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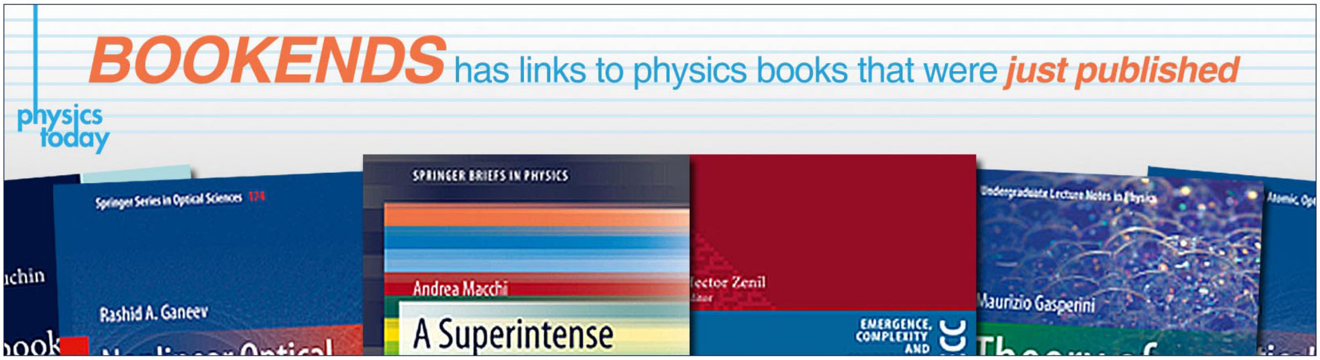

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Study of structure and luminescence of CdSe Nanocrystals obtained by ball milling

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The effect of mechanical milling on the structure and luminescent properties of CdSe powder has been investigated by means of cathodoluminescence (CL) in the scanning electron microscope, transmission electron microscopy (TEM) and x-ray diffraction. The starting powders were ball milled for times between 5 and 20h. TEM of the milled samples reveals the presence of nanocrystals with a wide range of sizes including nanocrystals of 10 nm and smaller. The CL spectra of the untreated samples show the characteristic band edge emission centered at 1.8 eV. In the milled samples a band centered at about 2.5 eV is observed which appears to be associated to the presence of nanocrystals. The evolution of defect structure with milling time has been monitored by recording infrared cathodoluminescence spectra. A partial phase transformation from wurtzite to zinc blende structure also has been observed. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1765858]

I. INTRODUCTION

Bulk CdSe has been extensively investigated in the lasts decades due to its application in photovoltaic cells, thin film transistor, optical-data recording, and other optoelectronic devices.[1] Recently, semiconductor nanocrystals have attracted attention due to their potential application in new optoelectronic devices such as light-emitting diodes,[2] nonlinear optical devices,[3] and fluorescent biological labels.[4] In particular, nanocrystalline CdSe exhibits quantum confinement effects which enables bandgap tuning from the near infrared (1.8 eV) to the blue-green region, thus being a good candidate for the fabrication of a variety of nanodevices.

In the recent years, nanocrystalline CdSe, as many other nanocrystalline semiconductors, has been obtained by several methods such as ion beam implantation,[5] chemical deposition,[6] sol-gel methods,[7] molecular beam epitaxy (MBE),[8] and metal-organic chemical vapor deposition (MOCVD).[9] However none of these methods allows, in principle, to obtain large quantities of material. Alternative methods as mechanical milling has been extensively applied to prepare nanocrystalline metallic materials[10] and recently has been also used to obtain semiconductor nanocrystals such as Si,[11] Ge,[11,12] ZnO,[13] or GaSb.[14] This technique opens the possibility to produce relatively large amounts of nanocrystalline material at low cost avoiding chemical contamination from the agents used in other synthesis methods. However, several problems related to mechanical damage and defect and oxide species formation during milling process have still to be overcome, since they can affect luminescence efficiency of the materials, which is of major importance to optoelectronic applications.

In this work, the formation of CdSe nanocrystals by ball milling and the luminescence of the nanocrystals as a function of the mechanical treatment are investigated. The structural characterization has been performed by means of x-ray diffraction (XRD) and transmission electron microscopy (TEM) and the luminescence properties have been studied by cathodoluminescence (CL) in the scanning electron microscope (SEM).

