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# Temperature-dependent interface evolution: Modeling of core-level photoemission results for V/Ge(111)

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High-resolution synchrotron-radiation core-level photoemission results are presented which show the evolution of the V/Ge(111) interface for temperatures between 300 and 643 K. These results have been analyzed quantitatively using an extension of a model developed by Butera, del Giudice, and Weaver to determine the range over which the various reaction products form at each temperature. We find that the reaction product $V_2Ge_3$ forms over a greater range of coverage with increasing temperature, that the amount of the Ge-in-V solution phase diminishes as thermal transport promotes $V_2Ge_3$ formation, and that a V-in-Ge solution phase forms, probably in the $V_2Ge_3$ grain boundaries. The effects of increasing the substrate temperature can be accounted for by a single activation energy which describes these growth profiles and allows the prediction of the interface evolution at any temperature in the range of study.

## INTRODUCTION

The physical and chemical properties of metal-semiconductor interfaces have attracted a great deal of experimental and theoretical interest.[1–13] Numerous studies have sought an understanding of the complex reaction chemistry and intermixing observed at interfaces, and great progress has been made. Although we are still far from being able to predict the properties of an interface as a function of temperature and growth conditions, ongoing investigations which focus on the reactivity of the constituents, the composition, spatial extent, and morphology of an interface at each stage in its development, the thermal and environmental stabilities of interfaces, and their electrical behaviors are making substantial headway.

In this paper we present results which shed light on the temperature-dependent evolution of a representative reactive metal-semiconductor interface—V/Ge(111). By using high-resolution synchrotron-radiation core-level photoemission, we have been able to follow the changing chemical environments of Ge atoms at the interface for temperatures $300 \leq T \leq 643$ K. We have used these results to examine the limitation of a recently developed model for the room-temperature evolution of that interface.[12] The goal of that model, and its extension here, was the elucidation of factors which govern the formation of reactive metal-semiconductor interfaces. Here, we show that it is possible to determine the temperature-dependent parameters which control the evolving interface.

The earlier study[12,13] showed that the V/Ge(111) interface is composed of the Ge substrate, a heterogeneous polycrystalline $V_2Ge_3$ phase which forms on the Ge substrate, a solid solution of Ge in V over the $V_2Ge_3$ phase, and an overlayer of pure V which terminates at the vacuum surface. We will show here that the $V_2Ge_3$ and the solution phases persist as the temperature is increased but that the spatial extent of each phase changes. The enhanced growth of the $V_2Ge_3$ phase follows an exponential of $-1/T$. Likewise, we show that there is a new phase which is formed as the temperature is increased, namely, a dilute V-in-Ge phase which probably grows in the $V_2Ge_3$ grain boundaries. The amount of this phase also increases exponentially as $-1/T$, with the same energy parameter as for the thickening of the $V_2Ge_3$ phase. These results show a metastable interface, but the modeling presented herein makes it possible to describe the evolution quantitatively over a wide range of temperatures.

## EXPERIMENTAL TECHNIQUES AND RESULTS

High-resolution core-level photoemission studies were conducted at the Wisconsin Synchrotron Radiation Center using the grasshopper Mark-II monochromator and beam line. The overall instrumental resolution was 250 meV (electrons plus photons). An etched Ge(111) wafer was cleaned by Ar-ion sputtering and thermal annealing cycles at 875 K. The cleanliness and quality of the surface was determined with Auger spectroscopy and valence-band photoemission. The temperature of the sample was controlled by a resistive heater attached to the holder. The temperature was stabilized before the first evaporation cycle was begun, and the overall thermal stability was ±5 K throughout each series of measurements. The results reported for each isotherm were found to be independent of time, indicating steady-state conditions. For each experiment, vanadium was evaporated onto the cleaned Ge(111) surface from a

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resistively heated molybdenum boat (pressure during evaporation better than $3\times10^{-10}$ Torr, operating pressure better than $5\times10^{-11}$ Torr, source to sample distance $\sim30$ cm, and the number of atoms deposited determined with a crystal oscillator).

