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Effects of copper doping on the electronic properties of CdS films sintered with $CdCl_2$

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Chlorine- and copper-doped polycrystalline CdS films were prepared by coating a slurry which consisted of CdS, $CdCl_2$, $CuCl_2$ and propylene glycol on a glass substrate and sintering in a nitrogen atmosphere, to investigate the effects of copper doping on the window properties of all-polycrystalline CdS/CdTe heterojunction solar cells. The variations of carrier concentration as a function of the amount of copper doping in CdS films which were doped with the order of $10^{18}\,cm^{-3}$ chlorine have been explained in terms of electronic compensation of the copper impurity. The variations of optical transmission spectra as a function of copper doping have been correlated with the variations of photoconductivity spectra. Even 10 p.p.m. copper in the sintered CdS films degrades the window properties of the CdS films significantly. The degradation is caused by reduced optical transmission rather than by an increase in electrical resistivity.

1. Introduction

CdS is a suitable window material for CdS/CdTe and CdS/Cu_2S heterojunction solar cells. The properties of polycrystalline CdS films produced by various methods for the purpose of reducing the production costs of heterojunction solar cells have been reported [1-4]. The method of coating and sintering is reported to be one of the most efficient ways to produce CdS/CdTe heterojunction solar cells [5-8].

Nakayama *et al.* [5] reported the production of sintered all-polycrystalline n-CdS/p-CdTe solar cells, doping gallium into the CdS and copper into the CdTe, with an efficiency of 8%. The doping of the copper into the CdTe was carried out by adding a copper impurity to the carbon paste which acts as an ohmic contact to the CdTe layer, and by subsequent heat treatment at a temperature in the region of 400° C which causes the interdiffusion of copper into the CdTe layer. They found that 50 to 100 p.p.m. copper results in the highest solar cell efficiency and that extended heat treatments reduce the efficiency of the CdS/CdTe solar cells, and suggested that extended heat treatment may cause interdiffusion of copper into the CdS layer through the CdTe layer, which increases the resistivity of the CdS layer and the series resistance of the solar cells. Most researches on copper-doped CdS, however, were performed for the purpose of studying the photosensitivity characteristics using CdS films with a high resistivity [9].

There is therefore ample necessity and interest to investigate the effects of copper doping on the electrical and optical properties of sintered CdS films. In the present paper we report the results of an investigation of the optical and electrical properties of CdS films as a function of the added amount of $CuCl_2$ and the sintering conditions.

2. Experimental procedure

CdS powder with 5N purity was used in the present investigation. Anhydrous $CuCl_2$ and $CdCl_2$ powders with 5N purity were used as the copper and chlorine dopant sources, respectively. The as-received CdS power with an average particle size of $0.45\,\mu m$ was calcined at 700° C for 2 h in nitrogen. A slurry consisting of the calcined CdS powder, now with an average particle size of $2\,\mu m$, 5 or 10 wt % $CdCl_2$, an appropriate amount of propylene glycol and various amounts of $CuCl_2$ were prepared by mixing with a mortar and pestle. Each slurry was coated on borosilicate-glass substrates using a screen printer with a 120 mesh stainless steel screen and was dried at 120° C for 2 h in air. The thickness of the dried films was approximately $50\,\mu m$. A dried CdS film was then placed in a quartz boat with a tight cover which had one hole with a diameter of 1 mm, and was sintered for one hour in a nitrogen atmosphere using a tube furnace with a quartz tube. The furnace was flushed with nitrogen and a nitrogen flow rate of $120\,cm^3\,min^{-1}$ was used to maintain the nitrogen atmosphere during sintering. Sintering and doping temperatures were varied from 625 to 675° C.

Ohmic contacts were made by coating with In-Ag paste and annealing at 200° C for 10 min in nitrogen. In some cases, the ohmic contacts were also made by depositing indium in 10^{-5} torr vacuum. Electrical resistivity was determined by measurement of the film thickness and by measurement of the sheet resistance of the films by a four-probe method. Carrier concentration and mobility were measured by the van der Pauw method. The temperature dependence of dark conductivity and the spectral response of photoconductivity were measured in an argon atmosphere. The optical transmittance and spectral response of the

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optical transmission were measured using a halogen lamp, monochromator and silicon photodiode. Photographs of surfaces and cross-sections were taken with a scanning electron microscope (SEM) to analyse the microstructure and to determine the film thickness.

