Binding-energy shifts from alloying at metal—compound-semiconductor interfaces

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One can relate the binding energy of a metal core level in a binary alloy as measured by photoemission to partial heats of solution. This principle is applied to explain the high-coverage behavior of cation core levels at metal—compound-semiconductor interfaces where alloying between the overlayer metal and the cation species is suspected or known to occur. Calculated and measured binding energies are compared for a wide range of noble and transition metals on GaAs and InP. Close agreement in many systems shows that alloying at these interfaces is more general than previously recognized. Implications of these results on previous interpretations of data will be discussed for specific interfaces. Limitations of the model and the extent of its applicability to other metal-semiconductor interface systems will also be outlined.

INTRODUCTION

The study of metal—compound-semiconductor interfaces by photoelectron spectroscopy has clearly demonstrated that in general such interfaces are nonabrupt, with intermixing and chemical reaction often affecting the interfacial region over a width ranging from several to tens of atomic layers at room temperature. In particular, in reactive systems deposition of the overlayer metal results in dissociation of the substrate, metal-anion compound formation, and metal-cation alloying. As more metal is deposited, outdiffusion of the substrate species is often observed, along with surface segregation effects. (Henceforth compound formation will be used to denote the reaction between the overlayer metal and the anion; alloying will refer to the reaction between the overlayer metal and the cation species.) One can get a rough indication of the relative importance of alloying and compound formation in a reaction at the interface by comparing the relevant heats of solution and formation. For most of the systems studied to date, the heats of anion compound formation are higher than or at least comparable to the heats of alloying, which accounts for the partial success of models predicting interface reactivity while neglecting alloying effects.[1] However, it has been pointed out by McGilp[2] that predictions of interfacial reactivity are most successful if both alloying and compound formation are taken into account. The reactive behavior is not only interesting from a fundamental standpoint, but is an extremely important consideration in the application of these interfaces. Large-scale alloying or reaction that can be induced by the elevated temperatures during fabrication procedures can have serious consequences for the electrical characteristics of the devices of which such interfaces are a component.

In this paper we are concerned with the behavior of the cation species in an interfacial reaction. We will restrict the discussion to Ga and In in the compound semiconductors GaAs and InP because of the availability of interface data for a wide range of overlayer metals. In all the experimental results quoted, the interfaces were formed by room-temperature deposition of the overlayer metal onto the cleaved (110) surface of n-type single crystals. The electronic structure of the near-surface region was monitored as function of metal coverage. The intensities of the semiconductor core levels with coverage gives an indication of the width of the interface. Relative intensities can give information about the composition of the interface. Much information is available as a function of depth at the interface; as one adds more metal, one is in effect probing regions lying further away from the interface on the metal-rich side.

Core-level binding-energy shifts and line-shape changes give information about chemical bonding. (Band-bending information can also be obtained. Here we discuss only shifts due to chemistry.) As an example, at most reactive interfaces there is clear evidence of compound formation which results in a binding-energy shift of the As $3d$ (P $2p$) signal. At the same time, there is often a shift of the Ga $3d$ (In $4d$) core level to a lower binding energy, approximating the binding-energy position of Ga (In) in the pure metal. This is taken as evidence of segregation of metallic islands or clusters. As the coverage increases, it becomes apparent that the segregated Ga (In) can largely be trapped near the interface; in other cases, it appears to noticeably segregate to the surface. In either case, at high coverages, the Ga $3d$ (In $4d$) core-level binding energy reaches an asymptotic value that often differs from the metallic position. This final binding energy also varies from system to system. The question is what determines this position.

The simple model proposed here assumes the environment of the Ga or In at high coverage to be very similar to that in an alloy with the overlayer metal, with the Ga (In) at infinite dilution. A simple calculation of the core-level binding energy expected for Ga (In) in dilute alloys illustrates that in all cases where alloying is suspected or known to occur at the interface, the binding-energy shift from the metallic position can be almost entirely accounted for by the effects of alloying. Implications of this result on previous interpretations of the data will be discussed for specific interfaces. Limitations of the model and the extent of its applicability to other metal—compound-semiconductor interfaces will also be outlined.

