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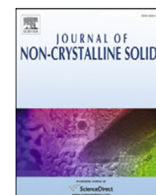

The influence of annealing temperature on the synthesis of silicon quantum dots embedded in hydrogenated amorphous Si-rich silicon carbide matrix

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ABSTRACT

Hydrogenated amorphous silicon carbide thin films (a-SiC:H) were prepared by plasma-enhanced chemical vapor deposition (PECVD) and thermal annealed at temperatures of 900, 1050, and 1200 °C, respectively. The influence of annealing temperature on the silicon quantum dot (QD) synthesis was investigated by Raman scattering spectroscopy, X-ray diffraction spectroscopy, and high-resolution transmission electron microscopy. The influence of annealing temperature on the chemical bonding configurations was revealed by Fourier transform infrared absorption microscopy. The element ratios of the as-deposited sample were deduced by X-ray photoelectron spectroscopy. Results reveal that the samples are in silicon-rich nature. Silicon in the as-deposited sample and the 900 °C annealed sample are amorphous. When the annealing temperature is increased to 1050 °C, crystal silicon QDs have come into being. The calculated number density is about $2.15 \pm 0.03 \times 10^{12}$ cm^{-2} and more than 80 ± 3% of the silicon QDs fall within a narrow size range of 2–3 nm. When the annealing temperature is increased to 1200 °C, the average size of crystal silicon QDs is tuned from 2.6 to 3.2 nm, while the crystallinity is enhanced from 56.7 ± 2.5 to 67.1 ± 1.5%. We attribute the influence of annealing temperature on the synthesis of silicon QDs to be dependent on the evolution of chemical bonding configurations and the agglomeration of silicon atoms from the host matrix.

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1. Introduction

Silicon nanocrystals dispersed in amorphous dielectric matrix have been paid extensive attention for their promising applications in silicon-based optoelectronic devices [1–3] and solar cells [4,5]. It's known that when the sizes of silicon nanocrystals are less than the silicon Bohr radius (~5 nm in diameter), they would behave as quantum dots (QDs) due to the quantum confinement effects [4]. For silicon QD size in range of 3–8 nm, the optical energy bandgap could be tuned from 1.3 to 1.65 eV [6]. Silicon QD superlattice is proposed for all-silicon tandem cell, whose efficiency limit would increase to 42.5% for 2-cell and 47.5% for 3-cell [7,8].

Considerable work has been done on the growth and characterization of silicon QDs in silicon oxide (SiO_2 or SiO_x) [9,10], silicon nitrides (Si_3N_4 or SiN_x) [11,12], and silicon oxytrides (SiO_xN_y) [13,14]. As a weaker polar dielectric matrix, silicon QDs in amorphous silicon carbide (SiC_x) might exhibit much larger quantum confinement behavior. Taking into account the lower barrier height of SiC_x (~2.5 eV), the barrier height of SiO_x and SiN_x are ~9 eV and ~5.3 eV, respectively, SiC is favorable for increasing the tunneling probability and in turn the carrier transport could be easier [15]. However, few experimental studies have been carried out on the preparation of silicon QDs in SiC matrix [16]. A full understanding about the synthesis of silicon QDs has been less documented, and the discussion is still open [17–19].

In this work, hydrogenated amorphous silicon carbide thin films (a-SiC:H) thin films were deposited by decomposition of silane (SiH_4) and methane (CH_4) and annealed at 900, 1050, and 1200 °C, respectively. The influence of annealing temperature on the synthesis of silicon QDs and the evolution of chemical bonding configurations have been investigated.

2. Experimental details

a-SiC:H thin films were deposited by 13.56 MHz capacitive-coupled plasma-enhanced chemical vapor deposition (PECVD) on (100) p-type crystalline silicon wafer and quartz plate simultaneously. The substrates were first cleaned with piranha cleaning solution (3:1 H_2SO_4:H_2O_2) and then rinsed in de-ionized water. A diluted HF acid (5%) dip was performed only for the silicon wafers to remove the native surface oxide for 180 s additionally. Prior to deposition, the chamber was evacuated down to a base pressure of ~5×10^{-5} Pa. Hydrogen-diluted 10% SiH_4 of 50 sccm and pure CH_4 of 10 sccm were then introduced to maintain a working pressure of 106.7 Pa. The substrate temperature, the power

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supply and the deposition time were kept at 200 °C, 160 mW/cm^2 and 90 min, respectively. After deposition, the samples were cut into four smaller parts. Three parts of them were annealed in a quartz tube furnace at 900, 1050, 1200 °C for 30 min in a flowing 99.999% N_2 atmosphere, respectively, and then were cooled down naturally to room temperature within the quartz tube furnace.

The synthesis of silicon QD was characterized by means of Raman scattering spectroscopy, X-ray diffraction spectroscopy, and transmission electron microscopy. Raman scattering measurements were carried out by HORIBA Jobin Yvon LabRAM Spectrometer (HR 800 UV) in backscattering configuration using the 514 nm line of Ar^+ laser, where the incident power was kept low to avoid crystallization and distortion of the spectrum. X-ray diffraction measurements was carried out by Philips's X'Pert Pro (XRD, PANalytical PW3040/60) with Cu Kα radiation ($\lambda = 1.540562$ Å) at a voltage of 40 kV and a current of 40 mA. The glancing angle between the incident X-ray and sample surface was 1.00 with a resolution of 0.01°. Crystalline silicon QDs were characterized directly on the 1050 °C annealed sample by transmission electron microscopy (TEM, JEM-2100F) in plan-view at a working voltage of 200 kV. The sample for TEM was prepared transparently by conventional mechanical polishing and Ar^+ thinning technology at room temperature. The element ratios were analyzed by X-ray photoelectron spectroscopy (XPS, VG Multilab 2000), using a monochromatic Al Kα (1486.5 eV) X-ray source and a hemispherical energy analyzer. The X-ray source power, instrument resolution, working pressure, and analyzed area of the samples were kept at 300 W, 0.47 eV, 6.67×10^{-8} Pa, and 0.36 mm^2, respectively. Before detections, the samples were sputtered using a beam of 3 kV × 2 μA Ar^+ bombardments for 270 s. The spectra were collected at 25 eV pass energy and the binding energy values were calibrated by using the contaminant carbon C1s = 284.6 eV. The narrow-scan peaks were fitted with Thermo Avantage® and a standard Smart background was used for fitting the spectra. Chemical bonding configuration behaviors were deduced from Fourier transform infrared absorption measurements (FTIR, VERTEX 70). The absorption of substrate was eliminated by a bare silicon wafer.