3. Results and discussion

It has been reported that $CdCl_2$ added in the slurry state evaporates during sintering through the opening between the boat and cover due to its high vapour pressure, and that the presence of the "right" amount of $CdCl_2$ remaining in the sample in the liquid state acts as a sintering aid [4]. Thus a quartz ampoule with a tight cover which had one 1 mm diameter hole was used to control the evaporation of $CdCl_2$ during sintering in the present investigation.

When the CdS film acts as the front contact as well as the window layer of a CdS/CdTe solar cell, a low value of electrical resistivity is necessary. The variations of electrical resistivity of CdS films which contained 10 wt % $CdCl_2$ and various amounts of $CuCl_2$ before sintering, sintered for 1 h in a nitrogen atmosphere at 625 and 650° C, are shown in Fig. 1. The

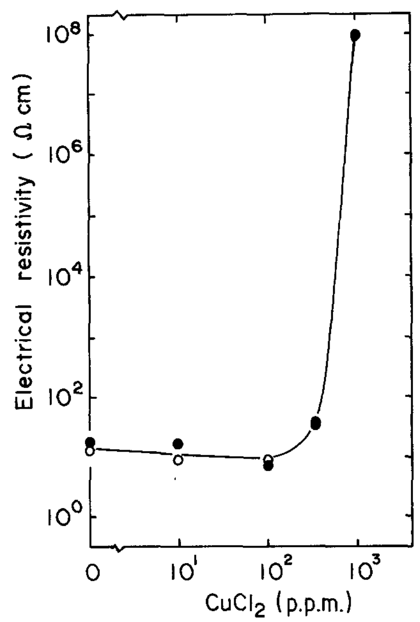

Figure 1 Electrical resistivity of CdS films which contained 10 wt % $CdCl_2$ before sintering and were sintered for 1 h at (○) 625 and (●) 650° C, as a function of the amount of $CuCl_2$ added.

