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Nonlinear Optical Properties of Al-Doped nc-Si-SiO_2 Composite Films*

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Abstract: The nonlinear optical properties of Al-doped nc-Si-SiO_2 composite films have been investigated using the time-resolved four-wave mixing technique with a femtosecond laser. The off-resonant third-order nonlinear susceptibility is observed to be 1.0×10^{-10} esu at 800nm. The relaxation time of the optical nonlinearity in the films is as short as 60fs. The optical nonlinearity is enhanced due to the quantum confinement of electrons in Si nanocrystals embedded in the SiO_2 films. The enhanced optical nonlinearity does not originate from Al dopant because there are no Al clusters in the films.

Key words: Si nanocrystals; composite films; third-order nonlinearity; time-resolved four-wave mixing
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1　Introduction

Materials with large third-order optical nonlinearity and fast response time are essential for photonic devices such as all-optical switches[1]. The third-order nonlinear optical response in semiconductor nanoparticles embedded in an insulating medium has received extensive attention. Yumoto *et al*.[2] observed optical bistability in CdS_xSe_{1-x}-doped glasses with 25ps switching time. Because of the technological importance of Si, great interest has arisen in Si nanocrystals (nc-Si) embedded in SiO_2 films formed by ion implantation and plasma-enhanced chemical vapor deposition (PECVD)[3~5]. Recently, we reported on the nonlinear optical response of nc-Si-SiO_2 films prepared by RF magnetron co-sputtering[6]. Many ways of doping silicon oxide films have also been applied to adjust the electron structure and to improve the stability and efficiency. Wu *et al*.[7] reported that the onset of bias voltage as well as the intensity of electroluminescence could be improved by adding a certain amount of Al into the silicon oxide films. Al-doped nc-Si-SiO_2 composite films could be promising materials for Si-based photoelectron device applications[16]. Studies on its third-order nonlinear susceptibility and relaxation time have seldom been reported. In this paper, we use the time-resolved four-wave mixing (FWM) technique with a femtosecond laser to study the optical nonlinearities of Al-doped nc-Si-SiO_2 composite films.

A number of researchers have measured the third-order nonlinear susceptibility through many methods in several time regions. In comparison with the Z-scan method, the FWM technique can be used to study not only the nonlinear susceptibility but the relaxation time as well. Transient coherent spectroscopy has been increasingly used to investigate the properties of the interactions among various elementary excitations in semiconductors. In the two-pulse self-diffracted FWM experiments, the two pulses create a transient grating and the diffracted signal is measured in a background-free direction[8]. The transient grating technique is a powerful tool for studying the nonlinear optical properties of semiconductor materials. We use this technique to study both the third-order nonlinear susceptibility and relaxation time of Al-doped nc-Si-SiO_2 composite films.

2　Experiment

RF magnetron co-sputtering and thermal annealing were used to prepare the Al-doped nc-Si-

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SiO_2 composite films. An 80mm SiO_2 plate was used as the target containing several Si chips and Al chips on the surface. The total surface area of Si chips and the total surface area of Al chips could be changed to adjust the contents of Si and Al in the films. The background vacuum and sputtering gas (pure Ar) pressures were 6×10^{-4} and 3.0Pa, respectively. The RF power was 300W. The Al-doped Si-rich oxide films were deposited on (100) oriented p-type Si substrates or silica glass slices. Then the as-deposited films were annealed in nitrogen ambient at different temperatures for 30min.

X-ray diffraction (XRD) measurements were carried out with a Bruker D8 Advance X-ray diffractometer. X-ray photoemission spectroscopy (XPS) was measured with a PHI Quantum 2000 scanning ESCA microprobe. The linear optical absorption properties of the films were measured with a Unico UV-2800H spectrometer.

Optical nonlinearities of Al-doped nc-Si-SiO_2 films were measured with a time-resolved four-wave mixing setup in the Key Laboratory of Optical and Magnetic Resonance Spectroscopy at East China Normal University. The experimental setup is shown in Fig. 1. The excitation source was a spectra-physics Ti: sapphire femtosecond laser with a central wavelength of 800nm, pulse-width of about 90fs and repetition rate of 1kHz. The excitation power was 60mW. The laser beam was split into two linearly parallel polarized beams, one beam as probe, which was delayed by T with respect to another beam as pump, and then the two split beams spatially overlapped on the sample. In this technique, two pulsed laser beams with wave vectors $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$ interfered in a sample to produce a diffracted beam in the direction $\boldsymbol{k}_3 = 2\boldsymbol{k}_2 - \boldsymbol{k}_1$[9]. The magnitude of the diffracted signal in the direction $\boldsymbol{k}_3$ was then recorded as a function of the time delay T. Signals detected by a photodiode were amplified by a lock-in amplifier and then sent into a computer.

