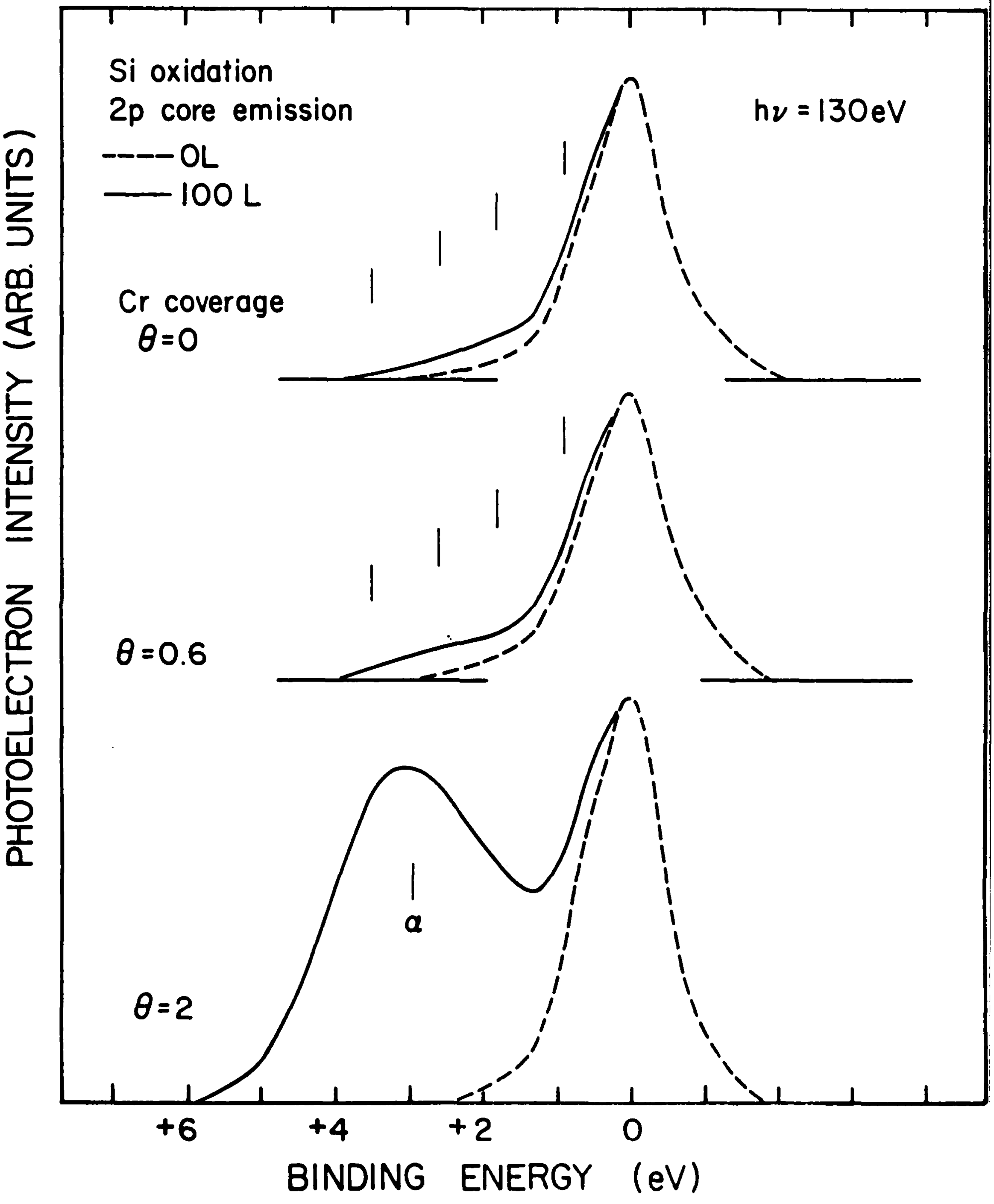
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