Effect of Copper and Chlorine on the Properties of SiO₂ Encapsulated Polycrystalline CdSe Films

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The effects of different copper doping concentrations on the properties of SiO₂ encapsulated CdSe films have been investigated. Two methods were used to dope the films with copper: ion implantation and diffusion from a surface layer. The room temperature dark resistivity of films annealed in oxygen at 450°C was found to increase as the copper concentration was increased until a maximum resistivity of 10⁸ ohm cm occurred at a copper concentration of 10²⁰ atoms cm⁻³. The room temperature resistivity in the light was found to be independent of the copper concentration and whether the films were annealed in argon or oxygen. During annealing the grains grew from 0.03 μm to 0.3 μm and this growth was independent of the doping or the annealing ambient. The energy levels, carrier mobilities, and microstructure of the annealed films were dependent on the method of doping. The ion implanted films had an additional energy level at 0.33 eV and their mobility was a factor of 4 smaller than films doped by the surface diffusion method, whose mobilities were 20 to 35 cm²V⁻¹ s⁻¹. The addition of chlorine to copper doped films had no effect on either the resistivity or photosensitivity but slowed the response times of the photocurrent by a factor of 10. No energy levels were observed which could be associated with the copper nor was the copper found to affect the density of the observed intrinsic levels at 0.65 and 1.1 eV.

**Key words:** Poly-Se, films, SiO₂ encapsulated, Cu-doped, Cl-doped

INTRODUCTION

The properties of CdSe thin films have been studied for various applications such as solar cells,1,2 photoluminescence,3 and photovoltaic devices and thin film transistors.4 For many of these applications highly resistive and photosensitive films are required. Numerous dopants, for example, oxygen,5 silver,6 and copper4,5 have been reported to increase the dark resistivity and photosensitivity of unencapsulated CdSe crystals and films and of these dopants probably copper has been most frequently studied. Generally, when CdSe crystals and films have been doped with copper they have also been doped with chlorine. The chlorine is termed a co-activator10 and is reported to increase the solubility of the copper in the CdSe by promoting the re-crystallization of the CdSe.

This paper reports a study of the effect on the microstructure, dark resistivity, photosensitivity, and response times of the photocurrent of annealing SiO₂ encapsulated CdSe films in oxygen and argon after doping with different copper and chlorine concentrations. To achieve the different dopant concentrations both ion implantation and diffusion from surface layers evaporated onto the surface of the CdSe were used.

In a recent paper11 the effect of annealing CdSe films in an oxygen atmosphere has been reported. In that work the films were coated with SiO₂ as the effect of annealing unencapsulated films in oxygen led to the formation of an incoherent oxide and a roughening of the film surface as well as an inevitable oxygen doping concentration gradient through the film with the semiconducting electrical properties being determined by an ill-defined layer within the film. The energy levels associated with the copper and the mechanism by which it increases the photosensi-
tivity and dark resistivity of CdSe films and crystals are still uncertain. Opik et al.\(^{12}\) postulated that the copper acts as an acceptor in CdSe by forming a complex with the \(V_{\text{Cd}}^-\) defect, i.e. \((\text{Cu}^+ + V_{\text{Cd}}^-)\). Robinson et al.,\(^{13}\) from photocurrent quenching measurements, reported a copper level situated at about 0.68 eV below the conduction band in copper doped crystals, which they did not consider to be a sensitizing center. Ture et al.\(^{14}\) reported a copper energy level at 0.73 eV to 0.76 eV below the conduction band which they postulated to be a sensitizing center. In contrast to Robinson et al. and Ture et al., Ermolovich et al.,\(^4\) from luminescence measurements, did not identify a copper level in their copper and lithium chloride doped films but attributed the observed increase in photosensitivity to an increase in the concentration of an intrinsic sensitizing center at 1.05 eV below the conduction band and a re-crystallization of the films.

