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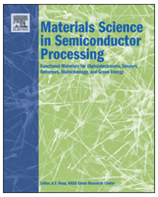

High thermal annealing effect on structural and optical properties of $ZnO–SiO_2$ nanocomposite

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ABSTRACT

The effect of annealing temperature on photoluminescence (PL) of $ZnO–SiO_2$ nanocomposite was investigated. The $ZnO–SiO_2$ nanocomposite was annealed at different temperatures from 600 °C to 1000 °C with a step of 100 °C. High Resolution Transmission Electron Microscope (HR-TEM) pictures showed ZnO nanoparticles of 5 nm are capped with amorphous SiO_2 matrix. Field Emission Scanning Electron Microscope (FE-SEM) pictures showed that samples exhibit spherical morphology up to 800 °C and dumbbell morphology above 800 °C. The absorption spectrum of $ZnO–SiO_2$ nanocomposite suffers a blue-shift from 369 nm to 365 nm with increase of temperature from 800 °C to 1000 °C. The PL spectrum of $ZnO–SiO_2$ nanocomposite exhibited an UV emission positioned at 396 nm. The UV emission intensity increased as the temperature increased from 600 °C to 700 °C and then decreased for samples annealed at and above 800°C. The XRD results showed that formation of willemite phase starts at 800 °C and pure willemite phase formed at 1000 °C. The decrease of the intensity of 396 nm emission peak at 900 °C and 1000 °C is due to the collapse of the ZnO hexagonal structure. This is due to the dominant diffusion of Zn into SiO_2 at these temperatures. At 1000 °C, an emission peak at 388 nm is observed in addition to UV emission of ZnO at 396 nm and is believed to be originated from the willemite.

1. Introduction

The past decade has witnessed the great deal of interest in the research of ZnO due to its wide and direct band gap of 3.3 eV and large exciton binding energy of 60 meV. The large exciton binding energy of 60 meV paves the way for an intense near-band-edge excitonic emission at room and higher temperatures, because this value is 2.4 times that of the room-temperature (RT) thermal energy ($k_BT=25$ meV) [1,2]. These properties made ZnO as an important material in short wavelength optoelectronic devices such as laser diodes, and light emitting diodes [1]. Apart from these applications, ZnO is also used as a color filter in flat panel displays, spectrum modification layer in solar cells, marker for cell labeling in medical tests [3,4]. Semiconductor nanocomposites are a new class of materials that gives very interesting properties that are different from the intrinsic properties of semiconductors. By proper choice of the matrix materials, tunable and desirable properties can be achieved. ZnO-based nanocomposites have been attracting considerable attention, because, the color property of ZnO nanoparticles can be tuned by varying their size. However, the major problem associated with nanoparticles is their vulnerability to aggregation. This is due to the fact that nanoparticles posses high surface to volume ratio or existence of relatively large percentage of atoms at the surface of nanosized solid materials. Because of the high specific surface area of the nanomaterials, the photo-generated

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carriers will be readily captured by the surface states. Consequently, the band edge emissions from ZnO nanoparticles will be quenched at nanodimensions.

This problem can be surmounted by embedding ZnO nanoparticles in materials which are having high dielectric constant. The SiO_2 matrix has been widely used as a host material for ZnO nanoparticles. The photoluminescence (PL) property of ZnO has been greatly enhanced by endowing them in SiO_2 matrix [5–7]. Importantly, the size can be effectively controlled by endowing ZnO nanoparticles in SiO_2 [7]. The tuning of the PL of ZnO was also achieved by embedding ZnO nanoparticles in SiO_2 matrix [8,9]. Moreover, high quantum efficiency was even obtained from silica coated ZnO nanoparticles [3]. Further, ZnO nanoparticles encapsulated with SiO_2 had shown strong quantum confinement effects and two photon absorption phenomenon [10,11]. Very recently, triangular core–shell ZnO/SiO_2 core/shell nanoparticles are also prepared for their applications in optoelectronics [12]. Due to the above mentioned fascinating structural and optical properties of ZnO–SiO_2 nanocomposites, they have become good optoelectronic materials. In our previous report, the effect of SiO_2 concentration on structural and optical properties of ZnO nanoparticles was studied [7]. To the best of our knowledge, the effect of high annealing temperature on the structure and optical properties of ZnO–SiO_2 nanocomposite is not addressed so far.

