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Interactions between (HgCd)Te and overlayers of intermediate reactivity (Ge, Ag, and Cu)

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The interactions between Ge, Ag, and Cu and both cleaved and sputtered (HgCd)Te substrates have been investigated using synchrotron radiation, and the results have been compared with those reported in the literature when available. Each of these overlayers forms tellurides with heats of formation near that of HgTe. Consequently, the extent of the interfacial reactions is intermediate between those occurring after deposition of reactive and unreactive metals and, in the absence of a large thermodynamic driving force for a reaction, is sensitive to the stability of the surface and the propensity of the overlayer to diffuse into the semiconductor. Ag readily diffuses into cleaved substrates, confirming earlier results. In contrast, it is trapped, at least partially, in the interfacial region of sputtered surfaces because of their increased reactivity, i.e., decreased stability. This increased reactivity of the sputtered versus cleaved surface is also demonstrated for Ge and Cu, where a greater fraction of the Hg is lost upon deposition. Our results show less Hg loss from cleaved surfaces than do the results of other work, which we attribute to differences in material or surface quality. The interactions between (HgCd)Te and intermediate overlayers are seen to serve as sensitive indicators of the surface stability.

I. INTRODUCTION

Recent studies of the interactions between (HgCd)Te and various deposited metallic or semiconductor overlayers[1-17] have been driven primarily by the use of (HgCd)Te as an infrared detector material and secondarily by the fact that (HgCd)Te is an unusual pseudobinary semiconductor alloy in which the two components (HgTe and CdTe) exhibit very different bond strengths and thermodynamic stabilities. The goals of these investigations are to improve contacts to future devices on (HgCd)Te and to increase our understanding of the reactivity of semiconductor alloy surfaces in general.

Because HgTe has a very low heat of formation,[18,19] interfacial reactions are ideally governed by the relative stability of HgTe and the tellurides of the overlayer metal or semiconductor. Although such a dependency is analogous to the behavior of other compound semiconductors,[20,21] it occurs to a greater degree. It is even more pronounced for the ternary compound than for HgTe alone, as a result of a destabilization of the Hg—Te bond by the CdTe component.[22-24] Recently, we have classified overlayers into four groups—ultrareactive, reactive, intermediate, and unreactive—based on the relative heats of formation of the different tellurides[8] (Fig. 1).

Ultrareactive overlayers include those elements, such as Ti (Ref. 9) and Sm (Ref. 12) that form tellurides more stable than CdTe. During their deposition, the exchange reactions

$$y\text{HgTe} + xM \rightarrow M_x\text{Te}_y + y\text{Hg} \qquad (1)$$

and

$$y\text{CdTe} + xM \rightarrow M_x\text{Te}_y + y\text{Cd} \qquad (2)$$

are both favorable. Consequently, an interfacial telluride is formed during the very initial stages of overlayer growth and the freed Hg and Cd are depleted from the semiconductor surface.

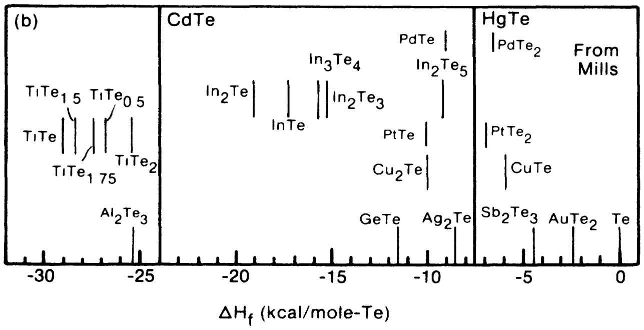

FIG. 1. Heats of formation of selected tellurides from Mills (Ref. 18) and Wagman *et al.* (Ref. 19).

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Similar interfacial behavior occurs during deposition of reactive metals with reaction (1) proceeding, but not reaction (2). This class, which includes Al,[1,4,5,14,15] In,[4,5] and Cr,[10,11] forms tellurides with heats of formation between those of HgTe and CdTe. As a result, Hg is lost from the interface as a thin-metal-telluride layer is formed. However, because the CdTe component is generally inert, after the HgTe is consumed from a thin surface region, no additional supply of Te is available, and further deposition results in growth of a metallic overlayer.

At the other extreme of reactivity, the unreactive overlayers, which are limited to Au (Refs. 3 and 6) and Sb (Ref. 25) (based on our classification), form tellurides that are even less stable than HgTe. Neither exchange reaction occurs, and a metallic overlayer grows from the very beginning with a stoichiometric semiconductor cation interface.

The intermediate group of overlayers exhibit behavior between that of the reactive and unreactive metals. These elements, which include Ge,[7,12] Ag,[12-15] Cu,[15,16] and Pt,[17] form tellurides with heats of formation very close to that of HgTe. As we will demonstrate in this paper, because the net energetics of reaction (1) are small, the occurrence and rate of an interfacial reaction can depend on other factors, such as surface preparation,[7] sample history, and heats of alloying.[15,17,26] Depending on the mechanisms involved, similar, but smaller, effects may also be present for unreactive overlayers.

In this paper, we report on the behavior of both cleaved and sputtered (HgCd)Te substrates upon deposition of Ge,[7] Ag, and Cu, and compare our results to those previously reported by others for Ag (Refs. 13–15) and Cu (Refs. 15 and 16) deposited on cleaved substrates. In general, cleaved surfaces are the least defective and least reactive of clean surfaces and provide a baseline for the understanding of the interfacial reactions. Nonetheless, cleaved (HgCd)Te surfaces are far from defect free as demonstrated by the nearly universal inversion of the surface region of *p*-type material; the occasional variability of the surface Hg concentration; the high concentration of dislocations, steps, and precipitates; and the rough surface morphology with regions of plastic deformation.[8,23,27] At the other extreme, sputtered surfaces are clean and reproducible, but highly damaged due to the creation of disorder and broken, distorted, or like-like bonds and the preferential sputtering of Hg.[5,7,28-31] As a result, sputtered surfaces,[32] in general, and sputtered (HgCd)Te surfaces,[7,8] in particular, are more reactive than the corresponding cleaved surfaces.

II. EXPERIMENT

The *p*-type $Hg_{0.7}Cd_{0.3}Te$ and $Hg_{0.8}Cd_{0.2}Te$ samples were obtained from Cominco American in two forms: elliptical wafers with $\{111\}$ faces and unoriented wafers. The oriented samples were cut into strips with $\langle 110 \rangle$ axes and cleaved *in situ* using a knife edge and anvil. Cleaved surfaces were nominally 2×3 mm^2 for $Hg_{0.8}Cd_{0.2}Te$ and 1×3 mm^2 for $Hg_{0.7}Cd_{0.3}Te$. The unoriented samples were ion bombarded in an introduction-preparation chamber with 1-keV Ar^+ ions. A few depositions for Ge were also made on sputtered *n*-type $Hg_{0.8}Cd_{0.2}Te$ substrates. To ensure that the sputtered surfaces were in equilibrium for our sputtering conditions, we examined the surface chemistry of specimens following different ion doses prior to the depositions.[5] [Previously, both cleaved (110) and the etched unoriented surfaces were sputtered and deposited with Au; no orientation dependence was found.[6]]

Measurements were made using a Perkin-Elmer double-pass cylindrical mirror analyzer (CMA) with preretarding grids at the University of Wisconsin's Synchrotron Radiation Center. For Ge, Ag, and some Cu experiments, a grasshopper monochromator on the 1-GeV storage ring was used, with the photon energies chosen to maximize the surface sensitivity of the data, i.e., photoelectron kinetic energies were $\sim$75–80 eV for each photoelectron peak of interest. For the remainder of the Cu experiments, a Seya monochromator on the 240-MeV (Tantalus) storage ring was used.

