Crystallization and optical properties of finite sized β-Ga_2O_3 in sol–gel derived Ga_2O_3:SiO_2 nanocomposites

Crystallization and optical properties of finite sized β-Ga$_2$O$_3$ in sol–gel derived Ga$_2$O$_3$:SiO$_2$ nanocomposites

Godhuli Sinha, Dibyendu Ganguli and Subhadra Chaudhuri[1]

Department of Materials Science, Indian Association for the Cultivation of Science, Kolkata-700 032, India

E-mail: mssc2@iacs.res.in (S Chaudhuri)

Abstract

Gallium oxide nanoparticles embedded in silica matrix with different molar ratios were synthesized by the sol–gel method. Powdered nanocomposite samples were annealed at 400, 500 and 900 °C. The gallium oxide nanoparticles (2–5 nm) crystallized in the β-phase at a very low temperature ($\sim$400 °C) as against the expected temperature ($>$700 °C), indicating a depression of crystallization temperature under the present condition. This may be a signature of the behaviour of confined nanosized particles. The indications of only Ga–O bonds and Si–O–Si bonds in FTIR spectra and peaks of gallium, oxygen and silicon in energy dispersive x-ray analysis (EDAX) confirmed the non-existence of any impurity. Room temperature photoluminescence study of the samples shows a strong blue emission at $\sim$460 nm.

1. Introduction

Gallium oxide is a wide bandgap, III–VI semiconductor material exhibiting polymorphism (α-, β-, γ-, δ-forms) under different conditions [1–3]. Among all the phases, the monoclinic β-Ga$_2$O$_3$ has been studied in the greatest detail because of its wide bandgap (4.8 eV) [3, 4] and good thermal and chemical stability. It has drawn significant attention from scientists because of its potential application in different fields as luminescent material [5, 6], UV emitter [5], gas sensor [7, 8], antireflection coating on GaAs [9], passivation coating [10] etc. It can also be used as a transparent conducting oxide [10–12]. Previously, Binet and Gourier [5] observed that specific excitation of the acceptor defects resulted in the blue luminescence of gallium oxide. With decrease in particle size some distinctive unique physical properties are expected from the nanostructures of gallium oxide as compared to bulk materials due to significant surface related defects originating from high ratios of surface to volume [13–16].

---

[1] Author to whom any correspondence should be addressed.

Theoretical and experimental studies on materials of nanometric size indicate that the optical properties of these materials depend highly on their sizes, especially when the size is comparable to the corresponding excitonic Bohr radius, i.e. when the quantum confinement effect is dominant. It is also very common to observe unusual phases when the materials are fabricated in nanocrystalline form [17, 18]. Mayo *et al* [17] observed that the phase transformation temperatures could vary linearly with particle size. For studying such properties of nanocrystalline materials, it is of course necessary to prevent the particles from coalescing together during and after synthesis.

Preparation of gallium oxide nanostructures can be successfully carried out by the physical evaporation technique [19–22], arc discharge and crystal assisted methods [23–25] and hydrothermal method [26]. There are various ways of preventing agglomeration of the nanoparticles, e.g. use of capping molecules during synthesis [27–30]. A bulk host material with higher bandgap and suitable porosity can also be used to confine the sizes of the synthesized nanoparticles. Previously, many researchers attempted to embed particles of different materials in suitable matrices [31–34]. Silica xerogel is a porous material and can be suitably used as a matrix, as its porosity can be controlled by preparation parameters [35]. The concave surface of the pores provides sites for nucleation and the pores provide spaces for crystal growth.

In this present course of work, gallium oxide quantum dots with specific sizes (2–5 nm), embedded in silica matrix, have been synthesized by the sol–gel method. The microstructural and optical properties of the composite materials have been studied systematically.

2. Experimental details

To prepare gallium oxide nanoparticles embedded in silica matrix, solutions were prepared in two parts. In the gallium oxide part gallium metal (Aldrich USA, 99.99%) was used as the precursor and for the silica part tetraethyl orthosilicate (TEOS, Merck Schuchardt) was used as the source of SiO_2.

First, gallium metal was dissolved into a calculated amount of HNO_3 and the pH value was maintained between 1 and 2. For SiO_2 matrix, TEOS was dissolved into ethanol–water mixture. For hydrolysis of TEOS a few drops of 0.1 N HCl were added to it as catalyst. The sol was stirred for 1 h. After this, the gallium part was added to the second part and the pH value of the mixture was adjusted to between 1 and 2. After stirring the mixture for another 1 h, the clear solution was heated at about 70 °C for 3.5 h to enhance the hydrolysis and condensation process. The clear gel obtained by this process was dried at 200 °C for 4 h. After this calcination process the gel became white and very porous.

