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Microstructure and Nonlinear Optical Properties of Very Small Size GaAs Nanogranulae Embedded in SiO_2 Matrix by Magnetron Co-Sputtering*

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Abstract: Microstructure of GaAs/SiO_2 nanogranular thin films fabricated by radio frequency magnetron co-sputtering technique and postannealing are investigated via atomic force microscope, X-ray diffraction, and Rutherford backscattering spectroscopy. The results show that GaAs nanocrystals with average diameters from 1.5nm to 3.2nm (depending on the annealing temperature) are uniformly dispersed in the SiO_2 matrices. GaAs and SiO_2 are found in normal stoichiometry in the films. The nonlinear optical refraction and nonlinear optical absorption are studied by Z-scan technique using a single Gaussian beam of pulse laser. The third-order nonlinear optical refractive index and nonlinear absorption coefficient are enhanced due to the quantum confinement effects and estimated to be $4\times10^{-12}m^2/W$ and $2\times10^{-5}m/W$ respectively in nonresonant condition, while $2\times10^{-11}m^2/W$ and $-1\times10^{-4}m/W$ respectively in quasi-resonant condition.

Key words: magnetron co-sputtering; GaAs nanogranula; microstructure; optical nonlinearity
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1 Introduction

III-V semiconductor/ medium nanogranular films have received considerable attention recently due to their large optical nonlinearity and the possibility of fast nonlinear response and therefore the promising applications in manufacturing novel devices of super-fast optoelectronics and photonics. GaAs/SiO_2 nanogranular films are the most promising in making ultra-fast optoelectronic devices due to its high electron mobility. Justus *et al.*[1] studied the nonlinear optical properties of quantum-confined GaAs nanocrystals in Vycor glass using the Z-scan method[2] and found that the measured nonlinear refractive index is an order of magnitude larger than that of bulk GaAs at 1060nm. Shi *et al.*[3] prepared GaAs/SiO_2 nanogranular films by magnetron co-sputtering technique and also use the Z-scan method to study the optical nonlinear properties of the films. They reported that the average diameter of the GaAs

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nanogranulae in the films was about 10nm and the third order optical nonlinearity was 7 orders of magnitude larger than that of the bulk GaAs at 632nm (near resonant). The Bohr radius of the exciton in bulk GaAs is 13nm which means the quantum confinement of the nanocrystals in the films prepared by Shi *et al.* is not very strong. What order of magnitude will the optical nonlinearities of a GaAs/SiO_2 nanogranular film reach if the average diameter of the nanocrystals in the film is much smaller than 10nm? To answer such a question is the purpose of this work that prepared GaAs/SiO_2 films with very small average size GaAs nanocrystals and studied their microstructures and the optical nonlinear properties.

2 Experimental details

The GaAs/SiO_2 nanogranular films were deposited by a co-sputtering technique in a radio frequency (RF) magnetron with a sputtering frequency of 13.56MHz. The target used was a SiO_2 glassy plate of 80mm in diameter which contained several chips of GaAs. The ratio of GaAs to SiO_2 in the films was mainly controlled by the effective surface area of the chips to that of the SiO_2 target and the input RF power. In this report, the ratio was 25% and the power varied from 110W to 130W. The back ground vacuum and sputtering gas (pure Ar) pressures were 2×10^{-4}Pa and 0.5Pa, respectively. The GaAs/SiO_2 thin films were deposited on polished silicon wafers or silica glass slices which were fixed on a hot (160℃) holder. Then the as-deposited films were annealed at different temperatures for 1h to form different average sizes of GaAs granules in the films. The surface morphology of the films was investigated by an atomic force microscope (AFM). The depth profiles of the compositions in the films were investigated by Rutherford backscattering spectroscopy (RBS). X-ray diffraction (XRD) experiments were carried out on a Siemens D5005 X-ray diffractometer with a conventional mode using CuKα1 radiation for investigating the phase structures of the films annealed at different temperatures. The examination of linear optical absorption properties of the films were carried out in a SHIMADZD UV-2501 PC spectrometer. Photoluminescence (PL) experiments were performed at a HITACHI F-4500 fluorescence spectrophotometer using an exciting wavelength of 200nm and a slit width of 10nm. The measurements of the optical nonlinear properties of the films were performed via a single Gaussian laser beam Z-scan technique. Figure 1 is the schematic diagram of the Z-scan experiment apparatus. A dye laser pumped by a XeCl Excimer laser (λ= 308nm) and operating at 450nm (near the absorption edges of the film measured) or 585nm (away from the absorption edges of the film measured) with a pulse duration of 8ns and a repetition rate of 10Hz was used as the excitation source. In the measurements the linear transmission of the collecting aperture was S= 0.3, and the focus length

