Surface & Coatings Technology xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Formation of luminescent Si nanocrystals by ion irradiation

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ARTICLE INFO

Article history:
Received 26 December 2015
Accepted in revised form 25 June 2016
Available online xxxx

Keywords:
Si nanocrystals
Atom beam sputtering
Ion beam irradiation
Luminescence

ABSTRACT

Intense red emission is achieved in silicon nanocrystals (SiNCs) grown by atom beam sputtering (ABS) followed by ion beam irradiation (IBI). The silicon rich silicon oxide thin films are grown by ABS technique with target consisting of 60% silicon-in-excess + SiO_2. To precipitate the excess silicon in the form of nanocrystals, samples were processed under IBI post deposition treatment. IBI of the films is carried out using a 160 MeV Ni^{+11} ion beam at fluences 5×10^{12}, 1×10^{13} and 5×10^{13} ions/cm^2. The transmission electron microscopy (TEM) studies reveal that the size of the nanocrystals increases monotonically as the ion fluence is increased. The IBI treated samples show almost monodispersion at all fluences and the size of the particles can be controlled precisely by ion fluence. The photoluminescence (PL) studies support the TEM results and an intense emission with a red shift is observed as the particle size is increased with an increase in ion fluence. The asymmetry in transverse optical (TO) vibrational mode in Raman spectra also suggests the formation of SiNCs in the SiO_2 films.

1. Introduction

Despite the fact of being the most studied and utilized material for microelectronic industry, bulk silicon is not appropriate for optoelectronic devices due to emission in infrared region. Since the discovery of luminescence from nano-dimensional silicon array [1], silicon based optoelectronics has gained a considerable research interest due to the full compatibility of this system with existing silicon based CMOS technology for the possibility of integrated silicon photonic devices [2,3]. Besides, photovoltaics [4], non-volatile semiconductor charge storage devices [5,6], light emitting diodes [7], laser [8], and biomedical applications [9] are other thrust areas of research with silicon nanocrystals (SiNCs) as key solution.

The underlying mechanism for the formation of highly stable, robust, economical, and luminescent SiNCs includes phase separation of non-stoichiometric-silicon rich silicon oxide (NS-SRSO) thin films by means of some activation. Hence, various growth methods have been explored so far for the preparation of NS-SRSO that includes silanol chemistry based plasma enhanced chemical vapor deposition (PECVD), pulsed laser deposition (PLD), ion implantation, magnetron sputtering, multilayer superlattice formation, thermal evaporation, and atom beam sputtering (ABS) etc [10–18]. In most cases, the precipitation of excess silicon takes place in the form of SiNCs in SiO_2 matrix by post-deposition treatments such as thermal annealing, rapid thermal annealing (RTA), strain etching, plasma treatments, laser irradiation, synchrotron irradiation, and ion beam irradiation (IBI) [19–21,23–25]. Among all these processes, ion implantation followed by high temperature thermal annealing is practiced the most, though the size distribution of SiNCs cannot be controlled in this process. To achieve high optical gain and high efficiency of photonic devices, controlled size, as well as size distribution of the SiNCs is the most common requirement, failing to which leads to deterioration of the performance of the devices.

In this article, formation of intense red luminescent and narrow size distributed SiNCs is presented utilizing ABS followed by IBI. Previously Warang et al. explored the effect of RTA on NS-SRSO grown by ABS and observed the formation of amorphous nano-clusters after RTA up to a temperature of 900 °C in N_2 environment for 1 min [17]. Conversely, our group achieved highly luminescent and nearly mono-dispersed SiNCs in silicon oxide matrix grown by ABS followed by RTA in Ar + 5% H_2 environment for 5 min at temperatures ranging between 800 °C and 950 °C at a step of 50 °C [18,26]. ABS has multifold advantages over conventional rf sputtering method such as 2″-diameter wide source of Ar beam, continuous substrate rotation, and comparatively less heating of the target during deposition that results in better uniformity of the films. Further, in rf magnetron co-sputtering process, due to the presence of magnetic field, there is higher sputtering from a narrow circular area that leads to the non-uniformity in the samples for large area deposition. IBI is a unique tool to synthesize and modify the material in a controlled way by providing local annealing with a very high quenching rate (10^5 K/s) that facilitates the nano-precipitation of excess silicon in the ion tracks and a narrow size distribution

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http://dx.doi.org/10.1016/j.surfcoat.2016.06.071
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Please cite this article as: N. Saxena, et al., Surf. Coat. Technol. (2016), http://dx.doi.org/10.1016/j.surfcoat.2016.06.071

can be achieved. The narrow size distribution and variation of SiNCs size with ion fluence lead to the intense emission from SiNCs that is not observed previously so far.

2. Experiment

The ABS set-up and the experimental parameters used for the deposition of NR-SRSO thin films are fully described elsewhere [18,27]. Briefly, sputtering target consisting of a fused silica disk of 3″ diameter with pieces of silicon (100) glued on it, covering an area of approximately 60% of the disk is used here. The deposition is carried out on silicon (100) wafer, optical grade quartz, and carbon-coated Cu grid substrates for different studies. The films on each substrate are then subjected to IBI using a 160 MeV Ni^{+11} ion beam from the 15 UD Pelletron Accelerator at Inter University Accelerator Centre, New Delhi, India. The irradiation is carried out at fluences 5×10^{12}, 1×10^{13} and 5×10^{13} ions/cm^2 at room temperature. The vacuum during IBI is maintained as 2×10^{-6} mbar. The beam is magnetically scanned over an area of 1×1 cm^2 of the sample to get uniform irradiation. The electronic energy loss, nuclear energy loss and the range of 160 MeV Ni ions in the films are 5.626 KeV/nm, 6.887×10^{-3} KeV/nm, and 35.77 μm, respectively, as calculated by the SRIM 2013 code [29].