In the present study, the influence of annealing temperature on structure and optical properties of ZnO–SiO_2 nanocomposite was investigated. As the temperature increased, the UV intensity of ZnO–SiO_2 nano;composite enhanced first until 700 °C and decreased for further rise in annealing temperature from 800 °C to 1000 °C. The decrease of UV emission intensity is due to the collapse of ZnO structure. It is observed that willimite phase formation started at 800 °C and completed at 1000 °C.

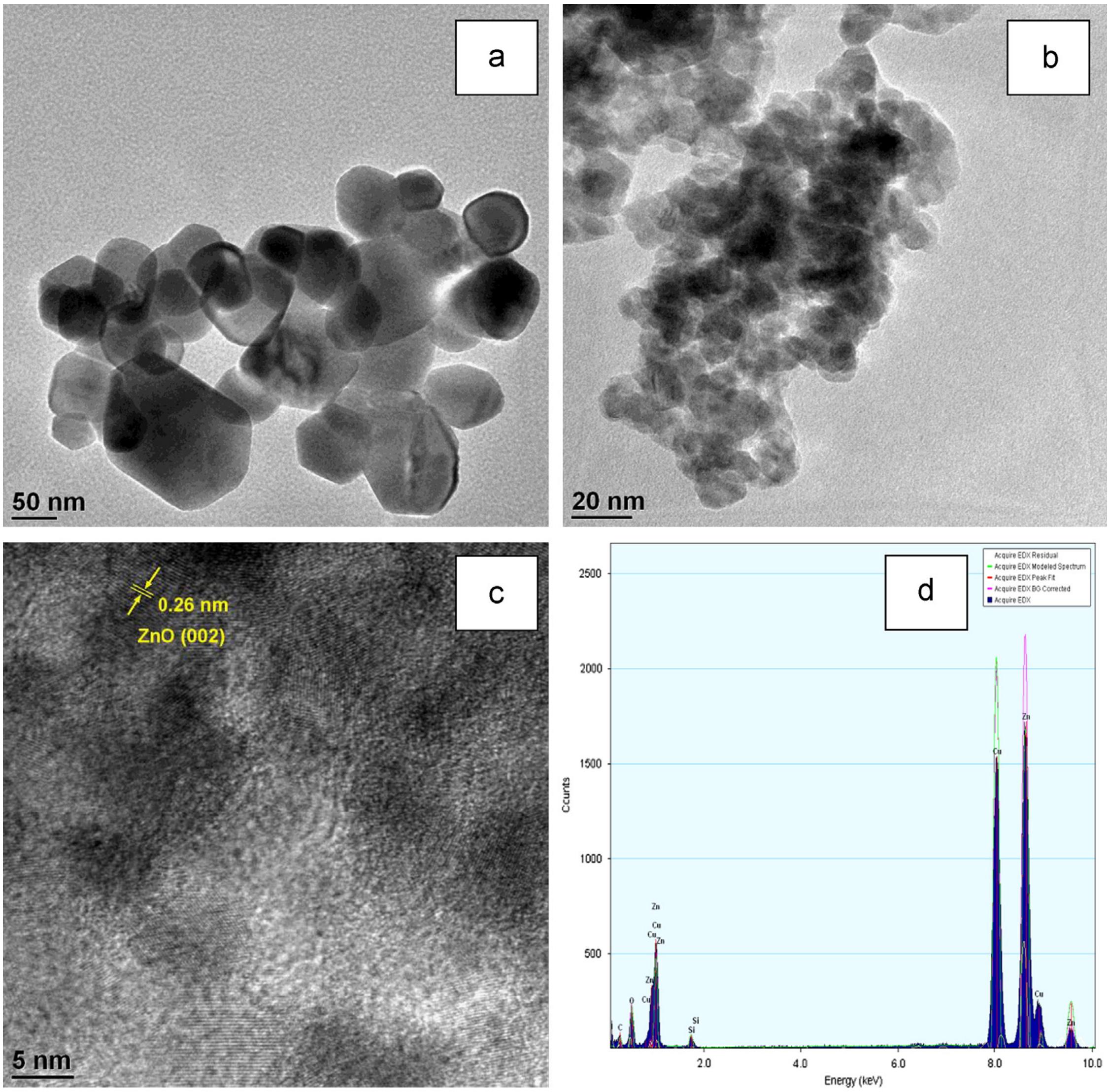

Fig. 1. HR-TEM pictures of ZnO (a) and ZnO–SiO_2 nanocomposite (b) and (c) and EDAX spectrum of ZnO–SiO_2 nanocomposite (d) annealed at 600 °C.

