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Tailoring the mechanical properties of sputter deposited nanotwinned nickel-molybdenum-tungsten films

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ABSTRACT

Advanced metallic alloys are attractive in microelectromechanical systems (MEMS) applications that require high density, electrical and thermal conductivity, strength, and dimensional stability. Here we report the mechanical behavior of direct current (DC) magnetron sputter deposited Nickel (Ni)-Molybdenum (Mo)-Tungsten (W) films annealed at various temperatures. The films deposit as single-phase nanotwinned solid solutions and possess ultra-high tensile strengths of approximately 3 GPa, but negligible ductility. Subsequent heat treatments resulted in grain growth and nucleation of Mo-rich precipitates. While films annealed at 600 °C or 800 °C for 1 h still showed brittle behavior, films annealed at 1,000 °C for 1 h were found to exhibit strength greater than 1.2 GPa and near 10% tensile ductility. In addition to the excellent mechanical properties, alloy films further exhibit remarkably improved dimensional stability – a lower coefficient of thermal expansion and greater microstructural stability. An excellent balance between mechanical properties and dimensional stability make sputter deposited Ni-Mo-W alloys promising structural materials for MEMS applications.

1. Introduction

Micro-electro-mechanical systems (MEMS) technology is entering a new era, requiring a wider range of functionality and the ability to survive in harsh environments, particularly elevated temperatures. Elevated temperature MEMS devices are of particular interest in: aviation, automotive, power generation, sub-sea drilling, and chemical processing industries, in which MEMS sensing and guidance in such harsh environments would provide enhanced feedback and control [1–4]. MEMS structures must also be mechanically robust. While typically this would imply the use of metallic alloys, inherently brittle materials such as silicon and silicon carbide enjoy widespread application as structural MEMS materials [5]. This has been accomplished through a combination of scale and the highly refined IC-based MEMS fabrication processes, which limit the possibility of critical flaws. The low thermal expansion of silicon is also beneficial in limiting thermal distortions, but significant junction leakage can result from temperatures above 120 °C [6]. Poor mechanical properties at elevated temperatures also preclude the use of silicon as a structural MEMS material at elevated temperatures [7,8].

The need for MEMS materials that can be used in extreme environments and at elevated temperatures calls for the reexamination and development of metallic alloys that can be fabricated and shaped on the micro-scale. Electrodeposited LIGA (German acronym for lithography, electroplating and molding) nickel (Ni) offers the capability to fabricate and shape high-aspect ratio structures, but it is generally deposited as pure nickel with highly variable properties that depend on deposition conditions and change rapidly with thermal exposure. Reduced grain sizes have been shown to dramatically increase the room temperature strength of Ni; however, grain growth at temperatures as low as 200 °C leads to a significant loss of strength [9,10]. Aluminum thin films have found application in micromirror arrays [11], and bulk metallic glasses offer easily adaptable and economic processing routes [12]. However, both are still limited by their temperature capacity. As such, recent attentions have shifted towards nickel alloys that are suitable for thin film applications and offer the

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potential to optimize high temperature strength.

Studies on electrodeposited nickel alloys with iron or cobalt showed that the mechanical properties could be significantly improved through grain refinement [13,14]. However, the major challenge of plating Ni, Co, and Fe is achieving the predetermined composition without co-deposition of less noble metal [15–17]. In addition, while Ni-Fe alloys exhibit high tensile strengths approaching 2 GPa, co-deposited sulfur migrates into grain boundaries when heat-treated above 300 °C [13]. Compositionally modulated nanostructure Ni-Mn alloys have been developed to obviate these problems and demonstrated room temperature yield strength of 1.25 GPa [18]. Recent studies have shown that the addition of small amounts of tungsten in solid solution significantly improves thermal stability and mechanical behavior [19–21]. Based on improved mechanical strength and stability, GE global research (GEGR) patented the design of a micro-switch structure using electroplated nickel alloys [4]. While electroplating has the advantage of depositing films at a fast rate, achieving the predetermined chemical composition without impurity elements being co-deposited is a challenge. Burns et al. [22] introduced sputter deposition as an alternate method with better control of the composition, and demonstrated that Ni-base superalloys consisting of seven elements can be sputter deposited with identical composition to the bulk. Further development of highly engineered metallic alloys that can be sculpted with submicron resolution would offer a wider range of functionality and could fuel an expansion of MEMS applications.

In this paper, we report microstructure evolution, mechanical behavior, and dimensional stability of sputter deposited nickel-molybdenum-tungsten (Ni-Mo-W) films annealed at elevated temperatures (600, 800, and 1000 °C). The films were deposited as single-phase nanotwinned solid solutions and show ultra-high tensile strengths up to 3.1 GPa [23]. After annealing at 1000 °C for 1 h, Ni-Mo-W films exhibit strength greater than 1.2 GPa with near 10% ductility. Our study suggests that sputter deposition combined with heat treatment may be an attractive route to manufacture advanced MEMS materials with tailorable properties. Coefficient of thermal expansion (CTE) measurements further prove that Ni-Mo-W alloys possess a remarkably lower CTE compared to pure Ni, which is advantageous for sensor applications.

