Journal of Non-Crystalline Solids 358 (2012) 3187–3192

Contents lists available at SciVerse ScienceDirect

Journal of Non-Crystalline Solids

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

# Interplay of ballistic and chemical effects in the formation of structural defects for Sn and Pb implanted silica

R.J. Green [a,*], A. Hunt [a], D.A. Zatsepin [b,c], D.W. Boukhvalov [d], J.A. McLeod [a], E.Z. Kurmaev [b], N.A. Skorikov [b], N.V. Gavrilov [e], A. Moewes [a]

[a] Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon, Saskatchewan, Canada S7N 5E2
[b] Institute of Metal Physics, Russian Academy of Sciences-Ural Division, 18 Kovalevskoi Str., 620990 Yekaterinburg, Russia
[c] Ural Federal University, 19 Mira Str., 620002 Yekaterinburg, Russia
[d] School of Computational Sciences, Korea Institute for Advanced Study (KIAS), Hoegiro 87, Dongdaemun-Gu, Seoul, 130-722, Republic of Korea
[e] Institute of Electrophysics, Russian Academy of Sciences-Ural Division, 620016 Yekaterinburg, Russia

ARTICLE INFO

*Article history:*
Received 10 July 2012
Received in revised form 5 September 2012
Available online 5 October 2012

*Keywords:*
Ion implantation;
X-ray absorption spectroscopy;
X-ray emission spectroscopy;
Density functional theory

ABSTRACT

The electronic structures of Sn and Pb implanted $SiO_2$ are studied using soft X-ray absorption (XAS) and emission (XES) spectroscopy. We show, using reference compounds and ab initio calculations, that the presence of Pb–O and Sn–O interactions can be detected in the pre-edge region of the oxygen *K*-edge XAS. Via analysis of this interaction-sensitive pre-edge region, we find that Pb implantation results primarily in the clustering of Pb atoms. Conversely, with Sn implantation using identical conditions, strong Sn–O interactions are present, showing that Sn is coordinated with oxygen. The varying results between the two ion types are explained using both ballistic considerations and density functional theory calculations. We find that the substitution of Pb into Si sites in $SiO_2$ requires much more energy than substituting Sn in these same sites, primarily due to the larger size of the Pb ions. From these calculated formation energies it is evident that Pb requires far higher temperatures than Sn to be soluble in $SiO_2$. These results help explain the complex processes which take place upon implantation and determine the final products.

## 1. Introduction

In recent years, ion beam synthesis has become a widespread and valuable technique for the modification of the structural, optical, electronic, and magnetic properties of semiconductors and dielectrics. These properties are often modified through the formation of nano-sized embedded aggregates, which can lead to phenomena such as intense photoluminescence, altered band structures, nonlinear optical effects, and superparamagnetism [1–3]. The materials synthesized with this technique have attracted attention as candidates for promising new applications in fields such as optoelectronics.

Ion implantation is known to be a very versatile technique for material synthesis as one can embed almost any elemental ion within almost any host material in a very controlled manner. The success of the ion beam synthesis technique, however, relies heavily on the careful consideration of the many processes which take place upon ion beam irradiation of a material [4]. Variations in any experimental parameters such as ion type, implantation energy, target compound, temperature, etc., can lead to strong variations in the final products. An often successful approach to understanding or predicting the final products of implantation is termed the *two-step model* (see, for example, Refs. [2,5]), which considers separately the effects of the high-energy physical step characterized by ballistic effects, and the subsequent low-energy chemical step based on thermodynamic considerations.

While the two-step model is often useful for predicting the physical and chemical states of an ion beam irradiated material, it is not always clear which step dominates for given implantation parameters. For example, high energy, high fluence implantation typically leads to more host damage. In such a case the ballistic effects are undoubtedly strong, but the severe rearrangement of the host structure due to ballistic effects consequently provides a prime situation for chemical reordering. For low fluence, low energy implantation, disturbance to the host is small, so both ballistic and chemical effects are somewhat reduced, likely leading to only interstitial ions in the extreme case. Thus, at the current time, it is often difficult to tell a priori what form the final product will take and why.

