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Temperature-dependent growth morphology of a semiconductor-metal interface: Ge/Ta(110)

M. W. Ruckman, M. del Giudice, and J. H. Weaver
Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

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The Ge/Ta(110) interface is studied as a function of Ge coverage and temperature ($25 \leq T \leq 980\,^{\circ}\mathrm{C}$) using synchrotron-radiation photoemission and low-energy-electron diffraction (LEED). Valence-band and core-level results indicate that no intermixing of the Ta or Ge atoms occurs across the interface at room temperature but that Ge/Ta interface states are formed. Comparison of the photoemission data with LEED results suggests that the low-coverage chemisorbed configuration evolves with coverage into a highly disordered Ge overlayer. Heating induces formation of a reacted overlayer with average composition $TaGe_2$. However, the initial reactive interdiffusion occurs at lower temperatures than those reported for the formation of bulk tantalum germanides. A model is presented for the morphology of the reacted layer.

I. INTRODUCTION

Interfaces between metals and semiconductors have been, and continue to be, the subject of intense study for a number of scientific and technological reasons.[1,2] Obvious goals of this research include a description of the metal-semiconductor interface chemistry on an atomic level, characterization of the interface electronic structure, and measurement of basic interface properties such as the Schottky barrier height which are relevant to electronic-device applications. Most studies of the initial development of these systems have focused on interfaces formed by depositing a metal film onto a semiconductor surface.[1] Growth morphologies which have been observed include epitaxy,[3] island or cluster formation,[4] exchange reactions,[5] and disruptive intermixing leading to the formation of reacted layers tens of angstroms thick.[6–12] Far fewer studies of the reverse situation exist, namely that of a semiconductor film deposited onto a metal. However, we believe such studies are important because inherently different kinetics may be involved and the potential for forming interfaces with different stoichiometries exist. Furthermore, they will be needed if we are to understand the processes controlling the fabrication of multilayer contacts[13] or three-dimensional integrated circuits.[14]

In this paper we examine the formation of the interface between germanium and tantalum and the subsequent behavior of that interface during heat treatment. Motivation for these experiments was provided by recent work by ourselves[15,16] and others[1,17] which showed that transition metals deposited onto simple semiconductor surfaces, including Ge(111) (Ref. 15) and Si(111) (Ref. 16), react to form intermixed layers at room temperature. Thus it was of interest to invert the metal-semiconductor junction to determine whether the overlayer is strongly or weakly bound to the substrate and whether the strength of the metal-semiconductor bond disrupts the substrate and facilitates reactive intermixing or stabilizes the interface.

Several factors influenced our choice of Ge and Ta for this study. First, the shallow Ta $4f$ and Ge $3d$ core levels are relatively sharp and have high photoemission cross sections at phonon energies less than 100 eV.[18] This made them ideal for studies at existing synchrotron radiation sources. In particular, we would use the changes in binding energies of the Ge $3d$ core to examine changes in the structural and chemical environments of the interface. Third, the intensity of the $5d$ valence-band emission relative to Ge-derived states made it possible to follow changes at the Ge/Ta interface for relatively thick (2–5 monolayers) Ge overlayers and identify interface states. Finally, the thermal and physical properties of Ta and Ge facilitated the creation of clean single-crystal substrates and straightforward deposition of Ge overlayers *in situ* under ultrahigh vacuum (UHV). Direct comparison of the Ge/Ta interface with the Ta/Ge interface was not possible because of the extremely high temperatures needed to evaporate Ta. Instead, we will compare our results to those found for V/Ge by del Giudice *et al.*[15]

II. EXPERIMENTAL PROCEDURE

Photoemission measurements using synchrotron radiation were done at the Wisconsin Synchrotron Radiation Center using the Mark V "grasshopper" monochromator and a photoelectron spectrometer which operates in the mid 10^{-11}-Torr range, as described elsewhere.[19] Photoelectron spectra collected using a photon energy of 21.2 eV (He I resonance) were conducted at the University of Minnesota in a UHV system which incorporates low-energy-electron diffraction (LEED) and Auger capabilities for sample characterization and structural studies. To enhance the resolution of the Ta $4f$ and Ge $3d$ core-level measurements reported here, the pass energy of the cylindrical-mirror photoelectron-energy analyzer (CMA) was set to give an effective monochromator-limited resolution of approximately 300 meV at 65-eV photon energy. The resolution for the valence-band studies conducted at 21.2 eV was estimated to be approximately 170 meV. Typical count rates were 10^4 sec^{-1} for the Ta $4f$ and Ge $3d$ cores and 10^5 sec^{-1} for the He I studies of the Ge/Ta valence bands. The choice of 65-eV photon energy for the Ge and Ta core-level studies represented a compromise between resolution, surface sensitivity, count rate, and a desire to avoid overlap with photon-stimulated Ta Auger peaks. The overall precision in determining the core-level binding energies was estimated to be 0.05 eV. The Ta(110) surface was oriented such that the sample normal was coincident with the CMA acceptance cone. Photons were *s* polarized and incident on the sample at ~45°.

