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Correlation between structure and electrical resistivity of W-Cu thin films prepared by GLAD co-sputtering

Raya El Beainou [a], Nicolas Martin [a,*], Valérie Potin [b], Paulo Pedrosa [a], Mohammad Arab Pour Yazdi [a], Alain Billard [a]

[a] Institut FEMTO-ST, UMR 6174 CNRS, Université Bourgogne Franche-Comté, 15B, Avenue des montboucons, 25030 Besancon Cedex, France

[b] Laboratoire Interdisciplinaire Carnot de Bourgogne (ICB), UMR 6303 CNRS, Université Bourgogne Franche-Comté, 9, Avenue Alain Savary, BP 47 870, F-21078 Dijon Cedex, France

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ABSTRACT

W-Cu thin films were co-deposited by magnetron sputtering using the glancing angle deposition (GLAD) method. The deposition angle of W and Cu targets was fixed at 80°, and their currents were inversely and systematically changed from 50 to 140 mA. Scanning electron microscopy, X-ray fluorescence spectroscopy, and X-ray diffraction were used to investigate the morphology and the elemental composition of the films. Electrical properties were also studied by the van der Pauw technique. An increase of the W target current and a decrease of the Cu target produced an improvement of the inclined columnar and porous structure. The W-to-Cu weight concentration ratio was tuned from 0.68 up to 19. W—Cu films exhibited a diffracted signal corresponding to the (100) planes of the *bcc* tungsten structure for the highest W current intensities whereas the (111) peak due to the *fcc* copper phase was measured when the Cu target current increased. The dc electrical resistivity measured at room temperature was gradually changed from 3.59×10^{-7} up to 9.90×10^{-6} Ωm by means of an inverse variation of W and Cu target currents. The Cu-rich films exhibited a non-reversible resistivity vs. temperature evolution due to thermal oxidation whereas those co-sputtered with the highest W target currents showed a sudden increase of resistivity when the temperature was above 400 K.

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1. Introduction

Though the growth of structured films from a single source became an established process, the GLancing Angle Co-Deposition (GLACD) with two or three sources has seldom been tried [1]. Zhou et al. [2] proposed the simultaneous deposition of two different materials from two opposite sputtering targets leading to the fabrication of two-component nanorod arrays. Other authors developed composite nanocolumns grown by oblique angle co-deposition from evaporation [3] or sputtering sources [4]. Recently, Liu et al. [5] prepared metallic glass nanostructures from a multitarget carousel oblique angle deposition system. All these recent studies extended the potentiality of the single source GLAD technique since the co-deposition does not solely control shapes and sizes of the nanostructures, but tunable compositions can be achieved.

Many kind of multi-components nanostructures can be reached by means of this GLAD co-deposition approach. The resulting composite architecture also depends on the starting materials which are implemented during the co-sputtering process. The combination of a nearly infinite number of materials can be used to design many new nanocomposites with different layered structures and/or nanorod morphologies. The GLAD co-deposition of metals [6], a metal with a semiconductor [7], a metal with an oxide [8] has ever been studied. To the best of our knowledge, a few studies report on W-Cu films prepared by simultaneous oblique sputter deposition of two separated metallic targets from different directions [9].

In this article, we report on the GLAD co-sputtering of W-Cu thin films by magnetron sputtering. These two metals were chosen because of the immiscibility character of the W/Cu binary system. W and Cu atoms actually prefer to form single element domains, which should favor well-defined interfaces between W and Cu phases in an oriented or normal GLAD columnar structure [10]. Former studies have ever been focused on immiscible W-Cu materials produced by conventional methods [11–14]. Non-equilibrium techniques such as ball milling [15], irradiation [16], electron-beam evaporation [17] led to the formation of metastable W-Cu alloys. Some metastable solid solutions or combinations of a solid solution and an amorphous phase have been proposed [18,19]. Several researches led to the conclusion that the final microstructure of W-Cu thin films and their stability strongly depend on the fabrication technique, operating conditions and composition [20–22].

In order to favor the growth of a two-component columnar structure, two opposite W and Cu targets focused on the center of the substrate were simultaneously sputtered using opposite oblique angles of

* Corresponding author.
E-mail address: nicolas.martin@femto-st.fr (N. Martin).

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80° from the substrate normal. Both target currents were systematically and inversely changed so as to tune the W and Cu concentrations in the films and to investigate the influence of each particle flux on the films' microstructure. Variations of electrical resistivity with the temperature are studied and discussed taking into account the tuneable composition, phases occurrence and microstructure changes, especially the W and Cu oxidation, which is favored by the voided architecture enhanced by the GLAD co-sputtering process.

2. Experimental details

Films were deposited by dc magnetron sputtering from tungsten and copper metallic targets (both are 51 mm diameter and 99.9 at.% purity) inside a home-made vacuum chamber. The experimental device was a 40 L sputtering chamber pumped down via turbo-molecular pump backed by a primary pump, allowing a residual vacuum of about 10^{-6} Pa. The targets were sputtered with an argon flow rate of 1.84 sccm and a constant pumping speed of 7.4 Ls^{-1}, which produced an argon sputtering pressure of 4.22×10^{-1} Pa. No external heating was applied during the growth stage and all depositions were carried out at room temperature. The incident angle was taken from the normal to the substrate and the normal of each target, namely α_{Cu} and α_W for Cu and W targets, respectively. It is also worth noting that the substrate holder can be rotated thanks to the ϕ angle, thus controlling the azimuthal position of the sample (not used in this study). The two incident angles of the particle flux were fixed at $\alpha_{Cu} = \alpha_W = 80°$. The distance between the center of the tungsten target and that of the substrate was 65 mm, while the distance between the center of the copper target and that of the substrate was 95 mm. Before depositing, all substrates were ultrasonically cleaned with acetone and ethanol for 15 min. Subsequently, they were rinsed in de-ionized water, dried and stored in desiccators.