In the current work we study the implantation of Pb and Sn ions into amorphous, bulk $SiO_2$, using periodically pulsed ion implantation and no thermal annealing. $SiO_2$ implanted with Sn [6–8] and Pb [9,10] has shown promise in past studies regarding the formation of metallic or oxide nanoclusters and subsequent non-linear optical properties and Coulomb blockade effects. A combination of X-ray absorption (XAS) and emission (XES) spectroscopy is used in the present work to closely study the structural and chemical effects of implantation.

---

[*] Corresponding author.
*E-mail address:* robert.green@usask.ca (R.J. Green).

0022-3093/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jnoncrysol.2012.09.014

Through analysis of the spectra we identify a significant presence of Sn–O bonding, and a prominent lack of Pb–O bonding. The results are explained using the two step model as well as ab initio calculations of formation energies of defect structures. Finally, we shed light on aspects of the ion implantation process which will be important for future studies.

## 2. Material and methods

The amorphous $SiO_2$ ($a$-$SiO_2$) samples used as targets for this study were 99.9% purity, plane-parallel glass plates measuring $1\times1$ $cm^2$ with surfaces of optical quality and thicknesses of ~0.7 mm. Separate samples were irradiated with $Sn^+$ and $Pb^+$ ions using a pulsed source with an ion beam current density of ~2–7 $mA/cm^2$, implantation energy of 30 keV, ion fluence of $5\times10^{16}$ $cm^{-2}$, and a pulse duration of 400 μs. The frequency of pulse repetitions was about 15 Hz and total implantation times were 3–4 min. The surface temperatures of the samples during $Sn^+$ and $Pb^+$ irradiation did not exceed 300 K due largely to the low currents used. No thermal annealing was performed after implantation. A high-purity $a$-$SiO_2$ sample was also left unirradiated for use as a reference material.

An additional reference material consisting of a $PbO/SiO_2$ mixture was synthesized via melting 99.9% purity PbO and $SiO_2$ in a corundum crucible under normal atmosphere. A ratio of 35:65 $PbO:SiO_2$ was used, and the mixture was kept at 1000–1300 °C for 3 h. The samples were then baked at 350–400 °C for 20 min and slowly cooled. All samples under study and references were prepared in the Ural Federal University (Yekaterinburg, Russia).

The penetration depths for $Sn^+$ and $Pb^+$ ions, as well as damage profiles for the $SiO_2$ host, were estimated using the SRIM program [11]. The program uses a *Monte Carlo*-based binary collision approximation to model the interaction of the ions with the solid. Simulations were performed using the same materials and implantation energies implemented in the experiment, and the implantation of a total number of $10^5$ ions was simulated in each case to obtain adequately converged profiles.

The electronic structure calculations of pure PbO, SnO, and crystalline $SiO_2$ were performed using the ab initio WIEN2k code [12] which is based on the full-potential augmented plane-wave method with scalar-relativistic corrections. The modified Becke–Johnson variant of the generalized gradient approximation (GGA-MBJ) exchange-correlation functional was used [13], and the ground state density of states (DOS) was calculated in each case. The atomic sphere radii (the cutoff radius between plane waves and spherical harmonics) were chosen as $R_{MT}=1.51$, 2.17, and 2.20 a.u. for the cations in $SiO_2$, PbO, and SnO, respectively, while for the O atoms they were 1.51, 2.17, and 1.75 a.u., respectively [14,15]. They were chosen in such a way that the spheres were nearly touching. The Brillouin zone integrations were performed with a $k$-point grid of up to 800 points and $R_{MT}^{min}K_{max}=7$ (the product of the smallest of the atomic sphere radii $R_{MT}$ and the plane wave cutoff parameter $K_{max}$) was used for the expansion of the basis set.

