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Mechanistic details of the formation and growth of nanoscale voids in Ge under extreme conditions within an ion track

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Abstract

The initial steps of Ge nanovoids formation have been studied. Two step energetic ion irradiation processes was used to fabricate novel and distinct embedded nanovoids within bulk Ge. The formation of voids in amorphous-Ge (a-Ge) and their size, and shape evolution under ultra-fast thermal spike within ion track of swift heavy ion, is meticulously expatiated using - formed in single ion track tends to attain spherical shape as the ion tracks overlap at about 1×10^{12} ions cm^{-2} and the void assumes prolate spheroid shape with major axis along the ion trajectory at sufficiently high ion fluences. Small angle X-ray scattering can provide information about primary stage of void formation hence this technique is applied for monitoring simultaneously their formation and growth dynamics. The results are supported by transmission (XTEM) and scanning (XSEM) electron micrographs. The multi-time-scale theoretical approach corroborate the experimental findings and relate the bow-tie shape void formation to density variation as a result of melting and resolidification of Ge within thermal spike generated along ion track plus non-isotropic stresses generated towards the end of the thermal spike.

Introduction

Nanostructured semiconductors have attracted widespread attention from broad scientific community due to their unique quantum-confined nanoscale properties. In particular, physical properties of micro and nanoporous semiconductors have been the subject of numerous studies during the past decades. Germanium (Ge) is one of these material receiving substantial attention which has been extensively investigated and matured to industrial applications recently. Moreover, fabrication of nano-scale voids in the bulk and on the surface of a-Ge is important as porosity plays an important role in visible photoluminescence [1,2] from porous Ge which is realized as a key to the future optoelectronic device fabrication. Porous materials can have numerous surface chemistry related applications due to the porosity induced increase in surface area [3]. Furthermore, through its tailoring, porous material can be functionalized and also used as filters [4], gas sensors [5], thermoelectric elements [6], solar cells [1] and high efficiency anodes for electric batteries [7].

Ion beam induced process is a superior technique to overcome the drawbacks of conventional methods of porous structures formation [2,8,9] as the latter incorporates chemical contamination in the sample along with the porous structures. Moreover, in conventional techniques, there is no uniformity of porosity and directionality e.g. $\langle 113 \rangle$ is a preferred direction in Si [10,11] that is quite unexplained still. As compared to the conventional porous structure fabrication method like anodization or chemical etching [8], ion beams may be used to synthesize pores with controlled size and positions without contamination. Production of these voids can be controlled by varying the ion beam parameters such as energy, fluence, angle of irradiation etc. [12,13]. This enables porous layer formation in pre-amorphized region with predefined three dimensional void structures. Furthermore, swift heavy ion (SHI) induced void formation is independent of their electrical properties and restricted to a-Ge only as c-Ge is rather insensitive to electronic energy loss (S_e) [3,14]. The fascinating applications underscore the basic interest in theoretical understanding of formation of voids in Ge using ion beam irradiation. Well-defined nanostructures were reported within amorphous Ge during bombardment with energetic heavy ions eventually resulting in nanohole patterns [15], nanoporous or sponge-like structures [16]. Moreover, nanoholes, nanodot pattern and porous structure formation at the surface has been reported in Ge under keV ion irradiation in recent years [17,18]. Despite the increasing interest in void formation in Ge, nanostructure formation on Ge surface due to high energy ion irradiation has been studied to a much lesser extent along with less understanding. Recently, the S_e effect of SHI on void formation in a-Ge layers is

reported by few groups. Gartner *et al.* [19] reported that outgoing shock waves, resulting from transient heating and expansion of the ion-track core due to SHI irradiation, is the origin of voids. Our group also studied response of pre-damaged Ge under 100 MeV Ag ions irradiation [20,21] to report the growth dynamics and shape evolution of voids [3]. For the sake of completeness, surface modification due to high energy ion irradiation in Ge and role of electronic sputtering on these surface pattern formations was also presented [14,22]. Ridgway *et al.* [13] reported the SHI induced bow-tie shape void formation resulting from the melting of Ge during thermal spike and its re-solidification. Due to detection difficulties of amorphous ion tracks in an amorphous matrix using transmission electron microscopy (TEM), the small angle x-ray scattering (SAXS) technique was employed by Ridgway *et al.* [13] for characterizing ion tracks and voids formed in single track. Moreover, glancing incidence small-angle x-ray scattering (GISAXS) is an effective means to quantify the growth dynamics of voids in terms of dimensions in both in-plane and out-of-plane orientations. GISAXS technique is well established and widely used to study formation and modification of nanostructures especially by ion beams [23-25]. This technique is suitable to study nano porous structures as X-ray scattering is highly sensitive to contrast of electron density in medium [26].

