Journal of Alloys and Compounds 715 (2017) 247–253

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Embedded Si nanoclusters in α-alumina synthesized by ion implantation: An investigation using depth dependent Doppler broadening spectroscopy

S.K. Sharma, P.K. Pujari*

Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai, 400085 India

ARTICLE INFO

Article history:
Received 14 February 2017
Received in revised form
24 April 2017
Accepted 27 April 2017
Available online 29 April 2017

Keywords:
Nanoclusters
Ion implantation
Doppler broadening
Positron annihilation spectroscopy
VEPFIT

ABSTRACT

Embedded Si nanoclusters in optically transparent host materials have shown potential applications in opto-electronic devices. Ion implantation followed by annealing at higher temperatures is considered a promising way to produce embedded nanoclusters in variety of host materials. In the present work, α-alumina crystals were irradiated with Si ion beam (50 keV) with varying total dose (1×10^{16}, 5×10^{16} and 1×10^{17} ions/cm^2). The ion implantation and vacancy defect profiles in alumina have been calculated using computer code SRIM. The irradiated samples were annealed at 500 and 1000 °C in a reducing atmosphere for 30 min. Depth dependent Doppler broadening measurements using high purity Germanium (HPGe) detector coupled to a slow positron beam were carried out on as-irradiated as well as annealed samples. The line shape (*S*- and *W*-) parameters showing contribution from valence (low momentum) and core (high momentum) electrons were evaluated from the positron implantation energy dependent Doppler broadened spectra. The *S-E* profiles of as irradiated samples indicated the formation of open volume defects in the damaged region. On annealing, *S-E* profiles are modified in the damaged region that is attributed to the formation of vacancy clusters and Si nanoclusters as confirmed through *S-W* correlation plots. The *S-E* profiles have been fitted using variable energy positron fit (VEPFIT) to evaluate the characteristic *S*-parameter corresponding to the damaged region. It is observed that ~90% of implanted positrons in the damaged region are confined to the Si nanoclusters due to their high affinity toward Si as compared to host material, α-alumina. The present study confirms that positrons are confined in embedded nanoclusters and acts as a self seeking probe for their characterization.

1. Introduction

Nanocrystalline silicon has attracted wide attention for its application in opto-electronics due to their charge storing capacity and intense photoluminescence [1,2]. Si nanocrystals embedded in SiO_2 has been extensively studied for its applications as charge storing and optoelectronic devices. Shrinking in dimensions of the charge storage devices has lead to search of materials with higher dielectric constant than SiO_2 but with similar insulating properties. Al_2O_3 with its dielectric constant twice as compared to SiO_2 is a promising choice for the purpose. The band gap of Al_2O_3 (9.2eV) is very much similar to band gap of SiO_2 (8.7 eV) [3]. Due to optical transparency of Al_2O_3, it can be considered as a suitable host for Si nanocrystals for its applications in opto-electronic devices. Nanocrystals formation in Al_2O_3 matrix has been achieved using combination of techniques such as co-sputtering [4], pulsed laser deposition [3], electrochemistry [5] and ion-implantation [6–8]. In ion implantation process, super saturated solution of implanted ions in the near surface region is annealed at higher temperature which leads to formation of embedded nanocrystals in the matrix. Formation of nanocrystals in a host matrix depends on the diffusion and solubility of the implanted ions. The opto-electronic properties of embedded nanocrystals depend on the size as well as local structure which in turn depend on the dose of implanted ions and annealing temperature and time. Various characterization techniques such as electron microscopy, X-ray diffraction, photo luminescence, Raman Spectroscopy, Fourier transform Infra red spectroscopy etc. are used to investigate the size as well as local structure of the embedded nanocrystals [8].

In last decade, depth dependent positron annihilation Doppler

* Corresponding author.
E-mail address: pujari@barc.gov.in (P.K. Pujari).

http://dx.doi.org/10.1016/j.jallcom.2017.04.285
0925-8388/

broadening spectroscopy (DBS) has been used to investigate the formation of vacancy defects as well as nanocrystals as a result of ion implantation followed by annealing [9–12]. Positron has high propensity for the low density regions (open volume defects) in a material. As a result, positron is a highly sensitive probe for the investigation of vacancy defects in crystalline materials. Positron annihilates with electron predominantly emitting two 511 keV photons in opposite direction. In materials, the annihilation photon energy (511 keV) is Doppler shifted by ΔE keV due to non-zero energy of annihilating positron-electron pair. The shift (ΔE) in the photon energy mainly depends on the momentum of annihilating electron in the direction of gamma emission (P_L) because positron is already thermalized. As a result of electron momentum distribution in a material, Doppler broadening of the annihilation peak (511 keV) occurs up to several keV which can be directly measured using a high purity Germanium (HPGe) detector due to its superior energy resolution. In case of positron trapping in vacancy defects, the overlap of valence and core electrons with positron reduces but the extent of reduction for core electron (high momentum region) is much higher as compared to valence electron (low momentum). In order to index this variation, the annihilation peak is characterized using two line shape parameters viz. *S*- and *W*- parameter which indicate the relative contribution in the low momentum (valence electron) and high momentum (core electron) region, respectively [12]. In last decade, it has been shown that positron is a self seeking probe for the embedded nanoclusters in variety of host materials. Positron annihilation technique has been successfully used to investigate the formation of Li clusters in Al_2O_3 [12], Cu clusters in Fe [13], Li [10], ZnO [14], Au [11,15], Zn [14] and CdSe [9] clusters in MgO. As mentioned before, embedded Si nanocrystals in α-alumina are shown to have potential application for opto-electronic devices; hence investigation on formation of these clusters using various techniques is required. In present study, role of ion implantation dose as well as annealing temperature on formation of vacancy defects and Si nanocrystals in α-alumina has been investigated using depth dependent positron annihilation Doppler broadening spectroscopy. The experimentally observed *S-E* and *W-E* profiles have been fitted using a computer program 'variable energy positron fit' (VEPFIT) [16]. The formation of Si nanoclusters has been confirmed through *S-W* correlation plots. The study shows that positrons act as self sleeking probe for embedded Si nanoclusters due to their confinement in the nanoclusters.