In order to study the mechanism by which the doping changes the dark and light resistivity of the SiO\(_2\) encapsulated CdSe films, thermally stimulated current (TSC), Hall, and resistivity measurements were made to determine the energy levels, mobilities, and carrier densities of the films. To determine the effect of the copper and annealing on the crystal structure, transmission electron microscopy (TEM), and focused ion beam (FIB) microscopy were used to examine the planar grain sizes and the grain structure through the thickness of the films.

**EXPERIMENTAL**

**Fabrication**

The substrates used were 125 × 125 mm, 1.5 mm thick NA45 glass supplied by Nippon Sheet Glass. After cleaning they were annealed in air at 500°C for 20 h to prevent any shrinkage during subsequent lower temperature processing. The substrates were then sputter coated with 120 nm of SiO\(_2\) to act as a buffer layer and 70 nm of ITO. The coated substrates were then annealed at 400°C in H\(_2\)/N\(_2\) to reduce the resistivity of the ITO from 10 to 10\(^{-3}\) ohm cm and patterned into the required electrical contacts by wet etching using HBr.

The CdSe was deposited by thermal evaporation over the whole substrate at a rate of 0.5 nm s\(^{-1}\) and a substrate temperature of 100°C to a thickness of 0.5 μm. The pressure before the CdSe deposition was 1 × 10\(^{-7}\) torr and at the end of deposition it had increased to 5 × 10\(^{-7}\) torr. The CdSe was then sputter coated in the same vacuum system with 120 nm of SiO\(_2\) and then baked at 350°C for 2 h in argon to improve the adhesion of the CdSe film. The SiO\(_2\) was etched into the required CdSe pattern using buffered HF. This pattern was then transferred to the CdSe by sputter etching away the exposed CdSe. The SiO\(_2\) was stripped using buffered HF and the films were doped by either evaporating a thin layer of the dopant onto their surface or by ion implantation. The films were then baked at 400°C in argon for 2 h to diffuse the dopant into the CdSe film. After baking the films were encapsulated with 0.4 μm of RF sputtered SiO\(_2\) and annealed in argon or oxygen at 450°C.

For the TSC measurements, capacitor structured samples were made by evaporating a 40 nm thick gold electrode of dimensions 4 × 1 mm onto the encapsula-
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Table I. Response Times of the Photocurrents (ms) of CdSe Films

<table>
<thead>
<tr>
<th>As-Deposited CdSe Films</th>
<th>Tₛ</th>
<th>Tₜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>as deposited</td>
<td>500</td>
<td>480</td>
</tr>
<tr>
<td>SiO₂ undoped</td>
<td>350</td>
<td>350</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>After SiO₂ Encapsulation of CdSe Films</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 × 10¹⁰ atoms cm⁻³</td>
</tr>
<tr>
<td>18 h O₂</td>
</tr>
<tr>
<td>8 × 10¹⁰ atoms cm⁻³</td>
</tr>
<tr>
<td>18 h O₂</td>
</tr>
<tr>
<td>40 h O₂</td>
</tr>
<tr>
<td>2 × 10¹⁰ atoms cm⁻³</td>
</tr>
<tr>
<td>40 h O₂</td>
</tr>
<tr>
<td>3 × 10¹⁰ atoms cm⁻³</td>
</tr>
<tr>
<td>40 h O₂</td>
</tr>
</tbody>
</table>

* Films were doped from different thicknesses of copper surface layers at the annealing stage at which their resistivities were a maximum after annealing at 450°C.

Table II. Response Times of the Photocurrent (ms) of Films Annealed in Oxygen or Argon at 450°C

<table>
<thead>
<tr>
<th></th>
<th>Oxygen</th>
<th>Argon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tₛ</td>
<td>Tₜ</td>
</tr>
<tr>
<td>Copper Doped*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 h</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>40 h</td>
<td>3</td>
<td>1.5</td>
</tr>
<tr>
<td>60 h</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Undoped</td>
<td>25</td>
<td>37</td>
</tr>
<tr>
<td>20 h</td>
<td>3</td>
<td>7</td>
</tr>
<tr>
<td>60 h</td>
<td>3</td>
<td>6</td>
</tr>
</tbody>
</table>

* 10¹⁰ atoms cm⁻³

tion layer of SiO₂ such that it overlaid the CdSe and ITO which was used as the bottom electrode.

