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Luminescence hydrogenated nanoamorphous Si films fabricated by reactive pulsed laser ablation

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ABSTRACT

Hydrogenated nanoamorphous Si (na-Si:H) films have been fabricated by reactive pulsed laser ablation technique with hydrogen as reactive gas. It is found that the hydrogen pressure has a great effect on both the structure and photoluminescence (PL) properties of the films. Increasing the hydrogen pressure leads to a structural transition of the films from amphorous Si to na-Si:H, and the PL center wavelength of the na-Si:H films is varied with the hydrogen pressure. The PL decay times of the na-Si:H films are in the nanosecond scale and are shorter on the high energy side of their PL spectrum. The results demonstrate that the na-Si:H films are promising candidates for visible, tunable and high-performance light-emitting devices.

1. Introduction

Since the first observation of strong visible luminescence of porous Si at room temperature [1], many efforts have been devoted to the fabrication of Si based light-emitting structure, aiming at applicable light-emitting devices to be implemented in optoelectronics [2–5]. High-efficiency room-temperature photoluminescence (PL) from several Si nanocrystals structures such as Si nanocrystals embedded in amorphous SiO_2 matrix has been confirmed [6]. However, PL from such a system is generally in the red or infrared range and post annealing at high temperature is usually necessary for the formation and crystallization of Si nanoparticles in SiO_x [7]. In contrast to bulk crystalline Si, the wider band gap of amorphous Si makes it easier achieving emission in short wavelength by quantum confinement effect of amorphous Si nanoparticles. Also, it has been reported that the radiative recombination rate for amorphous Si nanoparticles is two to three orders of magnitude higher than that for crystalline Si nanoparticles [8]. It is, therefore, expected that amorphous Si nanostructures might be promising candidates materials for visible, tunable, and high-performance light-emitting devices. Reactive pulsed laser ablation (PLA) is a versatile cold-wall technique for the growth of thin films and nanostructured materials. Here the interactions between ablated species and reactive background gases can control the stoechiometry of deposited films and the surface of synthesized nanoparticles [9,10]. This would be the case of use of hydrogen as background gas, as it is well known in hydrogenation of Si, where hydrogen terminates dangling bonds and improves the PL properties. Therefore, the synthesis of hydrogenated Si nanostructures by the reactive PLA is a promising technique to control the nonradiative recombination process which usually has important influence on PL.

In this paper, hydrogenated amorphous Si (a-Si:H) and hydrogenated nanoamorphous Si (na-Si:H) films were synthesized by reactive PLA technique at different hydrogen pressure. The effects of hydrogen pressure on the structure and PL properties of the prepared samples were discussed.

2. Experimental procedure

a-Si:H and na-Si:H films were fabricated on Si and quartz substrates at room temperature using a Lambda Physik XeCl excimer laser ($\lambda = 308$ nm, pulse length at half maximum: 15 ns) at a repetition rate of 5 Hz. After the deposition chamber was evacuated less than 3×10^{-5} Pa, the high purity (99.9999%) hydrogen gas was introduced into the chamber at a flow rate of about 8 sccm. The background hydrogen gas pressure, P, was varied from 1 to 500 Pa and maintained at a constant pressure during the deposition. A single crystalline Si disk was used as ablation target, which was rotated in order to avoid the formation of deep ablation grooves and hinder extensive particle formation. A 45 cm focal length fused silica lens was used to focus the incoming laser beam onto the target with an incident angle of 45°. The size of the irradiated spot on the target surface was 2×3 mm^2 and the average fluence was about 1.5 J/cm^2. The distance between the target and the substrate was kept at 35 mm. The deposition duration was 1 h for all samples.

Field emission scanning electron microscopy (FESEM) (FEI XL-30 at 15 kV) was employed to study the surface morphology of

