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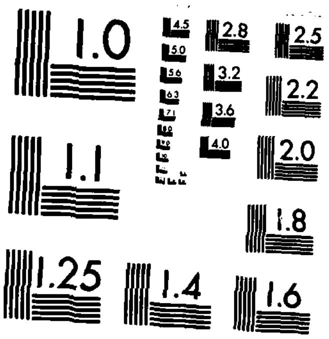

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and noble metals.

INTERFACE CHEMISTRY OF $Hg_{1-x}Cd_xTe$

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ABSTRACT

We present preliminary studies of room temperature formation of the $Hg_{1-x}Cd_xTe(110)$-Cr interface. For Cr coverages below 2Å, Cr atoms replace Hg atoms in a 10-13 Å-thick semiconductor layer while elemental Te is released at the surface. The typical high coverage interface morphology consists of an elemental Te surface, a metallic Cr film, a Hg-depleted subsurface layer where Cr is bonded to Te, and finally the ternary semiconductor bulk. This complex interface chemistry is compared with recent results for $Hg_{1-x}Cd_xTe$ interfaces with simple and noble metals.

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Mercury-Cadmium-Telluride is probably the most studied ternary semiconductor in recent years because of its widespread application for infrared detectors. The use of this material for device fabrication requires it to meet a number of challenges. Lattice, surface and interface instabilities in the alloy[1] are caused by the weakening of the Hg-Te bond relative to the Cd-Te bond.[2-3] Large changes in electronic properties are possible as a result of mechanical stress and may arise, for example, during metal contact fabrication. The relationship between local stoichiometry and semiconductor surface/interface properties is still largely unexplored. Recent pioneering studies have related the Schottky barrier height for the $Hg_{1-x}Cd_xTe$-Al[4] and $Hg_{1-x}Cd_xTe$-Au[5] interfaces to the non-stoichiometric composition of the semiconductor surface layer. In this paper we present preliminary results of investigations of the local morphology of the $Hg_{1-x}Cd_xTe(110)$-Cr interface. Results concerning the establishment of the Schottky barrier have been published previously.[6] To our knowledge this is the first investigation of a HgCdTe-refractory metal interface by means of surface sensitive techniques. Our study indicates that important differences exist in interface morphology and interface parameters (Schottky barrier height, interface width) relative to HgCdTe-noble and simple metal systems and emphasizes that careful analysis of the local environment of each elemental species during interface formation is the only way to obtain a complete picture of the local interface structure.

We performed synchrotron radiation photoemission measurements of interfaces prepared in situ by direct Cr sublimation on cleaved $Hg_{0.78}Cd_{0.22}Te(110)$ substrates. The HgCdTe single crystals were grown at McDonnell Douglas Research Laboratories using a modified Bridgman method. The bulk crystals exhibited a band gap of 0.175±0.01 eV and p-type conductivity with a room-temperature carrier concentration of 2×10^{16} cm^{-3} as determined from infrared transmission and Hall effect measurements, respectively. The samples were introduced into the photoelectron spectrometer (operating pressure $<5\times10^{11}$ torr) through a fast insertion device and cleaved in situ with varying degrees of success at obtaining mirror-like surfaces. Interfaces were prepared by Cr sublimation from a W basket at pressures $<5\times10^{-10}$ torr with coverage

Θ monitored by a quartz thickness monitor. The photoemission measurements were performed using monochromatized synchrotron radiation from a Grasshopper grazing incidence monochromator and the Tantalus electron storage ring at the Synchrotron Radiation Center of the University of Wisconsin-Madison. The photoelectrons were energy analyzed by means of a commercial double pass cylindrical mirror analyzer, with a typical overall resolution (electrons + photons) of 0.4-0.7 eV for $h\nu<90$ eV, and 0.8-1.0 eV at higher photon energies.

