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Micro-Raman and micro-PL investigation of ZnO: Cu nanowires for optoelectronic applications

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This work aims to study alterations in the crystalline structure of Cu doped ZnO nanowire clusters using micro-Raman spectroscopy and micro-photoluminescence (μ-PL) studies using the 325nm laser line of a He-Cd laser after transferring to a Si/SiO_2 substrate. The samples were prepared via the sol-gel route and doped at 0.1, 0.3, 0.5 and 0.8% of Cu concentrations on glass substrates. The coating solution was prepared using zinc acetate as the dissolved precursor material, with a molarity of 0.2M. Furthermore 2-methoxyethanol was used as a solvent and copper acetate for doping purposes. The stabilizer was mono-ethanolamine (MEA) with the molarity ratio of the stabilizer and zinc acetate being 1. Miro-Raman spectroscopy revealed that Cu causes at the interstitial sites a distortion in the ZnO lattice, breaking down its translational symmetry which leads to increased intensity of the A1(LO) polar optical phonon modes near 570-580 cm^{-1} as well as their broadening. Furthermore the μ-PL spectrum of the polycrystalline nanowires was characterized by a weak peak in the near-UV region due to the ZnO near-band-edge emission and a stronger broad peak in the visible as a result of the defect amount in the mid-gap region as well as green emission that is frequently associated to O-vacancies in ZnO.

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1. Introduction

In recent years ZnO nanowires have attracted much attention for their applications such as heterogeneous catalysts [1], antireflection coatings, optoelectronic devices as well as gas, chemical and biomolecular sensors. Additionally they make good candidates in UV lasing applications considering that ZnO is wide band gap semiconductor (~ 3.3eV) having an excitonic binding energy of approximately 60meV and exhibiting long term stability. In solar cells ZnO nanowires (wurzite structure) find applications as light emitter/detectors or transparent conductive electrodes due to their transparency in the visible region and low electrical resistivity. Additionally the manipulation of their properties by altering their size, shape and density is of significant interest in nanomaterial engineering due to the continuous need to improve their application performance. Doping is a common route in manipulating semiconductor material properties and in particular the use of Cu in ZnO doping has received increased attention due to its resulting in p-type thin films exhibiting room temperature ferromagnetism.

The present work aims to investigate the crystal quality, structural defects and disorders of Cu doped ZnO nanowires at 0.1, 0.3, 0.5 and 0.8% concentrations prepared using the sol-gel route [2,3]. There are a number of synthesis methodologies for one-dimensional ZnO (1-D) nanostructures such as metal organic chemical vapour depositions [4], pulsed laser deposition [5] and sol-gel routes [3]. Nanofabrication in general bottom up approaches compared to top-down routes produce less defects, higher homogeneity in chemical composition as well as better short and long range ordering. In particular the sol-gel route allows both for their convenient, inexpensive production while variations in temperature, molarity and PH lead to a variety of morphologies. Furthermore sol-gel routes allow for the preparation of porous materials whose pore-size distribution can be controlled both by the chemical composition of the precursor material as well as the processing conditions.

It is well known that transition metals such as Cu (1B group) are fast diffusers in semiconductors leading to the formation of (Cu_{zn}, Cu_i) centres. In particular copper atoms can replace substitutional or interstitial Zn atoms in the ZnO lattice leading to structural changes that in turn can alter optical as well as electron and thermal transport properties. In our work we aim to investigate the structure of the Cu:ZnO nanowires fabricated via the sol-gel route using micro-Raman spectroscopy [6] and micro-photoluminescent (μ-PL) studies [7], which can both facilitate the investigation of their crystallographic properties as well as providing useful information on the existence of secondary phases with a submicron spatial resolution. Purity, phase-transition, lattice distortion and site occupancy are information that might be obtained under ambient or controlled atmosphere and temperature. Despite the fact that structural analysis of such thin films commonly uses X-ray diffraction along with TEM investigations, micro-Raman spectroscopy and micro-photoluminescence can also be employed due to their ability to collect spectra from very small volumes of less than 1µm in diameter. Raman investigations can reveal subtle information regarding material crystallinity, polymorphism, phases as well as intrinsic stress and strain.

2. Materials and methods

The following chemicals were used in sample preparation: zinc acetate dihydrate [Zn(CH3COO)2·2H2O](99%, BDH Chemicals), copper II acetate monohydrate (QualiKems), 2-methoxyethanol anhydrous (99,8%, Sigma Aldrich), monoethanolamine (MEA, >99,5%,) (Sigma Aldrich).