In Figs. 1–3 we show high-resolution energy distribution curves (EDC's) for the spin-orbit-split Ge 3*d* core levels obtained at representative temperatures of 373, 459, and 643 K. In each figure the EDC in the bottom left is for the clean surface. The EDC's were scaled for visual clarity to be of approximately the same height, and backgrounds were subtracted. Corrections for changes in band bending have also been made, as discussed in Ref. 13. The effect of the V deposition is to induce a reaction product, labeled 1. This product grows with coverage $\Theta$, given alongside each EDC, but ultimately yields to a third component which appears at lower binding energy, labeled 2. The core-level shifts were $-0.5$ eV for the first reaction product and $-0.95$ eV for the second.[13] As can be seen by inspection, one effect of changing temperature is to prolong the coverage interval over which component 1 dominates.

As discussed elsewhere in detail,[13] line-shape decompositions of the complex core-level spectra make it possible to follow the coverage behavior of each component. To obtain the decompositions shown on the right of

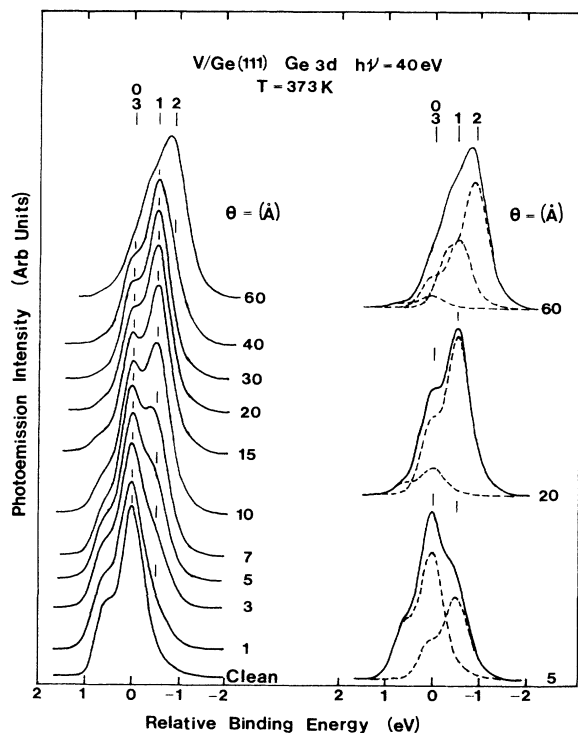

FIG. 1. Photoelectron energy distribution curves for the Ge 3*d* core level showing the evolution with coverage, $\Theta$, of the line shape at 373 K. Representative core-level decompositions are shown at the right. Component 0 corresponds to the substrate, component 1 corresponds to the $V_2Ge_3$ phase, component 2 corresponds to the Ge-in-V solution, and component 3 corresponds to the V-in-Ge solution.

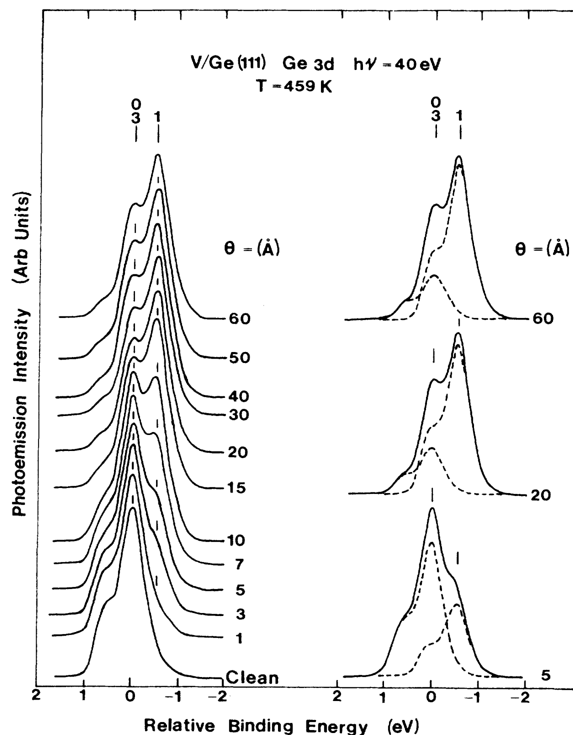

FIG. 2. EDC's for V/Ge showing the evolution of the Ge 3*d* line shape at 459 K.

