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YTTERBIUM MONOLAYER DIFFUSION BARRIERS AT Hg_{1-x}Cd_xTe/Al JUNCTIONS

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Abstract

Single layers of Yb at the $Hg_{1-x}Cd_xTe(110)$ interface prevent Al-Te reaction and dramatically increase the Hg concentration at the interface. Synchrotron Radiation photoemission studies of the interface as a function of Al deposition show a two orders of magnitude increase in the Hg/Te core intensity ratio as a result of the interlayer-induced change in atomic interdiffusion. Semi-empirical calculations of thermodynamic parameters following Miedema's model suggest that other rare earths should also act as effective diffusion barriers at Mercury-Cadmium-Telluride/reactive metal junctions.



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 $Hg_{1-x}Cd_xTe$ alloys are widely used in infrared detector technology because of their composition-dependent variable bandgap. Cutoff wavelengths in the $3-5\mu$ m and $8-12\mu$ m atmospheric transmission windows can be obtained through choice of a suitable Cd/Hg ratio in the bulk material. These alloys, however, exhibit a number of lattice, surface and interface instabilities that complicate material processing and device fabrication. The weakness of the binary Hg-Te bond is made more severe by the coexistence of Cd-Te and Hg-Te bonds in the matrix¹⁻², so that preferential loss of Hg and the formation of large concentrations of point defects have been observed as a result of metallization³⁻⁵, oxidation⁶⁻⁷, heating⁸, electron bombardment⁹, or a variety of other processing steps¹⁰.

It has been shown by several authors that the deposition of reactive metals such as Al. In or Cr onto the Mercury-Cadmium-Telluride surface results in atomic interdiffusion, preferential metal-Te reaction, and Hg-depletion of the near-surface region $^{3-5}$. The consequent change in local semiconductor stoichiometry may affect the Schottky barrier or induce inconsistencies in contact performance.

Earlier studies of metal contacts onto GaAs¹¹, Si¹², CdTe¹³ and InP¹⁴ semiconductor surfaces have shown that ultrathin interlayers predeposited onto the semiconductor surface prior to contact formation can modify atomic interdiffusion across the interface 11-14 and in some cases control the final value of the Schottky barrier height¹³⁻¹⁴. In this paper we present what is, to our **n** For knowledge, the first study of an effective monolayer reaction barrier between $Hg_{1-x}Cd_xTe$ and the reactive metal Al. Our results provide evidence that Yb interlayers can prevent Al-Te reaction and strongly reduce Hg-depletion at the interface. In general, our results suggest that monolayer diffusion barriers can be^{ition}/ Availability Codes

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effectively used to control the interface stability of $Hg_{1-x}Cd_xTe$ alloys, a class of materials for which interdiffusion and the resulting semiconductor disruption is especially severe.

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The use of rare earth interlayers has been considered on the basis of recent experimental studies¹⁴, and thermodynamic calculations. Our synchrotron radiation photoemission studies have shown that the rare-earth metals Yb and Sm induce a nonmonotonic variation of the Hg concentration in the interface region. For example, deposition of Yb initially causes a Yb-Te reaction leading to the formation of a Hg-depleted layer, but this initial stage is followed by a sharp transition (at an Yb thickness of 0.5 ML) to a stage where the Hg intensity recovers $20^{c}c$ of the initial value. We have suggested¹⁴ that this increase in Hg concentration is related to the formation of rare earth-rich metallic phases with high solubility for Hg. This interpretation is supported by thermodynamic parameters calculated through the semi-empirical Miedema alloying model.

In Table 1 we show the most stable telluride phases, the corresponding enthalpy of telluride formation, and the enthalpy of solution for Cd and Hg in a number of metal overlayers. For comparison we give in the first two rows of the table the enthalpy of formation of HgTe and CdTe. The telluride parameters were taken from ref. 15. The cation solution enthalpies were calculated by us through Miedema's model¹⁶⁻¹⁷. Values are given for both the divalent and the trivalent form of the rare earths Sm and Yb, and are compared with those of the reactive overlayers In, Cr and Al. Our experimental data show¹⁴ that Yb appears only in the divalent form at the Hg_{1-x}Cd_xTe/Yb interface, while for Sm a divalent-mixed valent transition is observed at metal coverage of about 4-5Å. For Yb we find a Hg solution enthalpy of -108.KJ/mol Hg and a YbTe formation enthalpy of -314 KJ/mol Te. If one compares these values with the telluride formation enthalpy a.d cation solution enthalpies of a typical "reactive" metal such as Al one should conclude that all of the interface reaction products between $Hg_{1-x}Cd_xTe$ and an Yb should be thermodynamically stable relative to reaction with Al. The pre-deposition of a thin Yb overlayer could therefore stabilize the semiconductor surface against further reaction with Al or In or Cr and control the stoichiometry of the interface region during contact formation. To verify this possibility, we have performed studies of $Hg_{1-x}Cd_xTe(110)/Al$ interfaces with and without thin interlayers of Yb.