Characterization of the CdSe Films

The resistivity measurements were made over the temperature range -100°C to 120°C in the dark and under illumination. The Hall measurements were carried out over the temperature range 60°C to 120°C in the dark and under illumination. The light source used was an unfiltered tungsten filament giving an illumination of 10 mW cm⁻². The magnitudes of the electric and magnetic fields used were 100 V cm⁻¹ and 0.5 T, respectively. The Hall resistivity bar was 10 mm long and 2 mm wide with 2 voltage arms separated by 3 mm.

In the TSC measurements an electric field was used to perturb the films. The TSC experimental procedure consisted of increasing the sample’s temperature to 120°C in the dark and at this temperature applying an electric field of +3 × 10⁵ V cm⁻¹ to the gold electrode which was maintained while the sample’s temperature was lowered to -120°C. At this temperature the polarity of the electric field was reversed and after 10 min, the sample’s temperature was ramped at 0.1°C s⁻¹ to 120°C and the current versus temperature profile was measured. Details and interpretation of this type of measurement have been outlined in a series of papers by Simmons et al. 15-17

The response times of the photocurrent were measured using a LED with an output of wavelength 750 nm and line width 20 nm. The electric field used was 100 V cm⁻¹ and the illumination at the surface of the sample was 1.3 mW cm⁻². The transient photocurrent was measured as a transient voltage across a resistor in series with the sample. The speed of response of the photocurrent data is presented as the rise time (Tₜ) and fall time (Tₛ) of the photocurrent. Tₛ is defined as the time required for the photocurrent to increase from 10% to 90% of its steady state value as the illumination is turned on while the Tₜ is defined as the time required for the photocurrent to decrease from 90% to 10% of its steady state value as the illumination is turned off.

Secondary ion mass spectroscopy (SIMS) analysis was performed with an Atomika 6500 SIMS system using a 5 kV Cs beam at an angle of 45° with electron beam compensation detecting negative secondary ions. The size of the crater was 100 × 40 μm. The SIMS system was calibrated for copper in the CdSe matrix by analyzing films ion implanted with known amounts of copper. A JEOL 120X transmission electron microscope was used to determine the planar grain sizes while a FEI FIB 200 focused ion beam system was used to determine the through grain structure of the films.

RESULTS AND DISCUSSION

Dark and Light Resistivity

Copper Doping by the Surface Evaporation Method

Figure 1 shows the maximum dark resistivities and corresponding light resistivities of SiO₂ encapsulated CdSe films doped with different copper concentrations by the surface method after annealing in oxygen at 450°C. The figure also shows typical values of the dark and light resistivities of an ‘as deposited’ film and of a copper doped and undoped film after the SiO₂ encapsulation. The values of the light and dark resistivities of the copper doped films were the same at the encapsulation stage regardless of the copper concentration. The response times of the photocurrents of these films are given in Table I.

Figure 2 shows a typical copper distribution in a CdSe film after 40 h annealing in oxygen at 450°C which was determined by SIMS for a film which was doped from a copper surface layer nominally 8 nm thick. The figure shows that this surface layer corresponds to an average copper concentration of 10²⁰ atoms cm⁻³.

Figure 3 shows the effect of annealing in oxygen and argon at 450°C on the dark and light resistivities of CdSe films surface doped to give an average copper
The concentration of $10^{20}$ atoms cm$^{-3}$. The effects of these anneals on the response times of the photocurrents are reported in Table II. To assess the relative effects of the argon and oxygen anneal to that of the copper doping, undoped films were annealed in argon and oxygen at 450°C. The resultant dark and light resistivities are also shown in Fig. 3 and their effects on the response times of the photocurrents are included in Table II.

