PERGAMON

Scripta mater. 44 (2001) 1841–1846

Scripta MATERIALIA

www.elsevier.com/locate/scriptamat

SYNTHESIS OF GaAs NANOPARTICLES EMBEDDED IN SiO_2 MATRIX BY RADIO FREQUENCY CO-SPUTTERING TECHNIQUE

U. Pal, A. Bautista-Hernández, N. Koshizaki*, T. Sasaki*, and S. Terauchi*

Instituto de Física, Universidad Autónoma de Puebla, Apdo. Postal J-48, Puebla, Pue. 72570, Mexico *National Institute of Materials and Chemical Research (NIMC), AIST, MITI, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan

(Received August 21, 2000)
(Accepted in revised form December 20, 2000)

Abstract—Nanoparticles of GaAs embedded in SiO_2 matrix were prepared by radio a frequency co-sputtering technique. The content of GaAs in the composite films was varied by varying the number of pieces of GaAs co-targets on a SiO_2 target. The as-grown composite films were amorphous in nature. the optical absorption spectra of the films revealed a large shift in the optical band gap of GaAs, which partly corresponds to the strong quantum confinement of electrons and holes in the nanoparticles and is partly due to their amorphous nature.

Keywords: Nanocomposites; Thin films; Optical properties; Quantum confinement

Introduction

The study of semiconductor nanocrystals has been an expanding field of interest in recent years. In semiconductor nanocrystals the band gap increases with decreasing diameter due to the spatial confinement of electrons and holes. Electronic states also become discrete with high oscillator strength (1). These zero dimensional semiconductors have many distinctive optical properties including super-radiant decay (2) and enhancement of nonlinear optical susceptibility (4,5). To obtain three dimensionally confined semiconductor systems, different groups have exploited a variety of techniques, for example: pyrolysis (6,7), liquid phase synthesis (8), co-sputtering (9–12), pulsed-laser abletion (13), spark processing (14), reduction of oxides (15), and ion-implantation (16–18).

The study of the formation and growth of these semiconductor nanocrystals in different commonly used host materials is necessary for understanding different material issues, as well as for controlling the nanocrystal fabrication to achieve the desired properties.

Co-sputtering has been utilized in this study as a method to produce semiconductor nanocrystals. This technique has been used in the past to produce several semiconductor nanocrystals like Si, Ge, CdS, etc. of a desired size and concentration and is extensively used in semiconductor technology.

This article presents a study on the growth of GaAs nanocrystals in SiO_2, a stable matrix with different contents of GaAs. The effect of the content of GaAs and subsequent process conditions on the formation, structure and optical properties of the nanoparticles have been studied.

