

# Nonlinear optical absorption and ultrafast optical response of un-doped and P-doped nanocrystalline Si/SiO<sub>2</sub> multilayers

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**Abstract.** The nonlinear optical properties and ultrafast optical response of Si/SiO<sub>2</sub> multilayers with and without phosphorus doping are comparatively studied in the present work. The enhanced nonlinear absorption and fast recombination process were observed after phosphorus doping, the defect states generated by high phosphorus doping was the possible origination. It was suggested that the nonlinear optical repose as well as the ultrafast dynamic process could be changed greatly via phosphorous doping, which provided a new approach to improve the performance of Si-based photonic devices.

## 1. Introduction

Nanocrystalline-Si (nc-Si) materials have been recently attracted much attention since they exhibit the intense photoluminescence as well as the large optical nonlinearities, which can be potentially applied in the future Si-based photonic devices [1,2]. However, the large nonlinear absorption and slow recombination process degrade extremely the photonic devices' performance, such as the modulation rate, gain bandwidth, wavelength conversation efficiency and so on [2]. In our previous work, the enhanced photoluminescence intensity and optical nonlinearities were observed, which was ascribed to the interface/surface states in nc-Si dots. It was found that the linear and nonlinear optical properties can be changed by altering the nc-Si dot size or post-annealing temperature [3,4]. Moreover, we found doping in nc-Si is another effective method to modify the chemical environment of nc-Si, and the density of interface/surface states could be continuously controlled, which made the nonlinear absorption coefficient reduced by 4 folds through phosphorus (P) doping [5]. Nevertheless, it was reported the nonlinear absorption increased after P doping, the impurity-related states below the conduction band induced by P doping was the major reason [6]. Meanwhile, the doping effect on the transient dynamics of nc-Si is still unclear.

Therefore, it is interesting to comprehensive understand the influences of P doping on nonlinear optical properties and transient process of nc-Si materials. In this work, we study the nonlinear optical properties and ultrafast optical response of Si/SiO<sub>2</sub> multilayers with and without P doping. It was found that P doping may tune the interfacial environment and induce new energy level, which could modify the nonlinear optical behavior and the initial carries dynamics of nc-Si/SiO<sub>2</sub> multilayers.

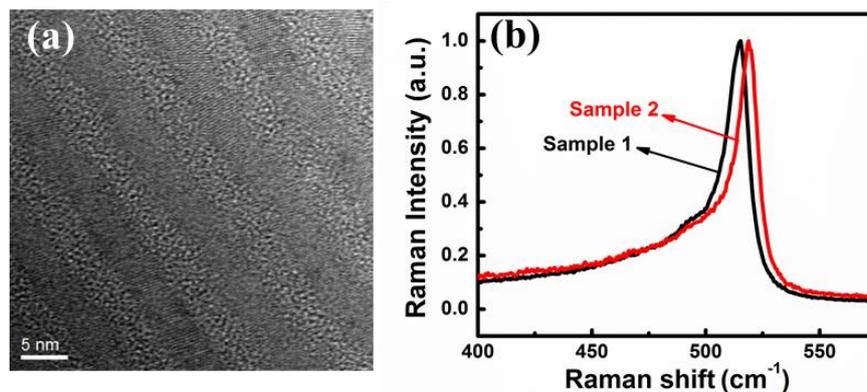


## 2. Experimental

The phosphorous-doped nc-Si/SiO<sub>2</sub> multilayers structures were fabricated by annealing the phosphorous-doped amorphous stacked structures deposited in conventional plasma-enhanced chemical-vapor system. The details of preparation conditions can be found elsewhere [3-5]. The thickness of the amorphous sublayers was about 4 nm, and the P doping concentration in nc-Si could be controlled by changing the gas flow ratio R ( $R = [\text{PH}_3] / [\text{SiH}_4]$ ). Here after, we denoted the samples prepared by  $R = 0$  and 5 as sample 1 and sample 2, respectively. The Z-scan technique was applied to measure the nonlinear optical absorption coefficient, a 100-fs mode-locked Ti-sapphire laser (Coherent Libra-HE) with a wavelength of 800 nm at 1 kHz was used as the excitation source. The pump and probe setup was utilized to monitor the temporal evolution of the photo-generated carriers. The mode-locked Ti: sapphire laser with fundamental frequency at 800 nm with 100-fs pulse duration were separated into two parts, one is the pump laser at 400 nm (3.1 eV) generated by frequency-doubled the fundamental frequency laser through a BBO crystal, the other one acts as the probe beam at 800 nm.