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RESULTS

Using a formalism outlined by Steiner and Hüfner,[3] one can relate the x-ray photoemission spectroscopy (XPS) binding energy of a metal-core level in an alloy to partial heats of solution. The basic idea is to calculate the binding energy as measured by photoemission by modeling the whole process as a Born-Haber cycle, as has been well described by Johansson and Mårtensson.[4] Under this approximation, if one writes the expression for the change in binding energy in going from an atom A in a solid made up of element $Z=A$ to the same atom in the binary alloy $M=A_xB_{1-x}$, then one gets the simple expression

$$\Delta E_A(x)=E(A;A_xB_{1-x})-E(A+1;A_xB_{1-x})+E(A+1;A)\ , \quad (1)$$

where $E(A;M)$ is the partial heat of solution of A in M and $A+1$ denotes the element with $Z=A+1$.

The sign convention taken is that if the solution of A in M is exothermic, then $E(A;M)$ is positive. (This is opposite to the normal convention.) This results in positive ΔE meaning an increase in the binding energy of the core levels of metal A in going from the metal to the alloy system.

In principle, given the relevant thermodynamic data, one can determine the binding-energy shift at any composition for any binary-alloy system. However, solution energies are known as a function of composition for only a few systems, and even in such cases the second term in (1), that involving three different elements, must be approximated. This last difficulty is avoided in alloy systems where $B=A+1$. It has been demonstrated that for these particular systems, the agreement between calorimetric measurements and heats of formation derived from XPS binding-energy shifts using this general formalism is extremely good.[5]

The analysis is also simplified for dilute alloys,[6] where A is in infinite dilution in B (i.e., as $x\rightarrow 0$). Equation (1) reduces to

$$\Delta E(A \text{ in } B)=E(A;B)-E(A+1;B)+E(A+1;A)\ . \quad (2)$$

Now only partial solution energies of binary alloys are involved. Measured values for ΔH_{sol} are available for a few alloy systems. More useful to the present work is the existence of a comprehensive table of calculated values of ΔH_{sol} for metal solutes at infinite dilution in a full range of transition-metal solvents,[7] derived from the semiempirical model of Miedema *et al.*[8] Using these values, one can calculate ΔE for many different alloy systems. (The heats of solution used are for liquid alloys. Although ΔH_{sol} for solid solutions can be significantly different, it turns out that the energy shifts which depend on differences in ΔH_{sol} are usually not significantly changed.)

TABLE I. Calculated and measured binding-energy shifts with respect to the metallic position for the In 4*d* core level, when In is in dilute solution in an overlayer metal. This table shows binding-energy shifts ΔE calculated for the cation species at infinite dilution in an alloy with the overlayer metals shown, compared with the shift observed for the Ga (In) core levels at high coverage at the corresponding metal-semiconductor interface. The first line gives the difference in binding energy of the cation core level in the semiconductor and in the pure metal. All subsequent binding-energy shifts are referenced to the metallic position. A negative value of ΔE indicates that the core level has lower binding energy in the alloy than in the pure metal. A plus or minus sign in parentheses means that the core level has not yet reached an asymptotic value, but continues to shift at the highest overlayer metal coverage studied, in the direction indicated. Also shown are calculated heats of alloying and compound formation, as per Miedema *et al.* (Ref. 7), to give an indication of the relative strength of overlayer-cation versus overlayer-anion chemistry. Measured values of the heats of formation are given in parentheses when available.

Metal	$\Delta H(M\text{In})$ (eV/atom)	$\Delta H(MP)$ (eV/atom)	ΔE_{calc} (eV)	ΔE_{expt} (eV)	Ref.	Note
In				−0.9	15	E(In metal) − E(In:InP)
Cu	−0.01 (−0.03)[a]	−0.36 (−0.33)[a]	−0.17	0.0	15,16	Strong intermixing, In surface segregation, extended phosphide phase
Ag	−0.05 (−0.09)[a]	−0.23 (−0.17)[a]	−0.06	0.0	18	Little intermixing, small In surface segregation
Au	−0.22	−0.18	−0.00	+0.4(−)	19	Strong Au-In alloying
Ni	−0.12	−0.63 (−0.57)[a,b]	−0.29	−0.3	20	Clear separation to binary compound and alloy
Pd	−0.65	−0.68	−0.22	−0.1	22	Strong intermixing, In surface segregation, extended phosphide phase
Co	−0.05	−0.65	−0.32	−0.1	23	
Cr	+0.15	−0.88	−0.50	−0.2	11	Strong reaction, metallic In segregation, phosphide formation
Ti	−0.26	−1.7	−0.77	−0.4(−)	24	

[a]Reference 17.
[b]Reference 21.

