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Electron and X-ray Diffraction Studies of Chemically Deposited Thin Films of Cadmium Selenide following Reaction with Mercury(II) Chloride Solution

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ABSTRACT

The reaction between thin films of CdSe and aqueous $HgCl_2$ was studied using electron diffraction (ED) powder X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). It was found that α-$Hg_3Se_2Cl_2$ is formed in the CdSe film following its reaction with 0.01 M $HgCl_2$ for a period of 5 minutes. Upon completion of the reaction of CdSe powder with 0.01 M $HgCl_2$, Hg_2Cl_2 is present in addition to α-$Hg_3Se_2Cl_2$ in a molar ratio of 1:3.1. The effect of air annealing on CdSe powder was also studied. Heating in air to 450°C for 1 hour resulted in an XRD pattern corresponding to the hexagonal form of CdSe.

INTRODUCTION

In previous work [1,2], changes in the electrical properties of chemically deposited thin films of CdSe were studied as a function of various treatments after deposition. The films were found to change from intrinsic to *n*-type conductors when they were heated in air at 450–500°C or when they were treated with aqueous $HgCl_2$ solution and then heated at 200°C. Analysis by means of X-ray photoelectron spectroscopy (XPS) has shown that both heated and unheated films have oxygen present in significant amounts and that mercury and chlorine are present in films treated with $HgCl_2$. The reaction between CdSe thin film and aqueous $HgCl_2$ can be thought of as in part due to the direct exchange of cations, which may be written as

$$\mathrm{CdSe(s)} + \mathrm{Hg^{2+}(aq)} = \mathrm{Cd^{2+}(aq)} + \mathrm{HgSe(s)}, \qquad \Delta G^\circ \leq -36.9\ \mathrm{kJ/mol} \quad [3]$$

The purpose of the present study is to examine in detail the changes in physical appearance and properties and in chemical composition of CdSe that occur as a result of these treatments.

EXPERIMENTAL

Thin films of CdSe were prepared by chemical bath deposition using *N,N*-dimethylselenourea, cadmium nitrate, sodium tartrate, and ammonium

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Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

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hydroxide, as described in a previous publication [2], with one major change. In order to examine these films using transmission electron microscopy (TEM) and selected area diffraction, the films were deposited on plastic rather than glass surfaces. Three different plastics were used: polyethylene, Xerox PP2200, and 3M Write-on film (3M I.D. No. 78-6868-1733-1). The latter two materials have commercial application for the preparation of overhead transparencies. In all cases, the deposition produced adherent films that had composition, as well as electrical and optical characteristics, essentially the same as those deposited on glass surfaces that were studied previously [3]. Some cadmium selenide films were then immersed in a solution of 0.01 M $HgCl_2$ for a period of 5 minutes followed by thorough rinsing with distilled water. After this film treatment, the substrates were immersed in methylene chloride following which thin films of CdSe separated cleanly from the surface of Xerox PP2200. (The films did not separate as cleanly from the other plastic surfaces.) These films were transferred to copper grids (200 mesh) and were utilized for electron diffraction (ED) and microscopic studies.

The CdSe bulk precipitate formed during the chemical bath deposition of the films was filtered, washed thoroughly with distilled water, and stored in a desiccator. This powder was subjected to heating in air at various temperatures as well as to reaction with 0.01 M $HgCl_2$ for several periods of time in order to get further information regarding the processes occurring in the films.

In addition to TEM and ED, XPS, and powder X-ray diffraction (XRD) were used to investigate the composition and structure of the films. The TEM and ED data were obtained from the JEOL JEM-2010 at the Texas A&M University Electron Microscopy Center operating at 200 kV with a high-resolution polepiece. The XPS studies were carried out on a Perkin-Elmer 5500 ESCA unit with Mg-K_α radiation. Powder XRD data were collected using Rigaku Denki Diffractometer and monochromatized Cu-K_α radiation.

