Structure and optical properties of Cd-substituted ZnO (Zn$_{1-x}$Cd$_x$O) nanostructures synthesized by the high-pressure solution route

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Abstract

We report the synthesis of Cd-substituted ZnO nanostructures (Zn$_{1-x}$Cd$_x$O with $x$ up to $\approx 0.09$) by the high-pressure solution growth method. The synthesized nanostructures comprise nanocrystals that are both particles ($\sim 10$–$15$ nm) and rods which grow along the [002] direction as established by transmission electron microscope (TEM) and x-ray diffraction (XRD) analysis. Rietveld analysis of the XRD data shows a monotonic increase of the unit cell volume with the increase of Cd concentration. The optical absorption, as well as the photoluminescence (PL), shows a red shift on Cd substitution. The line width of the PL spectrum is related to the strain inhomogeneity and it peaks in the region where the CdO phase separates from the Zn$_{1-x}$Cd$_x$O nanostructures. The time-resolved photoemission showed a long-lived ($\sim 10$ ns) component. We propose that the PL behaviour of the Zn$_{1-x}$Cd$_x$O is dominated by strain in the sample with the red shift of the PL linked to the expansion of the unit cell volume on Cd substitution.

1. Introduction

In recent years there has been renewed interest in studying the optical properties of ZnO nanocrystals. ZnO is a wide band gap (3.37 eV) semiconductor with large excitonic binding energy (59 meV) [1]. It can be used as an ultraviolet (UV) lasing material by stimulated emission of excitons at temperatures well above room temperature [2]. For controlled applications, band gap engineering is technologically very important. It is possible to tune the band gap of ZnO by alloying with suitable candidates. Isovalent substitution of Mg leads to enhancement of its band gap [3–5], whereas Cd incorporation reduces the same [6]. In nanocrystals, the band gap tuning can also be done by utilizing quantum confinements, which leads to a blue shift. The band gap engineering leads to a tuning of the PL emission energy and also a change of the lifetime of the emission. In the context of doped ZnO nanocrystals these issues, though studied in the past, have not been well understood.

In this paper we describe the synthesis of Zn$_{1-x}$Cd$_x$O nanostructures by an energy-efficient high-pressure solution route which can produce a large amount of Zn$_{1-x}$Cd$_x$O nanocrystals of good structural and optical qualities. The nanocrystals tend to have the shape of a nanorod. We show that such nanocrystals have near band edge PL that is red shifted significantly and have relatively large PL decay time ($\sim 10$ ns) as revealed through time-resolved PL measurements. The nanocrystals do not show the defect-related green emission often seen in ZnO nanostructures. We could also link the tuning of the band gap and the PL to the expansion of the unit cell as a result of the Cd substitution. The full width at half maximum (FWHM) of the near band edge emission band has been found to be linked to the strain inhomogeneity arising from the process of substitution.

The major challenge faced in the solution route synthesis process is that the CdO is formed at relatively high temperature (230 °C), which is much higher than the boiling point of most
of the solvents generally used for solution synthesis. Also because of different crystal structures of ZnO (wurtzite) and CdO (rock salt), they tend to get phase separated very easily. To overcome these problems, Zn$_{1-x}$Cd$_x$O has been synthesized in an autoclave at high pressure ($\approx$55 atm), which can increase the boiling point of solvents like ethanol which allow relatively higher temperature synthesis. At this high temperature and pressure, Zn$_{1-x}$Cd$_x$O nanostructures form along with CdO.

The nanostructures consisted of both particles and rods of good crystallinity and optical quality.

It is noted that many interesting structures of ZnO have been synthesized by self-assembly as well as by the vapour transport method [7–9]. But Cd-substituted ZnO has been prepared so far by only vapour phase methods. Epitaxial films of alloyed Zn$_{1-x}$Cd$_x$O grown on a substrate have been mostly fabricated by pulsed laser deposition (PLD) [6], molecular beam epitaxy (MBE) [10] and remote plasma-enhanced metal–organic chemical vapour deposition (RPE-MOCVD) [11]. Recently Zn$_{1-x}$Cd$_x$O nanorods have been fabricated by the thermal evaporation of precursors containing Zn and Cd [12]. Production of nanocrystals of Cd-substituted ZnO by vapour phase methods has its limitations, because it is expensive, and the materials obtained are in small quantities. Thus the synthesis of Cd-substituted ZnO nanostructures is a very desirable step. There are a large number of reports of the synthesis of undoped ZnO by solution or hydrothermal methods [13–16]. Undoped ZnO nanorods have been synthesized by a hydrothermal method very recently [17]. However, there has been no published report so far on the solution route synthesis of Zn$_{1-x}$Cd$_x$O nanostructures. Demonstration that one can produce band gap tuned good quality nanocrystals of Cd-substituted ZnO by a low-temperature solution route opens up the possibility of large-scale synthesis of this material.