The following observations and deductions can be made by a comparison of the data in Figs. 1 and 3 and Tables I and II:

a) The low value of the dark and light resistivities after the SiO$_2$ encapsulation can be attributed to ion and electron damage in the CdSe introducing shallow donor levels during the encapsulation process. The increase in both the dark and light resistivities after thermal treatment irrespective of the doping or annealing ambient is associated at least in part with removal of these levels.

b) On doping and annealing these encapsulated films three major effects can be observed:

i) An effect due to oxygen annealing where the dark resistivity of undoped films increases from 10 ohm cm to $10^4$ ohm cm (Fig. 3a).

ii) A thermal effect, seen on annealing in argon, where the dark resistivity of undoped films increase from 10 ohm cm in the encapsulated state to $10^4$ ohm cm (Fig. 3b).

iii) An effect due to copper doping (when the copper doping $\geq 10^{20}$ atoms cm$^{-3}$) which increases the dark resistivity by a further factor of 100, to $10^4$ ohm cm when the films are annealed in argon (Fig. 3b) and to $10^8$ ohm cm when the films are annealed in oxygen (Fig. 3a). This implies that as well as the thermal effects, both copper and oxygen are removing the donor levels and/or adding acceptor levels.

c) Figure 3 indicates that the increase in the room temperature photosensitivity of the doped ($\times 10^4$) and undoped ($\times 70$) CdSe films after annealing in oxygen is due to an increase in the dark resistivity of the films. The magnitude of the light resistivity is similar for both doped and undoped films whether annealed in argon or oxygen. This implies that at room temperature neither the copper nor oxygen affects the density of the centers which determine the magnitude of the room temperature photocurrent.

d) As the copper doping is increased both the dark resistivity and photosensitivity increase until a limit is reached at a concentration of $\geq 10^{20}$ atoms cm$^{-3}$ (Fig. 1b). This could be because of the solubility limit of copper in CdSe.

e) The response times of the photocurrents of all films decrease on annealing by at least an order of magnitude independent of doping or annealing ambient. The undoped films annealed in argon show the smallest change (from 500 ms to 3–45 ms). The response times of the photocurrents (1.5–3 ms) are for the films doped with copper concentrations $\geq 10^{20}$ atoms cm$^{-3}$ and annealed for $\geq 40$ h in oxygen at 450°C.

The decrease in the magnitude of the response time of the copper doped and undoped films during the oxygen and argon anneals could be due to a decrease in the density of the shallow levels. This would reduce the time required for equilibrium to be achieved between the photo-generated electrons and holes in the conduction and valence band and these levels. The faster response times of the copper doped CdSe films is explained by the copper acting as a fast recombination center.

Copper Ion Implantation

For comparison with the surface doping method the effect of ion implanting the copper was investigated. Three copper dosages $10^{14}$, $10^{15}$, and $10^{16}$ cm$^{-2}$ were implanted at an energy of 100 keV. The copper dosage of $10^{16}$ cm$^{-2}$ was chosen to give the same copper concentration in the CdSe films as that from the nominally 8 nm thick copper surface layer which
resulted in an average copper concentration of $10^{20}$ atoms cm$^{-3}$. SIMS data of a film ion implanted with a copper dosage of $10^{16}$ cm$^{-2}$ after 40 h annealing in oxygen at 450°C is shown in Fig. 2. It is evident that the concentration and distribution of the ion implanted copper is very similar to that resulting from a nominally 8 nm thick copper surface layer.

Figure 4 shows the effect of annealing in oxygen at 450°C on the dark and light resistivities of films implanted with copper while Table III reports the effect of these anneals on the speed of response of the photocurrent.

