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Raman measurements on nanocolumnar ZnO crystals

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Hexagonal zinc oxide nanocolumns have been grown on conducting F-doped SnO_2 substrates by galvanostatic electrodeposition. Raman and photoluminescence spectra of the ZnO nanocolumns have been measured in several samples with different size distributions as a function of the annealing temperature. Photoluminescence properties of ZnO nanocolumns are strongly influenced by the crystalline quality of the samples. The dependence of the crystalline quality of the samples on the growth parameters and annealing temperature is discussed. In particular, the Raman spectra of as-grown samples exhibit broad bands that correlate perfectly with the one-phonon density of states obtained from recent *ab initio* calculations.

1 Introduction

Zinc Oxide (ZnO) is a wide gap semiconductor that can be grown in nanostructured form by galvanostatic electrodeposition (ED). The physical properties of ZnO combined with its nanostructured form are suitable for luminescent and photovoltaic applications [1]. Nanocolumns obtained by ED exhibit a hexagonal structure whose dimensions can be controlled by means of the growth parameters [2].

The photoluminescence (PL) of the electrodeposited ZnO nanocolumnar samples, hereafter noted as ZED samples, is strongly influenced by the crystalline quality of the samples. In particular, the latter is greatly affected by the growth parameters of the as-grown samples and the subsequent annealing treatments. In this study we try to relate the size of the nanocrystals and the annealing temperature with the change of the Raman and photoluminescence spectra. Our goal is to improve the quality of the nanocrystals for luminescent applications and solar cells.

2 Experimental data and discussion

The electrodeposition procedure consists of a classical three electrode electrochemical setup and a solution containing 5×10^{-3} M $ZnCl_2$, 10^{-1} M KCl and dissolved oxygen in deionised water. A piece of conducting glass substrate was used as working electrode. A Pt electrode and Ag/AgCl reference electrode were also employed. Our ED process was performed onto glass coated with polycrystalline F-doped SnO_2. ED of ZnO onto other crystalline substrates like GaN has also been reported [3]. A potentio/galvanostat was used to keep a constant current density during the deposition. Three growth variables were controlled during the electrodeposition process, current density, deposition time and temperature of the working electrolyte. Samples were prepared under a current density of 2.5 mA/cm^2 at a relatively low

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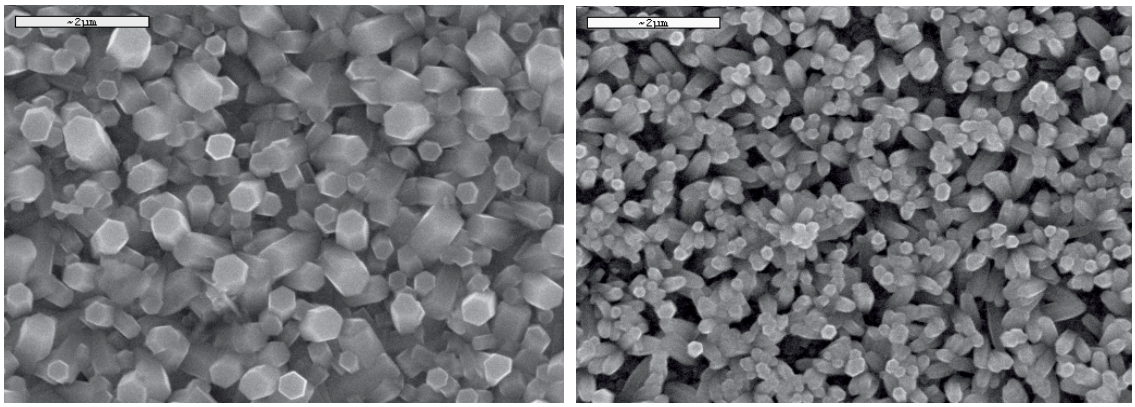

a) b)

Fig. 1 SEM micrographs of ZnO nanocolumns grown under different condictions: (a) ZED1 sample: $I = 2.5$ mA/cm^2; $t = 30$ min; $T = 65$ °C; (b) ZED2 sample: $I = 2.5$ mA/cm^2; $t = 10$ min; $T = 85$ °C.

temperature (between 65 and 85 °C). Deposition times ranged from 10 to 30 min. After deposition the samples were annealed between 200 and 400 °C for one hour in air atmosphere.

The unpolarized photoluminescence measurements have been performed in a backscattering geometry by placing them inside a helium close-cycle cryostat and using the 325.2 nm line of a HeCd laser for excitation at power levels of 30 mW. The emitted light was analysed by a Jobin–Yvon HR460 spectrometer using a GaAs photomultiplier tube (PMT) detector optimized for the UV-VIS range. The Raman measurements have been performed in backscattering geometry with a LabRam spectrometer (from Jobin–Yvon Horiba). The excitation line was provided by a 17 mW He–Ne laser at 632.8 nm focused into a 2 μm spot at the sample surface. The resolution was better than 2 cm^{-1}.

Figure 1 shows the SEM micrographs of two nanocrystalline ZnO samples used in this study (ZED1 and ZED2) and grown under different conditions of current intensity, deposition time and substrate temperature. The different size of the nanocrystals is evidenced in the micrographs and is mainly related to the different deposition time.