In present report, we utilized GISAXS and microscopy techniques (like TEM, SEM) to study the formation and growth dynamics of voids in a-Ge. A multi-time-scale theoretical approach including an asymptotical trajectory Monte Carlo (MC) calculation of the electron dynamics, a two-temperature model (TTM) description of the heat dissipation and a MD simulation of the atom dynamics for ion tracks in a-Ge is also used for corroborating the experimental findings. Using this novel approach, we have investigated the shape evolution of void in ion-track experimentally and substantiated theoretically.

Experimental Details

Pre-amorphization of c-Ge wafer was carried out using Ar ion implantation of four energies varying from 0.3 to 2 MeV resulting in an amorphous Ge layer of thicknesses $\sim 1.2 \mu\text{m}$ on c-Ge. The damage introduced by irradiation was estimated to be 7 DPA (displacement per atom) as calculated using Monte-Carlo simulation SRIM [27]. Subsequent irradiation was performed of these samples with 100 MeV Ag ions (nuclear stopping power $S_n = 0.1 \text{ keV nm}^{-1}$, $S_e = 16.4 \text{ keV nm}^{-1}$) [27] to ion fluences ranging between 1×10^{11} and $1 \times 10^{13} \text{ ions cm}^{-2}$. The beam was delivered from Pelletron accelerator at IUAC (Delhi), with controlled ion flux of $\sim 1 \times 10^{10} \text{ ions cm}^{-2} \text{ s}^{-1}$. Here S_n/S_e being $\sim 10^{-3}$, energy loss by electronic process dominates over nuclear

energy loss and ensuring uniform energy deposition within damaged layer due to significantly higher range of Ag ion ($\sim 12 \mu\text{m}$) as compared to the extent of the amorphous layers. Multiple techniques such as synchrotron based Glancing Incidence Small Angle X-Ray Scattering (GISAXS), Field Emission Scanning Electron Microscopy (FE-SEM) [MIRA-II LMH, TESCAN] in cross-section mode, Cross section transmission electron microscopy (XTEM) and Molecular Dynamics (MD) simulations have been applied to derive models that describe the formation and growth dynamics of open volume in a-Ge under energetic ion irradiation. Electron beam of energy 7 keV and 300 keV was used to capture the SEM and XTEM images, respectively. XTEM was performed in the present case using FEI, Tecnai, F30-ST. GISAXS measurements were performed at the SAXS beamline in synchrotron ELETTRA, Trieste (Italy) [28] using the X-ray beam with θ_i , with respect to the sample surface minimizes the undesirable scattering from the bulk and enhances the near-surface scattering. Hence, GISAXS spectra were recorded at an angle of incidence of 1° to maximize the contribution from the voids containing layer and to avoid contribution from the crystalline Ge beneath it. The scattering intensity spectra of x-rays were acquired by a two-dimensional position sensitive detector PILATUS 1M, placed perpendicular to the incident beam, at a detector to sample distance of $L = 2000 \text{ mm}$. These GISAXS spectra were recorded by keeping the experimental condition constant, like duration of measurement, glancing angle of x-ray and detector distance to avoid any uncertainty on comparing within the samples. A schematic diagram presenting the experimental setup is shown in figure 1. The wave vectors corresponding to incident (k_i) and reflected (k_r) beam form k_i and k_r with the sample surface, respectively. On the other hand, the angle subtended by the scattered wave with the x-axis is denoted by θ_f . Scattered intensity $I(q_y, q_z)$ recorded by the detector corresponds to a collective momentum transfer by an assembly of particles. The horizontal direction in the detector probes the reciprocal space along coordinate parallel to the surface. Therefore, q_y gives information about the correlations parallel to the surface like cluster correlation distance and cluster radii. The vertical direction in the detector probes the reciprocal space coordinate perpendicular to the surface. DPDAK software has been utilized to extract and integrate the line profiles (along y and z direction) from raw data [29]. The size distribution of voids was quantified by analysing the projected data using structure factor of different shapes for a best fit.