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Current density effects on the microstructure of zirconium thin films

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ABSTRACT

We investigate the effect of electrical current density below the electromigration failure limit in nanocrystalline zirconium thin films using in-situ Transmission Electron Microscope and molecular dynamics simulation. At least one order of magnitude higher growth was seen at current density of 8.5×10^5 A/cm^2 (Joule heating temperature 710 K) in 15 min compared to conventional thermal annealing at 873 K for 360 min. Simulation results support our hypothesis that the concurrent effects of electron wind force and Joule heating specifically target the grain boundaries, producing much higher grain boundary mobility compared to high temperature annealing alone.

Metallic materials show strong grain size dependence of their properties [1,2] across length scales [3], which has motivated the pursuit for microstructural optimization and control. Thermal annealing is one of the oldest example, where temperature is used as the stimulus for controlling grain size, phases and defect density. For most metals, this temperature is in the range of 0.3–0.4 T_m (where T_m is the homologous temperature). The applied temperature field is uniform, targeting both crystalline and defective regions. The process is time consuming in each of the phases of heating, temperature hold and cooling. This study proposes that electrical current could potentially achieve similar or higher grain boundary and defect mobility at lower energy and time input. This is because of pronounced scattering at the grain boundaries and defect sites [4,5], effectively enhancing atomic mobility exactly where it is needed for grain growth, and not uniformly across the material.

Current density effects are typically studied for degradation through electromigration [5,6]. Beyond a critical density, mass transport takes place due to the electron momentum transfer, particularly intensified at the defective areas. While it is unlikely that electrical annealing will replace conventional thermal annealing in the near future, we argue that its potential for higher atomic mobility is worth investigation at lower current densities. Other studies have focused on electro-plasticity [7], a phenomenon where electrical current flow induces plasticity in materials that are otherwise very hard and brittle. To study the fundamentals of electron transport effects on microstructures, we adopt a combined experiment-simulation approach. The experiments are performed inside a Transmission Electron Microscope (TEM). The high resolution imaging and diffraction modes make TEM first choice in visualization and characterization of microstructural changes (Zheng et al. [8]). The challenge in this technique is the very small work envelope of the TEM chamber, typically accommodating 3 mm diameter grids for specimens [9]. Computational modeling, such as molecular dynamic (MD) simulation has been used to study mechanical properties [10–12] and electro-migration failure [13]. The modeling challenges are in incorporating electron-matter interaction during transport directly. In our MD modeling approach, we represent the effect of the electrical current by applying an equivalent electron wind force and observe the resulting atomic/defect migration. The discrepancy in time and length-scales between experiment and modeling makes it impossible to achieve quantitative agreement. We therefore seek qualitative and mechanistic contributions from the computational modeling efforts to elucidate the experimental observations.

In this present study, we demonstrate the grain growth mechanism due to the electrical current flow in zirconium thin films. Zirconium is a transition metal with a hexagonal closed pack (hcp) lattice structure known for high melting point (2128 K), biocompatibility, good corrosion and radiation resistance, making it a popular choice in nuclear, aviation and surgical implant applications. We first evaporate about 140 nm thick, 99.97% pure zirconium films on silicon-on-insulator (SOI) substrates. The as-deposited films show near- amorphous structure. SOI substrate is used to co-fabricate a micro-electro-mechanical (MEMS) device with the specimen. The specimen is about 100 μm long, 5 μm wide. Standard photo-lithography, lift-off and deep reactive ion etching were performed on the wafer so that the actuator and heater structures were co-fabricated with the specimen which ensures perfect specimen alignment and gripping. Details of the device design and fabrication are given elsewhere [14]. Fig. 1a shows the zirconium thin film on MEMS device, where the heavily doped silicon structures act as electrodes. The device fits a TEM specimen holder with electrical biasing

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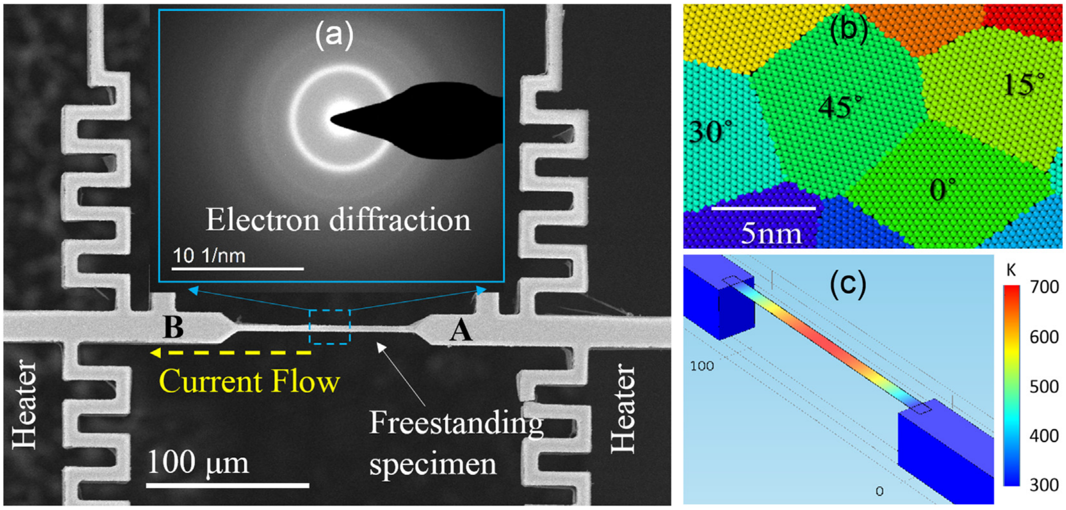