2. Experimental details

2.1. Synthesis of nanostructures

ZnO and Zn$_{1-x}$Cd$_x$O nanostructures were synthesized by a simple solution route using a mixture of cadmium acetate and zinc acetate in ethanol. For the synthesis of undoped ZnO nanostructures, 15 mM solution of zinc acetate dihydrate and 45 mM solution of sodium hydroxide were prepared in ethanol. The solution was sonicated until it became clear. The clear solution thus prepared was put in a Teflon-lined autoclave (pressure $\approx$55 atm) and kept inside an oven preset at 230°C. ZnO nanostructures of average size varying from 15–20 nm were formed after two hours of reaction within the autoclave. The nanostructure thus fabricated was sonicated for half an hour to get the proper size dispersion. To obtain the Zn$_{1-x}$Cd$_x$O nanostructures, an ethanol-based solution of zinc acetate dihydrate, cadmium acetate dihydrate and sodium hydroxide was prepared and similar steps as described above were followed. The dispersed solution contained two phases: hexagonal Zn$_{1-x}$Cd$_x$O of average size 15–20 nm and CdO of average size 70–80 nm having the rock salt structure. Precipitation of only CdO particles was possible by centrifuging the solution at 2000 rpm for one minute. The filtrate containing Zn$_{1-x}$Cd$_x$O was again centrifuged at 5000 rpm for four minutes to obtain the precipitate. The Zn$_{1-x}$Cd$_x$O precipitate was again dispersed in ethanol and centrifuged several times to wash the material.

2.2. Structural and optical measurements

X-ray diffraction (XRD) and inductively coupled plasma atomic absorption spectroscopy (ICP-AES) were carried out on precipitates dried at 120°C. The precipitate was re-dispersed in ethanol and taken in a cuvette for optical measurement. A crucial parameter in the synthesis of Cd-substituted ZnO is the determination of the exact Cd content. The Cd content $x$ was determined by ICP-AES as well as by energy dispersive x-ray (EDX) analysis. However, we found that the EDX analysis shows approximately 50% lower Cd content as compared to the ICP-AES method. We have considered the ICP-AES test results as a more accurate method due to its quantitative nature of calibration, which was done with the available standards.

The room-temperature optical properties were studied using a UV–visible spectrophotometer (Shimadzu UV-2450 [20]) and a xenon arc lamp as the illuminating source. The excitation wavelength used for the PL measurement was 325 nm. We carried out time-resolved photoluminescence (TRPL) measurements on the Cd-doped nanostructures. For time-resolved measurements, the samples were excited at 299 nm, by a pulsed light-emitting diode of 40 MHz repetition rate. The PL decay times were measured by using the time-correlated single-photon counting technique [22].

3. Results

3.1. Standardization of the method of synthesis and composition analysis

The synthesis of Zn$_{1-x}$Cd$_x$O nanostructures by the solution method is challenging for two reasons: (1) CdO is formed only at temperatures above 220–230°C. At temperatures below 100°C, synthesis by the acetate route leads to only CdCO$_3$ formation. Up to 170–180°C, Cd(OH)$_2$ is formed, and no incorporation of Cd into ZnO takes place. Incorporation of Cd in ZnO occurs only when the growth temperature is above 200°C. This necessitates a high-temperature solution route. (2) Because of the different structures of ZnO (hexagonal) and CdO (rock salt), they tend to get phase separated easily. Most of the Cd added to the solution leads to the formation of CdO and only a small part gets incorporated into the ZnO lattice.

To obtain higher temperatures, the reaction is made to happen within an autoclave working at 230–240°C. In this temperature range CdO is formed, and incorporation of Cd into ZnO is also initiated. The formation of CdO can be detected by visual observation. As soon as CdO formation starts, the bluish colour of the ZnO dispersion turns reddish. As the Cd concentration in the reactant is increased further, the
incorporation of Cd into ZnO takes place along with a phase segregation of CdO. The two phases thus formed have different sizes. While the Zn$_{1-x}$Cd$_x$O nanocrystals have an average size of $\sim$10–15 nm, the CdO particles have a much larger size, $\sim$80 nm. This difference in size allows us to separate the two phases by centrifugation. The subsequent compositional analysis and structural and optical studies were conducted after the two phases were physically separated.

