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Citation: AIP Conference Proceedings **1832**, 050020 (2017); doi: 10.1063/1.4980253
View online: http://dx.doi.org/10.1063/1.4980253
View Table of Contents: http://aip.scitation.org/toc/apc/1832/1
Published by the American Institute of Physics

Ion Induced Effects on the Dissociation of Silicon Nanoparticles

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Abstract. We report a detailed study on the dissociation of isolated silicon nanoparticles under high energy ion irradiation. Ultra-small (1-10 nm) colloidal silicon nanoparticles (Si NPs) have been synthesized by ablating porous silicon (pSi) in acetone using femtosecond laser pulses. Porous silicon was ablated, considering the fact that it contains a large number of light emitting silicon nanoparticles. The shape and size distribution of Si NPs was investigated by Transmission Electron Microscopy (TEM). The crystallinity of spherical Si NPs was confirmed by Selective Area Electron Diffraction (SAED).
Keywords: Porous silicon, Nanoparticles, Laser ablation, Irradiation, TEM
PACS: 78.55.Mb, 78.67.Bf, 79.20.Eb, 81.40.Wx, 87.64.Ee

INTRODUCTION

Porous silicon (pSi) and Si nanoparticles (NPs) are indispensable materials in the fields of nanotechnology and nanophotonics owing to their outstanding electronic and optoelectronic properties [1-2]. Synthesis, characterization and ion beam studies of pSi have been reported earlier [3]. It is possible to tailor the structural and optical properties of pSi by controlling various etching parameters during anodization [1]. The generation of silicon nanoparticles (Si NPs) by femtosecond (fs) laser ablation of Si under liquid environment has been demonstrated by many researchers [4]. In this paper, pSi is proposed as a seed material to synthesize colloidal Si NPs by using fs laser ablation. NPs prepared by laser ablation can be further modified by different post synthesis treatments. Swift Heavy Ion irradiation (SHI) is one of the important techniques used for tuning the size and shape of nanoparticles in a controlled manner [5,6]. There are few investigations on the effects of ion irradiation on structural and optical properties of nanostructured pSi prepared by anodic etching process [3]. The synthesis and growth of light emitting Si quantum dots in Silica matrix by low energy implantation and followed by irradiation with swift heavy ions have been reported by Kachurin et al. [7]. Saxena et al. [8] have reported the decomposition of SiO_x phase into Si and SiO_2 by 120 MeV Ni ion irradiation. They found size reduction, surface smoothness and shaping of nanostructures due to ion irradiation. Chaudhari et al. [9] have carried out the studies on swift heavy ion induced growth of nanocrystalline silicon in silicon oxide. In the present study we have investigated the ion induced modifications on nanoscale objects, in particular the dissociation of isolated Si NPs prepared by laser ablation.

EXPERIMENTAL

Ultra-small Si NPs were synthesized by subjecting the porous silicon targets to fs laser pulses under liquid environment. Porous silicon was prepared by anodic etching of p-type (100) Si (1-30 Ω-cm) for 10 min in 1:2:: HF: Isopropyl alcohol (IPA) solution at etching current density of J = 5 mA/ cm^2. Ultra-small silicon nanoparticles were prepared by ablating pSi target under acetone environment using a chirped pulse amplified Ti: sapphire laser system (Coherent Legend, ~2.5 W, 1 kHz) delivering nearly bandwidth limited laser pulses (Pulse duration of ~ 40 fs) at 800 nm. Pulse energy of 100 μJ was used for ablation which was carried out for ~40 minutes. The size distribution of NPs has been estimated by Transmission Electron Microscopy (TEM- Technai, equipped with a thermo-ionic electron gun working at 200 kV). The Energy Dispersive Spectroscopy (EDS-SEI Technai G2 S-T with 200 kV electrons) measurement was also performed to study the

DAE Solid State Physics Symposium 2016
AIP Conf. Proc. 1832, 050020-1–050020-3; doi: 10.1063/1.4980253
Published by AIP Publishing. 978-0-7354-1500-3/$30.00

chemical contaminations present in the sample. Further, irradiation was performed with 120 MeV Au ions at various fluences ranging from 5×10^{12} to 3×10^{13} ions/cm^2 using 15 MV pelletron accelerator at IUAC, New Delhi. The stopping and range of 120 MeV Au ions inside silicon were obtained by SRIM calculations [10]. The SHI irradiation effects on size and shape of Si NPs have been investigated by TEM.