TABLE II. Calculated versus measured binding-energy (BE) shifts with respect to the metallic position for the Ga $3d$ core level, when Ga is in dilute solution in an overlayer metal. See Table I caption for explanation of entries.

Metal	$\Delta H(M\text{Ga})$ (eV/atom)	$\Delta H(M\text{As})$ (eV/atom)	ΔE_{calc} (eV)	ΔE_{expt} (eV)	Ref.	Note
Ga				−0.9	25	E(Ga metal) − E(Ga:GaAs)
Cu	−0.12 (−0.10)[a]	−0.24	+0.07	≈+0.1	10	Strong intermixing, weak reaction Cu-Ga alloying (?)
Ag	−0.10 (−0.04)[a]	−0.16	+0.11		10	Abrupt interface, no reaction
Au	−0.35 (−0.14)[a]	−0.24	+0.52	+0.5	27	Strong intermixing, As surface segregation, Au-Ga alloying
Ni	−0.38	−0.49 (−0.37)[b]	+0.30	+0.2	20,28	Strong reaction, preferential As out-diffusion, Ni/Ga/As ternary phase (?)
Pd	−0.82	−0.78	+0.60	≈+0.2(−)	29	BE still decreasing at 50-Å Pd,As surface segregation, arsenide formation, alloying
Cr	−0.17	−0.50	−0.15	−0.35	30	Strong reaction, strong As out-diffusion, Cr-Ga alloying (?)
V	−0.29	−0.75	−0.34	−0.65	31	
Ti	−0.53	−1.1 (−0.78)[c]	−0.53	−0.9(−)	32	Strong reaction, strong Ti-Ga alloying
Re(3+) (Ce,Sm)	−0.76	−1.4 (−1.5)[d]	−0.49	−0.9	33,34	Strong reaction, Ga outdiffusion and alloying, arsenide formation in narrow interfacial region
Re(2+) (Yb)	−0.46	−0.94	−0.48	−0.9	35	

[a]Reference 26.
[b]Reference 17.
[c]Reference 21.
[d]Reference 18.

Tables I and II show binding-energy shifts ΔE calculated for the cation species at infinite dilution in an alloy with the overlayer metals shown, compared with the shift observed for the Ga $3d$ (In $4d$) core levels at high coverage at the corresponding metal-semiconductor interface. The shifts are measured with respect to the metallic position. Also shown are calculated heats of alloying and compound formation to give an indication of the relative strength of overlayer-cation versus overlayer-anion chemistry. These values are taken from Niessen *et al.*[7] for the equiatomic composition in all cases. Measured values of the heats of formation are given in parentheses as a comparison, when available.

DISCUSSION

The agreement between calculated and measured values of ΔE is quite close, particularly in those cases where the heat of alloying is large. In all cases the sign of the observed shift is predicted correctly.

There are a few general conclusions to be drawn about these results. The overall agreement shows that alloying at these interfaces is more general than previously recognized. The agreement is better for the InP results (Table I) than for the GaAs (Table II) since for InP, the heats of phosphide formation are generally much higher than the heats of alloying; in an interfacial reaction, the In liberated by phosphide formation is free to alloy with the overlayer metal at high coverage. For GaAs, the heats of Ga alloying and arsenide formation with a transition metal are often comparable so that treating the metal-GaAs system in terms of the thermodynamics of binary systems is probably a poorer approximation.

It is somewhat surprising that the general agreement between the calculated and the measured binding-energy shifts is so good. Over the whole range of overlayer metals there are large variations in the interfacial reactivity, and in the final interface morphology at high coverage. Nevertheless, the agreement with this simple model seems to imply that the cation behaves as if it is in a dilute alloy with the overlayer metal in many cases. This is mainly because at high metal coverages what remains on the surface is essentially the overlayer metal, with a small concentration of either the cation or the anion species. Thus as far as the cation is concerned, it is natural that it behave as if it were in a dilute alloy with the deposited metal, regardless of the details of the interfacial morphology.