Ta(110) samples were prepared *in situ* from ribbons ($5\times25\times0.002$ mm) cut from polycrystalline foils obtained from Johnson Matthey Inc. One or more Ta single crystals with typical dimensions exceeding 5 mm were generated by resistive high-temperature "flash" heating sufficient to partially melt the foils. Subsequent cleaning of the surface was also done by high-temperature heating. LEED studies of crystals produced by this method showed spot patterns (elongated hexagonal nets) which indicated preferential orientations with the [110] direction along the surface normal and the $[1\bar{1}0]$ and [001] directions parallel and perpendicular to the length of the Ta ribbon. Multiple spot patterns typical of either stepped surfaces or LEED reflections from multiple grains were often encountered. Samples were then repositioned until the simple elongated hexagonal spot pattern characteristic of LEED reflections from a single grain was obtained. LEED spot sharpness was comparable to that obtained in other studies involving sputter-annealed metal single-crystal surfaces.

Ge films were deposited by evaporation from tungsten wire baskets. During evaporations the chamber pressure never rose above 3×10^{-10} Torr. The Ta sample was recleaned and a new film was deposited whenever it became desirable to do so. An Inficon film thickness monitor was used to determine the evaporation rate and the Ge overlayer thickness. Selected Ge/Ta samples were resistively heated for studies of the effects of annealing on the interface. Surface temperatures were determined with an optical pyrometer with an estimated uncertainty of ~25°C. All other studies were conducted at room temperature. In this paper, Ge coverages are given in angstrom units and 3.3 Å would correspond to the equivalent of 1 monolayer (ML) of close-packed Ge surface atoms in a structure commensurate with the Ta(110) surface (1.29×10^{15} atoms/cm^2).

III. RESULTS AND DISCUSSION

A. Evaporated Ge overlayers

The aim of the room-temperature Ge/Ta(110) study was to investigate the details of the Ge-Ta interaction following Ge deposition onto a clean Ta(110) surface. Photoemission data combined with LEED results make it possible to address questions concerning atomic scale ordering, the existence of Ge-Ta bonding at the interface, the presence of reacted surface components, and the reaction kinetics and possible reaction mechanisms.

Qualitative information about the structure or morphology of the Ge overlayer on Ta(110) can be obtained from core-level photoemission measurements. In Figs. 1 and 2 we show photoemission spectra for the Ta 4*f* and Ge 3*d* core levels taken at 65-eV photon energy for coverages 0—23 Å. Not shown are results for a $\Theta=42$ Å Ge overlayer because the photoemission contribution for the Ta 4*f* levels was vanishingly small and the Ge 3*d* was essentially unchanged from that observed for $\Theta=23$ Å. Since the core levels have binding energies that differ by 5 eV, their photoelectron escape depths are comparable. As shown, the Ta 4*f* core levels show virtually no change in either shape [full width at half maximum (FWHM) equals 0.7 eV] or position ($4f_{7/2}$ binding energy equals 21.7 eV) over a wide range of Ge coverage. For the clean surface, we were unable to distinguish the surface-shifted Ta 4*f* core level[20] because the surface shift for Ta(110) should be approximately 0.1—0.2 eV,[21] i.e., half the value reported for Ta or W (111) (Ref. 22) or (100) (Ref. 23). The Ge 3*d* core levels show a small but steady shift to greater binding energy for coverages $0.5\leq\Theta\leq23$ Å (total shift 0.3 eV). The Ge 3*d* cores for $\Theta\leq1$ Å are featureless and almost symmetric with FWHM$=1.1$ eV but at higher coverage the Ge 3*d* emission increasingly resembles a poorly-resolved spin-orbit split doublet (FWHM$\simeq1.2$ eV for 23 Å). Spectra taken for cleaved Ge(111) under equivalent experimental conditions show much greater structure, including better resolved spin-orbit splitting (0.58 eV) and FWHM$=0.98$ eV as shown at the top of Fig. 2. From this we conclude that the apparent poor resolution for the Ge core levels, characterized by a reduction in the quality of the core energy distribution curves (EDC's) but with no apparent broadening, is physical not instrumental. This conclusion is supported by LEED investigations at 125-eV primary beam energies which showed that the evolving

