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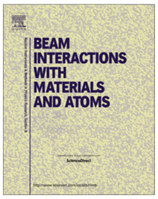

Competing effects of electronic and nuclear energy loss on microstructural evolution in ionic-covalent materials

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ABSTRACT

Ever increasing energy needs have raised the demands for advanced fuels and cladding materials that withstand the extreme radiation environments with improved accident tolerance over a long period of time. Ceria (CeO_2) is a well known ionic conductor that is isostructural with urania and plutonia-based nuclear fuels. In the context of nuclear fuels, immobilization and transmutation of actinides, CeO_2 is a model system for radiation effect studies. Covalent silicon carbide (SiC) is a candidate for use as structural material in fusion, cladding material for fission reactors, and an inert matrix for the transmutation of plutonium and other radioactive actinides. Understanding microstructural change of these ionic-covalent materials to irradiation is important for advanced nuclear energy systems.

While displacements from nuclear energy loss may be the primary contribution to damage accumulation in a crystalline matrix and a driving force for the grain boundary evolution in nanostructured materials, local non-equilibrium disorder and excitation through electronic energy loss may, however, produce additional damage or anneal pre-existing defects. At intermediate transit energies where electronic and nuclear energy losses are both significant, synergistic, additive or competitive processes may evolve that affect the dynamic response of materials to irradiation. The response of crystalline and nanostructured CeO_2 and SiC to ion irradiation are studied under different nuclear and electronic stopping powers to describe some general material response in this transit energy regime. Although fast radiation-induced grain growth in CeO_2 is evident with no phase transformation, different fluence and dose dependence on the growth rate is observed under Si and Au irradiations. While grain shrinkage and amorphization are observed in the nano-engineered 3C SiC with a high-density of stacking faults embedded in nanosize columnar grains, significantly enhanced radiation resistance is attributed to stacking faults that promote efficient point defect annihilation. Moreover, competing effects of electronic and nuclear energy loss on the damage accumulation and annihilation are observed in crystalline 4H-SiC. Systematic experiments and simulation effort are needed to understand the competitive or synergistic effects.

1. Introduction

Nanostructured materials provide the opportunity for tailoring physical, electronic, and optical properties for a variety of technological applications, including advanced nuclear energy systems. As the world increases its reliance on nuclear energy, there is an ever-increasing demand for radiation-tolerant materials that can withstand the extreme radiation environments in nuclear reactors, accelerator-based nuclear systems, and nuclear waste forms. Understanding radiation effects in materials with unique nanostructures is an urgent challenge, since it may hold the key to unlock the design of tailored materials for advanced nuclear

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energy systems. Ceria (CeO_2) is a well known ionic conductor that is also isostructural with urania- and plutonia-based nuclear fuels [1–4]. In the context of nuclear fuels, immobilization, and transmutation of actinides, CeO_2 is a model system for radiation effect studies. Covalent silicon carbide (SiC) is an important functional ceramic material [5–8] for high-power, high-frequency, and high-temperature electronic and space applications. As one of the key materials for nuclear energy applications [9–15], SiC is the critical matrix material in advanced composites (e.g., SiC fiber reinforced SiC matrix) being considered as accident tolerant cladding [11] for light water reactors (LWR) and structural components for advanced high temperature gas-cooled reactors (HTGR), and the first wall of fusion reactors [12]. As stated in the Light Water Reactor Sustainability Program [13], significant interest has been expressed in SiC ceramic matrix composites (CMCs) for use in revolutionary cladding materials. It has been proposed that SiC CMCs have the potential to allow more efficient operation during normal reactor operating conditions, operate with higher safety margins under accident conditions, and reduce the effects of severe accidents. SiC is also the principle material under consideration as the impermeable fission-product barrier coating in tristructural-isotropic (TRISO) coated fuel particles for both pressurized water reactors (PWRs) and HTGRs. Recent results on outstanding self-healing of irradiation-induced defects promoted by stacking faults in nanostructural engineered SiC [10] has attracted much attention, and also highlight the urgency to understand the defect dynamics to design, control or predict material performance. Understanding irradiation response of these ionic-covalent materials with and without nanoscale microstructures under ion beam irradiation has significant implication in advanced nuclear energy systems.

