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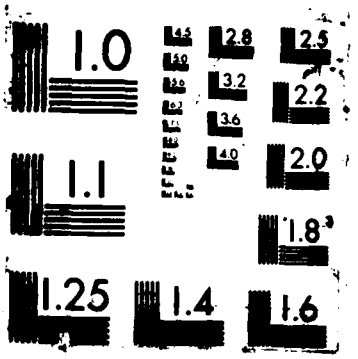
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SUMMARY ABSTRACT: CdTe(110)-Mn INTERFACE REACTION AND THE FORMATION OF NON-EQUILIBRIUM TERNARY SEMIMAGNETIC SEMICONDUCTOR ALLOYS

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In the past few years our understanding of the electronic properties of ternary semimagnetic semiconductors has been greatly improved by systematic photoemission spectroscopy studies of bulk single crystal alloys[1-5]. These materials can be synthesized in the form of high quality single crystals in a wide but limited range of composition (for example, $0<x<0.70$ for $Cd_{1-x}Mn_xTe$). They exhibit composition-dependent optical and transport properties and, because of the presence of Mn or Fe 3d orbitals, new magneto-transport and magneto-optical properties[6-9].

We have synthesized for the first time non-equilibrium ternary alloys through interface reaction in situ of CdTe single crystals and Mn thin films. We analyzed the electronic structure of these phases with synchrotron radiation resonant photoemission, and probed their composition through escape-depth-dependent core level photoemission. We also obtained for comparison results for bulk $Cd_{1-x}Mn_xTe$ single crystals cleaved in situ at composition x=0, 0.20, 0.32 and 0.68. The bulk data confirm that interface reaction is an effective method of producing non-equilibrium alloys, and allowed us an independent calibration of the composition of the surface alloy.

Details of the experimental procedure and sample preparation will be given in a longer forthcoming paper[10]. Oriented CdTe single crystals were cleaved in

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Because of the high stability of the divalent Mn atomic configuration Mn atoms diffuse readily in II-VI semiconductors. We have synthesized for the first time non-equilibrium ternary alloys through interface reaction in situ of CdTe single crystals and Mn thin films. We analyzed the electronic structure of these phases with synchrotron radiation resonant photoemission and probed their composition through escape-depth-dependent core level photoemission.

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situ in a photoelectron spectrometer at pressures in the 10^{-11}torr range. Sequential submonolayer deposition of Mn from a resistively heated source was performed in the same pressure range, with thickness monitored by a quartz microbalance. The substrate was at room temperature during deposition. Single crystals of bulk $Cd_{1-x}Mn_xTe$ alloys grown at Purdue University through a modified Bridgeman method were also cleaved in situ for comparison. Synchrotron radiation from the 1 GeV electron storage ring at the Synchrotron Radiation Center of the University of Wisconsin-Madison was monochromatized by a 3m toroidal grating monochromator and focused onto the sample. Angular integrated photoelectron energy distribution curves (EDC's) were obtained with a hemispherical energy analyzer. The overall resolution (electrons + photons) was typically 0.1eV in the 15-70eV energy range, and about 0.25eV in the 70-150eV range.

Representative EDC's for the valence band emission of the bulk ternary alloys at x=0, 0.20, and 0.68 are shown in the leftmost section of fig. 1. EDC's for the valence band emission from the CdTe-Mn interface appear in the rightmost section of fig. 1, at metal coverages of 0.2, 0.4, 1.0 and 3.0Å. In terms of the substrate (110) surface atomic density it is 1 monolayer = 0.83Å. The spectra of fig. 1 have been obtained at a photon energy of 50eV, near the Mn 3p-3d resonance[1], and emphasize the Mn 3d contribution. The EDC's for the bulk alloys have been normalized to the integrated Cd core intensity taking into account the Cd content from X-ray microprobe analysis[10]. The EDC's for the CdTe-Mn interface are shown in relative units. The zero of the binding energy scale corresponds to the position of the valence band maximum as derived from a linear extrapolation of the leading valence band edge.

The interface EDC's in fig. 1 show striking similarities with those of the ternary alloys. Emission features in the 0-2eV range, at 3.4eV and in the 5-9eV range reflect mostly 3d emission as demonstrated by resonance-antiresonance

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difference curves[7-10], or ternary-binary alloy difference curves[10]. A major emission feature in the 9-11eV range corresponds to the Cd 4d cores, that appear progressively attenuated with increasing coverage in the interface spectra. We note that no Fermi-level cut-off appears in the interface EDC's for coverages below 3 monolayers, that the valence band emission is dramatically different from that of an unreacted Mn film[10], and that the major Mn 3d feature appears at about 3.4eV in all interface and bulk alloy spectra.