II. EXPERIMENTAL METHOD

Commercially available CdSe powder with a nominal purity of 99.999% was used as starting material. Milling processes were performed in a centrifugal ball mill (Retsch S100) with 20 mm diameter agatha balls. Milling time was varied from 5 to 20 h.

Structural characterization of the samples was carried out by x-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD measurements were performed in a Philips Difractometer working at 45 kV and 40 mA, using Cu $K\alpha$ radiation. For the TEM measurements, a 300 kV Jeol 3000 TEM was used. Energy dispersive x-ray microanalysis in the TEM was also used for compositional examination of the samples.

In order to obtain disk shaped samples for the scanning electron microscopy experiments, the powders were compacted under a compressive load of 1 ton. Topography images were recorded in a Leica 440 SEM operating in emissive mode. CL measurements were performed at liquid nitrogen temperature in a Hitachi-2500 SEM with a beam energy ranging between 20 and 25 kV. Emission in the visible and near-infrared ranges was detected with a Hamamatsu R928 photomultiplier and a cooled ADC Ge detector, respectively. CL spectra were recorded using an Oriel 78215 computer controlled monochromator or a CCD camera with a built-in spectrograph (Hamamatsu PMA-11).

III. RESULTS AND DISCUSSION

XRD diffraction patterns of starting and milled samples are shown in Fig 1. After the milling process two different effects can be observed. As the milling time increases, the

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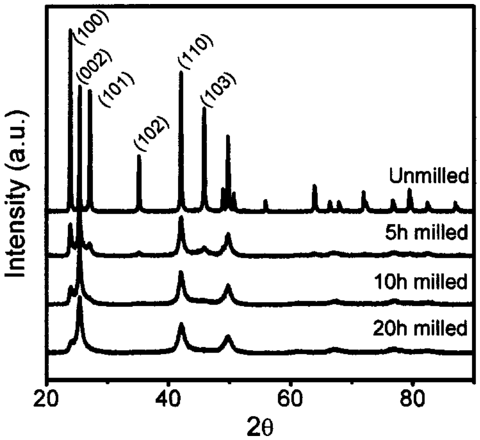

FIG. 1. XRD patterns of milled and nonmilled powders.

intensity of the (100), (101), (102), and (103) diffraction peaks associated to wurtzite phase, decreases, while peaks (002) and (110) still remain. The position of these last peaks can be also associated to (111) and (220) diffraction peaks of zincblende phase. Therefore, this fact indicates that a structural change from typical wurtzite to zincblende phase of CdSe has taken place, resulting in a mixture of both phases in the 20 h milled sample. Such a kind of structural transformation has been previously reported for ball milled CdS and CdSe powders.[15,16] On the other hand, a broadening of the diffraction peaks is detected due to the milling induced reduction of grain size. From Debye-Scherrer analysis, average crystallite sizes ranging between 40 nm in 5 h milled powders and 29 nm in the 20 h milled sample are obtained.

The presence of nanocrystals in the milled samples is further assessed by TEM measurements which show that the particles contain crystals with sizes of about 30–40 nm in agreement with the XRD results as well as smaller nanocrystals of sizes down to 10 nm and smaller as Fig. 2 shows. The existence of a wide crystallite size distribution has been previously observed in other ball-milled semiconductors.[11,12] It appears then that XRD measurements represent the average value of the size distribution, although smaller crystallites have been obtained after milling. Compositional analysis carried out by EDX on all the samples shows a nearly stoichiometric fraction of Cd and Se in the nanocrystals as well as in the starting material, furthermore, no oxygen has been detected.

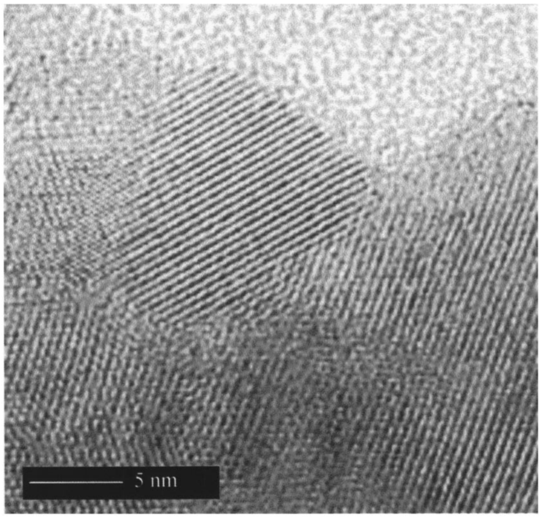

FIG. 2. TEM image showing a nanocrystal of about 6 nm size.

