



Mechanism of Formation of Highly Photosensitive CdSe/ZnO Composite Coatings Obtained by Sintering CdSe/ZnCl₂ Screen Printed Layers

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CdSe/ZnO composite coatings have been produced on glass substrates by sintering at 350 to 500°C screen printed layers of CdSe powder, ZnCl₂ flux (0.1 to 0.5 of flux to powder ratio) and propylene glycol. Depending on the composition of the paste and sintering conditions, photocurrent to dark current ratios of 10⁶ to 10⁸ are observed in the composite film under an intensity of illumination of ~2000 W m⁻². X-ray diffraction and X-ray fluorescence studies showed that the formation of the CdSe/ZnO composite takes place at temperatures of 350°C and above involving loss of nearly 75% of the chlorine at 350°C and a near total loss at 500°C forming a ZnO layer covering the CdS pigments. Loss of Zn through evaporation of ZnCl₂ and loss of Cd and Se through evaporation of CdCl₂ and Se formed in the sintering process are postulated and evidenced in X-ray fluorescence. The CdSe and ZnO components forming the highly photoconductive composite coating are of hexagonal phase with average grain size of 20-25 nm.

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Semiconducting sintered layers have been reported in the past for applications in photoconductive photodetectors,¹ photoelectrochemical,² and heterojunction solar cells,³⁻⁵ or as electrically conductive coatings^{6,7} which may be adapted for specific applications. The preparation of sintered layers involves the formulation of a precursor paste which is applied uniformly over a substrate by spin-coating, coating rod, doctor blade, or screen printing.⁸ In the preparation of n-type CdS films for solar cell applications,^{3,4} the paste is formed by mixing CdS pigments and CdCl₂ (flux, ~9% w/w) in a propylene glycol (binder) medium. The screen printed layers are sintered at temperatures of ~690°C for about 90 min. At such temperatures, the CdCl₂ melts (mp, 570°C) and covers the CdS pigments, resulting in the formation of a compact CdS:Cl layer of 50-150 Ω/□ at about 30 μm thickness.

We reported previously that if ZnCl₂ is used as flux, a highly photosensitive ZnCdS sintered layer is formed at sintering temperatures of ~400 to 500°C.⁹ Chlorine is almost entirely lost from the film as indicated by the high sheet resistance of ~10¹² Ω/□ of the coating. In the case of sintering a layer of CdSe + ZnCl₂ (flux), we found that a composite coating of the type CdSe + ZnO resulted.¹⁰ These coatings showed very high photosensitivities (photocurrent to dark current ratios) of ~10⁸ under 2 kW m⁻² tungsten halogen radiation. The near-linear variation of photocurrent with intensity of illumination of these coatings suggests photodetector applications.

In this paper we present details of the photoresponse characteristics of the CdSe/ZnO composite layers formed by sintering screen printed layers of CdSe powder and ZnCl₂ (flux) as a function of flux to powder weight to weight (w/w) ratio (FPR), sintering temperature, and duration of sintering. The composition of the sintered layers varies with the composition of the paste and the sintering conditions. We would suggest a mechanism for the formation of the layers, which not only involves a chemical conversion of ZnCl₂ to ZnO by reacting with atmospheric oxygen as previously thought, but also loss of material through evaporation. We consider these insights important for exploring possible applications of these coatings.

Experimental

Screen printing and sintering.—Chemical precipitation of CdSe powder.—The CdSe powder used in the present work was obtained

by a slow chemical precipitation, usually employed for the chemical bath deposition of CdSe thin films.^{11,12} The bath was prepared by the sequential addition of 30 mL of 0.1 M Cd(NO₃)₂·4H₂O (cadmium nitrate), 12 mL of 1 M sodium citrate, 1.5 mL of 30% (~1 M) ammonia (aq.), 30 mL of ~0.09 M *N,N*-dimethylselenourea (C₃H₈N₂Se) prepared in 0.01 M sodium sulfite, and taking the volume to 100 mL with deionized water. Except for *N,N*-dimethylselenourea which was prepared in our laboratory following the method reported in Ref. 13. All the other chemicals used were Baker Analyzed reagents. The bath turned orange in about 30 min due to the formation of a CdSe suspension, which eventually settled to the bottom. Sodium sulfite is introduced in the bath to inhibit the oxidation of selenide, as discussed in Ref. 14. The reaction was allowed to proceed at room temperature (25°C) for 16 h. At the end of this duration, the precipitate was separated by filtration, washed in deionized water, dried in air at 50°C in an oven, and stored for use in the preparation of a screen printing paste.