The tungsten and copper targets were dc sputtered in a pure argon atmosphere by systematically and inversely changing the current on each one. At first, the deposition rate of single tungsten and copper thin films was determined as a function of the applied target current. Two series of samples were initially produced. The first one was focused on the deposition of tungsten films using different W target currents from $I_W = 50$ mA to 100 mA. The second series was dedicated to the deposition of copper films with Cu target currents varying from $I_{Cu} = 50$ to 175 mA. The films' thickness was measured by means of a Tencor Alpha Step IQ profilometer and the rates were deduced from the deposition time. As expected, W and Cu deposition rates (R_W and R_{Cu}) as a function of the target current (I_W and I_{Cu}, respectively) both exhibited a linear evolution, according to the following equations:

$$R_W = 6.42 \times I_W - 239 \quad (1)$$

and

$$R_{Cu} = 2.85 \times I_{Cu} - 40.1 \quad (2)$$

respectively (coefficients were calculated from a linear fitting of the R_X vs. I_X plots). Afterwards, a third series of 8 of W-Cu thin films were deposited with different W and Cu current intensities from 50 to 140 mA. Copper target current was reduced from $I_{Cu} = 140$ down to 50 mA whereas that of tungsten was inversely changed from $I_W = 50$ up to 140 mA. For each run, the deposition time was adjusted in order to keep an overall thickness of the films close to 400 nm.

The morphology of W-Cu films deposited on silicon substrates was observed with a Dual Beam SEM/FIB FEI Helios 600i microscope on the fractured cross-section and on the top view. The elemental composition (weight concentration in W and Cu) of the films deposited on silicon substrates was determined by X-ray fluorescence spectroscopy using a Fischerscope X-ray XAN 315 system. Measurements of the weight concentration were performed at six different locations of the substrate. The spot size of XRF system is about 0.2–0.3 mm diameter. The composition was obtained for this given lateral dimension and gives an average value for the whole film thickness. The depositions were also characterized by X-ray diffraction (XRD). Measurements were carried out using a Bruker D8 focus diffractometer with a cobalt X-ray tube (Co $\lambda_{K\alpha1} = 0.178897$ nm) in a $\theta/2\theta$ configuration. Scans were performed with a step of 0.02° per 0.2 s and a 2θ angle ranging from 20 to 80°. The evolution of the W-Cu thin films electrical resistivity as a function of the temperature was assessed by the four-probe van der Pauw method. The measurements were carried out on glass substrates 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}). The metallic-like behavior of the W-Cu films was also characterized by calculating the *TCR* (temperature coefficient of resistivity) at 300 K (TCR_{300}).

3. Results and discussion

Fig. 1 shows the deposition rate of W-Cu thin films, produced with different W and Cu current intensities ranging from 50 to 140 mA. The measured rate corresponds to the film's thickness obtained by profilometry divided by the deposition time during co-sputtering of W and Cu targets. The added rate is calculated by adding W and Cu rate (R_W and R_{Cu} from Eqs. (1) and (2), respectively) when each target is singly sputtered. For all target currents, the measured rate is always lower than the added one. This discrepancy is especially significant for intermediate and nearly comparable W and Cu target currents. For the highest W or Cu currents, the measured rate tends to behave as those obtained with a singly sputtering target. By increasing a target current and reducing the other one, the particle flux of the most powered target prevails over the other flux incoming from the second target.

It is also interesting to remark that the minimum value of measured rate does not correlate with an equal W and Cu target current but is rather shifted to the lower W target current (i.e. $I_W = 70$ mA and $I_{Cu} = 100$ mA). Taking into account the sputtering yield of W and Cu for a given argon ion energy (e.g. $Y_{Cu} = 1.3$ and $Y_W = 0.32$ for $E_{Ar+} = 300$ eV [23]), one could expect a stronger influence of sputtered atoms from the Cu target on the measured rate. Due to the non-symmetric configuration of the co-sputtering system (distance between

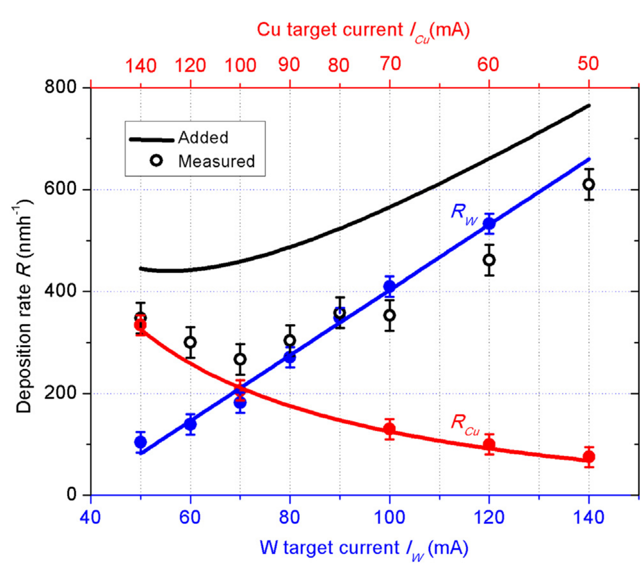

Fig. 1. Evolution of the deposition rate as a function the current intensities on tungsten and copper targets. The added rate was calculated from the single sputtering of W and Cu targets (cf. linear relationships R_W vs. I_W and R_{Cu} vs. I_{Cu} described in experimental details), i.e. $R_W + R_{Cu}$. Open symbols correspond to the deposition rate (Measured) from the co-sputtering of W and Cu targets. Current intensities I_W and I_{Cu} were inversely and systematically changed from 50 to 140 mA.

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