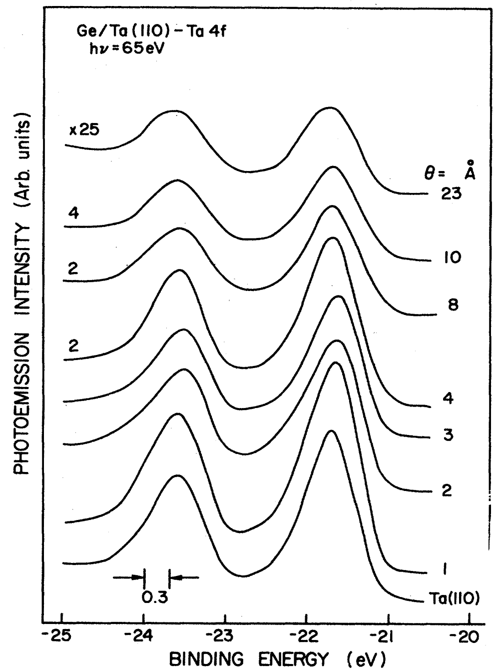

FIG. 1. Core-level results for the Ta 4*f* core at $h\nu=65$ eV for Ge overlayers on Ta(110). The lack of any change in line shape demonstrates either weak chemical interaction or absence of Ta atom outdiffusion. The incremental resolution is indicated by the horizontal line segment in the lower left-hand corner. Changes in intensity are indicated by the multiplication factors shown on the left-hand side.

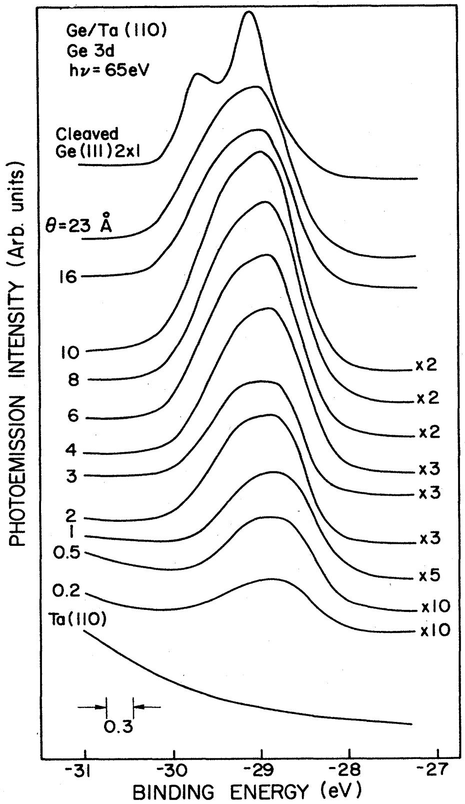

FIG. 2. Core-level results for the Ge 3*d* core level at $h\nu=65$ eV for Ge overlayers on Ta(110). The Ge 3*d* cores show a small shift to higher binding energy, little overall broadening, and ultimate development into a poorly resolved doublet with increasing Ge coverage. Included for comparison is an EDC from a cleaved Ge(111) surface. EDC's measured at lower Ge coverages have been enhanced by the multiplication factors shown on the right-hand side.

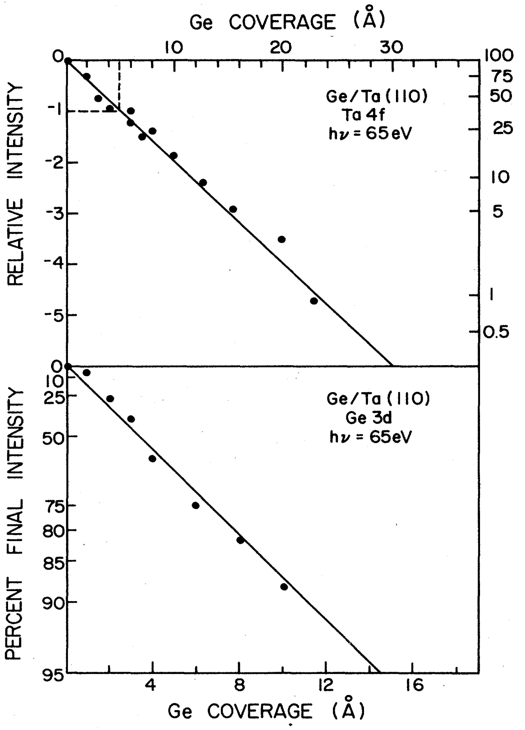

FIG. 3. Attenuation curve for the Ta 4*f* and growth curve for the Ge 3*d* core-level integrated intensities. The relative Ta 4*f* core-level emission was plotted logarithmically, the Ge 3*d* emission was plotted assuming that the integrated intensity followed the form $I(\Theta)/I(42)=1-e^{-\Theta/\lambda}$, where λ represents the mean free path for Ge 3*d* photoelectrons. The linear dependence of both the Ta 4*f* attenuation and the Ge 3*d* growth suggests that the Ge/Ta(110) interface is abrupt.