## 3. Discussion and results

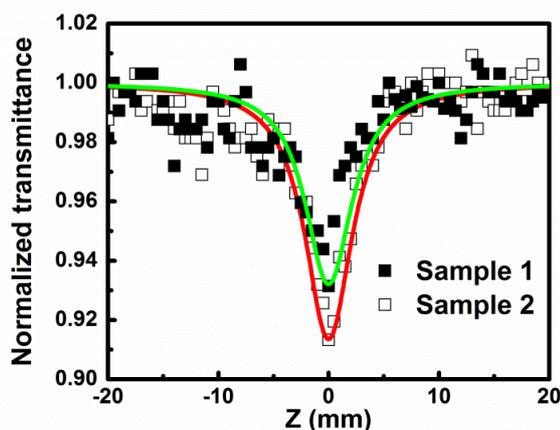
The formation of nc-Si after 900 °C annealing is confirmed by cross-sectional transmission electron microscopy (TEM) and the Raman spectra. Figure 1(a) shows the TEM image of nc-Si/SiO<sub>2</sub> multilayers, the dot size is about 4 nm which is uniformly distributed in the sample separated by the SiO<sub>2</sub> layers. It is found that the crystallinity is increased with increasing the doping concentration and annealing temperature [5], as shown in Figure 1(b).



**Figure 1.** (a) Cross-sectional TEM image and (b) Raman spectra of nc-Si/SiO<sub>2</sub> multilayers annealed at 900 °C.

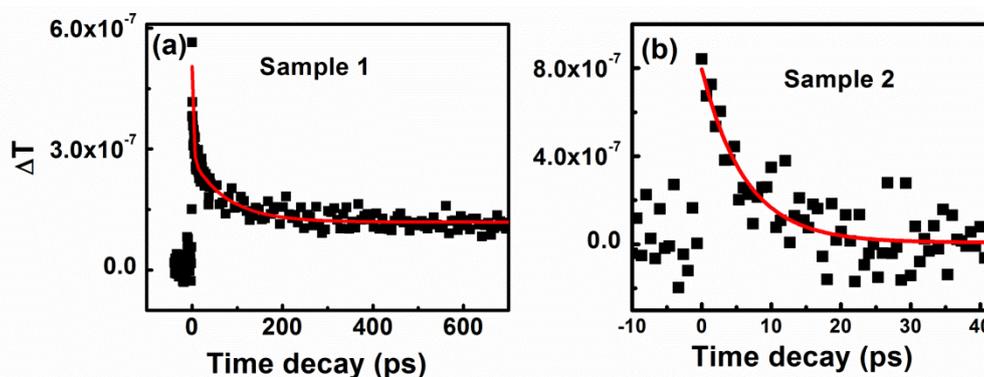
Figure 2 shows the normalized Z-scan transmittance traces of samples 1 and 2 in the open aperture configuration under laser intensity  $I_0 = 4.78 \times 10^{10} \text{ W/cm}^2$ . It is clear that both the Z-scan traces show a dip at the focal point, indicating nonlinear absorption (NLA) is the reverse absorption (RSA) process. In our previous work, it is found that the nonlinear optical absorption is changed with the annealing temperature as well as the nc-Si dot size. When the sample changes from amorphous phase to nanocrystalline state or increase the size of nc-Si dot, the nonlinear absorption turns from the reverse saturation absorption (RSA) to the saturation absorption (SA) process. It is proposed that the localized states at the nc-Si/SiO<sub>2</sub> interfacial region play the key role in the observed switching behaviours [3,4]. When the excitation intensity  $I_0$  is about  $3.54 \times 10^{11} \text{ W/cm}^2$ , the sample 1 shows the saturation absorption (SA) properties which is ascribed to the phonon-assisted one-photon transition process between the valence band and interface states in the gap [4]. We considered that the RSA property at low intensity ( $I_0 = 4.78 \times 10^{10} \text{ W/cm}^2$ ) is originated from the two step absorption process via the interface states [3].