RESULTS AND DISCUSSION

Figure 1 shows the formation of nanostructured porous silicon as a result of anodic etching of c-silicon. The width of pore walls and size of nanoparticles embedded between the pores decrease with increase in applied current density during anodic etching [3]. The thickness and porosity of pSi layer prepared at 5 mA/cm^2 current density is presented in the table-1. Further, this pSi sample has been subjected to fs laser pulses to synthesize colloidal ultra-small Si NPs in acetone (*label: SiNP-5*). TEM image shown in Fig. 2 confirms the formation of nearly spherical Si NPs by laser ablation. To determine the accurate size distribution of Si NPs, we have estimated the sizes of 500 particles in different regions of TEM grids. The corresponding histogram shows that the major portion of nanoparticles had diameters in the range of 7±3 nm (inset of Fig.2). Particle sizes of Si NPs estimated by different analytical techniques have been presented in table-2.

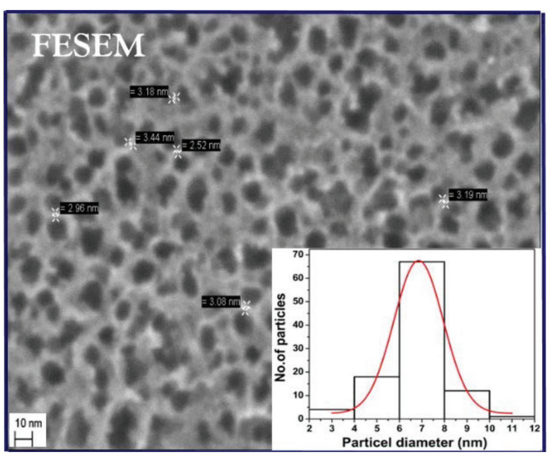

FIGURE 1: Surface morphology of porous silicon.

The chemical composition of the sample was extracted from EDS measurements and the data is shown in inset of Fig. 2. The observed peaks related to copper (Cu) is associated with TEM grids used in this study. Hence, the main constituents of this sample are found to be Si as expected and small amount of oxygen. Hence, this EDS measurement confirms the successful generation of impurity free ultra-small Si NPs with laser ablation of porous silicon. The HRTEM image of a single isolated Si NP presented in Fig. 3 shows the crystalline lattice fringes with lattice spacing of 0.31 nm corresponding to the inter-planar spacing of Si [111] planes. The selective area electron diffraction pattern shown in inset of Fig. 3 reveals the face centered cubic (fcc) structure of Si nanoparticles with a zone axis [111].

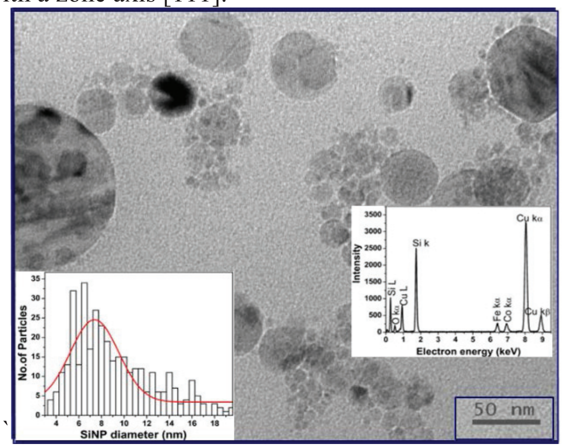

FIGURE 2: Distribution and corresponding histograms of Si NPs.

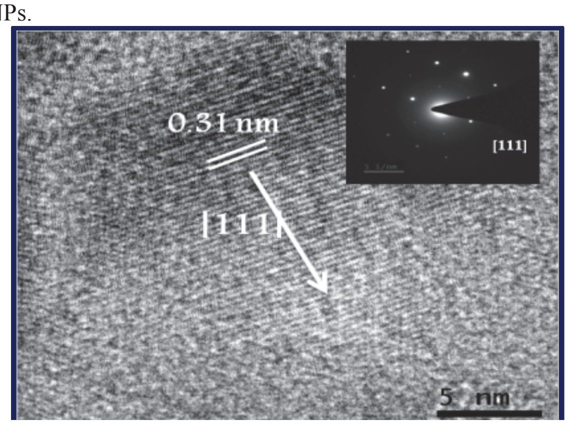

FIGURE 3: HRTEM image of a single Si NP (inset-SAED).