Ge overlayer is highly disordered (no new spots were observed). Instead, the effect of the overlayer was to attenuate the substrate pattern such that the Ta(110) pattern was lost by 1—2 ML coverage.

To assess the abruptness of the interface, we show in Fig. 3 the normalized logarithmic intensity for the Ta 4*f* core level and the percent final intensity for the Ge 3*d* core level as a function of Ge coverage. The results for Ta show a linear attenuation with increasing Ge overlayer thickness (0.9% of the original signal at $\Theta=23$ Å). For the Ge 3*d* core level, we again find a linear relationship between the emission intensity and the Ge overlayer thickness. From Fig. 3 we can see that the mean free path is ~5 Å for Ta 4*f* photoelectrons at this kinetic energy.

The results summarized in Figs. 1—3 indicate that the Ge/Ta interface is morphologically relatively simple. The variation in intensity of the Ta 4*f* emission can be explained by attenuation through a Ge overlayer with an escape depth of 5 Å. Since this is close to the escape depth predicted for crystalline Ge using the Seah-Dench value[24] for photoelectron kinetic energies of 30—40 eV, we believe that the resulting Ge overlayer is homogeneous and free of measurable amounts of dissolved Ta. Likewise, the absence of core-level chemical shifts is consistent with no intermixing. Comparison of our Ge 3*d* core-level results with those found for V deposited onto Ge(111) shows that our Ge 3*d* core-level spectra did *not* develop the one or more Ge 3*d* core-level components during the formation of the extended, reacted interface. The above finds imply that the Ge/Ta interface is *abrupt* or without atomic intermixing. The lack of structure in the Ge 3*d* core level, which at no time resembled either a cleaved or a sputter-annealed Ge surface, suggests that the Ge layer is highly disordered and possibly amorphous.[25]

Valence-band photoemission studies of Ge/Ta(110) were carried out to gain electronic structure information complementary to the morphological information obtained from the core-level studies. In Figs. 4 and 5 we show the effects of depositing Ge onto clean Ta(110). Figure 4 shows the valence-band EDC's with 21.2 eV, while more surface-sensitive photoemission spectra taken using 65 eV are shown in Fig. 5. The bottommost EDC corresponds to the Ta(110) substrate and EDC's offset vertically have increasing Ge coverages. The valence band EDC's taken at 65 eV are normalized by the factor given alongside each curve to maintain approximately constant peak intensity; those for $h\nu=21.2$ eV are shown without scaling and demonstrate the higher photoionization cross section for Ta valence states relative to Ge.

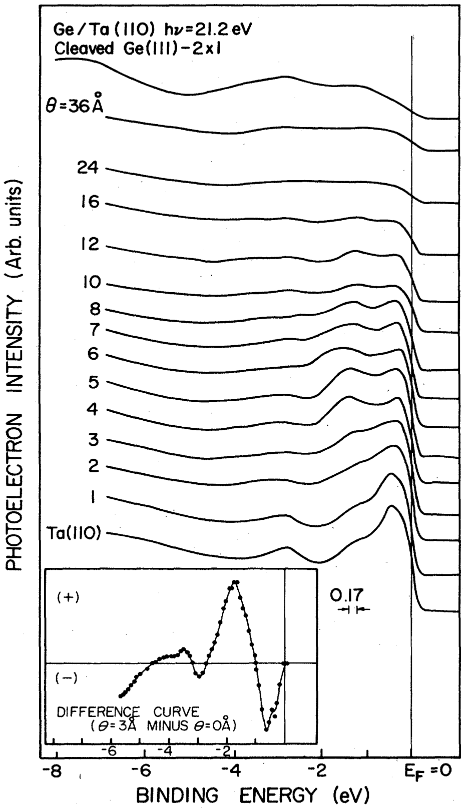

FIG. 4. Photoemission energy distribution curves for Ge overlayers on Ta(110) at $h\nu=21.2$ eV. Shown in the inset is the difference curve taken between the curve for clean Ta(110) and one covered with ~3 Å of Ge. Note the appearance of Ge-induced states at 1.7 and 3.8 eV below the Fermi level.

