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Evolution of embedded lithium nanoclusters in lithium implanted alumina

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HIGHLIGHTS

- Embedded Li nanoclusters are efficiently created by annealing Li implanted Al_2O_3 crystal.
- Depth dependent DBAR is a suitable method to characterize embedded nanoclusters.
- The formation of Li nanoclusters is assisted by vacancy migration to form clusters.
- At very high annealing temperature (>1000 °C), Li nanoclusters undergo breakdown.
- e^+ annihilation at V_{Al} site shows a unique observation i.e. a reduction in S-parameter.

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ABSTRACT

High dose of ion implantation followed by annealing is considered a feasible way to generate thermally stable nanoclusters inside a transparent host matrix. Low energy (50 keV) Li ions have been implanted into single crystals of alumina with different fluence (1×10^{15}–1×10^{17} ions/cm^2). The samples have been annealed at temperatures ranging from 500 to 1100 °C in air in step of 100 °C. Depth dependent Doppler broadening measurements have been carried out using high purity germanium detector coupled to a variable energy slow positron beam. Fractional area in the central and wing regions of Doppler broadened annihilation radiation spectrum, namely, S- and W- parameters, were evaluated from each spectrum. Any variation in positron annihilation probability with valence and core electrons which occurs on trapping of positrons at a defect site is reflected in these parameters. The effect of ion fluence and annealing temperature on evolution of defects and formation of embedded Li nanoclusters have been studied by indexing the variation in line shape S- (W-) parameter as a function of positron implantation depth. These studies supplemented by theoretical calculations confirm that with annealing up to 700 °C, vacancy clusters are created due to the aggregation of vacancies wherein Li nanoclusters are formed. On annealing at higher temperature, there is evidence for the breakdown of these Li clusters leaving behind vacancy clusters in the samples.

1. Introduction

Nanoclusters or nanocrystals of metals or semiconductors embedded in wide band gap ceramics display optical properties (linear or nonlinear) relevant to the field of opto-electronics [1–5]. In this regard, alumina is a suitable matrix due to its superior properties such as wide band gap, optical transparency, non-conducting and high melting temperature etc. [6]. Various techniques such as laser ablation, molecular beam epitaxy, gas phase condensation and solution chemistry etc. are used to synthesize the self-assembled nanoclusters. A more feasible way to generate thermally stable nanoclusters is to produce them inside a transparent host matrix. This can be achieved by high dose of ion implantation followed by annealing [1,7–13]. Synthesis of metal or semiconductor clusters such as Si in SiO_2; Cd and CdS in Al_2O_3; Li, Zn, Ag and Au in MgO etc. by ion implantation have already been reported [9,11,12,14]. During this process, a super saturated solution of implanted ions is produced at near surface region which leads to

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precipitation (formation of nanoclusters) on thermal annealing provided the implanted ion has low solubility in the host matrix. The structure and properties of nanoclusters mainly depend on their shape, size, distribution in the matrix and the lattice structure of host matrix itself. Hence, it is essential to understand the process of formation of such nanoclusters [15,16]. Investigation of embedded nanoclusters produced by multiple ion implantation and intermediate annealing steps has been proved to be an efficient method for these studies [17].

It is well known that mass and energy of the implanted ion, its solubility and diffusion in the host material are some of the crucial parameters governing the growth of the embedded nanoclusters. However, formation of the defects due to ion implantation and their behaviour with annealing can also play a crucial role in the nanocluster growth. Positron, due to its propensity for open volume defects is an established probe for the identification of the type and the size of defects. Positron being an antiparticle of electron, undergoes annihilation with electrons predominantly via 2γ photon mode. The annihilation photons (511 keV) are emitted collinearly in opposite direction. For electron-positron pair with non-zero energy, which is true for positron annihilation in any material, the photon energy is shifted from the value ~511 keV depending upon the momentum of annihilating pair (predominantly due to the momentum of electron as positron is thermalized) in the direction of γ-ray emission. The energy of photons produced by such event will be equal to $511 \pm \Delta E$. The term ΔE is called Doppler shift which is equal to $cP_L/2$, where c is speed of light and P_L is the momentum of annihilating pair in the direction of γ-ray emission (longitudinal component of momentum). The Doppler broadening of 511 keV peak ranges up to several keV and can be measured using a high purity Ge detector (HPGe) due to its superior energy resolution. The shape of the Doppler broadened annihilation peak is evaluated in terms of relative contribution to the central as well as wing regions, namely, *S*- and *W*- parameters, respectively. The primary contribution to *S*- and *W*-parameters arises from positron annihilation with low momentum (valence) and high momentum (semi-core or core) electrons, respectively. Any variation in positron annihilation probability with valence and core electrons which occurs on trapping of positrons at a defect site is reflected in these parameters. The *S*- and *W*-parameters show linear correlations for varying concentration of similar type of positron trapping sites.