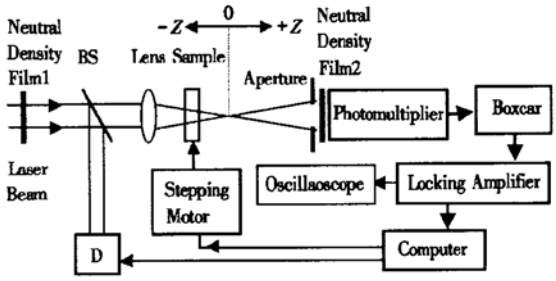

Fig. 1 Schematic diagram of the Z-scan experiment apparatus

of the lens was 6cm. The laser beam radius ω_0 at the focus (Z= 0mm) was 35μm for λ= 450nm or 37μm for λ= 585nm, and the corresponding diffraction length ($Z_0=\pi\omega_0^2/\lambda$) of the beam was 8.6mm or 7.4mm. The thickness (L) of the film annealed at 500℃ was 0.575μm, this make sure that $Z_0 \gg L$ and the film was absolutely thin. The position of the sample measured was controlled by a stepping motor which was controlled by a computer. The transmissibility for the different position of the sample at Z axle was detected by a photomultiplier. The

output of the photomultiplier would be averaged by a Boxcar first and then amplified by a locking-amplifier. Data would be collected and processed to be a T-Z curve by a computer at last. D is a photodiode for monitoring the incident laser intensity. The neutral density films 1 and 2 were used to regulate the incident laser intensities to the sample and to the photomultiplier respectively. The photomultiplier would work in linear state under the monitor of the oscilloscope.

3 Results and discussions

3.1 Microstructures of the films

Three-dimensional surface morphology images by AFM of the as-deposited film and the films annealed at different temperatures are shown in Fig. 2. It can be seen that the lower annealing temperature corresponds to smaller average grain size of the films and to a smoother film surface.