Analysis of the Zn$_{1-x}$Cd$_x$O nanocrystals by ICP-AES shows that the maximum observed Cd incorporation into the ZnO nanostructures corresponds to $x \approx 0.091$, which is comparable to that of some of the vapour-phase synthesized samples [23]. However, there are reports of some vapour-phase grown samples where a very high value of $x$ has been observed [24]. It appears that the measure of the exact amount of Cd incorporated in a sample is dependent on the analytical technique used. In figure 1 we show the exact value of $x$ as determined through ICP-AES analysis versus the molar fraction of Cd(CH$_3$COO)$_2$·2H$_2$O added in the Zn(CH$_3$COO)$_2$·2H$_2$O solution. As mentioned before, we use the ICP-AES data because it is a bulk analysis method that is based on quantitative standards. We feel that the difference in the Cd concentration analysed by the two techniques (EDX and ICP-AES) arises because, while the ICP-AES technique is averaged over the bulk, EDX is a surface-sensitive technique, being limited by the electron penetration depth, and what it reports is essentially the concentration near the surface. Due to the segregation of the CdO from the nanocrystals, there may be a concentration gradient, so the concentration decreases from the interior of the nanocrystals to the surface, and the difference in the Cd concentration seen by the two techniques may reflect this. The quantitative compositional analysis (irrespective of the technique used) establishes that the Cd incorporation is indeed very low due to the high lattice mismatch and difference in crystal structure of ZnO and CdO. We will see below that the incorporation Cd into ZnO gets limited because phase segregation occurs very early (at $x \approx 0.03$) in the growth process: the Zn$_{1-x}$Cd$_x$O nanocrystals physically separate out from the CdO crystals, those having relatively larger size.

3.2. Characterization by transmission electron microscopy

The size and microstructure of the undoped and doped samples have been investigated in detail using a transmission electron microscope (TEM). For low $x$ ($x < 0.03$) the nanostructures those are formed are predominantly spherical-shaped nanocrystals. As an example we show in figure 2(a) the particle size distribution of the undoped ZnO sample. The nanostructures are predominantly spherical in shape and the average size is $\sim$15–20 nm. This is similar to that found in the synthesis route under normal pressure and at temperature $70^\circ$C [5]. For particles with low values of $x$, the size distributions are very similar to those of the undoped nanocrystals. The lattice image (figure 2(b)) confirms the crystalline nature of the sample and the distances between two consecutive lattice fringes (2.41 Å) is similar to the interplanar spacing of the (101) set of planes, as indicated in the figure.

The spherical shape of the nanostructures no longer persists once significant Cd incorporation occurs. This is shown in figure 3. For $x = 0.065$, it can be seen that along with spherical nanocrystals one also sees the formation of hexagonal nanocrystals as well as the formation of nanorods, as marked in the figure. The nanocrystals have typical size from 15–20 nm for $x < 0.03$ to 10 nm for $x > 0.05$. The rods have typical diameter of $\sim$10–12 nm and length 20–25 nm. The histogram of the aspect ratio is shown in the inset of figure 3. The trend of rod formation persists to higher concentration of Cd and eventually the tendency for rod formation predominates. In figure 4(c) we show the HRTEM image of a single rod (formed at $x = 0.065$) which is aligned in the [002] direction.

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**Figure 1.** The value of the Cd content $x$ observed by ICP-AES analysis against the mixing of various amounts of Cd(CH$_3$COO)$_2$·4H$_2$O in the Zn(CH$_3$COO)$_2$·2H$_2$O solution.

**Figure 2.** (a) The average size distribution and (b) an HRTEM image of undoped ZnO ($x = 0$) nanostructures.
Figure 3. Growth of faceted nanocrystals along with hexagonal nanorods of Zn$_{1-x}$Cd$_x$O (indicated by arrows) for $x = 0.065$ is shown. The diameter distribution and aspect ratio distribution of the nanorods are depicted in the inset.

Figure 4. HRTEM images of the hexagonal nanoparticle and the nanorod are shown in figures 4(a) and (c) respectively. The FFTs of the lattice fringes of (a) and (c) are shown in (b) and (d) respectively. The growth direction of the single crystalline nanorods ([002]) can be seen.

The lattice spacing (2.68 Å) matches that of the interplanar spacing of the [002] set of planes. As shown in figure 4(d), the FFT (fast Fourier transform) of the lattice image confirms that the rods are single crystalline and have only [002] orientation as the growth direction. This preferred orientation has also been confirmed by the XRD data analysis, presented later on. For comparison, in figures 4(a) and (b) we show respectively the HRTEM image and its FFT of a spherical nanocrystal, which shows the hexagonal symmetry of the lattice. At higher concentration rods are synthesized in higher proportion but they retain their size and aspect ratio as well as the orientation [002]. The single-phase nature of Zn$_{1-x}$Cd$_x$O is confirmed from the TEM as well as by the XRD data for $x \leq 0.091$. There is no further incorporation of Cd in ZnO beyond this value of $x$. Addition of more Cd salt in the solution leads to the formation of more CdO.