Different techniques such as X-ray diffraction, photoluminescence, electron microscopy and Rutherford backscattering etc. are used to study the formation as well as structure of embedded nanoclusters. It has been shown that positron can act as a self seeking probe for nanoclusters embedded in a matrix provided positron has higher affinity towards nanoclusters compared to the host matrix [8,10,11]. Depending on the positron affinity difference between nanoclusters and host matrix, a large fraction of implanted positrons is confined to the nanoclusters. For example, 92% of implanted positrons were shown to be confined to Li nanoclusters embedded in MgO while the local fraction of Li at the implantation depth was just 1.3% [11]. These studies have paved the way for application of positron annihilation spectroscopy (PAS) in characterization of local structure of embedded nanoclusters.

PAS has been successfully used to characterize the Cu clusters in Fe; and Li, Au, Zn, ZnO, Cd and CdSe clusters in MgO [8,10,11,18–20]. In the case of Cu clusters in Fe and Li clusters in MgO, positrons are confined to nanoclusters mainly because of higher positron affinity as well as a coherent interface. On the other hand, positrons are mainly trapped at interface due to lattice mismatch as in the case of Zn as well as Au clusters in MgO. All these studies have shown that evolution of nanoclusters and associated defects can be indexed from Doppler Broadening of Annihilation Radiation (DBAR) measurements using variable energy positron beam technique. On the other hand, it has been reported that Li ion implantation in ZnO followed by annealing does not result in Li nanoclusters formation, reason for which is not well understood. In this case, the observed variation in *S*-parameter as a function of annealing temperature has been solely ascribed to the migration and aggregation of vacancy defects [21]. These necessitate further investigations to shed more light on the evolution of defects and nanoclusters as a result of ion implantation followed by annealing.

Al_2O_3 is a wide band gap material and has been used as a suitable host for creation of variety of embedded nanoclusters [9,12,22–25]. The positron affinity value for Al_2O_3 has been theoretically calculated by Slugen et al. [26] which is less compared to bulk Li. It implies that embedded Li clusters in Al_2O_3 can provide another suitable system for observing positron confinement. In order to study Li nanocluster formation mechanism in Al_2O_3 matrix, Li ion (50 keV) implantation has been carried out in α-Al_2O_3 crystals followed by thermal annealing at different temperatures. DBAR measurements are carried out in as-implanted and annealed samples to investigate the evolution of ion implantation related defects and embedded Li nanocluster. In order to supplement the experimental observations, positron annihilation parameters have been calculated in Al_2O_3 lattice with a variety of probable defects. Theoretical calculations are also carried out on Li cluster in Al_2O_3 to examine if positrons are confined to the cluster. On the basis of these results, a possible mechanism of Li nanoclusters formation in α-Al_2O_3 matrix is proposed.

2. Computational details and theoretical methodology

The ion implantation profile as well as the recoil defect profiles have been calculated using code SRIM [27,28]. At room temperature, α-Al_2O_3 is a trigonal crystal system (space group $R\bar{3}C$). For electron momentum distribution calculations, the alumina tetragonal supercell containing 120 atoms (24 units of Al_2O_3) with experimental lattice parameters as $a = b = 4.759$, $c = 12.993$ Å is chosen [29]. In the case of the lithium clusters in alumina, a 960 atom supercell is used for the calculations. Calculations of annihilation electron momentum distribution is carried out using density functional theory (DFT) employed in 'MIKA/DOPPLER package' [30]. The experimental lattice parameters without considering ionic relaxations are used for this purpose. The 'conventional scheme' is used in the calculations. The electron density of the solid is approximated by non-self consistent superposition of free atoms in the absence of positron according to 'conventional scheme'. The potential felt by the positron is also generated in a similar way [31]. The electron-positron enhancement factor was parameterized using gradient-corrected scheme. For performing the calculations, correlation potential developed by Arponen-Pajanne was used [32].

The theoretical electronic self-consistent calculations and ionic relaxation are performed using VASP package [33,34]. The electronic calculations were performed using accurate plane augmented wave (PAW) method as implemented in VASP [35,36]. The exchange correlation energy functional is used as given by Perdew, Burke and Ernzerhof (PBE) within the generalised gradient approximations (GGA) with the supercell approach [37]. The optimised plane wave basis cut-off (ENCUT = 300 eV) is used for all the calculations. The self-consistent total energy in ground state was obtained by the density-mixing scheme. Atomic positions were optimised to minimise the total energy of lattice using the conjugate gradient (CG) algorithm. The optimization of ionic relaxation procedure was truncated when the electronic energy and ionic forces lowers up to 10^{-4}eV and 10^{-3} (eV/Å), respectively for all the calculations. Gauss broadening up to 0.001 units is used to treat partial occupancies by Gaussian smearing and sometimes Fermi-smearing scheme. The unit cell of alumina is optimised for lattice