The Ge, Ag, and Cu overlayers were deposited by evaporation from a tungsten basket and their thicknesses monitored by a quartz oscillator. To avoid heating the (HgCd)Te samples while baking the main chamber, they were loaded into the introduction-preparation chamber and transferred afterwards. Operating pressures in the main chamber were in the low-10^{-8}-Pa range.

Peak intensities were obtained from the areas of the Te and overlayer photoelectron peaks and, because of their overlap, from heights of the Hg and Cd peaks. In most cases, the experiments were performed two or three times. The data we report are the average values. Reproducibility of the data was typically better than 20% as shown by the results reported in Refs. 3, 4, and 7. The greatest source of variability is the overlayer coverage, especially at very low coverages.

The intensity measurements of the semiconductor components were sometimes converted to atomic concentrations using sensitivity factors derived from the spectra of clean, cleaved surfaces. The surface compositions (neglecting the deposited element) were then plotted onto surface-behavior diagrams (SBD's).[33,34] This means of analysis has proven very useful in a variety of surface and interfacial studies including surface reactions,[34-36] adsorption,[35] overlayer deposition,[4] and sputter-depth profiles.[37,38]

The SBD's incorporate more data than conventional representations do and graphically illustrate the relationship between the three semiconductor constituents (Hg, Cd, and Te). As a result, they allow the initial (HgCd)Te surface to be characterized and interfacial behavior during deposition to be modeled. Because the ternary SBD's presented here suppress the absolute rate of attenuation of the semiconductor components and the rate of accumulation of the overlayer, in some cases more than one model of interfacial behavior is consistent with the SBD. When this happens, distinction between the models is readily achieved with the intensity-versus-coverage dependence of one component or similar information. Accordingly, SBD's and conventional data representations complement each other; the use of both means of analysis can provide a more complete understanding of the problem.

The use of the Hg-Cd-Te SBD's is illustrated in Fig. 2. The most likely scenarios for (HgCd)Te/overlayer structures are denoted as *A* (a constant semiconductor-component composition, allowing for scatter as the semiconductor signals become attenuated), *B* (evolution directly toward the Te vertex), *C* (evolution directly away from the Hg vertex), and combinations of these. In each scenario two semiconductor-overlayer interactions are feasible. Case *A* is consistent with an abrupt, stoichiometric interface and with in-diffusion of the metal across a stoichiometric interface. Case *B* would be indicative of a stoichiometric interface with out-diffusion of Te or an equal loss of Hg and Cd from the interface with or without Te out-diffusion. Finally case *C* implies either a loss of Hg from the interface with no out-diffusion or equal out-diffusion of Cd and Te. Differentiation between each pair of possibilities is easily made based on knowledge of the system or the signal-intensity variations of the appropriate element.

In the next section, we present the data obtained during our Ge, Ag, and Cu depositions on both cleaved and sputtered surfaces. Where available, we also include results reported by others for comparison. In the following section, we first examine the aspects of each deposition that are specific to that particular overlayer and then discuss the intermediate class of overlayers in general.

III. RESULTS

A. Ge

1. Cleaved surfaces

The Hg-Cd-Te SBD of Fig. 3 illustrates the behavior of the interface during Ge deposition. For comparison, similar representations of measurements following deposition of typical reactive and unreactive overlayers are given in Fig. 4. The SBD shows that during Ge deposition onto cleaved substrates the semiconductor-component composition evolves along a path directly toward the Te vertex. The evolutionary path indicates that the two cation signals are being attenuated at approximately the same rate, but that each is being attenuated faster than the Te signal—an observation also apparent from the conventional I/I_0 presentations of Fig. 5. This behavior is similar to that observed during deposition of Sb (Ref. 25) and Au (Refs. 3 and 8) except that the relative persistance of the Te is more pronounced, especially when compared to Sb, i.e., the points corresponding to 10–20-Å Ge are closer to the Te vertex than those corresponding to 10–20-Å Au or 10–20-Å Sb. Although it is not evident from the SBD, the difference in the rate of change of the semiconductor-component composition for Ge and Au depositions is caused by the slower attenuation of the cation signals in the Au case.

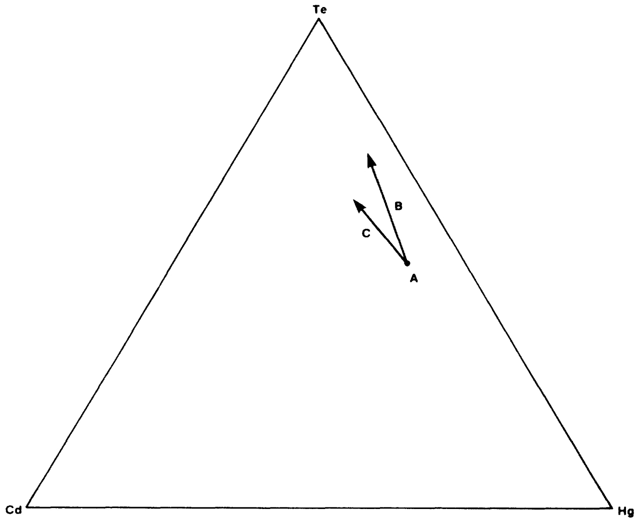

FIG. 2. SBD showing different evolutionary paths of the semiconductor-component composition during overlayer deposition.

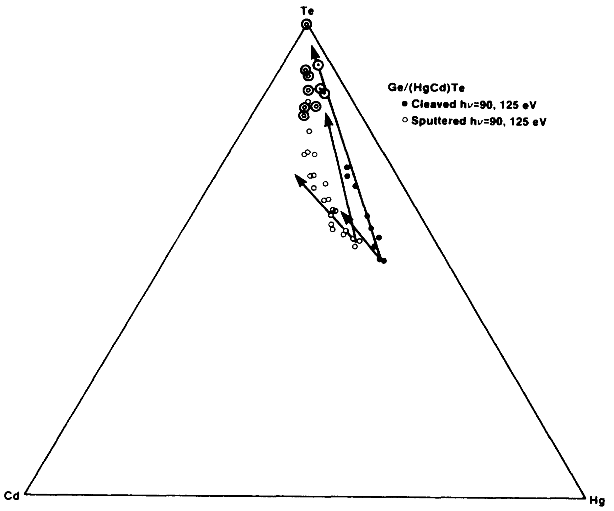

FIG. 3. SBD illustrating the evolution of the semiconductor-component composition during Ge deposition onto cleaved and sputtered substrates. Points representing deposition of 10–20 Å are circled.

During Ge deposition, the Te 4*d* peak gradually broadens, as reflected by the ratio of the valley between the two spin-orbit-split components to the $4d_{5/2}$ peak height (Fig. 6). This broadening begins at the lowest coverages and continues monotonically through the range of deposition.

A nearly identical behavior of the substrate is observed during Ge deposition on both $Hg_{0.79}Cd_{0.21}Te$ and $Hg_{0.72}Cd_{0.28}Te$ (Figs. 6 and 7). There is a similar small decrease in the [Hg]/[Cd] ratio and gradual broadening of the Te line.

The Cd and Te peaks shift by 0.1–0.2 eV to lower kinetic energies for both substrate compositions, but the Hg peak exhibits a small (<0.1 eV) shift in the opposite direction over the range of coverage examined here. In contrast, the Ge line shifts by ~ 0.8 eV to higher kinetic energy.