RESULTS AND DISCUSSION

Reaction of Thin Film CdSe with Aqueous $HgCl_2$. Electron microscopic examination and ED patterns of thin films of CdSe "as-prepared" and following the reaction with 0.01 M $HgCl_2$ were obtained. Figure 1 shows an electron micrograph of an as-prepared CdSe thin film, and Figure 2 shows the diffraction pattern obtained from it. The interplanar spacing of cubic CdSe [4(a)] at 3.51 Å was used as an internal standard in the analysis of the diffraction data. No evidence of an additional crystalline phase was found, as is indicated in Figure 2a, where no reflections were observed other than those expected for cubic CdSe.

The results of the microscopic examination of the CdSe films following treatment with aqueous $HgCl_2$ were similar to those observed for the untreated films. The diffraction results, however, were strikingly different in that distinct crystallites of a new phase were present, as indicated in Figure 2b by the presence of isolated diffraction reflections lying outside the CdSe diffraction rings. In addition to the exchange of cations, chlorine is taken up by the CdSe lattice and both Hg and Cd as well as Se and Cl were measured by means of XPS quantification using peak areas and the appropriate atomic sensitivity factors for the involved elements [5,6]. The charge balance in freshly deposited films was tested using the XPS quantification, and the result was that mol (Hg + Cd) = 1.08 mol (Se + Cl/2), an agreement well within the range of acceptable values. The relative numerical values for the uppermost layer of deposited film were as follows: Hg (24.1), Cd (1.3), Se (20.6), Cl (5.7), and O (1.5). The value of mol (Hg + Cd) = 1.02 mol (Se + O + Cl/2) was also obtained.

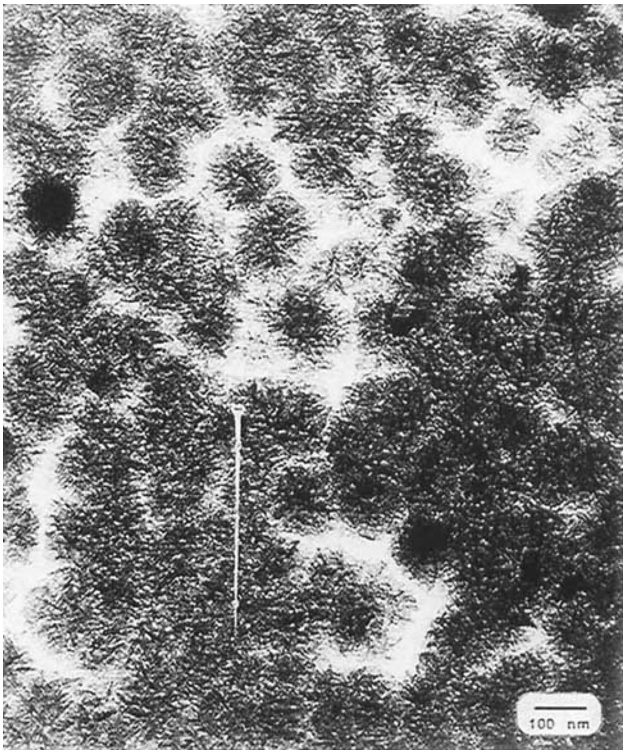

FIGURE 1 Electron micrograph of as-prepared CdSe thin film.

Extensive electron microscopic examination was carried out on a film that had been treated with $HgCl_2$, and the presence of well-defined individual small crystals embedded in CdSe was established. Figure 3 shows a selected area ED pattern of the CdSe film following immersion for 5 minutes in 0.01 M $HgCl_2$ solution, obtained by translating the grid in diffraction mode and recording on a standard video cassette tape. Seven