2. Materials and methods

Zinc nitrate hexa-hydrate [$Zn(NO_3)_2 \cdot 6H_2O$] and poly vinyl alcohol (PVA; Molecular Weight: 140,000) are received from Hi-Media. Tetraethyleorthosilicate (TEOS) was purchased from Sigma Aldrich. ZnO nanoparticles and ZnO–SiO_2 nanocomposites were prepared by the method described in our earlier work [7]. $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in minimum quantity of de-ionized water and stirred it for half an hour to get homogenous cationic solution. The metal nitrate to PVA ratio is maintained as 1:3. Required quantity of PVA was dripped slowly into de-ionized water for obtaining transparent and clear solution. Subsequently, the cationic solution was mixed with PVA solution under constant stirring and heating. The stirring and heating were continued until the gel like compound was formed. This gel type sample was dried at 150 °C for about 12 h in an oven for obtaining ZnO nanopowder. To prepare ZnO–SiO_2 nanocomposites, one gram of as prepared ZnO powder was added to the solution containing ethanol, distilled water, ammonia and TEOS and stirred for two hours. The molarity of this solution was chosen as 0.15 M. Later, the samples were filtered and washed with ethanol two to three times. At last, the samples were annealed in a programmable muffle furnace at different temperatures from 600 °C to 1000 °C at a rate of 2 °C/min to study the effect of annealing temperature on PL of ZnO–SiO_2 nanocomposite.

X-ray diffraction analysis of the samples was carried out on Inel-XRG 3000 equipped with Co Kα ($\lambda = 1.7889$ Å) radiation. The morphology and elemental analysis of the samples were carried out on the HR-TEM (JEOL 3010) operating at an accelerating voltage of 200 kV and having an Energy Dispersive Spectroscopy (EDS) attachment and FE-SEM. UV–vis absorption spectra are recorded on a Thermo Scientific spectrophotometer in diffusive reflectance mode with $BaSiO_4$ as reference material. The FT-IR spectra of ZnO–SiO_2 nanocomposite annealed at different temperatures were recorded from 400 to 4000 cm^{-1} with the Perkin Elmer Spectrum 100 model operating at a resolution of 4 cm^{-1}. PL measurements were performed on a Jobin Yuon spectrofluorometer having a 450 W xenon arc lamp as an excitation source.

3. Results and discussion

3.1. HR-TEM and FE-SEM analysis

Fig. 1 shows the HR-TEM images of ZnO and ZnO–SiO_2 nanocomposite. The average particle size of the ZnO nanoparticles calculated from Fig. 1(a) comes out to be 54 nm.