In Fig. 1 we show representative photoelectron energy distribution curves (EDC′s) for the valence band emission from the clean and Cr-covered semiconductor surface, at $h\nu=60$ eV. The EDC for the clean surface is in good agreement with the results of Silberman et al.[8] and Spicer et al.[9] and exhibits a Te p-derived density of states (DOS) feature within 3.5 eV of the Fermi level E_F and a second structure (4-7 eV) derived from unresolved Cd-s and Hg-s DOS features. Structure in the 8-12 eV binding energy range corresponds to the Hg $5d_{5/2}$ and $5d_{3/2}$ core levels and the unresolved Cd 4d doublet. This is more clearly seen from Fig. 2. In the left-most top section we show a decomposition of the core emission in terms of a Hg 5d lineshape (dashed line) and a Cd 4d line (dot-dashed line) for the clean HgCdTe surface. The Hg and Cd core lineshapes were obtained from HgSe and CdSe samples measured in the same experimental conditions. The emission from the Te 4d cores was also monitored with comparable surface sensitivity at $h\nu=110$ eV. As an example, we show in the right-most top section of Fig. 2 the Te4d line from a clean HgCdTe surface and from the same surface with 10 Å Cr coverage. The integrated intensities of the Hg, Cd and Te emission, normalized to the clean surface emission, is shown as a function of metal coverage in a semilogarithmic plot in the bottom-most section of Fig. 2.

The effect of Cr deposition can be seen in Figs. 1-2 from the fast attenuation of the Cd 4d and especially of the Hg 5d core emission. Solid lines in Fig. 2 correspond to exponential attenuation of the core emission. The resulting attenuation length of 0.7Å for the Hg 5d cores is far more rapid than can be reasonably expected from an escape-depth-driven mechanism, that would correspond to an attenuation length of 4-5Å. This indicates that Hg atoms migrate away from the surface layer. Since the binding energy of the Hg cores remains unchanged,[7] this process is likely to produce a surface layer completely depleted in Hg rather than a layer with graded Hg content, that would give rise to several inequivalent environments for Hg atoms within the sampling depth and possibly to broadening and shifts of the Hg 5d cores. Assuming a photoelectron escape depth of 4-5Å, the residual Hg5d emission observed at Θ=2 is consistent with complete Hg-depletion of a 13-16Å thick surface layer.

The relatively small attenuation of the Te 4d emission in Fig. 2 is mainly related to the presence of dissociated Te released at the overlayer surface. The existence of two different environments for the Te atoms at the interface is clearly shown in Fig. 3, where the experimental EDC's for the Te 4d core emission (solid line) can be successfully fitted (short-dashed line) in terms of two 4d components shifted ~.5 eV from each other. Escape depth-dependent studies[7] demonstrate that the Te II component corresponds to a Te-rich surface layer. Its binding energy corresponds to the one reported for elemental Te,[10] 0.4-0.5 eV above the Te 4d binding energy value for the clean HgCdTe surface. The Te I component starts at the clean surface binding energy value and then shifts 0.25 eV to lower binding energy as the Cr coverage increases up to 2Å. This may reflect the interaction of the Te I atoms with Cr, which has a lower electronegativity relative to Hg. The attenuation of the Te 4d emission as a function of metal coverage is shown in Fig. 4. The top section shows a semilogarithmic plot of the Te II integrated intensity, normalized to the clean surface Te 4d emission. The bottom-most section shows the analogous plot for the Te I component. Fig. 4 indicates that Te II is released at the surface for $0<\Theta<2$Å while Hg leaves the subsurface layer and Cr interacts directly with Te atoms (type I) in the semiconductor. The lower section of Fig. 4 shows that the Te I ($h\nu$=53 eV) attenuation for $\Theta>2$Å follows an exponential behavior with attenuation length of 7-8Å. Since this value is consistent, within experimental uncertainty, with the photoelectron escape depth, the Te I "substrate" emission shows, therefore, no evidence of Cr-Te interdiffusion at high metal coverage ($\Theta>2$).

For Θ<2 the Hg depletion of the surface layer and the shift of Te I 4d emission may both be related to the replacement of Hg-Te bonds with Cr-Te bonds. This is suggested by the difference in formation enthalpy of refractory metal tellurides relative to HgTe[11], that makes a Hg-Cr exchange reaction thermodynamically favored. This is supported by a comparison of the attenuation of the Hg emission with the Cr atomic density. At Θ=2 we have observed a 13-16Å Hg depletion layer from the film surface. The Te II surface contribution accounts for approximately 3Å.[7] The remaining 10-13 Å thick subsurface layer contains $1.2-1.5\times10^{15}$ atoms/cm^2, to be compared with a Cr coverage of 1.6×10^{15} atoms/cm^2 at Θ=2. Therefore the Hg attenuation is roughly consistent with a one-to-one exchange reaction between Cr and Hg atoms, followed by diffusion of the dissociated Hg away from the surface and subsurface layer.[12]

