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Thin Solid Films 516 (2008) 1350–1353
www.elsevier.com/locate/tsf

Insulator–conductor transition in $12CaO{\cdot}7Al_2O_3$ films: On the stability of the crystal lattice under Ar^+ bombardment

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Available online 5 April 2007

Abstract

Recent experimental studies suggest that thin films of a nano-porous complex oxide $12CaO{\cdot}7Al_2O_3$ (C12A7) are unusually stable under bombardment with energetic Ar^+ ions [M. Miyakawa et al., J. Appl. Phys. 97 (2005) 023510.]. We employ classical Molecular Dynamics to study the processes induced by knock-on collisions of Ar^+ with the C12A7 lattice. Our results suggest that such collisions predominantly affect the anion sublattice and form Frenkel defect pairs. We find that most of these Frenkel pairs are unstable and readily recombine with the extra-framework O^{2-} ions present in the lattice at stoichiometric concentrations of $\sim 1.2\times 10^{21}$ cm^{-3}. This process is further facilitated by fast diffusion of the extra-framework O^{2-} ions. These results provide a useful insight in the design of new radiation-resistant materials.

Keywords: Computer simulation; Ion bombardment; Radiation damage; Diffusion

1. Introduction

A complex oxide $12CaO{\cdot}7Al_2O_3$ (C12A7) exhibits properties that make it a promising new material for photo-electronic applications. As grown C12A7 is a transparent dielectric with the bulk band gap of over 6 eV. However, insulating C12A7 can be converted into a transparent conductor via several very different procedures including i) irradiation of the hydrogen-doped C12A7 with UV light [1], ii) exposure of insulating C12A7 to metal Ca vapour at high temperatures [2], and iii) bombardment of C12A7 thin films with heavy energetic particles, e.g. Ar^+, [3]. All of these procedures modify the atomic structure of "as grown" C12A7 in a way that results in the formation of a large concentration of conducting electrons but does not change its lattice.

The cubic unit cell of C12A7 contains two molecules of the $12CaO{\cdot}7Al_2O_3$ composite and can be represented by the chemical formula $[Ca_{24}Al_{28}O_{64}]^{4+}{\cdot}2O^{2-}$. The generalised cation $[Ca_{24}Al_{28}O_{64}]^{4+}$ defines the framework containing 12 cages per unit cell with each cage surrounded by eight first-neighbour cages and four second-neighbour cages, while the O^{2-} ions represent an example of the possible extra-framework species distributed over the framework cages (see Fig. 1). The extra-framework O^{2-} ions can be replaced by other species including H^- [1,4,5], O_2^- [6], Au^- [7], and electrons [2,8].

The extra-framework electrons in C12A7 are not associated with any particular lattice atoms. Instead, they localise in the framework cages, i.e. occupy the same sites, which would have been occupied by extra-framework anions. Therefore, these electrons are referred to as *electron anions* and C12A7 with all extra-framework ions being replaced by electrons is called *electride* (C12A7:e^-). The electron anions give rise to the electrical conductivity of the modified C12A7. At concentrations of the extra-framework electrons of the order of 10^{19} cm^{-3} C12A7 acquires a greenish colour but still retains its transparency in the visible range of photon energies [1].

Recent experiments have demonstrated that C12A7 films become conductive and acquire the greenish colour upon bombardment with energetic Ar^+ ions [3]. It has been suggested that collisions of Ar^+ ions with the lattice effectively 'kick out' the extra-framework oxygen atoms. As a result, part of the extra-framework O^{2-} ions is replaced with conducting electrons. It is important to stress that such modification was found to take place only if the films were heated to ~600 °C, i.e. in the hot implantation regime. Surprisingly, it has been found that

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doi:10.1016/j.tsf.2007.03.156

