Vol 14 No 10, October 2005
1009-1963/2005/14(10)/2145-04

Chinese Physics

© 2005 Chin. Phys. Soc.
and IOP Publishing Ltd

Photoluminescence and transmission spectra of nanocrystalline $GaAs_{1-x}Sb_x$ embedded in silica films*

Liu Fa-Min(刘发民)[a)†], Zhang Li-De(张立德)[b)], and Li Guo-Hua(李国华)[c)]

[a)] *Department of Physics, School of Science, Beijing University of Aeronautics and Astronautics, Beijing* 100083, *China*
[b)] *Institute of Solid State Physics, Chinese Academy of Sciences, Hefei* 230031, *China*
[c)] *National Laboratory for Superlattices and Microstructure, Institute of Semiconductors, Chinese Academy of Sciences, Beijing* 100083, *China*

(Received 1 March 2005; revised manuscript received 24 May 2005)

The composite films of the nanocrystalline $GaAs_{1-x}Sb_x$–SiO_2 have been successfully deposited on glass and GaSb substrates by radio frequency magnetron co-sputtering. The 10K photoluminescence (PL) properties of the nanocrystalline $GaAs_{1-x}Sb_x$ indicated that the PL peaks of the $GaAs_{1-x}Sb_x$ nanocrystals follow the quantum confinement model very closely. Optical transmittance spectra showed that there is a large blue shift of optical absorption edge in nanocrystalline $GaAs_{1-x}Sb_x$–SiO_2 composite films, as compared with that of the corresponding bulk semiconductor, which is due to the quantum confinement effect.

Keywords: nanocrystalline $GaAs_{1-x}Sb_x$, photoluminescence, transmission absorption, quantum confinement effect
PACC: 7855E, 7865K, 7865M

1. Introduction

The unique properties of nanocrystals and quantum dots have led to investigations of many techniques that can be used to synthesize these materials. Fabrication methods span a wide range including such techniques as the growth in sol-gel, chemical vapour deposition, laser ablation, and the growth by molecular beam epitaxy to form self-assembled quantum dots. One of the most versatile methods for fabricating nanocrystals and quantum dots involves magnetron co-sputtering. So far, many works have been reported for various glasses doped with semiconductor nanoparticles such as GaSb,[1−4] GaAs,[5] InAs,[6,7] CdSTe,[8] InGaAs[9] and GaN_xAs_{1-x}.[10] The ternary III-V compound $GaAs_{1-x}Sb_x$ epilayer has been shown to be a potentially important material for a wide range of opto-electronic device applications, including lasers[11−13] and light-emitting diodes[14,15] and detectors in the 1.3–1.6μm region desirable for fibre optical communication application. Although extensive work has been done on bulk $GaAs_{1-x}Sb_x$ alloys,[16−18] much less work has been reported on the growth and optical properties of nanocrystalline GaAsSb thin films. The growth and characterization of nanocrystalline $GaAs_{1-x}Sb_x$–SiO_2 composite films have been reported elsewhere.[19] In this paper we study the photoluminescence and transmission spectra of the $GaAs_{1-x}Sb_x$–SiO_2 composite films with the $GaAs_{1-x}Sb_x$ grains being of nanocrystal sizes, which are successfully deposited on glass and GaSb substrates by radio frequency (RF) magnetron co-sputtering.

2. Experimental procedure

A silica glassy plate of 60mm in diameter, together with several chips of polycrystalline GaSb and GaAs attached, was used as a target. In this work the effective sputtered area ratio of the semiconductor chips to silica plate was fixed at 23.1%. When the chamber was evacuated to a pressure of 2.7×10^{-3}Pa, high purity (99.9999 %) argon gas was introduced. During sputtering, the chamber pressure was maintained at 2Pa and the output voltage to RF sputter gun was 1000V. Then the films were grown in

*Project supported by the Aeronautics Science Foundation of China (Grant No 03G51069).
†E-mail: fmliu@buaa.edu.cn; fmliu@etang.com

situ at temperatures between 300°C and 650°C for 3h and formed various sizes of nanoparticles. The films were then characterized[19] by using x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and Raman scattering spectra.