The dried gel pieces were placed inside a horizontal tube furnace in an alumina boat and annealed at 400, 500 and 900 °C. At 400 °C, the annealing process was extended up to 11 h. For 500 and 900 °C, the annealing processes were maintained for 5 and 8 h. $Ga_2O_3:SiO_2$ nanocomposites were prepared with three different molar ratios of Ga_2O_3 and SiO_2, i.e. $Ga_2O_3:SiO_2 = 10:90$, 20:80 and 30:70.

The white powder thus obtained in each case was characterized by x-ray diffraction (XRD, Seifert 3000P). Microstructural studies of the products were carried out by transmission electron microscopy (TEM, JEOL JEM-2010). Selected area diffraction patterns (SAED) of samples were obtained. The compositions of the nanocomposites were also studied by energy dispersive x-ray analysis (EDAX). The samples were studied optically by FTIR (MAGNA-IR, 750 spectrometer) spectroscopy and UV–vis spectroscopy (Hitachi 3410). Photoluminescence studies were carried out with a luminescence spectrophotometer (Hitachi, F2500).
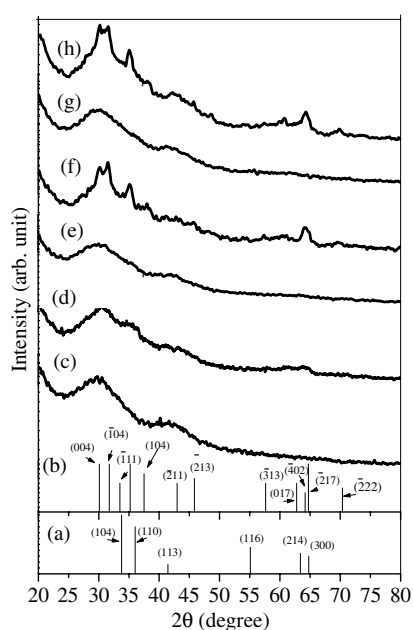
Figure 1. XRD pattern of Ga$_2$O$_3$:SiO$_2$ composite. (a) and (b) show the typical patterns of α- and β- phases (JCPDS 06-0503 and JCPDS 11-0370 respectively). (c), (e) and (g) show the XRD pattern of the composite samples annealed at 400 °C for 11 h with molar ratio 10:90, 20:80 and 30:70 respectively. XRD patterns of samples annealed at 900 °C for 8 h with molar ratios 10:90 (d), 20:80 (f) and 30:70 (h) have been shown.

3. Results and discussion

3.1. XRD study

X-ray diffraction patterns of Ga$_2$O$_3$:SiO$_2$ composites with molar ratios 10:90, 20:80 and 30:70, displayed in figure 1, confirm that gallium oxide particles embedded in silica matrix crystallize in the β-form of Ga$_2$O$_3$ under the given annealing conditions, i.e. 400–900 °C. Typical XRD patterns of α- and β-phases have been shown in figures 1(a) and (b) respectively. XRD patterns of the samples annealed at 400 °C for 11 h (molar ratios 10:90 (c), 20:80 (e) and 30:70 (g)) show that the particles of gallium oxide are not well crystallized, though they show a tendency to crystallize in monoclinic β-phase. In these patterns the signature of the formation of ($\bar{2}$02) and ($\bar{2}$11) planes can be observed clearly. In general, the β-phase has been considered to be the only stable phase of gallium oxide [1]. However, it has been shown in different reports [2, 3, 36–38] that α-Ga$_2$O$_3$ is easily obtained at relatively low temperature, and its conversion to the β-form requires a temperature >500 °C, sometimes with an intermediate temperature range where phases coexist, $\alpha \rightarrow \alpha + \beta \rightarrow \beta$. This shows that the α-phase can be described as the low temperature (up to 500 °C) polymorph of gallium oxide. In the present case, therefore, a high temperature polymorph (β-phases) is observed to form at a comparatively low temperature, where the low temperature α-form should apparently form [1–3, 36–38].

