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UV irradiation and H_2 passivation processes to classify and distinguish the origin of luminescence from thin film of nc-Si deposited by PECVD technique

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ABSTRACT

Synthesis and characterization of nanocrystalline silicon (nc-Si) deposited by plasma enhanced chemical vapor deposition method are reported. Optical and microstructural studies are carried out by UV–vis absorption spectroscopy, photoluminescence (PL), X-ray diffraction, high resolution transmission electron microscopy, selected area electron diffraction and Raman spectroscopy measurements. Two PL bands observed at peak energies of 1.86 eV and 2.23 eV. An intense debate as to whether the visible PL at room temperature originated from nc-Si as quantum confinement (QC) or defect state. We have used electron spin resonance and hydrogen (H_2) passivation processes to distinguish between defect state and excitons confined to the nc-Si as the source of the PL. We find that the origin of the PL in the sample can be controlled with the aid of ultra-violet (UV) irradiation to introduce defects, making them as the origin of the PL and then hydrogen passivation remove the defects, resulting in PL from QC states. i.e., Switching it from defect-related in the as-crystallized state to QC after passivation, and back to defect related after subsequent irradiation. The observations of the light emissions from nc-Si at energy of 1.8–2.5 eV should be very important for novel optoelectronic device applications of Si-based materials. In addition, this work opens up the possibility of growing nc-Si thin films at low deposition temperature with well-controlled PL origin.

1. Introduction

Very recently, optical properties, process and techniques such as luminescent labeling are widely used in biomedicine [1]. These techniques are noninvasive and can be employed for in vivo diagnostics such as the optical coherent tomography which is successfully employed to detect malignant tumors in vivo [2] and can also be employed in vitro diagnostics such as in vitro examination on infectious diseases based on a photoluminescence (PL) response [3]. Moreover, nanocrystalline silicon (nc-Si) and crystalline silicon (c-Si) forms the basis of just about all computing technologies on the planet, in the form of microelectronics. On the other hand, the possibility induction of light emission from Si, an indirect band gap material in which radiative transitions are unlikely, raises several interesting and technologically important possibilities, especially the fabrication of the truly integrated optoelectronic devices. In addition, the discovery of intense PL in the visible range from porous silicon (PS) [4] has given a strong impulse to a research activity devoted to the synthesis and characterization of nc-Si, Si nanocrystals embedded in a SiO_2 matrix, and Si quantum dots, wires, and pillars. Among these different nanostructures, nc-Si represent the most promising way to realize an efficient Si-based light source operating at room temperature due to their great stability, good efficiency, and its unique properties associated with the quantum confinement (QC) effect [4–8].

Nevertheless, the exact mechanism for light emission in nc-Si remains a matter of intense debate. A large volume of theoretical and experimental data are available in the literature, a detailed understanding of the origin and mechanism of PL have not been achieved yet [9–11]. Three models have played an important roles, are proposed to interpret the origins of the PL in nc-Si without classification and distinction between them. Those models are listed in following: (1) surface state model [12], (2) defects at the interface of Si/SiO_2 [13–15], and (3) pure quantum size effect (QSE) [8,16]. The PL spectrum is sensitive to the amounts of hydrogen and oxygen on the surface of nc-Si thin film [17,18]. For the pure QSE, it is

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well known that both the excitation process and the PL process originate from nc-Si [16].

In the present work, direct investigation on PL spectra of nc-Si thin film is reported, and the origin of the PL in nc-Si films is studied as the main purpose of this work. Moreover, an attempt was made to detect, distinguish, classify and control the origin of PL in nc-Si films by ultra-violet (UV) illumination and hydrogen (H_2) passivation processes. To achieve this purpose, nc-Si films were prepared by a plasma enhanced chemical vapor deposition (PECVD) technique and submitted to a systematic characterization using X-ray diffraction (XRD), Raman spectroscopy, high resolution transmission electron microscopy (HRTEM), electron spin resonance (ESR), optical property and PL under UV illumination and H_2 passivation processes.

2. Experimental

500-nm-thick nc-Si thin film was deposited on fused quartz, Si (1 0 0), and Corning 7059 glass substrates by PECVD using SiH_4/SiF_4 (+He)/H_2 gas mixtures. The details of the PECVD system used have been described elsewhere [19,20]. The gas flow rates of [SiH_4], [SiF_4] and [H_2] were 1.0 sccm, 10 sscm and 7.0 sccm, respectively. The deposition temperature, T_d, the supplied rf power, and gas pressure were fixed at 100 °C, 25 W, 0.25 Torr, respectively.

The nc-Si thin film preparation process can be divided into three steps. (1) The substrates were cleaned for 30 min using acetone and then ethanol in an ultrasonic cleaner. (2) The cleaned substrates were treated by exposing them for 20 min to either nitrogen or hydrogen plasma excited using radio frequency (RF) power of 90 W. (3) Finally, nc-Si film was deposited on the substrates, under the above fixed deposition conditions. Three different types of substrates were utilized throughout the present work, as mentioned above, depending on what type of characterization we want to do. The films were deposited on 0.3-mm-thick fused quartz substrates with an area of 10×20 mm^2 for PL and optical absorption measurements, and also on 0.3-mm-thick fused quartz substrates with an area of 3×20 mm^2 for ESR measurement. In addition, nc-Si thin films deposited on 0.3-mm-thick crystalline Si substrate with an area of 10×10 mm^2 for X-ray photoelectron spectroscopy (XPS) measurement, and on 0.3-mm-thick glass (Coring 7059) substrates with an area of 10×20 mm^2 for measurements of XRD and Raman scattering.

