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Alpha- vs. beta-W nanocrystalline thin films: A comprehensive study of sputter parameters and resulting materials' properties

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ABSTRACT

Tungsten thin films have exceptional thermal and mechanical properties, compared to other pure metal coatings, making them indispensable in many contemporary high-tech applications. Their superior properties, however, are strongly dependent on film microstructure, specifically including comprising phases, and hence, the employed deposition parameters, making a thorough process control essential. This study therefore investigates the different material properties of the bcc α and the A15 β phase of tungsten with respect to process parameters. The formation of β-W is mainly dependent on process gas pressure. While all films deposited at elevated pressure consist of β-W, the onset of β formation can already be observed for low pressure deposition, if magnetron power is reduced sufficiently. However, β-W formation for all deposition pressures can be suppressed by applying a substrate bias during deposition, leading to an α-W configuration. This indicates that the alpha-to-beta transition during film growth predominantly depends on adatom energy, rather than solely on the inclusion of residual impurities. Simultaneously, mechanical and electrical performance could be improved, while maintaining a nanocrystalline microstructure.

1. Introduction

Tungsten (W) is an extremely interesting material due to its unique properties, like its thermal stability (T_m = 3693 K [1]), high density (ρ = 19.30 g/cm^3 [1]), mechanical properties (H = 3.53–5.884 GPa; E = 407 GPa [1]), wear resistance [2] and electric conductivity (5.49 μΩ cm [1]). It is used in a wide variety of applications, such as diffusion barriers in interconnects [3,4], metallization layers, X-ray masks [5] and mirrors [6–8] and even nuclear applications [9]. Especially as thin film coatings, e.g. wear resistant coatings in micro-electro-mechanical systems devices [2,10,11], components and devices can profit from said properties without gaining much overall weight despite its high density [1]. Full microstructural control towards nanocrystalline morphology is expected to further promote these properties, especially with regard to thin film applications. Similarly improved properties, as increased hardness, enhanced toughness, or superior chemical, optical and magnetic properties, have already been achieved for other materials [12].

However, W can assume two different phases manifesting significantly different material properties. Its thermodynamically stable phase (α-W) with body centered cubic (bcc) structure has a higher electric conductivity [13]. In contrast, the metastable β phase with A15 structure [7,14] was reported to exhibit superior mechanical properties, i.e. higher hardness of 24.5 ± 1.6 GPa compared to 21.3 ± 1.1 GPa for the α-W configuration [15].

Current models describe the formation of β-W as a result of the interstitial incorporation of Ar, O and self-interstitials during deposition [6,13,15–17]. Despite the large number of investigations conducted, the discussion about the necessity of impurities in the process of β formation is not conclusive [13]. However, the most commonly identified factor promoting the formation of the β configuration is an increased deposition pressure [7,17–19]. Due to the strongly varying properties of the two possible phases, it is essential to establish a parameter framework that ensures reliable, as-deposited fabrication of nanostructured α-W.

In the present work a comprehensive parameter scan for magnetron sputter deposition is employed to determine a reproducible deposition route for nanocrystalline α-W thin films. The investigation shows how various deposition parameters such as magnetron power, deposition pressure, substrate rotation, deposition duration and substrate bias influence the structural, mechanical and electric properties of the resulting W films.

2. Experimental methods

2.1. Deposition

Prior to thin film deposition, the chamber was prepared by a bake-out for 10 h at 120 °C and by sputtering of Ti into the empty chamber

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(at least 2 min, 200 W, 0.67 Pa) to reduce residual hydrogen and oxygen contents. The resulting base pressure was better than $4.533 \cdot 10^{-7}$ Pa ($3.4 \cdot 10^{-7}$ Torr). Sputter deposition (PVD Products Inc., USA) was performed at ambient temperature onto Si (100) substrates with surface layers of 50 nm SiO_2 and SiN_x (Si-Mat Silicon Materials, Germany). Magnetron–substrate distance was 130 mm and surface normals were at an angle of 35° to each other. The W target (99.95% purity) had a diameter of 76.20 mm. Before deposition onto the substrate, target plasma was ignited and left running for 2 min with closed target shutter to remove potentially present surface contaminations. During sputtering, working pressure and an Ar flow of 10 sccm (99.998% purity) were kept constant. Across samples, target power, working pressure, deposition duration and substrate rotation were varied. Additionally, a negative direct current (DC) bias was applied to the substrate during deposition of several thin films.

Employed deposition pressures of 0.27, 0.40, 0.67, 3.33, 6.67 and 13.33 Pa correspond to 2, 3, 5, 25, 50 and 100 mTorr, respectively.

2.2. Characterization

Cross sections of the thin films were prepared employing a Hitachi IM 4000 broad ion beam (BIB) miller (Hitachi High-Tech, Japan). In preparation for the ion milling, the thin film samples were glued face to face to bare Si cover pieces with conductive silver paste in order to prevent surface damage and re-deposition during milling. Subsequently, the sandwich edge was ground with grit 500 and grit 4000 SiC grinding paper to achieve a sharp edge and flat surface over the whole side of the sandwich structure. In the BIB, the polished sample edge was placed in the ion beam with the bare side of the coated substrate directed toward the beam. Milling parameters were an acceleration voltage of 6 kV, ~140 μA ion beam current, 0.09 sccm Ar flow and ±40° swing angle at 23 reciprocations per minute for 1.5 h. These cross sections, as well as the corresponding film surfaces, were investigated utilizing an FEI Magellan 400 field emission gun extreme high resolution scanning electron microscope (SEM) (FEI Company, USA) to determine film thickness as well as film and surface morphology. SEM images were acquired at 5 and 10 kV acceleration voltage.