The calculated NLA coefficient for samples 1 and 2 is  $1.78 \times 10^{-7}$  cm/W and  $2.27 \times 10^{-7}$  cm/W, respectively, indicating that the density of states associated with two step process increased after high P doping, which is different from the P-doping in the nc-Si with the average size of 2 nm, where the NLA coefficient monotonously decreases with increasing P doping concentrations [5]. It is found that P atoms prefer to locate at the surface of nc-Si and passivate the dangling bond when the size of the nc-Si is small, while the substitutional doping may occur when the size of nc-Si is large. However, it is also worth noting that there is no obvious infrared absorption associated with the intra-valence-band transition can be observed at the high doping concentration. Therefore, the impurity-related states are not responsible for the observed nonlinear absorption phenomena. According to the ESR measurements, a kind of new defect states will be generated after high P doping concentration due to the damage of the Si crystalline lattice [7], which may play a great role in the increase of the nonlinear absorption coefficient.



**Figure 2.** Open aperture Z-scan traces of samples 1 and 2 annealed at 900 °C. The excitation wavelength and intensity are 800 nm and  $I_0 = 4.78 \times 10^{10}$  W/cm<sup>2</sup>, respectively. The solid lines are the fitting curves of the experimental data.

To further investigate the P doping effect on the transient dynamic process of Si/SiO<sub>2</sub> multilayers, the pump and probe measurements were carried out. Figure 3 (a) and (b) show the dynamics of transient transmission of samples 1 and 2 under 1 mW excitation. It is evident that all signals of transient transmission ( $\Delta T$ ) is positive, demonstrating the occurrence of transient bleach, which may originate from the occupation of the interface-related states by the photo-generated carriers. The ultrafast built-up time is less than 1 ps, illustrating that the excited-carriers generated by pump beam were trapped rapidly by the interface states of nc-Si/SiO<sub>2</sub> multilayers.



**Figure 3.** Dynamics of transient transmission of (a) sample 1 and (b) sample 2 annealed at 900 °C under pump power at 1 mW.

A two exponential decay function ( $y(t) = A + B_1 e^{-t/\tau_1} + B_2 e^{-t/\tau_2}$ ) was used to fit the decay time of sample 1, the obtained lifetime  $\tau_1$  and  $\tau_2$  are roughly about 2.9 and 78.2 ps, respectively. The fast component is attributed to the Auger recombination process, while the slow one may arise from the recombination process of electron-hole localized at interfaces states. Due to the limitation of pump-probe decay line, the long-lived lifetime can't be completely measured. However, the transient carrier dynamic of sample 2 can be well described by the single-exponential function ( $y(t) = A + B e^{-t/\tau}$ ) with decay time of  $\tau = 6.2$  ps, which may be ascribed to the process of strong Auger process and /or photo-excited carries trapped by defect states generated via high P doping. In this case, the long-lived lifetime is not obvious because of the generated carriers trapped rapidly by the nonradiative defect states.

#### 4. Conclusion

The un-doped and P-doped Si/SiO<sub>2</sub> multilayers with dot size of 4 nm were fabricated in PECVD system, the optical nonlinearities were investigated by the open aperture Z-scan technique, the NLA coefficients  $\beta$  increased through P-doping, which is ascribed to the new crystal defects states induced by high P doping. Meanwhile, the ultrafast optical response of Si/SiO<sub>2</sub> multilayers was explored by using pump and probe technique. It is shown that the carrier trapping process due to the nonradiative defect states influences the ultrafast optical response obviously.

#### Acknowledgment

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