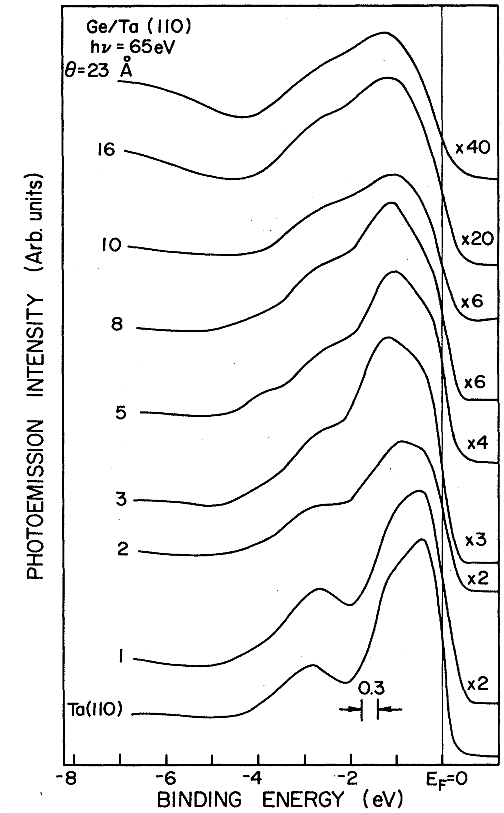

FIG. 5. Photoemission EDC's for Ge overlayers on Ta(110) at $h\nu=65$ eV normalized for variations of photon flux and scaled to approximately constant height. The scale factor is indicated on the right-hand side and the Ge coverage Θ on the left-hand side.

The EDC's taken at 21.2 eV show little change in the Ta-derived d states at very low Ge coverage beyond a diminishing of emission near the Fermi level, E_F, and growth of Ge-induced states. Difference curves obtained by subtracting each EDC from the next illustrate these changes more clearly. In the inset of Fig. 4, we show the cumulative difference between clean Ta(110) and Ta(110) covered by 3 Å of Ge. Enhanced photoemission is centered around -1.8 and -3.8 eV. Since the photoionization cross section of the Ge-sp states is low compared to that of Ta $5d$ states, we conclude that the emission at -1.8 eV indicates interface bonding states which are Ge induced but are mostly Ta in character. The valence bands taken at 65 eV exhibit similar changes for Ge coverage 2 to 8 Å with Ge-induced states growing 1–4 eV below E_F and the loss of the Ta substrate emission near E_F. Little or no modification of the valence band is observed at Ge coverages exceeding 20 Å at 65 eV (Fig. 5) and 30 Å at 21.2 eV (Fig. 4). Further, the Ta-derived features can no longer be identified in the valence band, the sharp Fermi edge characteristic of a metal is gone, and the Ge-Ta–induced interface states are lost by a gradual burial of the interface.

Our valence-band results show that the Ge adatoms interact strongly with the Ta(110) substrate during the initial stages of interface formation. The observed interface states resemble the metal-silicon bonding states reported by Weaver *et al.*[26,27] for transition-metal disilicides. Such hybrid states are reasonable because conditions are favorable for Ta d states to hybridize with Ge p states to form bonding and antibonding p-d combinations with little or no charge transfer.[28] The observed insensitivity of the Ta $4f$ core binding energy to the presence of Ge supports this conclusion.

The valence-band spectra for Ge overlayers can be analyzed by assuming that the results represent a superposition of photoemission from the Ge overlayer, the interface states, and the Ta substrate. Indeed, analysis of the valence-band spectra for $h\nu=21.2$ and 65 eV for a 5 Å thick Ge layer demonstrates that most of the photoemission signal from states near E_F is Ta derived. They are attenuated at $h\nu=65$ eV because of the greater surface sensitivity at that energy. At higher coverages, both the substrate and the interface states are attenuated by the Ge overlayer and the probed region increasingly resembles pure Ge, as shown at Θ~25 Å in Figs. 4 and 5. Comparison with valence-band results for cleaved Ge(111) shows that our thick film has none of the prominant band-structure features characteristic of an ordered Ge crystal. Instead, these results suggest that the overlayer is highly disordered, consistent with the appearance of the Ge $3d$ core EDC's.[25]