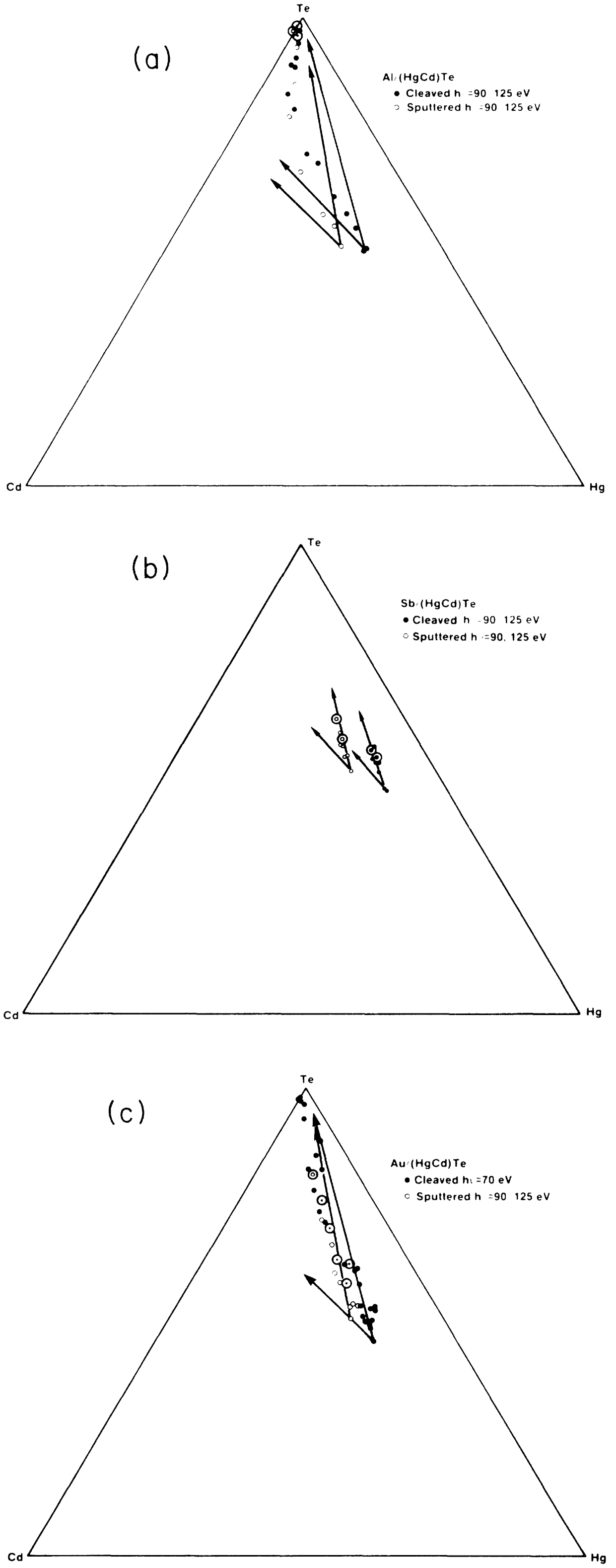

FIG. 4. SBD's illustrating the evolution of the semiconductor-component composition during deposition of reactive [(a) Al] and unreactive [(b) Sb and (c) Au] overlayers onto cleaved substrates. Points representing deposition of 10–20 Å are circled. Data are from Refs. 4, 25, and 3, respectively.

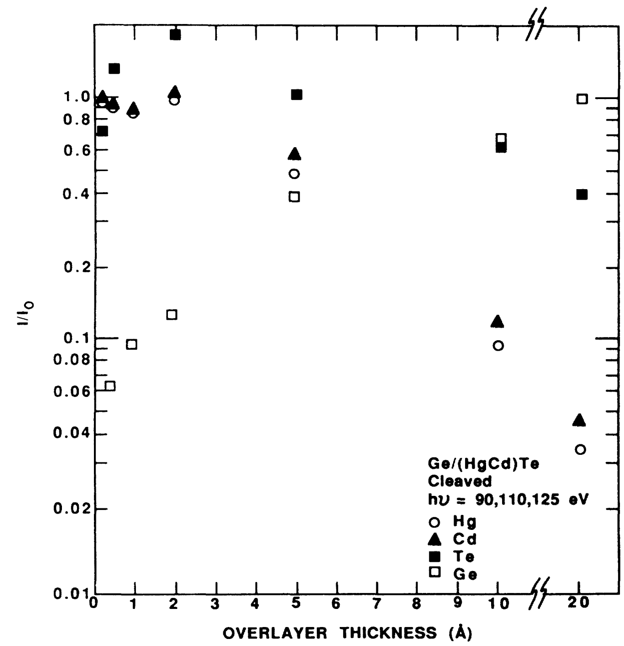

FIG. 5. Normalized intensities of the Hg, Cd, Te, and Ge signals as a formation of Ge coverage on cleaved substrates. The Hg, Cd, and Te signals are normalized to those of clean, cleaved substrates; the Ge signal is normalized to that of the highest coverage.

2. *Sputtered surfaces*

The initial sputtered surface is deficient in Hg with some enhancement of Cd (relative to Te) as previously shown.[5–8,28–31] The very broad Te peak of this surface (Fig. 6) reflects the presence of multiple Te chemical states, likely including normal (HgCd)—Te bonds, Te—Te bonds, and (HgCd)—Te bonds damaged by the ion bombardment.

Deposition of Ge onto sputtered substrates results in a two to threefold increase in the amount of Hg lost from the surface (relative to Cd) compared to cleaved substrates (Fig. 7). This greater Hg loss is also clearly indi-

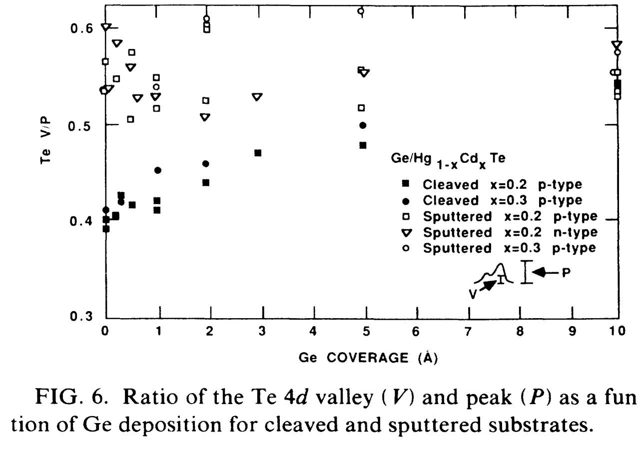

FIG. 6. Ratio of the Te 4*d* valley (*V*) and peak (*P*) as a function of Ge deposition for cleaved and sputtered substrates.

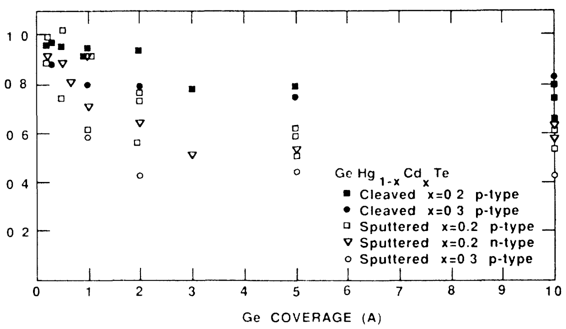

FIG. 7. [Hg]/[Cd] ratio as a function of Ge deposition onto both cleaved and sputtered surfaces (Ref. 7).

cated in the SBD of Fig. 3 where the semiconductor-component composition evolves along a path bowed away from that of the cleaved substrate (allowing for the difference in starting composition).

