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Surface segregation at metal–III-V-compound-semiconductor interfaces

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In this paper we analyze the results of a wide range of photoemission studies of metal–III-V-compound-semiconductor interface formation. We find that semiconductor atoms segregate to the vacuum surface of the metal overlayer in most cases and that the presence of these atoms accounts for the slow attenuation of the observed core emission intensities. A theoretical model is developed which predicts such segregation based on the cohesive energy and the relative atomic sizes of the substrate and overlayer species. Good agreement between the predictions of this model and experiment for GaAs and InP is achieved.

INTRODUCTION

In the past few years much experimental and theoretical work has focused on the properties of evolving metal-semiconductor interfaces.[1–28] These studies have clearly shown that interfaces formed by deposition of metal on atomically clean surfaces almost always exhibit metal-induced disruption of the substrate and subsequent intermixing of the atomic species.[7,8] Of the compound semiconductors, GaAs and InP have received the most attention, and the general behavior of such interfaces at room temperature is reasonably well delineated.[9–13] In these studies, surface-sensitive photoemission with synchrotron radiation has made it possible to follow interface formation at very low metal coverage and to discern the presence of substrate atoms in the overlayer at higher coverage, as recently reported by Weaver and co-workers,[14–16] Spicer and co-workers,[17–19] Ludeke and co-workers,[20–21] Williams and co-workers,[22,23] and others.[24–28]

It is now generally accepted that the deposited metal atoms induce substrate disruption and release the semiconductor species into the overlayer in most cases. For the reactive metals, there are reactions involving the metal and the anion. The resulting reaction products can be quite complicated and more than a single phase can be formed. Likewise, the cations released by substrate disruption can mix in the growing metal overlayers where they can form solid solutions. These conclusions are further supported by thermodynamical considerations. Indeed, inspection of the thermodynamical values of heats of formation[29,30] shows that metal-anion compound formation will usually be energetically favorable. In contrast, for many systems metal-cation reactions are not favorable and are not generally observed.

This paper focuses on the interesting observation that anion or cation species segregate to the free surface for a wide variety of metal–III-V-compound-semiconductor interfaces. The observation of surface segregation in metal–III-V-semiconductor systems enriches the phenomena of interface formation and, from another aspect, gives the possibility of understanding complicated interface behavior. Although this segregation has been noted, the mechanism which controls it has not been clear. The purpose of this paper is to develop a simple model for surface segregation for evolving metal-semiconductor interfaces. The starting point for this modeling is recent theories which have been developed to qualitatively interpret grain-boundary segregation and surface segregation on alloy systems. As we will show, our approach will yield excellent agreement when compared with the wealth of experimental information available in the literature, including our own experimental results and those of others.

SUMMARY OF EXPERIMENTAL RESULTS

Direct measurements of the spatial distribution of the various elements in an evolving interface are difficult. In some cases, such information has been obtained from sputter depth profiling or from polar-angle-dependent photoemission intensity profiling. A third technique involves the measurement of the core-level intensity as the kinetic energy of the photoelectron is changed, and hence the probe depth. These direct studies can provide clear evidence about the accumulation of semiconductor atoms on, or near, the free surface. Indirect studies are more common and include measurements of the core-level emission intensity of a particular element as a function of nominal metal coverage. Careful inspection of the attenuation curves based on intensity variations at high metal coverages gives insight into the change in atom concentration on the free surface and in the near-surface region.

The Ti/GaAs(100) system is an example of a reactive metal overlayer on GaAs(100). Recent sputter-profile studies of the intensity variation of the As $3d$, Ga $3d$, and Ti $3p$ emission measured after the growth of 100 Å of Ti on GaAs(100) showed that a significant amount of As accumulates on the free surface and only a very small quantity of As is dissolved in the Ti matrix. This interesting observation points to the possibility of anion segregation to the surface region of a reactive metal, a phenomenon which has only recently been noted. Detailed depth profiling for this Ti/GaAs system conducted for various metal coverages[31] indicate that for sufficiently thick metal overlayers (>20 Å) As keeps "floating" on the free surface, strongly suggesting a driving force which lowers the free energy of the system.

