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Fabrication of porous and pillar-shaped Mg by magnetron sputtering

B. Ham [a], A. Junkew [b], D. Bufford [b], R. Arróyave [a,b], X. Zhang [a,b,*]

[a] Dept. of Mechanical Engineering, Texas A&M University, College Station, TX 77843, USA
[b] Dept. of Materials Science and Engineering, Texas A&M University, College Station, TX 77843, USA

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ABSTRACT

We report on the synthesis of nanostructured Mg platelets with nanopores and Mg pillars by magnetron sputtering techniques under different deposition conditions. By varying deposition parameters, the morphology of Mg varied from fully dense epitaxial films to polycrystalline nanoporous structures containing hexagonal platelets. The influence of layer thickness, deposition rate, incidence angle and mode of deposition (DC vs. RF sputtering) on morphology of Mg was investigated. Mg nanopillars were formed via glancing angle deposition technique. Density functional theory (DFT) calculation was performed to examine the influence of surface diffusion on morphology of Mg films.

1. Introduction

Mg is a promising material for solid-state hydrogen storage as it absorbs a high weight percentage of hydrogen (exceeding 7 wt.%) in form of Mg hydride [1]. It is generally anticipated that porous and nanopillar Mg with enlarged surface areas may promote the kinetics of H sorption in Mg [2], hence it is desirable to have nanoporous and nanopillar Mg for hydrogen storage applications. Nanoporous Mg and Mg nanopillars may also have potential applications as biological implant to enhance the healing of bones [3]. In the following section, we will briefly summarize the Mg nanostructures that have been fabricated to date.

Mg nanoblades have been synthesized by glancing angle deposition technique [4]. Meanwhile thermal evaporation has produced Mg nanowires [5] and nanoprism [6]. The formation mechanisms for these nanofeatures are not clear, and the diameter of Mg nanowires spans across tens to hundreds of nanometers with a large diversity in length and morphology of wires.

Nanoporous Mg has not been properly fabricated to date. A popular technique to fabricate nanoporous precious metal films, such as Au, is chemical dissolution of (leaching) less noble elements, such as Ag from Au–Ag alloys [7–14]. The size of nanopores can approach tens of nm with good uniformity. This technique, however, is not applicable for the synthesis of nanoporous Mg, due to its significant chemical reactivity with water or dilute acids.

Magnetron sputtering is known to be a versatile technique to produce high quality films. At higher deposition rate, the density of sputtered films is typically higher than evaporated films, and a more compressive stress often develops [15]. Parameters such as the mode of deposition, deposition rate, kinetic energy of incoming adatoms and the incident angle may dramatically alter the microstructure and morphology of sputtered films. For instance studies comparing RF and DC magnetron sputtering on ZnO:Al [16], alumina [17], SiCN [18], and Al-doped ZnO [19] show that RF and pulsed magnetron sputtered coatings had much higher hardness than those of DC sputtered coatings due to the formation of continuous and dense surface with smaller grains.

In this work, a systematic study has been conducted to explore the effects of numerous parameters, including layer thickness, DC versus RF sputtering, deposition rate, texture of single crystal substrates, and varying deposition angles, on morphology of Mg films. By altering these deposition parameters, the film morphology varied from epitaxial dense films to films of varying porosity, and nanoscale pillars. Detailed microstructural characterizations and film stress measurements were conducted to examine the surface morphology and film growth mechanism. Density functional theory (DFT) calculations were performed to understand the drastic difference between morphology of DC and RF sputtered Mg films.

2. Experimental methods

Mg single layer films were deposited by DC and RF magnetron sputtering from high purity (99.99%) Mg targets. Mg films with layer thickness varying from 50 to 800 nm were deposited onto oxidized Si substrates with 1 μm thick amorphous SiO_2 (referred to as SiO_2 substrate hereafter). HF etched single crystal Si(111) substrates were also used for DC sputtering deposition. The chamber was evacuated to a base pressure of 6.6×10^{-6} Pa or better prior to depositions. For DC sputtering the deposition rate varied from 0.6 to 2.4 nm/s and Ar

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[*] Corresponding author at: Dept. of Mechanical Engineering, Texas A&M University, College Station, TX 77843, USA. Tel.: +1 979 845 2143.
E-mail address: zhangx@tamu.edu (X. Zhang).

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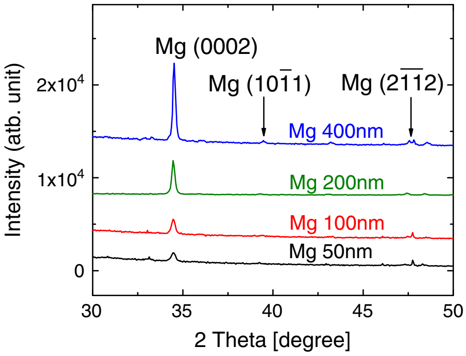

Fig. 1. XRD profiles of Mg films of various thickness, 50–400 nm, with (0002) texture on SiO_2 substrate. The peak intensity increased with increasing film thickness. All films were DC sputtered at a deposition rate of 2.4 nm/s with continuous rotation of the sample stage.

