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Anisotropic conductivity enhancement in inclined W-Cu columnar films

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ABSTRACT

Two immiscible metals (W and Cu) were deposited using two metallic targets by GLAD co-sputtering. A wet chemical etching technique was implemented to remove the copper and modify the typical inclined microstructure into a more porous architecture. The electrical resistivity behavior of the co-sputtered W-Cu film was characterized as a function of temperature before and after wet chemical etching. The results show that the columnar microstructure exhibits metallic-like electrical properties. The average DC electrical resistivity ρ changes from 1.66×10^{-5} Ωm to 4.28×10^{-5} Ωm after etching. The anisotropy at room temperature is A = 1.8 ± 0.1 for as-deposited W-Cu film and reaches 2.8 ± 0.1 after the etching procedure.

1. Introduction

GLancing angle deposition (GLAD) [1] is a recent method to produce highly porous thin films with tunable morphologies. GLAD thin films are known to exhibit many adjustable physical properties like electrical [2–4], optical [5], magnetic [6], frictional [7], and acoustic [8] anisotropy. Most studies reported on GLAD use a single source of deposition and control structural shapes by rotating the substrate around $\alpha$and φangles [1]. Another approach for nanostructuring involves here two immiscible metallic sources (e.g. tungsten and copper) [9,10], in order to produce a Janus-like columnar structure [11]. It is known that porous nanostructured films display interesting physical properties, thus making them ideal candidates for several applications such as birefringent materials, optical polarizers, gas sensors or catalysts [12,13]. To favor a more porous structure with high electrical anisotropy, one of the metal can be removed by using a wet chemical etching technique.

In this letter, we demonstrate the influence of structural morphologies on the electrical anisotropy in GLAD W-Cu nanostructured films. Morphological and structural properties of W-Cu thin films were characterized. The method proposed by Bierwagen et al. [14], which implements the van der Pauw configuration [15], was used to obtain the anisotropic electrical resistivity. The latter enhances after wet chemical etching due to a higher porous architecture.

2. Material and methods

W-Cu and W thin films were deposited by DC magnetron sputtering inside a 40 L homemade vacuum chamber at a base pressure below 10^{-5} Pa. Tungsten and copper metallic targets with a purity of 99.9 at % and a diameter of 51 mm, were used. The current of the tungsten target was fixed at I_W = 140 mA and that of the copper target at I_{Cu} = 50 mA for W-Cu films, and I_{Cu} = 0 mA for W films. All films were sputtered with an argon flow rate of 6.5 sccm and a pumping speed of 26 Ls^{-1} leading to an argon sputtering pressure p = 0.42 Pa. Glass and (1 0 0) silicon substrates were fixed at the center of the substrate holder which was inclined at an angle of 80°. The latter was at $d_{W\text{-}S}$ = 65 mm from the tungsten target and at $d_{Cu\text{-}S}$ = 95 mm from the copper target. The time of deposition was adjusted in order to have a thickness between 450 and 500 nm. More details about the experimental setup can be found in previous works [16,17].

The wet chemical etching of W-Cu thin films was carried out in a ferric chloride $FeCl_3$ solution at room temperature for an etching time of 1 min 30 s. Samples were then immersed in deionized water to stop the wet chemical etching process and remove the residue of ferric chloride. The morphology (surface and fractured cross-sections) of W-Cu thin films was viewed by scanning electron microscopy (SEM) in a Dual Beam SEM/FIB FEI Helios 600i microscope. Focused ion beam (FIB) was used to prepare the cross-section view and better distinguish the components before and after etching the copper. RMS roughness Rq, Skewness (Sk) and Kurtosis (Ku) of the surface was characterized by atomic force

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microscopy (AFM) using a Veeco Dimension 3100 Manual. The W and Cu weight concentrations of the film were determined by X-ray fluorescence (XRF) spectroscopy using a Fischerscope X-ray XAN 315 system and then the W and Cu atomic concentrations were calculated. The spot size of the XRF system is about 0.2–0.3 mm diameter. The error associated to the quantification of the atomic concentrations was ±5%. Measurements of the weight concentrations were performed at different locations on the sample and the results were averaged. The electrical resistivity was measured as a function of temperature by the four-probe van der Pauw configuration [15]. The measurements of the electrical resistivity were performed in air on films deposited on glass substrate in the temperature range of 298–473 K (1st cycle of 298–373 – 298 K with a ramp of 2 $Kmin^{-1}$ followed by a second cycle of 298–473 – 298 K with a ramp of 2 $Kmin^{-1}$). These two cycles and range of temperatures allow a progressive thermal oxidation of the films. The Bierwagen's method [14] was used to obtain the anisotropic electrical resistivity at room temperature.

3. Results and discussion

Fig. 1 shows the top and cross section SEM (with secondary electrons) views of W-Cu thin films before (a and b), and after (c and d) etching the copper. An inclined columnar structure with an angle of inclination $\beta = 48°$ in the W flux direction is clearly produced. Since W target is closer to the substrate holder than Cu target (65 mm and 95 mm, respectively) and due to the high current applied to the W target (I_W = 140 mA and I_{Cu} = 50 mA), columns are oriented following the W particle flux. Voids between the columns are also noticed with a column width (45–80 nm) perpendicular to the W and Cu fluxes. Such co-sputtering conditions lead to the formation of an elongated shaped columnar structure, which has an electrical anisotropic character of A = 1.8 ± 0.1. Films prepared with I_W = 140 mA and I_{Cu} = 50 mA are tungsten-rich with [W] = 77 ± 5 at% and [Cu] = 23 ± 5 at%, in agreement with those previously reported [16,17]. After etching the copper, the electrical anisotropy increases to A = 2.8 ± 0.1. This enhanced anisotropic behavior is due to the large number of voids in the W-Cu thin film after etching, as observed in Fig. 1(c and d), especially in the direction perpendicular to W and Cu fluxes.