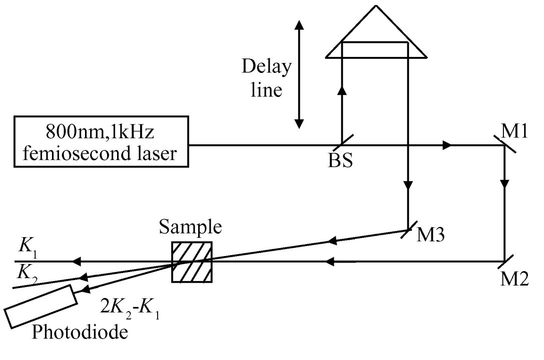

Fig. 1 Experimental setup for FWM measurements, where BS is a beam splitter, and M1, M2 and M3 are the reflective mirrors.

3 Results and discussion

The optical band gap E_g can be estimated by studying the dependence of the absorption coefficient α on incident photon energy $h\nu$. The relationship is given by

$$(\alpha h\nu)^{1/2} = B(h\nu - E_g) \tag{1}$$

where B is a constant. Figure 2 shows that the E_g for the films annealed at 800, 900, and 1000℃ is calculated to be 2.72, 2.43, and 2.36eV, respectively. This indicates that the smaller the average size of Si nanocrystals, the larger the optical band gap due to quantum confinement-related effects. In our FWM experiment, the incident photon energy corresponding to an excitation pulse central wavelength of 800nm is smaller than the optical band gap.

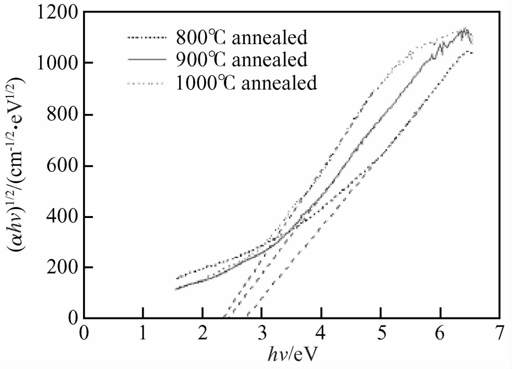

Fig. 2 Relationship between $(\alpha h\nu)^{1/2}$ and $h\nu$ of Al-doped nc-Si-SiO_2 film annealed at different temperatures

The FWM signal as a function of the delay time T for Al-doped nc-Si-SiO_2 film is shown in Fig. 3, in which the dots depict the experimental data and the curve is the fitting of a Gaussian function. In a two-level system, when the laser pulse width is proximate to the transverse relaxation time, the correlation signal is the convolution of the laser pulse with broadened systems[9]. Using the deconvolution method, the relaxation time is evaluated to be 60fs. Time-delayed four-wave mixing technique has become an important tool for investigating dephasing processes in gases, solids, and glasses. The temporal evolution of the FWM signal may yield information about the phase relaxation processes and the nature of the excited states. Because the electron-phonon interaction time is on the order of 100fs[11], phonon processes are not expected to be important in this study. The ultrafast optical response indicates the dominance of carrier-carrier scattering as the principal dephasing mechanism for the Al-doped nc-Si-SiO_2 films.

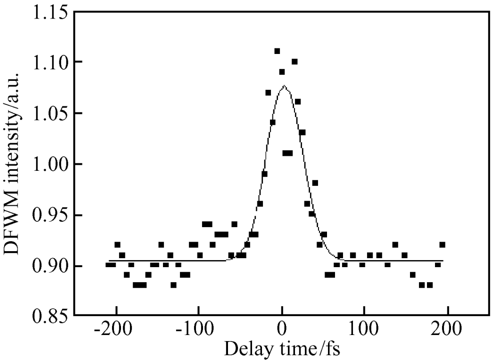

Fig. 3 FWM signal for Al-doped nc-Si-SiO_2 film versus delay time T

According to the reference measurement technique, the third-order susceptibility $\chi_S^{(3)}$ of the Al-doped nc-Si-SiO_2 film was measured relative to CS_2, a reference sample by which the diffracted signal was obtained under identical conditions. $\chi_S^{(3)}$ can be calculated using the equation[12]