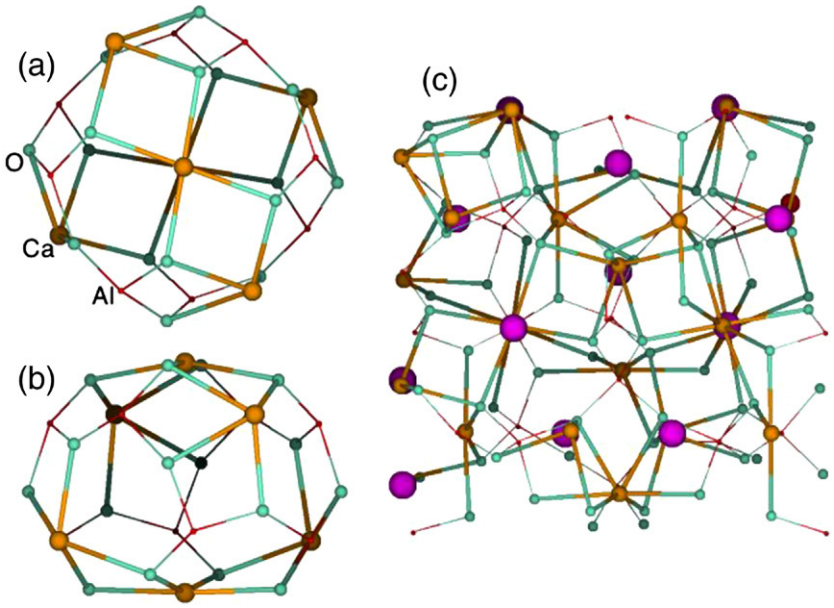

Fig. 1. C12A7 lattice structure: (a) and (b) show the top and side views of a single cage of C12A7 lattice; (c) 118-atom framework of a cubic unit cell. The positions of the cage centres are shown in (c) with large spheres. The extra-framework O^{2-} ions in (c) are not shown.

C12A7 framework sustains radiation doses of up to 500 displacements per atom (dpa) without apparent amorphisation or phase transformation.

In this work we investigate theoretically the mechanisms of radiation damage in C12A7 under bombardment with Ar^+ ions. The kinetic energy of incoming Ar^+ ions is absorbed via two channels: i) the electronic excitations, e.g. formation of electron-hole pairs, and ii) atomic displacements caused by knock-on collisions. The effect of the electronic excitations will be considered elsewhere. Here we only notice two points. First, the excited electrons are likely to neutralise the positive Ar^+ ions quickly since the electron affinity of the free Ar^+ ion is close to 15.8 eV. Second, since the C12A7 films are kept at the earth potential during Ar^+ bombardment, the excess holes will leave the system through the earth electrode. In the rest of the manuscript we concentrate on the modelling of the knock-on collisions induced by Ar^+ ions and their effect on the C12A7 lattice.

2. Details of the calculations

The impact of Ar^+ ions on the C12A7 lattice and the formation of defects were investigated using the classical Molecular Dynamics (MD) technique as implemented in the DL_POLY computer code [9]. Since most of the kinetic energy of Ar^+ ions is deposited inside C12A7 films at about 200 nm away from the surface [3], it is sufficient to consider C12A7 bulk using periodic model approach. We used a 944-atom super-cell constructed as $2\times2\times2$ extension of the smallest 118-atom cubic unit cell. The super-cell lattice constant is approximately 24 Å. The extra-framework oxygen ions were initially positioned in a subset of cages that provides the largest separation between them ($\sim$10 Å).

The interaction between the atoms was described using classical Buckingham-type inter-atomic potentials and a rigid atom approximation. The rigid atom parameters were obtained from the original set of the inter-atomic potentials developed for the shell model calculations of Al/Fe disorder in $Ca_2Fe_xAl_{2-x}O_5$ compounds [10]. The distance cutoff for both inter-atomic potentials and their derivatives with respect to the atomic coordinates was set to 7.0 Å. Formal atomic charges were used for Ca (+2), Al (+3), and O (−2) species. We have used the same set of parameters in an earlier study of O^{2-} diffusion in C12A7 [11]. Ar particle was represented using a neutral centre which interacts with other species via the Born–Mayer potential $A\exp(-r/\rho)$ with $A=10{,}000$ eV and $\rho=0.25$ Å.

First, super-cells containing an Ar particle in one of the cages, was equilibrated using constant pressure and constant temperature ensemble (NPT) with Berensden formulation of the external barostat and thermostat [12], where the external pressure and temperature were set to 0 Pa and 0 K respectively. Then the velocity of Ar particle was modified so as to reproduce its impact kinetic energies in the range of 10–600 eV. Several impact directions were randomly selected to provide statistical averaging. In each case velocities of all other ions of the system were adjusted so as to compensate the momentum of Ar particle. The dynamics of the system was then monitored for 1 ps with the time-step of 0.1 fs using the constant volume and constant energy ensemble (NVE). After that the system was quenched to $T=0$ K using NPT ensemble. During the quenching the temperature of the external thermostat was reduced with 10 K decrements and the system was allowed to run for 2 ps at each temperature with the time-step of 0.5 fs. The obtained structures were then compared to the initial system and the distribution of defects was analysed.

3. Results and discussion

To characterise the lattice damage induced by the Ar species we introduced a reference system. For that the initial system was