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Thermal conductivity of self-ion irradiated nanocrystalline zirconium thin films

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ABSTRACT

Thermomechanical stability and high thermal conductivity are important for nuclear cladding material performance and reliability, which degrade over time under irradiation. The literature suggests nanocrystalline materials as radiation tolerant, but little or no evidence is present from thermal transport perspective. In this study, we irradiated 10 nm grain size zirconium thin films with 800 keV Zr^+ beam from a 6 MV HVE Tandem accelerator to achieve various doses of 3×10^{10} to 3.26×10^{14} ions/cm^2, corresponding to displacement per atom (dpa) of 2.1 $\times 10^{-4}$ to 2.28. Transmission electron microscopy showed significant grain growth, texture evolution and oxidation in addition to the creation of displacement defects due to the irradiation. The specimens were co-fabricated with micro-heaters to establish thermal gradients that were mapped using infrared thermometry. An energy balance approach was used to estimate the thermal conductivity of the specimens, as function of irradiation dosage. Up to 32% reduction of thermal conductivity was measured for the sample exposed to a dose of 2.1 dpa (3 $\times 10^{14}$ ions/cm^2).

1. Introduction

Radiation in nuclear applications adversely influences the defect density and microstructure of the fuel cladding material. Energetic particles, such as neutrons, with sufficient kinetic energy knocks off atoms from their lattice sites of the cladding materials, creating defects associated with the missing lattice atoms (vacancies) and the dislodged atoms that reside in the lattice interstices. When the atomic displacement exceeds a threshold, this is followed by further displacement in the neighboring atoms in a cascaded manner [1]. The process takes time from femto to picoseconds and results in the partial recombination of the vacancy and interstitial point defects, while the remaining defects may agglomerate to form vacancy clusters and dislocation loops [2] due to their surface energy [3,4]. Depending on the radiation fluence, temperature and other harsh environmental factors, these one-dimensional defects lead to two and three dimensional defects dislocations and voids. The literature is well-established on the mechanical and microstructural aspects. However, thermal transport is also very important the materials are continuously exposed to intense radiation at high temperatures and the heat (with high flux) must be removed to ensure safety and reliability [5]. For example, radiation induced amorphization [2] can reduce thermal conductivity of metals. Similarly, oxidation or hydration can severely deteriorate both mechanical and thermal properties [6,7], which has led researchers to innovate on protecting the surfaces from radiation [8].

The motivation for this study comes from the application potentials of nanocrystalline materials, which are hypothesized to exhibit have better resistance to irradiation [9,10]. The hypothesis driving this area of research is that grain boundaries act as sinks for radiation induced defects [11,12]. Since the volume fracture of grain boundary atoms scales in a cubic power or grain size (the fraction can reach ~50% for grain size of ~6 nm [13]), the abundance of defect sinks may render nanocrystalline materials more radiation tolerant. However, the existing studies are mostly on mechanical properties and a limited literature is available on the thermal transport aspect in nanostructured nuclear materials [14]. Literature shows that the thermal conductivity of nanocrystalline metal films can be as low as one-third of the bulk value at room temperature and even smaller at lower temperature [15]. This not unexpected because when this grain approaches the electron mean free path (around 10 nm for Zr [16]), metallic thermal conductivity will experience enhanced scattering at the boundaries. First principles calculations show that lack of crystallinity reflected by vacancies and disorder as well as non-planarity/misorientation of grain boundaries contribute significantly to grain boundary reflectivity [17]. In the present study, we investigate thin films, for which surface scattering can play roles typically non-existent in bulk form. However, the literature suggests that the reduction in thermal conductivity is predominantly caused by grain-boundary and less by surface scattering [18].

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Accordingly, we propose that the large volume fraction of grain boundaries, compounded by the vacancies, interstitials and voids introduced by radiation, is not only expected to increase the thermal resistance, but also lattice resistance for grain sizes below the phonon mean free path [18]. We study self-ion irradiation in zirconium since the metal and its alloys are used as cladding material for the fuel rods in pressurized water reactors and boiling water reactors. This class of materials has low neutron cross-section [19], high hardness, and high corrosion resistance [20,21]. For metals, any change in thermal conductivity by high temperature irradiation (similar to cladding material environment) is recovered immediately due to annealing [22]. The focus of this study however is on the thermal transport in the nanocrystalline regime. Thermal conductivity measurement on irradiated materials is particularly challenging because the radiation fluence is strong function of the thickness. This means a spatial gradient of damage exists along the path of the neutrons or ions. Conventional thermal conductivity measurement techniques for bulk materials on the other hand assume microstructural homogeneity. Therefore, the underlying heat transfer models need to be adapted to capture these gradient effects accurately. Conventional technique, such as laser flash, 3-ω [23], thermo-reflectance [24], etc. can still be applied if a thin section specimen of uniform irradiation dosage is cut out from the bulk. Another way to avoid this problem is perform the irradiation experiments on thin film specimens, which results in approximately uniform damage throughout the cross-section.