Independent evidence of CdTe-Mn interdiffusion is provided by the coverage dependence of the core emission of the different elemental species. We measured the integrated intensity of the Cd 4d doublet (at $h\nu$=40 and 95eV) and of the Te 4d core levels (at $h\nu$=58 and 110eV) in order to obtain escape-depth-dependent information on the surface composition[10]. Since direct emission from the Mn 3p cores was insufficient to provide a reliable indication of the Mn concentration, we used the integrated area of the valence band resonance-antiresonance difference curves[10] to estimate the overall Mn emission intensity. The Mn emission in the submonolayer and monolayer coverage range increases with coverage at a rate that is less than 50% of that expected from the growth on an unreacted Mn film[10]. Correspondingly the Cd emission decreases at a rate that is more than twice that expected from layer-by-layer coverage of the CdTe substrates[10]. This suggests that for coverages up to 1-3Å, Mn diffuses into the semiconductor substrate displacing part of the Cd atoms in the matrix.

The decrease with coverage of the Te emission appears much slower than that of the Cd emission. The apparent Te/Cd ratio increases by a factor of 5 at 3Å coverage, further indicating a preferential Te-Mn interaction with Cd depletion[10]. Core emission data at different escape depth (3-10Å) show only small variations of the surface composition within the sampled depth, suggesting a substantial room temperature diffusion length for Mn in CdTe[10]. In fig. 1 a

weak metallic Fermi level emission is seen at 3Å coverage. However, only at much higher coverages (θ>20Å) the EDC's converge to a bulk-Mn emission spectrum, with intense emission at E_F and no evidence of the 3.4eV Mn 3d localized feature.

We can use the low-escape-depth Mn/Cd and Mn/Te emission intensity ratios from the ternary alloy to estimate the composition at the CdTe-Mn interface. Because of the relatively large Mn diffusion length an average stoichiometry can be defined in the first few monolayers of the semiconductor[10]. At coverages of 0.2, 0.4 and 1.0Å, respectively, the Mn/Cd and Mn/Te ratios are consistent with composition x=0.23±0.06, 0.35±0.09, and 0.74±0.19, respectively. At 3Å the presence of unreacted Mn prevents a rough estimate of this kind[10].

Binding energy and width of the main Mn 3d feature at 3.4eV remain unaffected by composition changes. In the picture proposed in ref. 5 the 3.4eV feature reflects complete ligand-induced screening of the d-hole ($d^5\underline{L}$ final state) and is therefore the one that can be more appropriately compared to the result of one-electron first-principle calculations. The agreement with the local density calculations of Wei and Zunger is remarkable[7-10]. If one considers the intensity of the different Mn emission features in the resonance-antiresonance difference curves[10] as a function of coverage, one observes that the emission intensity in the 0-2eV region follows closely the behavior of the major 3.4eV structure. The satellites in the 5-9eV range appear instead to increase in relative intensity at coverages near 3Å, were Fermi level emission is also observed. If the satellites correspond to the unscreened d^4 final state configuration, as proposed in ref. 5, one could expect them to increase in intensity when unreacted Mn is formed. On the other hand, the formation of a metallic Fermi-level should be accompanied by an effective d-hole screening due to the formation of d-bands, and the d^4 satellite should eventually disappear, so that this argument supports only in part the identification proposed in ref. 5.

In conclusion, we have shown that atomic interdiffusion at the CdTe-Mn interface can be exploited to synthesize ternary surface alloys in a wide range of composition, and that these alloys represent important test cases to verify our understanding of the electronic structure of semimagnetic semiconductors. This work was supported in part by the Graduate School of the University of Minnesota and by the Office of Naval Research. We thank J.K. Furdyna for providing us with the bulk crystals used in the present study and the whole staff of the University of Wisconsin-Madison Synchrotron Radiation Center (supported by NSF) for their cheerful support.