2. Experimental procedures

2.1. Specimen preparation and material characterization

A custom-built magnetron sputter deposition system, with a base pressure of 1×10^{-7} Torr, was used for depositing the Ni-Mo-W films at 2500 W (DC power) and using 1.0 mTorr of high purity argon. The DC power and Ar pressure adopted in this study were chosen to deposit films at high rate (comparable to electroplating) while ensuring low residual stress and a dense microstructure. The resultant deposition rate was 3.2 nm/s - much higher than previously reported for the sputter deposition of Ni films (0.7 nm/s [24]) and comparable to Ni films electroplated at a current density of 10 mA/cm^2 (3.3 nm/s [25]). Ni-Mo-W films were initially sputtered on a brass substrate and then peeled off to achieve freestanding films. After separating the films from the substrate, the films were cut into tensile geometries using wire electrical discharge machining (EDM) by sandwiching the films between two Ni plates with silver paint to ensure good electrical conductivity and to restrict movement during machining. The machined tensile specimens had an average thickness of 29 μm, gauge widths of 465 μm, and gauge lengths of 1.6 mm.

The chemistry of the deposited films was measured and compared using energy-dispersive spectroscopy (EDS) and wavelength dispersive X-ray spectroscopy (WDS) in a JEOL 8600 Superprobe with Ni, Mo and W crystals serving as standards. The measured chemical composition of the films used in the current study was $Ni_{83.6}Mo_{14}W_{2.4}$ (atomic percent).

The impact of heat treatment on the mechanical behavior was studied by annealing as-deposited films at 600, 800, and 1000 °C for 1 h in a custom-built vacuum furnace. The films were sandwiched between two alumina plates to avoid curling of the films during annealing, and the pressure was pumped below 10^{-6} Torr to limit oxidation. Microstructural changes resulting from the annealing process were observed via transmission electron microscopy (TEM). TEM samples were prepared using a Struers twin jet electropolisher and an electrolyte of 15 vol.% perchloric acid and 85 vol.% ethanol. TEM images were acquired using a Philips CM 300 microscope at 300 kV. The phase content and crystallographic texture of the films were assessed using X-ray diffraction (XRD), and further confirmed using TEM-based automated crystal orientation mapping (ACOM). The surface and cross-sectional microstructures of the samples were characterized using both a Tescan Mira field emission scanning electron microscope (SEM) and a FEI Strata DB235 Dual-Beam focused ion beam and scanning electron microscope (FIB/SEM).

2.2. Mechanical testing

Tensile specimens heat-treated at various temperatures were tested at room temperature using a custom-built micro-tensile testing setup consisting of a micro actuator, 111 N load cell, air bearing and a Pixelink digital camera [26]. All tensile tests were performed at a nominal strain rate of 2×10^{-5} s^{-1}. Surface images of the sample gauge section were captured every 1 s during testing, and these images were post-processed using a digital image correlation (DIC) technique to accurately measure strain in the gauge length [27,28]. For each annealing condition, three samples were tested at room temperature. All results showed good repeatability. The failure morphology of the deformed samples was further characterized using SEM, FIB, and TEM imaging. Hardness of the heat-treated films was measured by instrumented nanoindentation using iNano (Nanomechanics inc.) equipped with a diamond Berkovich tip (Supplementary materials).

3. Experimental results

3.1. XRD result of the deposited films

X-ray diffraction (XRD) data from the sputter deposited $Ni_{83.6}Mo_{14}W_{2.4}$ films annealed at different temperatures are compared with polycrystalline Ni (sputter deposited at 200 W and 2 mTorr argon pressure) in Fig. 1. The as-deposited alloy film was found to be a supersaturated single-phase nickel solid solution alloy with preferred (111) out-of-plane texture [23], which is consistent with the quench rates of the high-energy sputtering process. While the diffraction profile from the film annealed at 600 °C is nearly identical to that of the as-deposited film, diffraction profiles from films annealed at 800 °C and 1000 °C clearly include both (200) and (311) reflections. This is indicative of recrystallization, which will be discussed in section 4. The XRD reflections for the solid solution alloy are slightly shifted as compared to the sputter deposited polycrystalline Ni peaks, and this is attributed to increased lattice spacing due to the addition of Mo and W atoms [29]. The measured lattice parameter for the $Ni_{83.6}Mo_{14}W_{2.4}$ films is 0.36 nm, which is comparable to Ni-W [30–32] and Ni-Mo [33,34] alloys with similar level of dissolved solutes.