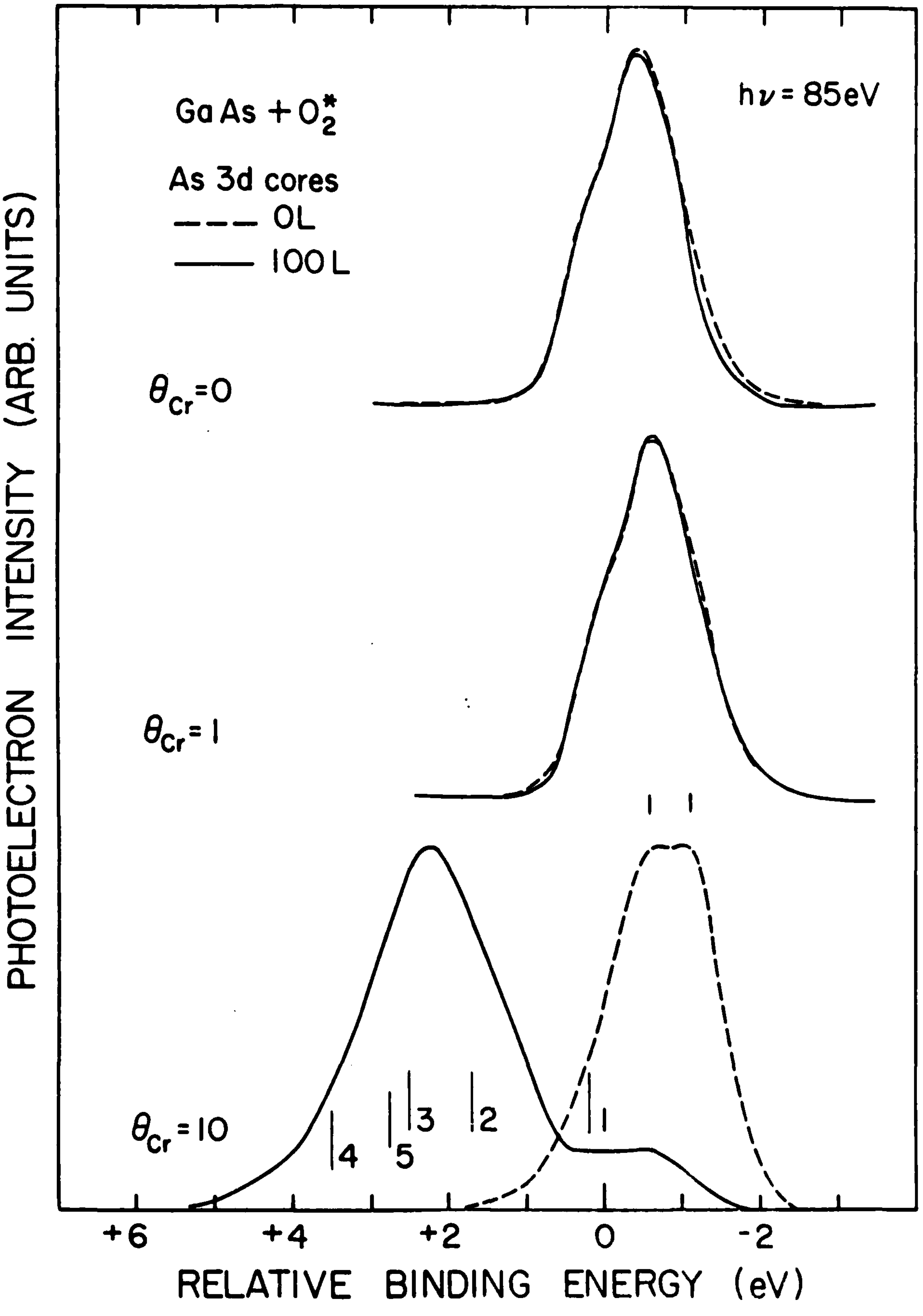
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