2.1. Preparation of the Cu: ZnO nanowires

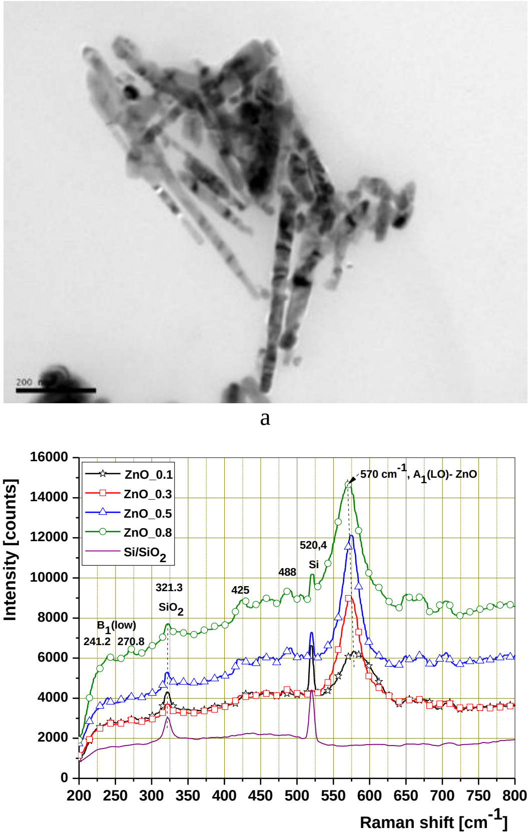
We have prepared 0.1, 0.3, 0.5 and 0.8 %Cu doped ZnO thin films using the sol-gel route. The coating solution was prepared using zinc acetate as the dissolved precursor material, with a molarity of 0.2M, while 2-methoxyethanol was used as a solvent. Copper acetate was employed as the doping material. The stabilizer was monoethanolamine (MEA) and the molarity ratio of the stabilizer and the zinc acetate was 1. Initially the solutions were stirred under a constant temperature of 60°C for 30 minutes. After the stabilizer was added the solution was further stirred for an hour at the same temperature and then allowed to age for 24 hours before it was used as a coating on glass substrates. The rotation speed of the spin coated was 2000RPM for 30 seconds. After that each coating was heated at 150°C for 10mins and in total 7 layers were prepared for each sample. Finally all samples were annealed at 400°C for 1 hour to obtain homogeneous and uniformly covered surfaces.

3. Results and discussion

3.1. Micro-Raman measurements

A micro-Raman study was employed to investigate the structural properties of $ZnCu_xO$ polycrystalline nanowires using the 325 nm He-Cd laser line. The nanowires to be measured were transferred to Si/SiO_2 substrates in order to avoid the strong luminescence that originates from glass and misrepresent the measured spectra. A TEM image of the measured nanowires clusters is shown in Fig. 1a. Typically the Raman spectra of undoped hexagonal ZnO at room temperature is made up of (4) peaks at 100, 380, 437, and 580 cm^{-1}, which correspond in turn to its E_{2L}, $A_1(TO)$, E_{2H}, and $A_1(LO)$ fundamental phonon modes. Occasionally at 204 cm^{-1} the Raman peak present is related to the $2E_{2L}$ second-order phonon mode. [8,9].

The Raman spectra of the Cu-doped ZnO nanowires with different Cu concentrations are shown in Fig. 1b in comparison with the Si/SiO_2 substrate Raman spectra. All the samples show expressive $A_1(LO)$ polar optical phonon modes appearing near 570 -580 cm^{-1}, which are related to defect complexes containing oxygen vacancies and zinc interstitials in zinc oxide [8,10]. Intensity of $A_1(LO)$ phonon mode in Raman spectra increased with the increase of Cu content up to 0.5% together with decreasing the FWHM as shown in Fig. 1b.