The formation energy modeling was carried out using the first-principles pseudopotential method as implemented in SIESTA [16]. All calculations were performed using the Perdew–Burke–Ernzerhof variant of the generalized gradient approximation (GGA–PBE) [17] for the exchange-correlation potential. The atomic positions were fully optimized until the inter-atomic force was less than 0.04 eV/Å. A $2\times2\times2$ supercell containing 108 (36 silicon and 72 oxygen) atoms was utilized. All calculations were carried out for an energy mesh cutoff of 360 Ry and $k$-points of $4\times4\times4$ Monkhorst–Pack mesh [18]. To verify the performance of the pseudopotentials we performed an optimization of the crystal structure for bulk $\alpha$-quartz, silicon, tin and lead. In all cases the obtained deviation between experimental and calculated values of lattice parameters was less than 1.5%. The chemisorption energy has been calculated with the help of the standard formula $E_{chem}=(E_{Q+X}-(E_Q-E_{Si}+E_X))/n$, where $E_{Q+X}$ is the total energy of quartz supercell with an X impurity in a Si substitutional position, $E_{Si}$ and $E_X$ are the total energies per atom of silicon and impurity in a bulk phase, respectively, $n$ is a quantity of impurity atoms and $E_Q$ corresponds to the total energy of pure $\alpha$-quartz.

Soft X-ray emission spectra (XES) were measured using Beamline 8.01 of the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory [19]. The beamline uses a Rowland circle type diffraction grating spectrometer with a 90° scattering angle and the incident radiation is plane-polarized in the horizontal direction. Soft X-ray absorption spectra (XAS) were measured using the Spherical Grating Monochromator (SGM) beamline of the Canadian Light Source (CLS) at the University of Saskatchewan [20]. Spectra were collected using the total fluorescence yield detection scheme, again with horizontal plane-polarized incident radiation.

## 3. Results

Fig. 1 shows the simulated depth distributions of the Pb and Sn ions in $a$-$SiO_2$, using the parameters implemented in our experiment and displacement energies of 15 eV and 28 eV for the Si and O atoms of the host, respectively. These simulations provide a very good estimate for the ion distribution within a host for specific implantation parameters. We do note, however, that large fluences (such as those used in this work) may lead to non-negligible density changes in the target during implantation, resulting in an overall slightly shallower ion range than predicted. One can observe from the simulations that Pb and Sn are expected to penetrate similar distances into the $SiO_2$ on average. The ion range calculated for Pb implantation is 20.1 nm, whereas that for Sn is 20.8 nm. Additionally, we see that for the case of Pb the distribution is more spatially localized than that for Sn. We note that the scales for the upper and lower panels have the same values to help show that the Sn concentration does not peak as high as for Pb, and that the ions are distributed in a more gradual nature.

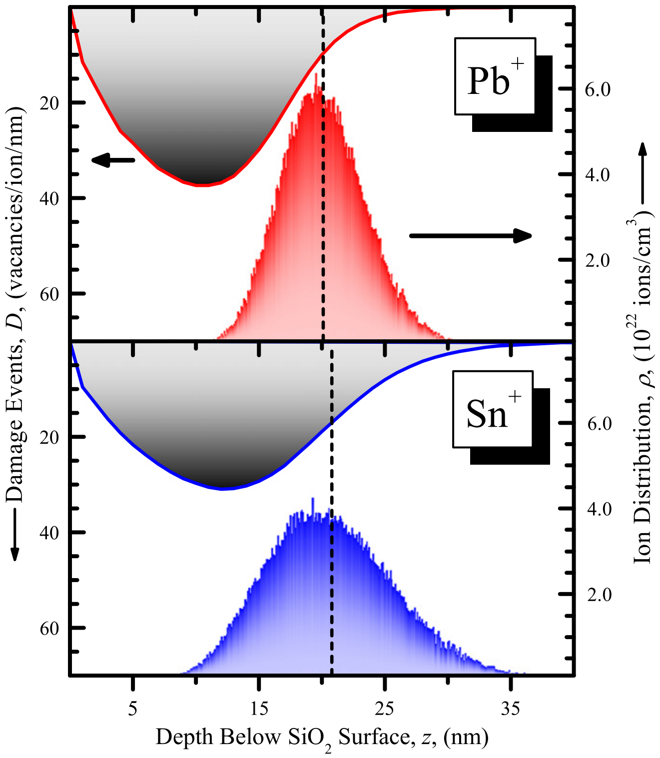

**Fig. 1.** Ion depth distributions and host damage of $Pb^+$ and $Sn^+$ implanted in $SiO_2$. The profiles were simulated using the SRIM program [11] with the experimental implantation parameters given in Section 2.