3.3. Structural analysis from x-ray diffraction data

The structural analysis of the powdered x-ray diffraction data of the Zn$_{1-x}$Cd$_x$O nanostructures was carried out extensively by using the Rietveld method [25]. The XRD patterns of the Zn$_{1-x}$Cd$_x$O alloy nanostructures are shown in figure 5. The XRD data analysis also allows us to establish the range of Cd concentration in which phase segregation occurs. We could go to a maximum Cd incorporation of $x = 0.091$, as stated before. It can be seen in figure 5 that, at $x \approx 0.091$, there is a segregated phase of CdO that coexists with Zn$_{1-x}$Cd$_x$O nanostructures. The nanocrystals have wurtzite structure (peaks are indexed), as that of the parent ZnO ($x = 0$). However, the peak positions shift to lower 2θ values due to the Cd incorporation, signifying a change (increase) in the lattice constant. (Note: we also find from the XRD data that a CdO phase appears at a rather low level of $x = 0.03$. However, as mentioned before most of the Cd forms the CdO phase with nanoparticles with average size $\sim$70–80 nm. We have separated out the CdO particles by centrifuging,
and the XRD data show are only from the \( \text{Zn}_{1-x}\text{Cd}_x\text{O} \) nanostructures with average size \( \sim 10–20 \) nm, which are single phase.) The XRD data along with the TEM data presented before establish that the high-pressure solution route can be used to synthesize nanocrystals of single-phase \( \text{Zn}_{1-x}\text{Cd}_x\text{O} \) alloy of good crystallinity.

The texture growth of rods in the nanostructure synthesis as the Cd content is increased, as seen in the TEM images, is also clearly seen in the XRD data. The relative intensity of the Bragg peak due to [002] planes of the wurtzite structure increases with the increase in Cd content. This fact can be clearly seen from figure 6, where the intensity ratios of the Bragg peaks (100) and [002] to the maximum intensity peak (101) of the wurtzite phase have been plotted with the increase in Cd content. The important observation is that the intensity ratio [002]/(101) increases sharply up to \( x = 0.03 \), beyond which it saturates. To establish that the growth occurs preferentially in the [002] direction, we have plotted for comparison the intensity ratio of (100)/(101) peaks, which has a more or less constant value. This confirms the increase in the preferred growth of rods aligned in the [002] direction as we increase the Cd concentration. The [002] direction is an easy axis of growth for ZnO and most nanorod formation in ZnO occurs in this orientation.

There is yet another important observation that accompanies the process of texturing. The XRD peaks of the wurtzite phase show enhanced full width at half maximum (FWHM) values for higher Cd content. We have carried out a Williamson–Hall analysis [26] of the XRD data. The analysis shows that the increase in the XRD line width occurs due to an enhancement of the inhomogeneous strain (which we refer to as the microstrain) as well as due to a decrease in the average size of the \( \text{Zn}_{1-x}\text{Cd}_x\text{O} \) nanostructures with the increase in Cd content. The enhancement of the microstrain, as seen through the XRD analysis, also broadens the FWHM of the PL peak, as we see later on. The observed increase in strain values can be due to the effect of fluctuation in the Cd concentration, as previously suggested by Makino et al [6].

**Figure 6.** The intensity ratios of the Bragg peaks (100) and [002] to the maximum intensity peak of the wurtzite structure (101) have been plotted against the Cd content \( x \). The enhanced intensity ratio of [002]/(101) peaks indicates an increase in the preferred orientation in the [002] direction. In comparison the value of the (100)/(101) ratio is mainly unchanged as the Cd concentration is changed.

Variations of the lattice parameters and crystallite sizes were obtained from the Rietveld analyses of the observed XRD data. As the Cd content is increased, the peak positions of the XRD data shift to lower angles due to increase in lattice volume which is caused by the incorporation of Cd\(^{2+}\) ions having higher ionic radii (0.97 Å) in place of the Zn\(^{2+}\) ions (0.74 Å) in the ZnO lattice [27]. The calculated profile matches well with the observed data, as shown in figure 5. In this least-square refinement the peak shape is assumed to be pseudo-Voigt. The residues of the fitting for all the data are indicated in figure 5. We have noted before (as measured through the HRTEM observation) that enhanced incorporation of Cd in ZnO also changes the growth morphology. We could find a signature of this in the analysis of the XRD data. We find that the average size of the \( \text{Zn}_{1-x}\text{Cd}_x\text{O} \) nanostructures was observed to decrease from 15–20 nm (\( x = 0 \)) to 10 nm for \( x > 0.05 \). Beyond that the size remains constant.