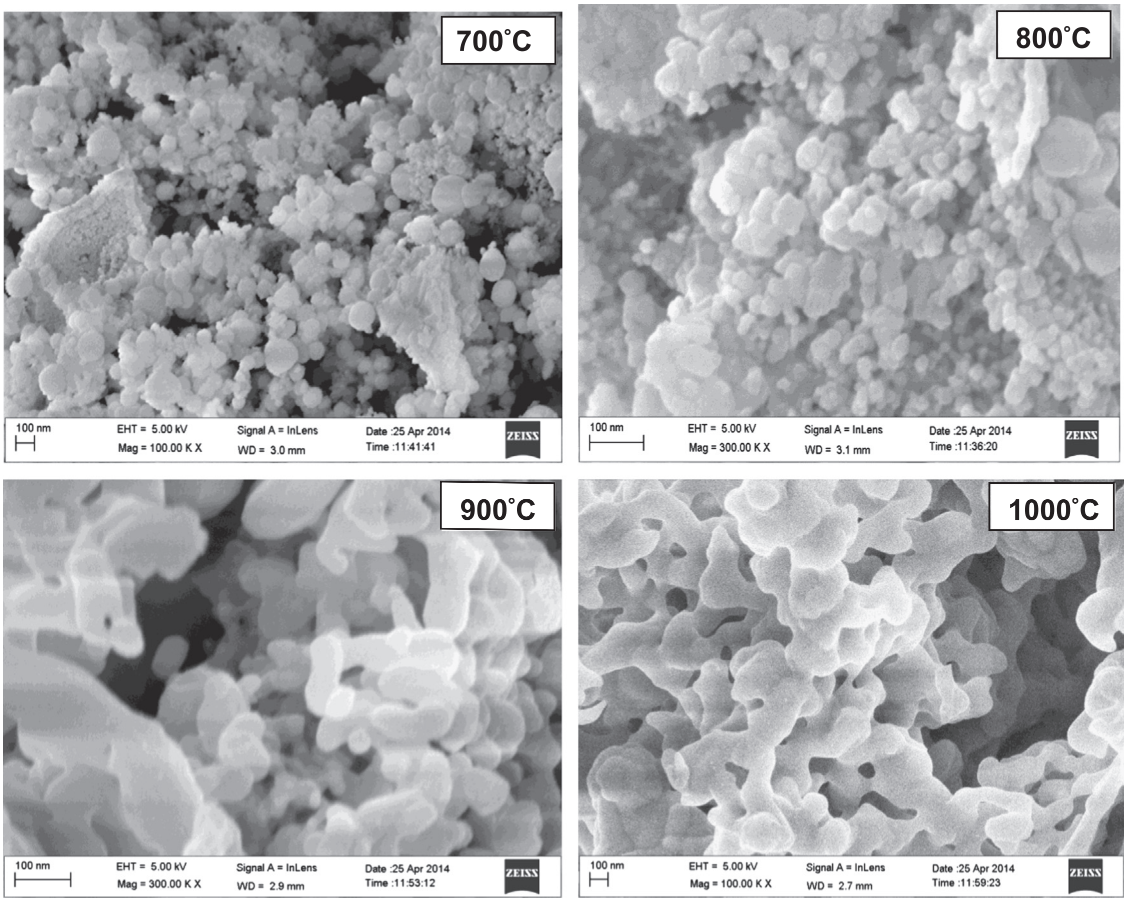

Fig. 2. FE-SEM pictures of ZnO–SiO_2 nanocomposite annealed at various temperatures.

The ZnO nanoparticles are in polyhedral shape. It is evident from Fig. 1(b) that the size of ZnO nanoparticles has been reduced to 5 nm with SiO_2 capping. All the ZnO nanoparticles are successfully capped with SiO_2 by using this simple two step method. It is shown in Fig. 1(c) that the lattice fringes of ZnO nanoparticles that are capped with SiO_2. The lattice spacing of 0.26 nm marked in Fig. 1(c) belongs to the (002) plane of wurtzite ZnO structure. The elemental analysis was carried out by using the energy dispersive spectroscopy. Fig. 1(d) shows the signals related to Zn, O and Si which confirmed the presence of these elements in the ZnO–SiO_2 nanocomposite. The other signals such as Cu and C are due to the carbon coated copper grids used for TEM analysis. These results also infer that there are no impurity elements in the samples. The morphology change of ZnO–SiO_2 nanocomposite with increase of annealing temperature is studied using FE-SEM. Fig. 2 shows the FE-SEM images of the nanocomposite annealed at various temperatures. From Fig. 2(a and b) it is clear that ZnO–SiO_2 nanocomposite exhibits spherical morphology at 700 °C and 800 °C but at higher temperatures such as 900 °C and 1000 °C, dumbbell like structures were formed. Due to the very small size of the ZnO nanoparticles inside the SiO_2 matrix, the particle size cannot be estimated from these pictures. Ultimately, these pictures show that significant change in morphology occurs above 800 °C.