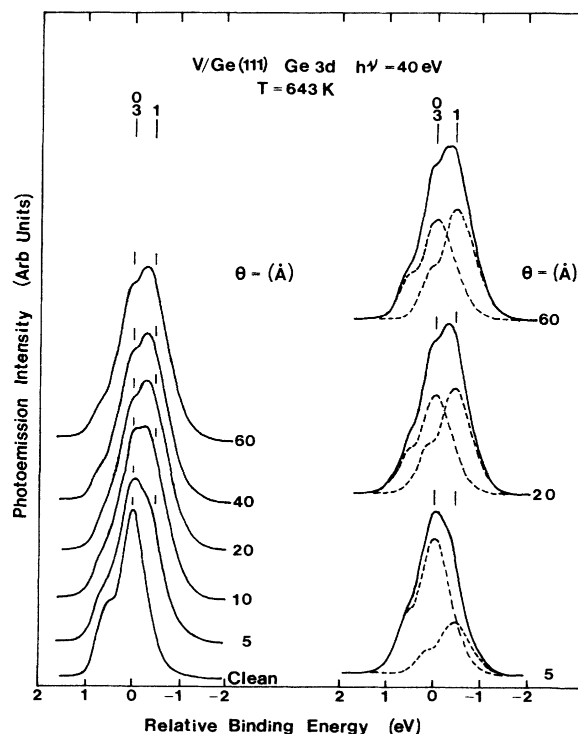

FIG. 3. EDC's for V/Ge showing the evolution of the Ge 3*d* line shape at 643 K.

Figs. 1–3 (and others not shown), we used line shapes derived from the clean surface, with the surface component mathematically removed,[13,14] to build the spectra for all coverages. The binding energy of each species was held fixed throughout the fitting procedure and only the relative intensities of the components were allowed to vary. As noted above,[13] the first reacted species corresponds to $V_2Ge_3$ and the second corresponds to the solid solution of Ge in V. The present set of decompositions indicate that the regions under investigation are composed of distinct chemical environments which can be identified from the room-temperature analyses.[13] This is a fundamental observation, and its validity is demonstrated by the quality of the fits and their self-consistency for all coverages and temperatures. Furthermore, the results of Figs. 1–3 show that a previously unobserved component must be introduced at high temperature to account for emission at the same binding energy as the substrate; in the figures we show these with labels 0 and 3.

In Fig. 4 we show the normalized attenuation curves $\ln[I(\Theta)/I(0)]$ corresponding to the V/Ge(111) interface obtained at 300, 373, 423, 459, 523, and 643 K. In each case the different symbols represent the substrate, the first reacted phase, the second reacted phase, and the total integrated Ge 3*d* intensity, as determined from the decompositions of Figs. 1–3. These attenuation curves make the point quantitatively that the spatial extent of the $V_2Ge_3$ phase extends to higher coverage as the temperature increases and its relative amount increases. Simultaneously, the amount of the second phase decreases and, by 459 K, it is present in an amount that is too small to be detected when $\Theta < 60$ Å. These results show that by 459 K the formation of $V_2Ge_3$ is strongly favored over the formation of the Ge-in-V solution phase. Furthermore, there is core emission which persists at the same energy as the substrate and is spectroscopically indistinguishable from the substrate. The amount of this component increases with temperature. Clearly, these results show that the effect of temperature is to modify the distribution of Ge in the interface and to induce the formation of a phase not seen at low temperature. Although spectroscopically indistinguishable, it can be identified through its attenuation profile and we estimate its growth (and the attenuation of the substrate) by the dashed lines in the intermediate coverage regime ($\sim$20–30 Å).

In order to see the evolving core-level line shapes and the growth of this new component, we show in Fig. 5 the EDC's measured at a fixed nominal coverage of 40 Å