The lattice parameters \( (c \text{ and } a \text{ axes}) \) extracted by Rietveld analysis show that they increase monotonically as the Cd content is increased. The change is small but it is distinct. In figure 7 we show the variation of the unit cell volume \( (V = 0.866a^2c) \) and the microstrain as well as the \( c/a \) ratio as a function of the Cd content. The cell volume increases by nearly 0.8% on Cd substitution. It is interesting to note that the small yet distinct compaction of the lattice does not preserve the \( c/a \) ratio. Most of the change occurs in the parameter \( a \), which increases by 0.3%, while the parameter \( c \) expands only by 0.19%. This reduces the \( c/a \) ratio. Here we note that the expansion of the unit cell volume on Cd substitution can be thought of as a ‘negative pressure’ arising from the larger Cd ions. The negative pressure is not hydrostatic and leads to
been found in films grown by the vapour phase method [6]. Increase of the unit cell volume on Cd substitution has also Cd substitution. The changeover occurs at $x \approx 0.03$. Determination of the band gap is not possible, due to the broad nature of the absorption.

preferential compaction of $a$, leading to a smaller $c/a$ ratio. Increase of the unit cell volume on Cd substitution has also been found in films grown by the vapour phase method [6].

From figure 7 it appears that there are two stages in the Cd substitution. The changeover occurs at $x \approx 0.03$. Below $x = 0.03$ the nanocrystals are predominantly spherical. In this region the microstrain increases till the CdO separates out, which occurs beyond $x = 0.03$. Above $x = 0.03$, when the CdO separates out, the growth leads to nanorod formation; these rods have preferential orientation along [002]. The intensity ratio [002]/(101) shown in figure 6 reflects this change of stage at $x \approx 0.03$. The intensity ratio saturates beyond $x = 0.03$, indicating preferential growth of [002]-oriented nanorods. Figure 7 also indicates that, beyond $x = 0.03$, the phase separation releases some of the microstrain in the lattice.

The detailed structural investigations presented before have established that single-crystalline nanocrystals as well as rods of well characterized structural quality can be synthesized by the high-pressure solution route. The structural studies have also established some of the subtle features in the growth of Cd-substituted nanocrystals; in particular, the stages of growth as well as rods with textured structure are interesting observations that have not been reported before. There is a continuous expansion of the unit cell volume on Cd substitution with a small reduction in the $c/a$ ratio of the lattice constants.

3.4. Optical properties

Below we present the results of the optical studies of nanocrystals dispersed in ethanol. The concentration of the final solution was maintained at 2 mM. Investigation of the optical properties of the chemically synthesized alloy $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ nanostructures is a principal motive of the present investigation. The structural studies presented above show the quality of the material grown and also reflect the small yet distinct changes in the crystal lattice that are likely to have an impact on the optical properties. We have investigated the change in the absorption, the photoluminescence (PL) and also the time-resolved PL (TRPL) in these materials at room temperature. These measurements allow us to assess the utility of these chemically synthesized materials for application as a band gap engineered optical material [6].

3.4.1. UV–visible absorption. One of the important effects of Cd incorporation into ZnO is the reduction of its direct band gap value, as has been seen in vapour phase synthesized $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ nanostructures. The band gaps of the alloy nanostructures were determined by monitoring the onset of the fundamental absorption edge. As shown in figure 8, a sharp peak appears in the absorption spectra of undoped ZnO nanostructures even at room temperature, due to the large excitonic binding energy (59 meV) of ZnO [1]. The absorption curves shift to lower energy for the alloy nanostructures. The absorption edge can be clearly identified from the optical absorption up to $x < 0.03$. Beyond that the absorption edge gets blurred, probably due to the appearance of a large number of disordered induced states within the band gap and partially due to the CdO present along with the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ nanostructures. The shift in the band edge (for $x < 0.03$) as a function of $x$ is shown in figure 10. The direct band gap value of the undoped ZnO nanocrystals ($\sim 3.37$–$3.45$ eV) is found to be $3.37$ eV, which is the fundamental absorption edge of the bulk ZnO. In the size regime we are working in, no quantum confinement effect has been observed [28]. One can see a monotonic decrease of the gap with increase of the Cd content. (Note that although we have observed a decrease in the average size of the nanostructures on Cd incorporation, the size is still larger than the size range where quantum confinement effects (diameter $<5$ nm) can alter the band gap. Even if there is any effect of quantum confinement, this will reduce the extent of red shift.) Thus the limited absorption data can be analysed to establish that the absorption edge of the chemically synthesized $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ nanostructures can also be red shifted as in the vapour phase grown materials, and that the shifts are comparable [23].