Figure 2 shows the low-temperature photoluminescence (PL) spectra of the ZED1 samples after annealing at 200, 300 and 400 °C, respectively, during 1 hour. At low temperatures (15 K), the PL spectra of nanocolumnar ZnO samples exhibit a sharp bound exciton (BE) emission line at around 369 nm followed by the free exciton associated LO-phonon replica around 373.7 nm (FE + LO). These peaks can be

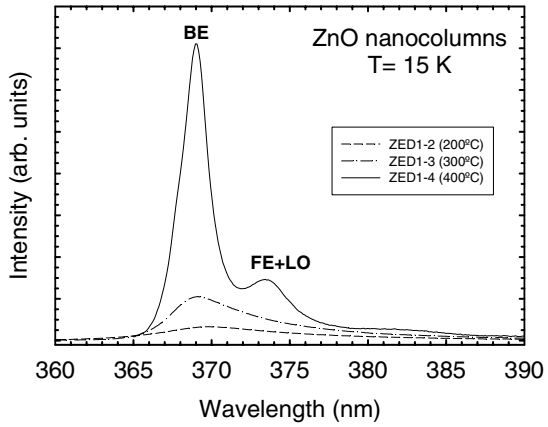

Fig. 2 Low-temperature photoluminescence spectra of nanocolumnar ZnO crystals after annealing at different temperatures.

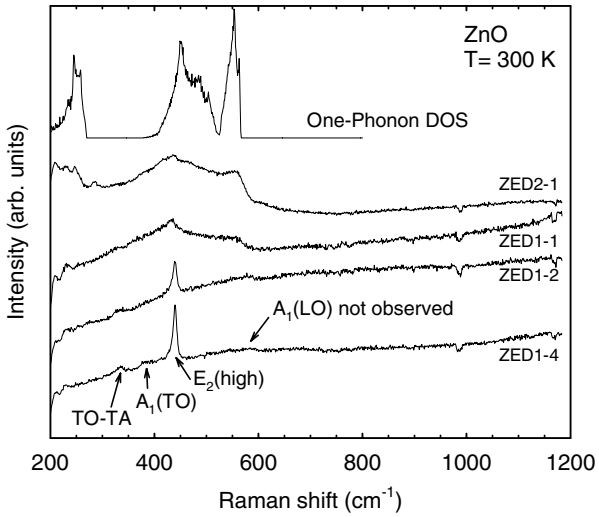

Fig. 3 Room-temperature Raman spectra of nanocolumnar ZnO crystals as a function of the column size and annealing temperature. ZED1-1 and ZED2-1 correspond to as-grown crystals, ZED1-2 and ZED1-4 correspond to the ZED1 sample after annealing at 200 and 400 °C, respectively. The calculated one-phonon density of states from first principles in Ref. [7] is also shown for comparison.

only observed for nanocrystalline samples after annealing the as-grown samples at 400 °C. Only a broad PL band is observed if the annealing is performed at a lower temperature. A similar emission has been found for single crystals [4]. The lack of any PL activity prior to annealing has been attributed to the presence of non–radiative defects which are removed during annealing. In fact, intense PL emission of ZED samples can be observed even at room temperature after annealing above 400 °C.

In order to follow the effect of the annealing process on the crystalline quality of nanocolumns we have performed Raman scattering measurements as a function of the annealing temperature. Figure 3 shows the room-temperature Raman spectra of the two unannealed ZED samples (labelled as ZED1-1 and ZED2-1) as well as the room-temperature Raman spectra of the ZED1 sample after annealing at 200 °C (ZED1-2) and at 400 °C (ZED1-4).

The as-grown samples exhibit similar Raman spectra, but the sample with the smaller column size (ZED2) shows a Raman spectrum with stronger features. The features of the Raman spectra of these samples do not correspond to the usual first-order Raman modes [5], which are not observed. It is well known that zone edge phonons, corresponding to large wave vectors, appear only in high-order Raman scattering and are sensitive to short-range disorder.

For partially disordered systems, this results in the damping of the two-phonon Raman amplitude [6]. In fact, this happens in our Raman spectra where no signal of the large two-phonon peak corresponding to the 2LO around 1100 cm^{-1} is observed. Instead, our Raman spectra of as-grown samples show broad features at smaller wavenumbers that resemble very much to the one-phonon density of states (DOS), as calculated recently from first principles [7] (see Fig. 3). This result indicates that our as-grown samples are partially disordered ZnO crystals, specially the ZED2 sample with the smaller nanocolumn sizes.

The effect of annealing on the crystalline quality of the nanocrystals was evidenced in the features shown by the Raman spectra. Figure 3 also shows the room-temperature Raman spectra for the ZED1 sample after several annealing temperatures. The Raman spectrum clearly changes with the annealing temperature. After annealing at 200 °C, the one-phonon DOS spectra has almost disappeared from the Raman spectrum whereas it appears the E_2(high) first-order Raman peak at the Γ-point of the Brillouin zone. Finally, after annealing at 400 °C, the Raman spectrum corresponds totally to the first-order Raman phonons at the Γ-point of the Brillouin zone. This means that the ZnO nanocrystals, now recrystallized, exhibit a longer range order than as-grown crystals. The lack of observation of the two-phonon features after annealing at 400 °C seems to indicate that there is still a small disorder present in the samples. The recrystallization process as a function of temperature observed in the Raman spectra are in clear agreement with the observation of the photoluminescence in annealed samples above 400 °C.

3 Conclusions

In summary, Raman and PL spectroscopy of electrodeposited ZnO nanocrystals has been used to determine the effect of crystalline quality on the luminescent properties of ZnO nanocolumns. The dependence of these spectra on the annealing temperatures has allowed us to understand the evolution of PL in the annealed samples. This behaviour is now well understood if we consider the as-grown samples as partially disordered structures with a large concentration of non-radiative defects. The decrease of the non-radiative defects due to the recrystallization process subsequent to annealing permits the observation of PL signal even at room temperature due to the strong emission efficiency of this material.

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