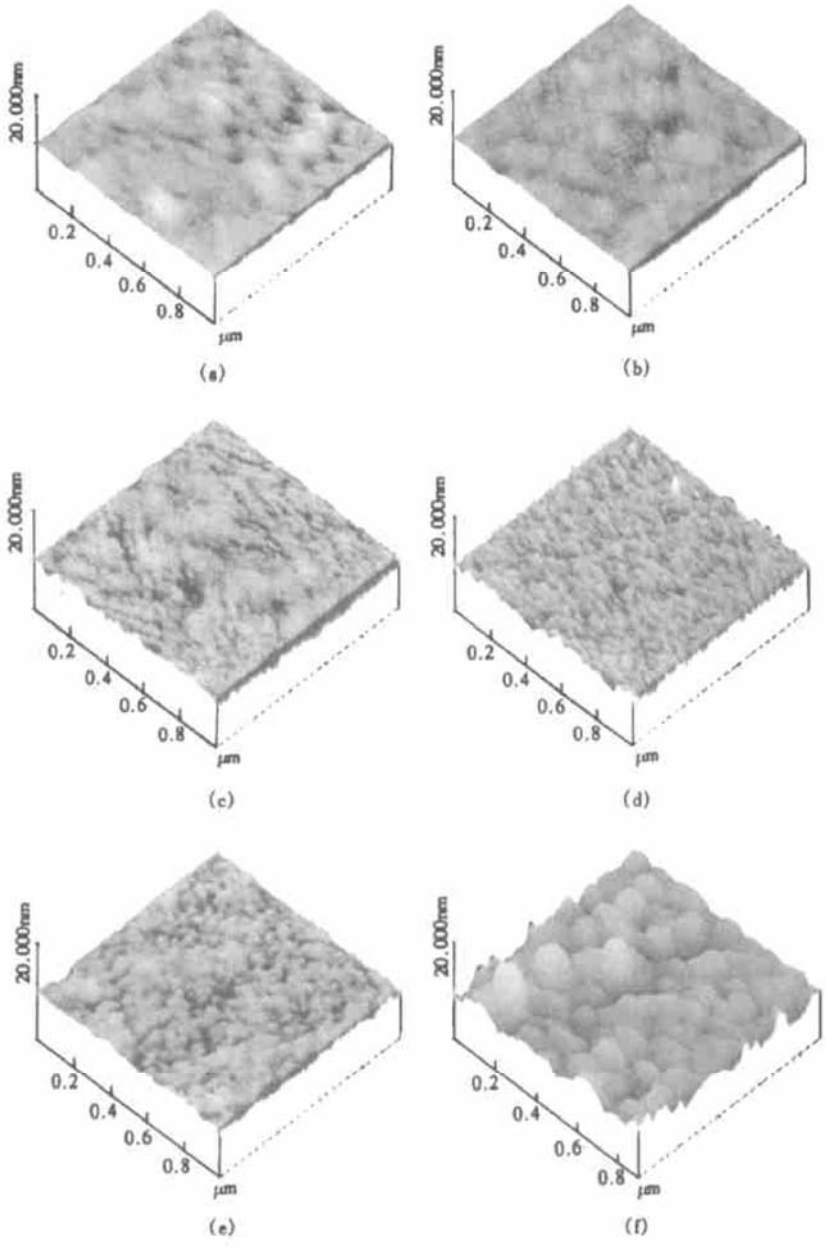

Fig. 2 AFM images of the surfaces of the GaAs/SiO_2 nanogranular films(T_a: annealing temperature) (a) as-deposited; (b) T_a= 300℃; (c) T_a= 350℃; (d) T_a= 450℃; (e) T_a= 500℃; (f) T_a= 550℃

Experimental results of RBS for the films annealed at different temperatures are shown in Fig. 3. Component content depth profile analysis on Fig. 3 indicates that GaAs and SiO_2 exist in normal stoichiometry in all the films and the distribution of GaAs granule are constant in all the films.

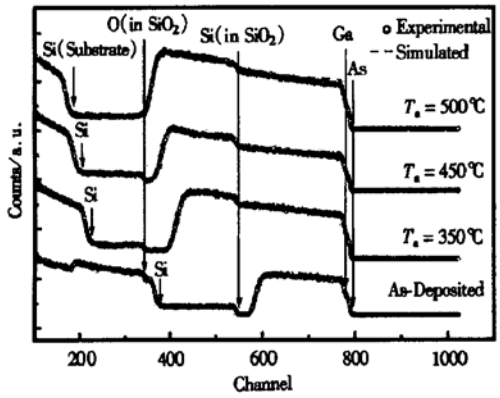

Fig. 3　RBS spectra of the as-deposited film and the films annealed at 350, 450 and 500℃ repectively(T_a: annealing temperature)

XRD patterns of the films are showed in Fig. 4. For the films annealed at 550℃, there are three peaks at $2\theta = 27.041°$, $45.348°$ and $53.729°$ in the pattern, which can be indexed as the face-centered cubic GaAs (111), (220), and (311) diffractions respectively. Comparing to the standard positions of the peaks, the angular shifts of the three peaks are 0.26°, 0.24° and 0.19° respectively. The shifts may origin from the relative changes of the d values in a group of crystal plane, namely $\langle \Delta d/d \rangle_{hkl}$, in different GaAs nanocrystals. It also can be seen that the widths of the peaks get narrower with the increase of annealing temperature which indicate that the higher the annealing temperature, the larger the average size of GaAs nanogranulae in the films. The average GaAs nanogranulae diameters in the films annealed at 550, 500, 450 and 350℃ can be evaluated from the FWHM of the (111) diffraction lines to be 3.2, 2.0, 1.6 and 1.5nm respectively according to the Scherrer formula[3] $D = 0.9\lambda/\beta\cos\theta$, where λ is the wavelength of the X-ray source, and β is the FWHM in radian of the X-ray diffraction peak at the diffraction angle θ. These values are all much smaller than the Bohr diameter of exciton in bulk GaAs. Hence, the motion of excitons in GaAs nanocrystals will be strongly affected by the quantum confinement.