In studies of a chemically very different system,[32] Au/GaAs(100), polar-angle-dependent x-ray photoemission was used to investigate the elemental distribution in the overlayer. These results clearly showed a high concentration of both Ga and As on the free surface and in the near-surface region. A series of recent investigations of metal-overlayer formation on GaAs(110) and InP(110) based on core-level studies using high-resolution synchrotron-radiation photoemission showed that the anion or cation intensities generally attenuate much more slowly than they should if they were covered up by the growing metal overlayer. Further, the slopes for these attenuation curves at high coverages differ from metal to metal and from substrate to substrate.

It is now well known that surface chemical reactions induce surface morphology changes and intermixing. In most cases these chemical reactions dominate in the low-metal-coverage range at room temperature, but, as the amount of deposited metal increases, the reaction becomes diffusion limited and can be neglected. If the intermixed region is covered up in a layer-by-layer fashion by the metal overlayer, then the attenuation of the substrate emission should have the mean free path of the photoelectrons as a characteristic length scale. If the experimental results show slower attenuation at high coverages, there is reason to consider metal-cluster formation, continuous out-diffusion of semiconductor atoms into the overlayer, or semiconductor-atom segregation to the free surface.

With the exception of a few metals, such as Al, Ag, and In deposited on III-V semiconductor substrates, there is no strong evidence for metal-cluster formation at high coverages (this is especially true for the reactive metals where the photoemission intensity of the substrate signal is rapidly attenuated, even if the total is not). On the other hand, the low solubilities of semiconductor atoms in the metal matrix strongly argues that continuous out-diffusion with high concentration in the overlayer is very unlikely. We can therefore regard the slow attenuation of emission from substrate elements as indicating a high concentration of these atoms on and near the free surface, i.e., surface segregation. Of course, a careful analysis of the details for each of these systems is always needed before we can definitely attribute the observed low attenuation slope to surface segregation.

From the literature,[14,33–37] we can see that for the same metal overlayer (Fe, Cr, Ti, for example), the attenuation curves for In have lower slopes than those of Ga, implying that In has a greater tendency for surface segregation than Ga. Similarly, comparing metal-InP, metal-GaAs, and metal-InSb (Ref. 38) systems for the same metal overlayer, Sb has the strongest surface segregation, As has medium surface segregation, and P has very weak, or negligible, surface segregation. In addition, we have examined the experimental results from a wide variety of studies of the type described above for metal overlayers grown sequentially on GaAs and InP under ultrahigh-vacuum conditions. These results are summarized in Tables II and III where we report surface segregation of Ga and As in GaAs and In and P in InP, respectively. These results are the basis for comparison with the theoretical model developed in the next section.

THEORETICAL MODEL

In the earliest theory of atomic segregation, which was specific for grain boundaries, McLean[39] proposed a model where the solute atoms were assumed to populate grain boundaries and lattice sites with an energy difference, ΔE, the free energy of segregation. His analysis led to a phenomenological expression for surface segregation which was supported by several experiments,[40] but the problem still remained as to how to evaluate ΔE, and to what parameter it can be correlated.

Basically, the treatment of segregation has considered the preferential decoration of an AB alloy surface by atoms of species A. One reason that this occurs is that the A atoms have lower surface energy than do B atoms. Another involves the relative sizes of A and B, thus the strain energy associated with dissolving larger A atoms in the B matrix. When there exists a C species which covers the surface of the AB alloy, then A atoms have a greater tendency to move to the surface to react with C if A atoms are more reactive with species C. From a thermodynamic point of view, surface segregation in alloys is due to lowering the surface free energy by atom exchange between surface and bulk sites to gain the bonding and the strain energies and to the chemical activity of the different species, if there is any. Since the photoemission experiments that we will discuss were all conducted in ultrahigh vacuum, we can assume that there are no chemically active C atoms on the surface to induce preferential segregation so that the third factor of chemical reactivity can be neglected.