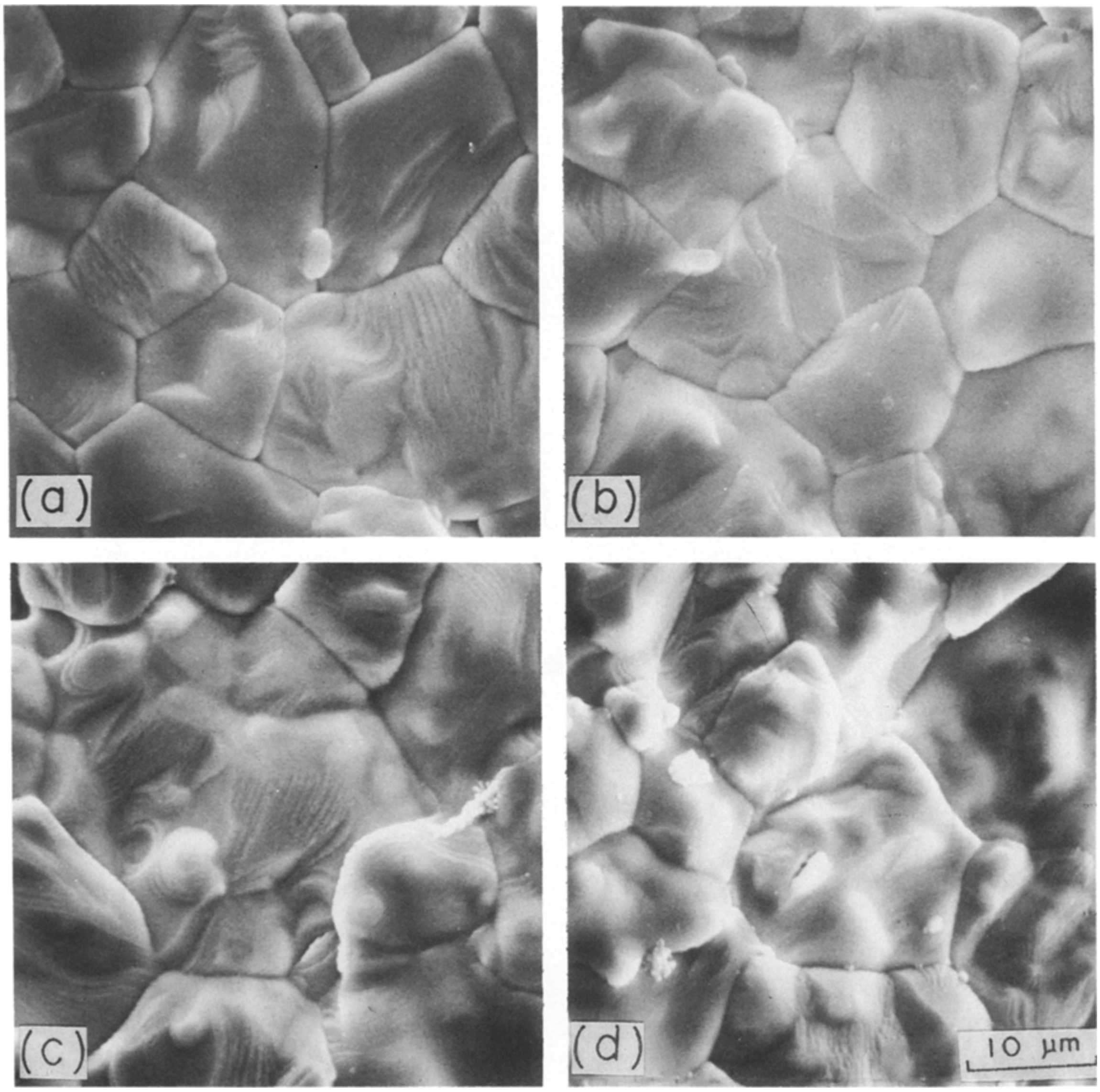

Figure 2 SEM photographs of the surfaces of sintered CdS films which contained 10 wt % $CdCl_2$ and (a) 0, (b) 10, (c) 100 and (d) 1000 p.p.m. $CuCl_2$ before sintering, sintered at 625° C.

resistivity of the sintered CdS films without any $CuCl_2$ is about 10 Ω cm, and the resistivity is almost constant up to 100 p.p.m. $CuCl_2$ addition and then increases sharply for the sample that contained 1000 p.p.m. $CuCl_2$. An examination of the microstructures of CdS films which contained 10 wt % $CdCl_2$ and various amounts of $CuCl_2$, sintered in the temperature range 625 to 675° C, showed that all the sintered films were dense with few voids. Typical microstructures for those films sintered at 625° C for 1 h are shown in Fig. 2. The average grain size and pore fraction determined by the average area method were almost independent of the amount of $CuCl_2$ added and were 15 μm and less than 0.01, respectively.

Fig. 3 shows the variation of electrical resistivity of CdS films which contained 5 wt % $CdCl_2$ and various amounts of $CuCl_2$ before sintering, sintered for 1 h in nitrogen at various temperatures as a function of the proportion of $CuCl_2$ added. Again, the resistivity of the sintered CdS films does not change significantly up to 100 p.p.m. $CuCl_2$ addition and then increases sharply in the sample that contained 1000 p.p.m. However, the resistivity of a given composition, i.e.