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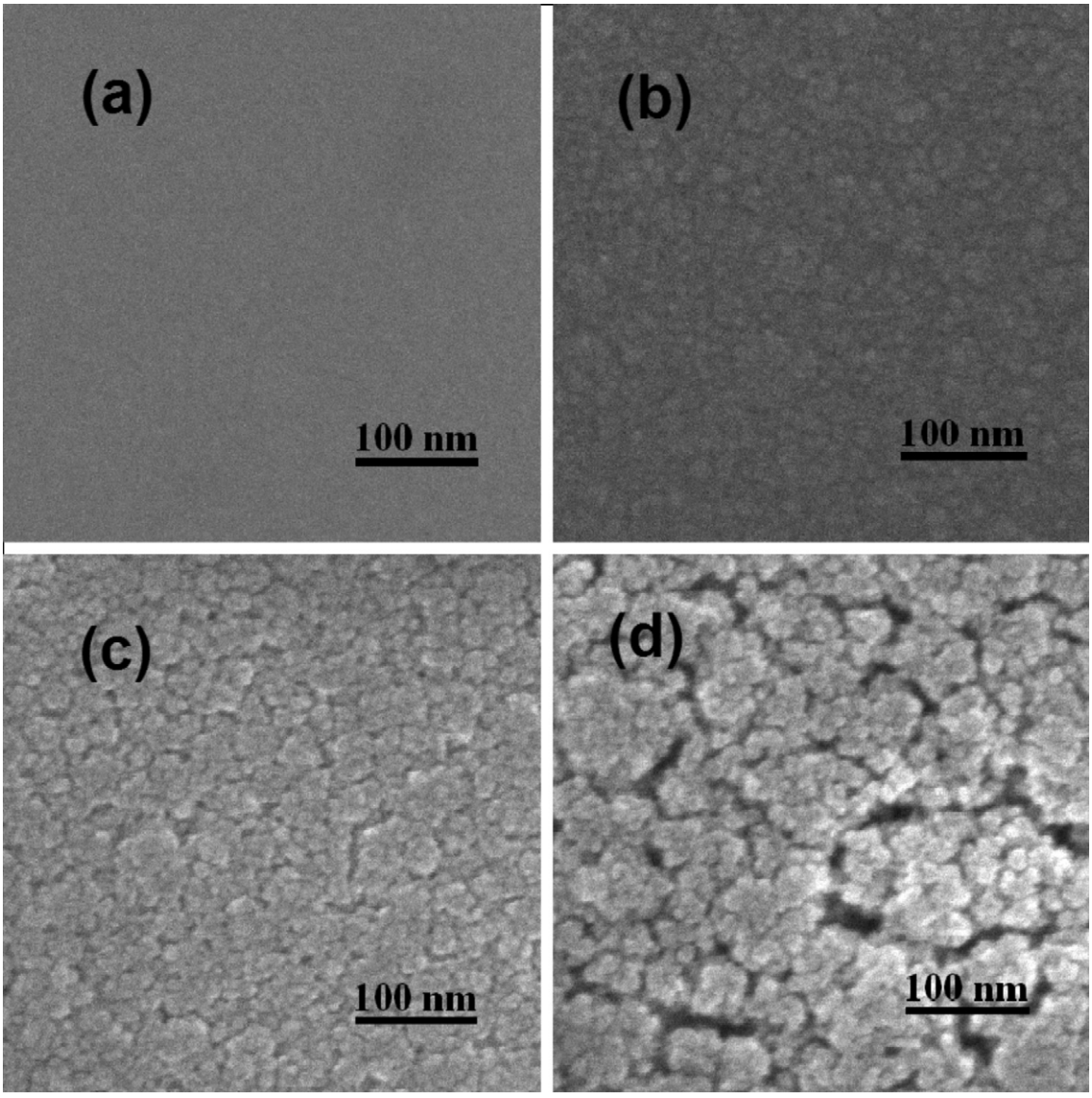

Fig. 1. FESEM images of the samples deposited at different *P*: (a) 50 Pa, (b) 100 Pa, (c) 300 Pa, (d) and 500 Pa.

the films. Infrared absorptions were measured with a TENSOR-27 Fourier transform infrared (FTIR) spectrophotometer. Raman scattering spectra measurements were performed in a Jobin Yvon T64000 spectrometer with an Ar^+ laser (532 nm) as the excitation source. Steady-state and time resolved PL spectra were measured at room temperature with an Edinburgh FLS920 fluorescence spectrometer equipped with a 450 W Xe lamp, a 375 nm picosecond pulse laser and a time-correlated single photon counting card.

3. Results and discussion

Fig. 1(a)–(d) displays the FESEM surface images of the samples deposited at various *P*, which are strongly depend on the *P* values. The FESEM image of the sample deposited at $P = 50$ Pa shows a very smooth surface on which no grains could be observed. Similar FESEM surface image is also observed for the samples deposited at $P = 1$ and 30 Pa, which are not shown here. These results suggest that the samples deposited at $P \leq 50$ Pa have a continuous, totally amorphous, film structure. For the samples deposited at $P \geq 100$ Pa, the SEM images show a rough and porous surface consisting of aggregates of small nanoparticles. Umezu et al. [11] have also reported the fabrication of hydrogenated Si nanostructures using PLA in hydrogen background gas. They have also found that there exists a critical hydrogen gas pressure value, where a continuous a-Si:H film is obtained. When the background gas pressure is higher than the critical value hydrogenated Si nanostructures are produced. The hydrogenated Si nanostructures have a hierarchical structure composed of surface hydrogenated silicon nanocrystallites as the primary structure and aggregates of the nanocrystallites as a secondary structure. However, further analysis (below) will show that all the small nanoparticles in our samples deposited at 100 Pa or above are purely amorphous phase, which is different from the results of nanocrystallite reported by Umezu et al. [11] In addition, it can be seen that the nanoparticles average size and the surface porosity of these samples seems to increase as *P* increases from 100 to 500 Pa.

The Raman scattering and FTIR spectra were measured *ex situ* to evaluate the crystallinity and local bonding structure of the deposits. The inset of Fig. 2 shows the Raman scattering spectrum of a typical sample deposited at $P = 500$ Pa. A broad peak at 480 cm^{-1} can be seen, which relates to the amorphous Si phase. Raman scattering spectra of the other samples (not shown) also exhibit similar