Screen printing and sintering process.—To prepare the screen printing paste, approximately 300 mg of the CdSe powder and different quantities (30-150 mg) of ZnCl₂ (flux) was ground finely in an agate mortar. The flux to powder weight to weight (w/w) ratio, FPR, is therefore 0.1 to 0.5. Sufficient quantity of propylene glycol was added to this mixture and ground again to get a uniform paste. The paste was screen printed on clean microscope glass slides (7 × 25 × 1 mm) using a 120T polyester screen (~325 mesh; sieve opening, 44 μm; polyester filament diam, 30 μm). The screen printed layer was dried in an oven at 100°C for about 1 h and the sintered in air at temperatures varying from 350 to 500°C for duration of typically 1 h in a Thermolyne furnace. Such temperatures are above the melting point (283°C) of ZnCl₂. Thus, the sintering process would initially lead to distribution of CdSe pigment in the ZnCl₂ melt. Subsequently various physicochemical processes may set in. This will lead to the formation of a composite layer. These physicochemical processes are the subject of the present study. Typical thickness of the sintered composite layer formed about 20 μm. The sintered coatings showed good adherence to glass substrates for sintering temperatures >350°C and FPR >0.1. Hence the studies were made on coatings prepared with FPR greater than 0.1 and sintering temperature greater than 350°C, but less than 500°C because the substrates utilized were of glass.

Characterization of the films.—The X-ray diffraction (XRD) patterns of the coatings were obtained on a Siemens D-500 diffractor

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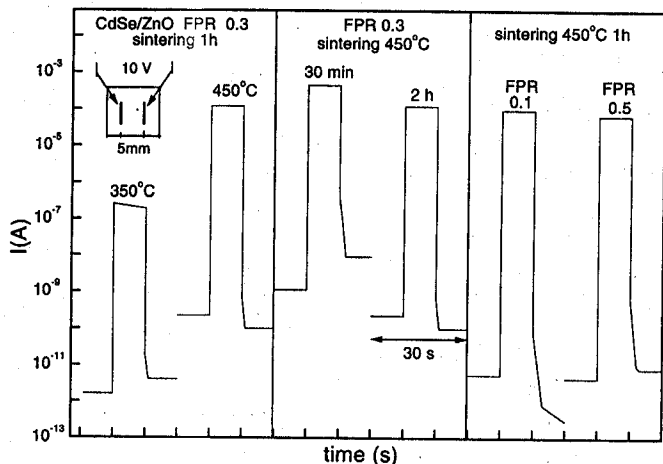


Figure 1. Photocurrent response in screen printed CdSe/ZnO layers prepared with different (FPRs) and different sintering conditions. Illumination, 2 kW/m^2 tungsten-halogen radiation during 10 to 20 s; bias 10 V applied across silver paint electrodes 5 mm long with 5 mm separation.

eter using Cu $K\alpha$ radiation. The X-ray fluorescence (XRF) spectra for Cd, Zn, Cl, Se, and S were recorded on a Siemens SRS 303 spectrometer using an LiF(100) analyzer crystal, $2d = 0.4027 \text{ nm}$, to detect $K\alpha_{1,2}$ radiation from Zn and Se; an LiF(110) crystal $2d = 0.2848 \text{ nm}$, to detect Cd $K\alpha_{1,2}$ emission; and pentaerythrite, $2d = 8742 \text{ nm}$, to detect S $K\alpha_{1,2}$ emission and Cl $K\alpha$ emission.

Diffuse reflectance spectra of CdS powder and the coatings as a function of sintering temperature were recorded on a Shimadzu UV-3101PC UV-vis-near infrared spectrophotometer employing an integrating sphere attachment. To measure the photocurrent response, silver paint electrodes of 5 mm length at 5 mm separation were painted on the coatings. The samples were kept inside a dark measurement chamber for 1-2 h under 10 V bias across the electrodes. The photocurrent response was measured with 10 s under the dark, followed by 10 s under the illumination with 2 kW/m^2 tungsten halogen lamp, and the final 10 s under the dark decay mode after shutting off the illumination. A computerized data acquisition system recording the data every 0.5 or 0.1 s was used.

Results and Discussion

Photocurrent response.—Figure 1 shows the photocurrent response of the sintered composite layers formed under different conditions from screen printed CdSe-ZnCl₂ coatings. The sheet resistance in the coatings in the dark varies in the range of 10^{10} - $10^{13} \Omega/\square$. This is much higher than the sintered layers of CdS of comparable thickness formed for solar cell application (50 - $150 \Omega/\square$).⁴ The photosensitivity, which may be defined in these cases as the ratio of the maximum photocurrent to the initial dark-current, is 10^6 to 10^8 . Such photosensitivity is associated with intrinsic semiconductor layers. The ease of formation of these sintered layers having such photosensitivity, is the continuing attraction for this technique for various applications. It is therefore worth while investigating the mechanism of formation of this coating and its composition, the subject of this paper.

