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Sputtered Hf–Ti nanostructures: A segregation and high-temperature stability study

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ABSTRACT

High-temperature stability and segregation tendency of a Hf–Ti alloy is investigated using specimens sputtered in monolithic and multilayer configurations. Upon annealing at 800 °C for 96 h, the alloy shows segregation of Hf and Ti at the nanoscale even though the bulk Hf–Ti phase diagram predicts a homogeneous solid solution. The length scale of segregation is found to depend upon the initial as-deposited structure, with the monolithic film showing Ti segregation at grain boundaries, and the multilayered specimens showing a nanostructure of Hf-rich grains and Ti-rich intergranular amorphous regions. The multilayer specimens exhibit similar post-annealing grain diameters even when the initial layer thickness is varied. Thermodynamic Monte Carlo simulations show a solid solution when the bulk constraint is imposed, in line with the phase diagram expectation, and a polycrystalline nanostructure with solute segregated intergranular regions with full equilibration, in general agreement with the experimental observations.

1. Introduction

Nanostructured materials have many attractive properties, but they generally exhibit poor thermal stability due to their myriad interfaces, which can both act as channels for diffusion and drive grain growth by providing excess free energy [1–4]. Some nanostructured materials, such as Al and Pd, can show appreciable grain growth even at room temperature [5,6]. This grain growth severely limits the materials' application relevance, since their properties often degrade with increasing grain size.

Several techniques have been introduced to limit grain growth in nanostructured materials. Methods which focus on the kinetics of the system include the addition of solutes or second-phase particles which pin the grain boundaries or retard their movement [7–12]. On the other hand, techniques which focus on thermodynamics do not simply slow the grain boundary migration, but relieve the grain boundary excess energy by the addition of solutes [13–15]. One model built on this approach examined the energetics of different grain sizes and compositions, and classified many binary systems by their proclivity for nanograin stability [16,17]. In line with predictions, the W–Ti system was experimentally demonstrated to have stabilized nanograins at elevated temperatures (1100 °C) [18]. However, in that study the nanograined material was produced by a ball-milling technique, which can result in chemical contamination, as well as a microstructure that is rich in dislocations and other defects, all of which affect the energetics of the system [19,20].

To minimize the influence of such processing-related artifacts, the present study uses magnetron sputtering to synthesize nanostructured Hf–Ti materials, with the goal of testing their thermal stability for different initial grain sizes. While the thermal stabilities of ternary systems containing Hf and Ti have been investigated for shape memory alloys and metallic glasses, an investigation into the nanograin stability of the binary Hf–Ti system at high temperatures

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is lacking [21–23]. The aforementioned thermodynamic stability model has suggested that the Hf–Ti system could be either stable or metastable in a nanograin configuration [17], interestingly, in a temperature range where the two elements are fully miscible [24]. In order to control the initial nanostructure, the Hf–Ti samples were sputtered as nano metallic multilayers, with alternating nanometer thick layers of pure Ti and co-sputtered Hf–Ti. The use of this multilayered geometry allows for control of the grain size (which correlates to the layer thickness) and provides the ability to distribute the Ti in nanoscale proximity to the Hf-rich regions, which should lower the kinetic barrier between the initial and expected equilibrium microstructures.

2. Methods

2.1. Experimental

Samples were synthesized using DC magnetron sputtering, with two sputtering sources being used to deposit Hf and Ti onto (100) Si substrates. The sample descriptions are shown in Table 1, where Samples A and B consist of alternating pure Ti and co-sputtered Hf–Ti layers. The following sputtering conditions were used: 60 Watts for Ti, 200 Watts for Hf, and a 0.67 Pa Argon pressure, with the on-times for the Hf source being varied to produce samples with differing layer thicknesses.

An XP-2 profilometer (AMBiOS) was used to measure as-sputtered sample thicknesses, after which the samples were removed from the Si substrates. The samples were then subjected to an 800 °C heat treatment for 96 h under vacuum (pressure $\approx 4 \times 10^{-4}$ Pa) in a GSL1100X tube furnace (MTI Corporation). The heat treated samples will be referred to as HT-Sample A and HT-Sample B. At the end of the heat treatment, quenching was performed in low vapor pressure oil (Invoil 705, Inland Vacuum Industries) without breaking the vacuum. The samples were then removed from the oil and cleaned with ethanol. Samples for transmission electron microscopy (TEM) were prepared by Focused Ion Beam (FIB) liftout using a JIB-4500 FIB (JEOL). TEM, scanning TEM (STEM), and Energy Dispersive X-ray spectroscopy (EDX) were performed in a JEM-2100F transmission electron microscope (JEOL). A JSM-7001 scanning electron microscope (SEM) was used to determine global compositions by EDX (JEOL).