A comparison of Figs. 1, 3, and 4 indicates that the resistivities of the films implanted with a copper dosage of $10^{14}$ cm$^{-2}$ and the changes in these properties on annealing in oxygen are similar to those of undoped films annealed in oxygen while the properties of the films implanted with a copper dosage of $10^{15}$ cm$^{-2}$ and the changes in these properties on annealing in oxygen are similar to those of the films doped with copper concentrations $<10^{20}$ atoms cm$^{-3}$ by the surface method.

A comparison of Figs. 3 and 4 and Tables II and III indicates that the resistivities and response times of the photocurrents for the films doped with an average copper concentration of $10^{20}$ atoms cm$^{-3}$ by both methods with similar heat treatments are comparable which supports the SIMS analysis of similar copper concentrations and distributions.

**Chlorine Ion Implantation**

To investigate the effect of doping with both copper and chlorine, CdSe films doped with an average copper concentration of $10^{20}$ atoms cm$^{-3}$ by the surface method were ion implanted with a chlorine dosage of $10^{18}$ cm$^{-2}$ at an energy of 100 keV. After encapsulation with SiO$_2$, the films were annealed for 40 h at 450°C in oxygen. This resulted in films with similar dark and light resistivities to the equivalent copper doped films but which had significantly longer $T_2$s and $T_3$s of typically 30 ms and 60 ms, respectively.

Since the speed of response of the photocurrent of the films doped with copper by the surface method and by ion implantation were similar, this implies that the slower speed of response of the photocurrent of the chlorine implanted CdSe films is due to the presence of the chlorine and not to the implantation process.

Yodogawa, from TSC measurements on chlorine doped films, reported an energy level associated with chlorine at 0.04 eV below the conduction band. Therefore, the observed increase in response times of the chlorine doped films could be due to the time required for steady state conditions to be achieved by the electrons between this shallow level and the conduction band as the illumination is turned on and off.

**Micro-Structure**

Figure 5a and b shows a bright field TEM micrograph and a selected area diffraction pattern (SADP) micrograph of a CdSe film doped with $10^{20}$ atoms cm$^{-3}$ of copper by the surface method after 40 hours annealing in oxygen at 450°C. From the SADP the crystal structure of the copper doped CdSe was determined to be wurtzite which is the same structure reported by Aven and Prener for undoped CdSe crystals and Naguib for polycrystalline CdSe films.

The average grain sizes, determined by averaging

<table>
<thead>
<tr>
<th>Grain Size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Deposited</td>
</tr>
<tr>
<td>Adhesion Ar Brake (350°C, 2 h)</td>
</tr>
<tr>
<td>Ar Diffusion Brake (400°C, 2 h)</td>
</tr>
<tr>
<td>20 h O$_2$ (450°C)</td>
</tr>
<tr>
<td>40 h O$_2$ (450°C)</td>
</tr>
</tbody>
</table>
over 100 grains) of the CdSe films doped with $10^{20}$ atoms cm$^{-3}$ of copper after various heat treatments, are reported in Table IV. The results indicate that large grain growth occurs when the films were baked above 350°C. The grain sizes of undoped films were found to be very similar in size to those of the copper doped films which indicates that the copper does not cause pinning of the grain boundaries (GBs). Similarly, both Boer et al.21 and Svechnicov et al.22 have reported that copper does not cause pinning of GBs.

Figures 6 and 7 show FIB prepared cross sections of films doped with $10^{20}$ atoms cm$^{-3}$ of copper by the surface method and by ion implantation, respectively, after 40 h annealing in oxygen at 450°C. The SiO$_2$ encapsulant of the sample shown in Fig. 7 was removed by wet etching. This was to reduce the required milling time when the sample was SIMS analyzed. The platinum layers on the top of the cross sections were deposited to reduce the ion damage to, and rounding of the top surface during the ion milling. Details of the preparation of cross sections using a FIB workstation can be found in the literature.23,24 The cross sections were imaged using an ion beam current of 12 pA and the emitted secondary electrons. Figure 6 shows that the grain structure through the thickness of the film doped by the surface method consists mainly of single grains. The contrast between the grains in the images results from ion channeling due to the different crystal orientations. Figure 7 shows that the through structure of the ion implanted films is similar, apart from 90 nm to 110 nm near the surface which consists of small grains. The lack of contrast between the small grains suggests that this region consists of grossly disordered material implying that the ion implantation process has damaged the CdSe matrix and that this damage has not been annealed out during the subsequent heat treatments.