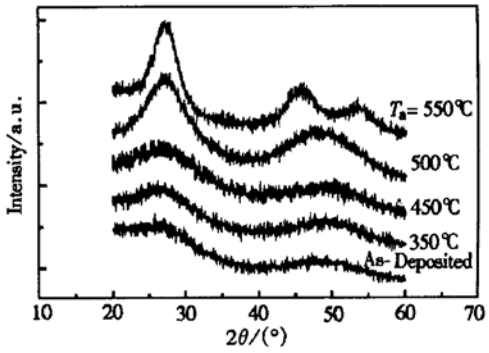

Fig. 4　XRD patterns of the as-deposited film and the films annealed at different temperatures (T_a: annealing temperature)

3.2 Linear optical properties of the films

Figure 5 shows the optical absorption and PL spectra of the film annealed at 500℃. The absorption edge is much blue shifted with respect to that of the bulk GaAs crystal (886nm). A distinct spike (spike C) presents at the ultraviolet in the absorption spectrum of the film. In fact, all the films annealed at (or higher than) 500℃ possess this feature which is clearly different from the featureless absorption spectra exhibited in many litera-

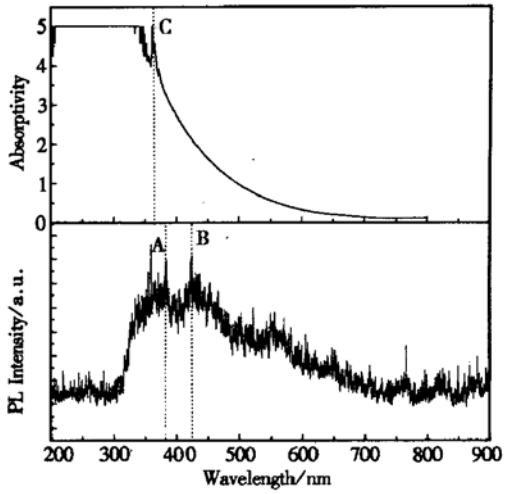

Fig. 5　Absorption and PL spectra of the film annealed at 500℃

tures[3~6] and may mean that the size distribution of the GaAs nanocrystals in the films is smaller than those in the samples reported in the literatures. The spikes may result from the transition of the electrons from the split-off band to conduction band by optical absorption. There are many peaks in the room temperature PL spectrum. The separation between peaks A and B is quite closed to the spin-orbit splitting ($\Delta = 0.35$eV) of bulk GaAs. This might imply that peak A results from the radiative recombination of the electron-split-off hole pairs and peak B from that of the quantum confined electron-heavy hole pairs. These are quite similar to those exhibited in the PL spectra of InAs/SiO_2 composite films[7].

3.3 Nonlinear optical absorption and refraction

The Z-scan experiment was performed at $\lambda = 585$nm and 450nm separately for the film annealed at 500℃ to investigate the optical nonlinear property of the film at different resonance conditions and compare with the results obtained by other authors. Figure 6 shows the relations between the normalized transmittance $T(Z)$ and the distance of Z from the focus at $\lambda = 585$nm which is off-resonant to the average band gap energy of the nanocrystals in the film. Figure 6(b) shows the opened-aperture Z-scan curve. As one can see that the curve is quite symmetric with respect to the focus ($Z = 0$mm) where it is minimum. Thus a positive intensity dependent nonlinear absorption effect is observed. Since the incident photon energy is 1eV lower than the energy of the absorption edge, the direct transition probability of the electrons from the valence band to the conducting band by single photon absorption is very small, and so is the transition to the surface states due to the forbidden transition of the dipole moment. Hence the nonlinear absorption would be two-photon absorption. The two-photon absorption coefficient β can be estimated at 2.2×10^{-5}m/W by fitting the following equation (1) to the experimental data:

$$T(Z, s=1) = \sum_{m=0}^{\infty} \frac{[-q_0(Z)]^m}{(m+1)^{3/2}} \quad \text{for } |q_0| < 1, \tag{1}$$

where

$$q_0 = \frac{\beta I_0 (1 - e^{-\alpha L})}{(1 + Z^2/Z_0^2)\alpha} \tag{2}$$

where α is the linear absorption coefficient, L is the thickness of the film, I_0 is the intensity of the laser beam at the focus ($Z = 0$), and Z_0 is the diffraction range of the beam. In this fitting, $\alpha = 7.9\times10^5 m^{-1}$, $I_0 = 2.7$MW/cm^2, $m_{max} = 13$, and $q_0 = 0.26 < 1$. The theoretical curve which is the fit of equation (1) to the experimental data is also depicted in Fig. 6(b).