XRD patterns of the samples annealed at 900 °C with molar ratios 10:90 (d), 20:80 (f) and 30:70 (h) clearly show that under this annealing condition the particles are well crystallized in stable β-phase. Using the Scherrer equation,
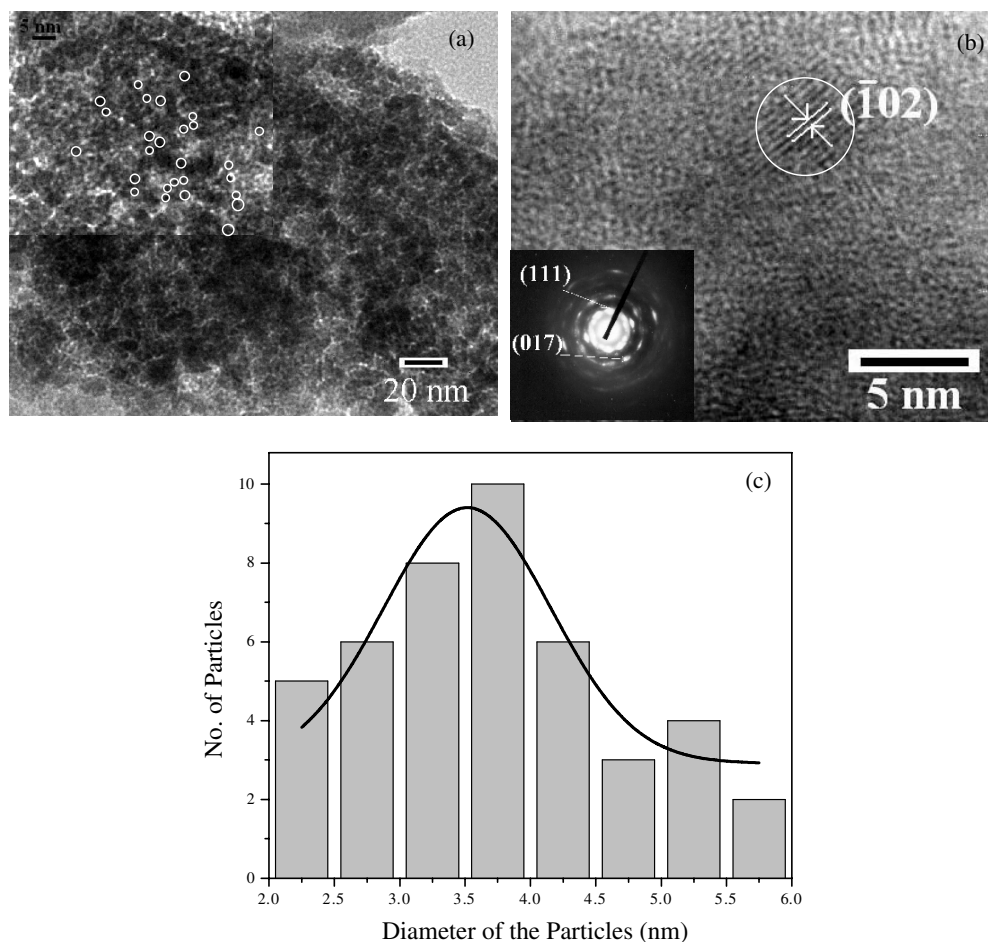
$$r = \frac{k\lambda}{B \cos \theta}$$

Figure 2. (a) TEM of Ga$_2$O$_3$:SiO$_2$ composite with molar ratio 20:80 (annealing temperature = 400 °C) (inset: gallium oxide nanoparticles embedded in silica matrix). (b) HRTEM of a nanoparticle of gallium oxide in silica background (inset: SAED pattern of the corresponding sample). (c) Histogram of particle size distribution of this sample.

where r is the crystallite size, λ is the x-ray wavelength (1.5418 Å for the Cu Kα radiation), B is the broadening of the diffraction line, θ is the Bragg angle and k is a constant approximately equal to unity, the crystallite sizes of Ga$_2$O$_3$ in Ga$_2$O$_3$:SiO$_2$ composites with molar ratios 10:90, 20:80 and 30:70 (annealed at 900 °C/8 h) are calculated. For these three cases the crystallite sizes are 1.20, 1.81 and 1.90 nm respectively. From the above observations it can be said that very small crystallites of gallium oxide formed in the composites with different molar ratios.