Hall and Resistivity

Figures 8 and 9 show Hall and resistivity results for films doped with a copper concentration of $10^{20}$ atoms cm$^{-3}$ by the surface method and by ion implantation, respectively after 40 h annealing in oxygen. The mobilities and carrier densities were not measured below 60°C because of the high resistivities of the films. The room temperature resistivities, mobilities, and carrier densities, extrapolated from the high temperature values as well as the activation energies of the mobilities and carrier densities, $E_m$ and $E_c$, measured over the temperature range 60°C to 100°C, are given in Table V.
Table V. Room Temperature Hall and Resistivity Data for CdSe Films Doped with $10^{19}$ Atoms cm$^{-2}$ of Copper after 40 h Annealing in Oxygen at 450°C

<table>
<thead>
<tr>
<th>Copper Doped by the Surface Evaporation Method</th>
<th>Light Off</th>
<th>Light On</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$ (Ω cm)</td>
<td>$10^7 - 10^8$</td>
<td>$10^9 - 10^{10}$</td>
</tr>
<tr>
<td>$n$ (cm$^{-3}$)</td>
<td>$10^9 - 10^{10}$</td>
<td>$10^{11} - 10^{12}$</td>
</tr>
<tr>
<td>$\mu$ (cmV$^{-1}$s$^{-1}$)</td>
<td>20–35</td>
<td>20–35</td>
</tr>
<tr>
<td>$E_g$ (eV)</td>
<td>0.65 ± 0.03</td>
<td>1.10 ± 0.01</td>
</tr>
<tr>
<td>$E_a$ (eV)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Copper Doped by Ion Plantation

<table>
<thead>
<tr>
<th>$\rho$ (Ω cm)</th>
<th>$10^7 - 10^8$</th>
<th>$10^9 - 10^{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$ (cm$^{-3}$)</td>
<td>$10^9 - 10^{10}$</td>
<td>$10^{11} - 10^{12}$</td>
</tr>
<tr>
<td>$\mu$ (cmV$^{-1}$s$^{-1}$)</td>
<td>5–10</td>
<td>8–15</td>
</tr>
<tr>
<td>$E_g$ (eV)</td>
<td>0.33 ± 0.03</td>
<td>0.65 ± 0.03</td>
</tr>
<tr>
<td>$E_a$ (eV)</td>
<td>1.10 ± 0.01</td>
<td>1.0 ± 0.02</td>
</tr>
</tbody>
</table>

Fig. 10. TSC spectra of a CdSe film doped with $10^{19}$ atoms cm$^{-2}$ of copper after 40 h annealing in oxygen at 450°C, (■) by the surface evaporation method, (●) by ion implantation.

The data show that the mobility of the ion implanted films is activated only in the dark and is a factor of 4 smaller than that of the surface doped films. This difference could be due to the ion implantation process having created defects, which on annealing accumulate either at the GBs or at the interface between the disordered and crystalline region and which trap charge and thus increase the scattering thereby reducing the mobility. The reduction in the activation energy and the increase in the magnitude of the mobility of the ion implanted films on illumination can be ascribed to the photo-generated free holes recombining with the charge trapped at the GBs or the interface between the disordered and the crystalline region.