Figure 2 shows the photocurrent response of the composite layer formed with FPR of 0.2 (w/w) and sintering at 400°C for 1 h. Electrodes were printed in the form of a light-dependent resistor (LDR). The data acquisition rate was 10/s. The photocurrent rise time is $<0.1 \text{ s}$, at which 90% of the maximum photocurrent is registered. In the photocurrent decay, there is a slow varying component due to charge carrier detrapping; the extent of which depends on the sintering process. Another feature is that the dark current after illumination drops below the steady-state level before the illumination, seen in Fig. 1. This is due to chemisorption of oxygen at the grain

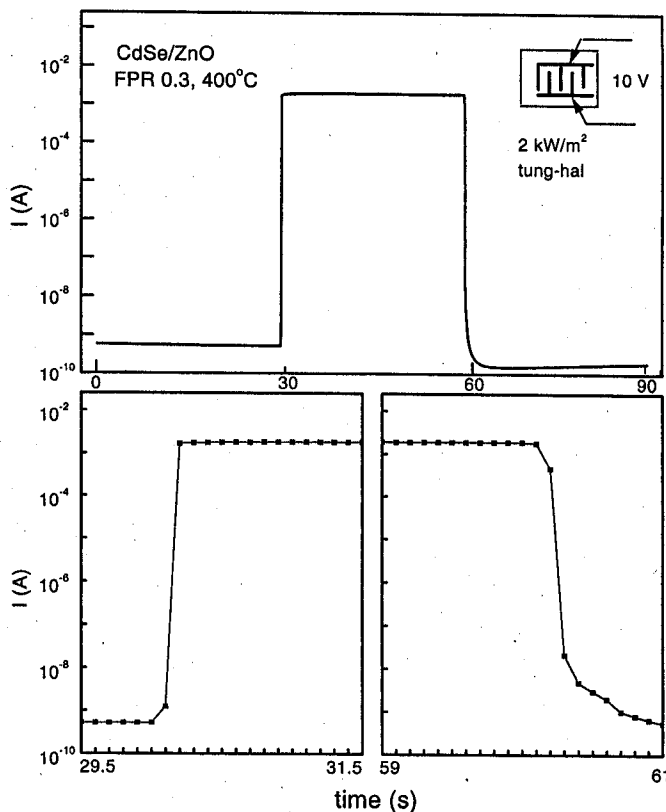


Figure 2. Photocurrent rise and decay in a CdSe/ZnO screen printed composite layer prepared using FPR 0.3 and sintered at 400°C for 1 h.

boundaries creating O^-/O_2^- , making use of the photogenerated electrons, which will reduce the electron drift mobility.¹⁵ The dark current values return to the original steady-state values in about 30 min.

In the following discussion it is established that the sintered layers are CdSe/ZnO composites. We have reported in our earlier papers^{11,12} that CdSe thin films obtained from the same bath as used here for the precipitation of CdSe powder shows high photosensitivities of 10^6 to 10^8 after they are annealed in air at 350 - 450°C . Similarly for ZnO films produced by pyrolysis of chemically deposited ZnS thin films at 400° - 500°C , photosensitivities of 10^4 to 10^6 are typical.¹⁶ In the present case the ZnO component is formed by pyrolytic conversion of ZnCl₂ at similarly high temperatures. The observation from the results in Fig. 1 that the photosensitivities are not strongly dependent on the FPR suggests that the overall photosensitivity of the composite layers is actively contributed by the CdSe as well as ZnO components.

Optical properties.—In order to obtain a value for the effective optical bandgap of the composite coatings we recorded the diffuse reflectance spectra of the CdSe powder and that of the sintered layer formed at different temperatures, as shown in Fig. 3. The optical bandgap might be estimated from these curves by the following procedure. The intensity of the reflected light, at any wavelength, $I_\lambda = I_{\lambda 0} e^{-(\alpha d)}$, where α is the absorption coefficient and d , an effective thickness for the radiation of wavelength, λ . In the region of strong optical absorption, at wavelengths slightly above the threshold of optical absorption, $\lambda_g \text{ (nm)} = 1240/E_g$ (where E_g in electronvolts is the bandgap energy). The absorption coefficient α for CdSe and most other semiconductors are in the 10^3 to 10^5 cm^{-1} range.¹⁷ This suggests that at a thickness of 10 - $0.1 \mu\text{m}$ into the material, the intensity would drop to $1/e$ ($e = 2.718$) of the initial value. In the present case of sintered layers, the layer thickness is about $20 \mu\text{m}$, and hence a total absorption of the radiation and