Our suggestion of a Hg-Cr exchange reaction for 0<Θ<2 is based on a) the thermodynamic trends b) the Hg depletion of the surface layer and its quantitative relationship with Θ c) the binding energy change of the Te I 4d line for Θ<2. More quantitive studies of the Te I 4d and Cr 3p core intensities, as well as of the Cr 3p binding energy are in progress to confirm this picture.[13] We emphasize that the term "exchange reaction" is used here to summarize a process in which initially Hg atoms are bonded to Te atoms in the homogeneous semiconductor and, upon Cr deposition, the surface and subsurface layers appear depleted of Hg while Cr-Te bonds are established.[15]

As for the Cd atoms in the interface region, at this preliminary stage it is not possible for us to determine if and to what extent a Cr-Cd reaction takes place. If it does, it cannot involve more than 10-15% of the Cd atoms in the subsurface region. A more complete discussion of this point will have to wait for a future report.[7]

The description of the $Hg_{1-x}Cd_xTe(110)$-Cr interface formation process that stems from this work is rather complex. At low metal coverages (Θ<2Å) Cr atoms replace all the Hg atoms in a 10-13 Å thick layer of the semiconductor, while some Te atoms are released from the semiconductor and form an elemental Te layer at the surface. Further Cr deposition (Θ>2Å) gives rise to a metallic Cr film covered by the dissociated Te species. This picture is rather different from the one proposed for the HgCdTe-Au[5] and HgCdTe-Al[4] interfaces. For HgCdTe-Au, Davis et al.[5] did report significant Te outdiffusion in the Au film, but no chemical shift of the Te 4d core was observed, leading to the conclusion that elemental Te was not the dominant species present. Furthermore, no change in the Hg/Cd ratio was observed at low metal coverage, when a 0.2 eV decrease of the band bending was observed relative to the clean surface. For the HgCdTe-Al interface, Daniels et al.[4] do not present any Te core data, but observe Hg-depletion near the surface and a large decrease of the Hg/Cd ratio at low metal coverage. An apparent 0.2 eV change of the interface position of the Fermi level was related by these authors to the variation of the Hg/Cd surface ratio. In the case of the $Hg_{1-x}Cd_xTe(110)$-Cr interface one has to distinguish the properties of the relatively thin surface and subsurface layers from those of the underlying semiconductor bulk. The subsurface layer forms with the exchange reactions that yield the apparent dramatic variations observed in the Hg/Cd ratio. The surface layer is constituted of dissociated Te that seems only a by-product of the exchange reaction that takes place in the subsurface layer. The information on the underlying "near-surface" bulk is carried primarily by the residual Hg 5d core emission, while the Te core and valence band emission primarily reflect the surface and subsurface electronic structure. We did not observe any variation in the Hg 5d core binding energy throughout the coverage range explored and we suggest that neither the local stoichiometry nor the band bending in the near surface region is affected by the reactions that take place in the two uppermost layers. In particular, interface reactions do not change the n-degenerate character[6] of the near-surface region.

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7. A description of the deconvolution procedure for the Hg 5d and Cd 4d cores, as well as of the Te 4d lineshape analysis will be presented in a longer paper: A. Franciosi, P. Philip and D.J. Peterman, unpublished.

8. J.A. Silberman, D. Laser, I. Lindau, and W.E. Spicer, J. Vac. Sci. Technol. 21, 154 (1982).

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11. The equilibrium phase diagram of the Cr-Te binary system is still not completely understood. The existence of CrTe, Cr_3Te_4, Cr_2Te_3, $CrTe_2$ and Cr_7Te_8 have been proposed, in some cases following observation of relatively wide ranges of homogenuity of the $Cr_{1-x}Te$ alloy, ranges associated with the coexistence of two or more of the above sthoichiometries. See for example, F.A. Shunk, Constitution

of Binary alloys, 2nd supplement, McGraw-Hill Book Co., New York, 1969.

The standard formation enthalpies of Cr tellurides are not known. However, their higher stability relative to HgTe is expected from a number of thermodynamic trends. Apart from the lower electronegativity of Cr relative to Hg, that suggest a larger ionic contribution to the bonding, we note that the known formation enthalpies of refractory metal tellurides are all well above the value of -7.6 k cal/mole appropriate for HgTe. In particular, most values are in the -20 to -40 k cal/mole range (for example TiTe -29.9; MnTe -26.6; $MoTe_2$ -32; WTe_2 -32; etc.) and none was reported below the ~-13.5 k cal/mole value of $NiTe_{1.1}$ and Ti_2Te. See K.C. Mills, Thermodynamic Data For Inorganic Sulphides, Selenides and Tellurides, Butterworths, London, 1974. Therefore, the formation of Cr-Te phases at the HgCdTe-Cr interface should be thermodynamically favored, at the expenses of the weaker Hg-Te bonds.