2.2. Modeling

A lattice Monte Carlo method was used to simulate the equilibrium structure of a binary alloy at finite composition and temperature by considering both chemical and topological arrangements. Each lattice site maintains two state variables: the chemical type, which can be assigned as a solvent or solute atom, and the grain number, which denotes the group of atoms that belong to the same grain. The model accounts for mixing interactions within granular and intergranular regions using two different interaction energies, ω_c and ω_{gb}, respectively, and the details on bond energy calculations can be found in Ref. [25]. The structure evolves by changes in the chemical distribution and grain structure. A chemical switch selects two lattice sites at random and exchanges their atom types. A grain switch allows a lattice site next to a grain boundary to change its grain allegiance. For the hexagonal close packed lattice used in the present study, if such a lattice site is surrounded by 11 or 12 neighbors of the same grain number, the majority grain number is attempted. Otherwise, the grain number of one of its neighbors across a grain boundary or a unique grain number (which represents nucleation of a new grain) is attempted. A switch that evolves the system to a lower energy state is always executed, while a switch that evolves the system to a higher internal energy E_2 relative to the initial internal energy E_1 is accepted at a probability $e^{\frac{-(E_2-E_1)}{kT}}$, where k is the Boltzmann constant and T is the absolute temperature.

The structure is initialized in a randomized state, with regard to both chemical and grain number distributions, at 10,000 K and slowly cooled at a rate $\frac{-(T_{\mathrm{step}}-T_{\mathrm{final}})}{5000}$, where the denominator is in units of Monte Carlo steps, until the final temperature $T_{\mathrm{final}} = 1073$ K is reached. During each Monte Carlo step, one switch per atom is attempted on average across the whole system at the intermediate temperature T_{step}. A total of 100,000 Monte Carlo steps are performed, which is found to achieve an equilibrated state (i.e., slower cooling produces the same essential state) for the present conditions. Periodic boundary conditions were imposed on the three principal axes, and all simulations employ a hexagonal close packed lattice with 560 × 560 × 6 sites, which is equivalent to 180 nm in width and encompasses a total of 1,881,600 atoms. All simulated structures that follow are presented in a cross-sectional view onto a (001) plane.

For simulation of the Hf–Ti system studied here, we use the bond energies $E_c^{\mathrm{HfHf}} = 1.61$ eV, $E_c^{\mathrm{TiTi}} = 1.25$ eV, $E_c^{\mathrm{HfTi}} = 1.42$ eV, $E_{gb}^{\mathrm{HfHf}} = 1.58$ eV, $E_{gb}^{\mathrm{TiTi}} = 1.22$ eV, and $E_{gb}^{\mathrm{HfTi}} = 1.44$ eV, where the subscript indicates a bond in a crystal (c) or grain boundary (gb) region, and the superscript denotes the chemical pair. Other relevant material parameters are the atomic volume $\Omega_{\mathrm{Hf}} = 13.44$ cm^3/mol, $\Omega_{\mathrm{Ti}} = 10.64$ cm^3/mol, hexagonal close-packed (HCP) coordination number of 12, and grain boundary thickness of 0.5 nm. These bond energies yield reasonable values for the pure component grain boundary energies $\gamma_{0,\mathrm{Hf}} = 0.72$ J/m^2, $\gamma_{0,\mathrm{Ti}} = 0.68$ J/m^2, as well as the bulk interaction energy ω_c of 13 meV and the grain boundary interaction energy ω_{gb} of −39 meV.

3. Results and discussion

3.1. Microstructure and grain evolution

The microstructures of the as-sputtered samples are shown in the cross-sectional TEM images in Fig. 1. Fig. 1a and c are bright-field TEM (BF-TEM) images of Sample A and B, respectively. The bright layers are Ti, the dark layers are Hf–Ti, and the growth direction is vertical, as indicated by the arrow. EDX scans by SEM showed overall compositions of approximately 23 at% Ti for Sample A and 24 at% Ti for Sample B. Fig. 1b and d are dark-field TEM (DF-TEM) images of Sample A and B, respectively. There is a columnar structure in the as-sputtered samples, and strong Hf (002) diffraction spots, as indicated by the inset selected area

Table 1
Multilayered Hf–Ti sample descriptions.

Sample name	Hf–Ti layer thickness (nm)	Ti layer thickness (nm)	Overall sample thickness (μm)	Composition (at.% Ti)
Sample A	15	2	1.6	23
Sample B	40	5	2.1	24