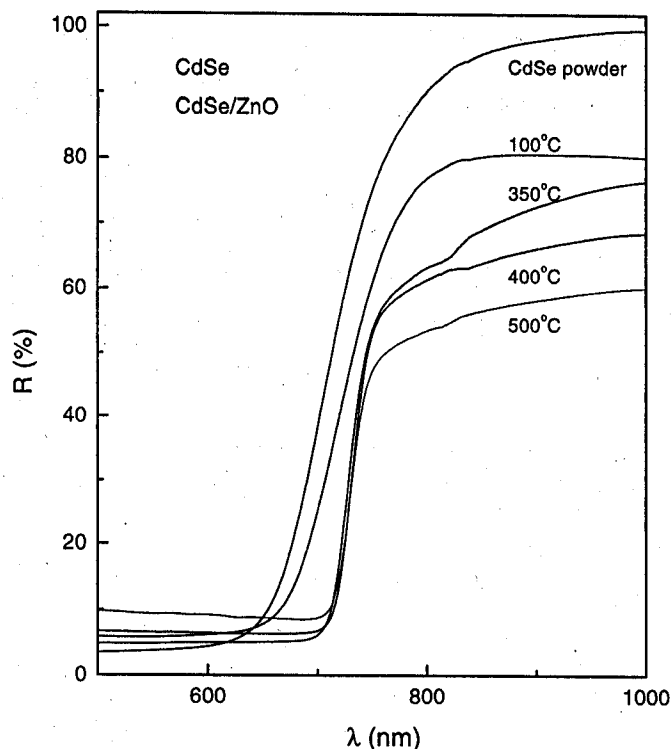


Figure 3. Diffuse reflectance spectra of CdSe powder and of CdSe/ZnCl₂ screen printed layers sintered at different temperatures in air for 1 h each.

near-zero diffuse reflectance would be observed toward shorter wavelengths. This is observed in Fig. 3. The CdSe powder (as collected in a filter paper and dried at 50°C) was compacted into the sample holder of the diffuse reflectance attachment to record the reflectance values; in all other cases, the sintering temperature of the screen printed layers on glass substrates are given.

An interpolation of the plots of $(\alpha d)_\lambda^2 = \{\ln[100/R(\%)]\}^2$ vs. the photon energy, hc/λ (where h is the Planck's constant and c , the velocity of light) gives an estimate of the bandgap energy in the case of direct gap materials. Figure 4 shows these plots obtained from the data given in Fig. 3. In the case of CdSe powder samples, the optical bandgap is the highest, 1.78 eV, which is within the values (1.75–2.18 eV along different directions) reported for crystalline CdSe in hexagonal structure.¹⁸ After sintering the layer at 350 to 500°C, the bandgap decreases to about 1.68 eV. The shift in the bandgap to lower values with annealing in polycrystalline semiconductors is associated with increase in the grain size.¹⁹

In the following section we shall see that at 350–500°C, the screen printed layer transforms to a composite layer of CdSe pigments in a ZnO matrix, formed through the decomposition of ZnCl₂ flux. The high photosensitivity of the layers shown in Fig. 1 testifies to the fact that the ZnO component is also photosensitive. In the case of photosensitive ZnO thin films obtained through pyrolytic conversion of ZnS at similar temperatures, the optical bandgap is about 3.7 eV.¹⁶ Due to the onset of optical absorption at 1.68 eV in the sintered CdSe/ZnO layers arising due to the CdSe component, the optical absorption of ZnO is not explicit.

Crystalline structure of the coatings.—Figure 5 shows the XRD patterns recorded for the screen printed and sintered layers prepared with FPR of 0.3 and sintered at different temperatures for 1 h each. The patterns of the layers sintered at 100°C show only broad peaks corresponding to CdSe. This indicates that the CdSe powder collected as precipitate from the chemical bath is of very poor crystallinity. In addition, there are also some minor peaks attributable to ZnCl₂.