Hall and resistivity measurements were also made on undoped CdSe films after 40 h annealing in oxygen. The mobilities of these films were of the order of 100 cm$^2$ V$^{-1}$ s$^{-1}$ which is about 4 times larger than that of the films doped with copper by the surface method while the measured carrier activation energy was 0.33 eV. As the dark resistivity of the copper doped films were at least 10$^5$ times higher than that of the undoped films this implies that the major change in resistivity of the copper doped films is due to a reduction in the carrier concentration.

Similar activation energies have been reported before in the literature.12,13,18,20,26 Opik et al.12 performed resistivity measurements on CdSe crystals doped with $7 \times 10^{18}$ atoms cm$^{-3}$ of copper by the surface method and reported a carrier activation energy of 1.02 eV which is similar to the value of 1.1 eV observed in this work. The other two activation energies of 0.33 and 0.65 eV reported in Table V have been observed in undoped CdSe crystals and films which suggests that these energy levels are not due to the copper. Yodogawa15 ascribed the level at 0.65 eV to be due to selenium vacancies and Robinson et al.13 reported that the level at 1.1 eV was a state involving native defects such as cadmium vacancies. However, without any direct evidence indicating that these levels are vacancies, such as from electron spin resonance measurements, these levels could be due to impurities substituting on the lattice sites.

TSC Results

Figure 10 shows the TSC spectra for films doped with copper concentrations of $10^{19}$ atoms cm$^{-2}$ by the surface method and by ion implantation, respectively, after annealing for 40 h in oxygen at 450°C. Both types of films had a TSC peak between 70°C and 80°C but only the ion implanted films had a TSC peak at 0°C. It was found that with repeated measurements on the same sample that one of two different TSC peaks of comparable maximum current occurred between 70°C and 80°C and that these two TSC peaks never occurred together. The cause was not deduced and any correlation between perturbation history and peak occurrence was not established. Using the initial rise27 method the activation energy determined for the TSC peak at 0°C was 0.33 eV and those for the two TSC peaks between 70°C and 80°C were 0.65 eV and 1.1 eV.

TSC spectra on undoped films, after similar heat treatments, showed only the TSC peaks between 70°C and 80°C and again these two TSC peaks were never observed together. The average TSC current at the maximum of these TSC peaks and the activation energy were $10^7 - 10^8$ eV.
energies were the same as those of the copper doped films which implies that these TSC peaks cannot be attributed to the copper.

The activation energy of 0.33 eV determined for the TSC peak at 0°C, which was only observed in the ion implanted films, is the same as \( E_c \) determined for the undoped annealed films. This implies that this TSC peak is due to an intrinsic defect and that the implantation process increases the density of this defect.

The activation energies and the average magnitudes of the maximum currents of the TSC peaks for the copper doped and undoped films are given in Table VI.

A comparison of Tables V and VI show that the energy levels determined in the TSC measurements are very similar to those obtained from the resistivity measurements.

Simmons et al.\(^2\) showed that in TSC capacitor measurements the area under a TSC peak is proportional to the density of the center. As the area under the TSC peaks for the copper and undoped films in this work are similar this implies that the copper is not affecting the density of the observed centers.

**IDENTIFICATION OF THE COPPER CENTER**

Many authors\(^3\)-\(^5\) have reported the level at about 1.05 ± 0.05 eV below the conduction band and different properties and interactions with copper have been reported for it. Robinson et al.\(^6\) reported that this level was a defect involving native acceptors and identified this as the main sensitizing center in their copper doped films but found no evidence of any association of this level with the copper level they also observed. Conversely, Ermolovich et al.\(^2\) reported an increase in the magnitude of the luminescence peak associated with this level in their copper doped films relative to their undoped films while, Opik et al.\(^10\) postulated that the copper acts as an acceptor in the CdS:Cu by forming a complex with this level.

In this work the TSC measurements showed that the density of this level was similar for both the copper and undoped films, which implies that the copper is not affecting the density of this level. Thus, our results agree with Robinson et al.\(^6\) and differ from those of Ermolovich et al.\(^2\) and with Opik's et al.\(^10\) postulation.