Williams and Nason[41] calculated the free energy of segregation using a layer-by-layer model of the surface and considering nearest-neighbor bonding in the regular solution model. They showed that such an energy per mole decreases when one atom of A is removed from the bulk and placed on the surface and an atom of B is transferred in the reverse direction. Wynblatt *et al.*[42] summed over all nearest-neighbor bonds with energies (negative values) ε_{AA}, ε_{AB}, and ε_{BB} being assigned to AA, AB, and BB neighbors, respectively, and concluded that the free energy of segregation per atom can be expressed as

$$\frac{\Delta E}{N}=\tfrac{1}{2}Z_v(\varepsilon_{BB}-\varepsilon_{AA}) +2\omega[Z_1(X_A^b-X_A^s)+Z_v(X_A^b-\tfrac{1}{2})] \;, \tag{1}$$

where $\omega=\varepsilon_{AB}-\frac{1}{2}(\varepsilon_{AA}+\varepsilon_{BB})$ is the alloy regular solution parameter, N is Avogadro's number, and Z_1 and Z_v are the atomic coordination number in one layer and the atomic coordination to one of the adjacent layers, respectively. In principle, the effects of successive layers away from the surface should also be considered since the composition of the second layer can differ from that of the bulk for nonzero values of ω. On the other hand, Seah[43] assumed that all compositional variations occurred in the topmost atom layer and noted that this approximation simplified the analysis while introducing errors that were negligible compared with errors encountered elsewhere.

The bond strengths ε_{AA} and ε_{BB} are best derived from the values of the molar surface energies γ_A and γ_B of the two constituents. At zero kelvin, these energies can be expressed as

$$\gamma_A=-\tfrac{1}{2}Z_v\varepsilon_{AA}N,\; \gamma_B=-\tfrac{1}{2}Z_v\varepsilon_{BB}N \;. \tag{2}$$

ω can be calculated[44] from tabulated values of the enthalpy of mixing, H^m, using

$$\Omega=N\omega=\frac{H^m}{ZX_A^bX_B^b} \;, \tag{3}$$

where Z is the coordination number. Thus, the free energy of segregation can be written

$$\Delta E=\gamma_A-\gamma_B+2\Omega[Z_1(X_A^b-X_A^s)+Z_v(X_A^b-\tfrac{1}{2})] \;, \tag{4}$$

Williams and Nason evaluated ε_{AA} and ε_{BB} in terms of the molar sublimation enthalpies. Seah[43] later approached the problem by relating surface energies to the melting points of the segregant and matrix atoms, with substantially improved agreement.

In our treatment of the parameters of Eq. (4), we correlated the surface segregation energy with the cohesive energies rather than with the melting points of the species involved. This seems more reasonable since the main difference between solid and liquid states involves the transition from long-range to short-range atomic order without breaking atomic bonding. Thus, it induces only a small change in bond strength. Instead, the cohesive energy involves bond breaking and conversion to the atomic orbital configuration from a solid-state configuration and should represent a better approach in modeling the surface-segregation mechanism.

Finally, to calculate the strain energy released when solute A atoms are allowed to segregate from the bulk to the surface, Burton and Machlin[45] and Wynblatt and Ku[42] wrote the difference of strain energy of a solute atom A at the surface and in the bulk as

$$E_{\text{str}}=\frac{24\pi kGa_Ba_A(a_B-a_A)^2}{3ka_A+4Ga_B} \;, \tag{5}$$

where k is the solute bulk modulus, G is the solvent shear modulus, and a_B and a_A are the appropriate radii for solvent and solute atoms in their pure states. From Eq. (5) we can see that the strain energy is always released when atom A is replaced from bulk to surface, in spite of whether a_A is bigger than a_B, because ΔE depends on the square of the difference in atomic radii. However, Tsai *et al.*[46] pointed out that current atomic calculations indicate that there is no appreciable relaxation of atomic positions about a vacancy because of the hard-core repulsion of nearest-neighbor interactions. Thus, the strain-energy term includes only the surface free energy for solute atoms larger than the solvent atoms. For smaller solute atoms, the strain term can be ignored.