12. The local Cr/Te ratio in the subsurface region near the HgCdTe-Cr interface can be roughly estimated at $\Theta=2$ from the number of vacant Hg sites and by the number of Te atoms initially in the subsurface layer minus those that segregated at the surface and do not react with Cr. The result is consistent with CrTe, Cr_3Te_4, Cr_7Te_8 and possibly with Cr_2Te_3 stoichiometries, within the relatively large experimental uncertainty.

13. Studies of the Cr 3p line require complex deconvolutions of the Cr 3p and Te 4d lines at photon energies near threshold. The Cr 3p line is partially superimposed on the Te $4d_{3/2}$ component. Due to centrifugal barrier effects emission from the Cr 3p states can be emphasized relative to the 4d emission for photon energy near threshold while it is negligible, for example, in the spectra of Fig. 3, obtained at $h\nu=110$ eV.

14. See, for example, L.J. Brillson, Surf. Sci. Rep. 2, 123 (1982) and references therein.

15. The expression "exchange reaction" does not imply here as in the

case of GaAs-Al[16] that the adatom (Al) takes up cation (Ga) sites in the lattice, forming an ordered reacted layer (AlAs) of the same crystal structure. A conclusion of this kind would require a detailed structural analysis by means of LEED or SEXAFS or other scattering techniques that is not available at the present time.