The as-deposited and irradiated films were characterized for structural studies and optical properties. The thin films deposited and irradiated on silicon substrate are investigated by Fourier transform infrared spectroscopy (FTIR) measurements using Thermo Nicolet NEXUS 670 FT-IR with a resolution of 4 cm^{-1} (Thermo Fisher Scientific, Waltham, USA). The micro-Raman spectroscopy of the samples are carried out using a Renishaw Invia Raman microscope (Renishaw plc, Gloucestershire, United Kingdom) with a 514-nm excitation wavelength of an Ar-ion laser. Photoluminescence (PL) spectroscopy studies are carried out using HORIBA Jobin Yvon LabRAM 800 HR (NJ, USA) after exciting at a wavelength of 488 nm from Ar^+ ion laser at room temperature. The samples deposited and irradiated on optical grade quartz substrates are studied by UV–vis absorption spectroscopy (Hitachi 3300 UV/visible spectrophotometer; Hitachi High-Technologies Corporation, Tokyo, Japan). The transmission electron microscopy (TEM), and high-resolution transmission electron microscopy, studies are carried out using a Tecnai G20-stwin microscope (FEI Company, Shanghai, China) operating at 300 kV equipped with a LaB_6 filament and a charge-coupled device camera having a point resolution of 1.44 Å and a line resolution of 2.32 Å.

3. Results and discussion

To visualize the formation of embedded SiNCs in NS-SRSO thin films by means of IBI, TEM studies are carried out and shown in Fig. 1a–d. Fig. 1a shows the TEM image of the as-deposited NS-SRSO thin film that clearly reflects the uniformity of the film grown by ABS in contrast to PLD where micron sized droplets are ablated and get deposited on the substrate. No signature of nanophase or any debris is found in the ABS deposited NS-SRSO thin films rather an amorphous phase of Si-SiO_2 nanocomposite may be present as shown in Fig. 1a. After IBI of the films at a fluence of 5×10^{12} ions/cm^2, the bright field TEM images visualize the presence of very small SiNCs of the size 3.51 ± 0.076 nm as can be seen in Fig. 1b. The size distribution of the SiNCs is shown in the inset of Fig. 1b, that indicates a narrow size distribution of SiNCs. The size of the SiNCs is found to increase on increasing the ion fluence, though the size distribution is found to decrease. This is due to the formation of overlapping ion tracks at higher fluences leading to broadening in the track diameter and thereby the size of the SiNCs increases. The sizes of SiNCs are observed as 4.59 ± 0.057 nm and 5.29 ± 0.034 nm

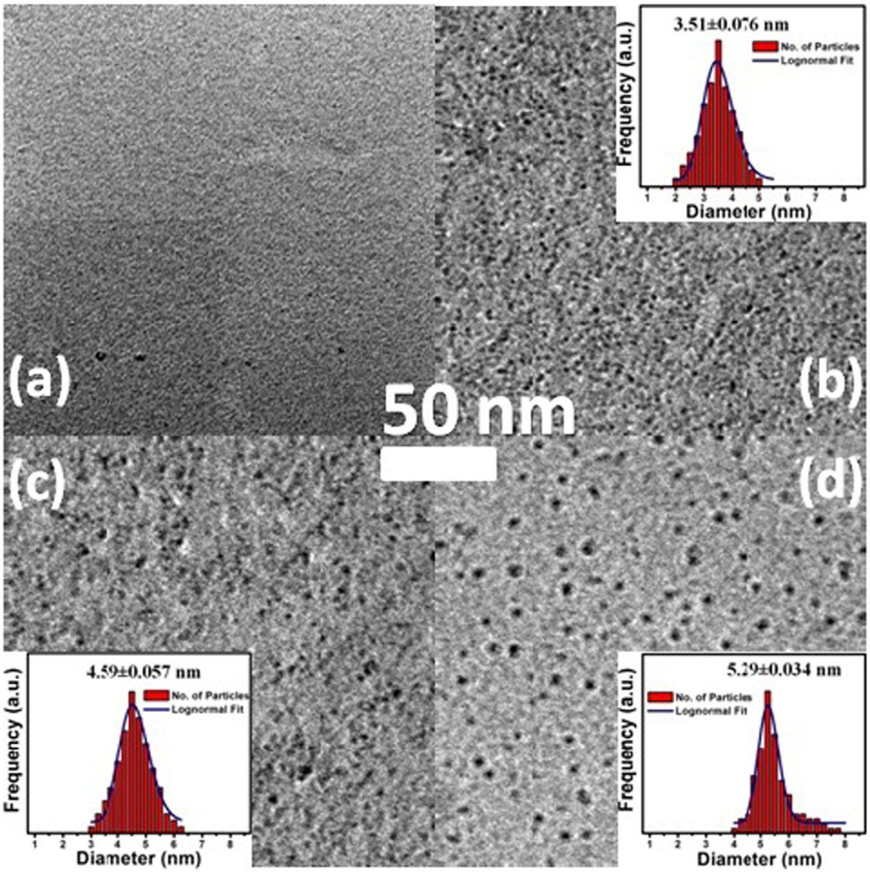

Fig. 1. TEM images of (a) as-deposited Si rich SiO_2 film, (b) irradiated at 5E12 ions/cm^2, (c) 1E13 ions/cm^2 and (d) 5E13 ions/cm^2 of 160 MeV Ni^{+11} ion beam. Insets show corresponding size distributions.

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