Sector Sector

Our experiments were conducted on single crystals of $Hg_{0.78}Cd_{0.22}Te$ obtained from Cominco Inc. The crystals (3x3x10mm in size) were cleaved in the photoelectron spectrometer at pressures in the 10⁻¹¹ torr range. Metal overlayers were deposited *in situ* by direct sublimation from resistively heated sources with coverage monitored by a quartz thickness monitor. Synchrotron radiation from the 1 GeV electron storage ring at the Synchrotron Radiation Center of the University of Wisconsin-Madison was used to obtain angular integrated photoelectron Energy Distribution Curves (EDC's) of the valence band, Hg 5d, Cd 4d. Te 4d, Yb 5p and Al 2p core levels. Selected results are shown in fig. 1-2 with metal coverages given in angstroms. In terms of the surface density of atoms on the $Hg_{1-x}Cd_xTe(110)$ surface, 1 ML= 6.76×10^{14} atoms/cm² corresponds to 1.12Å of Al or 2.78Å of Yb.

In the left-most section of fig. 1 we show high resolution EDC's (overall resolution-electrons + photons-of 0.15eV) for the Al 2p core emission from the $Hg_{1-x}Cd_xTe(110)/Al$ interface as a function of Al coverage. The EDC's have been approximately normalized to the same peak height to emphasize lineshape changes. The vertical bar marks the position of the Al 2p core level in metallic Al. from ref. 18. Only at the highest Al coverages explored does the Al 2p emission show a metallic Al component. At all coverages, high binding energy Al

2p contributions are related to Al-Te reacted species at the interface. Chemical shifts of up to 1.6eV of the Al 2p line have been observed also by other authors⁴, and have been interpreted as the result of Al₂Te₃ formation. In our study the high resolution employed allowed us to identify a number of Al-Te reacted features that were not resolved in earlier studies of the $Hg_{1-x}Ce_xTe/Al$ interface¹⁷. In the right-most section of fig. 1 we show the effect of predepositon of a monolayer of Yb on the $Hg_{1-x}Cd_xTe$ surface prior to Al deposition. At all Al coverages the Al 2p lineshape appears similar to the metallic Al 2p lineshape¹⁸, with no evidence of Al-Te reacted components within the experimental uncertainty. A 0.4eV shift to lower binding energy relative to the metallic position is observed at the lowest Al coverages and is related to Al-Yb interaction. Calculated solution enthalpies for Al atoms in Yb suggest that such an interaction is thermodynamically possible- H_{sol} (Al:Yb)=-29/8 KJ/mol Al-and should correspond to a decrease in binding energy of -0.3eV for the Al 2p core levels, as determined from a Born-Haber cycle calculation in the equivalent-core approximation¹⁷.

The data of fig. 1 provide evidence that Yb monolayers act as diffusion barriers and prevent Al-telluride formation. Whenever Yb coverages below a monolayer were explored, the interlayer was found to be only partially effective in preventing Al-Te reaction¹⁷.

The effect of Yb interlayer on the Hg concentration at the $Hg_{1-x}Cd_xTe/Al$ interfaces is depicted in fig. 2. In the bottom-most section of fig. 2 EDC's for the valence band, Hg 5d (8-10eV) and Cd 4d (10-11eV) core emission from the $Hg_{1-x}Cd_xTe/Al$ interface in the presence of a 1 ML Yb interlayer are shown as a function of Al coverage. The bottom-most EDC corresponds to the clean surface emission prior to Yb deposition. Upon deposition of 3Å of Yb, the characteristic $4f^{13}$ final state multiplet appears within 4eV of the Fermi level E_F , the Hg 5d

core emission intensity is at about 20% of the initial value, while the Cd intensity is reduced to about 1% of the clean surface value because of the very short Yb escape depth¹⁷.