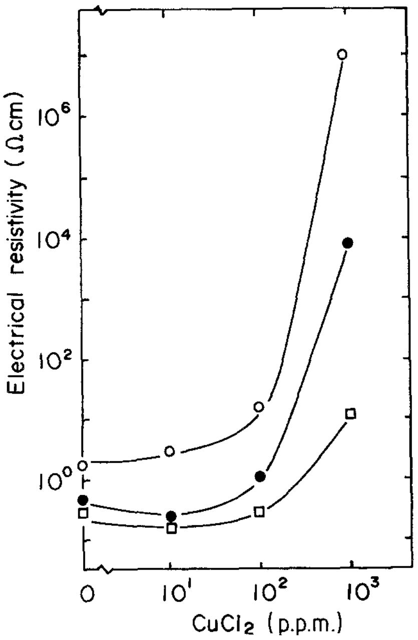

Figure 3 Variations of electrical resistivity of CdS films which contained 5 wt % $CdCl_2$ before sintering as a function of $CuCl_2$ added; temperature (○) 625, (●) 650, (□) 675° C.

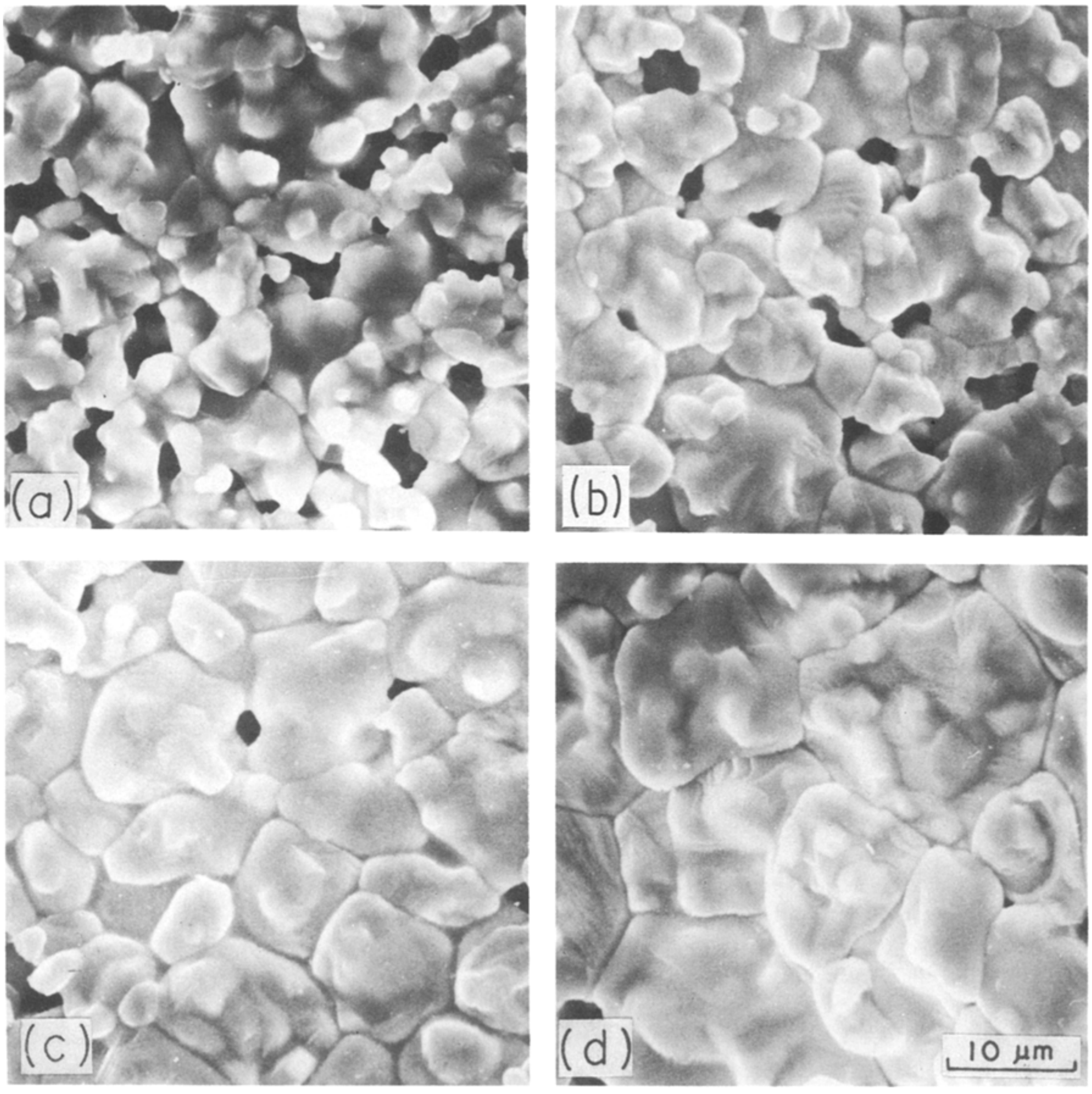

Figure 4 Microstructures of sintered CdS films which contained 5 wt % $CdCl_2$ and (a) 0, (b) 10, (c) 100 and (d) 1000 p.p.m. $CuCl_2$ before sintering, sintered at 625° C.

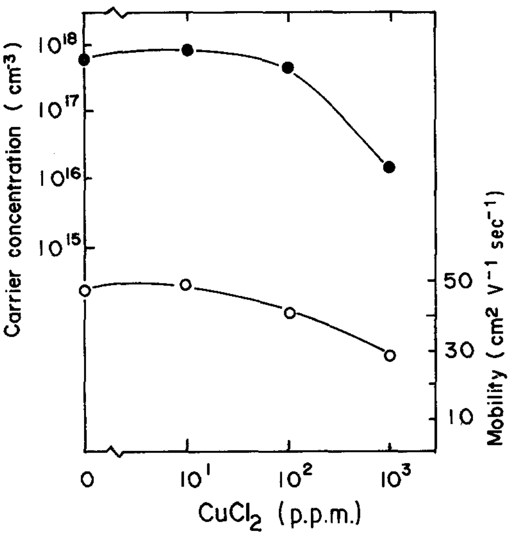

Figure 5 (●) Electron concentration and (○) mobility of sintered CdS films against amount of $CuCl_2$ added. The films contained 5 wt % $CdCl_2$ before sintering and were sintered at 675° C.

with a certain amount of $CuCl_2$, decreases with increasing sintering temperature. For the specimens which contained up to 100 p.p.m. $CuCl_2$ before sintering the resistivity decreases from ~ 10 to $0.5\,\Omega$ cm, while the resistivity decreased from 10^7 to $10\,\Omega$ cm for the specimens which contained 1000 p.p.m. $CuCl_2$, when the sintering temperature was increased from 625 to 675° C. The microstructures of CdS films which contained 5 wt % $CdCl_2$ and various amounts of $CuCl_2$, sintered at 625° C for 1 h, are shown in Fig. 4. Comparing with Fig. 2, we see that the CdS films which contained 5 wt % $CdCl_2$ before sintering are more porous than those which contained 10 wt % $CdCl_2$. It can be seen in Fig. 4 that the average grain size increases while the porosity decreases as the amount of $CuCl_2$ increases, indicating that the $CuCl_2$, with a melting temperature of 498° C, also enhances the sintering of the CdS films. The enhancement of sintering by a small amount of $CuCl_2$ appears to be negligible for the samples that contained 10 wt % $CdCl_2$, which may be because 10 wt % $CdCl_2$ is sufficient for liquid-phase sintering.

It is worthwhile to note from Figs 1 and 3 that when the films were sintered at 625 or 650° C, the resistivities of the CdS films which contained 10 wt % $CdCl_2$ are larger than those which contained 5 wt % $CdCl_2$, in spite of their denser microstructures (Figs 2 and 4). It has been reported that the presence of $CdCl_2$ in the sample after sintering causes an increase in the resistivity of sintered CdS films [4, 6]. The energy-dispersive analysis of X-rays (EDAX) data for samples which contained 10 wt % $CdCl_2$ before sintering indicated indeed the presence of chlorine after the sintering.