Although the Hg lost is independent of the type (n or p) of the substrate, it does appear to be dependent on the CdTe fraction, or x value, with the higher-x-value substrate exhibiting a greater decrease in its Hg concentration relative to the initial surface (Fig. 7). In absolute terms, the difference is even greater because the $x=0.3$ surface loses more Hg during ion bombardment than the $x=0.2$ surface (under our sputtering conditions).[5]

The behavior of the Te $4d$ line from sputtered substrates is very different from that observed with cleaved substrates. The Te peak from the clean, sputtered surface is very broad, and sharpens, during the initial stages of overlayer growth. At intermediate coverages (up to the highest measured for Ge), it begins to broaden and, at 10-Å Ge, converges to the same width as that from the Ge-covered cleaved substrate.

In contrast, the trends in energy of the spectral features from the sputtered surface are similar to those observed from the cleaved surface: Cd and Te—a 0.1–0.2-eV decrease in kinetic energy; Hg—a small (<0.1 eV) increase; and Ge—a somewhat larger (~ 1.0 eV) increase. The energies from the sputtered surfaces are very close to those from the cleaved surfaces, i.e., the increased inversion reported below and in other cases does not appear to be present here.

B. Ag

1. Cleaved surfaces

The valence-band and core-level spectra of cleaved (HgCd)Te before and after deposition of Ag are shown in Fig. 8. Qualitatively, the figure shows that (1) the semiconductor components are attenuated very little, even at high-Ag coverages; (2) the Hg intensity decreases only slightly faster than that of Cd; and (3) the Ag peak grows slowly. The relationship between the Hg, Cd, and Te is illustrated in the SBD of Fig. 9 which also presents results from similar cleaved surfaces reported by Friedman *et al.*[13,14] using Mg $K\alpha$ photons ($h\nu=1253.6$ eV) and from the sputtered surfaces discussed below.

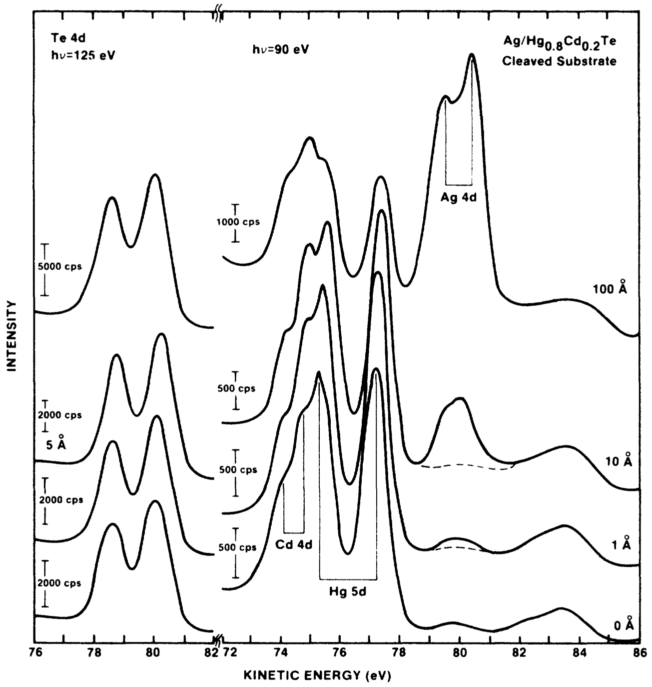

FIG. 8. Valence-band and core-level spectra for cleaved $Hg_{0.8}Cd_{0.2}Te$ substrates as a function of Ag coverage.

The SBD of the current Ag measurements on cleaved surfaces shows that the semiconductor-component composition remains nearly constant for coverages less than 20 Å. At higher coverages, the composition evolves along line B of Fig. 2 (the line representing a stoichiometric interface and out-diffusion of Te). Howev-

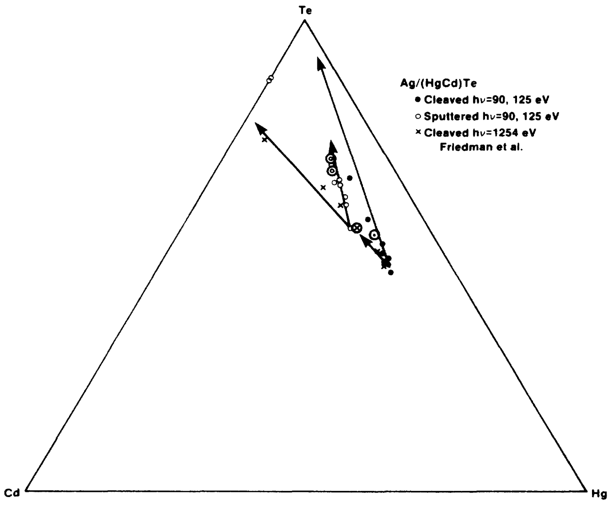

FIG. 9. SBD illustrating the evolution of the semiconductor-component composition during Ag deposition. Results are shown for cleaved and sputtered substrates and for the cleaved surfaces reported by Friedman *et al.* (Refs. 13 and 14). Points representing deposition of 10–20 Å are circled.

er, at all coverages, the composition is closer to that of the cleaved surface than that observed during either Au or Al deposition (but similar to that with Sb deposition).

The normalized intensity measurements (Fig. 10) indicate little attenuation of the substrate components in our measurements. The Hg signal intensity exhibits our largest decrease—~25% at 100-Å Ag—while the Te signal actually increases in intensity by ~50% at 100-Å Ag. By comparing the rise of the Ag and Ge (Fig. 5) signals during their respective depositions (e.g., 0.08 versus 0.38 at 5 Å), the slow buildup of Ag at the surface is also evident. For additional comparison, the figure also includes the normalized Hg intensity from Friedman *et al.*[13,14] to show the major difference between the two measurements. (Intensities of the other components are similar in the two experiments.)

The Te 3*d* peak from this particular cleave was slightly broader (by ~10% as reflected by the peak-to-valley ratio) than those cleaves used in the Ge study. [Such small cleave-to-cleave variations are frequently seen with (HgCd)Te;[8] however, they do not appear to affect the chemical behavior of the metal-(HgCd)Te interface.] During the first few Å of Ag coverage, the Te 4*d* peak narrows slightly until it resembles the initial peak of the other samples (Fig. 11). At higher coverages, the trend seems to reverse and the peak slowly becomes broader.

Also during the initial stages of deposition, the spectral features of the semiconductor components generally shift to 0.1–0.2 eV higher kinetic energy, indicating less band bending of the inverted surface. Such a shift is opposite of that observed in the case of Ge overlayer formation.