3.2. *X-ray diffraction analysis*

The influence of temperature on the structure of ZnO–SiO_2 nanocomposite was studied using the XRD patterns of samples annealed at various temperatures from 600 to 1000 °C. Fig. 3 displays the XRD patterns of the ZnO–SiO_2 nanocomposite annealed at different temperatures. Fig. 3 shows that the wurtzite structure of the ZnO nanocrystals unaffected up to 700 °C. The diffraction peaks are positioned at 2θ values 37.47°, 40.79°, 42.81°, 56.96°, 68.12°, 75.97° etc. These peak positions correspond to the (100), (002), (101), (102), (110) and (103) diffraction planes of ZnO wurtzite structure. As can be seen from the picture, diffraction peaks are broadened and shifted towards higher angle side with rise in temperature from 600 °C to 700 °C. Generally, particle size increases as the temperature increases. As a result of it, the full width at half-maximum (FWHM) of the diffraction peaks decreases. Here, the FWHM of the diffraction peaks increased with rise in temperature from 600 to 700 °C. Hence, the broadening of the diffraction peaks of ZnO nanocrystals should not be due to the enhancement in the particle size. Another important parameter which causes the broadening of XRD peaks is strain. The strain induced in the ZnO nanocrystals can be understood as follows: as the temperature increases, the ZnO nanocrystals tries to grow to larger sizes but their growth might be hindered by the surrounding SiO_2 matrix. As a result of this opposition force to the growth of ZnO nanocrystals, strain would be developed. Consequently, the diffraction peaks of ZnO were shifted towards higher angle side with rise in temperature from 600 °C to 700 °C. Hence, it can be conclude that the broadening and the shift of diffraction peaks of ZnO nanocrystals are purely due to the strain induced in the ZnO nanocrystals by the surrounding silica network. As can be seen from Fig. 4 the formation of willemite (Zn_2SiO_4) started at 800 °C. It was reported that ZnO is the dominant diffusing species in ZnO/Al_2O_3 couple at higher temperatures greater than 700 °C [13]. It is believed that the same can also be true in the case of ZnO/SiO_2 due to the similarities between SiO_2 and Al_2O_3 such as amorphous nature and large optical band gap. Moreover, the activation energy of the ZnO surface diffusion (158 kJ/mol) [14] is much lower than that of bulk diffusion (347–405 kJ/mol) [15]. Hence, the ZnO atoms which are at the surface will dominantly diffuse towards silica matrix and induces the formation of Zn_2SiO_4. This process of diffusion increases rapidly with increase in temperature. Consequently, willemite (Zn_2SiO_4) formation progressed with increase in temperature and at 900 °C willemite became the main phase. Though the willemite formed at 900 °C, traces of ZnO appeared in the sample. However, pure willemite phase was formed at 1000 °C.

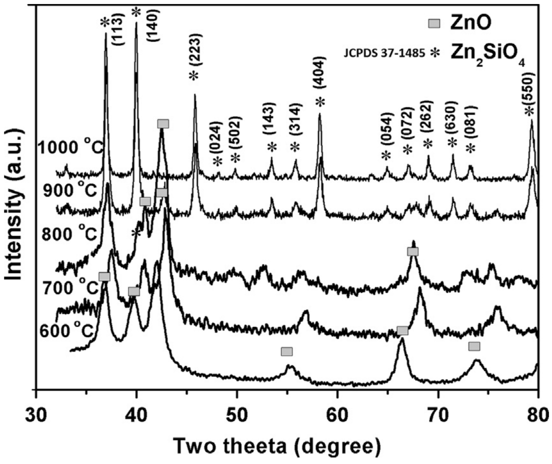

Fig. 3. XRD patterns of ZnO–SiO_2 nanocomposite annealed at various temperatures.

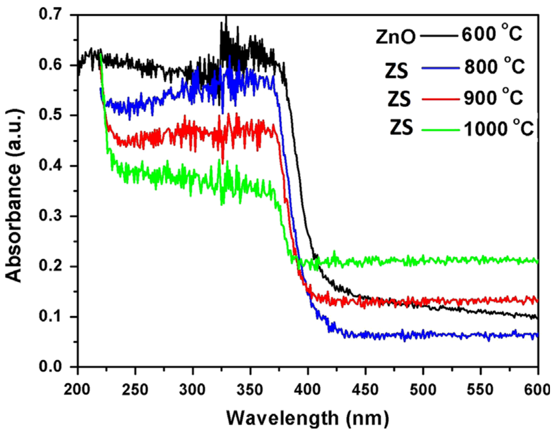

Fig. 4. UV–vis absorption spectra of ZnO–SiO_2 nanocomposite annealed at various temperatures.