3.4.2. Photoluminescence. A clearer signature of the red shift on Cd substitution can be seen from the photoluminescence data. The photoluminescence (PL) spectra of pure ZnO and $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ nanostructures were measured with an excitation of $325$ nm. The emission spectra taken with $325$ nm excitation are shown in figure 9. The undoped ZnO nanostructures show sharp emission in the UV region ($P_1$) at $371$ nm (3.345 eV). The emission at $371$ nm has been established due to exciton recombination. A broad and weak emission ($P_2$) is also observed at $389$ nm (3.189 eV), the exact nature of which has not been identified, but it arises also from excitons that are bound to defects [29]. We do not see any green emission at $\sim 450$–$500$ nm which has been seen in a number of nanoparticles of ZnO [5]. The green emission is typically taken as a signature of defects (like oxygen vacancies) in the ZnO [30]. (Note: in most nanocrystals and quantum dots of ZnO the emission at room temperature occurs at around $3.25$–$3.35$ eV. While in bulk single crystals at room temperature the UV emission at $\sim 3.3$ eV is attributed to free excitons, the UV emission in nanocrystals and quantum dots is due to
Figure 9. The room-temperature emission spectra for $x = 0$, $x \approx 0.034$ and $x = 0.091$ are shown in figure (a)–(c) respectively. The $P_1$ emission band of $\text{Zn}_1-x\text{Cd}_x\text{O}$ nanostructures shows a red shift due to the incorporation of Cd, as indicated in the figure.

The $\text{Zn}_1-x\text{Cd}_x\text{O}$ nanostructures show $P_1$ emission, as in the case of undoped $\text{ZnO}$, and there is no significant shift in the position of the $P_1$ component on Cd substitution. However, the relative contribution of this line to the total emission reduces significantly. The emission line $P_1$ which is unchanged on Cd substitution is most likely the emission from the small amount of pure $\text{ZnO}$ nanostructures that is left undoped and mixed in the $\text{Zn}_1-x\text{Cd}_x\text{O}$ nanostructures.

The main change occurs in the broad peak $P_2$, which shows a gradual red shift as well as enhanced intensity due to the incorporation of Cd. The gradual red shift of the emission energy of $P_2$ with Cd content is shown in figure 10. For the highest Cd content ($x = 0.091$) $P_2$ occurs at 417 nm (2.976 eV), which is 213 meV red shifted from the undoped $\text{ZnO}$. In figure 10 we also show the intensity ratio of the two peaks ($P_2/P_1$) as a function of $x$. The figure shows the shift in the intensity as the alloying takes place. However, after the first stage of growth ($x \approx 0.03$) the ratio saturates.

A substantial change in the PL characteristics can be seen in the line width of the $P_2$ band. The full width at half maximum (FWHM) of the $P_2$ line changes as the Cd concentration increases (see figure 11). It can be seen that the dependence is not monotonic. It first increases with $x$, reaching a maximum at $x \approx 0.04-0.045$, and then decreases again. For the line $P_1$, the FWHM is more or less constant, but it shows a shallow peak near the composition range where the FWHM of the line $P_2$ also shows a peak. We note here that the line width appears to have a relation to the microstrain, whose variation with $x$ is shown in figure 7. The microstrain reaches a maximum for $x \approx 0.03-0.04$. We discuss this issue more later on.

3.4.3. Time-resolved photoluminescence. We have collected time-resolved photoluminescence (TRPL) data from nanocrystals of $\text{Zn}_1-x\text{Cd}_x\text{O}$. The representative data taken from three compositions are shown in figure 12. The TRPL data were obtained on the $P_2$ line after excitation at 299 nm. The lifetime decay curves have been resolved into three components by deconvolution fitting of the data with the relation

$$I(t) = \sum_{i=1-3} A_i \exp(-t/\tau_i).$$
The parameters $A_i$ ($i = 1, 2, 3$), which give the weight of the components and the decay time constants $\tau_i$ ($i = 1, 2, 3$) of the transients, are shown in table 1. The first observation that we make is that there is actually an increase in all the decay time constants on Cd substitution. The natural decay time of free excitons in ZnO is rather small and in the range of 1 ns. The decay times observed here are larger, suggesting that the emission mainly involves localized excitons. The change in the decay time constant on Cd substitution is different for the three components. It is marginal for the longest time constant $\tau_3$ ($\sim 10\%$), noticeable for the intermediate time constant $\tau_2$ ($\sim 25\%$) and substantial for the shortest time constant $\tau_1$ ($\sim 100\%$), which increases from 266 ps to 544 ps. We find that the maximum decay occurs through the process that has the longest decay time constant $\tau_3$ ($\approx 9–10$ ns), which has a relative weight of nearly 50%, and there is a very little change in its weight on alloying.