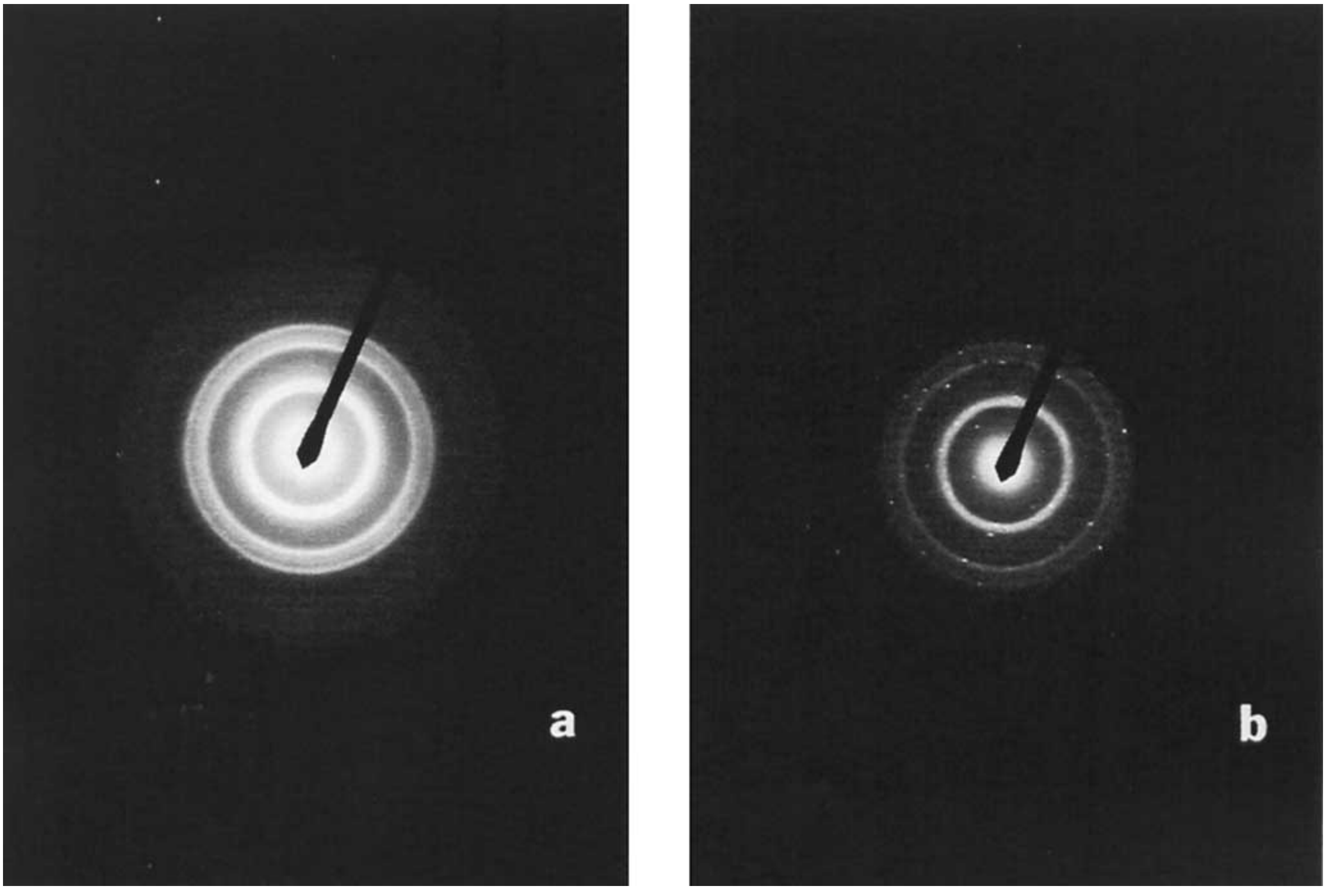

FIGURE 2 Electron diffraction pattern obtained from (a) as-prepared CdSe thin film and (b) CdSe after immersion for 5 minutes in 0.01 M aqueous $HgCl_2$.