3.2. Microstructural study

Transmission electron microscopic data (figures 2 and 3) reveal that the gallium oxide nanocrystals are dispersed in silica xerogel. Figure 2(a) shows a transmission electron microscopic image of Ga$_2$O$_3$:SiO$_2$ composite with molar ratio 20:80 annealed at 400 °C for 11 h. It is clear from the inset of figure 2(a) that the nanoparticles of gallium oxide annealed at 400 °C for 11 h are dispersed in silica matrix in such a way that sometimes two or more particles
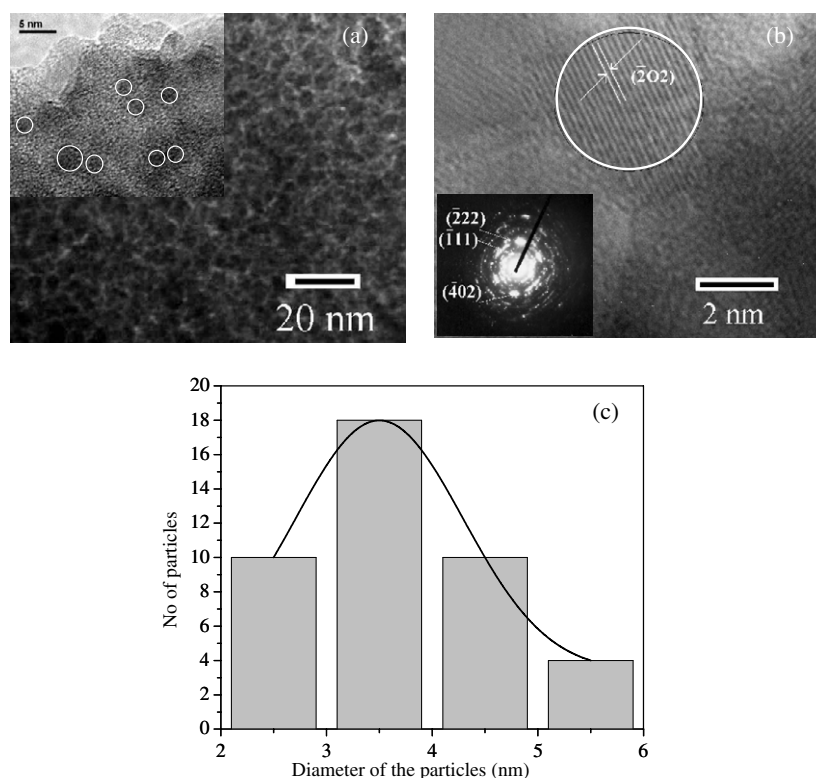
Figure 3. (a) TEM of Ga$_2$O$_3$:SiO$_2$ composite with molar ratio 20:80 (annealing temperature = 900 °C) (inset: gallium oxide nanoparticles embedded in silica matrix). (b) HRTEM of a nanoparticle of gallium oxide in silica background (inset: SAED pattern of the corresponding sample). (c) Histogram of particle size distribution of this sample.

coalesce together to form a larger one, though the individual particles are discernible for size measurement. These particles are spherical in shape. Figure 2(b) shows a high resolution TEM image of the samples annealed at 400 °C for 11 h (molar ratio 20:80). The fringe pattern in the figure indicates the formation of the ($\bar{1}$02) plane of the β-phase. The inset of figure 2(b) shows the SAED pattern of the sample, which also indicates the formation of β-phase of gallium oxide clearly. Figure 2(c) presents the size distribution of the particles of the Ga$_2$O$_3$:SiO$_2$ composite with molar ratio 20:80 and annealed at 400 °C for 11 h. The diameter of the particles varies between 2 and 5.8 nm. The Gaussian fit of the histogram gives the average diameter of the particles to be $\sim$3.51 nm. Figures 3(a) and (b) show TEM and HRTEM images of the nanocrystals of gallium oxide dispersed in silica matrix with Ga$_2$O$_3$:SiO$_2$ molar ratio 20:80 annealed at 900 °C for 8 h. The inset of figure 3(a) shows that the gallium oxide nanocrystals are dispersed in the matrix in such a way that the particles are not coalesced together to form larger particles. As the samples were annealed at 900 °C, there was expectedly a shrinkage of the gel matrix, causing shrinkage of pores housing the gallium oxide particles; this caused the formation of smaller particles slightly smaller particle as observed in this present case. The shapes of these particles are also spherical. The inset of figure 3(b) shows the SAED pattern of this sample. The fringe pattern and SAED pattern indicate that the gallium oxide nanoparticles crystallize in monoclinic β-phase. Figure 3(c) indicates the particle size distribution of the sample annealed at 900 °C for 8 h. The sizes of the particles vary between 2 and 5 nm. The
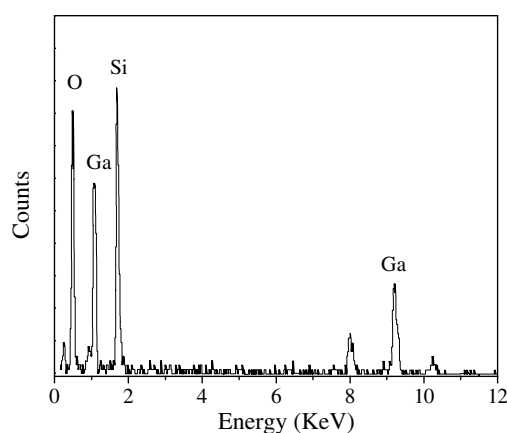
Figure 4. EDAX pattern of a representative sample.

mean diameter of the particles observed from the Gaussian fit of the histogram is ∼3.5 nm. Previously Aubay and Gourier [39] calculated the Bohr radius for shallow donors of gallium oxide as 18 Å. So the sizes of the gallium oxide particles in the present work are comparable to the corresponding Bohr radius and they are expected to show the size confinement effect.