2. Experimental

Si ion (50 keV) implantation on α-alumina has been carried out using a Low Energy Accelerator Facility (LEAF) at Bhabha Atomic Research Centre, Mumbai. α-Alumina (12 × 12 mm) sample was exposed to Si beam (current ~ 200 nA, size ~ 10 mm^2) for varying time to achieve the total implantation doses 1×10^{16} (Sample A), 5×10^{16} (Sample B) and 1×10^{17} (Sample C) ions/cm^2. No cooling arrangements are made for the sample cooling through irradiation. The samples were annealed at 500 and 1000 °C for 30 min in reducing atmosphere (Ar + 10% H_2). The ion implanted as well as annealed samples (after each annealing step) were characterized using Depth dependent Doppler broadening spectroscopy. The measurements were carried out using HPGe detector having energy resolution 1.4 keV at 514 keV of ^{85}Sr, coupled to slow positron beam. The details of this set up can be found elsewhere [17]. The positron energy is varied from 0.2 keV to 12.2 keV by floating the sample at requisite voltage and Doppler broadening spectra were acquired (total counts ~ 2×10^5 counts). The *S*-parameter was calculated as fractional area in the low momentum region (511.000 ± 0.682 keV), and the *W*-parameter was calculated as area under 3.18 keV window centered at (511.000 ± 5.25 keV) in the high momentum regions.

3. Results and discussion

Implantation profile of 50 keV Si ions in α-alumina calculated using computer code SRIM-2013 [18] is shown in Fig. 1. The profile shows that the range of Si ions is ~42 nm with straggling of 15.3 nm. Ion implantation causes atom displacements into the lattice resulting in the formation of vacancy defects. Fig. 2 shows the Al and O vacancy distribution profiles as a result of Si ion implantation. It is observed from these figures that the vacancy distribution profiles are rather broad compared to the Si ion distribution profile. The peak position of the vacancy distribution profiles is ~30 nm which is less as compared to range of the implanted ions. The ion implantation profile as shown in Fig. 1 can be divide into four regions viz. surface region (SR; 0–5 nm), tail region (TR; 5–30), Cascade region (CR: 30–100 nm) and non implanted region (NIR: beyond 100 nm). Surface region may have artifacts due to preexisting defects like stacking faults as well as sputtering due to ion implantation. TR represents the region where nuclear stopping is not predominant in the energy loss process of the implanted ion. CR represents the region of nuclear stopping of the implanted ions wherein most of the implanted ions are stopped which generally occupy the interstitial positions in the host material. Beyond CR, ion implantation effects are non significant and the region is termed as non implanted region (NIR).

Fig. 3 shows the *S-E* profiles of the pristine and Si ion implanted samples. The mean implantation depth <z> (nm) shown on the top axis in the figure is calculated using Equation (1) where ρ (g/cc) and *E* (keV) are the density of material and energy of implanted positrons, respectively [19].

$$\langle z \rangle = \frac{40}{\rho} E^{1.6} \tag{1}$$

The *S-E* profile of pristine sample is typical of crystalline materials. The *S*-parameter initially decreases and reaches a plateau at higher positron implantation energy. The observed profile is attributed to the back diffusion of positrons to the surface where they predominantly annihilate via a positronium like state resulting in high value of *S*-parameter at surface. With the increase in implantation energy, the fraction of positrons reaching to surface reduces and a constant *S*-parameter value characteristic of the bulk material is obtained. On Si ion implantation, the changes are observed in *S-E* profiles in positron energy range 1–4.5 keV (damaged Region, DR) corresponding to positron implantation depth 10–112 nm. This region corresponds to the TR as well as CR

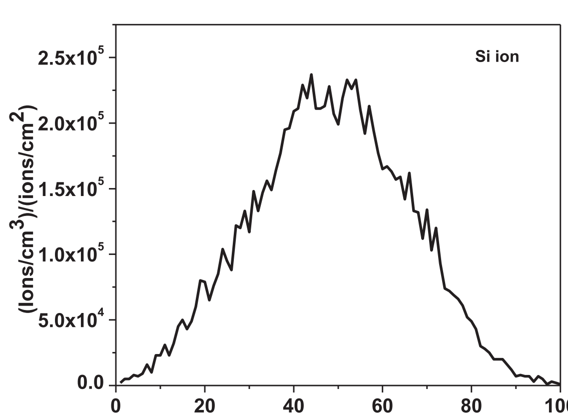

Fig. 1. Implantation profile of 50 keV Si ions in α-Al_2O_3 using code SRIM.