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Correlation of photoluminescence measurements with the composition and electronic properties of chemically etched CdTe surfaces

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We have performed photoluminescence (PL) measurements on chemically etched single-crystal p-CdTe. In addition, x-ray photoemission measurements have been used as a guide to surface stoichiometry for each chemical treatment. The relative intensities of the 0.875 ± 0.005 eV and 1.125 ± 0.005 eV PL bands are seen to be linked to the preferential depletion of either Cd or Te from the CdTe surface. Furthermore, the energies of these deep level transitions measured at $T = 4$ K show remarkable agreement with the two values of Schottky barrier, $\Phi_b = 0.72 \pm 0.02$ eV and $\Phi_b = 0.93 \pm 0.02$ eV, normally obtained at room temperature for Au and Sb contacts to n-CdTe.

Chemical etching remains the most important way of preparing semiconductor surfaces for device applications. Very often the electrical behavior of metal-semiconductor contacts is significantly influenced by the etching procedure; this is particularly so for the metal-CdTe interface. This system, therefore, is an attractive one as a vehicle to explore the manner in which electrical contacts are affected by surface layers and associated interface states. In a previous publication[1] it has been shown that Schottky barrier heights at Au-CdTe and Sb-CdTe interfaces depend strongly on the choice of chemical etchant used to prepare the surface prior to metallization. When the n-CdTe surface was etched with a Br methanol solution, barrier heights of either 0.72 ± 0.02 eV or 0.93 ± 0.02 eV were measured. Exactly which value was obtained appeared to depend on the fine details of the etching process, in a manner that was difficult to control. It was found, however, that etching solutions which left the CdTe surface slightly deficient in Te produced barrier heights of 0.93 eV only. Analysis of the experimental data led to the suggestion that the pinning levels associated with the 0.72 and 0.93 eV barrier heights are due to defects near the surface of the CdTe, with the defect type and concentration depending on the etching procedure.

In this letter we describe an investigation of chemically treated CdTe surfaces by photoluminescence (PL) spectroscopy. We show that the different chemical treatments which influenced barrier height measurements also lead to drastic changes in the PL spectra. Furthermore, the deep levels identified in these PL spectra appear to mirror the pinning behavior observed in the Schottky barrier measurements, clearly indicating that the PL technique is a most valuable tool to investigate the electronic structure of the metal-CdTe interface and the influence of deep levels on Fermi level pinning. Photoluminescence has, of course, been used very successfully to probe the influence of surface preparation on the surface recombination velocity for GaAs[2] and InP,[3,4] and has also revealed cleavage-induced defect levels near the surface of InP[5] single crystals. Other workers[6] have also related the position of the Fermi level at annealed Au-CdTe interfaces to specific transitions observed in the PL spectra of these interfaces.

The single-crystal material used in this study was of low resistivity ($\sim 60\ \Omega$ cm) p-type CdTe purchased from Eagle Picher Inc., USA. To ensure that all the etches were applied to the same material, all the samples used were cut from the same crystal. The surfaces were initially polished to a finish of 0.25 μm using diamond paste and then degreased with acetone. They were then treated with the following etches. (a) Bromine/methanol (Br/Me): ~ 2 min immersion in a 1% bromine in methanol solution. (b) Br/Me + KOH: As for (a), followed by ~ 3 min in 1 M KOH in methanol solution. (c) Br/Me + hydrazene: As for (a), followed by ~ 3 min in hydrazene-hydrate. (d) Br/Me + reducing etch: As for (a), followed by ~ 4 min in a hot (80–90 °C) solution of 0.5 M $Na_2S_2O_4$ and 2 M NaOH in de-ionized water. (e) Oxidizing etch: ~ 20 s immersion in a solution containing 5 g of $K_2Cr_2O_7$, 10 ml of conc. HNO_3, and 20 ml of de-ionized water. (f) Oxidizing etch followed by reducing etch.