$$\chi_S^{(3)} = \chi_R^{(3)} \left(\frac{I_S}{I_R}\right)^{1/2} \left(\frac{n_S}{n_R}\right)^2 \frac{d_R}{d} \times \frac{\alpha d}{1 - e^{-\alpha d}} e^{\alpha d/2} \quad (2)$$

where I_R and I_S are the peak values of the diffracted signal of CS_2 and the sample respectively, n_R and n_S are the corresponding refractive indices, d_R is the length of CS_2, and d is the thickness of the sample. The value of n_R is 1.62, and the value of $\chi_R^{(3)}$ for CS_2 has been estimated to be 1.0×10^{-13} esu on the femtosecond time scale by Minoshima *et al*.[13]. From Eq. (2), the value of $\chi_S^{(3)}$ is evaluated to be 1.0×10^{-10} esu. The incident photon energy in our FWM experiment is smaller than the optical band gap. Under this off-resonant excitation condition, the linear absorption at 800nm is weak, whereas two-photon absorption is the origin of the nonlinear absorption[14]. The thermal effect is assumed to be negligible in the femtosecond region. Therefore, the value of the nonlinear susceptibility should be closer to the real value. Prakash *et al*. studied the third-order nonlinear susceptibility $\chi^{(3)}$ of silicon nanocrystals embedded in the SiO_2 medium by the Z-scan method using a femtosecond laser at wavelength of 813nm. The absolute values of $\chi^{(3)}$ are in the range from 10^{-10} to 10^{-9} esu when the silicon nanocrystal size varies from 2 to 0.5nm[1]. Our result for $\chi^{(3)}$ of Al-doped nc-Si-SiO_2 is of the same order of magnitude as that reported by Prakash.

The nonlinear optical properties are closely related to material structure. The structure of the films was characterized by XRD and XPS. In XRD patterns of the film annealed at 800℃, there is a peak at $2\theta \approx 69^\circ$, which can be indexed as the Si (400) diffraction peak. There is no diffraction peak related to Al. The average size of Si nanocrystal diameter in the films annealed at 800, 900, and 1000℃ can be evaluated from the FWHM of the diffraction lines to be 7.1, 9.5, and 10.4nm, respectively, according to the Scherrer formula $D = 0.9\lambda/\beta\cos\theta$, where λ is the wavelength of the X-ray source and β is the FWHM in radians of the X-ray diffraction peak at the diffraction angle θ. This indicates that the higher the annealing temperature, the larger the average size of Si nanocrystals. The average size of Si in Al-doped samples is larger than that in undoped samples at the same annealing temperature[6] because Al-induced crystallization takes place during thermal annealing[10].

The composition of a film stripped by an Ar^+ was measured by XPS. Figure 4 shows the characteristic spectra of Al2p and Si2p. The two peaks of the Si2p characteristic spectra at 99.6 and 103eV correspond to elemental silicon and silicon dioxide, respectively[10]. XRD and XPS results show the formation of Si nanocrystals embedded in the SiO_2 matrix. Quantum confinement of electrons in nc-Si could enhance the nonlinear optical properties of the films. The characteristic peak of Al2p shows that the peak position is 75.25eV, corresponding to that of AlO_x[10]. FTIR spectra of Al-Si-SiO_2 film and Si-SiO_2 film are shown in Fig. 5. In comparison with undoped film, for Al-Si-SiO_2

film there is an absorption peak at 675cm^{-1} corresponding to the Si-O-Al stretching vibration mode. XPS and FTIR results indicate that Al doping in the films is oxidized. Wang *et al*. proposed that during annealing, Al atoms could take O out of SiO$_2$ to form alumina[16]. We know that the enhanced optical nonlinearity does not originate from Al nanoparticles because there are no Al clusters in the films.