For the other two molar ratios, i.e. 10:90 and 30:70, TEM studies (not shown here) yielded similar results. The particle sizes varied between 2 and 5 nm. SAED patterns (not shown) of the samples annealed at 400 °C for 11 h and 900 °C for 8 h for both molar ratios indicated the signature of the formation of β-phase.

From the previous studies [1–3, 36–38], as indicated above, it is confirmed that at the temperature of 400 °C the polymorph expected to crystallize should be the α-phase. However, in the present case, both XRD and HRTEM studies confirm that the nanoparticles crystallize in the β-phase. This extension of the high temperature β-phase into the low temperature zone is apparently because of the capping effect of silica, which confines gallium oxide particles to very small size (2–5 nm) [17, 18]. The theories explaining the presence of high temperature phases at low temperature include the lack of nucleation sites [40], internal pressure due to particle curvature [41], surface energy difference between polymorphs [42], nature of the environment [43] etc. The most direct effect, however, is that of particle size, and it has been demonstrated in several systems [42, 43] that finite size of particles rules thermodynamic stability of phases.

The composition of a representative composite sample was analysed by EDAX, as shown in figure 4, indicating that there is no significant trace of any impurity.

3.3. Optical properties

Figure 5 shows a comparative study of FTIR spectra of gallium oxide quantum dots embedded in silica matrix with molar ratios (a) 10:90, (b) 20:80 and (c) 30:70, annealed at 900 °C for 8 h. A broad intense peak in the range of 2900–3800 cm^{-1} is a characteristic of the spectrum. A band represented the stretching mode of isolated –OH groups has been reported at ∼3740–3750 cm^{-1} [35, 44, 45]. Hydroxyl groups partially involved in hydrogen bonding also show a band in this region. A band in the region 3650–3200 cm^{-1} can be linked to stretching modes of strongly hydrogen-bonded –OH groups in chains of different lengths. In the present case, the samples were annealed up to 900 °C for 8 h, therefore the broad peak in the abovementioned
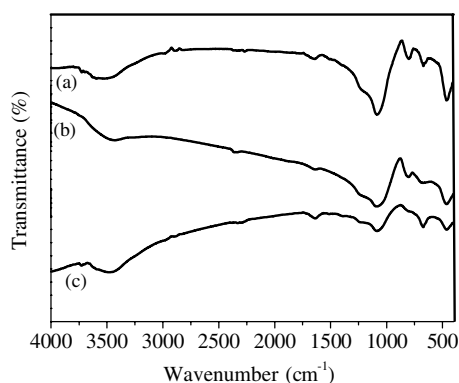
Figure 5. FTIR spectra of the Ga$_2$O$_3$:SiO$_2$ composites with molar ratio (a) 10:90, (b) 20:80 and (c) 30:70.
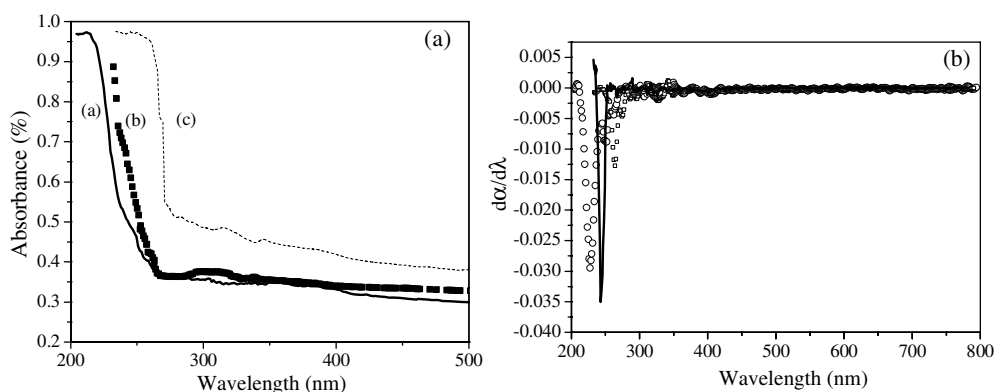

