Positron trapping at divacancies in thin polycrystalline CdTe films deposited on glass

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We have performed positron annihilation experiments on CdTe films grown by vacuum evaporation at 220 °C on both plain glass and indium-tin-oxide-coated glass substrates. By checking the linearity of the valence annihilation parameter $S$ versus the core annihilation parameter $W$ we introduce a method to analyze the data which directly shows that the same vacancy defect can be present in all the films. By comparing the core annihilation parameter at the defect to that at the $V_{Cd}$ vacancy we can identify this defect as the divacancy $V_{Cd}V_{Te}$. Its concentration in the films decreases from about $10^{18}$ to less than $10^{16}$ cm$^{-3}$ after annealing in air at 400 °C for about 30 min. Chlorine doping seems to stabilize the divacancies.

The $n$-CdS/p-CdTe heterojunction solar cell is currently a leading contender for a low cost thin film solar cell for terrestrial use. Deposited as thin polycrystalline layers onto SnO$_2$-coated glass by a variety of scaleable techniques the device is under industrial development by a number of European, American, and Japanese companies. Presently efficiencies in excess of 14% and 10% have been reported for laboratory scale devices and larger area modules, respectively. The CdTe thin film may be deposited by a variety of techniques, but usually requires post-deposition processing to render it type and sufficient conducting for use in a solar cell. Typically, this entails "dipping" the CdTe layer into a solution of CdCl$_2$ in methanol (MeOH), followed by a heat treatment in air at 300–400 °C for about 30 min. The procedure was developed empirically, and the underlying physical mechanisms of the process are not known and are currently the subject of much research. The present positron annihilation study was intended to show whether there were any changes in the vacancy distribution between the as-deposited and treated CdTe films.

Positron diffusion and annihilation are very sensitive to negatively charged and neutral vacancy-type defects in semiconductors and provide a direct method for their detection. To investigate the thin CdTe films we use a slow positron beam and perform Doppler broadening measurements. We introduce a new way to use the valence and core annihilation Doppler parameters $S$ and $W$. By checking the linearity of the $S$ vs $W$ function we can directly show that the same vacancy defect can be present in all the films.

Three types of CdTe films have been investigated: (a) as grown; (b) heat treated at 400 °C in air for 30 min; (c) dipped in CdCl$_2$/MeOH and heat treated as in (b). The films (Table I) were deposited at 220 °C onto glass or indium-tin-oxide (ITO)-coated glass by vacuum evaporation from the congruent sublimation of the compound at 750 °C. A molecular beam epitaxy In-doped CdTe layer (ZD16, $n=1.3 \times 10^{17}$ cm$^{-3}$), grown on a CdZnTe substrate (4% Zn) at 200 °C was also measured for comparison with the films. Positron annihilation in the films is studied as a function of depth by recording the $\gamma$-annihilation line, $E_\gamma=511$ keV±$\Delta E_\gamma$, as a function of positron energy $E$ (Ref. 5). The 511 keV annihilation line is Doppler broadened, $\Delta E_\gamma$, due to the momentum of the annihilating electron–positron pair. The momentum distribution is characterized by the line shape parameters $S(W)$ defined as the relative number of annihilation events in the centroid (wings) of the 511 keV line. Annihilations with low (high) momentum electrons fall to the energy window of $S(W)$. Therefore, mainly valence electrons contribute to $S$ whereas only core electrons are represented in $W$. The annihilation parameters at the defect, $S_d$ and $W_d$, can be used as fingerprints of the open volume of the defects. The larger the open volume, the lower the core annihilation parameter $W_d$ and the higher the valence annihilation parameter $S_d$.

In a variable energy slow position beam at the Helsinki University of Technology positron energy was varied between 0.1 and 25 keV. This energy range corresponds to a mean penetration depth, $\langle z \rangle = 68 [E(\text{keV})]^{1.6}$ Å, of up to 1.2 μm in CdTe. Positrons are stopped well before the substrate since all the films are more than 3 μm thick. For each positron energy, the 511 keV annihilation line was measured using an intrinsic Ge detector with an energy resolution of 1.64 keV at 1.33 MeV gamma energy ($^{60}$Co). The energy windows set in the experiments were $0<|\Delta E_\gamma|<0.83$ keV for the valence annihilation parameter $S$ and $2.49$ keV<$|\Delta E_\gamma|<7.30$ keV for the core annihilation parameter $W$.