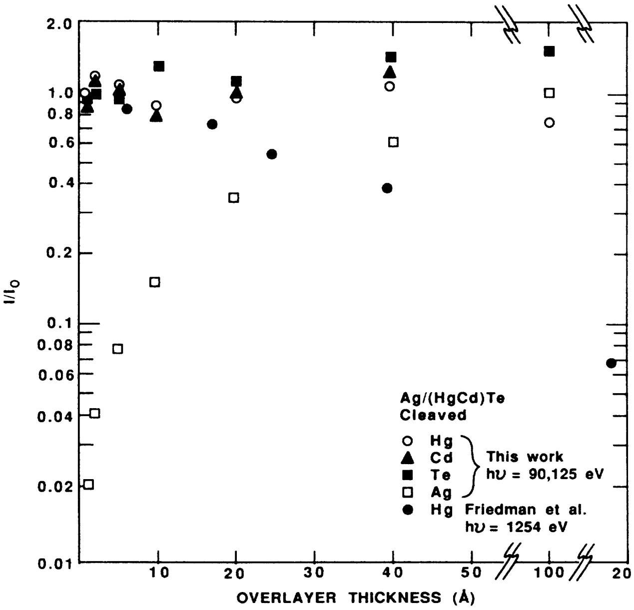

FIG. 10. Intensities of the Hg, Cd, Te, and Ag signals as a function of Ag coverage on cleaved substrates. The Hg, Cd, and Te signals are normalized to those of the clean, cleaved surface; the Ag signal is normalized to that of the highest coverage. Also shown are the normalized Hg intensities of Friedman *et al.* (Refs. 13 and 14).

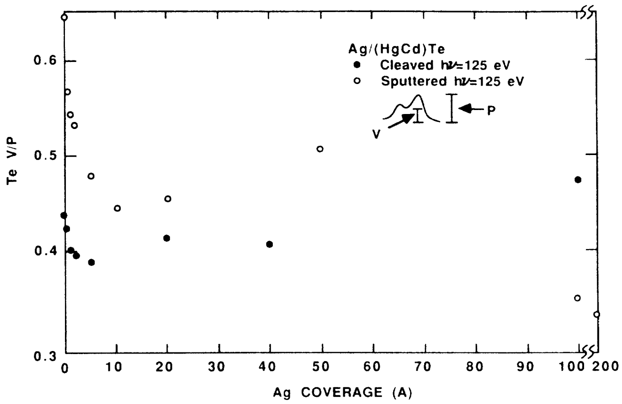

FIG. 11. Ratio of the Te 4*d* valley (*V*) and peak (*P*) as a function of Ag deposition for cleaved and sputtered substrates.

At higher coverages, there is no clear trend of energy shifts for either the semiconductor components or Ag.

2. Sputtered surfaces

The Ag deposition onto sputtered substrates can be divided into two regimes: coverages less than ~50 Å and coverages greater than ~50 Å. In the first regime, the sputtered surface exhibits the same behavior as that of the cleaved surface (present results) as shown in the SBD of Fig. 9, where the semiconductor-component composition again evolves slowly along the same path (allowing for the different initial compositions)—directly toward the Te vertex. The Te peak of the sputtered surface also sharpens (Fig. 11), but to a much greater extent than that of the cleaved surface due to its initial broadness with the sputtered surface.

The key difference between the behavior of the two substrates in this coverage range is the Ag signal (Fig. 12). It increases much faster (about 5 times) on the ion-bombarded surface than on the cleaved surface during the initial stages although at high coverages (> 40 Å), the two surfaces exhibit similar Ag signals.

At high Ag coverages, the sputtered surface behaves very differently, i.e., the Hg signal, but not those of Cd and Te, attenuates completely. Concurrent with this extinction of the Hg signal is a sharpening of the Te peak (Fig. 11).

Unlike the case of the cleaved surface, peak energies from the sputtered surface exhibit no consistent trends indicative of changes in the band bending. However, throughout the deposition sequence, each spectral feature occurs at 0.2–0.3 eV lower kinetic energy than the corresponding feature from the cleaved surface. This reflects an increased inversion of the sputtered surface.[5] At low coverages (< 2 Å), the Hg peak does not exhibit this 0.2–0.3-eV shift, which suggests the formation of less tightly bound Hg species during ion bombardment. Other individual peak shifts include a 0.3-eV shift to higher kinetic energy for the Ag 4*d* peak during the first Å of deposition and a decrease in kinetic energy for the Cd 4*d* peak at very high coverages.

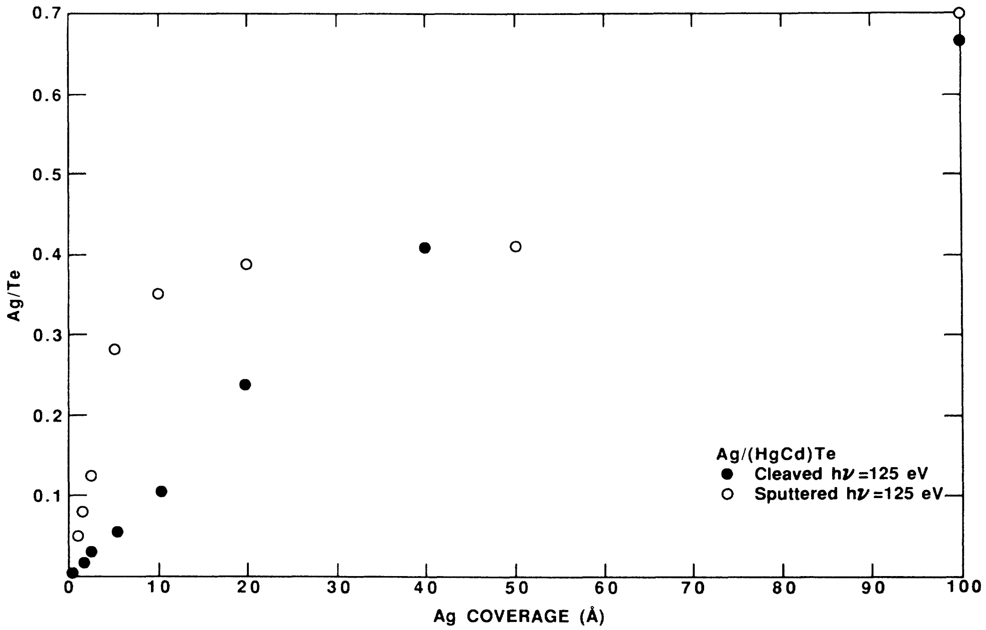

FIG. 12. Ag intensity, normalized to the initial Te intensity, as a function of Ag deposition. Results are shown for cleaved and sputtered substrates and for the cleaved surfaces.

C. Cu

1. Cleaved surfaces

Figure 13 illustrates the behavior of the (HgCd)Te surface upon deposition of Cu as measured by us at $h\nu=90$ eV and by Friedman *et al.*[16] at $h\nu=1254$ eV. According to our data, the surface composition evolves directly toward the Te vertex—an approximately equal attenuation of the Hg and Cd signals and a persistence of the Te signal. this progression is much like that observed during Au or Ag deposition on cleaved surfaces [Figs. 4(c) and 9, respectively) except that it is quicker, i.e., the cation signals are attenuated, relative to that of Te, faster for Cu than for either Au or Ag.

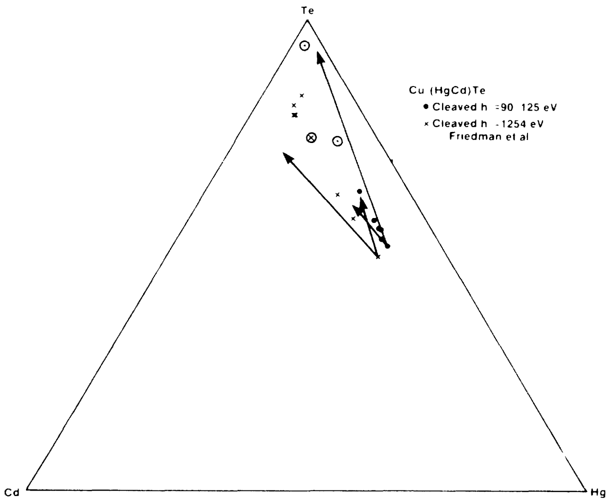

FIG. 13. SBD illustrating the evolution of the semiconductor-component composition during Cu deposition onto cleaved substrates. Also shown are results from Friedman *et al.* (Ref. 16) with $h\nu=1254$ eV. Points representing deposition of 10–20 Å are circled.