Figure 6. (a) Comparison of absorption spectra of Ga$_2$O$_3$:SiO$_2$ composites with molar ratio 10:90 (a), 20:80 (b) and 30:70 (c). (b) Comparison of $\frac{d\alpha}{d\lambda}$ versus wavelengths spectra of Ga$_2$O$_3$:SiO$_2$ composites with molar ratio 10:90 (open circle), 20:80 (solid line) and 30:70 (open square). For each case the annealing temperature is 900 °C.

region may be associated with for example isolated –OH groups. The three peaks at 1080, 796 and 460 cm^{-1} are the characteristics of Si–O–Si vibrational mode [46]. The peak at the highest frequency mode, i.e. at about 1080 cm^{-1}, with the strongest intensity (among the three), is due to antisymmetric stretching. The bands at 796 and 460 cm^{-1} can be assigned to symmetric stretching and optical rocking motions respectively [45]. The peaks at 1635 and 680 cm^{-1} are due to Ga^{3+} ion at the surface [47] and the Ga–O band respectively and indicate that gallium is present in the sample with Ga–O bonding.

Figure 6(a) shows the comparison of optical absorbance versus wavelength spectra of Ga$_2$O$_3$:SiO$_2$ composites with different molar ratios, (a) 10:90, (b) 20:80 and (c) 30:70. All the samples were annealed at 900 °C for 8 h. To record the optical absorption spectra an equal amount (by weight) of each sample was taken and dispersed into triple distilled water. It is clear from figure 6(a) that the absorption band shifts slightly towards longer wavelengths with increasing molar percentages of gallium oxide in the samples. Bandgap values of the composite powder samples can be obtained by plotting the derivative of absorbance of the corresponding sample. Figure 6(b) shows a comparative study of $\frac{d\alpha}{d\lambda}$ versus λ traces of the foresaid samples. A hint of a slight increasing trend of bandgap values of samples with decreasing molar percentage
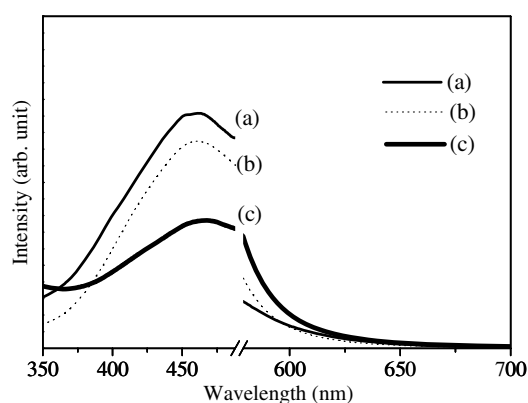
Figure 7. Comparison of PL spectra of Ga_2O_3:SiO_2 composites with molar ratio 10:90 (a), 20:80 (b) and 30:70 (c). For each case annealing temperature is 900 °C.

of gallium oxide can be observed in the figure. Thus E_g of Ga_2O_3:SiO_2 composite with molar ratio 10:90 is 5.51 eV. For the samples with molar ratios 20:80 and 30:70 the bandgap values are 5.12 and 4.70 eV. From the previous studies, it can be concluded that the bandgap value of gallium oxide strictly depends on its preparation condition [12, 48, 49]. The significant deviation of bandgap for low-Ga_2O_3 composites of this work from that of the corresponding bulk material (4.9 eV [5]) is considered to be an effect of the nanosize of β-Ga_2O_3 particles embedded in the silica matrix. However, the deviation of the values among themselves is not so clear in view of the little variation of particle size as a function of the Ga_2O_3:SiO_2 molar ratio.