The total surface free energy of segregation can now be written

$$\Delta E=(\gamma_A-\gamma_B)+V\Omega+W(a_A-a_B)^2 \;, \tag{6}$$

where the coefficients V and W must be determined by comparison with experiment. Seah[43] showed that V is

TABLE I. A list of the melting temperatures, cohesive energies, and atom sizes of elements of importance for the metal-III-V-compound-semiconductor systems under examination here. Part of the data was taken from Ref. 29. Atom sizes were obtained by calculations shown in text.

Element	Melting temp. (°C)	Cohesive energy (kJ/mol)	Atomic size (Å)
Ag	961.9	284.9	2.57
Al	660	329.7	2.55
As	817	302.5	2.79
Au	1064	368.2	2.57
Ce	799	423	3.27
Co	1495	428.4	2.22
Cr	1857	398	2.29
Cu	1063	337.6	2.28
Fe	1535	415.5	2.28
Ga	29.8	273.6	2.70
Hf	2227	619	2.81
In	156.6	243	2.97
Mn	1244	283.3	2.33
Ni	1455	430.1	2.22
P	590	332.2	2.67
Pd	1554	376.6	2.45
Pt	1772	565.7	4.36
Ru	2310	648.5	2.39
Sb	630.5	264.4	3.12
Sc	1541	377.8	2.92
Sm	1077	206.7	3.21
Ta	2996	782	2.63
Ti	1660	469.9	2.61
Tl	303.5	182	3.06
V	1890	514.2	2.42
W	3410	849.8	2.51
Yb	819	152.1	3.46

TABLE II. Comparison between theoretical predictions and experimental results of Ga and As surface segregation for metal-GaAs semiconductor systems. Y denotes that segregation is predicted, N denotes that there is no segregation, and A denotes that we cannot predict (abstain).

Metal overlayer	Ga segreg. predicted by cohesive energy	Ga segreg. predicted by melting temp.	Ga segreg. predicted by strain energy	Expt.	As segreg. predicted by cohesive energy	As segreg. predicted by melting temp.	As segreg. predicted by strain energy	Expt.	Ref.
Ag	N	Y	Y		Y	Y	Y		
Al	Y	Y	Y	Y	Y	N	Y		25,47
Au	Y	Y	Y	Y	Y	Y	Y	Y	11,32,48
Ce	Y	Y	A	Y	Y	N	A	Y	11,49
Co	Y	Y	Y	N	Y	Y	Y	Y	16
Cr	Y	Y	Y	Y	Y	Y	Y	Y	50
Cu	Y	Y	Y	Y	Y	Y	Y	Y	51
Fe	Y	Y	Y	N	Y	Y	Y	Y	52
Hf	Y	Y	A		Y	Y	A		
In	N	Y	A		Y	N	A		
Ir	Y	Y	Y		Y	Y	Y	Y	24
Mn	Y	Y	Y		N	Y	Y		
Ni	Y	Y	Y		Y	Y	Y		
Pd	Y	Y	Y	Y	Y	Y	Y	Y	53
Pt	Y	Y	A		Y	Y	A		
Ru	Y	Y	Y		Y	Y	Y		
Sc	Y	Y	A		Y	N	A		
Sm	N	Y	A	N	N	Y	A	N	54
Ta	Y	Y	Y		Y	Y	Y	Y	24
Ti	Y	Y	Y	Y	Y	Y	Y	Y	21,55
Tl	N	Y	A		Y	N	A		
V	Y	Y	Y	Y	Y	Y	Y	Y	15
W	Y	Y	Y		Y	Y	Y		
Yb	N	Y	A	N	N	A	A	N	56

TABLE III. Comparison between theoretical predictions and experimental results of In and P surface segregation for metal-InP semiconductor systems, analogous to those of Table II.