PL measurements were carried out at $T = 4$ K using a Ge detector and excitation from a 10 mW He-Ne laser ($\lambda = 632.8$ nm). The excitation intensity was ~ 100 mW/cm^2 and all measurements were completed within 48 h of the samples being etched. X-ray photoemission (XPS) measurements were taken with a VG Scientific ESCALAB, using an experimental configuration which has been described elsewhere.[1]

Figure 1 contains typical XPS spectra, in this case for p-CdTe surfaces etched with Br/Me, Br/Me + KOH, and Br/Me + reducing agent. For the stoichiometric clean cleaved CdTe surface, the ratio of the areas associated with the Cd $3d$ and Te $3d$ peaks (Cd $3d$/Te $3d$) is around 0.7. This reference point allows the stoichiometry of the surfaces leading to the spectra shown in Fig. 1 to be estimated. Clearly the Br/Me etched surface, with a Cd $3d$/Te $3d$ ratio of 0.34 appears deficient in Cd. Chemical etching with Br/Me + KOH gives a ratio of 0.67, close to stoichiometry, whereas Br/Me + reducing agent yields a ratio of 0.87, indicating a slight deficiency of Te. The combination of Br/Me with hydrazene has a Cd/Te area ratio of ~ 0.85 while the oxidizing etch and oxidizing plus reducing etches show values of 0.26 and 0.71, respectively. The observed trend agrees well with our earlier XPS data for n-CdTe. In addition, in these spectra there is an increased oxygen content, in the form of Te oxide, since these surfaces had been exposed to the atmosphere for longer times.

Figure 2 displays PL spectra for the six surfaces studied,

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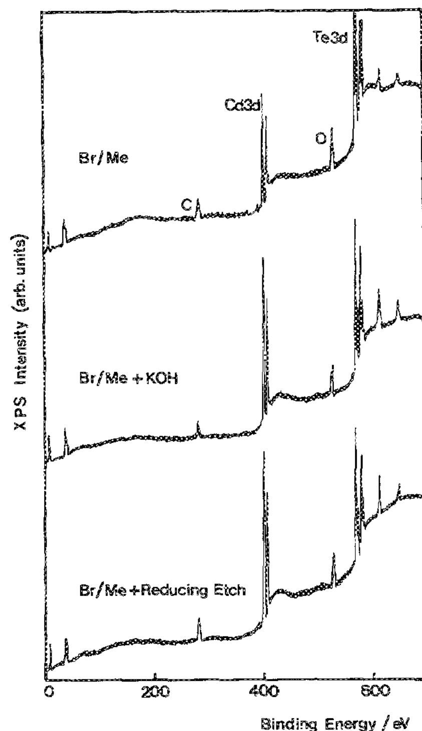

FIG. 1. X-ray photoelectron spectra for single-crystal p-type CdTe etched in different ways.

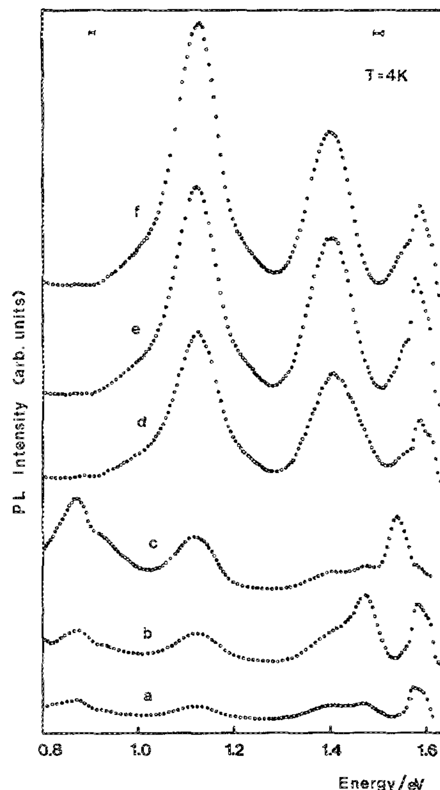

FIG. 2. Photoluminescence spectra for p-CdTe samples chemically treated with (a) oxidizing etch, (b) oxidizing + reducing etches, (c) Br/Me, (d) Br/Me + reducing etch, (e) Br/Me + KOH, and (f) Br/Me + hydrazine.

each spectrum being plotted in unit energy bandwidth. No correction has been made for the response of the detection system as the responsivity of the Ge detector is known to vary smoothly over this energy range and the spectrometer does not introduce any sharp anomalies either. The two horizontal bars at the top of the figure depict the resolution of the spectrometer at 0.9 and 1.5 eV, respectively. The Br/Me-etched surface shows a PL band at 0.875 ± 0.005 eV (~ 0.9 eV) which is more intense than the PL peaks at 1.125 ± 0.005 eV (~ 1.1 eV) and 1.400 ± 0.005 eV (~ 1.4 eV). The surfaces which have been treated with an oxidizing etch and a combination of oxidizing + reducing etches also contain a contribution at ~ 0.9 eV in their PL spectra, although in both cases the intensity is lower. Dramatic changes occur when a second treatment is used after the initial etch with Br/Me solution. The PL band at ~ 0.9 eV disappears completely, and the intensities of the peaks at ~ 1.1 and ~ 1.4 eV increase greatly. These three surfaces have previously been observed to be close to stoichiometry or deficient in Te.[7–9]