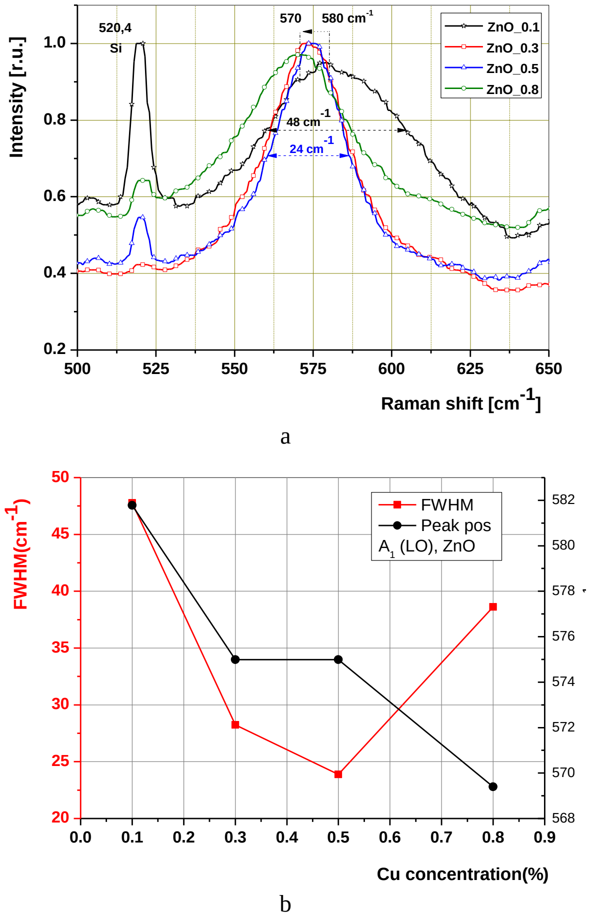


a

b

Fig. 1. a/ TEM image of the nanowire cluster and b/ Raman spectra of ZnO :Cu nanowires with different Cu concentration

After incorporating Cu in ZnO, the $A_1(LO)$ peak (phonon mode) broadened and shifted about 10 cm^{-1} towards lower energy (Fig. 2a,b) as a result of Cu accumulation at the interstitial sites leading to distortion in the ZnO lattice, breaking down its translational symmetry and leading to an increased intensity of the $A_1(LO)$ polar optical phonon modes near 570-580 cm^{-1} as well as their broadening (Fig. 2a,b).



a

b

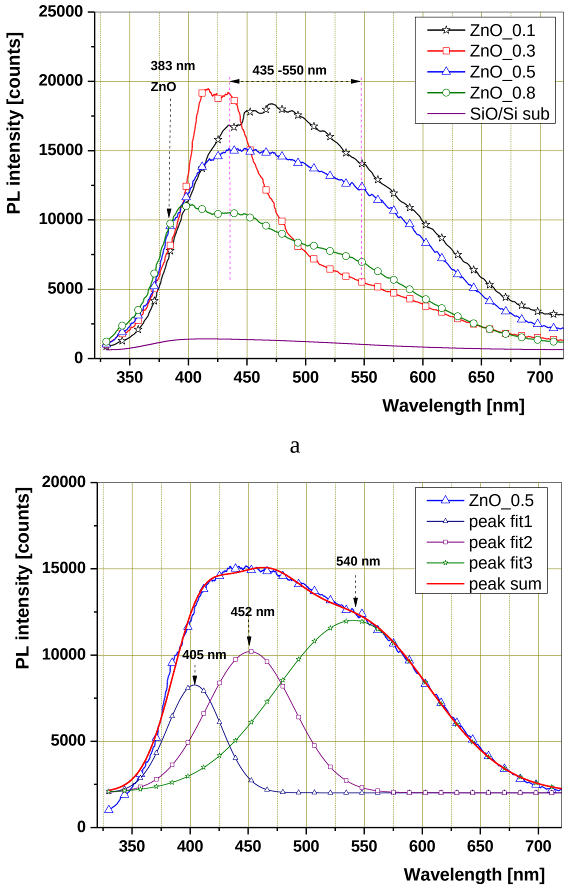
Fig. 2. a) Comparison of A_1(LO) phonon mode intensity of ZnO:Cu for different concentration b) change of FWHM and position of A_1(LO) phonon mode in dependence of Cu concentration

The increase of Cu concentration over 0.5% to 0.8% causes the decrease of A_1(LO) phonon and increase of the FWHM in the Raman spectra. Additionally, broad Raman peaks appeared at about 420-490 cm^{-1} for the Cu-doped samples, which was assigned as the interfacial surface phonon mode in the literature [8,11]. Similarly the Raman peaks at about 240-270 cm^{-1} could be associated to the lattice-host intrinsic defects as a result of doping, something that has been commonly observed when ZnO has been doped with various other elements [8,12]. Several authors have assigned this anomalous vibration mode to the B_1_low silent mode due to its closeness to the position of theoretically calculated B_1 mode at 261 cm^{-1} [13].