Photoluminescence (PL) spectra were carried out using a Jobin-Yvon HRD-I double grating monochromator with a microscope and detected by an APD CSW-202A cooled GaAs photomultiplier operating in photon counting mode. The step was 0.5nm and the count time of the detector ranged from 0.5 to 1s. A He-Cd laser operating at 325.0nm was used as the excitation source with excitation level of 250W/cm^2. A resolution of 0.5nm was used in our measurements. All PL spectra were recorded at 10K by attaching the sample in the cold finger of an APD refrigeration system. The measured spectra have been corrected according to the system response.

3. Results and discussion

The spectral position of the 10K excitonic photoluminescence peaks of $GaAs_{0.57}Sb_{0.43}$ nanoparticles depends on the nanocrystal size as shown in Fig.1.

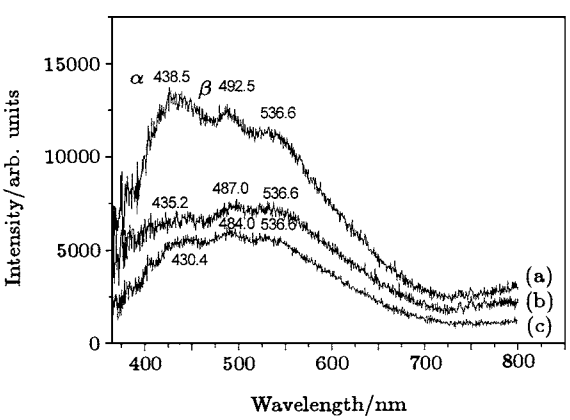


Fig.1. 10K photoluminescence of nanocrystalline $GaAs_{0.57}Sb_{0.43}$ –SiO_2 composite films versus the mean size of $GaAs_{0.57}Sb_{0.43}$ nanocrystals (a) 4.8 nm, (b) 4.1 nm, (c) 3.8nm.

The large blue shift of this band suggests that the band correspond to the electron hole pair recombination with at least one carrier being deeply localized. One can see three blue peaks in the PL which depend on the size of $GaAs_{0.57}Sb_{0.43}$ nanocrystals. Figure 1(a) shows the 10K excitonic photoluminescence of nanocrystalline $GaAs_{0.57}Sb_{0.43}$–SiO_2 composite film grown at 673K for 3h. The size of $GaAs_{0.57}Sb_{0.43}$ nanocrystals is about 4.8nm. Three PL peaks at 447.7, 492.5 and 536.6nm come in sight. Figures 1(b) and (c) show the 10K excitonic photoluminescence of nanocrystalline $GaAs_{0.57}Sb_{0.43}$–SiO_2 composite film grown at 623 and 573K for 3h, respectively. The sizes of these $GaAs_{0.57}Sb_{0.43}$ nanoparticles are about 4.1 and 3.8nm, respectively. One can see three PL peaks (435.2, 487.0, and 536.6nm) in Fig.1 (b) and three PL peaks (430.4, 484.0 and 536.6nm) in Fig.1(c).

GaSb has a band gap of 0.72 eV at room temperature and is a direct band gap material. At low temperatures, GaSb bulk has two main PL peaks at the positions of 1.5938μm (0.778 eV) and 1.5576 μm (0.796eV).[20] The observed PL peaks of bulk GaSb are the conduction to valence band transition and the free excitons to neutral acceptor excitons transition, as shown in Fig.2. Apart from these two PL peaks, there is much weak radiative transition across the band gap.

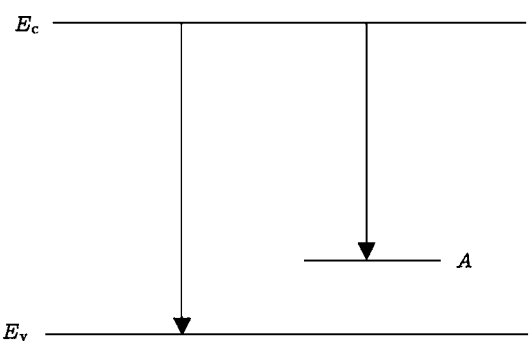


Fig.2. The principle figure of electron-hole pair recombination across the band gaps. $E_c \rightarrow E_v$ is the band to band transition, and $E_c \rightarrow A$ is the free excitons to neutral acceptor excitons transition.