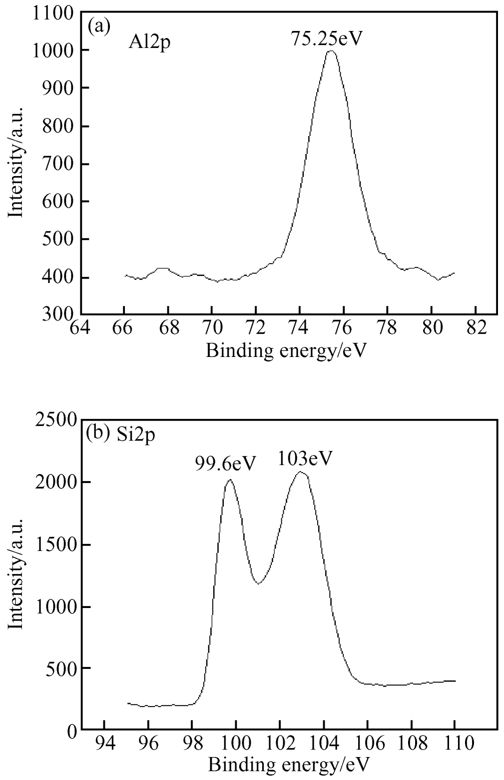

Fig. 4 XPS Al2p (a) and Si2p (b) spectra of Al-doped nc-Si-SiO$_2$ film

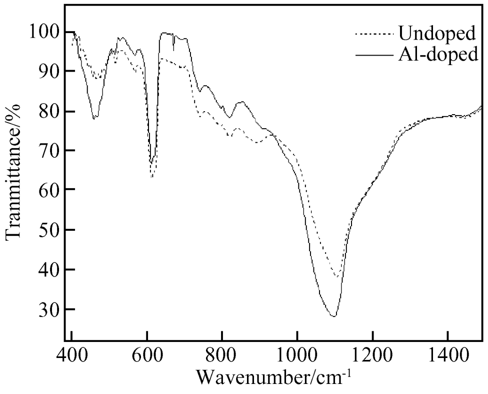

Fig. 5 FTIR spectra of Al-Si-SiO$_2$ film and Si-SiO$_2$ film

Cotter *et al*.[15] used the two-band effective-mass model modified to incorporate the effect of quantum confinement and found that the quantum confinement of electrons in small semiconductor particles causes the nonlinear optical properties in the off-resonant regime to differ markedly from those of bulk semiconductors. The real and imaginary parts of $\chi^{(3)}$ are directly related to the nonlinear refractive index and two-photon absorption coefficients, respectively. Prakash *et al*. presented a systematic study on the correlation between third-order nonlinear susceptibility $\chi^{(3)}$, silicon nanocrystal size, linear refractive index, and optical band gap[1]. Their study suggests that large third-order nonlinear coefficients observed for small nanocrystals are due to an increased quantum confinement effect. In this study, XRD and XPS results show the formation of Si nanocrystals embedded in the SiO$_2$ matrix. The enhanced optical nonlinearity in the Al-doped ncSi-SiO$_2$ films can be attributed to three-dimensional quantum confinement[15]. The value of $\chi^{(3)}$ in Al-doped samples is smaller than that in the undoped samples[6]. This is ascribed to the larger average size of nc-Si in Al-doped samples in comparison with that in undoped samples due to the quantum confinement effect.

4 Conclusion

RF magnetron co-sputtering and thermal annealing were used to prepare Al-doped nc-Si-SiO$_2$ composite films. The nonlinear optical properties of the films were studied using time-resolved FWM. The off-resonant nonlinearity is predominantly electronic in origin. The ultrafast optical response indicates the dominance of carrier-carrier scattering as the principal dephasing mechanism. The optical nonlinearity is enhanced due to quantum confinement of electrons in Si nanocrystals embedded in SiO$_2$ films.

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掺Al的纳米Si-SiO_2复合薄膜的光学非线性特性*

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摘要： 采用时间分辨四波混频方法，用钛宝石飞秒激光器测量了掺Al的纳米Si-SiO_2复合薄膜的光学非线性特性. 得到薄膜非共振三阶非线性极化系数为1.0×10^{-10}esu，弛豫时间为60fs. 分析认为薄膜的光学非线性增强来源于SiO_2镶嵌的纳米Si中电子的量子限制效应，而不是来源于Al杂质，这是因为Al易被氧化，薄膜中没有形成Al团簇.

关键词： 纳米Si；复合薄膜；三阶非线性；时间分辨四波混频

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