Robinson et al.,\(^6\) using photoconductivity measurements identified a copper level at 0.68 eV below the conduction band and another level at 0.6 eV below the conduction band in both copper doped and undoped crystals. Similarly, Ture et al.\(^11\) using photoconductivity and deep level transient spectroscopy (DLTS) measurements observed a level at 0.63 eV to 0.67 eV below the conduction band in both their copper doped and undoped crystals and an additional level at 0.73 eV to 0.76 eV below the conduction band in their copper doped crystals. In this work a similar energy level, the level at 0.65 ± 0.03 eV, was observed in the TSC measurements on the copper and undoped films. Thus, this is possibly the same level as the 0.6 eV level observed by Robinson et al.\(^6\) and the level between 0.63 and 0.67 eV observed by Ture et al.\(^11\). Therefore, in this work, unlike that of Robinson et al. and Ture et al., but similar to the work of Ermolovich et al.,\(^2\) no energy level was observed which can be directly associated with the copper.

**SUMMARY**

1) Grain growth of the films was independent of doping or whether the films were annealed in argon or oxygen. For 0.5 μm thick films the planar grain size grew from ~0.03 μm ‘as deposited’ to 0.34 μm after extended anneals. SADP showed that the crystal structure of the annealed films is wurtzite and FIB microscopy showed that the grain structure through the thickness of the films consisted mainly of single grains.

2) The dark resistivity of the copper doped films annealed in oxygen at 450°C were found to increase as the copper concentration increased until a maximum resistivity of 10⁸ ohm cm occurred at an average copper concentration of 10²⁵ atoms cm⁻³. A comparison between the effects of annealing copper doped and undoped films in both oxygen and argon indicated that both copper and oxygen have an important role in removing shallow donors from the films.

3) The increase in the magnitude of the photosensitivity for both doped and undoped films is due to an increase in the dark resistivity. The magnitude of the photosensitivity in the light is similar for both doped and undoped films suggesting that neither the copper nor the oxygen affect the density of the centers that determine the magnitude of the room temperature photocurrent.

4) The response times of all films decrease on annealing by at least an order of magnitude independent of doping or annealing ambient with the fastest response times (1.5–3 ms) for the films doped with a copper concentration of 10²⁵ atoms cm⁻³ and annealed for ≥ 40 h in oxygen. The decrease in the magnitude of the response time on heat treatment is ascribed to a decrease in the density of the shallow levels. The faster response times of the copper doped films is explained by the copper acting as a fast recombination center.

5) The addition of chlorine to copper doped films had no effect on resistivity and photosensitivity but slowed the response times by a factor of 10. This was attributed to a shallow level associated with the chlorine.

6) TSC measurements on films doped with a copper concentration of 10²⁵ atoms cm⁻³ by the surface method indicated the presence of energy levels at 0.65 and 1.1 eV. These levels were also observed in TSC measurements on undoped films and so they cannot be solely attributed to the copper.

7) Doping the films with a copper concentration of 10²⁵ atoms cm⁻³ by ion implantation gave films with similar dark and light resistivities and photosensitivities to those doped with the same copper concentration by the surface method. How-
ever, FIB microscopy and TSC, resistivity and Hall measurements showed that ion implantation created differences relative to the films doped by the surface method. The FIB microscopy analysis indicated that the copper implanted films had a highly disordered layer near their surface while the TSC and resistivity measurements showed that these films had an additional energy level at 0.33 eV. The Hall measurements showed the mobility of these films were a factor of 4 smaller than those of the films doped by the surface method. These differences were attributed to the ion implantation process having created defects in the CdSe films that are not annealed out during the subsequent heat treatments.

8) No energy levels were observed which could be associated with the copper nor was the presence of the copper found to affect the density of the observed energy levels at 0.65 eV and 1.1 eV.

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REFERENCES