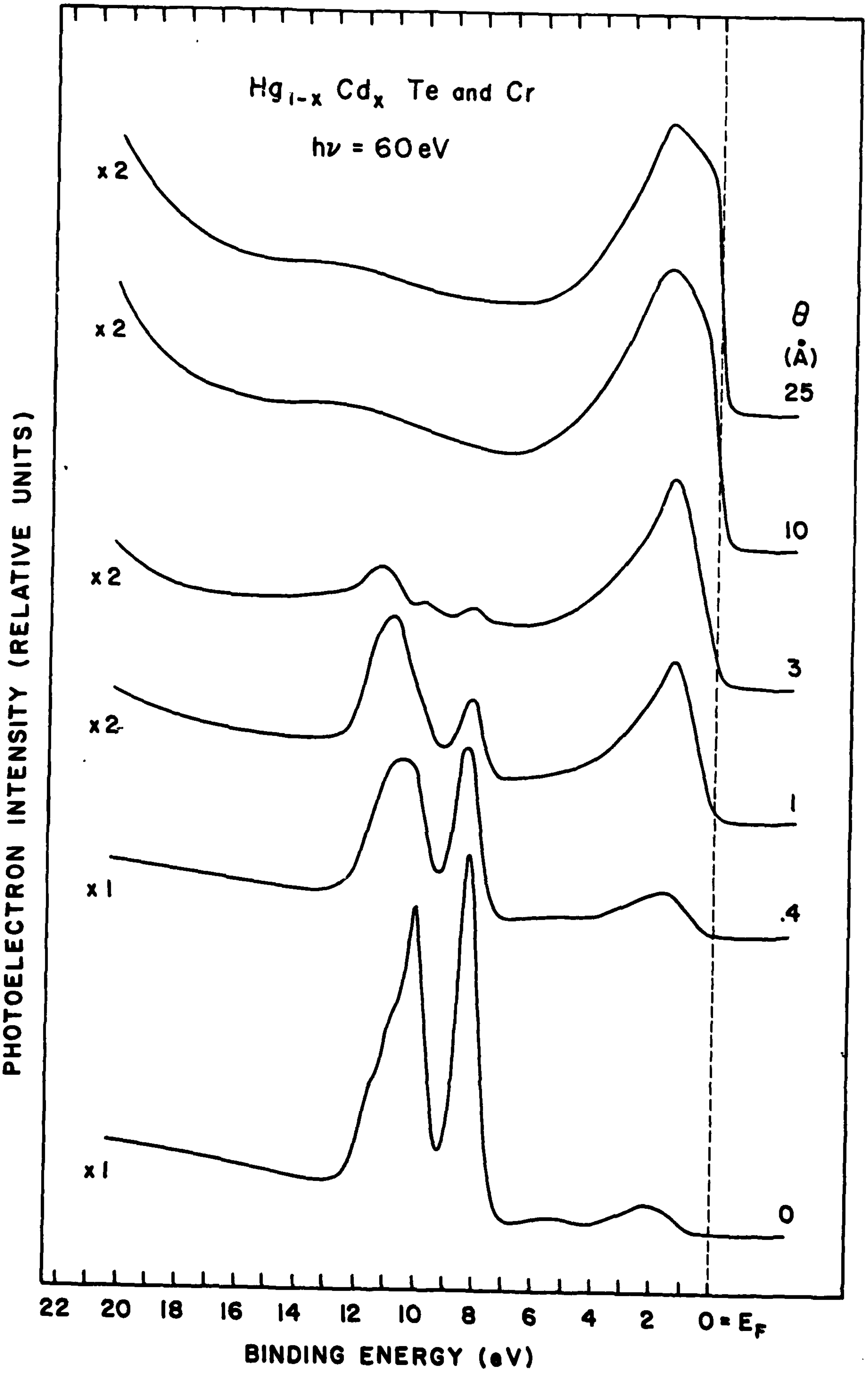
Figure Captions

Fig. 1 - EDC´s for the valence bands and Hg $5d_{5/2}$, Hg $5d_{3/2}$ and Cd 4d core levels (tic marks) for the $Hg_{1-x}Cd_xTe(110)$-Cr interface. The spectra are given in relative units and the topmost EDC´s are shown expanded by a scale factor of 2.

Fig. 2 - Top, left: decomposition of the Hg5d (dashed line) and Cd 4d (dot-dashed line) core emission from the clean HgCdTe surface. Top, right: Te 4d emission at $h\nu=110$ eV, for the clean HgCdTe surface and for the HgCdTe-Cr interface at $\Theta=10$. Bottom: integrated intensity of the Hg 5d, Cd 4d and Te 4d core emission is shown in a semilogarithmic plot after normalization to the clean surface emission and to monochromator output.

Fig. 3 - Te 4d core emission from the $Hg_{1-x}Cd_xTe$-Cr interface. Solid line: experiment. Shrot-dashed line: result of a best fit in terms of a Te I subsurface component (long-dashed line) and a Te II surface component (dot-dashed line).

Fig. 4 - Semilogarithmic plot of the integrated intensity of the Te 4d core emission from the $Hg_{1-x}Cd_xTe$-Cr interface, normalized to the Te 4d emission from the clean surface. Top: The Te II component corresponds to dissociated Te released at the surface during the first interface formation stage. Bottom: The Te I component corresponds mostly to Te atoms in the subsurface layer, where the Cr-Hg exchange reaction takes place for $\Theta<2$Å.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x 2
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(Å)
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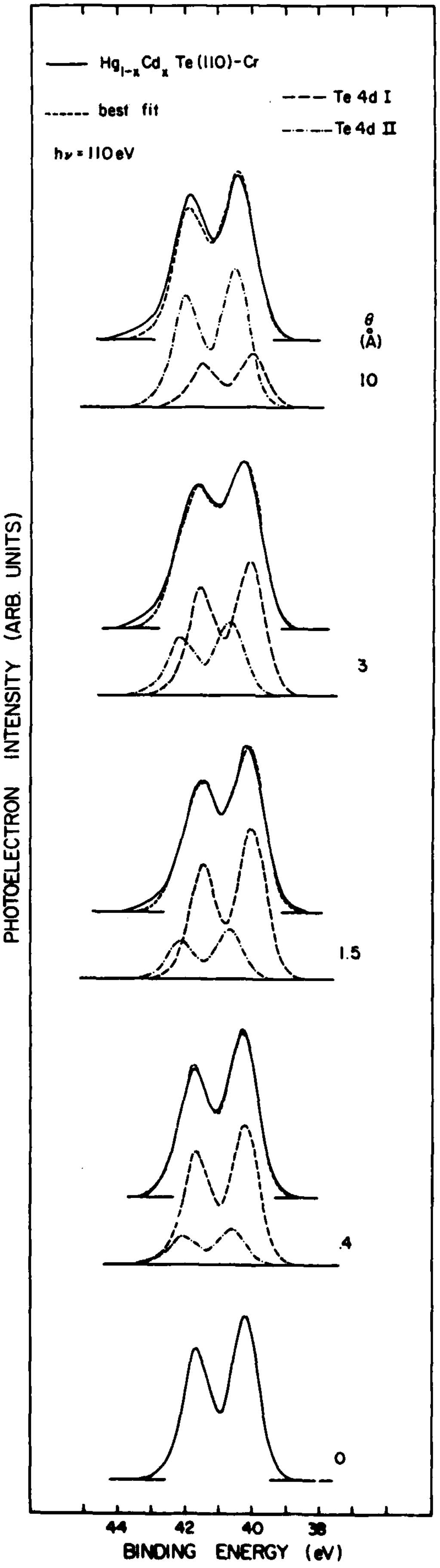