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The data were analyzed with the VEPFIT program. The films were found to be homogeneous at depths larger than 0.2 μm and so each film can be characterized by a valence (core) annihilation parameter $S_{\text{film}}(W_{\text{film}})$. As seen in Table I, $S_{\text{film}}$ and $W_{\text{film}}$ parameters vary strongly from one film to the other. The lowest $S_{\text{film}}$ value is observed in the CdTe (In) molecular-beam epitaxy (MBE) layer and the highest in the CTD1 film. The $W$ values reach also extrema in these two films but, as it should be, in a reverse way to $S$. The variations of $S_{\text{film}}$ and $W_{\text{film}}$ indicate that the films contain vacancy-type defects. The films which contain the highest density of defects are the as-grown CTA and CTD1 films. The MBE layer where the value for $S_{\text{film}}(W_{\text{film}})$ is the lowest (highest) contain the lowest density of defects.

When a fraction $f_d$ of positrons annihilated from only one other state $d$ than the bulk, $S_{\text{film}}$ and $W_{\text{film}}$ take the average value

$$S_{\text{film}} = (1 - f_d)S_b + f_d S_d,$$
$$W_{\text{film}} = (1 - f_d)W_b + f_d W_d. \quad (1)$$

by eliminating the fraction $f_d$ one obtains a linear relation between $S_{\text{film}}$ and $W_{\text{film}}$:

$$S_{\text{film}} = S_b + R_d(W_b - W_{\text{film}}), \quad (2)$$

where the slope $R_d$ is characteristic of the steady state $d$

$$R_d = \frac{S_d - S_b}{W_b - W_d}. \quad (3)$$

To determine whether positrons annihilate from the bulk state and only one other state $d$ in the films it has been proposed earlier to calculate the ratio $R = (S_{\text{film}} - S_b) / (W_b - W_{\text{film}})$ and check its invariability. Instead of using this method which requires that $S_b$ and $W_b$ are known, we propose rather to check whether the $S_{\text{film}}$ and $W_{\text{film}}$ parameters are linearly related according to Eq. (2). If the measured $(S_{\text{film}},W_{\text{film}})$ values in the different films lie on a straight line on the $(S,W)$ plane, it means that the films contain defects for which the defect parameter $R_d$ [Eq. (3)] is the same and given directly by the slope of the line. The simple and straightforward way to explain that $R_d$ can remain constant when the concentration of defects varies in the different films is to attribute the positron trapping to the same vacancy-type defect in all the films.

In Fig. 1 we plotted the valence annihilation parameter, $S_{\text{film}}$, as a function of the core annihilation parameter, $W_{\text{film}}$. It is obvious that all experimental points fit well to a straight line. This suggests that the films contain the same vacancy-type defect characterized by the value $R_d = 2.02(2)$ determined from Fig. 1 by linear regression. Its concentration varies from one film to the other.

It is noticeable in Fig. 1 that the data for the MBE layer fall also on the same straight line as those for the films. This leads us to conclude that the MBE layer contains either (i) the same vacancy-type defects as the films but at a smaller concentration, or (ii) is free of them. This MBE layer gives the lowest $S$ parameter (and highest $W$) we have so far measured in various other CdTe materials. Consequently, we consider in the following that the parameters in this layer are characteristic of the free bulk annihilation with the values $S_b = 0.561(1)$ and $W_b = 0.0428(1)$.

One can also read directly in Fig. 1 that the relative change from bulk annihilation to annihilation in the CTD1 film is 4% for $S$ and 30% for $W$. These relative changes are larger than those measured for monovacancies in various

![FIG. 1. Valence annihilation parameter $S$ as a function of core annihilation parameter, $W$, in vacuum evaporated thin CdTe films (●) and defect-free CdTe (n, $n=1.3 \times 10^{17}$) MBE layer (○). For comparison, the $(S,W)$ curve is also shown for $V_{Cd}$ vacancies detected in bulk crystals (□) (see Ref. 8). Right and upper axes give the relative values of the annihilation parameters compared to the bulk.](image-url)
TABLE II. Experimental core annihilation parameter \((W_i)\) and theoretical relative core annihilation probability \((A_i^f)\) in defect-free CdTe, monovacancies of both lattice sites and divacancy.