Fig. 1. TEM and MD experimental setups, (a) Scanning electron micrograph of the MEMS device showing the current flow through the specimen. Inset shows diffraction pattern at 0 A/cm^2 current density. (b) Atomistic simulation cell with grains oriented at different angles. (c) Multiphysics simulation of sample with actual geometry, resistance and current density.

capability. In a typical experiment, we pass electrical dc current through the electrodes A and B (as shown in Fig. 1a) to conduct the electrical annealing without damaging the specimen. The inset of Fig. 1a shows the TEM diffraction pattern of a specimen before passing electrical current, where the completely diffused rings suggest near-amorphous (<5 nm grain size) microstructure. Accordingly, the ten grain MD simulation specimen (Fig. 1b) cell was prepared with similar grain size but different orientations. We also performed multi-physics simulation of the temperature field due to Joule heating using COMSOL®. In the in-situ TEM experiments, we passed dc current through the specimen. Since TEM cannot measure temperature field, this information was obtained from multiphysics simulation of the specimen with actual geometry, resistance and current density. Fig. 1c shows the temperature profile along the specimen at a current density of 8.5×10^5 A/cm^2 under vacuum condition mimicking the TEM chamber. The highest temperature is about 710 K and is seen in the middle section of the specimen.

The grain growth mechanism in zirconium due to the electrical current flow was studied using classical MD simulation conducted by LAMMPS [15] software using Embedded Atom Method (EAM) potential [16]. We used a time step of 0.5 fs. Voronoi tessellation based simulation cells of hcp zirconium were built with 10 numbers of grains with an average size of 8 nm. These grain sizes were chosen to mimic the as-deposited specimen as well as grain size distribution in the earlier phases of electrical annealing. We also orient the grain at different angle such as 0°, 5°, 10°, 15°, 30°and 45° as shown in Fig. 1b, while 0° angle lies along $[1\bar{2}10]$ direction and [0001] direction corresponds to film normal i. e., c-axis. The model was checked for any overlapping of atoms at the grain boundaries. Energy minimization was carried out using conjugate-gradient (CG) method followed by NPT dynamics for several thousand steps in LAMMPS. To indirectly model the electrical current effects, we apply equivalent wind force on each atom, obtained from the Huntington-Grone [17] ballistic model. The electron wind force on each atom is calculated using the following equations [18]:

$$F_{wind} = Z^* \times e \times j \times \rho \tag{1}$$

where, Z^* is effective valence number, e is electron charge, j is the current density and ρ is the specific resistivity of zirconium. In our present simulation, we consider Z^* as 3.4 [19] and ρ as 421 n$\Omega \cdot$m [20]. During our simulation, we maintained periodic boundary conditions in all directions. Verlet algorithm was employed for time integration during the NPT dynamics. Electron wind force was applied on individual atom followed by energy minimization and NPT dynamics run. We conduct our simulation at 710 K considering Joule heating effect during the current flow through the sample.

Fig. 2 shows the experimentally observed grain growth during the dc current passage through the specimen inside a Tecnai LaB$_6$ TEM. We allowed 5 min between two consecutive current increments. It is possible to induce grain growth at lower current density at the expense of significant amount of time. Thus, our experimental results can be considered to be at accelerated electrical loading conditions. During the experimentation, we also take TEM BF and selected area electron diffraction (SAED) to probe the grain growth. Fig. 2a–c show the TEM BF and associated SAED images on the microstructural evolution. Starting from near-amorphous grains, we observed very fast grain growth around current density of 8.5×10^5 A/cm^2 (Fig. 2b), where the microstructural changes were discernible within time increments of few minutes. Accelerated loading at current density of 1.1 $\times 10^6$ A/cm^2 led to vigorous grain growth, discernible in few seconds. Fig. 3b and e show the TEM diffraction patterns for the initial and final conditions in only 15 min time span. The clearly resolved spots in Fig. 3e represent the grain growth similar to that seen in the bright field images.

To assess the effectiveness of electrical current annealing, we also performed thermal annealing on specimens. To see any appreciable growth, we had to anneal the specimen at 873 K with total processing time of 360 min (equal heating, holding and cooling period of 120 min). The process was very slow, taking 24 times as much time as allowed in the current annealing experiment. Fig. 3 shows the comparative picture, clearly showing current annealing to produce at least one order of magnitude larger grain size. This is also reflected by the more resolvable spots in Fig. 3e compared to Fig. 3b, where the diffraction pattern of thermally annealed specimen shows only diffused ring patterns. Finally, absence of any damage in Fig. 3d confirms that electrical annealing can take place below the electro-migration failure current density threshold.

To explain the observed performance, we hypothesize that current annealing efficiently annihilates defects and dislocations localized around defective regions such as grain boundaries. Electrical current annealing involves both electron wind force (electron momentum transfer occurring at defect (vacancy, dislocation, grain boundaries and triple points) and Joule heating ([21,22]). It is well known that grain boundary (GB) atoms are relatively at higher energy state than the equilibrium. This is due to the strain field associated with the defects. Therefore, the momentum transfer effect is more pronounced at the GB region. It is important to distinguish this effect from Joule heating, which arises due to the solids resistance to electron flow. Joule heating also