One important consideration is the possibility of surface segregation. The surface energies of the simple metal

(Ga,In) are much smaller than those of the transition metals, and so one might expect surface segregation or at least surface enrichment in the cation species.[9] However, we have shown that the observed shifts can be accounted for by the effects of alloying for a wide variety of overlayer metals, and so secondary effects, if present, make a relatively small contribution to the total shift. Since the relative concentration of the cation metal at the surface is small, one could expect alloying to make some contribution to the binding-energy shift, even if the Ga (In) remained segregated as the pure element, surrounded by the overlayer metal.

Although in principle the comparison between the calculated and the measured binding-energy shifts applies strictly to the situation at high coverage when the interface is fully formed, it does provide some insight into the chemistry of the cation species in general that can be applied to what is observed at lower coverages. For example, the calculated values allow the distinction of different alloying behaviors that appear similar as far as the shift of the cation core level is concerned. We contrast the Cu/GaAs and Cr/InP interfaces, both cases in which the cation core level reaches a final position near the value for pure Ga (In) metal. For Cu/GaAs, strong intermixing at the interface is reported.[10] The Ga $3d$ core level exhibits a slight broadening at high coverage, but remains essentially at the metallic Ga position. The calculation shows that any shift due to alloying would be small, and so the lack of a large shift in the Ga $3d$ should not be taken as an indication of the absence of strong alloying behavior. Cr on InP is another system where the binding-energy shift is small,[11] but in this case, the measured shift is much smaller than the calculated value for the dilute alloy, and so one can reasonably assume that the In segregates as pure metal and resists the tendency to alloy with the Cr. This is consistent with the fact that the heat of alloying between the two metals is positive.

One might imagine extending this work further by studying the behavior of the cation core-level binding energy as a function of coverage at the interface in conjunction with the predicted variation in binding energy with composition calculated by the approach of Steiner and Hüfner.[3] (It is also possible to calculate the energy shifts using a simpler formalism due to Verbeek.[12]) This work would have to be carried out and discussed on a case-by-case basis, as the details of the interfacial reactive behavior can vary significantly from system to system. The agreement between calculated and measured thermodynamic quantities used in the estimation of the binding energy is another consideration. The next best step in testing the general applicability of this approach would be to examine an interfacial system for which the interfacial behavior is well characterized, and the relevant thermodynamic data are available.

One point that must be kept in mind in comparing the photoemission results from different papers is that the value of the binding-energy shift quoted can vary by as much as ≈ 0.2 eV because of differences in the details of the data reduction. One principal source of discrepancies is the separation of the core-level shift due to chemical effects from the rigid shift due to band bending. Since all the quoted measurements were taken on n-type crystals, the shifts due to band bending and alloying are both to lower binding energy. Particularly in reactive systems, there can be shifts and changes in core-level line shape even at very low metal coverages, before the band bending is complete, and so the separation of the shift due to just alloying can be quite difficult. Another difficulty is in judging whether or not the cation core level has reached a "final" position at the highest metal coverage studied in a given paper. The coverage required for the core level position to stabilize is somewhat ill-defined, and varies strongly from system to system; it depends on the degree to which the substrate and overlayer intermix. It also depends on the experimental conditions, in particular on the surface sensitivity of the measurement.

The agreement is bad for refractory metal (Ti), and rare-earth- (RE) metal overlayers; the measured shift is considerably higher than the calculated value. This is in part due to a failure of the calculated values for solution energies in these systems. The Miedema scheme is a semiempirical model with parameters fixed by fits to a large number of alloy systems, the great majority involving a transition metal as one or both of the two components. Thus, it is alloys of two transition metals for which the predictions of the theory work best. A tabulation of calculated and experimental values by deBoer *et al.*[13] for alloys with electropositive metals (Sc,V,Ti) demonstrates that calculated heats of solution of Ti in Al, Si, and Ge are within $\approx 20\%$ of measured values, which is certainly reasonable agreement. However, the value of ΔE depends on the differences in heats of solution between different elements and, as seen in a study of binding-energy shifts in dilute alloys,[6] cases in which calculated values of ΔE are considerably more positive than measured values all involve alloys with electropositive metals (Ti,Zr). One can, in principle, adjust the empirical parameters used to calculate ΔH_{sol} in order to optimize the values for a restricted class of alloys, but in this case, where good values for electropositive metals alloyed with column-III, -IV, and -V metalloids are required, if a sufficient base of data was available to adjust the model, then it would be almost easier to use the data in a more direct comparison, rather than to work through a model.