Metal overlayer	In segreg. predicted by cohesive energy	In segreg. predicted by melting temp.	In segreg. predicted by strain energy	Expt.	P segreg. predicted by cohesive energy	P segreg. predicted by melting temp.	P segreg. predicted by strain energy	Expt.	Ref.
Ag	Y	Y	Y		N	Y	Y	Y	9,57
Al	Y	Y	Y	Y	A	Y	Y		9,58–61
Au	Y	Y	Y	Y	Y	Y	Y	Y	60,62,63
Ce	Y	Y	A	Y	Y	Y	A	Y	33
Co	Y	Y	Y	Y	Y	Y	Y	N	34
Cr	Y	Y	Y	Y	Y	Y	Y	N	35,64
Cu	Y	Y	Y	Y	Y	Y	Y	Y	61,63,65
Fe	Y	Y	Y	Y	Y	Y	Y	N	36
Ga	Y	N	Y	Y	N	N	A		22
Hf	Y	Y	Y		Y	Y	A		
Mn	Y	Y	Y	Y	N	Y	Y		64
Ni	Y	Y	Y	Y	Y	Y	Y	Y	9,63,66
Pd	Y	Y	Y	Y	Y	Y	Y	Y	9,67
Pt	Y	Y	A		Y	Y	A		
Ru	Y	Y	Y		Y	Y	Y		
Sc	Y	Y	Y		Y	Y	A		
Sm	N	Y	A		N	Y	A		
Ta	Y	Y	Y		Y	Y	Y		
Ti	Y	Y	Y	Y	Y	Y	Y	N	37
Tl	N	Y	A	N					58
V	Y	Y	Y		Y	Y	Y		
W	Y	Y	Y						

nearly unity and the second term is typically only 4% of the first term. The magnitude of W depends on a_A and a_B through the atomic size dependence of the moduli k and G; W will be equal to zero for $a_A < a_B$. Because of complications in evaluating W, we do not try to determine which term in Eq. (6) is more important, cohesive energy or strain energy, for a given system. Instead, we include the predictions from bonding energy and strain energy separately in Tables II and III. However, as discussed above, the strain energy plays a role only when a_A is bigger than a_B, and in many cases it is the bonding energy (cohesive energy) that plays a key role in determining surface segregation. With Eq. (6) we can predict whether surface segregation is energetically favorable for any metal–III-V-compound-semiconductor system.

In Table I we summarize the melting temperatures T^{melt}, the cohesive energies E_{coh}, and the atom sizes a_A, of elements of importance for the metal–III-V-semiconductor systems under examination here. T^{melt} and E_{coh} were taken from Ref. 29. a_A is calculated in angstroms according to the relation

$$a_A = \left[\frac{10^{24} A_A}{N \rho_A} \right]^{1/3} , \tag{7}$$

where A_A denotes atomic weight, ρ_A is the density of metal, and N is Avogadro's number. a_A should be deduced from lattice-parameter changes as the solute enters the solvent but, for a qualitative study, Eq. (7) is an adequate approximation. The predictions concerning the segregation of Ga and As in metal-GaAs systems are summarized in Table II and those for In and P segregation in metal-InP systems are summarized in Table III.