To clarify the variation of the electrical resistivity as a function of the amount of $CuCl_2$ added, carrier concentration and mobility were measured by the van der Pauw method. Fig. 5 shows the variation of electron concentration and electron mobility of CdS films which contained 5 wt % $CdCl_2$ and were sintered at 675° C for 1 h in nitrogen, as a function of the amount of $CuCl_2$ added. The electron concentration is about $10^{18}\,\mathrm{cm}^{-3}$; it corresponds approximately to the solubility of chlorine in CdS at this temperature, and agrees well with values reported previously [4]. The electron concentration stays at about the same value for the specimens which contained $CuCl_2$ up to 100 p.p.m. and decreases to about $10^{16}\,\mathrm{cm}^{-3}$ for the sample that contained 1000 p.p.m. $CuCl_2$. The electronic activity of copper in CdS is not precisely known but Kukk and Altosaar [10] observed that the carrier concentration of chlorine-doped CdS does not change when it is doped with a copper concentration less than the chlorine concentration, and it decreases sharply when the copper concentration exceeds the chlorine concentration. The doping behaviour of copper in CdS films during sintering is not reported but it may be reasonable to assume that most of the copper present in the form of $CuCl_2$ before sintering diffused into grains and doped the CdS films under the sintering conditions used in the present investigation, since the diffusion length of copper in CdS is very large (e.g. 21 μm for 500° C for 1 h). The value of 100 p.p.m. $CuCl_2$ is equivalent to $10^{18}\,\mathrm{cm}^{-3}$ in CdS. It appears, therefore, that the doped copper atoms act as acceptors and compensate the donor impurity (chlorine) as long as uncompensated donors exist, and the excess copper impurity forms a complex defect state which is not active electronically.

As can be seen in Fig. 5, the electron mobility decreases gradually with increasing $CuCl_2$. According to Seto [11] and Baccarani *et al.* [12], in the case of $LN_d > N_t$ where L is the grain size, N_d the doping concentration and N_t the trap density of the grain boundary, the potential barrier of the grain boundary is given by

$$\Phi = \frac{(qN_t)^2}{8\varepsilon N_d}$$

where Φ is the potential barrier height and ε is the permittivity of the semiconductor. It is reported that the trap density of sintered CdS films is about $5 \times 10^{11}\,\mathrm{cm}^{-2}$, almost independent of grain size [4]. Thus the barrier height of a grain boundary should be inversely proportional to the carrier concentration. The measured values of the activation energy of sheet resistance were 0.028, 0.016, 0.028 and 0.033 eV for the samples that contained 0, 10, 100 and 1000 p.p.m. $CuCl_2$, respectively. Comparing these values with the carrier concentrations in Fig. 5, they are generally consistent with the theory. Thus the electrical resistivity of the sintered CdS films which were doped with $10^{18}\,\mathrm{cm}^{-3}$ chlorine is not affected significantly by doping with copper up to 100 p.p.m.

The CdS films to be used as a window layer of CdS/CdTe heterojunction solar cells should have high optical transmittance as well as low electrical resistivity. Measurement of the optical transmission spectra of the sintered CdS films using conventional equipment was difficult due to the roughness of the sintered surface which causes diffuse scattering. An attempt to measure the transmission spectra was therefore made using a silicon photodiode, whose front cover had been removed to give a flat surface, in contact with the CdS film, and measuring the photodiode current both without and with the sintered film

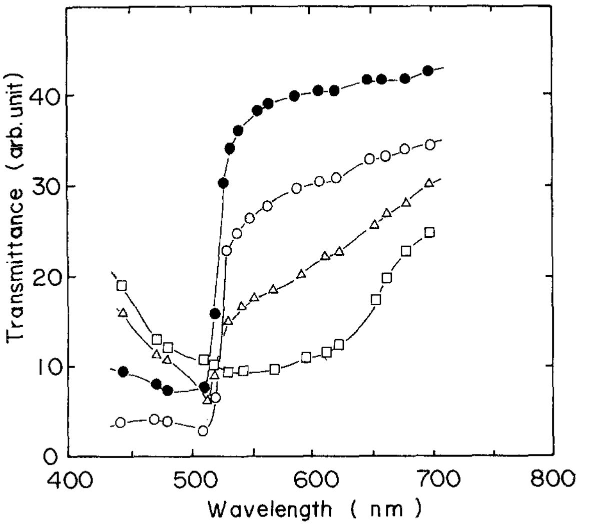

Figure 6 Optical transmission as a function of wavelength for CdS films which contained 10 wt % $CdCl_2$ and various amount of $CuCl_2$ and were sintered at 625° C: $CuCl_2$ content (●) 0, (○) 10, (△) 10^2 and (□) 10^3 p.p.m.

between the light source and the photodiode. The ratio of the two photodiode current readings was taken as a measure of the optical transmission.