The effect of Al deposition is a slow attenuation of the Yb 4f and Hg 5d features without any evidence of Al-induced Hg-depletion of the interface. In the to section of fig. 2 we show the Hg/Te (solid line) and Al/Te (dashed line) photoemission intensity ratios as a function of Al coverage, as derived from the integrated intensity of the Hg 5d_{5/2}. Te 4d and Al 2p core levels. Results are shown for the Hg_{1-x}Cd_xTe/Al interface (squares, case A) and for a similar interface in the presence of an Yb monolayer diffusion barrier (triangles, case B). In the absence of a Yb interlayer (case A) one observes a rapid decrease of the Hg emission intensity and a shift to increasing binding energy of all semiconductor features reflecting a change in band bending^{4,17}. The Hg/Te ratio in fig. 2 decreases to zero within experimental uncertainty at about 20Å Al coverage. The Al/Te ratio increases slowly reflecting Al-Te reaction, island-growth of the metal overlayer and possible Te outdiffusion and segregation in the Al film^{4,17}.

In the presence of a Yb interlayer (case B) both Hg-depletion and Te outdiffusion are strongly reduced. The Hg/Te ratio at Al coverages above 10Å shows an increase of over two orders of magnitude relative to the previous case. The Al/Te ratio increases initially (Al coverage below $2^{\text{Å}}$) at an apparently similar rate. Al-Te interaction in case A and Al-Yb interaction in case B¹⁷ are responsible for this behavior. In the presence of the Yb interlayer, however, the Al/Te ratio increases rapidly toward high-coverage values that are approximately a factor of two higher than in case A. Possible changes in the island morphology of the Al overlayer and segregation phenomena have to be taken into consideration to account for the detail in the coverage-dependence of the Al 2p

integrated intensity. This point will be addressed in a longer forthcoming paper¹⁷.

Yb In conclusion. shown that interlayers we have the at $Hg_{1-x}Cd_{x}Te(110)/Al$ interface control atomic interdiffusion. The lack of Altelluride-related Al 2p core features, the persistence of the Hg 5d signal at high Al coverages and the dramatic increase in the Hg/Te ratio provide evidence that a single Yb monolayer is sufficient to prevent Al-Te reaction, stabilize the Hgconcentration at the interface and reduce Te outdiffusion. Our thermodynamic calculations suggest that other rare earth interlayers (Sm) may act as effective diffusion barriers during $Hg_{1-x}Cd_xTe$ /reactive metal contact formation.

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Table Captions

Table 1. Thermodynamic parameters calculated from the semiempirical model of Miedema *et al.*¹⁶⁻¹⁷. Column 1: metal atom Column 2: most stable metal-telluride solid phases, from ref. 15. Column 3: metal-telluride formation enthalpies from ref. 15. Columns 4 and 5: heats of solution for isolated Cd and Hg atoms, respectively, in the overlayer.

Ta	ble	1
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Metal (M)	Most stable telluride	H _f telluride (KJ/mol Te)	H _{sol} (Cd:M) (KJ/mol Cd)	H _{sel} (Hg:M) (KJ/mol Hg)
Hg	HgTe	-31.8		
Cd	CdTe	-101.		- ·
ſn	In_2Te	-79.8	+1.7	-3.4
Cr		~	+ 19.0	+67.9
Al	Al_2Te_3	-106.	+14.7	+17.2
Sm^{2+}	SmTe	-310.		
Sm ³⁺	$\mathrm{Sm}_{2}\mathrm{Te}_{3}$	-265.	-141.	-173.
Yb^{2+}	YbTe	-314.	-74.1	-108.
Үb ³⁺		·	-140.	-172.

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Figure Captions

- Fig. 1 High resolution EDC's for the Al 2p core emission as a function of Al coverage θ are shown with (right) and without (left) a 3Å Yb interlayer. The vertical bars mark the position of the Al 2p core level in metallic Al from ref. 18. All spectra have been approximately normalized to the peak intensity in order to emphasize lineshape changes. Binding energies are referred to the Fermi level E_F .
- Fig. 2 Bottom: EDC's for the valence band, Yb 4f (0-4eV), Hg 5d (8-10eV), and Cd 4d (10-11eV) emission from the $Hg_{1-x}Cd_xTe/Al$ interface in the presence of a 3\AA (=1ML) Yb interlayer are shown as a function of Al coverage θ . The bottom-most EDC's corresponds to emission from the clean $Hg_{1-x}Cd_xTe(110)$ surface.

Top: Hg/Te (solid line) and Al/Te (dashed line) intensity ratios as derived from the integrated intensity of the Hg $5d_{5/2}$. Te 4d and Al 2p core levels are shown as a function of Al coverage θ . The squares (case A) mark the results in the absence of a Yb diffusion barrier, the triangles (case B) depict the results in the presence of a Yb monolayer at the interface.



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