Like Ag deposition, Cu deposition results in a broadening of the Te 4*d* line, indicating multiple local environments for Te. However, in this case, the broadening begins at a much lower coverage (~2 Å instead of 20 Å) and reaches approximately the same value at 5–20 Å as the Ag-covered surface does at 100 Å. A comparable broadening of the Te 3*d* line is also reported by Friedman *et al.*,[16] but beginning at their lowest coverage shown (~0.5 Å).

During other Cu depositions, measurements were taken at lower photon energy. Because the Te signal was not measured, these results cannot be displayed on an SBD, but must be presented in more conventional formats. The [Hg]/[Cd] ratio as a function of Cu coverage is shown in Fig. 14 for photon energies of 90 and 26 eV. Also shown are the corresponding quantities from the results of Friedman *et al.*[16] Our Cu results show significant variation with photon energy: The more surface-sensitive measurements ($h\nu=90$ eV) indicate a comparatively small (30%) loss of Hg relative to Cd in the first 10 Å of Cu deposition [one monolayer of Cu corresponds to 0.80 Å (Ref. 16)]. The less surface-sensitive measurements ($h\nu=26$ eV), on the other hand, show a continual decrease in the relative Hg concentration over the entire range of coverages at a rate intermediate between those observed with the reactive and unreactive overlayers[3–6] until ~80% of the Hg in the near-surface region is missing. This variation with surface sensitivity—increasing [Hg]/[Cd] ratio with decreasing surface sensitivity—is the opposite observed for In.[4,5]

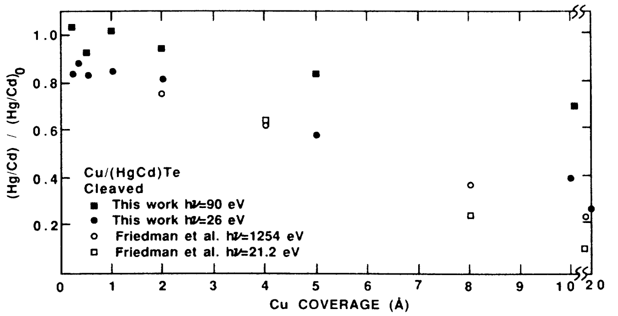

FIG. 14. [Hg]/[Cd] ratio as a function of Cu deposition onto cleaved substrates for $h\nu=90$ and 26 eV. Also shown are results from Friedman *et al.* (Ref. 16) with $h\nu=21.2$ and 1254 eV.

For these Cu-deposition measurements, the Cd signal decreases according to a photoelectron attenuation length of ~9 Å; that of Hg decreases with an attenuation length of ~4 Å. Although the value for Cd is near the lower limit of that expected for photoelectrons with 10-eV kinetic energy, the value for Hg is unreasonable[39]—indicating a depletion of Hg from the interface.

Similar to Ag deposition we observe a small (0.1–0.2 eV) shift to higher kinetic energy of the spectral features in the very early stages corresponding to less band bending of the initially inverted surface. This shift remains essentially constant up to our highest coverage of 20 Å.

2. *Sputtered surfaces*

The normalized [Hg]/[Cd] ratio of sputtered $Hg_{0.8}Cd_{0.2}Te$ and $Hg_{0.7}Cd_{0.3}Te$ surfaces is shown in Fig. 15 as a function of Cu coverage. Also indicated are the corresponding values from the cleaved surface. Although the differences are not as pronounced as in the case of Ge deposition, there is a distinctly larger decrease in the cation ratio (~33% greater decrease at 10 Å) of the sputtered specimens than in that of the cleaved specimens. In absolute terms, the decrease of Hg would be even larger for sputtered surfaces because of their initial Hg depletion.[5–8,28–31] Even though surfaces of different compositions exhibit varying degrees of Hg depletion during ion bombardment under our experimental conditions,[5–8] little difference between their normalized [Hg]/[Cd] ratios is observed at our higher Cu coverages (> 5 Å).

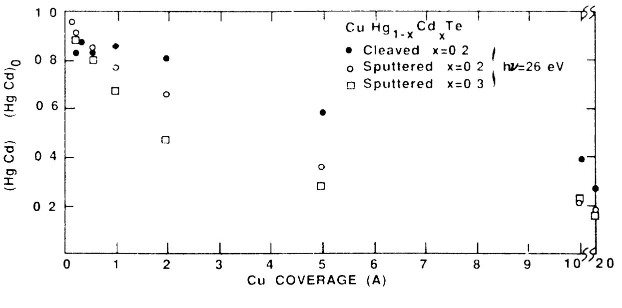

FIG. 15. [Hg]/[Cd] ratio as a function of Cu deposition onto both cleaved and sputtered surfaces.

There is almost no change in band bending of sputtered surfaces with Cu deposition; energies of the spectral features remain within 0.1 eV of their values on the clean, sputtered surface. Like the case of most deposition experiments,[5] features from the sputtered surface appear at several tenths of an electron volt lower kinetic energy than the corresponding feature from the cleaved surface at all coverages, including zero.

IV. DISCUSSION

A. Ge

The behavior of cleaved substrates upon Ge deposition is very similar to that observed during Au deposition, i.e., Ge acts as an unreactive overlayer. No difference in behavior of $x=0.21$ and $x=0.28$ substrates was seen despite the general weakening of the Hg—Te bond with increasing CdTe fraction.[22–24] This suggests that the energetics of exchange reaction (1) are sufficiently negative for Ge that the alloying effect does not alter the degree of reaction.

The increased Hg loss from the sputtered substrates is attributed to the increased surface damage due to the ion bombardment, which makes the surface more reactive. Such defects allow reaction (1) to proceed until their supply is exhausted. The increased Hg loss for $x=0.28$ material relative to $x=0.21$ material probably is a manifestation of the weakened Hg—Te bond during alloying which also causes the increased preferential sputtering of Hg.[5]

Both *n*- and *p*-type sputtered surfaces behave identically, indicating that the annealing procedure used to convert the substrate to *n*-type must not have significantly weakened the Hg—Te bond or created defects that promote Hg loss. Such defects have been suggested[23] to explain the enormous loss of Hg observed from the surface region of other *n*-type material exposed to UHV.[40] Although these defects might occur, our results indicate that they are not a necessary consequence of the formation of *n*-type material.

The large energy shift of the Ge line over our coverage range indicates that Ge, at low coverages, forms a complex with Te on the surface even though a complete exchange reaction does not occur and, at higher coverages, forms an elemental overlayer. This initial complex would likely involve the cleavage- and sputter-induced defects present on the surface; the slightly greater energy shift observed with the sputtered substrates suggests a more tightly bound complex, such as GeTe, formed with the elemental Te resulting from the ion bombardment. In both cases, the limited reaction is likely the origin of the outdiffusing Te.

The energy shifts of the semiconductor components may represent a small increase in the band bending of the already inverted surface. In this case, Ge, an amphoteric dopant, diffuses into the semiconductor and acts as a donor, in a manner analogous to Si.[41] The zero shift of the Hg line then would actually be a positive-kinetic-energy chemical shift which would reflect a less electropositive nature. Such a change in bonding might arise from the Ge-Te complex formed during the initial deposition stages.

