Effects of deposition and post-fabrication conditions on photoluminescent properties of nanostructured Si/SiOx films prepared by laser ablation

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Abstract

Pulsed Laser Ablation (PLA) from a Si target in an inert He ambient has been used to produce Si/SiO_x nanostructured thin films on Si substrates. After the film exposition to atmospheric air, they exhibited photoluminescence (PL) signals with peak energy between 1.58 and 2.15 eV. It was found that both natural and thermal oxidation of the films can cause dramatic changes in PL properties giving rise to the appearance or considerable enhancement of fixed PL peaks around 1.6-1.65 and 2.2-2.25 eV. Quite different time-dependent PL degradation behavior under continuous laser irradiation gives an evidence for different mechanisms responsible for the PL peaks. Possible origins of PL are discussed.

Keywords: pulsed laser ablation, silicon nanoparticles, photoluminescence

1. Introduction

Because silicon is an indirect band gap material with a small band, it cannot emit visible light. This property significantly complicates the spreading of Si-based technologies to optoelectronics. However, recent observations of visible PL in porous silicon [1] and in other Si-based nanocrystalline structures (see, e.g., [2]) gave a promise for the development of some applications.

Pulsed Laser Ablation (PLA) is one of the best candidates for the production of the Si-based nanocrystallites [3-6]. Due to the peculiarities of laser plasma formation and evolution, Si nanoscale clusters can be effectively produced by laser ablating a Si target into an inert gas ambient (see, e.g. [7]). Si/SiO_x films fabricated by PLA were found to contain Si nanoscale particles and exhibit visible PL [3-6, 8]. Nevertheless, many aspects of the phenomenon remain unclear, and the physical origin of the observed photoluminescence is still controversial.

In this paper, we study PL properties of Si-based films produced by PLA and the effect of post-deposition oxidation. In the PL studies, the main attention has been given to the visible and near-infrared spectral ranges (S-band), which are the most important for optoelectronics applications.

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2. Experimental setup

The ablation of material from a rotating Si target was produced by a pulsed KrF laser ($\lambda = 248$ nm, pulse length 15 ns FWHM, repetition rate 30 Hz). The radiation was focused on a focal spot 2x1 mm^2 on the target at the incident angle of 45°. The fluence was 7-10 J/cm^2 giving a radiation intensity of about $5 \cdot 10^8$ W/cm^2. The laser-induced plasma plume expanded perpendicularly to the target surface. The substrates, identical to the target, were placed on a rotating substrate holder at 2 cm from the target. The deposition was carried out in He at a constant ambient pressure. The pressure P of He was varied in different experiments between 50 mTorr and 10 Torr. The chamber was pumped down to $P = 2 \cdot 10^{-7}$ Torr before filling with the gas. After several thousand laser shots, the thickness of the Si film on the substrate was $100 - 500$ nm. In addition, a technique of thermal evaporation from a Si target in vacuum has been used for comparative tests. A powder from a Si wafer with the same parameters was evaporated under the residual pressure of 10^{-7} Torr from a tantalum boat onto a Si substrate maintained at room temperature. The boat to substrate distance was about 15 cm, and the deposition rate was 0.1-0.2nm/s. In some cases, the deposited films were annealed at 800° C in atmospheric air for 10 minutes.

For the PL measurements, the samples were illuminated by the radiation of cw Ar* laser (model INNOVA 100) with the wavelength 488 nm. The power was 10 mW and the power density was estimated to be 30 W/cm^2. The PL spectra were measured at room temperature using a double spectrometer (model U100, Instruments SA) and GaAs photomultiplier (Hamamatsu Photonics). To determine the composition of the surface layer, we also analyzed the deposited films by X-ray photoemission spectroscopy (XPS) at a base pressure of $2 \cdot 10^{-8}$ Torr using a Perkin-Elmer 5500 system.
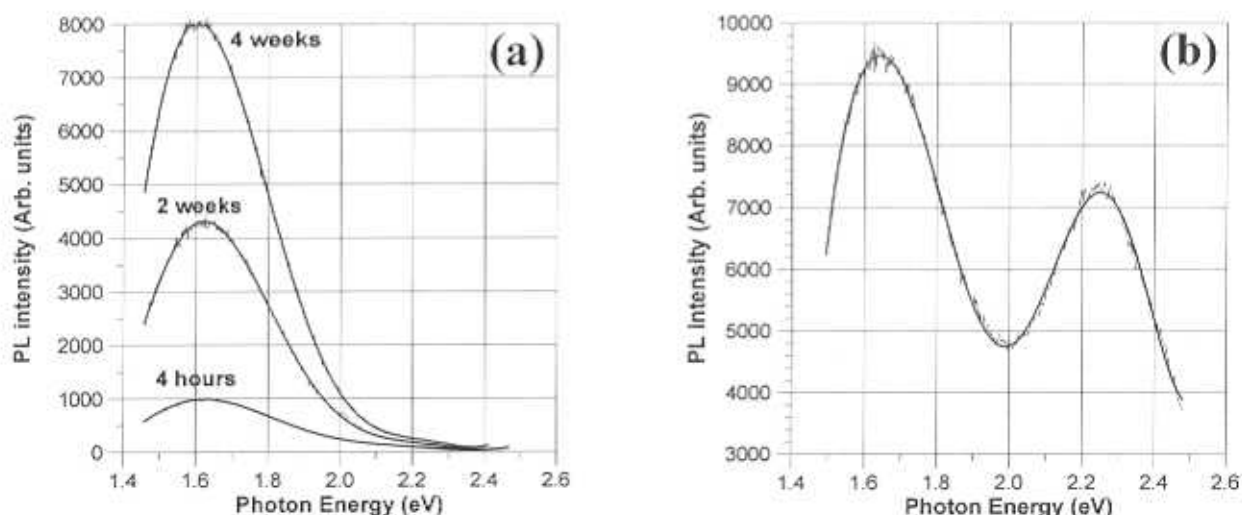