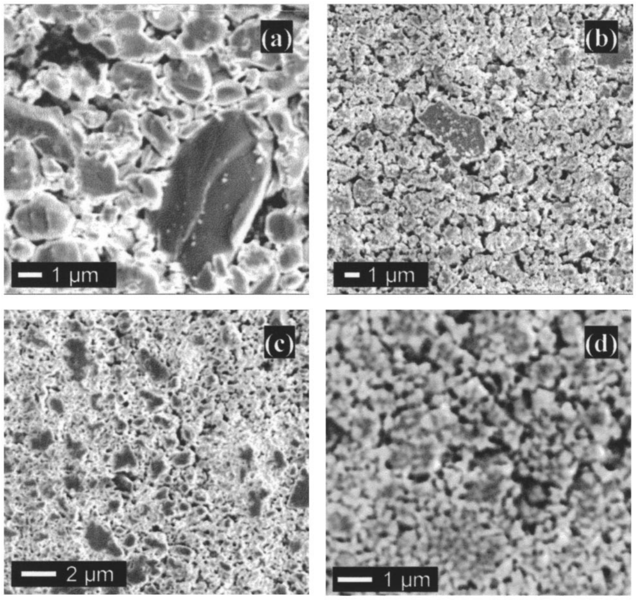

FIG. 3. Topography images acquired by SEM in (a) starting material, (b) 5 h, (c) 10 h, and (d) 20 h milled powders.

The evolution of the particle size and morphology with milling treatment was observed by SEM in the secondary electron mode (Fig. 3). In nonmilled powders [Fig. 3(a)] grains with sizes ranging from hundreds of nanometers to a few microns can be observed. During milling the particle size was found to decrease and to become more homogeneous. In the samples milled for 5 and 10 h, small particles of about 300 nm coexist with larger grains with sizes of several microns [Figs. 3(b) and 3(c)]. However, in the powders milled for 20 h [Fig. 3(d)], aggregates of smaller particles (100 nm) and a more homogeneous size distribution are observed.

Normalized CL spectra of the samples in the visible range are shown in Fig. 4. The spectra are corrected for the system response. In the nonmilled sample (solid line), an emission band centered at 1.8 eV is observed. Since the band gap value of wurtzite CdSe is 1.84 eV at liquid nitrogen temperature, this band can be associated to band-to-band and shallow levels transitions in the material. In addition, as we will discuss later, an increase of the CL intensity at lower energies is detected due to the existence of deep levels. No emission at energies above 1.9 eV is detected. After short milling times (square symbol), band edge emission is still observed and a new broad emission band in the range 2.0–3.0 eV arises. The relative intensity of this band as compared with the band edge emission is observed to increase in the spectra recorded from 10 and 20 h milled samples (dotted and dashed line, respectively). In these cases the band is centered at about 2.5 eV.

CdSe nanocrystals and quantum dots have been obtained previously by several methods. Photoluminescence (PL) and

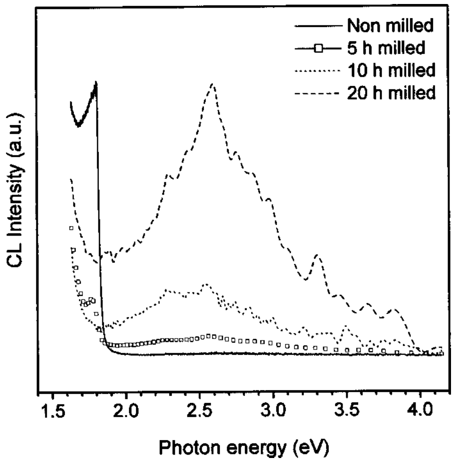

FIG. 4. Normalized CL spectra in the visible range recorded at 20 kV and 85 K of nonmilled powders (solid line), 5 h milled (square symbol), 10 h milled (dotted line), and 20 h milled (dashed line) samples.