4. Discussions

In this section we discuss the physical implications of some of the important observations that came out from this work. The issues that we discuss are about growth, PL properties and what appears to us as the essential role of the lattice strain on Cd substitution that affects the growth and phase separation as well as the PL property.

4.1. Growth

We find that the growth of the nanocrystals changes characteristics when the Cd is gradually substituted. The two phases in growth, with a change at $x \approx 0.03$, were pointed out before (see section 3.2). One of the observations about the growth is that when the Cd concentration increases the average size of the nanocrystals grows to about half of the size obtained in the undoped case, and there is formation of nanorods with [002] growth direction that predominates near the higher range of Cd concentration. We propose to explain this observation in the following manner. It is known that, in solution phase, if the initial nucleation process is fast, the growth generally occurs by such coarsening process as Oswald ripening (OR), which is diffusion limited, or through the aggregation by orientation (AO) that leads to ordered growth of nanocrystals with different morphology [33]. The growth of nanorods of ZnO as has been observed by us is likely due to the AO process, which is similar to the growth of TiO$_2$ nanocrystals from solution [33]. The occurrence of the AO process as an alternate growth process occurs when a diffusion-dependent process like OR or direct precipitation from solution gets limited. The size-limited growth of nanocrystals on Cd substitution is a manifestation of the reduction of such diffusion-dependent pathways. Two processes can limit the diffusion-dominated processes. The presence of strain on Cd substitution can limit growth, as has been observed in a number of crystal growth processes [34, 35]. This occurs due to increase of free energy of the strained nanocrystals. Another alternate reason can be the presence of Cd$^{2+}$ ions. The incorporation of Cd into ZnO during the growth occurs through absorption of Cd$^{2+}$ ions on the surfaces of the growing crystals. It is known that the absorption of ions can limit the growth rate in the solution growth process [36]. To summarize this part, the presence of strain and/or adsorption of Cd$^{2+}$ ions can limit the growth through a diffusion-limited process leading to growth by AO that gives rise to nanorods with [002] orientation.

4.2. Photoluminescence

The effects of the Cd substitution are clearly apparent on the PL properties. The main effect is indeed on the emission line $P_2$. This line red shifts and broadens (as revealed through the enhancement of the FWHM). This red shift is substantial and is similar to that found in the vapour phase grown samples. The position of the line $P_2$ appears to be tagged to the red shift of the band edge with the Stokes shift remaining nearly constant.
on Cd substitution. (Note: the data for band edge shift are limited to $x < 0.03$.)

In ZnO crystals it has been shown that a hydrostatic pressure can blue shift the band gap [37]. In films of wide band gap semiconductors like ZnO grown on substrates with lattice constant mismatch, the PL is shifted by the in-plane strain arising due to the mismatch [38]. It has been shown that in films with compressive strain, the PL is blue shifted, while tensile strain leads to red shift. We propose that a partial contribution to the red shift of the PL in Zn$_{1-x}$Cd$_x$O nanostructures, which is a consequence of the red shift of the band edge, arises due to the strain produced by the Cd substitution. It need be noted that in the substituted alloy Zn$_{1-x}$Cd$_x$O, which is a mixed crystal, one would expect that a contribution to the decrease in the band gap on Cd substitution will also arise as the end member CdO (though of a different crystal structure) has a smaller band gap. The Cd substitution that leads to an expansion of the unit cell can be interpreted as a ‘negative’ pressure producing a similar effect to that of a tensile strain in a film. It is proposed that the ‘negative’ lattice pressure produced by the Cd substitution is the cause of the red shift seen in the PL. In figure 13 we plot the red shift of PL line ($P_2$) as a function of the unit cell size. One can see the smooth variation of the PL line with the unit cell volume.

The line width of the main PL line as measured by the FWHM has a severe sensitivity to the inhomogeneous lattice strain (microstrain) that develops during the process of Cd substitution. As can be seen from figure 7, the microstrain reaches a maximum for $x \approx 0.03$–0.04. This is the region where the segregation of the CdO occurs, and this phase separation actually reduces the microstrain somewhat. The FWHM of the PL reflects this variation of the microstrain and reaches a shallow maximum for $x \approx 0.04$–0.045 (see figure 11). A similar trend, although much weaker, is seen in the FWHM of the line ($P_1$), also suggesting that the broadening of the PL line is predominantly due to the strain homogeneity arising due to the Cd substitution.