2. Experimental setup and results

To study the role of irradiation on thermal transport in nanocrystalline materials, we developed a micro-electro-mechanical (MEMS) setup that integrates thin film specimens with micro-heaters. The design is essentially a version of the technique developed by Shi et al. [25], adopted for freestanding thin films. The essence of the design is to suspend the specimen between micro fabricated heaters. The specimen is then heated to establish a temperature gradient so that the data can be used in a thermal conductivity model. Shi et al. used electrical resistance based thermometry at the two ends of the specimen, which is modified by using a thermal (infrared) microscope for enhance spatial mapping. Fig. 1 shows the device design where the freestanding thin film specimen is co-fabricated with the micro-heaters. First, the thin film (100 nm-thick zirconium) is deposited by physical vapor deposition (PVD) on silicon-on-insulator (SOI) wafer with 20 μm-thick device layer silicon. Alternatively, a thin section coupon can be nano-manipulated on to this device if the specimen is obtained from bulk material. The deposition is a traditional lift-off process where an inverse pattern of photoresist is created on the SOI substrate using standard photolithography. After the deposition, the unwanted photoresist is removed thereby leaving zirconium specimen in the desired pattern. After a second lithography process, the device layer silicon in the exposed areas is etched by SF_6 plasma using a deep reactive ion etch (DRIE) process. The third lithography step is done on the back side of the handle layer silicon and a similar DRIE process removes the exposed silicon. The buried oxide (BOX) layer is etched away in CF_4 plasma using standard reactive ion etch (RIE) process, leaving the specimen freestanding.

Individual dies containing multiple partially processed samples were ion irradiated with an 800 keV Zr^+ beam using the 6 MV HVE Tandem accelerator at Sandia's Ion Beam Lab. Ion irradiation is a popular surrogate for neutron irradiation with advantages of (a) faster experimentation since damage rates (~10^{-2} dpa/s) are higher compared to the typical ~10^{-7} dpa/s for actual reactors (b) no residual radioactivity hazard and (c) precise control of irradiation conditions [26]. The ion energy was chosen based on a SRIM simulations [27] to have the majority of the ion species past through the Zr film leaving a relatively uniform damage profile, as a function of depth in the Zr. All of the irradiations occurred at nominally room temperature with a rastered ion beam at the maximum dose rate achievable that day. The six doses that were achieved were 3×10^{10} ions/cm^2, 3×10^{11} ions/cm^2, 3×10^{12} ions/cm^2, 3×10^{13} ions/cm^2, 3×10^{14} ions/cm^2 and 3.26×10^{14} ions/cm^2. Damage

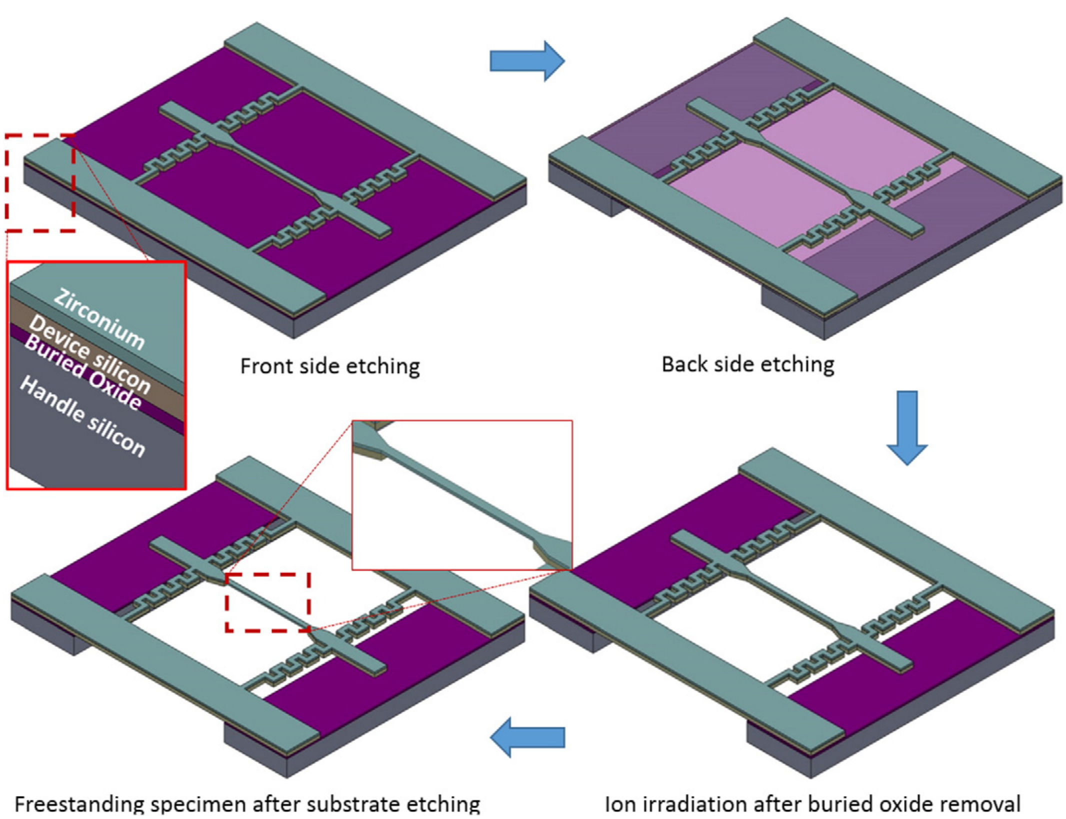

Fig. 1. Fabrication scheme of co-fabricating freestanding thin film specimens with MEMS heaters for thermal conductivity measurements.