Comparison of the PL spectra in Fig. 2 reveals the presence of up to seven transitions. These can be grouped as follows: transitions involving deep levels at 0.875, 0.92, 1.125, 1.4, and 1.475 eV; edge transitions at 1.54 and 1.59 eV. The latter contain a number of separate lines[10] which are not resolved in our data. We shall concentrate on the PL peaks which involve deep levels, namely the transitions around 0.9, 1.1, and 1.4 eV. The exact nature of the recombination centers which lead to these PL bands remains unclear.[11] However, the PL transition at ~ 0.9 eV is most intense for the Br/Me-etched surface which appears to be deficient in Cd. Similarly, the 1.1 and 1.4 eV PL features are most noticeable for surfaces which tend towards stoichiometry or Te deficiency. The 1.1 eV transition has previously been linked to a simple Te defect.[12]

Diodes formed by evaporating Au or Sb onto Br/Me-etched surfaces of n-CdTe usually show barrier heights Φ_b of 0.72 ± 0.02 eV or 0.93 ± 0.02 eV at room temperature.[13] The likelihood of obtaining $\Phi_b \sim 0.93$ eV has been shown to be increased by following the initial Br/Me etch with treatment in KOH.[1] The probability of obtaining the higher barrier is enhanced further by using Br/Me + hydrazine or Br/Me + reducing agent. If we allow for the CdTe band gap being ~ 0.16 eV larger at $T = 4$ K than $T = 300$ K, then there appears to be remarkable agreement between $\Phi_b \sim 0.72$ eV and the PL transition at 0.875 ± 0.005 eV, as well as $\Phi_b \sim 0.93$ eV and the PL transition at 1.125 ± 0.005 eV. The PL spectrum for the Br/Me-etched surface shows the most intense deep level emission at ~ 0.9 eV. Hence, we suggest that Au/n-CdTe or Sb/n-CdTe diodes possessing values of $\Phi_b \sim 0.72$ eV are more likely to occur for CdTe surfaces where the 0.9 eV PL transition is more intense than the PL peak at 1.1 eV. Likewise, barrier heights of ~ 0.93 eV are more probable for these metals on CdTe surfaces where the PL transition at 1.1 eV dominates. Obviously, this is a qualitative assessment which will depend on the etchant concentration and the effective etching time. For example, both Br/Me and the oxidizing etch are known[14] to deplete Cd from the surface of cadmium telluride. The difference in composition between these two etched surfaces is reflected by their PL spectra in Fig. 2. It has also been shown[1] that Au or Sb diodes fabricated on n-CdTe surfaces treated with an

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oxidizing etch give $\Phi_b \sim 0.93$ eV, unlike the Br/Me-etched surfaces which show either $\Phi_b \sim 0.72$ eV or $\Phi_b \sim 0.93$ eV. Examination of the PL spectrum which corresponds to the oxidizing etch reveals that the 0.9 and 1.1 eV PL bands have approximately the same intensity, which suggests that it is more likely that diodes formed on this CdTe surface will give $\Phi_b \sim 0.93$ eV. A further point to note is that CdTe surfaces deficient in Cd exhibit a much lower overall PL intensity than the more stoichiometric or slightly Te-deficient surfaces. This can be ascribed to increased surface recombination, and a similar increase in surface leakage currents is observed[15] for diodes prepared on CdTe surfaces which are deficient in Cd.

In conclusion, we have carried out photoluminescence measurements on single-crystal *p*-CdTe and shown that the spectra are dramatically influenced by the chemical etching treatment to which the surface has been subjected. Two deep levels observed in these spectra appear to be closely correlated to the appearance of two values of Schottky barrier height at ~ 0.72 and ~ 0.93 eV for Au and Sb contacts on *n*-CdTe. XPS investigations demonstrate that different chemical treatments alter the stoichiometry of the CdTe surface and indicate that the deep levels observed with photoluminescence are related to anion and cation deficiencies for this semiconductor.

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