It is interesting to note that Wall *et al.*[12] report different behavior upon Ge deposition: Although they found energy shifts for the Cd, Te, and Ge peaks very similar to those reported here, they observed a large loss of Hg from the surface region, similar to that seen during deposition of reactive metals. We will discuss possible explanations for these differences in subsection D.

B. Ag

The very slow attenuation of the semiconductor components and the slow buildup of Ag make Ag deposition unique among all (HgCd)Te-overlayer systems reported to date. Friedman *et al.*[13,14] concluded that the Ag is displacing the Hg in the lattice and diffusing into the semiconductor to a depth greater than 100 Å. The slow increase in the Ag signal could be caused by one of several phenomena: (1) a small sticking coefficient for Ag on (HgCd)Te;[13,14] (2) clustering or island formation of Ag; (3) nearly equal out-diffusion of Hg, Cd, and Te into the Ag overlayer; or (4) in-diffusion of Ag into the (HgCd)Te.[13,14]

As discussed by Friedman *et al.*[13,14] a small sticking coefficient is inconsistent with the results. Because the sticking coefficient of Ag onto Ag is not small, once an Ag monolayer was deposited onto the (HgCd)Te, the rate of increase in the Ag signal would be dramatic. Such an acceleration of the coverage was seen in neither experiment, indicating that this is not the mechanism controlling Ag deposition.

Island formation could also attenuate the substrate signals more slowly than expected from laminar deposition. It too would require a two-stage attenuation behavior, but in the opposite sense—a relatively rapid initial attenuation as the islands are nucleated and a slower attenuation as the islands grow. Such behavior has been observed for Al,[4] In,[4] and Au,[3] for example, but is not seen here where the data indicate little, if any, attenuation, with peak intensities remaining strong even at the highest coverages.

Diffusion of the semiconductor or overlayer constituents, then, is likely to be responsible for the Ag/(HgCd)Te behavior. Out-diffusion of Te and Cd has been observed in Pt overlayers[17] and was explained by the large heat of cation alloying in Pt.[42,43] Such out-diffusion is also predicted for Pd (Ref. 44) and, possibly Au, but not for Ag where Hg and Cd exhibit low heats of alloying.[17] Instead, the Ag/(HgCd)Te interface must be governed by in-diffusion of Ag, as originally suggested by Friedman *et al.*[13,14] However, the displacement of Hg by Ag is not necessarily the diffusion mechanism as evidenced by the persistence of the Hg signal during our experiments.

Silver, like the other group-I*B* elements (Cu and Au), is a known rapid diffuser in (HgCd)Te.[45–47] In the case of a low-temperature anneal for *n*-type conversion, Schaake and coworkers[47,48] have shown that dislocations are formed in the skin region and that Ag is gettered to the core-skin boundary. These results suggest that the in-diffusion of Ag seen here and by Friedman *et al.*[13,14] may be governed by the high level of defects present on the cleaved (HgCd)Te surface,[27] which could provide a rapid means of diffusion of Ag away from the surface even at ambient temperature. Such a mechanism is also supported by the more rapid increase in the Ag signal upon deposition onto sputtered surfaces. Although the sputtered surface is very defective, its defects are of a different nature—the breaking or distortion of bonds, formation of like-like bonds, and disruption of long-range order. These defects tend to make the surface more reactive, as indicated by the Ge and Cu depositions, and trap the Ag at the surface, causing a more rapid buildup. The trapping is evidenced by the small chemical shift of the Ag peak seen only from sputtered substrates; this indicates formation of an Ag-Te complex. (Ag exhibits only a narrow range of chemical shifts.[49,50]) Depending on the diffusion mechanisms, the Ag buildup might also be augmented by the formation of an amorphous region during ion bombardments; the disruption of long-range order would eliminate some of the dislocations and other defects that enhance diffusion—a process analogous to the formation of amorphous diffusion barriers.

C. Cu

The variation of the [Hg]/[Cd] ratio with photon energy during Cu deposition onto cleaved surfaces is consistent with the model proposed by Friedman *et al.*,[16] where both Hg and Cd are partially depleted from the surface region with the Cd deficiency being localized at the interface and the Hg deficiency having a broader spatial extent. In this model, the more surface-sensitive measurements would probe the region where both were depleted and could indicate an unchanged [Hg]/[Cd] ratio; in contrast, the less surface-sensitive measurements would also probe the region where only Hg was depleted leading to a reduction in the Hg/Cd ratio. This same trend is continued with measurements at $h\nu=21$ eV (Ref. 16) which have the least surface sensitivity—they indicate an even greater reduction in the cation ratio. (In comparison, the photon energy dependence of the [Hg]/[Cd] ratio during In deposition is in the opposite direction and is explained by a thin, but greater Hg depletion at the interface with little, if any, decrease in the Cd concentration.)

Depletion of Hg from the interfacial region is also indicated by more rapid attenuation of its signal than could be expected from electron-attenuation-length considerations. A similar, but less severe, depletion might also be true for Cd because its attenuation length (~ 9 Å) is lower than that normally determined for 10-eV electrons in Cu (15–20 Å);[39] however, the evidence is less clear cut in this case. Unlike Friedman *et al.*,[16] we see no suggestion of Cd outdiffusion although our highest coverages are considerably less than theirs. Nonetheless, we do see the nearly universal outdiffusion of Te.

The proposed structure of Friedman *et al.* is consistent with the data and their variation with photon energy, but a mechanism that describes the formation of the Cd-deficient region is needed. Such a Cd depletion is difficult to explain thermodynamically, especially since such a region was not seen during Al deposition[4] where the driving force, either from the energetics of reaction (1) or from lattice-disruption considerations due to the Hg depletion or from the heat of condensation of the metal, should be greater (or at least the same). The small, but favorable, heat of alloying of Cd in Cu (Ref. 17) possibly may combine with the other phenomena to provide a small amount of Cd depletion. However, at present the formation of the Cd depletion is not fully understood.

Another explanation for the greater relative reduction in the Hg signal in the data of Friedman *et al.*[16] compared to that of ours, but not for the variation of Hg behavior reported here for samples investigated with different photon energies, is the greater tendency of at least some of their surfaces to lose Hg as demonstrated in the different Ag deposition experiments. However, this scenario can explain the data only if each individual surface is arbitrarily assigned the appropriate degree of susceptibility to Hg loss to fit the model in an *ad hoc* manner. This susceptibility is likely to depend on the particular boule from which a sample was obtained, its history, and the type and concentration of cleavage-induced defects. Consequently, the variation would generally be expected to be systematic—an expectation supported by the consistency within each laboratory for each other overlayer studied. Thus, this mechanism is believed to play only a minor role in this set of experiments; it is not inherent to the measurements of the different groups.

As in the case of Ge deposition, sputtered substrates lose a greater fraction of their initial Hg from the surface region. Again we attribute this to the lower stability of the sputtered surface due to ion-bombardment-induced damage.