Before and after etching, W-Cu thin films exhibit nearly the same RMS roughness with Rq = 5.0 ± 0.1 nm from AFM measurements. Skewness (Sk) and Kurtosis (Ku) of as-deposited W-Cu films are Sk = 0.42 ± 0.01 and Ku = 2.8 ± 0.1, respectively. After etching, Kurtosis is kept nearly constant with Ku = 2.9 ± 0.1, whereas Sk = $-5.6 \times 10^{-3} \pm 10^{-4}$. This means that the height of the column remains unchanged. It is worth noting that a negative value of Sk confirms a change in the symmetry of the surface profile, which implies that the columns become sharper due to the copper etching. One may suggest that small and thin columns are predominantly etched (probably Cu-rich) rather than elongate ones, which also modify the surface profile.

Fig. 2a and b are SEM cross-section observations with backscattered electrons after FIB preparation of W-Cu films before (a) and after etching (b). The presence of large white columns show that this structure is tungsten-rich (in agreement with the chemical composition by XRF). Fig. 2a shows that a single column grows into a dense thin lateral structure composed of 2 components (W and Cu), up to 100 nm. Afterwards, the white columns become larger and voids appear between the columns. For the largest columns, W and Cu metals are clearly observed and exhibit a Janus-like structure. Fig. 2b shows more voids between the largest columns, and no Cu can be clearly distinguished for a thickness higher than 200 nm. However, for the first 100 nm, a dense columnar structure with W/Cu alternations still remains. An anisotropic architecture with an increasing porosity is produced after a few tens nanometers of the film thickness (shadowing effect becomes efficient). It means that the wet chemical etching reaches only a part of copper

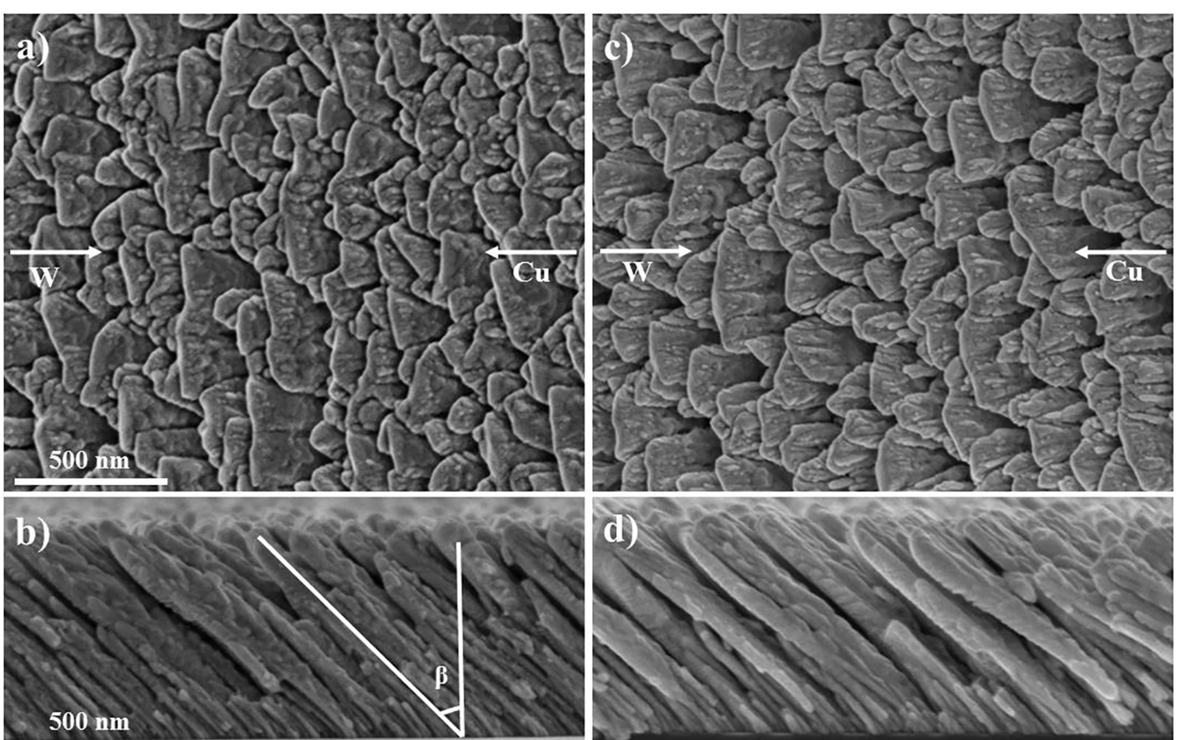

Fig. 1. SEM images of a) the plan view and b) the cross-section with secondary electrons of a W-Cu thin film prepared with I_W = 140 mA and I_{Cu} = 50 mA. c) Plan and d) cross-section views of the same W-Cu thin film after wet chemical etching. Arrows indicate W and Cu fluxes.