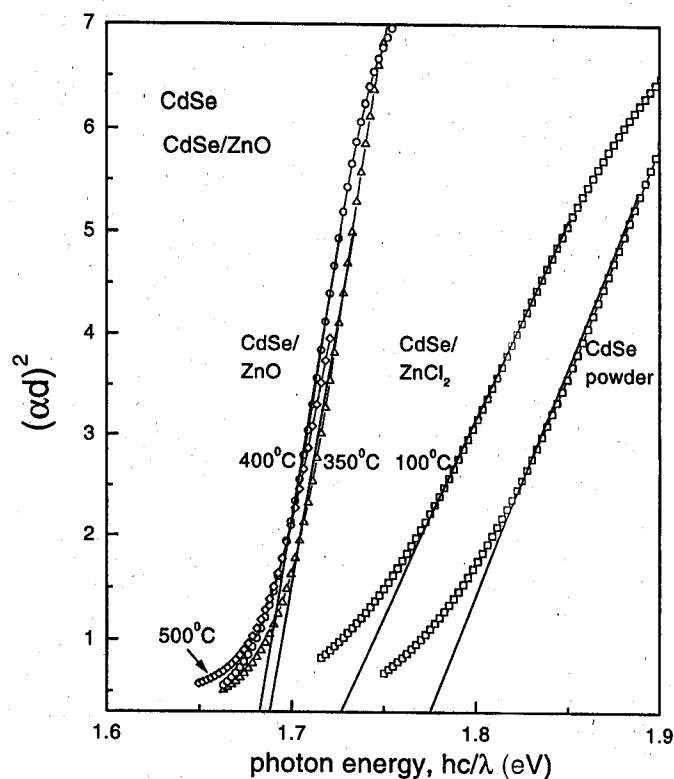


Figure 4. Plots of square of the product of absorption coefficient (α) and an effective thickness (d) as a function of photon energy, obtained from the data in Fig. 3.

The XRD patterns of the layers formed at sintering temperatures of 350 to 500°C illustrate the dominant presence of the hexagonal phase of CdSe (JCPDS 8-0459) as well as that of ZnO (JCPDS 36-1451). The smaller peak intensities of ZnO is due to the relatively low abundance of this material in the composite. The relatively smaller atomic scattering factors of Zn and O compared to that of Cd and Se also are a contributing factor. The crystalline grain diameters (D) for the ZnO and CdSe components in the composites were evaluated from the full width in radian (β) at half maximum intensity of the peaks mentioned, the Bragg angle (θ) and the wavelength of X-ray ($\lambda = 0.1054$ nm), using the relation,²⁰ $D = 0.9\lambda/(\beta \cos \theta)$. Under the different sintering conditions used here, the composites obtained showed grain size of ~24 nm for the CdSe component and ~20 nm for the ZnO component. Relative peak intensities due to the CdSe component correspond to that of the JCPDS standard for hexagonal phase CdSe (8-0459) in the case of layers produced at sintering temperatures 350, 400, and 450°C. For the layers formed at 500°C, the (002) peak intensity improves and surpasses that of (011) peak. This is accompanied by a reduction in the relative intensity of the (-120) peak. This suggests some degree of preferential orientation of the crystalline grains with the c axis perpendicular to the plane of the substrate setting in at this temperature.

Figure 6 shows the XRD results on layers prepared at different FPR and sintered at 450°C for 1 h each. The XRD pattern of CdSe powder annealed at the same temperature is also shown. The significant effect seen here is the substantial orientation of crystallites with c axis perpendicular to the plane of the substrates in the layer formed using FPR 0.5. The other is the presence of a peak associated with the formation of CdSeO₃ in the case of CdSe powder. This is eliminated in the sintered layers, in which the ZnO matrix effectively protects the CdSe pigments from reaction with atmospheric oxygen.

The peaks of small intensities appearing in the $2\theta = 10$ to 20° in the case of sintered layers, seen in Fig. 5 and 6, may be associated

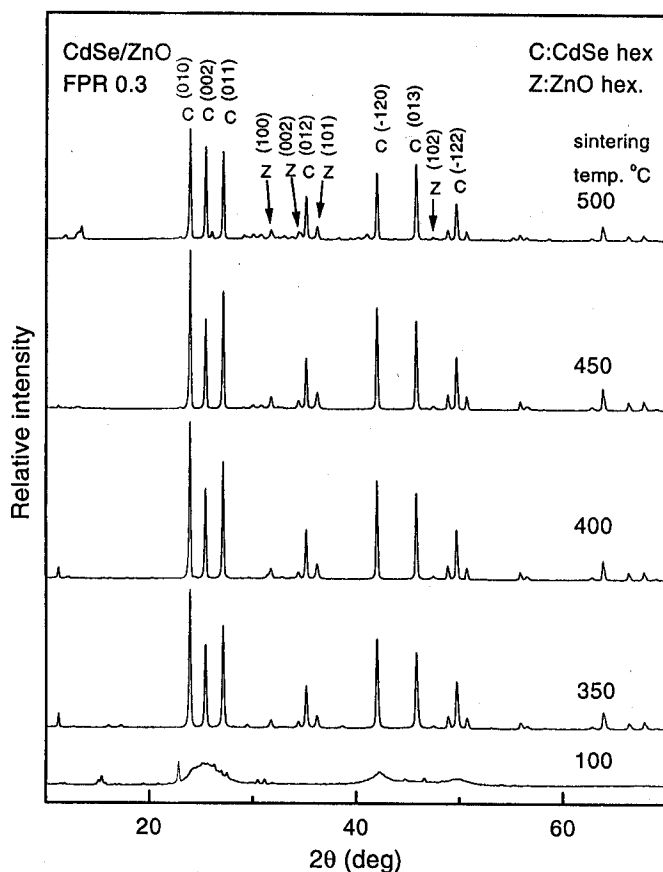


Figure 5. XRD patterns of CdSe/ZnO composite layers prepared using FPR 0.3 and sintering at different temperatures for 1 h each.