According to the virtual-crystal approximation (VCA),[21] the direct band gap E_Γ of the solid solution $GaAs_{1-x}Sb_x$ is defined by the following linear combination:

$$E_\Gamma = xE_{GaSb} + (1-x)E_{GaAs}, \qquad (1)$$

where E_{GaSb} is the band gap of bulk GaSb, and E_{GaAs} is the band gap of bulk GaAs. So we can estimate that the direct band gap E_Γ of the bulk $GaAs_{0.57}Sb_{0.43}$ has a band gap of 1.12 eV at room temperature, which is in good agreement with that reported in Ref.[22]. Thus, there are larger blue shifts of optical absorption edge of the nanocrystalline $GaAs_{0.57}Sb_{0.43}$–SiO_2 composite films than that of bulk $GaAs_{0.57}Sb_{0.43}$ semiconductor. This blue-shift behaviour of the absorption edge originates essentially from the quantum confinement effect.[23,24] Brus[23] pointed out that if the Bohr radius a_B of the exciton in the bulk material is much

larger than that of the nanoparticles, then the quantum confinement is obvious, in which the confinement energy dominates over the Coulomb interactions. According to the effective mass model, Bohr radius a_B has been taken as

$$a_B = 4\pi\varepsilon_0\varepsilon h^2/4\pi^2\mu e^2, \qquad (2)$$

where ε_0 is the vacuum dielectric constant, ε the relative dielectric constant, h the Planck constant, μ the reduced mass of an electron-hole pair, and e the electronic charge. Obviously, the PL peaks of $GaAs_{0.57}Sb_{0.43}$ nanocrystals have larger blue shifts than that of $GaAs_{0.57}Sb_{0.43}$ bulk from the data mentioned above. One usually uses Varshni formula[25,26] to describe the variation of semiconductor band gap with temperature at low temperatures.

$$E_g(T) = E_g(0) - AT^2/(T+B). \qquad (3)$$

For bulk $GaAs_{0.57}Sb_{0.43}$, the band gap as a function of temperature can be described as follows:

$$E_g(T) = 1.215 - 3.3\times10^{-4}T^2/(T-14.9). \qquad (4)$$

So we estimate the band gap E_g (10K)=1.222eV by using Eq.(4) for bulk $GaAs_{0.57}Sb_{0.43}$.

The radius of Bohr exciton is estimated as about 15.9nm for $GaAs_{0.57}Sb_{0.43}$ bulk from formula (2), and the size of the $GaAs_{0.57}Sb_{0.43}$ semiconductor crystallite ranges from 4 to 6nm. Therefore, the strong quantum confinement leads to a blue-shifted PL peak. From the effective mass approximation, for a spherical nanoparticle of diameter d, the variation of band gap of semiconductor nanoparticles corresponding to the bulk case is expressed as

$$\Delta E_g = E - E_g \approx h^2\pi^2/2d^2\mu - 1.8e^2/2\pi\varepsilon\varepsilon_0 d + \text{smaller terms}, \qquad (5)$$

where μ is a reduced mass of an electron-hole pair, ε_0 and ε are the dielectric constants of vacuum and the semiconductor respectively, h is Planck's constant, and e is electronic charge. From Eqs.(3), (4) and (5), the band gap energy shifts of PL peaks as functions of the size of nanocrystals are shown in Fig.3. These show that the experimental data are basically in agreement with the quantum confinement theory.