3.3. UV–vis analysis

Further, the absorption spectra of ZnO–SiO_2 nanocomposite annealed at 600 °C, 700 °C, 800 °C, 900 °C and 1000 °C were measured. Fig. 4 shows the absorption spectra of the ZnO nanoparticles and ZnO–SiO_2 nanocomposite annealed at various temperatures. The absorption spectra of ZnO–SiO_2 nanocomposite annealed at 600 °C, 700 °C and 800 °C are appears to be the same. Hence for the sake of clarity, only the absorption spectrum of sample annealed at 800 °C is shown in Fig. 4. The ZnO nanoparticles annealed at 600 °C showed an absorption edge at 379 nm. The absorption edge of ZnO–SiO_2 nanocomposite annealed at 800 °C suffers a blue-shift from 379 nm to 369 nm. This shift is due to the decrease of the particles size with SiO_2 capping as we observed in our previous study [7]. As the annealing temperature increased from 800 °C to 1000 °C, there is decrease in the absorption peak intensity along with the shift of the peak towards lower wavelength. From the FE-SEM and XRD results discussed above, the decrease of the peak intensity can be attributed to the deterioration of the crystal quality of ZnO. These results also indicates that pure willemite (Zn_2SiO_4) phase was formed at 1000 °C. Hence the absorption spectrum at 1000 °C purely belongs to the willemite phase and the shift towards lower wavelength is due to the relatively larger band gap (5.5 eV) of willemite.

3.4. FT-IR analysis

Fig. 5 shows the FT-IR spectra of ZnO–SiO_2 nanocomposite annealed at various temperatures. Two peaks positioned at 1095 cm^{-1} and 962 cm^{-1} can be seen in the IR spectrum of ZnO–SiO_2 nanocomposite annealed at 700 °C. These peaks are assigned to asymmetric stretching modes of Si–O–Si vibrations and stretching modes of surface silanol groups ($\equiv$Si–OH) [7]. With increase of temperature, the intensity of 1095 cm^{-1} peak gradually decreased and shifted to 1118 cm^{-1} but the peak at 962 cm^{-1} disappeared completely. This result suggests that Si atoms are replaced by Zn ions to form Si–O–Zn bonds. Further, significant changes in the FT-IR spectra were observed for temperatures higher than 700 °C. As the annealing temperature increased up to 800 °C, new vibrational bands were developed at 474, 577, 617, 867, 896, 930, 977 cm^{-1}. The vibrational bands at 474 and 577, 617 cm^{-1} are due to the bending vibration of O–Si–O bond and vibration of ZnO_4 group respectively [16]. It is also observed that intensities of 577 and 617 cm^{-1} bands enhanced with increase of temperature. It implies that the ZnO_4 group units enhanced with temperature by replacing the Si atoms. The group of vibrational bands observed between 1000 and 800 cm^{-1} attributed to SiO_4 tetrahedron vibration. The presence of the vibrational bands of SiO_4 and ZnO_4 groups suggests the formation of the Zn_2SiO_4 phase.

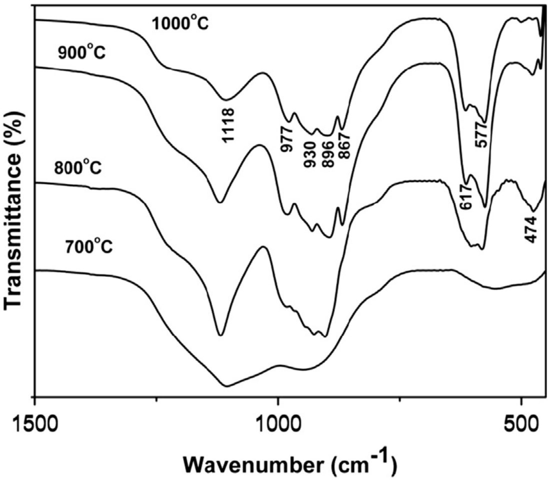

Fig. 5. FT-IR spectra of ZnO–SiO_2 nanocomposite annealed at various temperatures.