with the formation of $\text{ZnSO}_3 \cdot 2.5\text{H}_2\text{O}$ (JCPDS 11-0105) and $\text{Zn}_3\text{O}(\text{SO}_4)_2$ (JCPDS 31-1469). The source of sulfur here is the chemically precipitated CdSe. In chemical bath deposition or precipitation of metal selenides, the source of selenium is usually sodium selenosulfate, selenourea, or dimethyl selenourea.¹¹⁻¹⁴ In all these cases, the bath also contains sodium sulfite, which prevents the oxidation of selenide to elemental selenium. We have recently reported ion beam analysis of copper selenide thin films prepared by different routes and detected the presence of sulfur at 1 to 4 atom % in many cases.²¹ In the present case, the bath contained dimethylselenourea and sodium sulfite as the antioxidant. A coprecipitation of small quantities of CdS might be possible. All the sintered layers in the present case indicated the presence of sulfur in XRF studies.

XRF studies on elemental composition in the layers.—Figures 7 show the variation in the intensities of $\text{K}\alpha$ -XRF peaks due to Zn, Cd, Cl, Se, and S of the screen printed layers prepared with FPR 0.3 and subjected to sintering in air for 1 h each at the temperatures mentioned. This suggests that the following processes might take place during the sintering process.

The variation in the peak heights of Cd and Se is monotonic; thus they maintain the same atomic ratio in the sintered layers irrespective of the sintering temperature. The ratios of the peak intensities of these elements in the XRF spectra of the layers sintered at higher temperatures as compared with that of those done at 100°C suggest the loss of the elements from the layer during sintering. This loss is about 15% of CdSe when the layer is sintered at 350–400°C and is nearly 22% after sintering at 500°C. Hexagonal CdSe possesses a melting point of 1514°C and hence may be rated as a stable material. In a layer prepared with FPR 0.3, the molar abundance ratio of ZnCl_2 to CdSe is $0.3 \times (191.4/136.3) = 0.42$, where the numbers inside the parentheses are the molecular masses of CdSe (191.4) and

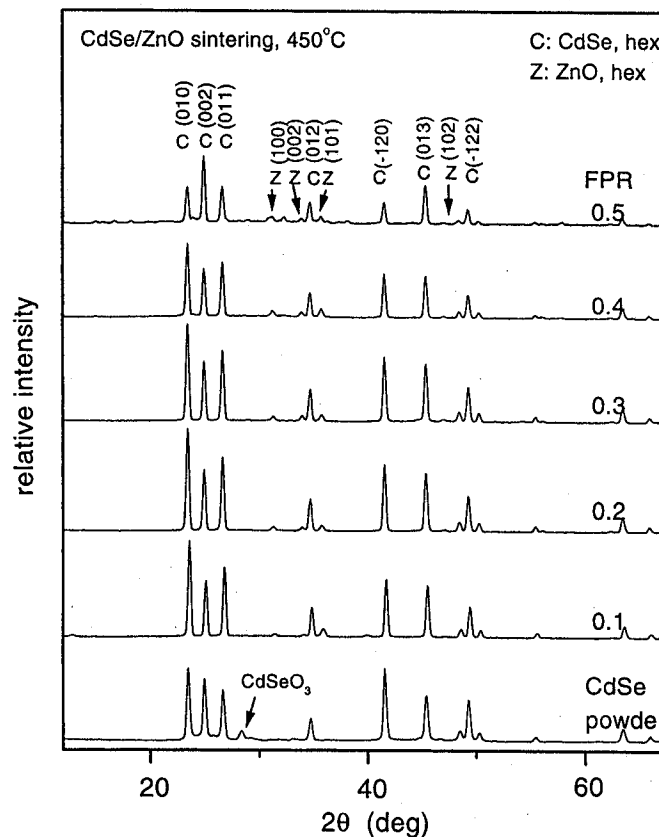


Figure 6. XRD patterns of CdSe/ZnO composite layers prepared using different FPR and sintered at 450°C for 1 h.

ZnCl_2 (136.4). We suggest the loss of Cd and Se/S through the partial conversion of CdSe as well as of the subsidiary material CdS to CdCl_2 and subsequent evaporation. The loss of Zn is higher: 22% when the layer is sintered at 400°C and 40% when sintered at 500°C. The most drastic loss is of Cl during the sintering: 85% of the element is lost during sintering at 400°C and 96% during sintering at 500°C. Loss of sulfur is about 30% at 400°C and 65% at 500°C. The relatively rapid loss of S may also result from its high vapor pressure over the layer during the sintering.