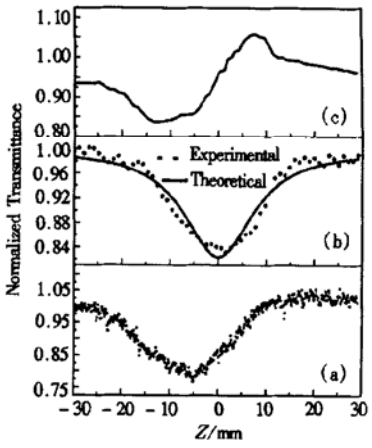

Fig. 6 Normalized Z-scan data at $\lambda = 585$nm for the film annealed at 500℃ (a) with a closed aperture; (b) with an opened aperture; (c) obtained from the operation of dividing data A by data B

Figure 6(a) is the closed-aperture Z-scan curve. The magnitude of the maximal normalized transmittance at the positive Z direction is only just a little larger than 1. In other words, the amplitude of the valley (at $Z < 0$) is much larger than that of the peak (at $Z > 0$) which indicates the strong offset of the nonlinear absorption against the nonlinear refraction. We can remove the influence of the nonlinear absorption from Fig. 6(a) via dividing the data by the corresponding data in Fig. 6(b), and obtain a new $T(Z)$-Z curve in Fig. 6(c) where ΔT_{pv} (the difference of the normalized trans-

mittance between the peak and the valley) agrees to within ±10% of that obtained from a purely refractive Z-scan[2]. The nonlinear refractive index γ can be estimated at 4.4×10^{-12} m^2/W from Fig. 6 (c) according to the following formula[2]:

$$\gamma = \frac{\Delta T_{pv}}{0.406(1-s)^{0.25}kL_{eff}I_0} \qquad (3)$$

for $\Delta\Phi \leqslant kL_{eff}\lambda I_0 \leqslant \pi$. Here, $\Delta\Phi$ is the nonlinear phase shift (in this estimation, $\Delta\Phi \leqslant 0.61 < \pi$), $k = 2\pi/\lambda$, and $L_{eff} = (1-e^{-\alpha L})/\alpha$ is the effective thickness of the film.

Figure 7 shows the Z-scan curves for the film at $\lambda = 450$nm which is in quasi-resonant with the average band gap energy of the nanocrystals in the film. In these measurements, the laser beam intensity I_0 (at $Z = 0$nm) is 2.5MW/cm^2. The curve in Fig. 7(a) is the closed-aperture Z-scan data. The nonlinear refractive index γ can be estimated at 2.3×10^{-11} m^2/W according to Fig. 7 (a) and formula (3). In this estimation, $\alpha = 2.87\times10^6$ m^{-1}, and $\Delta\Phi = 2.3 < \pi$. Figure 7(b) depicts the opened-aperture Z-san data and the theoretical fit with $\beta = -1.3\times10^{-4}$ m/W using formula (1) and (2), where $m_{max} = 13$, and $|q_0| = 0.91 < 1$.

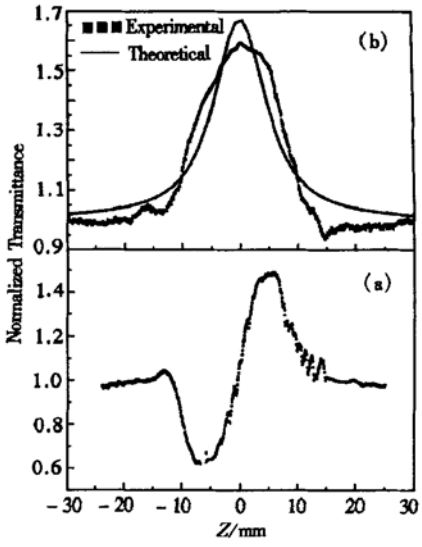

Fig. 7　Z-scan curves at $\lambda = 450$nm for the film annealed at 500℃　(a) with a closed aperture; (b) with an opened aperture

A comparison of our Z-scan data to those of other authors is shown in Table 1 below:

Table 1　Comparison of experimental values of the nonlinear refractive index γ and absorption coefficient β

Material	λ/nm	Nonlinearity category	γ/(m^2·W^{-1})	β/(m·W^{-1})	Reference
GaAs/SiO_2 nanogranular film	585	Nonresonant	4.4×10^{-12}	2.2×10^{-5}	This work
GaAs/SiO_2 nanogranular film	450	Quasi-resonant	2.3×10^{-11}	1.3×10^{-4}	This work
GaAs/SiO_2 nanogranular film	632	Quasi-resonant	4×10^{-10}	2×10^{-3}	Ref. [4]
GaAs/Vycor glass nanogranular film	1064	Nonresonant	3.4×10^{-16}		Ref. [1]
Bulk GaAs crystal	1064	Nonresonant	3.3×10^{-17}	2.6×10^{-10}	Ref. [8]