pressures of 0.08, 0.33, and 0.57 Pa were used. However as Ar pressure has little influence on morphological evolution of DC sputtered Mg films, only results obtained at 0.33 Pa are shown in this paper and compared to RF sputtered Mg films. RF sputtering was performed at 1.6 nm/s under ~0.33 Pa Ar pressure. It should be noted that all aforementioned films (DC vs. RF sputtering) were performed while the sample stage was rotating continuously during depositions. Although substrates were angled at 45° relative to central axis of sputtering gun, continuous rotation led to either dense or porous Mg films (no pillars). To fabricate Mg pillars, sample stage rotation was first disabled. The substrates were arranged either at 45° or 5° with respect to the central axis of the sputtering gun, i.e. nearly parallel to the direction of deposition flux when tilted at 5°. X-ray diffraction (XRD) experiments were performed on a Bruker-AXS D8-focus Bragg–Brentano X-ray diffractometer (Cukα radiation). Scanning electron microscopy (SEM) was performed using JEOL JSM-7500F microscope operated at 5 kV. Transmission electron microscopy (TEM) studies were carried out on a JEOL 2010 transmission electron microscope operated at 200 kV. Substrate curvature was measured before and after deposition using a Dektak-150 profilometer to calculate film stress.

3. Computational methods

To calculate surface diffusivity of Mg atoms, DFT calculations were performed based on pseudo-potentials as implemented in the Vienna ab initio simulation package (VASP) [20,21]. A clean Mg (0001) surface consisted of a 13-layer slab (8 Mg atoms/layer) adjacent to 20 Å of vacuum was constructed. By adding one Mg atom on the surface, the configuration contains a total of 105 Mg atoms. The projector augmented-wave (PAW) pseudo-potentials with the generalized

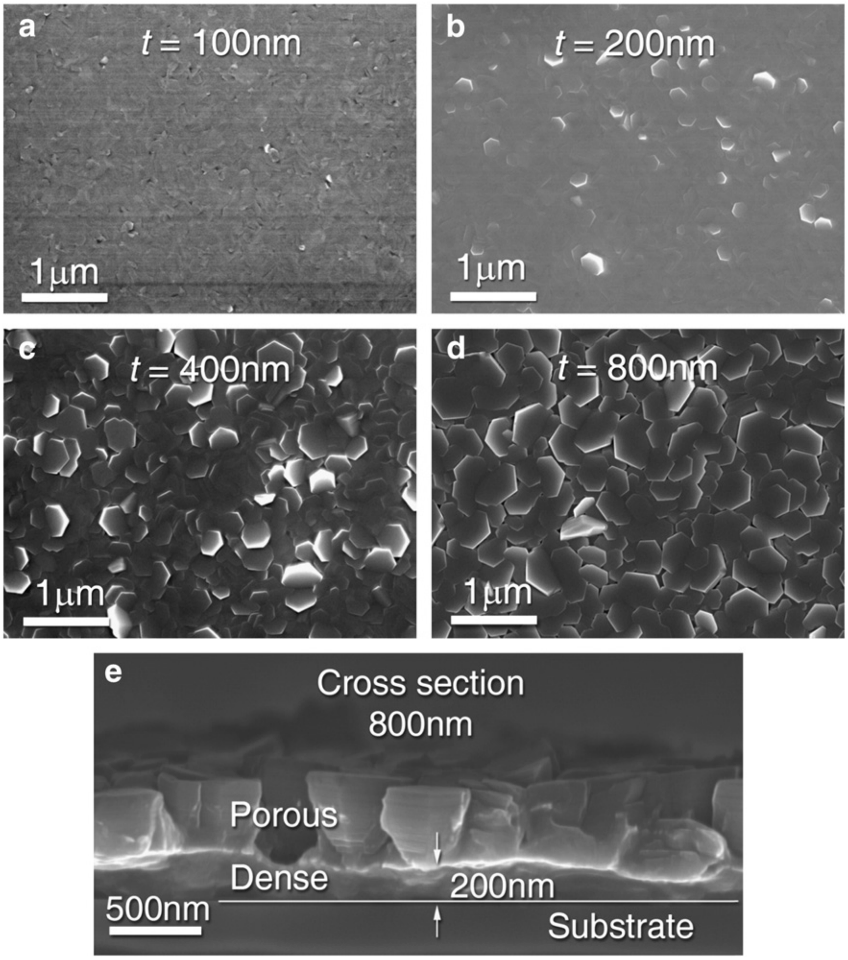

Fig. 2. (a–d) Plan-view SEM micrographs illustrate morphological evolution of DC sputtered Mg films (t = 100, 200, 400, 800 nm) at a deposition rate of 2.4 nm/s on SiO_2 substrates. Mg 100 nm film in (a) showed predominantly smooth surface decorated with few half hexagonal plates. There was increasing porosity and density of hexagonal plates with greater diameters when films grew thicker (200–800 nm) shown in (b–d). Mg 800 nm film showed abundant nanopores. (e) Cross-sectional SEM micrograph of the same Mg 800 nm film reveals the porous columnar structure. A 200 nm thick dense layer adjacent to substrate was identified.