The calculation is expected to be still worse for RE alloys, since in these cases, neither of the constituent metals is a transition metal. In addition, the Miedema model treats atomic size effects in only a cursory fashion, and the approximations made are expected to be poor when the sizes of the atomic species are very different, as they are for a RE atom, in comparison to Ga or In.

It is interesting to compare the behavior of the cation and the anion core levels at highest coverage. A recent paper by Grioni *et al.*[14] tabulates As $3d$ core-level positions at high coverage for various reactive metal—GaAs interface systems. What they find is that in general after an interfacial reaction, the As $3d$ has two distinct core-level positions: one due to a reacted phase at the interface, denoted by As-II, and a second that becomes dominant at high coverage, denoted by As-III. In their model of interface formation, As-II is regarded as a stable arsenidelike phase, and As-III as a phase more dilute in As,

where perhaps As is in solution in the overlayer metal. In some sense, the final phase for the As is then analogous to our picture for the Ga metal at high coverage. One could in principle then try to predict the binding energy of the As-III phase with a similar calculation.

In practice, there are several problems with this calculation. The first is trivial: The Miedema formalism[8] does not extend to the $Z+1$ element for As (Se) and so the heats of solution involving Se must be estimated by alternate means. We calculated binding-energy shifts for As in dilute solution in several metals for which some thermodynamic information was available. In all cases, the shifts were not close to the measured values, but the estimation of the relevant heats of solution may not have been correct. The second problem is more fundamental: The Born-Haber cycle used to model the photoemission process assumes a fully screened final state, and so it may not be appropriate to treat the nonmetallic anion or such a specie in a nonmetallic environment. If the As (P) segregates at the surface, then one can also anticipate cluster size to affect screening as well.

There are other reasons to suspect that the As-III position cannot be modeled in the same way as the Ga shift. One point is the fact that the As-III position is almost the same for all the metals studied, whereas an alloying shift, or a shift due to compound formation, would vary with different metals. (This is precisely the behavior of the As-II position, which is due to an arsenidelike phase: The values range from $+0.25$ to -1.0 eV with respect to the clean GaAs substrate position.) The origin of this shift is then something that does not depend strongly on the bonding with the overlayer metal. Arsenic is known to segregate at the surface at high metal coverage for many of these interfaces, but the binding energy for pure As is higher than the value for the GaAs substrate, whereas the As-III peak lies at -0.6 ± 0.2 eV for all the metals reported.

In summary, alloying effects have been shown to account for binding-energy shifts for Ga (In) peaks at high overlayer coverages, in systems where alloying is known to occur. Although other contributions to this shift are surely important, the agreement between calculation and data is good, and the availability of calculated values for a wide variety of elements will make the general applicability of this approach easy to check in the future. The results also demonstrate the validity of the structural models proposed for the relevant metal—III-V-compound semiconductor interface systems.

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[1]L. J. Brillson, C. F. Bruckner, N. G. Stoffel, A. D. Katnani, and G. Margaritondo, Phys. Rev. Lett. **46**, 838 (1981).

[2]J. F. McGilp, J. Phys. C **17**, 2249 (1984).

[3]P. Steiner and S. Hüfner, Acta Metall. **29**, 1885 (1981).

[4]B. Johansson and N. Mårtensson, Phys. Rev. B **21**, 4427 (1980).

[5]P. Steiner and S. Hüfner, Solid State Commun. **37**, 79 (1981).

[6]P. Steiner, S. Hüfner, N. Mårtensson, and B. Johansson, Solid State Commun. **37**, 73 (1981).