Raman scattering, XRD, TEM, and XPS characterizations were performed on the samples deposited on the quartz plates. FTIR measurements were performed on the samples deposited on the crystalline silicon substrates.

3. Results and discussion

Fig. 1 displays the Raman scattering measurements obtained from the as-deposited sample and the samples annealed at 900, 1050 and 1200 °C, respectively. Before measurement, the system was calibrated with a single crystal Si wafer, whose Raman shift peak is at about 521 cm^{-1}. For the as-deposited sample, the spectrum exhibits one broad peak at about 472.8 cm^{-1} with the full width at half maximum (FWHM) of 93.5 ± 2.8 cm^{-1}. The 900 °C annealed sample also exhibits one broad peak in the same behavior, but whose peak has shifted to about 477.5 cm^{-1} and FWHM has decreased to 83.7 ± 0.13 cm^{-1}. When the annealing temperature is further elevated to 1050 °C, the spectrum exhibits two peaks: one is sharper asymmetrical and the other is broad weak. The sharper asymmetrical peak has shifted to about 514.0 cm^{-1} and the FWHM has decreased to 16.1 ± 0.10 cm^{-1}. The low-energy tail has extended down to 290 cm^{-1}. The broad weak protuberance is located at about 952.1 cm^{-1}. The 1200 °C annealed sample exhibits one significantly sharper asymmetrical peak and one enhanced broad weak protuberance in the same behavior as that of the 1050 °C annealed sample. The significantly sharper peak is also at about 514.0 cm^{-1}, but the FWHM has decreased further to 8.3 ± 0.07 cm^{-1}.

The 472.8 cm^{-1} peak could be attributed to scattering by the transverse optical (TO) mode of Si—C and/or Si—Si vibrations in the amorphous matrix, suggesting that the as-deposited sample is in completely amorphous feature [20,21]. The shifts to 477.5 cm^{-1} could be ascribed to the presentation of ultra-small silicon particles, but whose number-density is quite small [22]. It is well known that Raman spectroscopy is sensitive to local atomic arrangements and lattice vibrations [23,24]. The grain size-related effects as well as compressive stress within the material usually result in a low-frequency asymmetric broadening and a high low-number shift of the first order Raman band from 521 cm^{-1} of bulk crystalline Si [25–27]. Thus, the asymmetrical low-frequency shift of the 1050 °C and 1200 °C annealed samples demonstrate the formation of crystalline silicon particles. The left axis in Fig. 2 shows the trend of FWHMs. It has been reported that FWHM of Si—Si peak increases with decrease in order and decreases with increase in order [28]. Thus the continuous decrease of FWHM also reveals the increase in order or the synthesis of crystalline silicon particles in the samples.

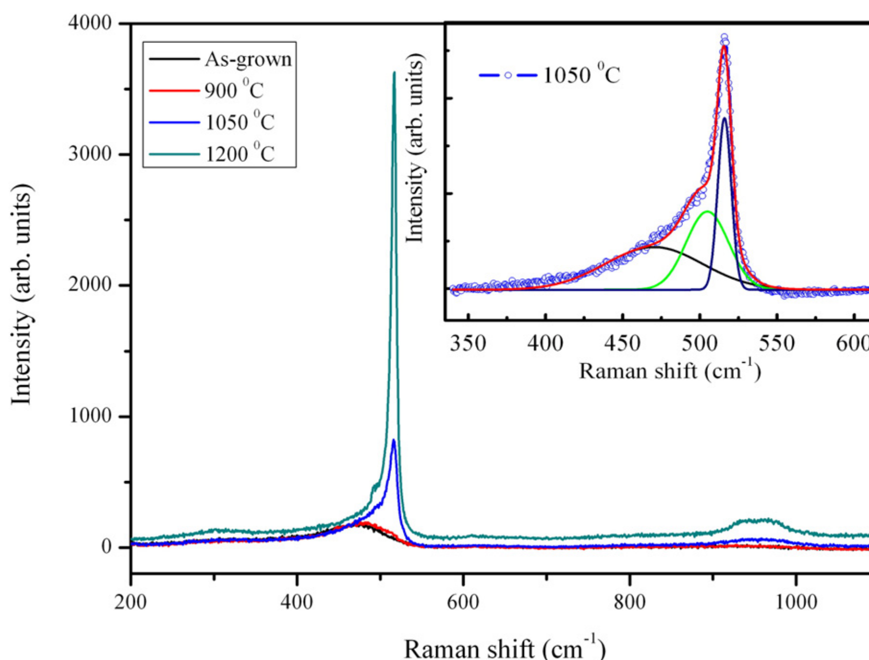

Fig. 1. Raman scattering measurements of the as-deposited sample and the samples annealed at 900, 1050, and 1200 °C, respectively, in range of 100–1200 cm^{-1}. The inset shows a typical deconvolution of the spectrum of the 1050 °C annealed sample in range of 300–580 cm^{-1}.

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