D. Intermediate overlayers in general

The observed behavior for (HgCd)Te upon deposition of overlayers of intermediate reactivity is summarized in Table I and can be compared with that reported for reactive and unreactive overlayers. The similarity between the heats of formation of HgTe and of tellurides of the intermediate overlayer elements allows the interfacial reactions between (HgCd)Te and these overlayers to be governed by such other factors as surface treatment,[7] material history, heats of alloying of the cations into the overlayer,[17] and proclivity of the overlayer element to diffuse into the semiconductor. The last two factors can also influence the behavior of unreactive overlayers as well. Because the deposited element is not trapped at the interface, as in the case of reactive and ultrareactive metals with the formation of a telluride, it is free to diffuse into the (HgCd)Te as is the case with Ag and, to a much lesser extent, Cu.[16] (A small amount of diffusion is likely in most of the cases examined so far because changes in the band bending of the semiconductor correspond to the dopant character of the overlayer.) The large-scale diffusion can be enhanced by the cleavage-induced defects on the surface,[27] which allow the deposited atoms to readily leave the surface. In this case, ion bombardment reduces the diffusion by trapping the deposited atoms via the formation of tellurides or similar complexes and, possibly, by annihilating dislocations and other defects via the formation of an amorphous surface region. As a result of its rapid diffusion, an element such as Ag would be an unsuitable contact material unless the surface could be prepared in such a way as to trap it at the interface. Even though Cu is also considered a rapid diffuser in (HgCd)Te,[45–47] it does not exhibit the same behavior following deposition on cleaved substrates. This dissimilari-

TABLE I. Behavior of (HgCd)Te upon deposition of overlayers.

Overlayer	Reference	Class	Cleaved substrate	Sputtered substrate
Ag	This work	Intermediate	Ag in-diffusion little Hg loss	Little Ag in-diffusion Little Hg loss (≤ 50 Å) Large Hg loss (≥ 100 Å)
Ag	Friedman *et al.*[a]	Intermediate	Ag in-diffusion large, slow Hg loss	
Ag	Wall *et al.*[b]	Intermediate	Ag in-diffusion large, slow Hg loss	
Cu	This work	Intermediate	Intermediate Hg loss (measurement $h\nu$ dependent)	Increased Hg loss
Cu	Friedman *et al.*[b]	Intermediate	Intermediate Hg loss (measurement $h\nu$ dependent) limited Cd out-diffusion	
Ge	This work	Intermediate	Little Hg loss	Increased Hg loss
Ge	Wall *et al.*[b]	Intermediate	Large, rapid Hg loss	
Pt	Friedman *et al.*[d]	Intermediate	Large Hg loss Cd out-diffusion	
Al	Davis *et al.*[e]	Reactive	Large, rapid Hg loss	Large, rapid Hg loss
Au	Davis *et al.*[f]	Unreactive	Little Hg loss	Possible small increase in Hg loss

[a] References 13 and 14.

[b] Reference 12.

[c] Reference 16.

[d] Reference 17.

[e] References 4 and 5.

[f] References 3 and 6.

ty suggests that the two metals diffuse by different mechanisms.

Large-scale outdiffusion of the cations into the overlayer did not occur for the overlayers discussed here, but has been reported for Pt (Ref. 17) and Pd (Ref. 44). For these elements, the high heats of alloying the cations into the overlayer is the factor governing the interfacial behavior. Based on the heats of formation of their tellurides (Fig. 1), both of these elements would be considered intermediate overlayers; however, the effect of a high heat of alloying would be to shift the energy balance of the exchange reactions (1) and (2) to the right, reflecting a negative heat of the Hg or Cd alloyed in the overlayer. Thus, some overlayers that would otherwise be considered intermediate would act reactive, and others that would nominally be unreactive would appear intermediate.

The intermediate class of overlayers is unique in that its members are sensitive to the reactivity of the (HgCd)Te surface. This was first demonstrated by Ge deposition,[7] and was illustrated here for the other overlayers also. One means to change the reactivity is ion bombardment. Because the driving force of exchange reaction (1) is near zero, small changes in the stability of the Hg—Te bond can allow the reaction to proceed and the freed Hg to leave. The ion bombardment results in a number of damaged bonds. Some of these distorted or broken bonds are sufficiently weakened so that the overlayer telluride is formed and the loss of Hg from the interface is increased. (The formation of a telluride from Te—Te bonds is favorable in all cases, including unreactive overlayers; however, since there is no Hg associated with this reaction, there is no change in the [Hg]/[Cd] ratio.)

Although no differences were seen from cleaved substrates of different compositions, changes were detected from different sputtered substrates. The increased relative loss of Hg from the higher CdTe-fraction material is attributed to the small decrease in stability of the Hg—Te bond due to alloying.[22–24] This weakening of the Hg—Te bond results in an increase in the preferential sputtering of Hg (Ref. 5) and, apparently, in the number of damaged bonds.

Ion bombardment, however, is an extreme means of increasing the reactivity. Dramatic differences have also been seen in some of the results from different research groups. They were particularly evident with our results for Ag deposition on cleaved surfaces and those of Friedman *et al.*[13,14] and Wall *et al.*[12] Likewise, apparent differences in behavior have been seen for Ge deposition on cleaved surfaces.[7,12] In both cases, the Martin Marietta–Wisconsin measurements showed significantly less Hg loss. Four possible causes for these differences can be proposed: material, cleavage, deposition, and photon energy. We obtained our material from Cominco American in oriented wafer form, whereas Santa Barbara Research Center (SBRC)–Stanford and McDonnell-Douglas–Minnesota grew their own and cut it into rods. There may be some inherent difference in material so that we observe less Hg loss. Indeed, as mentioned earlier, such material differences between the SBRC material and German material have been proposed[23] to explain the high loss of Hg from surfaces of the latter that were cleaned in UHV.[40] Alternatively, because our cleaved surfaces are smaller, especially along the direction of crack propagation, they may have fewer cleavage-induced defects. Other variations in experimental procedure, such as the temperature of the (HgCd)Te during deposition, might also lead to increased Hg loss. Because each group nominally uses the same procedure, the variations are expected to be small. Nonetheless, they cannot be eliminated as causes contributing to the observed differences in behavior.

Finally, each experimentor uses a different set of photon energies and, hence, electron attenuation length(s). Consequently, in principle, structures can be proposed that would be consistent with different results. Such a model was used to explain the Cu results but cannot explain the differences noted following the Ag and Ge depositions for two reasons. (1) The differences between the Ag measurements of this paper and of Friedman *et al.*[13,14] and between the Ge measurements of this paper and of Wall *et al.*[12] are too large to allow a thin-Hg-rich layer on top of a Hg-depleted region. (2) The results of Friedman *et al.*[13,14] and of Wall *et al.*[12] are very similar to each other although the latter used a photon energy closer to that of the present results than to that of the former.

In any case, these differences have been reported only for the intermediate class of overlayers; any changes in surface or material reactivity should not affect the strong driving force of reaction (1) for reaction metals or the unfavorable energetics of the reaction for unreactive metals. Instead, the results show that the interactions between (HgCd)Te and intermediate overlayers can serve as a sensitive indication of the stability or reactivity of the substrate surface.

V. SUMMARY AND CONCLUSIONS

We have examined the interactions between Ge, Ag, and Cu and both cleaved and sputtered (HgCd)Te surfaces and, where available, have compared our results to those previously reported. Each of these overlayers forms tellurides with heats of formation near that of HgTe. As such, the interfacial interactions are governed by other factors, including stability of the surface and diffusion into the substrate. Specifically, Ag was found to diffuse into cleaved surfaces as initially reported by Friedman *et al.*[13,14] but not into sputtered surfaces where it is trapped at the interface. Both Cu and Ge also exhibit increased interfacial reactions on sputtered substrates and cause an increased relative loss of Hg. When the current results are compared with those of others, significant differences in the amount of Hg lost from the interface are seen for Ag and Ge. These differences are believed to be dependent on material and surface quality. They demonstrate that the interactions between (HgCd)Te and intermediate overlayers can be sensitive to the stability of the substrate surface.

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