3.4. Photoluminescence study

Figure 7 shows photoluminescence spectra of Ga_2O_3:SiO_2 composites with molar ratios (a) 10:90, (b) 20:80 and (c) 30:70. All the samples were annealed at 900 °C for 8 h. Under the excitation at about 260 nm, gallium oxide nanoparticles show a strong blue emission at ~460 nm. A similar observation has been made by other workers examining the photoluminescence of low dimensional Ga_2O_3, e.g. nanowires [20] and nanorods [26]. In the present case the relative peak intensity of the composite sample with molar ratio 10:90 is the strongest. The peak intensity goes down with increasing proportion of gallium oxide. However, no blue shift can be observed with decreasing molar ratio of gallium oxide in the composite. The capping of Ga_2O_3 particles leading to only insignificant difference of size in the different cases of composition and annealing, is apparently the reason for this. Binet and Gourier [5] described the blue luminescence of gallium oxide nanoparticles as a result of transfer by tunnel effect of an electron from a donor cluster to a hole trapped at an acceptor site. However, a fast electron–hole recombination occurs at the acceptor site with strong electron–phonon coupling giving rise to blue luminescence [50, 51]. In the present case the blue luminescence can be demonstrated in a similar way. Figure 8 shows a schematic diagram of blue luminescence of gallium oxide. Finally, the absence of the photoluminescence peaks for β-Ga_2O_3 in the UV and green regions [5], and also those due to the silica host [52] in figure 7, clearly indicates non-interference of the confining host, and also impurities such as dopant in the spectrum. The absence of any significant impurities is already indicated in figure 4. These observations apparently increase the possibility of use of the prepared materials in blue luminescent devices with tailorable intensity of luminescence.
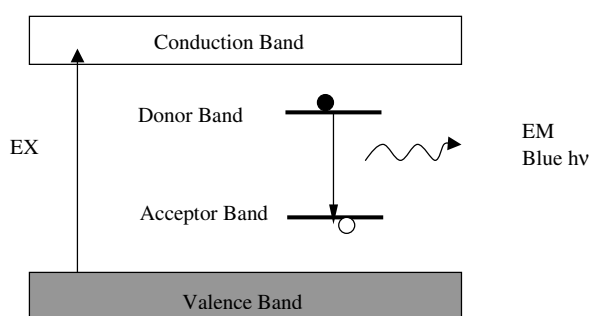
Figure 8. Schematic diagram of the blue luminescence of β-Ga$_2$O$_3$ (after [5]).

4. Conclusion

Ga$_2$O$_3$:SiO$_2$ nanocomposites with molar ratio 10:90, 20:80 and 30:70 were prepared by the sol–gel method. Annealing of the samples was carried out at 400, 500 and 900 °C. Particle diameter of gallium oxide varied from 2 to 5 nm. Though α-Ga$_2$O$_3$ has been obtained in various investigations as the low temperature (up to $\sim$500 °C) crystalline phase [2, 3, 37, 38], XRD and HRTEM investigation in the present work indicated formation of β-Ga$_2$O$_3$ already around 400 °C for each molar ratio. This probably indicates the role of the confined size of the gallium oxide particles in the depression of polymorphic transformation of the β-phase. Due to a very strong capping effect of the silica matrix, the particle sizes of gallium oxide varied only slightly with increasing annealing temperature and proportion of gallium oxide in the composite. The optical bandgap was observed to increase slightly with the decrease of proportion of gallium oxide in Ga$_2$O$_3$:SiO$_2$ composites in low-Ga$_2$O$_3$ samples. A blue luminescence (at about 460 nm) was observed to be exhibited by the samples, probably because of the recombination of an electron, originating from a donor vacancy, with a hole trapped in an acceptor vacancy.

References

[1] Roy R, Hill V G and Obson E F 1952 *J. Am. Chem. Soc.* **74** 719
[2] Tas A C, Majweski P J and Aldinger F 2002 *J. Am. Ceram. Soc.* **85** 1421
[3] Sinha G, Adhikary K and Chaudhuri S 2006 *Opt. Mater.* at press
[4] Tippin H H 1965 *Phys. Rev.* **140** A316
[5] Binet L and Gourier D 1998 *J. Phys. Chem. Solids* **59** 1241
[6] Hao J and Cocivera M 2002 *J. Phys. D: Appl. Phys.* **35** 433
[7] Ogita M, Saika N, Nakanishi Y and Hatanaka Y 1999 *Appl. Surf. Sci.* **142** 188
[8] Pohle R, Fleischer M and Meixner H 2000 *Sensors Actuators* B **68** 151
[9] Rebien M, Herion W, Hong M, Mannaerts J P and Fleischer M 2002 *Appl. Phys. Lett.* **81** 250
[10] Passlack M, Schubert E F, Hobson W S, Hong M, Moriya N, Chu S N G, Konstadinidis K, Mannaerts J P,
        Schnoes M L and Zydzik G J 1995 *J. Appl. Phys.* **77** 686
[11] Edwards D D, Mason T O, Goutenoire F and Poeppelmeier K R 1997 *Appl. Phys. Lett.* **70** 1706

[12] Hajnal Z, Miro' J, Kiss G, Re'ti F, Dea'k P, Herndon R C and Kuperberg J M 1999 *J. Appl. Phys.* **86** 3792

[13] Fu L, Hu P, Xiao K, Yu G and Zhu D 2003 *Chem. Mater.* **15** 4287

[14] Sharma S and Sunkura M K 2002 *J. Am. Chem. Soc.* **124** 12288

[15] Geng B, Zhang L, Meng G, Xie T, Peng X and Lin Y 2003 *J. Cryst. Growth* **259** 291