PII: S1359-6462(01)00804-1

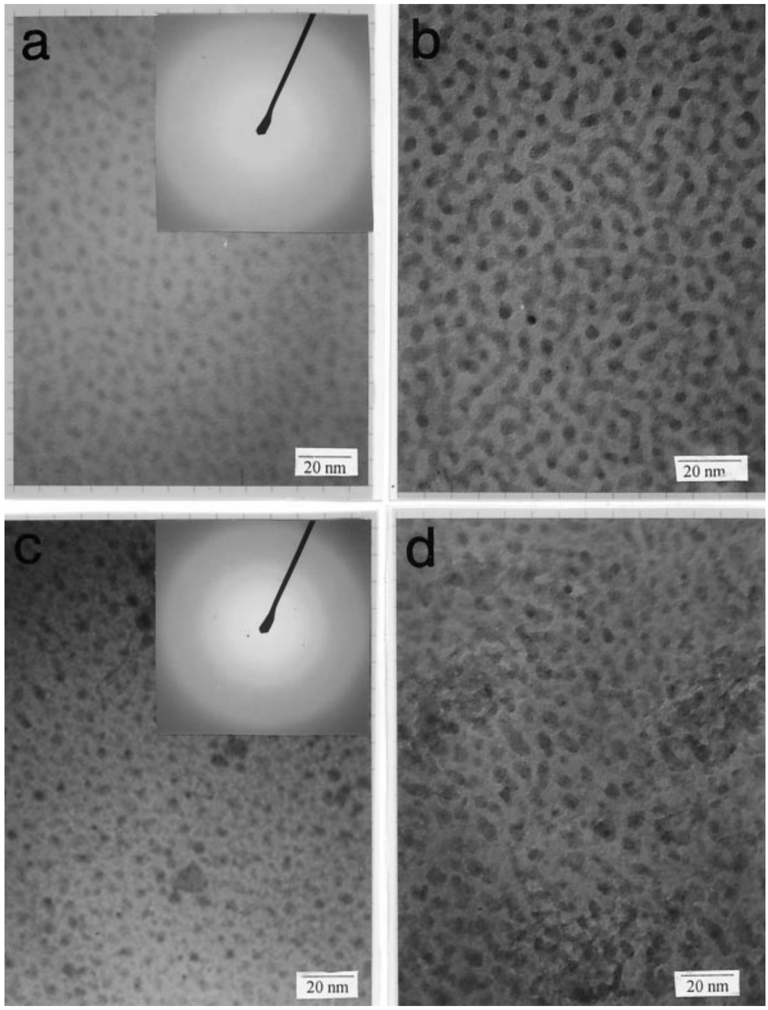

Figure 1. TEM micrographs for the as-grown samples prepared with a) 4 pieces, b) 8 pieces, c) 12 pieces and d) 16 pieces of GaAs co-targets. The insets show the corresponding TED patterns.

Experimental

The GaAs nanoparticles were formed in a SiO_2 matrix by co-sputtering a SiO_2 (10 cm diameter) target with different pieces of GaAs (3 mm $\times$ 3 mm $\times$ 0.2 mm) co-targets on quartz substrates. The composite films were deposited at 10 mTorr argon pressure and with 100 W r.f. power for 90 minutes. To control the content of GaAs in the composite films the number of co-targets was varied on the SiO_2 target. Depending on the content of GaAs, the thickness of the films was varied from 620 nm to 1191 nm. The films were annealed at different temperatures (200–800°C) in Ar atmosphere for 2 hrs. For transmission electron microscopy (TEM) and transmission electron diffraction (TED) observations, composite films of about 30 nm thickness were grown on carbon coated NaCl subs-trates and transferred to the copper grids. A JEOL JEM2000-FXII electron microscope was used for TEM and TED observations. A Shimadzu UV-3101PC double beam spectrophotometer was used to record the absorption spectra of the samples.

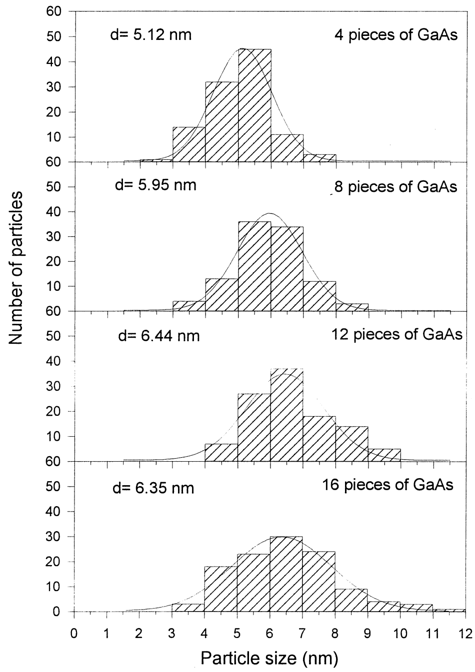

Figure 2. Size distribution of GaAs nanoparticles for the films containing different GaAs content.

Results and Discussion

In Figure 1, the TEM micrographs of the samples prepared with different GaAs content are presented. We observe the formation of nanoparticles homogeneously distributed in the matrix. The size of the particles increased gradually with the increase of GaAs content. Figure 2 shows the size distributions of the nanoparticles formed in the composites containing different GaAs contents. The mean diameters of the particles in the films prepared with 4, 8, 12 and 16 pieces of GaAs co-targets were 3.7, 4.7, 5.7, and 6.0 nm respectively. With the increase of annealing temperature, in general, the size of the particles decreased. In Figure 3, the size distribution of the particles for the samples prepared with different GaAs content and annealed at 800°C are presented. With the increase of the content of GaAs in the films, the nanoparticles became interconnected and then the connecting bonds broke to form smaller particles. The as-grown GaAs nanoparticles were amorphous in nature (ref. Figure 1). Upon annealing at temperatures 200°C or higher, the particles achieved a fibrus or crystalline structure. Figure 4 shows the optical absorption spectra of the GaAs particles in the as-grown films. The spectra are significantly blue shifted from the bulk absorption edge of 867 nm because of strong quantum confinement. A similar observation is made by Hirasawa et al. (11) for their GaAs nano-particles prepared by digital sputtering. The increase of the energy gap (ΔE) of the GaAs particles with mean diameter of 3.7, 4.7, 5.7, and 6.0 nm are 4.17, 2.4, 1.57 and 1.15 eV respectively.