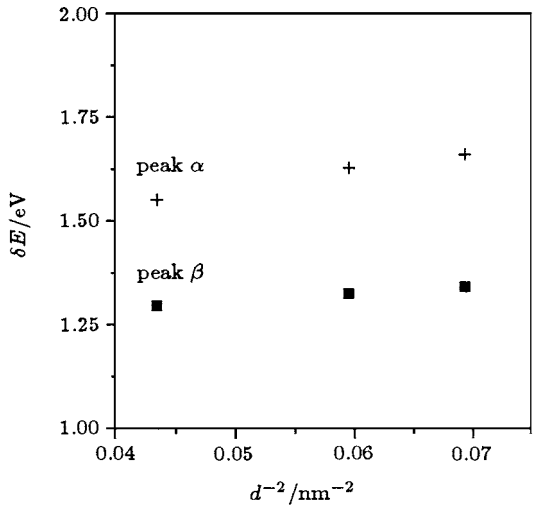


Fig.3. The band gap energy shift of PL peak versus the size of nanocrystals.

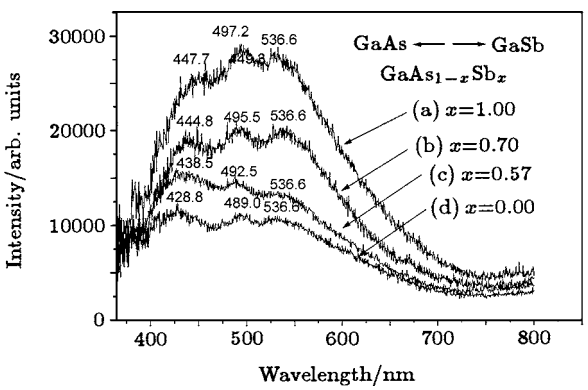


Fig.4. 10K photoluminescence of nanocrystalline $GaAs_{1-x}Sb_x$–SiO_2 composite films.

Figure 4 shows 10K photoluminescence of nanocrystalline $GaAs_{1-x}Sb_x$–SiO_2 composite films, where Fig.4(a) shows the 10K excitonic photoluminescence of nanocrystalline GaSb–SiO_2 composite films grown on the GaSb substrate. There are three PL peaks at the positions of 444.7, 495.5, and 533.6 nm. Figures 4(b), (c), and (d) show the 10K excitonic photoluminescence of nanocrystalline $GaAs_{1-x}Sb_x$–SiO_2 composite films grown on the GaSb substrate for x=0.70, 0.57, 0, respectively. We can also see three PL peaks at the positions of (444.8, 495.5, 536.6nm), (438.5, 492.5, 536.6nm), and (428.8, 489.0, 536.6nm) for Fig. 4(b), (c), and (d) respectively. The two films were grown at the same condition (673K, 3h) and the sizes of GaSb nanocrystals in the films are about 4.9 nm. These results can be explained by quantum confinement effect mentioned above.

The optical transmittance spectra of nanocrystalline $GaAs_{1-x}Sb_x$–SiO_2 composite films are shown

in Figs.5 (a), (b), (c) and (d) for x=0.26, 0.49, 0.57, and 0.67, respectively.

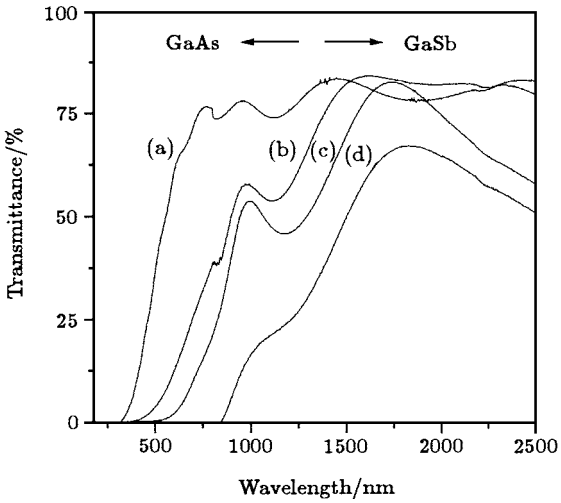


Fig.5. Optical transmittance spectra of nanocrystalline $GaAs_{1-x}Sb_x$–SiO_2 composite films (a) x=1, (b) x=0.70, (c) x=0.57, (d) x=0.