Fig. 1, (a) PL spectra from a Si/SiO$_x$ film deposited by PLA under $P = 2$ Torr after different times of the film exposition to dry ambient air, (b) PL spectrum from the film after 8 weeks of the exposition to humid air (relative humidity 90-95%).

3. Experimental and discussion

In our experiments, PL signals were observed only after the exposition of the films to oxygen, i.e. after the replacement of He in vacuum chamber by atmospheric air. PL spectra could differ for the films prepared under different deposition conditions. For example, a change of the He pressure from 3 Torr to 150 mTorr in different deposition experiments caused a progressive blue shift of the PL peak position from 1.58 eV to 2.15 eV. However, a wider displacement of the PL peak position by this

method was problematic. Under the pressures above 3 Torr, PL peaks remained always around 1.57 – 1.6 eV, while their intensity significantly decreased. On the other hand, the decrease of the pressure below 150 mTorr caused a dramatic decrease of plasma plume intensity, which led to a weak and hardly reproducible PL signal. Nevertheless, maximum PL intensities were found to be remarkably different for the peaks within the 1.58 – 2.15 eV range. The most intense PL signals were at about 1.60 – 1.65 eV, while PL intensities of other peaks could be weaker by orders of magnitude. Note that similar dispersion of PL spectra was previously observed with Si-based films deposited on peripheral parts of target surface by PLA in He [8]. A correlation of the blue shift of the spectra with a recorded decrease of average particle size enabled to attribute the PL origin to quantum size effect [1].

The experiments showed that some samples manifested considerable enhancement of PL efficiency with time of the film exposition to ambient air. In particular, for the films deposited at 2-3 Torr, we observed a progressive increase of PL intensity at about 1.6-1.65 eV during 8-10 weeks of natural oxidation in clean atmospheric air as shown in Fig. 1 (a). During the oxidation, the PL intensity increased by almost an order of magnitude, while PL peak position remained stable or slightly red-shifted. It is necessary to note that the increase was much weaker or absent for other PL bands. A set of special tests showed that the increase rate of 1.6-1.65 eV signals could be accelerated by an increase of the air relative humidity. Furthermore, a prolonged storage of samples in relatively humid atmosphere could lead to the appearance of an additional PL peak at about 2.2-2.25 eV as shown in Fig. 1 (b). Thus, post-deposition oxidation process can significantly influence on PL properties of Si-based films. An XPS analysis of the upper film layer confirmed the presence of oxygen-related compounds in the film composition, namely the SiO_x complexes with x between 0 and 2. The value of x increased with time to air exposition, which was probably connected with an increase of relative contribution of the growing SiO_2 superficial layer in the XPS signal.
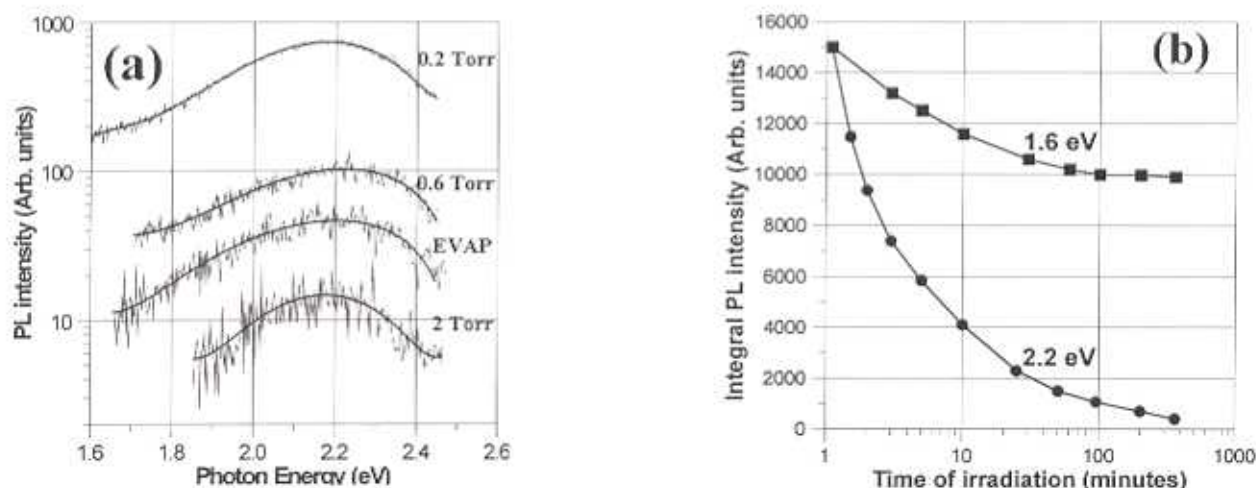