Swift Heavy Ion (SHI) Irradiation effects on Si NPs

We have performed SHI-irradiation on Si NPs generated by laser ablation. The colloidal Si NPs generated on pSi target prepared at J=5 mA/cm^2 was drop-casted onto TEM grid for SHI-irradiation. The amount of energy deposition and consequent damage creation in nano-scale objects decreases with increase in incident energy, which is contrary to the situation observed in bulk Si [11,12]. The degree of disorder depends on nanoparticle size due to its large surface to volume ratio. Fig. 4 depicts the effects of 120 MeV Au ion irradiation on isolated Si NPs at different fluences (5×10^{12}, 1×10^{13} and 3×10^{13} ions/cm^2). The formation of smaller Si species in the vicinity of isolated Si NPs was observed as a result of sputtering during ion irradiation. From data presented in Fig. 4, the boundaries of irradiated Si NPs were found to be hazy and the haziness was found to increase with increasing fluence. This observation gives a clear understanding of collective electronic and nuclear energy deposition on Si NPs, which is responsible for breaking of Si-Si bonds. The broken bonds collectively agglomerated to form smaller Si NPs under SHI-irradiation.

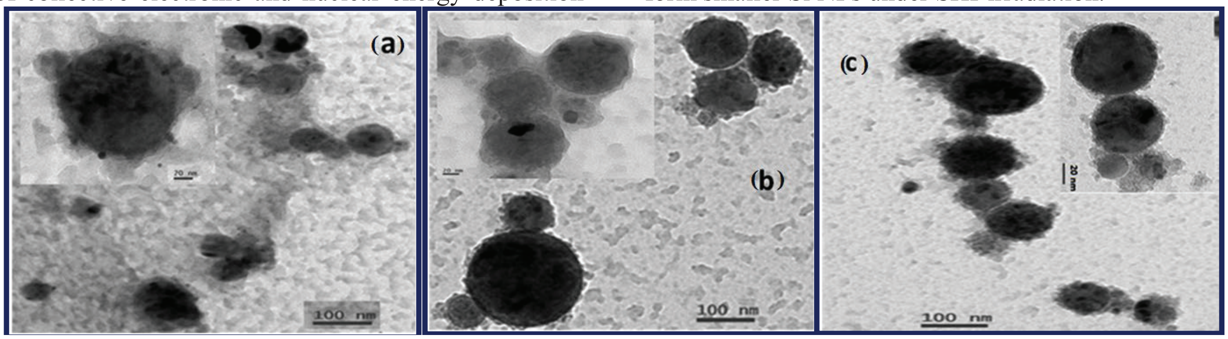

FIGURE 4: TEM images of Si NPs irradiated by 120 MeV Au ions at fluences of a) 5×10^{12} ions/cm^2 b) 1×10^{13} ions/cm^2 , and c) 3×10^{13} ions/cm^2.

TABLE 1: Physical and optical parameters of pSi used for laser ablation.

pSi target used for ablation	Estimated thickness of pSi layer (μm)	Porosity of pSi layer (%)	PL peak position (nm)	Average diameter of pore walls (nm)
pSi-5 mA/cm^2	1.89 ± 0.29	71	651	6.9 ± 0.07

TABLE 2. Particle sizes of Si NPs estimated by different analytical techniques.

Sample label	Estimated average Particle diameters d (nm)		
	TEM	Raman	UV-Vis
Si NP-5	7.6 ± 3.0	5	9

CONCLUSIONS

Ultra-small silicon nano-particles were synthesized by ablating porous silicon using femto second laser in liquid medium. The size distribution of silicon nanoparticles is estimated to be in the range of 1-10 nm by different analytical techniques. HRTEM image of a single isolated Si NP shows the crystalline lattice fringes with lattice spacing of 0.31 nm corresponding to the inter-planar spacing of [111] planes in Si lattice. The crystalline structure of the generated silicon nanoparticles have been confirmed by SAED. The dissociation of Si NPs has been observed in the boundary of isolated Si NPs when subjected to high energy heavy ion irradiation. This observation gives a clear understanding of collective electronic and nuclear energy deposition on nano scale objects.

ACKNOWLEDGMENTS

VSV thanks CSIR New Delhi for RA in the Emeritus Scientist project awarded to APP. We thank IUAC, New Delhi for high energy ion beam facility. SVSN and SVR thank UPE-II, UoH for partial financial support.

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