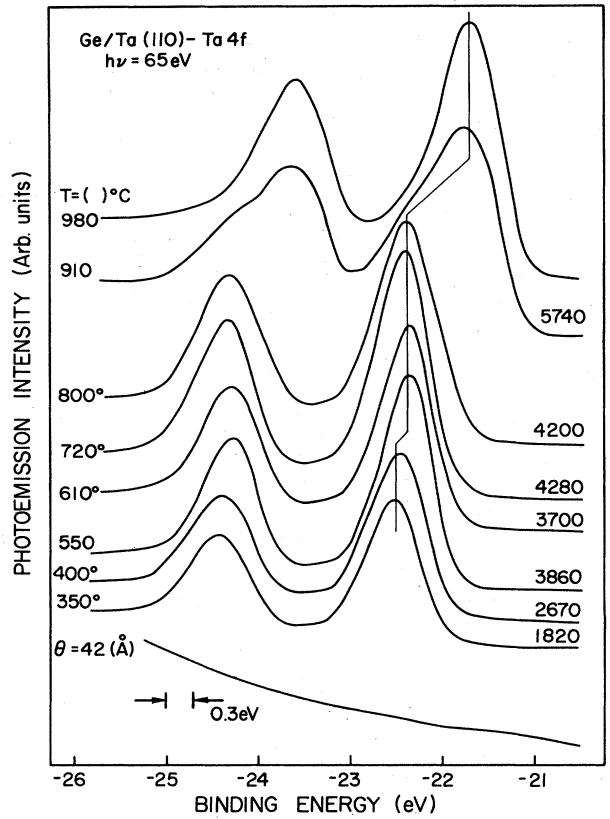

FIG. 6. Ta 4f core-level results for thermally processed Ge/Ta overlayers heated until approximate equilibrium had been established. The vertical line marks the position of the principle Ta $f_{7/2}$ component and suggests that two distinct Ta-Ge reacted phases exist, one more Ge-rich and another characteristic of the "fully-reacted" phase. Heating beyond 850° C leads to the appearance of Ta metal states. Integrated intensities are included on the right-hand side of the figure.

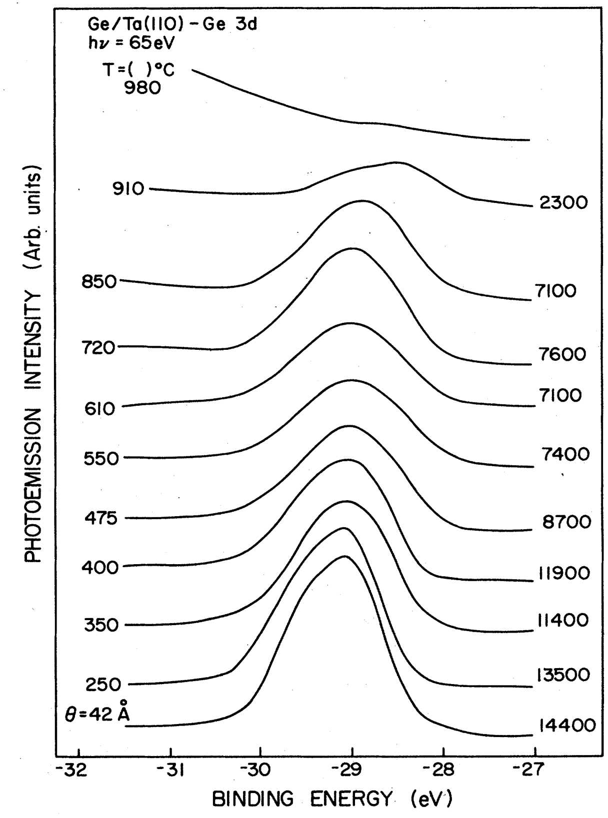

FIG. 7. Ge 3d core-level results for thermally processed Ge/Ta heated until approximate equilibrium had been established. Note the slight Ge 3d core-level shift to lower binding energy and the small broadening of the Ge 3d core accompanied by a loss of line shape at the onset of Ta outdiffusion into the Ge overlayer. The removal of Ge at high temperatures is accompanied by a large Ge core-level shift indicative of the formation of a very dilute Ge/Ta phase. Intensity variation is demonstrated by the change in integrated intensity shown on the right-hand side.

B. Thermally stabilized intermixed Ge-Te layers

The room-temperature results presented above indicate that the Ge/Ta(110) interface does not intermix. Nevertheless, several stable Ta-Ge compounds can be synthesized by heating bulk Ge-Ta composites.[29,30] To examine the temperature range of stability of our abrupt interface, we therefore performed a series of experiments which involved thermal treatments. These were conducted by resistively heating the substrate to the desired temperature for intervals of time sufficient to reach steady state, as judged by changes in the EDC's (typically 5-min intervals). Dramatic changes were found in the valence-band and core-level photoemission spectra which demonstrate that Ta could be driven into thick overlayers to produce an intermixed region with the approximate composition $TaGe_2$.