Fig. 2, (a) PL spectra (in logarithmic scale) after the thermal annealing the films deposited by PLA at different pressures, and by a thermal evaporation (EVAP); (b) Dependence of integral PL intensities for 2.2 and 1.6 eV peaks on the excitation irradiation time (in logarithmic scale).

It was found that thermal annealing of fresh samples resulted in dramatic changes in PL properties. In this case, only PL spectra with the same peak around 2.2-2.25 eV were observed for all films prepared under different pressures of He as shown in Fig. 2 (a). It is necessary to note that the annealing of relatively old and strongly oxidized samples led to considerable decrease or disappearance of the 1.6 eV peak. To understand the origin of 2.2 eV PL, we carried out a comparative experiment with Si-based amorphous films deposited by thermal evaporation from a Si target in vacuum, which is known to provide relatively large dimensions of deposited particles. Our experiments did not reveal

3

visible PL from as-deposited films and the films did not exhibit PL even after a prolonged (for several months) air exposition. Nevertheless, the thermal annealing of the films led to a similar PL spectrum with a peak at 2.2-2.25 eV as shown in Fig. 2 (a). Such a coincidence of PL peak positions gives a clear evidence for similar final microstructures of thermally annealed particles for the films deposited by different methods. This suggests that in the case of 2.2 eV PL laser ablation technique produces amorphous films with a certain morphology and mechanical properties, while the luminescent particles are produced during the oxidation process of these amorphous films.

Finally, we examined the time-dependent degradation of the PL spectra in air for the fabricated Si/SiO$_x$ films. In these experiments, the evolution of the PL spectra was recorded while an Ar$^+$ laser beam continuously illuminated the films prepared under different conditions. As shown in Fig. 2 (b) the 2.2 eV band suffered a dramatic PL intensity degradation after few minutes of the continuous illumination. This phenomenon of 2.2 eV PL degradation was observed for all samples prepared by different methods. However, 1.6 eV PL manifested quite different degradation properties. After slight decrease during the first minutes of the experiment, the PL intensity remained stable even after 6 hours of the continuous illumination. Such a difference in PL properties gives an evidence for a different PL mechanisms responsible for 1.6 and 2.2 eV peaks. Nevertheless, strong connection of these peaks to the oxidation processes makes possible suggestion about the same origin of the peaks.

Different mechanisms can be involved in generation of PL from the deposited Si/SiO$_x$ films. Dispersed spectra for fresh samples prepared under different deposition parameters could be explained by a carrier recombination between quantum confined states in the nanoscale particles [1]. The decrease of average particle size with a decrease of He pressure [5,6] and correlations of the average particle size with PL peak position [8] confirm the possibility of this mechanism. In this case, an air passivation of the nanocluster film is necessary to saturate dangling bonds and thus reduce nonradiative recombination channels. Nevertheless, other mechanisms may not be ruled out completely. For example, a mechanism of radiative recombination through localized defects in SiO$_2$ [9] also admits a variation of PL peak position with a variation of oxygen content [10]. Nevertheless, it is the most probable that fixed intense peaks around 1.6-1.65 eV and 2.2-2.25 eV are related to surface chemistry reactions between the nanocluster film and oxygen. In particular, similar 1.65 eV PL signals were observed for Si-based films fabricated by an optical breakdown in silane after the growth of oxide layer [2]. The origin of 1.65 eV PL was satisfactorily explained by a recombination through an interfacial layer between the c-Si core and the a-SiO$_2$ surface layer [2]. On the other hand, 2.2-2.25 eV PL could be explained by a formation of some oxygen-related compounds or localized defects in SiO$_2$ structure. In any case, a clear identification of the PL mechanism requires further detailed study of mechanical, structural and PL properties of the deposited and annealed films. These investigations are in progress.

In conclusion, Si/SiO$_x$ nanostructured films have been fabricated by PLA. The films exhibited visible PL with peak energy depending on deposition conditions. Surface chemistry interactions related to different oxidation processes were found to affect considerably the PL properties of the films.

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