Raman spectra were obtained utilizing the laser light at 488 nm using a cooled photomultiplier tube (Hamamatsu R649S) and a double monochrometer (Jobin Yvon RAMANOR HG 2S). The Raman spectra consist of a narrow line at 520 cm^{-1} due to a crystalline phase (c-phase) and a broad line around 480 cm^{-1}, due to an amorphous phase (a-phase). When the film includes smaller crystallites with a structure between that of a-Si and c-Si, the Raman peak arising from the crystallites may have a frequency between 480 cm^{-1} and 520 cm^{-1}, i.e. intermediate phase silicon structure (IPSS), as will be shown later. Besides, the structural properties were also investigated using an XRD apparatus (Shimadzu XD-D1), employing a diffractometer with a slit width of 0.1 mm set at the front of the detector. Moreover, characterization of crystal size was performed by using HRTEM. TEM was conducted at 200 kV with a JEOL JEM-2100 F-UHR field emission instrument equipped with a Gatan GIF 2001 energy filter and a 1k-CCD camera in order to obtain EEL spectra. The ESR spectrum was observed at room temperature using an X-band spectrometer (JEOL, JESRE 1X) with the magnetic-field modulation frequency of 100 kHz. From the ESR spectrum, we calculated the g-value and the spin density, N_s, using the integrated intensity for simplicity.

The optical transmission spectra were measured using an UV/VIS/NIR spectrophotometer (JASCO V-570). PL was analyzed using a Jobin Yvon RAMANOR HG 2S spectrometer coupled with a cold photo-multiplier tube (Hamamatsu Photonics R649S). The 488 nm Ar-ion laser with power of 200 mW was used as the PL excitation source. UV light was irradiated to the samples under vacuum and N_2 atmosphere with UV lamp (110 W samco SUV40S) for 3 h, using a UV band-pass filter (UV-D33). The spectrum of the excitation UV source showed a strong peak at 253.7 nm and subpeaks at 313.2, 360 and 404.7 nm. For the plasma-assisted hydrogenation (H_2 passivation), the RF power and duration were 5 W and 60 min, respectively.

3. Results and discussion

Fig. 1 shows the Raman spectra for as-deposited nc-Si thin film, UV illumination (irradiation), and H_2 passivation, respectively. As revealed in this diagram, a strong Raman peak at around 520 cm^{-1} arising from the crystalline phase is observed. The most surprising feature of the results shown in Fig. 1 is that a shoulder peak appeared at around 493 cm^{-1} which is due to very small crystallites for the sample after UV illumination and H_2 passivation.

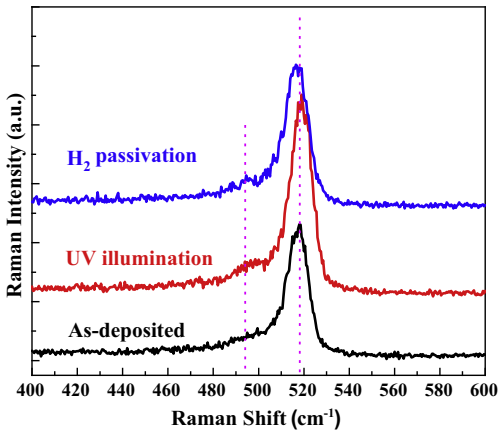

Fig. 1. Raman spectra for as-deposited nc-Si thin film, UV illumination (irradiation), and H_2 passivation.

The observed peak at 493 cm^{-1}, which is located between the continuous random network a-phase and the well ordered c-phase, i.e. IPSS, is considered to be associated with dilated bonds at the grain boundaries [21] or to tensile strained Si-Si bonds at grain boundaries [22]. It is suggested that nc-Si film is included a very small crystallites with the IPSS as mentioned before.

In addition, we find that the intensity of the Raman peak increases with UV illumination, but that component (crystalline phase) decreases after H_2 passivation. Moreover, it is found that the peak frequency of the 520 cm^{-1} component shifted toward a higher frequency side after UV illumination. On the other hand we can see opposite behavior, i.e. the peak shifted toward a lower frequency side, after H_2 passivation. Such crystalline component shifts may be due to either a change in the stress or structure of the nc-Si thin film and are controlled by vibration of the electronic polarization for constituents in the nc-Si thin film.

Fig. 2 shows the XRD spectra for as-deposited nc-Si thin film, UV illumination, and H_2 passivation, respectively. As seen in Fig. 2, the XRD spectra from (1 1 1) and (1 1 0) planes are observed. In addition, the intensity of the (1 1 0) increases and the intensity of the (1 1 1) decreases after UV illumination and H_2 passivation. Thus, under the condition of the UV illumination and H_2 passivation the nc-Si thin film exhibits a dominant (1 1 0) texture. As shown in Figs. 1 and 2, the Raman shift of the 520 cm^{-1} component (crystalline phase) is found to correspond well with the shifts of the (1 1 1) and (1 1 0) planes after UV illumination. The growth orientations

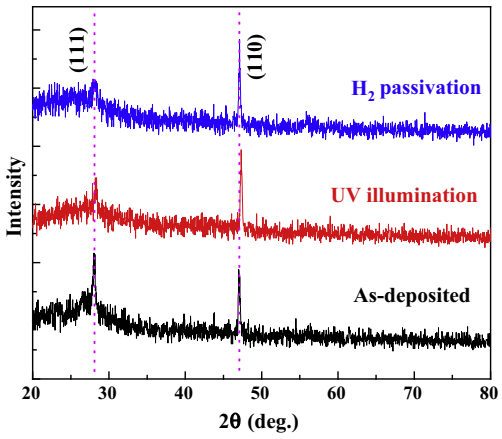

Fig. 2. XRD spectra for as-deposited nc-Si thin film, UV illumination, and H_2 passivation.