3.2. Micro-photoluminescence characterization

Micro-photoluminescence (μ-PL) was used to study the optical properties of the ZnO:Cu nanowires. Fig. 3a below shows the μ -PL spectrum of the polycrystalline nanowire clusters using the 325nm He-Cd laser line. In particular a weaker peak is observed in the UV region as a result of ZnO near band edge emission, while the broad and stronger peak in the visible is due to the defect level in the mid gap region. It should be noted that crystal defects in crystals can be due to foreign atoms at a regular lattice site (substitutional) or between lattice sites (interstitial). Additionally they could arise as a result of missing lattice atoms, antisite defects or Frenkel defects. The broad visible emission band could be deconvoluted in to three Gaussian shaped components peaked around 540 nm, 452 nm and 405 nm as shown in Fig. 3b.

Emission at 405 nm and 452 nm can be due to the recombination of electrons at Zn_i and holes in the valence band, while the strong green emission peak at 540nm is the result of O antisites, interstitial oxygen, and Zn antisites in the oxide [14,15].



a

b

Fig. 3a). Micro-Photoluminescence spectrum of ZnO:Cu nanowire clusters with different Cu concentration and b)multiple peak fit of PL spectra with Cu concentration 0.5%

4. Conclusions

In conclusion, we investigated the optical properties of Cu doped ZnO nanowire clusters for 0.1, 0.3, 0.5 and 0.8% concentrations prepared by using the sol-gel route. For low doping concentrations, most of the incorporated Cu ions occupy the ZnO lattice interstitial sites while higher Cu ions concentrations modify the probability of excitonic transitions as well as visible luminescence of ZnO, originating from defect states such as oxygen vacancies and Zn interstitials. This was confirmed by the PL spectrum measurements of Cu doped ZnO nanowire clusters which show a weaker peak near the UV region and a stronger broad peak in the visible region in dependence on Cu concentration. In Raman spectra the accumulation of Cu at the interstitial sites causes a distortion in the ZnO lattice, breaking down its translational symmetry and increasing the intensity of the A_1(LO) polar optical phonon modes. This effect is responsible for the frequency shift and broadening of the Raman active A_1(LO) polar optical phonon mode in dependence on Cu concentration. The increased A_1(LO) polar optical phonon intensity and decrease of FWHM shows improvement of Cu incorporation into the ZnO lattice at Cu concentration around 0.5 %.

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References

[1] Y. Zhang, M. K. Ram, E. K. Stefanakos, D. Y. Goswami, Journal of Nanomaterials **2012**, 624520 (2012).
[2] A. Kołodziejczak-Radzimska, T. Jesionowski, Materials **7**, 2833 (2014).
[3] Kai Loong Foo, Uda Hashim, Kashif Muhammad, Chun Hong Voon, Nanoscale Res Lett. **9**(1), 429 (2014).
[4] A. Fontcuberta, C. Chennupati, J. Phys. D: Appl. Phys. 47 (2014).
[5] S. Carlo Casari, Andrea Li Bassi, Journal of Optics Research **12**(3-4), (2011).
[6] C. S. S. R. Kumar, Springer-Verlag, Heidelberg, 2012.
[7] G. Gilliland, Materials science & engineering. R, Reports **18**, 99 (1997).
[8] R. S. Zeferino, M. B. Flores, U. Pal, J. Appl. Phys. **109**, 014308 1 (2011).
[9] A. Khan, Alim, J. Appl. Phys. **97**, 124313 (2005).
[10] T. M. Khan, B. Hussain, Int. J. Chem. Mater. Sci. **3**(1), 1 (2015).
[11] B. Jusserand, M. Cardona, Topics in Applied Physics, edited by M. Cardona and G. Güntherodt _Springer, Heidelberg **66**, 48 (1989).
[12] F. J. Manjón, B. Marí, J. Serrano, A. H. Romero, J. Appl. Phys. **97**, 053516 (2005).
[13] J. Serrano, A. H. Romero, F. J. Manjón, R. Lauck, M. Cardona, A. Rubio, Phys. Rev. B **69**, 094306 (2004).
[14] P. K. Samanta, S. K. Patra, A. Ghosh, P. Chaudhuri Roy, International Journal of NanoScience and Nanotechnology **1**(1-2), 81 (2009).
[15] B. Sen, M. Stroncio, M. Dutta, Journal of Electronic Materials **40**(9), 2015 (2011).

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