In Figs. 6 and 7 we show the changes observed in the Ta 4f and Ge 3d core-level spectra as a function of heat treatment. The starting point was the Ge/Ta(110) interface produced by room-temperature deposition of 42 Å of Ge onto the freshly cleaned surface. Initially the Ta 4f cores were absent, consistent with the results of Fig. 3 which showed $I(42\ \text{Å})/I(0) \simeq 2\times 10^{-4}$. Heating to 350 °C caused Ta to reappear and produced a slight reduction in the integrated intensity of the Ge 3d cores. In Fig. 6 we show alongside each EDC the integrated total 4f emission. As can be seen, the 4f emission then increased about twofold with heating from 350 to 610 °C, changed relatively little from 610 to 800 °C, and then increased significantly when the temperature exceeded 850 °C. From this we conclude that Ta intermixes with the Ge overlayer by 350 °C, but that the stable interface region was not reached until ~550°C. Indeed, the results of Fig. 6 show a 4f binding energy variation of 0.1 eV as temperature increases from 400 to 550 °C, representing the transition from what is probably an under-reacted, Ta-deficient to a fully-reacted interface phase. Comparison with results for the clean surface shown at the top of Fig. 6 indicates that this final phase is characterized by a Ta 4f component shifted 0.7 eV with respect to Ta metal. The sharpness of the resulting Ta 4f doublet (comparable to that of the clean surface with FWHM of 0.625 eV) and the absence of other Ta 4f core-level components suggests that the Ta-Ge reacted layer is characterized by a narrow range of

Ta atomic environments. The lack of a metallic Ta 4*f* core level suggest that the Ta-Ge—reacted overlayer is free of segregated metallic Ta.

The Ge 3*d* core levels displayed in Fig. 7 show no change until the onset of Ta intermixing at ~350°C. At that point, a shift of approximately 0.1 eV to lower binding energy was observed, there was no change in FWHM (1.2 eV), and a small reduction in intensity occurred. Further heating to ~475°C, corresponding to the temperature which induced formation of the fully-reacted phase, produced the Ge 3*d* emission with the greatest FWHM (1.4 eV) but no change in center of mass was observed. The intensity of the Ge core level was relatively constant until ≥800°C; at 910°C our results show a shift of ~0.5 eV and a great reduction in intensity corresponding to the loss of Ge from the surface.[31] LEED studies of the reacted Ta-Ge surface compound again showed no evidence of long-range order until the substrate temperature exceeded 900°C, at which point the underlying Ta(110) pattern was recovered.

We can estimate the Ta-Ge stoichiometry in the reacted overlayer by examining the intensities of the Ta and Ge core levels. The Ta concentration was determined using the method applied by Minni[32] to compute alloy compositions using Auger lines. Elemental sensitivity factors were inferred from the strength of the photoemission core levels for clean Ta and a thick Ge film. We found that the stable Ge-Ta phase observed between 550 and 800°C had a Ta concentration of ~55 mol %. Our data therefore suggest that heating triggers an interface reaction and increases intermixing so that an overlayer of $TaGe_2$ average composition is formed.

Bulk results reported by Shunk[29] and Moffat[30] reveal that $TaGe_2$ is stable over the range of temperatures examined in this study and is the most stable phase formed by reacting Ge with Ta metal. $TaGe_2$ was found to decompose at 1280±20°C into Ta_2Ge and a Ge-rich liquid. The solid solubility of Ta in Ge ranged from 14.7×10^{-2} at. % at 850°C to 7.9×10^{-3} at. % at 775°C. Insufficient data exist for Ta/Ge to produce a complete phase diagram. The results presented here are consistent with the reported bulk data in that we find evidence for Ta outdiffusion into the Ge overlayer and the formation of a compound with $TaGe_2$ stoichiometry. Furthermore, our interface compound is stable over a wide temperature range and decomposes at 910°C. This is significantly less than reported for bulk $TaGe_2$, suggesting that the interface-produced phase is less stable than the bulk phase.

In order to determine the ease of diffusion of Ta through this reacted layer into a Ge overlayer, we produced a fully-reacted region and deposited Ge onto it. At room temperature, there appeared to be no outdiffusion of Ta through this Ge/Ge-Ta layer. Studies of the attenuation of the Ta emission showed exponential behavior, analogous to that discussed above for the Ge/Ta(110) interface. As expected, however, Ta outdiffusion was observed as soon as the temperature was increased.

In Fig. 8 we show valence-band spectra which further illustrate the effect of thermal processing of thick Ge overlayers on Ta. The EDC's at the bottom of Fig. 8 for a 24-Å Ge overlayer show no evidence for Ta emission. Heating to 350°C enhances emission at E_F and increases the overall photoemission intensity, indicating a change to the metallic state in the overlayer and the presence of Ta. For the temperature range 550—800°C, valence-band spectra show increasing emission near E_F due to the formation of the final reacted phase. The valence-band spectra in that range are similar to EDC's obtained by Weaver *et al.*[26] for $TaSi_2$ insofar as the nonbonding Ta *d* and hybrid Ta-*d*/Ge-*p* states within ~4 eV of E_F are concerned. The deeper valence-band features are not visible in the present experiments, perhaps because of the choice of photon energies here. Above ~800°C Ta metal states appear in the valence band, consistent with the loss of Ge and the formation of a clean Ta(110) surface.