[16] Chun H Y, Choi Y S, Bea S Y, Seo H W, Hong S J, Park J and Yang J 2003 *J. Phys. Chem.* B **107** 9042

[17] Mayo M J, Suresh A and Porter W D 2003 *Rev. Adv. Mater. Sci.* **5** 100

[18] Frey M H and Payne D A 1996 *Phys. Rev.* B **54** 3158

[19] Dai Z R, Pan Z W and Wang Z L 2002 *J. Phys. Chem.* B **106** 902

[20] Gundiah G, Govindaraj A and Rao C N R 2002 *Chem. Phys. Lett.* **351** 189

[21] Zhang H Z, Kong Y C, Wang Y Z, Du X, Bai Z G, Wang J J, Yu D P, Ding Y, Hang Q L and Feng S Q 1999 *Solid State Commun.* **109** 677

[22] Wu X C, Song W H, Huang W D, Pu M H, Zhao B, Sun Y P and Du J J 2000 *Chem. Phys. Lett.* **328** 5

[23] Han W Q, Redlich P K, Ernst F and Rühle M 2000 *Solid State Commun.* **115** 527

[24] Choi W B, Lee N S and Kim J M 2000 *Adv. Mater.* **12** 746

[25] Liang C H, Meng G W, Wang G Z, Wang Y W, Zhang L D and Zhang S Y 2001 *Appl. Phys. Lett.* **78** 3202

[26] Zhang J, Liu Z, Lin C and Lin J 2005 *J. Cryst. Growth* **280** 99

[27] Chen X, Shi W, Xia J, Cheng P, Zhao B, Song H B, Wang H G, Yan S P, Liao D Z and Jiang Z H 2005 *Inorg. Chem.* **44** 4263

[28] Liu J, Ong W, Kaifer A E and Peinador C 2002 *Langmuir* **18** 5981

[29] Zhang H, Yang D, Ma X and Que D 2005 *Mater. Lett.* **59** 303

[30] Sui Z M, Chen X, Wang L Y, Xu L M, Zhuang W C, Chai Y C and Yang C J 2006 *Physica* E **33** 308

[31] Que H, Cao C, Wang D and Zhu H 2006 *Mater. Chem. Phys.* **96** 296

[32] Yang Y, Tran C, Leppert V and Risbud S H 2000 *Mater. Lett.* **43** 243

[33] Gorai S and Chaudhuri S 2006 *Mater. Sci. Eng.* B **126** 97

[34] Chakrabarti S, Ganguli D and Chaudhuri S 2003 *J. Phys. D: Appl. Phys.* **36** 146

[35] Brinker C J and Scherer G W 1990 *Sol–Gel Science* (San Deigo, CA: Academic) chapter 3

[36] Fleischer M, Hollbaner L, Born E and Meixner H 1997 *J. Am. Ceram. Soc.* **80** 2121

[37] Sinha G, Adhikary K and Chaudhuri S 2005 *J. Cryst. Growth* **276** 204

[38] Sinha G, Ganguli D and Chaudhuri S 2006 communicated

[39] Aubay E and Gourier D 1993 *Phys. Rev.* B **47** 15023

[40] Tolbert S H and Alivisatos A P 1994 *Science* **265** 273

[41] Skandan G, Foster C M, Frase J, Ali M N and Parker J C 1992 *Nanostruct. Mater.* **1** 313

[42] Zhang H and Banfield J F 1998 *J. Mater. Chem.* **8** 2073

[43] Wu N L, Wu T F and Rusakova I A 2001 *J. Mater. Res.* **16** 666

[44] Fidalgo A, Nunes T G and Ilharco L M 2000 *J. Sol–Gel Sci. Technol.* **19** 403

[45] Innocenzi P, Falcaro P, Grosso D and Babonneau F 2003 *J. Phys. Chem.* B **107** 711

[46] Galeener F L 1979 *Phys. Rev.* B **19** 4292

[47] Petre A L 2001 *Thermochim. Acta* **379**

[48] Ueda N, Hosono H, Waseda R and Kawazoe H 1997 *Appl. Phys. Lett.* **71** 933

[49] Kim H G and Kim W T 1997 *J. Appl. Phys.* **62** 2000

[50] Kim H W and Kim N H 2005 *J. Alloys Compounds* **389** 177

[51] Villora E G, Hatanaka K, Odaka H, Sugawara H, Muira T, Fukumura H and Fakuda T 2003 *Solid State Commun.* **127** 385

[52] Kohketsu M, Kawazoe H and Yamane M 1987 *Diffus. Defect Data* **53/54** 127