Mechanical characterization was performed by nanoindentation with a TriboIndenter (Hysitron Inc., USA) and Berkovich tip in load control mode. For every sample, 5 measurements for each of 10 different peak forces (1500 μN–6000 μN, 500 μN steps) were performed. Loading and unloading time were kept constant at 5 s without dwell time. Drift was monitored before loading and corrected for after the measurement. The data was analyzed by the Oliver–Pharr method [20].

Phase analysis and estimation of grain sizes were carried out by X-ray diffraction (XRD) on an X'Pert Pro diffractometer (PANalytical, Netherlands) with Cu–Kα radiation ($\lambda = 0.154056$ nm). θ–2θ scans were obtained over the range of 20–100°, with 0.033° step size. An offset of 5° in Ψ, relative to the surface normal, was chosen for the θ–2θ scans to avoid diffraction peaks of the substrate. To exclude false single phase detection due to strong texture, XRD scans with a 2θ range of 5° and step size of 0.050°, centered on peak positions of non-detected phases, were performed over a Ψ range of 0–74° with 2° step size, Ψ being the angle around the in-plane sample axis in the diffraction plane (Ψ-scan). Assuming random in-plane crystallite orientation of the films with out-of-plane texture, these multiaxial measurements provide evidence to allow exclusion of the presence of the second W phase. Grain size was then determined by applying Scherrer's equation [21,22] to the ordinate-intercept of acquired Williamson–Hall plots [23].

Surface roughness data was obtained by atomic force microscopy (AFM) on a Cypher (Asylum Research, USA). For analysis, roughness raw data was fitted by 1st order flattening and 2nd order XY planefit with the Asylum Research module to IGOR Pro (WaveMetrics Inc., USA).

Thin film resistivity was determined by the Van der Pauw method [24]. The setup is composed of a cylindrical four point probe head (Jandel Engineering Ltd., UK; square tip alignment, 0.635 mm tip spacing, 200 μm tip radii), an N6752A power module (Agilent Technologies Inc., USA) to supply 0.02 A and an NI 4351 voltage meter (National Instruments Corporation, USA). After settling of the applied current, a current measurement, followed by 50 voltage measurements, was acquired and current injection direction rotated by 90°. The cycle was performed four times providing four averaged resistance values from which resistivity was calculated [25].

3. Results

3.1. Thin film deposition

A summary of deposited thin films is given in Table 1. The table gives an overview of deposition parameters and, partly, of the resulting thin films' characteristics. Thin films in the table are arranged according to the pressure they were deposited at. Within the pressure regimes (0.27, 0.67, 3.33, 6.67, 13.33 Pa), the order follows magnetron power and deposition duration. Films deposited under negative substrate bias are combined in a separate category.

Thin film growth rates against deposition pressure are plotted in Fig. 1. It can be seen that generally, for standard deposition (no substrate bias), increasing deposition pressure results in higher growth rates Γ. However, growth rates peak at intermediate pressures. After reaching a maximum at 6.67 Pa, normalized growth rates decrease again for even higher deposition pressures.

It is further apparent that a negative bias applied to the substrate can significantly reduce thin film growth rates. This decline can be observed for both, high and low deposition pressures.

3.2. Phase analysis

While low pressures (0.27 Pa) lead to pure α-W films, the first onset of β phase formation can be observed at 0.67 Pa. At this pressure, however, the (200) β-W reflection at 35.53° is only present when applying a very low magnetron power (50 W). Further increasing deposition pressure to 3.33 Pa then yields a thin film dominated by, if not purely consisting of, the β phase. These results agree with other investigations [7]. For even higher pressures of 6.67 and 13.33 Pa, the (200) β-W reflection is clearly visible. The coexistence of an additional α phase for these pressures cannot be excluded simply by θ–2θ measurements, as the peak at ~40° can originate from either (110) α- or (210) β-W, which are reported for 40.265° and 39.885°, respectively [26,27]. To exclude the presence of β-W in films identified as "single phase" α-W via θ–2θ scans, and vice versa, XRD scans were performed over a Ψ angle ranging from 0°–74° and a 5° 2θ range. These scans were centered at $2\theta = 35.5°$ and $2\theta = 58.0°$ for samples exhibiting only α and β reflections in θ–2θ line profiles, respectively. The Ψ-scans do not indicate a second phase for films deposited at low pressures (0.27 and 0.67 Pa) displaying only the α-W phase. Among 13.33 Pa films, however, multiaxial scans reveal a weak (200) α-W signature for films deposited with high (245 W) magnetron power. The intensities, however, hardly exceed the scans' noise levels. Films demonstrating this behavior of an "elevated noise" were marked with (+α-) in Table 1 to indicate the possibility of an α presence. Nevertheless, this observation coincides with a shift of the dominating reflection from ~35° to ~40° in the single axis diffraction profiles. Independent of deposition pressure, films deposited under negative substrate bias show no indication of the β-W phase. A deposition at 3.33 Pa, however, appears to result in a strongly textured, pure β-W thin film. Neither measurements along θ–2θ, nor with varying Ψ, indicated a reflection that could clearly be attributed to the α phase.

Deposited metallic thin films typically exhibit stresses of the order of 0.01–1 GPa that can be compressive or tensile in nature [28]. It can be seen from Fig. 2 that the diffraction peaks for 0.27 Pa are shifted to slightly lower angles compared to the indicated literature values [26].