According to Smith[9], the nonlinearities of our sample measured at 450nm and of the sample in Ref. [4] can be referred to as "resonant nonlinearities", because they corresponds to real light-induced absorption change. The change of the former is induced by light with energy near the average band gap energy, and is caused by the electrons excited to the conduction band of the material (single-photon absorption). The change of the latter is induced by light with energy near the energy difference between level 1P and level 1S, and is caused by the electrons excited from 1S to 1P (two-photon absorption). The nonlinearities of the others described in Table 1 can be referred to as "nonresonant nonlinearities", because the nonlinear effects occur for light energy significantly less than the band gap of the nonlinear materials. Such nonlinearities can be described as arising from virtual transitions (two-photon absorption). It is comprehensible that the values of γ and β at 450nm are about one order of magnitude larger than those at 585nm respectively for our sample, for resonant nonlinearities tend to be larger due to light close to the band gap of the sample. The values of γ and β of our sample at 585nm are all about 5 orders of magnitudes larger than those of the bulk GaAs

crystal. We attribute this to the strong quantum confinement of the excitons in the GaAs nanocrystals. From Table 1, the values of γ and β of our sample at 450nm are about one order of magnitude smaller than those of Ref. [4] respectively though the average nanocrystals size in our sample would be much smaller than that in the sample of Ref. [4] and hence the corresponding quantum confinement effect presented in our sample would be much stronger than that presented in the sample of Ref. [4]. This interesting phenomenon may result from the measurement mode of the Z-scan experiments. The major difference between two experiments is that we took a pulse laser while Shi *et al.* took a continuous one. According to Dvolak *et al.*[5] and Battaglin *et al.*[10], continuous laser would exacerbate nonlinear refraction and nonlinear absorption (especially the excited-state absorption) furthermore than a pulse laser in Z-scan experiments. As to the GaAs/Vycor glass materials, the reason for the lower enhancement of the nonlinearities may be that there are much less GaAs nanocrystals formed in the materials compared with the materials by magnetron co-sputtering.

4 Conclusion

In conclusion, the characterization on GaAs/SiO_2 nanogranular films by AFM, XRD, and RBS shows the formation of higher quality GaAs nanocrystals in the films at higher annealing temperature and the stoichiometric relation between GaAs and SiO_2. Very large absorption edge blue shift with respect to the bulk GaAs crystal and the corresponding ultraviolet PL due to the strong quantum confinement have been observed in the optical spectra. The nonlinear refractive index and nonlinear absorption coefficient of the GaAs/SiO_2 nanogranular film were estimated at $2\times10^{-11}m^2/W$ and $1\times10^{-4}m/W$ respectively in quasi-resonant condition, while at $4\times10^{-12}m^2/W$ and $2\times10^{-5}m/W$ respectively in nonresonant condition. The greatly enhanced optical nonlinearities in the film were caused by the strong quantum confinement. The discrepancy between the optical nonlinearities of our sample and those of the sample of Shi *et al.*[4] may result from the difference of the lasers used.

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磁控共溅射 $GaAs/SiO_2$ 细小纳米颗粒镶嵌材料的结构和非线性光学性质*

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摘要: 应用磁控共溅射技术和后退火方法制备了 $GaAs/SiO_2$ 纳米颗粒镶嵌薄膜，并分别应用原子力显微镜、X 射线衍射和卢瑟福背散射实验来观测薄膜的形貌、相结构和化学组分. 结果表明 GaAs 纳米颗粒的平均直径很小(约为 1.5~ 3.2nm)，且均匀地分布于 SiO_2 之中，薄膜中的 GaAs 和 SiO_2 组分都符合化学计量关系. 应用脉冲激光高斯光束对薄膜的光学非线性进行了 Z 扫描测试和分析. 结果表明，薄膜的三阶光学非线性折射率系数和非线性吸收系数都由于量子限制效应而大大地增强，在非共振条件下，它们分别约为 $4\times10^{-12}m^2/W$ 和 $2\times10^{-5}m/W$，在准共振的条件下，它们分别约为 $2\times10^{-11}m^2/W$ 和 $-1\times10^{-4}m/W$.

关键词: 磁控共溅射; GaAs 纳米颗粒; 微观结构; 光学非线性

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