<table>
<thead>
<tr>
<th>(W_i)</th>
<th>(V_{Cd})</th>
<th>(V_{Te})</th>
<th>(V_{Cd}-V_{Te})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0428</td>
<td>0.03646</td>
<td>(0.03646)</td>
<td>0.03085</td>
</tr>
<tr>
<td>0.12772</td>
<td>0.07254</td>
<td>0.09695</td>
<td>0.060288</td>
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<td>0.3303</td>
<td>0.3026</td>
<td>0.3761</td>
<td>0.3117</td>
</tr>
<tr>
<td>1</td>
<td>0.846</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.831</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(A_i^f = \frac{\lambda_f}{\lambda_f + \lambda_i^f} \)  \(\lambda_i^f\) is found by measuring the ratio \(W_i/W_{i'}\) and \(A_i^f = A_i^f/\lambda_i^f\) is given by Table II, the relative core annihilation parameter \(A_i^f\) calculated for the perfect lattice, \(V_{Cd}\), \(V_{Te}\), and \(V_{Cd}-V_{Te}\) can be compared to the \(W\) values determined for the perfect lattice, \(V_{Cd}\) and the vacancy cluster in the film. The value of the state \(i\), \(A_i^f\), is calculated from Eq. (4) by using the \(\lambda_i^f/\lambda_i^f\) core (valence) annihilation rate calculated by Puska et al. The calculated values are only reported for the perfect lattice, \(V_{Te}\), \(V_{Cd}\), and \(V_{Cd}-V_{Te}\) because there are no calculations available for multiple vacancy clusters (tri-, quadrivacancies).

In Table II, the fraction \(X_i^f = W_i/A_i^f\) is 0.33 for the perfect lattice, 0.5026 for the \(V_{Cd}\) monovacancy, and 0.5117 for the \(V_{Cd}-V_{Te}\). As this fraction is about the same in \(V_{Cd}\) and \(V_{Cd}-V_{Te}\), we can compare the change induced in \(A_i^f\) from \(V_{Cd}\) to \(V_{Cd}-V_{Te}\) to those induced in \(W\) from the \(V_{Cd}\) vacancy to the vacancy cluster. They are in good agreement, about 16% for \(W\) and 17% for \(A_i^f\). This leads us to conclude that the divacancy can already account for the change observed in \(W\) and therefore we identify the vacancy cluster to a \(V_{Cd}-V_{Te}\) divacancy.

We can calculate the trapping rate \(\kappa_d\) at the divacancy in the different layers by using \(\kappa_d = \chi_d(S-S_0)/(S_d-S)\). Its relative variation from one layer to the other (see Table I) enables us to follow that of the divacancy concentration since \(\kappa_d\) is directly proportional to it. The following conclusions can be drawn. (i) Annealed layers contain less divacancies than unannealed layers. The annealing at 400 °C can reduce the divacancy concentration by an order of magnitude. (ii) The annealing is less effective if the film is CdCl₂ dip coated before annealing. The divacancy concentration decreases by a factor of 5 instead of 20. This suggests chlorine diffusion in the film and interaction of Cl atoms with the divacancies. (iii) Deposition on CdTe/110 glass at 220 °C seems to generate as much as (or even more) divacancies than direct deposition, but reproducibility needs to be checked to confirm this conclusion.

The position trapping coefficient at \(V_{Cd}-V_{Te}\) being unknown, we can only estimate the divacancy concentration. We may assume that the trapping coefficient at \(V_{Cd}-V_{Te}\) is about the same or higher than in \(V_{Cd}\). Taking the values of 10⁻⁷ cm² s⁻¹ for \(V_{Cd}\), the divacancy concentration is then 2 x 10¹⁸ cm⁻³ or less in the 400 °C annealed CTB film which contains the lowest concentration. The concentration increases to 10¹⁹ cm⁻³ in the as-grown CTA layer.

In summary, by implanting monoenergetic positrons at various depths in thin CdTe films we found that they contain divacancies in homogeneous concentration at depths larger than ~0.2 μm.