3.5. PL analysis

Fig. 6 shows the PL spectra of ZnO–SiO_2 nanocomposite annealed at temperatures of 600 °C, 700 °C, 800 °C, 900 °C and 1000 °C. The pristine ZnO nanoparticles showed only a sharp and intense UV peak positioned at 396 nm when excited with 353 nm excitation wavelength [17]. The intensity of the UV emission peak of ZnO nanoparticles enhanced with SiO_2 capping and the possible reasons were discussed in detail elsewhere [7]. Another peak at 453 nm in all PL spectra is due to the substrate which is used to

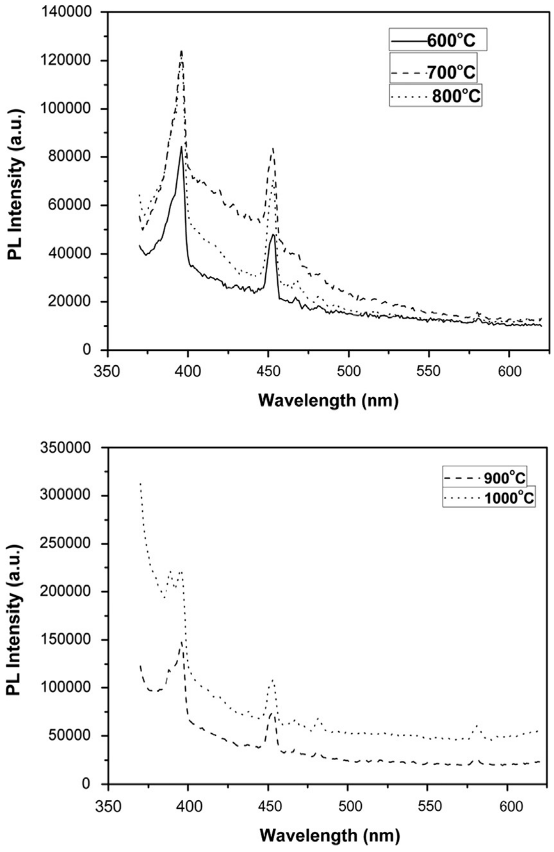

Fig. 6. PL spectra of ZnO–SiO_2 nanocomposite annealed at various temperatures.

hold the sample for PL measurement [17]. As the ZnO–SiO_2 nanocomposite annealed from 600 °C to 1000 °C, the intensity of the UV peak centered at 396 nm enhanced for temperature of 700 °C. At 700 °C, there is also an enhancement in the intensity of defect related emissions between 400 nm and 500 nm. This defect emission positioned approximately at about 440 nm in the blue region of the spectrum. Hence this defect emission is called blue emission and is assumed to be due to the zinc interstitials [18]. The increase in the 396 nm emission peak may be due to the improvement in the crystallanity and increase in defect emission is presumed to be due to the strain induced at the interface of ZnO and SiO_2. Further increase in temperature to 800 °C causes intensity of the defect emission to decrease while maintaining the same UV emission intensity. It is speculated to be due to the relaxation of the strain due to the diffusion of Zn into SiO_2. At temperatures 900 °C and 1000 °C, the intensity of the 396 nm peak reduced and another emission peak appeared at 388 nm. The decrease in the intensity of 396 nm emission peak is obviously due to the collapse of ZnO wurtzite structure. The emission peak observed at 388 nm for annealing temperatures at and above 800 °C is due to the Zn_2SiO_4 phase. This result also indicates that pure willemite formed at 1000 °C.

4. Conclusions

In conclusion, the effect of temperature on structure and PL properties of ZnO–SiO_2 nanocomposite was studied. It was observed from the XRD analysis that willemite phase started forming for temperatures greater than 800 °C and completed at 1000 °C. The position of the absorption edge did not change as the temperature increased from 600 °C to 800 °C. The intensity of the absorption peak decreased at 900 °C and 1000 °C and there is shift to lower wavelength at 1000 °C. This shift is attributed to the relatively larges bandgap of willemite than ZnO. The intensity of the PL peak positioned at 396 nm increased until 700 °C and then decreased for further increase in temperature to 1000 °C. These results indicate that active interaction between ZnO and SiO_2 takes place for temperatures greater than 800 °C. The decrease in the intensity of PL peak is due to the collapse of the ZnO hexagonal structure and formation of willemite. It was also observed that an emission peak at 388 nm is developed for temperatures greater than 800 °C. This peak is presumed to be due to the willemite phase.

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