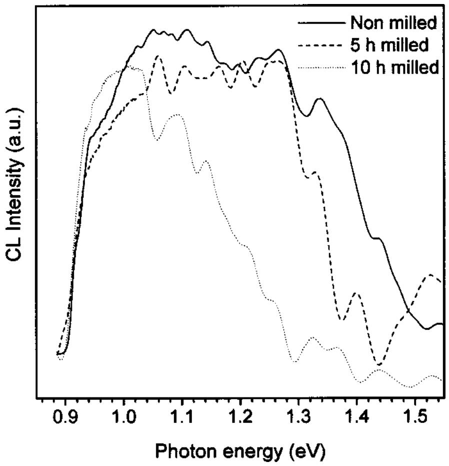

FIG. 5. Normalized CL spectra recorded at 20 kV and 85 K on nonmilled (solid line), 5 h milled (dashed line) and 10 h milled (dotted line) samples.

CL investigations performed in these materials showed the appearance of luminescence bands at energies higher than the bulk band gap. In particular, Yamakawa *et al.*[8] have reported a broad luminescence band centered at 2.49 eV in CdSe quantum dots of 15–40 nm in size grown by MBE, and Litvinov *et al.*[17] have found similar bands peaked at 2.6 eV in quantum dots grown by the same technique. The emergence of these emissions in the visible range has been explained by quantum confinement effects. In our case, XRD and TEM measurements show the existence of nanocrystals in the milled samples, therefore, the 2.5 eV CL band could be associated to these noncrystals. These effects have been also described in other ball milled semiconductors as Si (Ref. 3) and Ge (Ref. 4).

According to Brus,[18] the size dependent band gap energy in the quantum confinement regime can be calculated by

$$E_g^* = E_g + \frac{\hbar^2\pi^2}{2\mu R^2} - \frac{1.8e^2}{\varepsilon}\frac{1}{R},$$

where μ is the reduced mass, ε is the dielectric constant, and R the radius of the nanocrystals. Taking m_e^{eff}, m_h^{eff}, and ε as 0.11, 0.45, and 10.2, respectively, an approximate mean diameter of 6–7 nm is obtained for a band gap of 2.5 eV. However, although crystallites of this dimension are observed by TEM in the milled samples, the very broad CL band centered at 2.5 eV cannot be explained by quantum confinement in crystallites of 6–7 nm. As described above a wide range of grain sizes is present in the samples, which would contribute to the band broadening and on the other side surface states in the crystallites influence the luminescence spectra. The effect of surface states on the nanocrystals luminescence has been discussed for different materials, specially for the case of porous and other forms of nanocrystalline silicon and germanium. Adsorbed species and the presence of oxides or amorphous material at the crystallite surface lead to luminescence emission which does not correspond to that to be expected from a pure quantum confinement effect, e.g., Refs. 19 and 20.

Although EDX measurements do not reveal the presence of oxygen in the milled samples and oxides are not detected by XRD, the formation of small amount of CdO during milling cannot be ruled out, However, since the band gap of CdO is located at 2.3 eV,[21] the existence of this compound would lead to luminescence emissions at this and lower energies and therefore only the low energy part of the observed broad band peaked at 2.5 eV would be influenced by the possible presence of oxide.

CL spectra in the near-infrared range also change from nonmilled to milled powders (Fig. 5). Spectrum of starting material (solid line) shows a broad deep level emission band located in the range 0.9 eV–1.5 eV. The asymmetric shape of this emission suggests the existence of several components. Deconvolution of the spectrum in Gaussian peaks reveals at least three components centered at about 1.05, 1.33, and 1.40 eV, respectively. Brasil *et al.*[22] have observed in polycrystalline CdSe films two PL bands peaked at 1.35 and 1.01 eV, close to the CL bands observed here, which are associated to V_{Se} and O_{Se} defects, respectively. In addition a CL band centered at 1.40 eV observed in ion implanted CdSe crystals, has been associated to V_{Cd}-donor complexes.[23] The infrared CL signal in milled samples decreases drastically, probably due to an increase of nonradiative centers produced during the milling process. This assumption is supported by the fact that the intensity decreases as the milling time increases. The CL signal in the 20 h milled samples is too faint, which prevents the acquisition of spectra. The spectrum corresponding to 5 h milling (dashed line) is rather similar to that recorded from the nonmilled sample, only a decrease of the relative intensity in the region between 1.3 and 1.5 eV can be observed. Changes in the spectrum of the 10 h milled sample (dotted line) are more important showing the quenching of the 1.40 eV and 1.33 eV bands while the 1.05 eV emission still remains. The observed behavior can be tentatively explained by a competition mechanism between both emissions. During the milling process, some of the oxygen of the atmosphere can incorporate to Se lattice positions leading to a decrease of V_{Se} concentration and a subsequent decrease of the intensity of the V_{Se} related 1.35 eV band. In addition it appears that mechanical milling causes the reduction of the CL related to

V_{Cd}-donor complexes either by the reduction of its concentration or by the generation of defects introducing nonradiative recombination paths.