Hg1-x Cdx Te (110)-Cr
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Te 4d II
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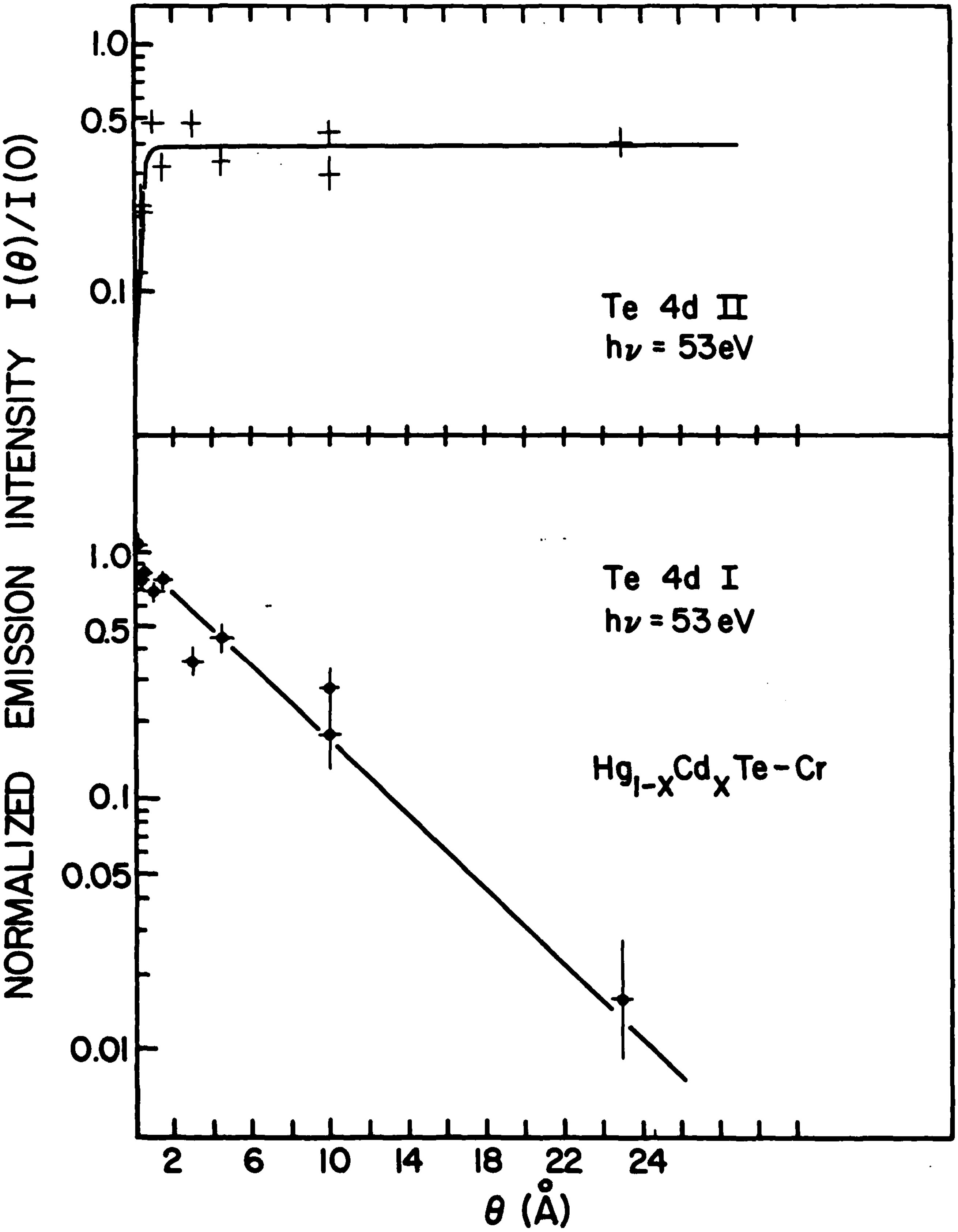

NORMALIZED EMISSION INTENSITY I(θ)/I(0)
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0.5
0.1
Te 4d II
hν = 53eV
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0.5
0.1
0.05
0.01
Te 4d I
hν = 53 eV
Hg1-xCdxTe-Cr
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22
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θ (Å)

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