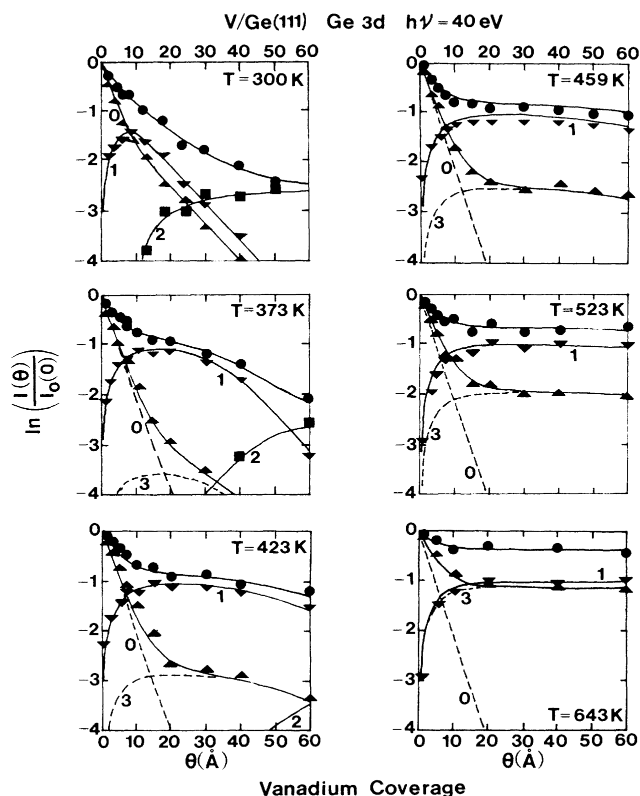


FIG. 4. Ge 3*d* core level attenuation curves, defined as the emission at some coverage Θ normalized to that of the clean surface of bulk sensitive core-level spectra. Component-specific spectra are shown based on the core-level decompositions of Figs. 1–3. The substrate is labeled 0 and is seen to decay rapidly with V coverage. Component 1, the $V_2Ge_3$ phase, is seen to increase in amount as the temperature increases. Component 2, the Ge-in-V solution, decreases in amount as the temperature increases and cannot be detected for $T > 423$ K. Component 3, the V-in-Ge solution, increases with temperature and equals component 1 at 643 K.

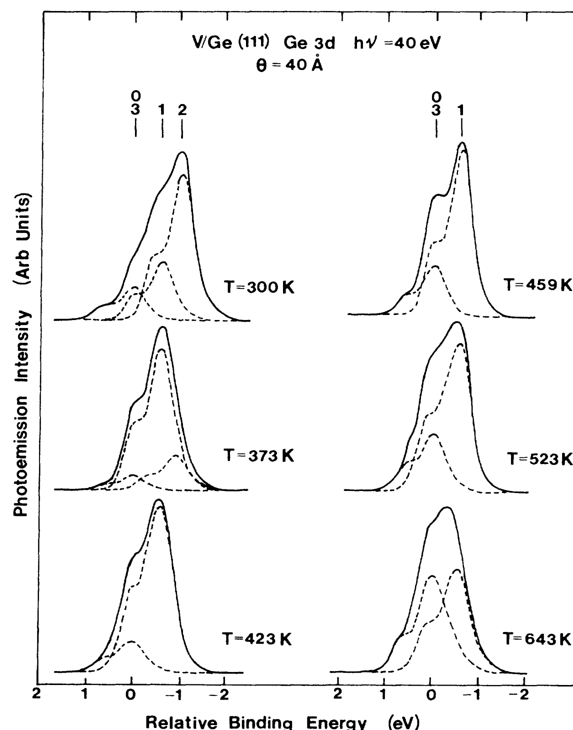


FIG. 5. Ge 3*d* EDC's for a fixed coverage of 40 Å summarizing the effects of temperature on the line shape, and hence constituency of the interface.

for temperatures $300 \leq T \leq 643$ K. As with the other EDC's, the photoelectron mean-free path is $\sim 20$ Å and this guarantees that there is residual substrate emission at 300 K. The emission from the $V_2Ge_3$ phase is stronger than that of the residual substrate but the dominant emission is from the Ge-in-V solution (component number 2). By 459 K the solution phase has vanished and the $V_2Ge_3$ component is dominant. From Fig. 4 we can also see that the total Ge $3d$ emission is $1/e$ of its clean-surface value at 459 K, compared to $1/e^2$ for 300 K. By 643 K, there is approximately equal emission from $V_2Ge_3$ and the new phase and there are copious amounts of Ge within the probe depth of the photoelectrons.

## DISCUSSION

At any metal-semiconductor interface, reaction is controlled by the availability of suitable numbers of atoms of each species and the heats of formation of the reaction product(s). Once reaction is initiated, there must be mass transfer across the reacted region so that the balance of metal and semiconductor atoms is sufficient to continue the reaction. The free energy of the reaction provides the driving force for this diffusion. The reaction product which forms also serves to limit its own growth since the amount of reactants available for reaction decreases with increasing interlayer thickness (diffusion). Hence, a thin metastable interface region forms with spatial extent which varies from system to system. This appears to be the general rule for interface formation, with refinements as appropriate for epitaxial systems or systems which are effectively nonreactive.