[7]A. K. Niessen, F. R. de Boer, R. Boom, P. F. deChâtel, W. C. M. Mattens, and A. R. Miedema, Comput. Coupling Phase Diagrams Thermochem. **7**, 51 (1983).

[8]A. R. Miedema, P. F. de Châtel, and F. R. de Boer, Physica (Utrecht) **100B**, 1 (1980).

[9]A. R. Miedema, Z. Metallkd. **69**, 455 (1978).

[10]Cu,Ag/GaAs: S. H. Pan, D. Mo, W. G. Petro, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. B **1**, 593 (1983).

[11]Cr/InP: R. S. List, T. Kendelewicz, M. D. Williams, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. A **3**, 1002 (1985).

[12]B. H. Verbeek, Solid State Commun. **44**, 951 (1982).

[13]F. R. de Boer, R. Boom, and A. R. Miedema, Physica **101B**, 294 (1980).

[14]M. Grioni, J. J. Joyce, and J. H. Weaver, J. Vac. Sci. Technol. A (to be published).

[15]Cu/InP: T. Kendelewicz, W. G. Petro, I. A. Babalola, J. A. Silberman, I. Lindau, and W. E. Spicer, Phys. Rev. B **27**, 3366 (1983).

[16]Cu/InP: L. J. Brillson, C. F. Bruckner, A. D. Katnani, N. G. Stoffel, and G. Margaritondo, J. Vac. Sci. Technol. **19**, 661 (1981).

[17]O. Kubaschewski and C. B. Alcock, *Metallurgical Thermochemistry*, 5th ed. (Pergamon, Oxford, 1979).

[18]Ag/InP: I. A. Babalola, W. G. Petro, T. Kendelewicz, I. Lindau, and W. E. Spicer, Phys. Rev. B **29**, 6614 (1984).

[19]Au/InP: W. G. Petro, T. Kendelewicz, I. A. Babalola, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. A **2**, 835 (1984).

[20]Ni/InP,GaAs: T. Kendelewicz, M. D. Williams, W. G. Petro, I. Lindau, and W. E. Spicer, Phys. Rev. B **32**, 3758 (1985).

[21]D. D. Wagman *et al.* The NBS Tables of Chemical Thermodynamic Properties, edited by D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall [J. Phys. Chem. Ref. Data Suppl. **2**, 111 (1982)].

[22]Pd/InP: T. Kendelewicz, W. G. Petro, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. A **2**, 542 (1984).

[23]Co/InP: T. Kendelewicz, Phys. Rev. B **34**, 558 (1986).

[24]Ti/InP: T. Kendelewicz (unpublished results).

[25]Ga/GaAs: P. Skeath, I. Lindau C. Y. Su, and W. E. Spicer, Phys. Rev. B **28**, 7051 (1983).

[26]B. Predel, J. Chem. Phys. **74**, 827 (1977).

[27]Au/GaAS: W. G. Petro, I. A. Babalola, T. Kendelewicz, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. A **1**, 1181 (1983).

[28]Ni/GaAs: M. D. Williams, W. G. Petro, T. Kendelewicz, S. H. Pan, I. Lindau, and W. E. Spicer, Solid State Commun. **51**, 819 (1984).

[29]Pd/GaAs: T. Kendelewicz, W. G. Petro, S. H. Pan, M. D. Williams, I. Lindau, and W. E. Spicer, Appl. Phys. Lett. **44**, 113 (1984).

[30]Cr/GaAs: J. H. Weaver, M. Grioni, and J. J. Joyce, Phys. Rev. B 31, 5348 (1985).
[31]V/GaAs: M. Grioni, J. J. Joyce, and J. H. Weaver, J. Vac. Sci. Technol. A 3, 918 (1985).
[32]Ti/GaAs: C. E. McCants (private communication).
[33]Ce/GaAs: J. H. Weaver, M. Grioni, J. J. Joyce, and M. del Giudice, Phys. Rev. B 31, 5290 (1985).
[34]Sm/GaAs: M. Grioni, J. J. Joyce, and J. H. Weaver, Phys. Rev. B 32, 962 (1985).
[35]Yb/GaAS: J. Nogami, M. D. Williams, T. Kendelewicz, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. A (to be published).