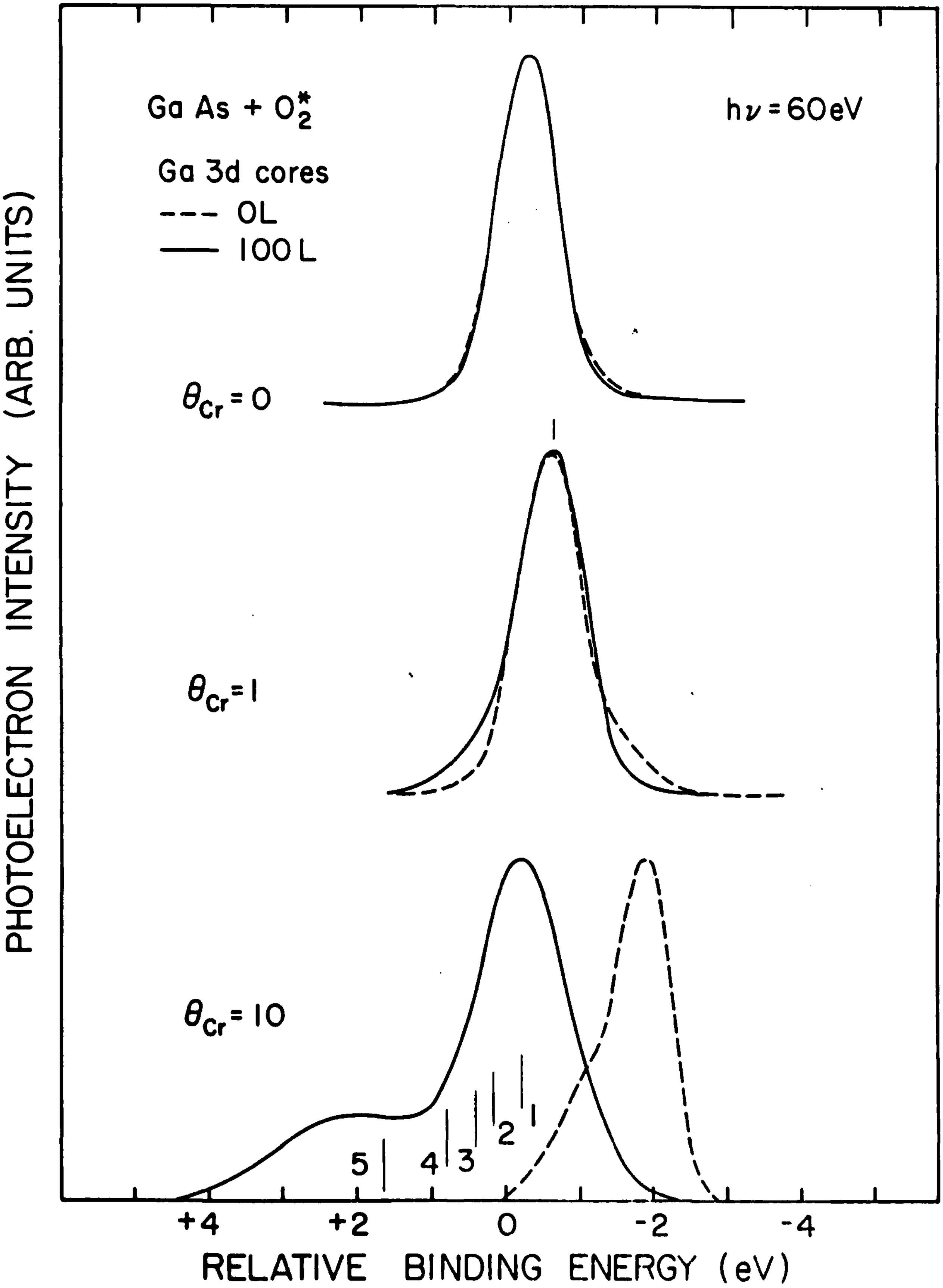

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