Figure 8 is a plot of the atomic ratio of Cl/Zn and Zn/Cd estimated from the peak heights, assuming an atomic ratio of 2 for Cl/Zn and 0.42 (for FPR 0.3, as mentioned above) for Zn/Cd. The relative loss of Zn compared with Cd and of Cl compared with Zn are both noted.

Mechanism of formation of the sintered CdSe/ZnO screen printed layers.—At sintering temperatures, $>300^\circ\text{C}$, the ZnCl_2 flux in the screen printed layers should melt (melting point 283°C). If we assume the mass densities of crystalline CdSe of hexagonal phase (5.81 g/cm³) and of solid ZnCl_2 (2.9 g/cm³), the volume by volume ratio of flux to powder is approximately double that of FPR. Thus for a layer prepared at an FPR of 0.3, the ZnCl_2 melt will be 60% of volume as of CdSe powder. In that case, in a reaction with atmospheric oxygen, ZnCl_2 would be totally converted into ZnO (mass density, 5.5 g/cm³) a composite layer of CdSe/ZnO would be formed. The volume by volume ratio of ZnO matrix and CdSe powder would be roughly the same as FPR. Thus, in a composite layer formed by sintering a screen printed layer of FPR 0.3, with complete conversion of the flux, the ZnO matrix will be about 23% in volume and CdSe, 77% in volume. This conversion is illustrated in Fig. 9, which additionally shows a growth in the size of the crystalline grain inside the CdSe powder in the sintered layer.

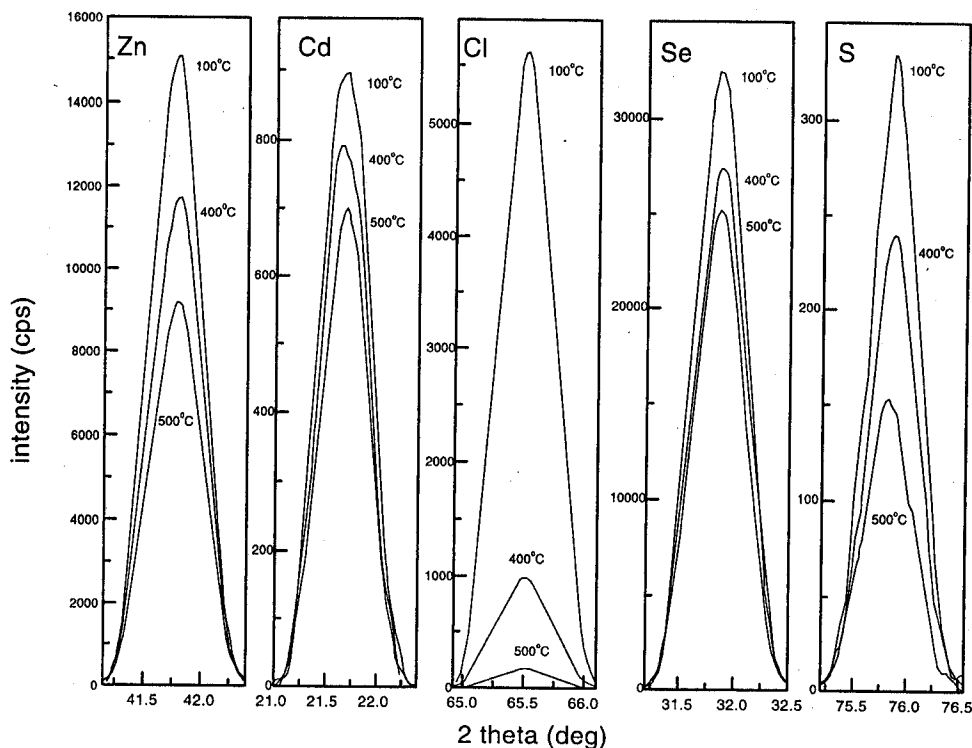


Figure 7. Variation in the intensities of $K\alpha$ XRF lines of Zn, Cd, Cl, Se, and S recorded for CdSe-ZnCl₂ layers dried at 100 as well as those sintered 400 and 500°C for 1 h each; FPR, 0.3.

Following the XRD and XRF results presented above, the loss of Cl from the screen printed layers during the sintering process may be assigned to the following three mechanisms

1. Evaporation of CdCl₂ (melting point, 570°C and boiling point, 967°C),²² formed from reaction of ZnCl₂ with CdSe or trace CdS, resulting in the loss of Cd and of Se/S as elemental Se/S (melting

point of Se, 217°C and boiling point, 685°C) as well. The formation of CdCl₂ during the formation of sintered ZnCdS layers from CdS + ZnCl₂ paste was reported before.⁹

2. Evaporation of ZnCl₂ (melting point, 283°C and boiling point 732°C),²² resulting in the loss of Zn as well. The relatively low melting point of ZnCl₂ and its ready availability in the form of flux would lead to a relatively higher loss of Zn, seen in Fig. 7.