In a recent paper[12] we assumed that the distance dependence of the available reactants would control the probability of formation of a given product and that it was possible for a two-phase region to exist which could be accounted for by using a linear level rule. In effect, this described a heterogeneous reaction with the possibility of phase 1 and phase 2 growing simultaneously at different parts of the surface. This required the existence of critical coverages corresponding to the beginning and end of the two-phase region(s). The success of this simple model rested in the fitting of photoemission core-level results, like those of Fig. 1, for V/Ge, Ce/Ge, and Ce/Si interfaces formed at room temperature. With this model it has been possible to gain information about the number of phases formed, their compositions, and their spatial extent as a function of the amount of metal deposited.

When temperature is elevated during interface formation, there will be enhanced reaction-induced diffusion through the reacted region and a correspondingly larger amount of the first product, consistent with the formation of thick reacted films and the results of Figs. 1–5. This implies that the values of the critical coverages for the two-phase region increase with temperature. Since these critical values are controlled by diffusion through the reaction-activated region, they should exhibit an exponential dependence on temperature and be amenable to an Arrhenius description.

In the Appendix we reiterate the critical expressions that make it possible to determine the normalized photoemission intensities for the reaction products corresponding to $V_2Ge_3$ and the Ge-in-V solution. These expressions can be applied to the results at any temperature (Figs. 1–3) provided that only the two reaction products form. However, the results obtained through these temperature-dependent studies provide strong evidence for the formation of a product which has a binding energy that is indistinguishable from that of the substrate. The contribution of this component cannot be predicted by the Butera–del Giudice–Weaver (BGW) model. Detailed analysis has, however, shown that its presence is related to the $V_2Ge_3$ reaction product (which thickens with temperature) and that its amount, relative to $V_2Ge_3$, is constant for a given temperature.

There are several possibilities that would account for the third reaction product. First, it could be due to a surface-segregated layer of Ge atoms. These Ge atoms would, however, produce an emission intensity which would be essentially constant with metal coverage and might increase with temperature. Such segregation has been observed for a number of metal-semiconductor interfaces, such as anion segregation at Co/GaAs (Ref. 15) or Au/GaAs (Ref. 2) interfaces. Its appearance is correlated to the disruption of the substrate, release of the semiconductor atoms, and the low solubility of the dissociated species in the growing metal overlayer.[2,15] This appears to be highly unlikely for a system with as high a reactivity as the V/Ge system since the surface Ge would react with the incoming V atoms to form a solution. Furthermore, we know that it is possible to extinguish the Ge emission by depositing thick V films. Such segregation would require a low solubility of Ge in the reaction products, but this presents a problem with regard to the required reaction-induced diffusion. We conclude that this possibility is unlikely.

Second, the new emission could be due to interstitial Ge atoms within the reaction products. The solubility of this Ge solute would increase exponentially with temperature and, although there may indeed be a small contribution of such atoms, the observed emission at the highest temperature requires the solubility to be $\sim 30\%$. We consider this to be unrealistic in light of the extremely low solubility of Ge in the V-Ge compounds reported in the literature.[16]

The third and most likely source for the additional emission comes from the formation of a new reaction product which is Ge rich. From conventional diffusion considerations for an $A$-$B$ couple, there will be a concentration gradient across the interfacial region for $A$ atoms diffusing into $B$, and conversely. When $A$ is a reaction product ($V_2Ge_3$ in our case) in contact with an infinite source of $B$ (Ge atoms), there will again be a concentration gradient as Ge out-diffuses across the $V_2Ge_3$ region. The most likely paths for such diffusion are grain boundaries. Locally, it is reasonable that $V_2Ge_3$ would be converted to the next richer Ge phase. This process will be enhanced at higher temperature and would scale with the amount of $V_2Ge_3$ present. Likewise, since the phase that is richer in Ge than $V_2Ge_3$ is

the solid solution ($V_2Ge_{98}$ at the eutectic temperature), the binding energy of Ge would be indistinguishable from that of bulk Ge. Because the Ge content is large, a relatively small amount of this phase will have a major impact on the observed photoemission spectra, as shown in Figs. 4 and 5.