We can obviously see a red shift of the absorption edge with increasing content of Sb. The lines of absorption edge for x=0.26, 0.49, 0.57, and 0.67 are 334.0, 435.6, 561.0, and 852.8nm, respectively. In addition, one can notice that as expected the absorption edge of nanocrystalline $GaAs_{1-x}Sb_x$–SiO_2 composite films is blue shifted if the Sb content decreases.

4. Conclusion

In summary, we have investigated the nanocrystalline $GaAs_{1-x}Sb_x$–SiO_2 composite films grown by radio frequency magnetron co-sputtering. We have observed the 10K optical transition from PL spectra in $GaAs_{1-x}Sb_x$ nanocrystals as their sizes change. It is shown that the PL peaks have large blue shifts compared with that of corresponding $GaAs_{1-x}Sb_x$ bulk semiconductor, which originates from the quantum confinement effect. Optical transmission data exhibit a large blue shift with respect to that of the bulk semiconductor due to the strong quantum confinement effect.

References

[1] Liu F M and Zhang L D 1999 *J. Crystal Growth* **204** 19
[2] Liu F M and Zhang L D 1999 *Semicond. Sci. Technol.* **14** 710
[3] Liu F M, Wang T M and Zhang L D 2002 *Acta Phys. Sin.* **51** 183 (in Chinese)
[4] Liu F M, Wang T M and Zhang L D 2004 *Chin. Phys.* **13** 2169
[5] Shi W Z, Lin K X and Lin X Y, 1997 *J. Appl. Phys.* **81** 2822
[6] Shi J, Zhu K, Zheng Q, Zhang L, Ye L, Wu J and Zuo J 1997 *Appl. Phys. Lett.* **70** 2686
[7] Shi J, Zhu K and Zhang L 1999 Solid *State Commun.* **110** 645
[8] Jain R K and Lind R C 1983 *J. Opt. Soc. Am.* **73** 647
[9] Steffen R S, Koch T H, Oshinowo J, Faller F and Forchel A 1996 *Appl. Phys. Lett.* **68** 223
[10] Luo X D, Sun B H and Xu Z Y 2005 *Acta Phys. Sin.* **54** 2385 (in Chinese)
[11] Tabatabie N, Stillman G E and Chin R 1982 *Appl. Phys. Lett.* **40** 415
[12] Nahory R E, Pollack M A, Beebe E D, Winter J C D and Dixon R W 1976 *Appl. Phys. Lett.* **28** 19
[13] Wang F Z,Chen Z H, Liu Y, Huang S H, Bai L H and Shen X C 2005 *Acta Phys. Sin.* **54** 434 (in Chinese)
[14] Nahory R E, Pollack M A, Beebe E D and Winter J C D 1975 *Appl. Phys. Lett.* **27** 356
[15] Cho A Y, Casey H C and Foy J P W 1977 *Appl. Phys. Lett.* **30** 397
[16] Cohen R M, Cherng M J, Benner R E and Stringfellow G B 1985 *J. Appl. Phys.* **57** 4817
[17] Cherng M J, Stringfellow G G and Cohen R M 1984 *Appl. Phys. Lett.* **44** 677
[18] Peter M, Herres N, Fuchs F, Winkler K, Bachem K H and Wagner J 1999 *Appl. Phys. Lett.* **74** 410
[19] Liu F M, Zhang L D and Li G H 2000 *Thin Solid Films* **375** 284
[20] Su Y K and Chen S M 1993 *J. Appl. Phys.* **73** 8349
[21] Deibuk V G and Studenets V I 1999 *Semiconductors* **32** 944
[22] Chen A B and Sher A 1994 in *Semiconductor Alloys—Physics and Materials Engineering* (New York: Plenum Press)
[23] Brus L 1986 *J. Phys. Chem.* **90** 2555
[24] Kayanuma Y 1988 *Phys.Rev.* B **38** 9797
[25] Bellani V, Lernia S D, Geddo M, Guizzetti G, Bosacchi A, Franchi S and Magnanini R 1997 *Solid State Commun.* **104** 81
[26] Varshni Y P 1967 *Physica* **34** 150