3. As Cl₂ resulting from the formation of ZnCl₂, seen in the XRD patterns of Fig. 5 and 6, through the reaction, ZnCl₂ + 1/2 O₂ → ZnO + Cl₂.

The continued presence of Cl in the layers sintered at 400 and 500°C at about 15 and 4%, respectively, of the original value, must be as either ZnCl₂ or CdCl₂. This is because, the atomic distribution of Cl in the form of either ZnO:Cl or CdSe:Cl would have led to a relatively low sheet resistance of the layers, many orders lower than 10¹⁰ to 10¹³ Ω/□ estimated from the photocurrent response curve:

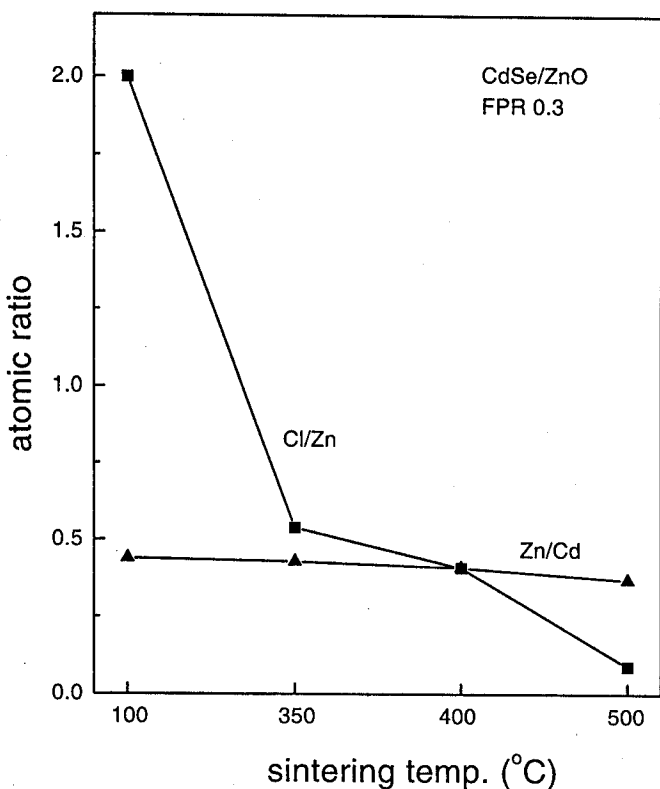


Figure 8. Atomic ratios estimated from XRF peaks of Fig. 7 and 8 for CdSe/ZnO sintered layers; FPR, 0.3.

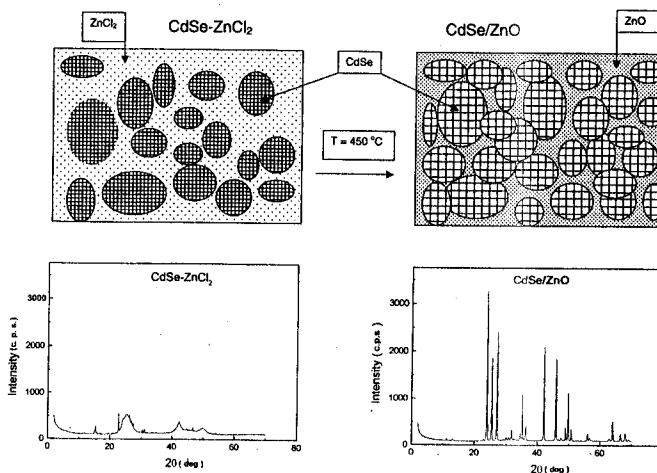


Figure 9. Schematic representation of the conversion of the screen printed CdSe/ZnCl₂ layer to sintered CdSe/ZnO layer at 450°C.

of Fig. 1. Such layers also would not have shown the high photosensitivity shown in Fig. 1 and 2.

Conclusions

In this paper we have illustrated the high photosensitivity obtained in sintered composite layers of CdSe/ZnO produced at 350 to 500°C. The stability of these layers such as in an acidic medium for photoelectrochemical cell applications, etc., would be decided by the processing condition and the composition (CdSe/ZnO content) of the layer. Using XRD and XRF results we proposed a mechanism for the formation of these composite layers, taking into account the crystalline phases present and the relative abundance of the elements. We consider that this understanding would promote efforts to utilize these layers for optoelectronic applications, which require semiconductor layers of high photosensitivity in the visible region and are produced by a relatively simple technique at a relatively low temperature.

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