In the Appendix we have described the mathematical formalism needed to treat the growth of the V-in-Ge solution phase along with the $V_2Ge_3$ and Ge-in-V phases with the explicit assumption that the new phase grows in the grain boundaries of $V_2Ge_3$ and is therefore related to the amount of $V_2Ge_3$. Equations (A1)–(A3) describe a reaction-induced diffusion process in which the supply of semiconductor atoms is the limiting factor. As long as the amount of Ge atoms is large enough to support the formation of $V_2Ge_3$, a single phase is present. When the impinging metal atoms exceed the necessary 2:3 ratio for $V_2Ge_3$ formation, the system enters a two-phase region consisting of $V_2Ge_3$ and a Ge-in-V solution. The beginning of this two-phase region is characterized by the parameter $\Theta_2$. $\Theta_1^*$ refers to the end of the two-phase region where only the Ge-in-V solid solution is formed. These parameters, together with $\alpha$ which describes the relative amount of V-in-Ge solution, are found to be dependent on temperature and are given in Table I. Our analysis clearly shows that the V-in-Ge solid solution is produced simultaneously with the $V_2Ge_3$ compound. The Ge content in this solid solution is so high that the Ge 3*d* binding energy is indistinguishable from that of the substrate. The fits to the experimental results shown as solid lines in Fig. 4 are quite remarkable.

The experimental results and their fittings show that the parameters $\Theta_2$, $\Theta_1^*$, and $\alpha$ increase rapidly with temperature. In order to determine the form of the temperature dependence for these parameters, we assumed an Arrhenius behavior of the form $x = A\exp(-E^*/RT)$ where $E^*$ is an activation energy for the diffusion process across the reaction-activated region. The applicability of this form is demonstrated through the results of Fig. 6 where we show that $\Theta_1^*$, $\Theta_2$, and $\alpha$ all depend exponentially on temperature and, most importantly, have the same slope. The fact that the same activation energy $E^*$ applies to all the parameters is strong evidence that the mechanism controlling the two-phase region (consisting of phases 1 and 2) is coupled to, if not the same as, that responsible for the formation of the final V-in-Ge solution. Thus we can write for the V/Ge(111) system that the temperature-*dependent* parameters have the form

$$\Theta_2 = 8.6\times10^2\exp(-3930/RT) ,$$

$$\Theta_1^* = 1.0\times10^4\exp(-3930/RT) ,$$

and

$$\alpha = 6.1\exp(-3930/RT) ,$$

where the units of coverage are angstroms. As listed in Table I, the temperature-*independent* parameters are the atomic fraction of Ge in phase 1, $C_1 = 0.60$ corresponding to the empirical formula $V_2Ge_3$; the atomic fraction of Ge in phase 2, $C_2 = 0.10$ corresponding to the Ge-in-V solution; the activation energy $E^* = 3.93$ kcal/mol; the universal photoelectron mean-free path $\lambda_0 = 20$ Å; and the material-specific mean-free paths $\lambda_1 = 12$ Å and $\lambda_2 = 15$ Å. Once these parameters have been evaluated, the interface evolution can be calculated for any intermediate temperature up to the maximum temperature and coverage of this work. In addition, insight into the evolution for temperatures outside the range of this work can be approximated, as long as there are no new phases which form.

TABLE I. Parameters used to obtain the fits between Eqs. (A1)–(A3) and the experimental results of Figs. 1–5. Temperature-*independent* parameters used in fitting included the photoelectron mean-free paths through different materials ($\lambda_0 = 20$ Å, $\lambda_1 = 12$ Å, $\lambda_2 = 15$ Å), the nominal concentrations of the phases ($C_1 = 0.60$ or $V_2Ge_3$, $C_2 = 0.10$ or nominal $V_9Ge$), and the activation energy $E^* = 3.93$ kcal/mol. Temperature-*dependent* parameters corresponding to coverages at which phase 2 starts to form, $\Theta_2$, phase 1 stops forming, $\Theta_1^*$, and the amount of phase 3, $\alpha$.