4.3. Essential role of strain in the Cd-substituted ZnO

The dependence of the position of the PL line on the cell volume as well as the line width of the PL line on microstrain strongly suggests a link between the emission process and the strain. It has been seen in a number of random substitution alloy semiconductors (e.g., CdS$_{1-x}$Se$_x$) [39] that the disorder due to random substitution can lead to smearing of the band edge absorption as well as broadening of the PL line. Its origin is thought to be fluctuations (static) in the band gap due to random fluctuations in compositions. In addition, the strain field can also lead to exciton localization [40]. The large absorption in the Zn$_{1-x}$Cd$_x$O nanostructures in the subband gap region suggests the presence of disorder-induced states from the random substitution. It is likely that the microstrain seen in the Cd-substituted samples arises from the randomness of the substitution process. The Cd substitution sites can provide the excitonic binding sites. This type of strain-induced localization can trap the excitons, and can lead to large PL decay times, as has been seen in this investigation.

5. Conclusion

We show that a high-pressure solution route can be used to successfully synthesize nanostructures of Zn$_{1-x}$Cd$_x$O. The maximum Cd incorporated is $x \approx 0.09$. The synthesized nanostructures comprise nanocrystals that are both hexagonal particles ($\sim 10$–$15$ nm) and rods which grow along the [002] direction. The synthesis of the nanostructure is accompanied by phase segregation of CdO that separates out as large ($\sim 70$ nm–$80$ nm) particles. The Cd incorporation enhances the unit cell volume, and the optical absorption edge as well as the photoluminescence emission shows a red shift. The Cd incorporation is like a ‘negative pressure’ that is similar to a tensile strain. We find a close link of the strain to the PL properties where the microstrain broadens the PL line width. The time-resolved photoluminescence showed a long-lived ($\sim 10$ ns) component. We suggest that the long lifetime arises from exciton localization due to the disorder created by the random strain field.

Cd substitution on the one hand can tune the band gap and on the other can give rise to phosphors due to relatively long-lived PL; however, it loses the sharp excitonic emission that characterizes undoped ZnO.

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References

[1] Pearton S J et al 2003 J. Appl. Phys. 93 1–3
[2] Bagnall D M, Chen Y F, Zhu Z, Yao T, Koyama S, Shen M Y and Goto T 1997 Appl. Phys. Lett. 70 2230–2
[3] Lee C Y, Tseng T Y, Li S Y and Lin P 2005 Nanotechnology 16 1105–11
[4] Ohtomo A, Kawasaki M, Koida T, Masubuchi K, Koinuma H, Sakurai Y, Yoshida Y, Ysuda T and Segawa Y 1998 Appl. Phys. Lett. 72 2466–8
[5] Ghosh M and Raychaudhuri A K 2006 J. Appl. Phys. 100 034315
[6] Makino T, Segawa Y, Kawasaki M, Ohtomo A, Shirotki R, Tamura K, Yasuda T and Komnna H 2001 Appl. Phys. Lett. 78 1237
[7] He F Q and Zhao Y P 2006 Appl. Phys. Lett. 88 193113–6
[8] Li C, Fang G, Su F, Li G, Wu X and Zhao X 2006 Nanotechnology 17 3740–4
[9] Lazareck A D, Clouter S G, Kuo T F, Taft B J, Kelley S O and Xu J M 2006 Nanotechnology 17 2661–4
[10] Sakurai K, Kubo T, Kajita D, Tanabe T, Takasu H, Fujita S and Fujita S 2000 Japan. J. Appl. Phys. 39 L1146–8
[11] Shigemori S, Nakamura A, Ishihara J, Aoki T and Temmyo J 2004 Japan. J. Appl. Phys. 43 L1088–90
[12] Wang F Z, Ye Z Z, Ma D W, Zhu L P, Zhuge F and He H P 2005 Appl. Phys. Lett. 87 143101
[13] Wang Z L 2004 J. Phys.: Condens. Matter 16 R829–58
[14] Xu F, Yuan Z-Y, Du G-H and Ren T-Z 2006 Nanotechnology 17 588–94
[15] Le H Q, Chuah S J, Loh K P, Fitzgerald E A and Koh Y W 2006 Nanotechnology 17 483–8
[16] Li F, Ding Y, Gao P, Xin X and Wang Z L 2004 Angew. Chem. 116 5350
[17] Xu C X, Wei A, Sun X W and Dong Z L 2006 J. Phys. D: Appl. Phys. 39 1690
[18] JEOL Ltd. 1-2, Musashino 3-chome Akishima, Tokyo 196-8558, Japan
[19] PANalytical B.V., Lelyweg 1, 7602EA ALMELO, The Netherlands
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