IV. CONCLUSIONS

In summary, CdSe nanocrystals have been obtained by ball milling. XRD and TEM results show the existence of crystallites of a few nanometers size although a wide range of sizes is observed. CL spectra of the milled samples show an emission band centered at 2.5 eV which appears to be related to the presence of nanocrystals. In addition, the defect structure of the samples also changes during milling, as the quenching of CL bands at 1.35 and 1.40 eV shows.

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[1] R. Tenne, R. Jäger-Waldau, M. Lux-Steiner, E. Bucher, J. Rioux, and C. Levy-Clement, Phys. Rev. B **42**, 1763 (1990).
[2] A. P. Alivisatos, Science **271**, 933 (1996).
[3] D. Nesheva, Z. Levi, Z. Aneva, V. Nikolova, and H. Hosmeister, J. Phys.: Condens. Matter **12**, 751 (2000).
[4] M. Bruchez, Jr., M. Moronne, P. Gin, S. Weiss, and A. P. Alivisatos, Science **281**, 2013 (1998).
[5] W. Hipp, H. Karl, I. Groβhans, and B. Strikzker, Mater. Sci. Eng., B **101**, 318 (2003).
[6] X. W. Zhou, R. F. Lin, and X. R. Xiao, Appl. Surf. Sci. **119**, 203 (1997).
[7] R. Reisfeld, J. Alloys Compd. **341**, 56 (2002).
[8] I. Yamakawa, M. Ichida, S. V. Sorokin, A. A. Toropov, A. N Titkov, S. V. Ivanov, and A. Nakamura, J. Lumin. **87–89**, 384 (2000).
[9] J. Rodríguez-Viejo, K. F. Jensen, H. Mattoussi, J. Michel, B. O. Dabbousi, and M. G. Bawendi, Appl. Phys. Lett. **70**, 2132 (1997).
[10] C. C. Koch, Nanostruct. Mater. **2**, 109 (1993).
[11] C. Díaz-Guerra, A. Montone, J. Piqueras, and F. Cardellini, Semicond. Sci. Technol. **17**, 77 (2002).
[12] E. Nogales, A. Montone, F. Cardellini, B. Méndez, and J. Piqueras, Semicond. Sci. Technol. **17**, 1267 (2002).
[13] R. Radoi, P. Fernández, J. Piqueras, M. S. Wiggins, and J. Solís, Nanotechnology **14**, 794 (2003).
[14] S. Borini, B. Méndez, and J. Piqueras, J. Appl. Phys. **94**, 7729 (2003).
[15] K. Durose, A. T. Fellows, A. W. Brinkman, G. J. Russell, and J. Woods, J. Mater. Sci. **20**, 3783 (1985).
[16] A. G. Lehman, M. Bionducci, and F. Buffa, J. Non-Cryst. Solids **232–234**, 421 (1998).
[17] V. G. Litvinov, V. I. Kozlovsky, and Y. G. Sadofyev, Phys. Status Solidi B **229**, 513 (2002).
[18] L. Brus, J. Phys. Chem. **90**, 2555 (1986).
[19] O. Blis, S. Ossicini, and L. Pavesi, Surf. Sci. Rep. **264**, 1 (2000).
[20] T. Oku, T. Nakayama, M. kuno, Y. Nozue, L. Reine Wallenberg, K. Niihara, and K. Suganuma, Mater. Sci. Eng., B **B74**, 242 (2000).
[21] F. P. Koffyberg, Phys. Rev. B **13**, 4470 (1976).
[22] M. J. S. P. Brasil, P. Motisuke, F. Decker, and J. R. Moro, J. Phys. C **21**, 3141 (1988).
[23] C. B. Norris, J. Appl. Phys. **53**, 5177 (1982).