of the most promising of these single-crystal patterns were selected and measured with their *d* spacings, calculated using the cubic CdSe reflection at 3.51 Å as an internal standard. Attempts were made at first to interpret the ED patterns [7] based upon known crystalline compounds containing Hg, Cl, and O [8], and agreement was obtained with the monoclinic form of $Hg_3O_2Cl_2$ [4(b)]. To verify these results, a small quantity of CdSe powder (0.08 g) prepared under the same conditions as those used to prepare thin films (but in the absence of any substrate) was immersed in 0.01 M $HgCl_2$. The mixture was stirred at room temperature for various periods of time, and powder XRD patterns of the precipitates were taken. New reflections appeared in these patterns, and an examination of the powder diffraction files [4(c)] suggested that a selenium isomorph of α-$Hg_3S_2Cl_2$ was present. The structure of the synthetic material was determined most recently by Frueh and Gray [9]. The cell edge for the selenium analogue was taken to be 9.06 Å. Further calculations with the ED data gave a good fit for this material with errors in calculated interplanar angles less than 3° and in *d* values less than 0.2 Å. The intensities and *d* values of the powder data agree well with those calculated for this compound [10].

After lengthy immersion in $HgCl_2$, two solid phases were identified: α-$Hg_3Se_2Cl_2$ and Hg_2Cl_2 [4(d)]. Figure 4 shows XRD powder patterns measured for CdSe, CdSe treated with $HgCl_2$ (0.08 g CdSe with 40 mL 0.01 M $HgCl_2$ for 2 days and 0.08 g CdSe with 100 mL 0.01 M $HgCl_2$ for 3 weeks). Figure 5 shows the XRD pattern of CdSe following a reaction period of 3 weeks together with simulated XRD patterns for α-$Hg_3Se_2Cl_2$ and Hg_2Cl_2 [10]. The reaction is essentially complete after a 3 week period, as confirmed by XPS analysis, which showed that the ratio mole (α-$Hg_3Se_2Cl_2$)/moles (Hg_2Cl_2) was 3.1 and that cadmium was essentially absent. The overall reactions that occur are

$$2CdSe(s) + 3HgCl_2(aq) = 2CdCl_2(aq) + \alpha\text{-}Hg_3Se_2Cl_2(s) \qquad \text{(i)}$$

$$CdSe(s) + 2HgCl_2(aq) = CdCl_2(aq) + Hg_2Cl_2(s) + Se(s) \qquad \text{(ii)}$$

No indication of the presence of crystalline Se could be found in the powder diffraction data, although

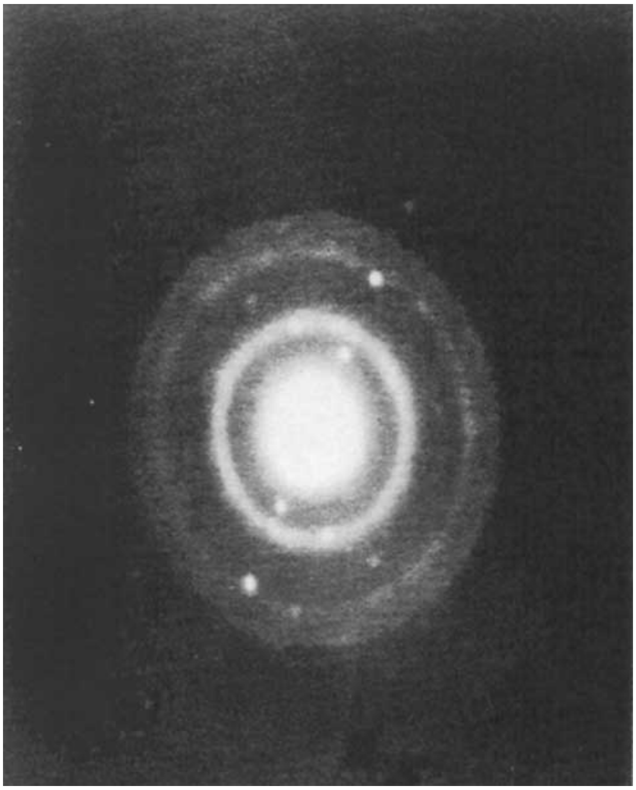

FIGURE 3 Selected area transmission electron diffraction pattern obtained from CdSe thin film following immersion in 0.01 M $HgCl_2$ for a period of 5 minutes. The reflections lying outside the CdSe diffraction rings indicate the presence of the new phase, α-$Hg_3Se_2Cl_2$.