DISCUSSION

According to Eq. (6), we use data taken from Table I to predict the existence of surface segregation shown in Tables II and III for metal-GaAs and metal-InP systems, respectively. The first column shows the prediction with account taken of only the cohesive energy; the second considers only the melting temperature, and the third for strain energy. The fourth column gives experimental results where Y means the existence of surface segregation, N means absence of surface segregation, and A means that one cannot predict yes or no (abstain). From Table I we see that the cohesive energy of In is lower than that of Ga and that the atomic size of In is larger than that of Ga. From our model, considering either the gain in cohesive energy or the gain in strain energy, we should therefore expect that In has a greater tendency to surface segregate than Ga for a given metal overlayer. Indeed, when we compare the results for overlayers of Ti, Cr, and Fe on GaAs and InP, we can clearly see this trend. The In intensities decrease much more slowly than do those of Ga, and In has a greater tendency to segregate to the surface.

When the metal atoms from the vapor phase reach the III-V semiconductor surface, they can break anion-cation bonds of the substrate, release the dissociated anions and the cations, and react with the anions to form new chemical products if the metal is reactive. Due to disorder and the random distribution of different atoms in the interfacial region during the deposition process, some anions may escape without forming compounds with metal atoms. When compound formation is very favorable, the anions are mostly strongly bonded to the metal atoms and they are less likely to diffuse from interface to the vacuum surface at room temperature. This corresponds to chemical trapping in the interfacial region.[7] Only those anions can diffuse to the surface which can escape from chemical trapping and only when segregation is favored by a gain in surface energy. Hence, for reactive metal deposition we must consider the effect of chemical trapping as well as the cohesive energy and strain energy. The absence of P surface segregation for the Co, Cr, and Fe on InP interface systems is plausibly connected with phosphide compound formation and P trapping near the buried interface, and the failure of our prediction is mainly due to this phenomenon, which is not taken into consideration in our model.

The chemical reactivity of P is greater than that for As which, in turn, is greater than that for Sb as can be seen from their electronegativities and the heats of compound formation between metal and anion. The greater the reactivity of the anions, the less intense will be the surface segregation. This implies that the lower chemical reactivity of Sb may induce more intense surface segregation compared to As and P. Furthermore, Sb atoms are the largest among the pnictides and P atoms are the smallest (excluding Bi). From the point of view of strain energy, we should also expect that Sb would segregate most readily. This would predict that the tendency to surface segregate would diminish from Sb to As to P for the same metal overlayer. The results from Refs. 14 and 33–37 confirm this since most of the P atoms are trapped near the interface for metal-InP systems and we have not observed any P surface segregation for Fe, Cr, Co, and Ti overlayers on InP. For metal-GaAs systems, we see As surface segregation for the same Fe, Cr, Co, and Ti overlayers, although the segregation is very weak. In metal-InSb systems we have found very strong surface segregation for Co and other metals.[38]

From Tables II and III we can see the agreement between our predictions and the experimental results is quite good, with deviation observed for only a few systems. Our theoretical considerations are all based on the thermodynamic equilibrium state but interface formation is limited by diffusion and the systems need not reach equilibrium. In practice, many systems are not in equilibrium. The kinetic process is always associated with the diffusion of the segregant. In turn this is related to the amount of substrate disruption, to metal-anion compound formation, and to the morphological distribution of the reaction products. Clearly, these interfacial regions are more complicated than AB alloy surfaces and the details differ from system to system. It is therefore not surprising that our simple model fails in a few systems. Indeed, it is remarkable that it works so well in so many systems. That success implies that, although the interface is very complicated, the cohesive energy and the strain energy are key factors which control the process of surface segregation. To demonstrate this is equivalent to demonstrating the essence of surface segregation for metal–III-V-compound-semiconductor interfaces.

In conclusion, we have presented a modified theoretical model which describes surface segregation in binary alloy systems and have applied it to surface segregation for metal–III-V-compound-semiconductor interfaces. Our simple model is direct and does not need laborious calculations. By using some elemental considerations, it can predict what may happen when a thick metal layer is deposited onto III-V semiconductor substrates. The general agreement between the predictions and experiment indicates the utility of the simple model.

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