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Short communication

Enhancing crystallization of silicon nanocrystal embedded in silicon-rich oxide by ion beam-assisted sputtering

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ABSTRACT

This study examined the material and optical properties of Si nanocrystals (NCs) embedded in Si-rich oxide (SRO) films prepared through ion beam-assisted sputtering (IBAS). Transmission electron microscopy and grazing-incidence X-ray diffraction revealed that IBAS improved the formation of the Si NCs in the SRO films. The size and density of Si NCs were predominantly controlled by IBAS with varying anode voltage. The photoluminescence levels of the SRO films were enhanced, which was associated with the quantum confinement effect of the Si NCs. The benefits of an Ar ion beam used on the SRO films are discussed in this paper. The results indicate that IBAS is a promising approach for the development of highly efficient Si-based optoelectronic devices.

1. Introduction

Since the discovery of light emission from porous Si, Si nanocrystals (NCs) have attracted significant attention for use as light emitters, memory devices, and solar cells, as well as for other optoelectronic applications that exploit quantum confinement effect (QCE) and size-tunable bandgaps [1–4]. Materials featuring Si NCs embedded in Si-rich oxide (SRO) are promising candidates for development; they have been applied to Si-based light sources because the radiative recombination probability of electron–hole pairs in Si NCs can be obviously improved [5]. The standard approach for nucleation of Si nanoaggregates and formation of Si NCs is post-annealing at temperatures higher than 900 °C [6].

SRO films can be prepared using various approaches such as plasma enhanced chemical vapor deposition, ion implantation, sputtering, and evaporation [7–10]. Sputtering outperforms other deposition methods because sputtering provides benefits, such as low substrate temperature, low cost, and strong adhesion to substrates. In addition, ion beam techniques have been developed for the deposition of optical thin films, and can be used together with evaporation to improve film quality [11]. However, few studies have examined combined sputtering and ion beam systems, mostly because of the difference of working pressures between the sputtering process (10^{-3} Torr) and the ion source process (10^{-5} Torr) [11,12]. Previously, we demonstrated that ion beam-assisted sputtering (IBAS) for SRO/SiO_2 superlattices can increase crystallinity and activate a defect emission that yielded a spontaneous white photoluminescence (PL) [13]. Moreover, IBAS is a versatile technique that can produce high-quality films without additional substrate heating, enabling deposition at room temperature [14,15].

In this letter, we report concerning Si NCs embedded in a single SRO layer prepared through IBAS with varying anode voltage. The results show that the ion source influenced the size, density, and crystallinity of these Si NCs and enhanced the degree of phase separation. The PL emissions from these SRO films were enhanced by IBAS.

2. Experimental details

The SRO films were deposited on p-type (100) Si wafers. Radio frequency sputtering of a pure Si target (110 W) and an Ar ion beam with a gas mixture of Ar (20 sccm)/O_2 (0.3 sccm) were both employed to prepare SRO films at a pressure of 1 mTorr. IBAS used an ion source with anode voltages of 0 V, 40 V, and 80 V; the products were labeled as 0 V, 40 V, and 80 V samples, respectively. The Ar ions from the ion source impinged on the substrate simultaneously with the deposited SRO films. The thickness of the SRO films was measured as approximately 170 nm by using an ellipsometer (J.A. Woolam/M2000-DI). Post-annealing was performed with forming gas (95% N_2+5% H_2) for phase separation at 1000 °C for 3 h in a conventional quartz-tube furnace. High-resolution transmission electron microscopy (HR-TEM, JEOL/JEM-2100) was used to investigate the lattice of crystalline Si. The

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crystalline properties of the samples were also analyzed through grazing-incidence X-ray diffraction (GIXRD, Siemens/D5000) using Cu Kα radiation with a wavelength of 0.154 nm. X-ray photoelectron spectroscopy (XPS, ULVAC/PHI Quantera SXM) with a monochromatic Al Kα excitation source (1486.6 eV) was used to identify the oxidation states and the compositions of the SRO films. Room-temperature PL spectroscopy (Horiba/Jobin Yvon Labram spectrometer) was carried out to observe the emission properties of the SRO films. The excitation source was a 532 nm laser line and the spectrum ranged from 650 to 1000 nm.

3. Results and discussion

Cross-sectional HR-TEM was performed to observe the existence of Si NCs in the SRO films that had been prepared using IBAS with various anode voltages. As shown in Fig. 1(a)–(c), the crystallinity levels of the Si NCs were recognized and randomly distributed in the SRO matrix. Results showed a single Si NC smaller than 4 nm [Fig. 1(d)] with a lattice separation of 0.313 nm [Fig. 1(e)]. The lattice fringes were very close to the Si bulk value of 0.31 nm. In addition, the mean sizes of the Si NCs for the 0 V, 40 V, and 80 V samples were 2.3 ± 0.4 nm, 3.6 ± 0.7 nm, and 6.1 ± 0.8 nm, respectively, which suggested that the sizes of the Si NCs were proportional to the anode voltage. The densities of the Si NCs determined from HR-TEM for the 0 V, 40 V, and 80 V samples were $6.2 \times 10^{16}/\mathrm{cm}^3$, $2.6 \times 10^{17}/\mathrm{cm}^3$, and $1.0 \times 10^{17}/\mathrm{cm}^3$, respectively, indicating that IBAS increased the phase separation and formation of the Si NCs within the oxide matrix. However, the reduction of density for the 80 V sample was due to a number of small Si NCs that had aggregated to form a large Si NC.