| $T$ (K) | $\Theta_2$ | $\Theta_1^*$ | $\alpha$ |
|---|---|---|---|
| 300 | 1.1 | 14 | |
| 373 | 4 | 51 | 0.030 |
| 423 | 8 | 93 | 0.057 |
| 459 | 11 | 137 | 0.082 |
| 523 | 20 | 233 | 0.141 |
| 643 | 40 | 464 | 0.319 |

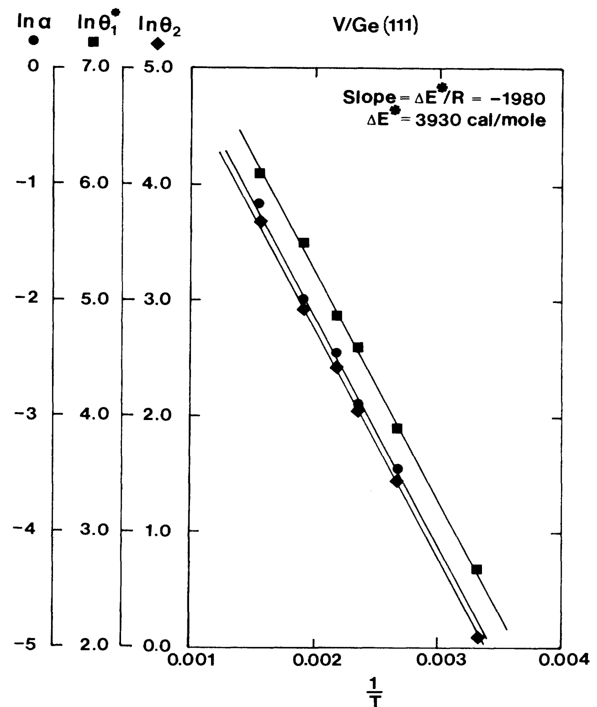


FIG. 6. Arrhenius plot showing that the activation energy and the critical coverages for the two-phase region exhibit the same temperature dependence, thereby indicating common physical origins.

The experimental results and the analysis presented above indicate that the interface is composed of the solid solution of Ge in V, the compound closest to the lowest eutectic, and the solid solution of V in Ge. The amounts of each as a function of metal deposition are temperature dependent and the results can be fit with the modified BGW model. A highly schematic description of the morphology of the interface at various temperatures is shown in Fig. 7. Note that the V-in-Ge solution can extend from the substrate to the site of formation of both the first and second reaction products, forming as it should in grain boundaries. Indeed, Ge diffusion is most likely to occur via these grain boundaries. Note also that although the stoichiometries of the solution phases vary with distance from their boundaries, we have out of necessity assumed them to be constant.

This work represents a quantitative second step in describing the development of reactive metal-semiconductor interfaces, building on the results of Refs. 12 and 13. It is, however, still only at the phenomenological level. Efforts are underway to develop a better understanding of the reaction-induced diffusion mechanism which controls interface formation for these systems and to determine the atom-specific properties and interactions which control the reactions.

## ACKNOWLEDGMENTS

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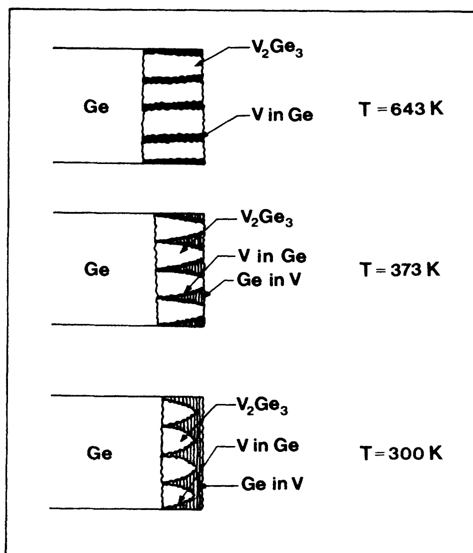


FIG. 7. Highly schematic representation of the evolving V/Ge interface. A cross section of the thick film at 300 K would show the Ge substrate and the three reaction products. Increasing the temperature results in the enhancement of $V_2Ge_3$ and the V-in-Ge solution, but the loss of the Ge-in-V solution due to mass transport across the interface.

## APPENDIX: EXTENSION OF THE BGW MODEL

The BGW model was developed to fit the experimental core-level photoemission data when the interface was produced on a room-temperature substrate. It was necessary to extend the model to account for the behavior of the emission occurring at the substrate binding energy, as shown in Figs. 1–5.