Energy deposition to both target electrons and atoms from radiation–solid interactions has a broad impact in many energy-related technologies and applications including obvious impact of the development of radiation-tolerant materials for nuclear energy and high-energy accelerator applications. While it is well accepted that the interaction of energetic ions with solids initiates a cascade of energy transfer processes on both the electronic and atomic structures, the mechanisms of damage production, for much of the past few decades, are considered as two non-correlated processes: direct knock-on displacements at low energies and extreme electronic ionization/excitation at high energies. At low energies (keV), kinetic energy is effectively transferred to the atomic structure through the nuclear stopping cross section, target atoms are directly displaced from their lattice sites, and defects are produced via atomic collision cascades. For high energy heavy ions (MeV to GeV), often referred to as swift heavy ions, electronic energy loss can be more than two orders of magnitude higher than nuclear energy loss, and nuclear energy loss is, therefore, negligible. Swift heavy ions [16–20] first transfer their energy to the loosely bound target electrons initiating a cascade of secondary electrons that spreads radially within femtoseconds. After some time delay, the energy is gradually transferred into atomic motion through electron–phonon coupling within sub-picoseconds, thereby initiating a thermal spike that can modify the atomic structure of the target [16–19]. At intermediate transit energies where electronic and nuclear energy losses are both significant ($\sim$0.5–50 MeV, or from 1 to a few hundreds of keV/amu), synergistic [21,22], additive [22] or competitive [23] processes may affect the dynamic response to irradiation. In recent years, the importance of these ionization effects and the coupled processes has become increasingly recognized for both metals [24–26] and ceramics [21,22,27–29]. The design of radiation tolerant materials, control of materials modification, and creation of defect structures to tailor materials properties demand a comprehensive understanding and predictive models of energy transfer and exchange processes. Understanding the coupling of electronic and atomic processes in this intermediate energy regime is critically important to predict and control material properties in many energy-related technologies.

2. Experimental procedure

2.1. Film deposition

Nanocrystalline CeO_2 films were deposited on Si (100) wafers by ion beam assisted deposition (IBAD) technique (Mill Lane Engineering, Lowell, MA) at room temperature at the Nanotechnology Laboratory of the University of Nebraska Medical Center [30,31]. IBAD combines evaporation with concurrent ion beam bombardment in a high vacuum environment. Low energy ions with a depth penetration of typically less than 20 nm were employed to produce engineered nano-crystals “stitched” to the Si substrate. The IBAD technique greatly enhances adhesion by *in situ* removing of contaminants prior to deposition, increasing substrate/film atom reactivity, generating a nanoscopically rough surface/interface, creating more nucleation sites, enhancing surface mobility of the deposited atoms, and decreasing the formation of interfacial voids. Ion bombardment may also be utilized for controlling other film properties [32], such as surface morphology, density, stress level, crystallinity, grain size, grain orientation and chemical composition. In the current study, the substrates were cleaned by an *in situ* argon ion beam with energy of 300 eV at a total current of 200 mA. During e-beam evaporation at room temperature, the CeO_2 target was bombarded at 500 eV with current of 50 mA. During deposition, oxygen was backfilled to ensure stoichiometry, and low current argon ions were used to enhance the adhesion between the CeO_2 film and the substrate. All depositions were performed in an ultra-clean vacuum system with a base pressure at 10^{-8} Torr and a working pressure of 10^{-4}–10^{-5} Torr.

Nanostructurally engineered 3C-SiC (NE-SiC) films were deposited on Si (100) wafers by low pressure chemical vapor deposition (LPCVD) process utilizing dual precursor feed gases [10]. The primary feed gases are DCS (H_2SiCl_2), acetylene (C_2H_2), and ammonia (NH_3). With adjustment of the ammonia flow rate, the n-type doping of the 3C-SiC film can be controlled to a specific doping concentration on the order of 10^{18} cm^{-3}. The initial step for a typical SiC LPCVD process involves a carbonization stage, in which an ultra-thin carbon film is deposited on the silicon substrate to facilitate proper film quality and to promote stoichiometry. Since the growth is a reaction rate limited process, the process temperature is set at 1173 K to control the growth rate according to the Arrhenius relationship with respect to temperature. In order to generate a stress matrix consisting of compressive or tensile stresses thin films, the pressure of the LPCVD process was adjusted. Initial stress of the as-deposited films were determined by profilometry measurements at three angles relative to the main flat of the (100) silicon wafer.

2.2. Film irradiation

Room temperature ion irradiations were carried out using the 3.0 MV tandem accelerator facilities at the UT-ORNL Ion Beam Materials Laboratory (IBML) located at University of Tennessee (http://ibml.utk.edu/) and at the Environmental Molecular Sciences Laboratory (EMSL) within the Pacific Northwest National Laboratory (PNNL). The samples were mounted onto a molybdenum plate using double-sided carbon tape so all the sample surface can be irradiated. During the irradiation, the ion beam was rasterred over the sample surface to ensure uniform ion bombardment. Overlapping irradiations of the CeO_2 films by 1 MeV Si and 3 MeV Au ions were carried out at room temperature to ion fluences adding up to 3.5×10^{16} cm^{-2}. Two NE-SiC nanocrystalline