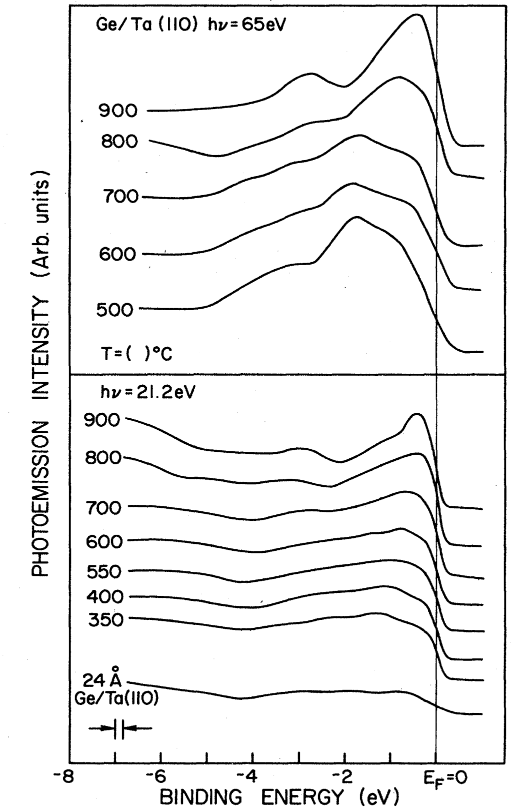

FIG. 8. Valence-band photoemission EDC's for thermally stabilized Ge/Ta overlayers at $h\nu=21.2$ and 65 eV. The introduction of Ta into the Ge overlayer sharpens the Fermi level and produces several new states within 5 eV of the Fermi level. Loss of Ge at high temperatures leads to a recovery of the Ta metal valence band.

Insight into the nature of the structure of the intermixed region can be inferred from extended x-ray absorption fine structure (EXAFS) and x-ray scattering experiments for Ge-rich and metal-rich amorphous Mo-Ge films prepared by sputtering.[33] Those results indicated that the structure of the amorphous film is determined by the strong covalent interaction between Mo and Ge. This favored structures with a single Mo environment and a range of environments around Ge. For relatively low Mo concentrations this produced a structure in which each Mo atom was surrounded by Ge atoms. These compounds were still metallic because the Fermi level falls in an area with a high density of states.[34] Generalizing to the Ta-Ge system, we suggest that the net effect of introducing Ta into a Ge overlayer is to establish covalent bonds between Ta and its nearest-neighbor Ge atoms. Our results supports this morphology for Ta-Ge since we observe a single well-defined Ta $4f$ signature and poorly-defined Ge $3d$ signatures. The observed large shift of the Ta $4f$ level (0.7 eV) and the minimal changes in the $3d$ binding energy can also be understood with this local-configuration model.[28] Since each Ta atom has a shell of several Ge atoms, any charge redistribution from Ta to Ge will be most easily seen in the Ta core shifts.

IV. CONCLUSIONS

We have studied the formation of the Ge/Ta(110) interface with LEED and photoelectron spectroscopy. The main results are as follows. First, the Ge/Ta(110) interface is abrupt with no evidence for intermixing at room temperature. Comparison of our results for Ge/Ta(110) with results obtained for V/Ge(111) demonstrates that the interface reactions are quite different. In particular, the Ge $3d$ core components observed during the evolution of the V/Ge interface are not observed for Ge on Ta(110)—for V/Ge it was always possible to fit the Ge $3d$ core line shape with distinct doublets, changing only their relative intensities. Similarly, the Ta $4f$ cores show nothing indicative of a modified Ta atom environment as the Ge coverage increases. Second, evidence was found for the existence of Ge-induced interface states in the valence band at -1.7 and -3.8 eV. Third, we find that Ge in thick Ge overlayers is probably in a highly disordered structure and possibly amorphous. LEED studies found no evidence for the formation of an ordered Ge overlayer at any coverage. Fourth, heating triggers a reaction which introduces significant amounts of Ta into Ge overlayers which have an average composition of $TaGe_2$ but no indication of extensive crystallinity. In this overlayer, we propose that Ta atoms are coordinated with a cage of Ge neighbors, consistent with EXAFS and x-ray results for Mo-Ge.

ACKNOWLEDGMENTS

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