Fig. 6 shows the spectral response of the optical transmission of the CdS films which contained 10 wt % $CdCl_2$ and various amounts of $CuCl_2$ before sintering and were sintered at 625° C for 1 h in nitrogen. As can be seen from their microstructures in Fig. 2, the pore fraction of the sintered films is almost independent of the copper content. For the sample which was not doped with copper, the transmission increases sharply at the wavelength of 510 nm which corresponds to the energy band gap of CdS. For an irradiation energy less than the band gap (longer wavelength), the transmission decreases with increasing amounts of copper. Thus doping of even 10 p.p.m. reduces the optical transmission significantly.

Since the microstructures of these films showed not much difference between them, the photoconductivity of these films was measured. Fig. 7 shows the spectral response of the normalized photocurrent of CdS films. The photocurrent shows a sharp peak near 510 nm and low values for longer wavelengths. However, the photocurrents under an illumination of photon energy less than the band gap are much larger in the sample that was doped with 100 p.p.m. copper than in the undoped sample. It is reported that the energy levels formed by copper impurity in CdS are 0.6 and 1.0 eV above the valence band [9]. The determination of the impurity level by photoconductivity method appears to be difficult for heavily doped samples. It appears, however, that the decrease in the optical transmission for longer wavelengths for the copper-doped CdS films in Fig. 6 is caused by optical absorption by the copper impurity level in the CdS film.

4. Conclusion

The effects of copper doping on the electrical resistivity and optical transmission of sintered CdS films have been investigated by forming slurries which consisted of CdS, $CdCl_2$, $CuCl_2$ and propylene glycol, followed by coating the slurry on amorphous glass substrates using a screen-printing method and sintering in nitrogen. The doping of copper up to 100 p.p.m. does not affect the electrical resistivity of sintered CdS films which were doped with the order of 10^{18} cm^{-3} chlorine. The doping of 1000 p.p.m. copper reduces the electron concentration of the heavily doped CdS film to the order of 10^{16} cm^{-3} due to the compensation of donor impurities by the copper. The dependence of the electron mobility on the copper doping is mainly influenced by the electron concentration, which affects the barrier height of the grain boundary. The optical transmission of the sintered CdS films decreases sharply with an increase in copper doping due to the absorption of illumination by copper-associated defect levels.

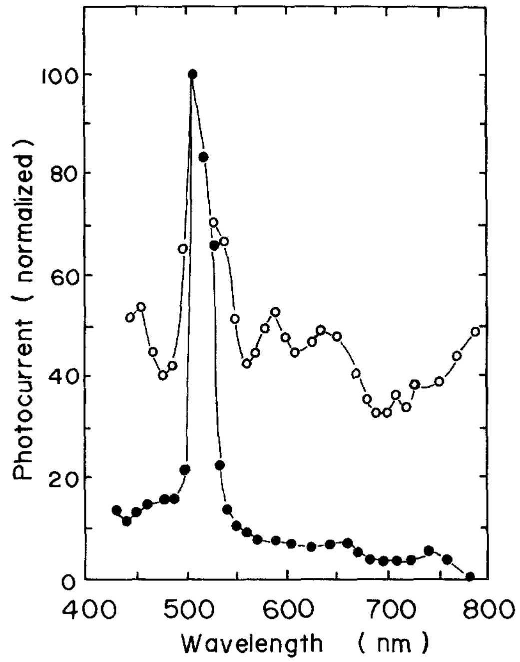

Figure 7 Spectral responses of photoconductivity of sintered CdS films which contained 5 wt % $CdCl_2$ and (●) 0 p.p.m. or (○) 100 p.p.m. $CuCl_2$. The films were sintered at 625° C.

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