ΔE was calculated from the following simple model (19)

$$\Delta E = \frac{\hbar^2 \pi^2}{2R^2}\left[\frac{1}{m_e^*} + \frac{1}{m_h^*}\right]$$

where $m_e^* = 0.067m_0$ and $m_h^* = 0.45m_0$ are the effective mass of electrons and holes respectively, and R is the radius of the particles. For particle size of 3.7, 4.7, 5.7, and 6.0 nm, the calculated

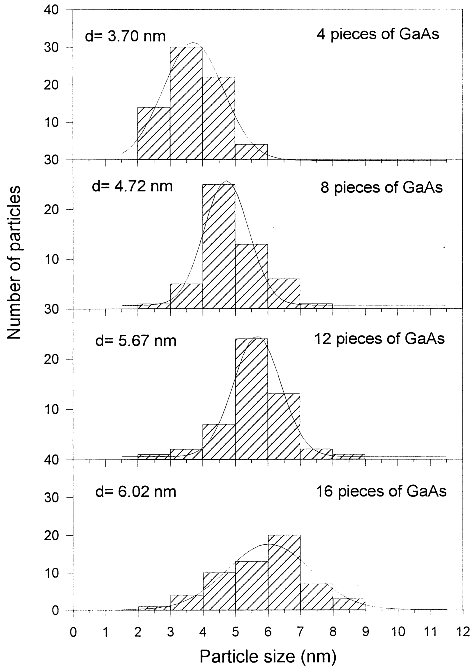

Figure 3. Size distribution of GaAs nanoparticles for for the films containing different GaAs content. the films with different GaAs content and annealed at 800°C.

values of ΔE are 1.87, 1.28, 0.80 and 0.71 eV, respectively. The blue shift observed in the experimental absorption spectra, therefore, shows a weaker dependence on particle size than the analytical model. The experimental ΔE was about two times larger than the calculated values. One of the most plausible explanation of this difference is the deviation of the particles from spherical shape, which is assumed in the model used for calculating ΔE. We assume that the GaAs particles were grown on the substrates two-dimensionally. The surface coverage ratio of GaAs particles to the substrate increased linearly with the increase of GaAs content. The height of the particles is thin enough to make quantum confinement in the direction normal to the substrate surface stronger than that in the other directions and hence a larger blue shift in the band gap than the calculated shift for the particle size determined from the projected particle surface area of the two-dimensional TEM images is observed. However, the effect of the amorphous nature of the particles and the higher effective mass of electrons and holes in small particles might have some contribution in the shift of band gap.

Conclusions

GaAs nanoparticles of different sizes embedded in SiO_2 were prepared successfully by r.f. co-sputtering. The size of the particles increased with the increase of GaAs content in the films and decreased on increasing the temperature of annealing. Further investigation is in progress to correlate the band gap shift for the GaAs nanoparticles with its crystallinity.