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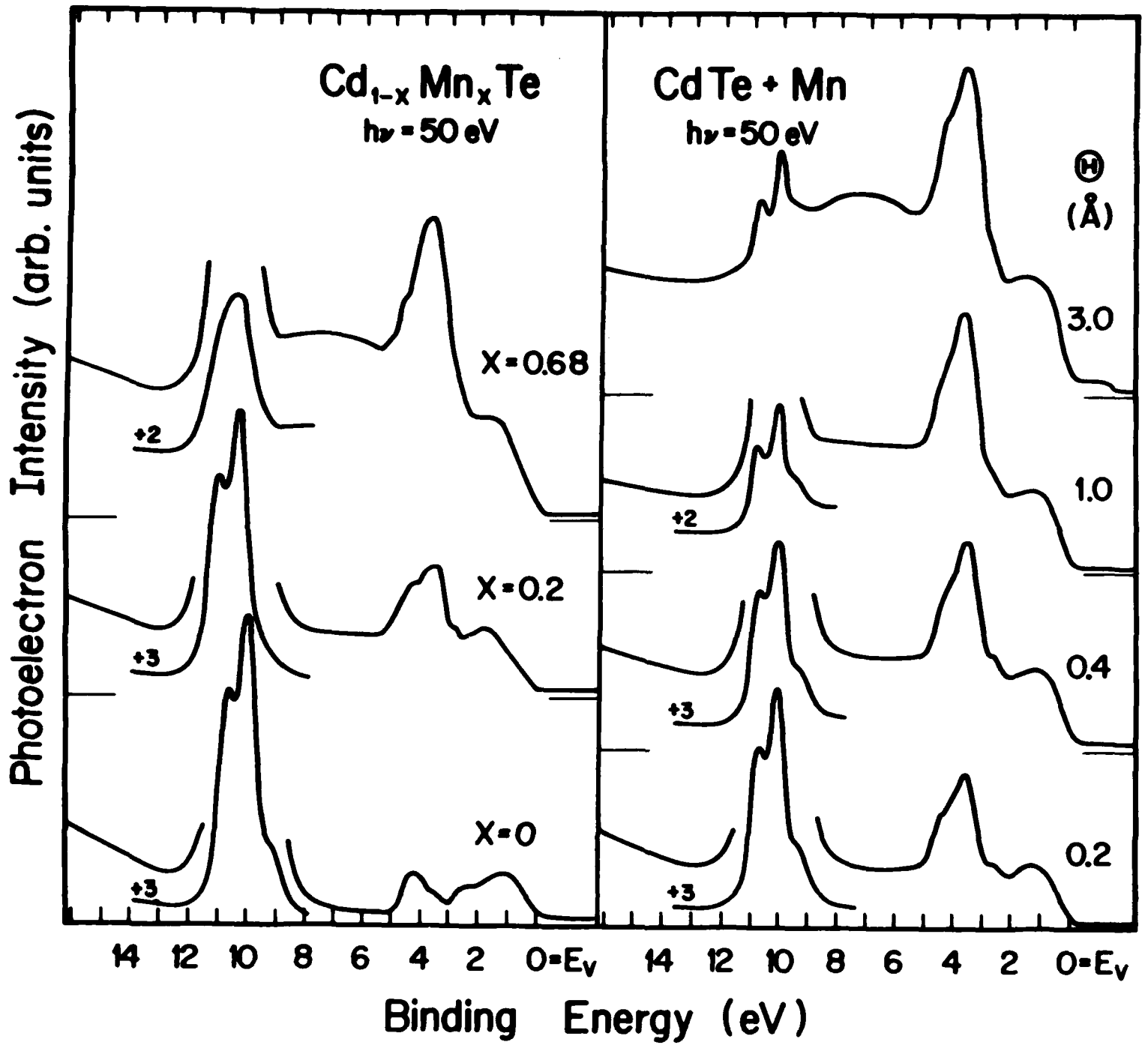
10. A more extensive report will appear elsewhere: A. Wall, A. Raisanen, S. Chang, N. Troullier, A. Franciosi, R. Reifenberger, and U. Debska, to be published.

Figure Captions

Figure 1

Left: Photoelectron energy distribution curves (EDC's) for the valence band emission of cleaved $Cd_{1-x}Mn_xTe$ alloys at x=0, 0.20 and 0.68. The Cd 4d integrated emission was used to normalize the spectra to the bulk composition, as measured through X-ray microprobe analysis. The photon energy of 50eV corresponds to the Mn 3p-3d resonance and enhances the Mn 3d contribution.

Right: EDC's for the valence band emission from the CdTe(110)-Mn interfaces as a function of metal coverage θ. For θ<3Å atomic interdiffusion yields ternary semimagnetic surface semiconductor alloys.


Cd1-x Mnx Te
hν = 50 eV
CdTe + Mn
hν = 50 eV
Θ (Å)
3.0
1.0
0.4
0.2
X = 0.68
X = 0.2
X = 0
+2
+3
+2
+3
+3
Photoelectron Intensity (arb. units)
14 12 10 8 6 4 2 0=EV
14 12 10 8 6 4 2 0=EV
Binding Energy (eV)

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