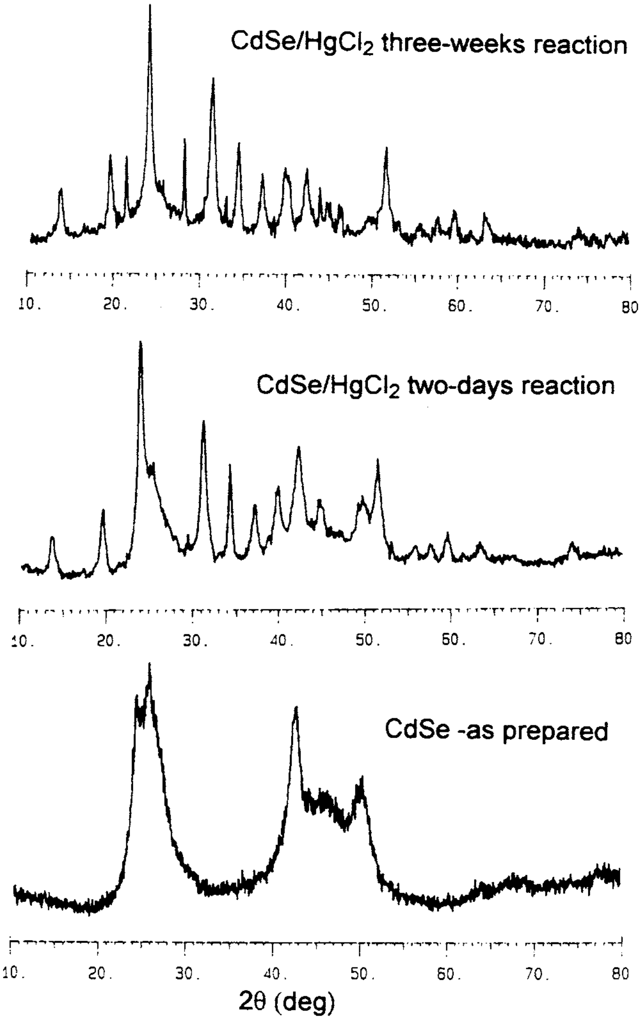

FIGURE 4 Copper K_α X-ray powder diffraction patterns of as-prepared CdSe and of CdSe following reaction with 0.01 M $HgCl_2$ for two periods of time, 2 days and 3 weeks.

some generally high background seems to be present in the region between $d = 3$ Å and $d = 4$ Å. Puff and coworkers [11,12] carried out detailed studies of the reactions between mercury chalcogenides and $HgCl_2$ and established the structures of some of the products of these reactions including α-$Hg_3S_2Cl_2(s)$. The reaction analogous to (i), between HgSe(s) and aqueous $HgCl_2$, produced α-$Hg_3Se_2Cl_2(s)$, but the reaction between HgSe(s) and aqueous $HgCl_2$, analogous to (ii), is not spontaneous since

$$HgSe(s) + HgCl_2(s) = Hg_2Cl_2(s) + Se(s),$$
$$\Delta G^\circ = 2.86\ \text{kJ/mol} \qquad [3]$$

and the chemical potentials, μ, are $\mu(HgCl_2, 0.01\ M) < \mu\ (Hg_2Cl_2, s)$.