The derivation of the general expressions which describe the intensity of any core component during the evolution of the interface can be found in Appendix A of Ref. 12 and will not be repeated here. A few expressions are, however, necessary and can be summarized briefly. From Ref. 12 the Ge photoemission intensity originating from phase 1, normalized to the substrate intensity for the clean surface, is

$$I_1(\Theta)/I_s(0)=C_1(\lambda_1/\lambda_0)[1-\exp(-t_1/\lambda_1)] \times[(1-\chi)+\chi\exp(-t_2/\lambda_2)] , \quad (A1)$$

and that of the second phase

$$I_2(\Theta)/I_s(0)=\chi C_2(\lambda_2/\lambda_0)[1-\exp(-t_2/\lambda_2)] , \quad (A2)$$

where the function which describes the partitioning between phase 1 and phase 2, $\chi$, is taken to have a lever-rule form, namely

$$\chi=0 \text{ for } \Theta_1<\Theta<\Theta_2 ,$$

$$\chi=(\Theta-\Theta_2)/(\Theta_1^*-\Theta_2) \text{ for } \Theta_2<\Theta<\Theta_1^* ,$$

and

$$\chi=1 \text{ for } \Theta_1^*<\Theta<\Theta_2^* ,$$

and the following are definitions: $C_i$ is the atomic fraction of semiconductor in phase $i$; $\Theta$ is the amount of metal deposited (in angstroms); $\Theta_i$ is the coverage at which phase $i$ begins to form; $\Theta_i^*$ is the coverage at which $i$ ceases to form; $\lambda_i$ is the photoelectron mean-free path through phase $i$; $\lambda_0$ is the mean-free path extracted from the universal curve; $\chi$ is the fraction of metal involved in formation of phase 2; $(1-\chi)$ is the fraction of metal involved in formation of phase 1; $t_i=(1-\chi)[1/(1-C_1)](\Theta-\Theta_1)$ is the amount of phase 1 that forms per amount of metal deposited, and $t_2=\chi[1/(1-C_2)](\Theta-\Theta_2)$ is the amount of phase 2 that forms per amount of metal deposited. Equations (A1) and (A2) thus describe the emission from the two reaction products and the substrate as phase 1 forms, grows, competes with phase 2, and is replaced by phase 2, which in turn is also covered by pure metal.

In order to apply these expressions to the data obtained in our temperature-dependent investigation, it was necessary to account for the appearance of the V-in-Ge product. For this phase, together with the spectroscopically indistinguishable substrate, we can write

$$I_3/I_0=\alpha[1-\exp(-t_1/\lambda_1)][(1-\chi)+\chi\exp(-t_2/\lambda_2)] , \quad \text{(A3)}$$

$$I_s/I_0=[\exp(-t_1/\lambda_1)\exp(-t_2/\lambda_2)] , \quad \text{(A4)}$$

thus

$$(I_3+I_s)/I_0=I_3/I_0+I_s/I_0 , \quad \text{(A5)}$$

where $\alpha$ is the fraction of Ge in the V-in-Ge phase; $1-\exp(-t_1/\lambda_1)$ expresses the assumption that the formation of V in Ge is related to the amount of $V_2Ge_3$; $\exp(-t_1/\lambda_1)$ is the attenuation factor due to the presence of $V_2Ge_3$; and $\exp(-t_2/\lambda_2)$ is the attenuation factor due to the presence of the V-in-Ge solution. The total Ge intensity is then $I_T/I_0=I_1/I_0+I_2/I_0+I_3/I_0+I_s/I_0$. The assumptions upon which the above are based are (1) diffusion of semiconductor and metal atoms can only occur while the interface is activated by the reaction, (2) reaction occurs simultaneously at both the semiconductor interface and the vacuum interface, and (3) the observed products are related to the bulk phase diagram and the solid-solution phases are related to the eutectics which form between the pure elements and the compounds. Assumptions (1) and (2) are necessary to produce the lever-rule regions and allow the reactions to stop at a given temperature. The cessation of reaction allows for the eventual covering up of the surface by the metal. Assumption (3) is required to accommodate the presence of the simultaneous growth of the $V_2Ge_3$ compound and the V-in-Ge solid solution.


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