The selected area diffraction pattern (SADP) of the SRO films is shown in Fig. 2. The ratio of radius for the first three diffraction rings was $\sqrt{3}:\sqrt{8}:\sqrt{11}$, yielding a diamond cubic structure. The SADP was indexed as (111), (220), and (311) according to the selection rule of bulk Si [16]. The nearly continuous rings were suggestive of random orientation of the neighboring crystallites. Notably, the obvious rings in Fig. 2(b) and (c) indicated that the IBAS samples had strong crystalline structures.

To further illustrate the crystallinity of the samples, the diffraction patterns measured using GIXRD are presented in Fig. 3. The 2θ diffraction peaks at 28.4°, 47.4°, and 56.3° corresponded to (111), (220), and (311) planes of crystalline Si, respectively. The XRD patterns showed high intensity for the sample fabricated with an anode voltage of 40 V, indicating that application of an ion source during film deposition enhances the crystallization process during high-temperature annealing. However, for the sample fabricated at an anode voltage of 80 V, the XRD intensity was slightly lower than that of the 40 V sample, but still higher than that of the 0 V sample because of the reduced density of Si NCs. The average grain size (L) of the Si NCs was estimated using Scherrer's formula [17]:

$$L = (K \bullet \lambda)/(B \bullet \cos\theta) \quad (1)$$

where K is a shape factor, which is considered to be 0.9 in this case; λ is the wavelength of the X-ray, B is the value of full-width at half-maximum, and θ is the Bragg angle. Using Eq. (1), the grain sizes for the 0 V, 40 V, and 80 V samples were calculated to be 1.8 nm, 2.9 nm, and 4.7 nm, respectively. The Scherrer broadening size (L), the length of columns of cubic cells aligned perpendicularly to the set of diffracting lattice planes, was used to calculate the minimum sizes of the crystallites. The spherical shape of an Si NC with a diameter (d) is given by [16,18]:

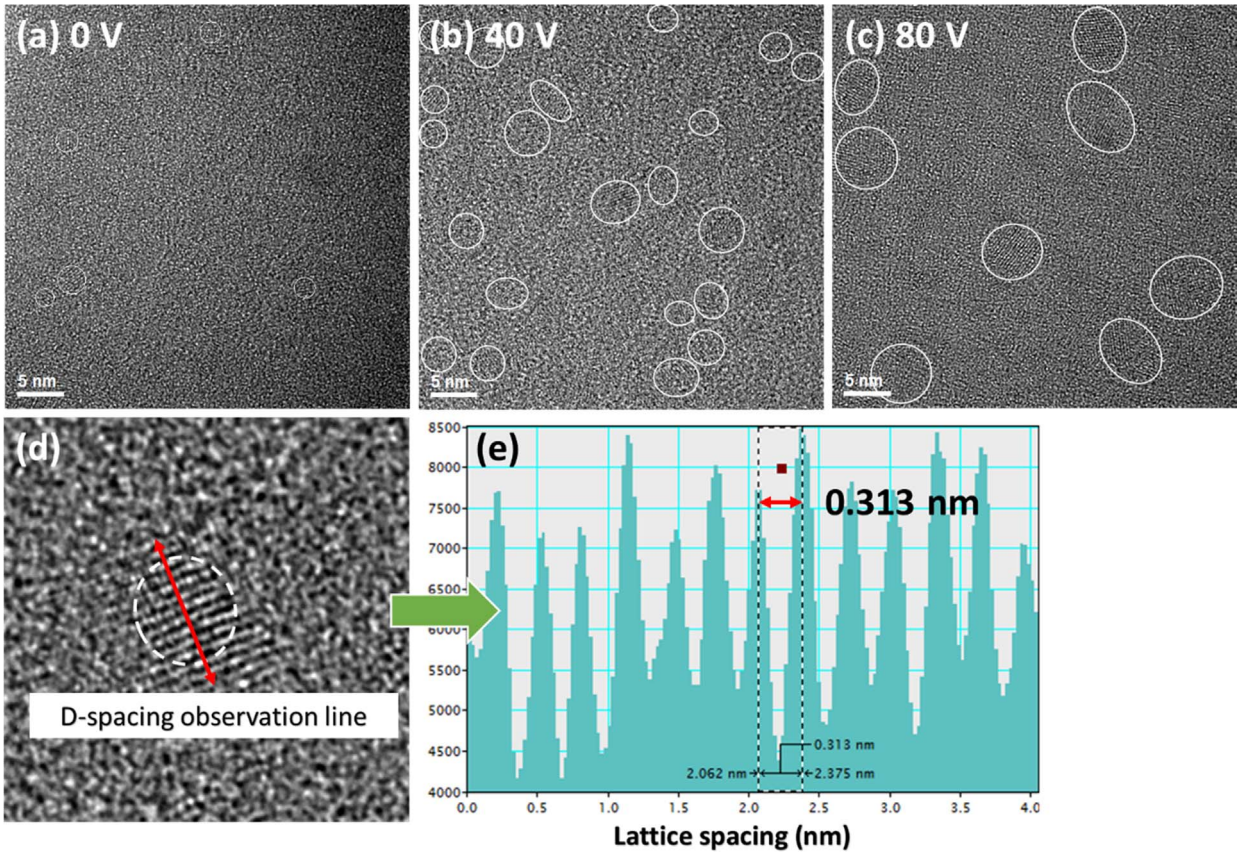

Fig. 1. HR-TEM images of the SRO films with anode voltage of (a) 0 V, (b) 40 V and (c) 80 V. The visible Si NCs are highlighted in white circles. Fig. (d) and (e) show an enlarged TEM view of the single Si NC and d-spacing in (111) lattice fringe, respectively.