Air Annealing of CdSe. Previous work [1] has shown that CdSe thin films are of poor crystallinity. X-ray diffraction peaks are not detectable in the XRD spectra. However, well-defined peaks corresponding to the hexagonal form of CdSe can be observed following air annealing of the films at 450°C for 1 hour. In order to further investigate the thermal transformations of CdSe, powder collected from the deposition bath was heated in air at 450°C. Figure 6 shows the XRD patterns for as-prepared CdSe as well as CdSe heated at 450°C for 1 hour and simulation patterns for cubic and hexagonal CdSe. It can be seen that the freshly deposited precipitate had only the poorly defined pattern characteristic of cubic CdSe that was reported previously for films of CdSe deposited on glass [1,2]. When CdSe was heated in air at 450°C, two obvious changes in its X-ray pattern occurred. First, the lines in the pattern became very sharply defined and are characteristic of hexagonal CdSe [**4(e)**] rather than cubic CdSe. Second, three additional reflections (d_{hkl} = 3.08, 1.92, and 1.60 Å) of a new phase appeared in the pattern that could be ascribed to partial oxidation of cadmium selenide. Extended heating (450°C, 24 hours) yielded a complex XRD pattern, indicating the probable formation of a number of oxidation products. This situation is analogous to the air heating of CdS, whereby several oxidation products are formed [13].

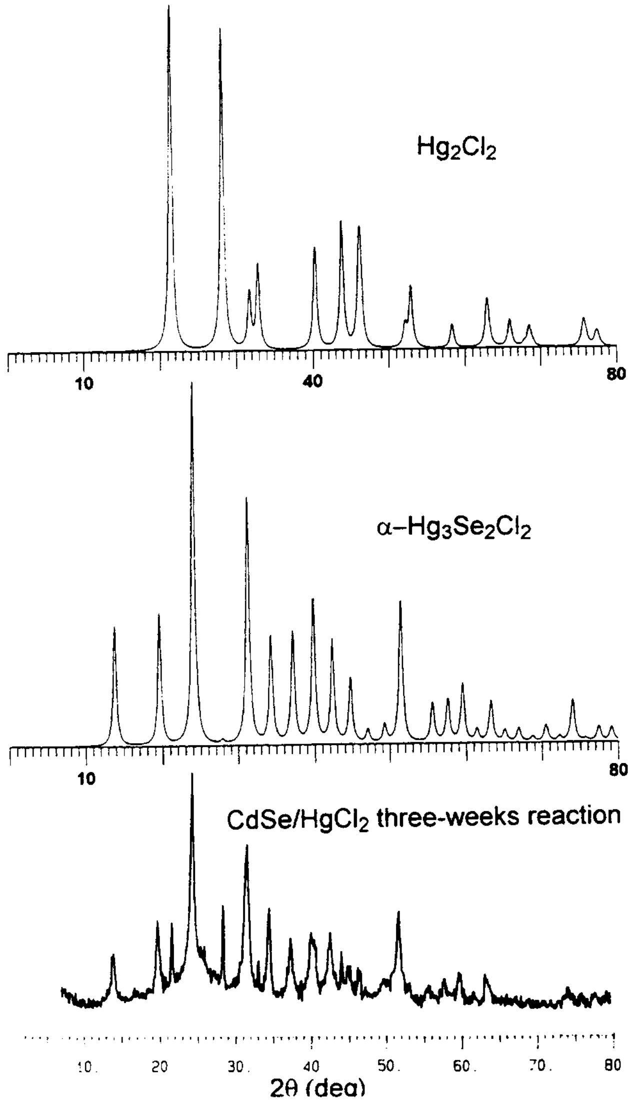

FIGURE 5 Copper K_α X-ray powder diffraction pattern of as-prepared CdSe following reaction with 0.01 M $HgCl_2$ for a period of 3 weeks and simulated powder diffraction patterns for the products of the reaction, α-$Hg_3Se_2Cl_2$ and Hg_2Cl_2.

CONCLUSIONS

The reaction between thin film and cadmium selenide powder with aqueous $HgCl_2$ has been studied by EM, ED, XRD, and XPS. In addition to the direct cation exchange, analysis of the ED pattern produced by CdSe thin films, which underwent reaction with 0.01 M $HgCl_2$ for a 5 minute period, and XRD patterns of CdSe powder treated with 0.01 M $HgCl_2$ for 3 weeks revealed the occurrence of the following reactions:

$$2CdSe(s) + 3HgCl_2(aq) = 2CdCl(aq) + \alpha\text{-}Hg_3Se_2Cl_2(s)$$

$$CdSe(s) + 2HgCl_2(aq) = CdCl_2(aq) + Hg_2Cl_2(s) + Se(s)$$

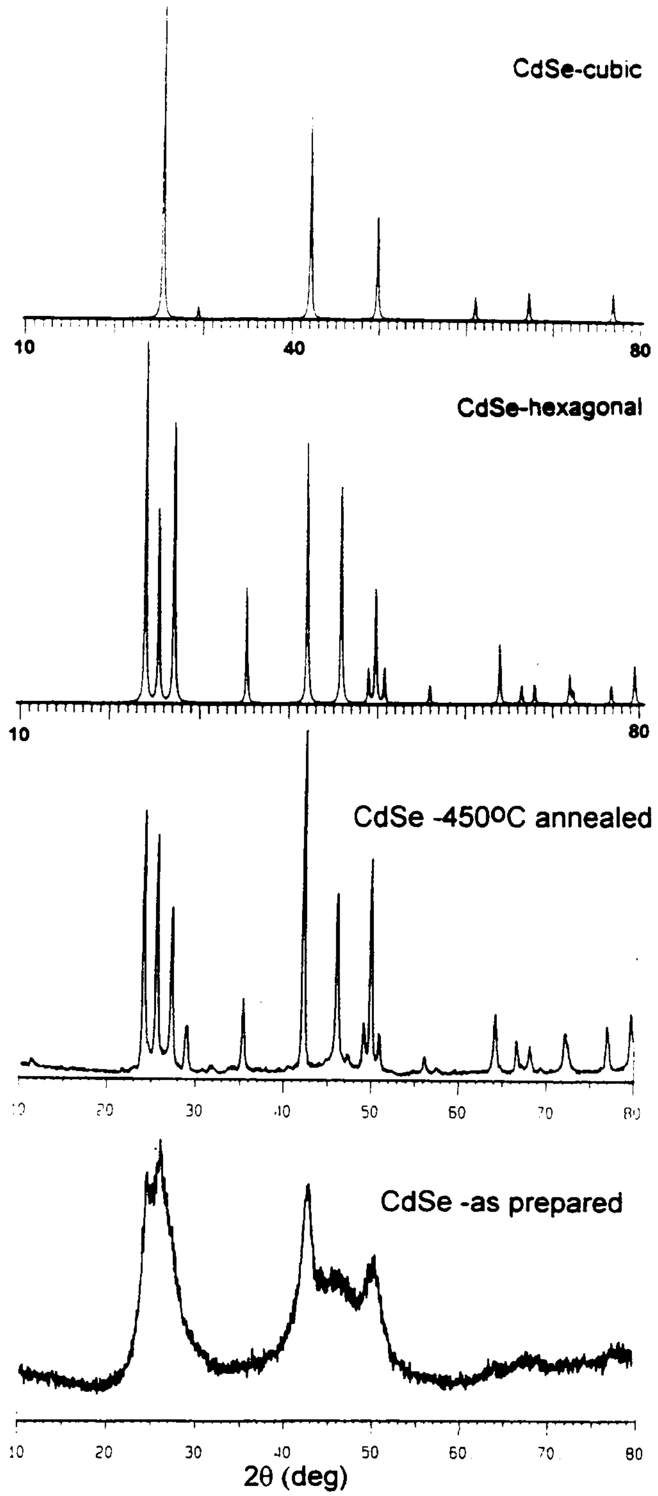

FIGURE 6 Copper K_α X-ray diffraction patterns of as-prepared CdSe and of CdSe following 1 hour heating in air at 450°C. The simulated powder diffraction pattern for the hexagonal and cubic forms of CdSe are provided for comparison.

Heating CdSe powder in air to 450°C brought about a transformation from a poorly crystalline cubic material to a well-defined hexagonal form of CdSe, as revealed by observed XRD patterns, in agreement with previous results on air-heated CdSe thin films [1,2]. The presence of additional XRD peaks not belonging to hexagonal CdSe indicates the presence of an oxidation product. This product has not yet been identified, and further experiments are being undertaken to establish its identity.

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