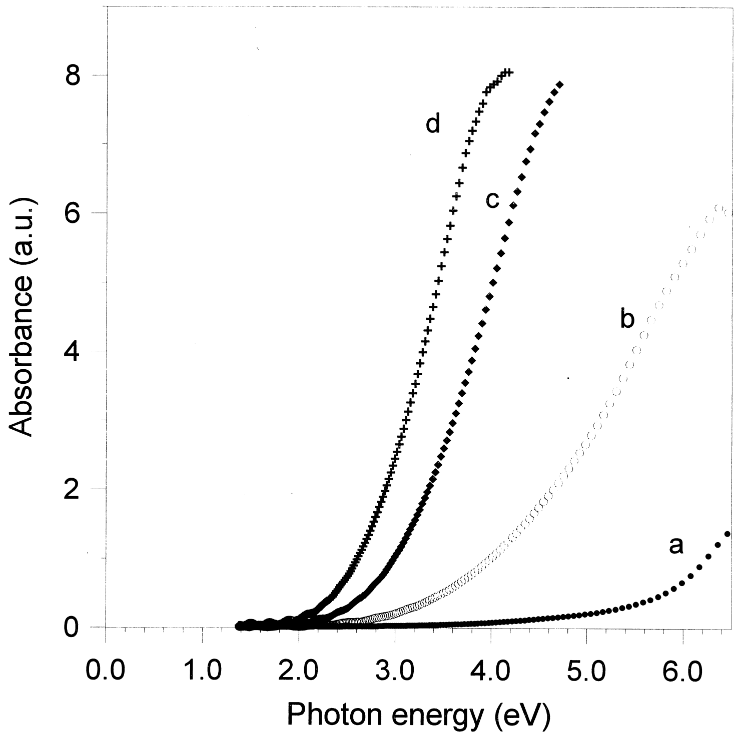

Figure 4. Optical absorption spectra for the films prepared with different GaAs content a) with 4 pcs. of GaAs, b) with 8 pcs. of GaAs, c) with 12 pcs. of GaAs and d) with 16 pcs. of GaAs.

Acknowledgments

The work is partially supported by CONACyT (Grant No. 28380 E), Mexico. U.P. thanks AIST, Japan, for awarding fellowship.

References

1. L. Brus, Appl. Phys. A. 53, 465 (1991).
2. E. Hanamura, Phys. Rev. B. 38, 228 (1988).
3. T. Takagahara and E. Hanamura, Phys. Rev. Lett. 56, 2533 (1996).
4. S. Schmitt-Rink, D. A. B. Miller, and D. S. Chember, Phys. Rev. B. 35, 8113 (1987).
5. P. C. Sercel, W. A. Saunders, H. A. Atwater, K. J. Vahala, and R. C. Flagan, Appl. Phys. Lett. 61, 696 (1992).
6. K. A. Littau, P. J. Szajowiski, A. J. Miller, A. R. Kortan, and L. E. Brus, J. Phys. Chem. 97, 1224 (1993).
7. C. B. Murray, D. J. Norris, and M. G. Bawendi, J. Am. Chem. Soc. 115, 8706 (1993).
8. H. Uchida, C. J. Cruts, P. V. Kamat, K. M. Jones, and A. J. Nozik, J. Phys. Chem. 96, 1156 (1992).
9. H. Nasu, J. Matsuoka, and K. Kamiya, J. Non-Cryst. Solids 178, 148 (1994).
10. M. Fujii, Y. Inoue, S. Hayashi, and K. Yamamoto, Appl.Phys. Lett. 68, 3749 (1996).
11. M. Hirasawa, N. Ichikawa, Y. Egashira, I. Honma, and H. Komiyama, Appl. Phys. Lett. 67, 3483 (1995).
12. U. Pal and J. Garcia-Serrano, Solid St. Commun. 111, 427 (1999).
13. E. Werawa, A. A. Seraphin, L. A. Chiu, C. Zhou, and K. D. Kolenbrander, Appl. Phys. Lett. 64, 1821 (1994).
14. M. H. Ludwig, R. E. Hummel, and S. S. Chang, J. Vac. Sci. Technol. B12, 3023 (1994).
15. D. C. Paine, C. Caragianis, and Y. Shigesato, Appl. Phys. Lett. 60, 2886 (1992).
16. T. Shimizu-Iwayama, K. Fujita, S. Nakao, K. Saitoh, T. Fujita, and N. Itoh, J. Appl. Phys. 75, 7779 (1994).

17. J. G. Zhu, C. W. White, J. D. Budai, S. P. Withrow, and Y. Chen, J. Appl. Phys. 78, 4386 (1995).
18. V. Zhu, C. W. White, J. D. Budai, S. P. Withrow, and Y. Chen, Mater. Res. Soc. Symp. Proc. 358, 175 (1995).
19. L. Brus, J. Phys. Chem. 90, 2555 (1986).