Deposition and structure of W-Cu multilayer coatings by magnetron sputtering

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Abstract. W-Cu-W multi-layer metallic coatings are designed and deposited by d.c. magnetron sputtering on a Fe substrate. Correlations between the deposition parameters, such as target power and Ar gas pressure, and the film characteristics are investigated. Especially, deposition parameters for a dense W-Cu multilayer coating are discussed. Coatings exhibit small grain sizes and a dense surface structure for high target power and low argon pressure leading to dense and well adhesive films.

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1. Introduction

Tungsten, as a high atomic number (high-Z) and refractory material, has attracted considerable interest for their potential use in the ITER plasma facing components, microelectronic technology due to its excellent thermal and electrical properties [1, 2, 3]. In addition, tungsten -based coatings [15, 16]. have been developed for applications in the field of wear- or erosion-resistant components, high-temperature/high-vacuum environments, such as W-C, W-Si, W-N, W-Re, W-La_2O_3 [4, 5, 6, 7]. On the other hand, due to very high thermal conductivity and fracture toughness, Cu and its alloys have been widely used as heat-sink in high heat flux plasma facing components. So W-Cu becomes an attractive candidate material for the heat-sink, plasma experiments as well as armor [4, 8, 9]. Because there is (almost) no mutual solid solubility, only W-Cu pseudo-alloys, as a composite material, are produced. From a research point of view, how to obtain a dense structure and how to overcome the big mismatch of thermal expansion remain open questions. The fine grain and compositionally/functionally graded design were discussed [4, 10, 11] as an alternative route. However, W-Cu coatings were mostly fabricated by mechanical alloying of their powder mixtures [12, 13]. So far there have been little studies reported on a W-Cu multi-layer coating by physical vapor deposition (PVD). It is well known that, in PVD technology, the physical properties of sputtered tungsten or copper films depend strongly on the deposition parameters, especially those controlling the kinetic energy of depositing species. For example, Hubler et al [14] claimed that the kinetic energy must be controlled in the (best) energy range of 5 to 30 eV per atom. From 0.1 to 10 eV, the film growth mechanism changes from an island-growth mode toward a layer-by-layer mode, below about 5 eV, the energy is ineffective for changing the physical process. Above about 30 eV, defects are introduced into the film by displacement damage. The deposition flux and the energy of the atoms and ions on the substrate determine the deposition rate and the film characteristics, respectively [15, 16]. Furthermore, the flux and energy are mainly controlled by the deposition variables: target power (involving voltage and current), working pressure (involving gas species and mass flow), substrate temperature, substrate bias voltage, target to substrate distance (d_{T-S}) In the present paper, a W-Cu multi-layer films have been deposited onto a Fe substrate at room temperature by d.c. magnetron sputtering. The most important deposition parameters: target power including target current and voltage, Ar gas pressure were investigated in order to elucidate how the deposition parameters affect the film characteristics (density, structure) and the physical properties (adhesion). Good adhesion and dense structure are preliminary requirements for thermal stability and good behaviour in plasma conditions.

2. Experiments

A magnetron sputtering deposition system (APRIM VIDE), with three independently biased d.c. planar magnetron targets, is used to sputter W and Cu (one target is idle).

The resulting plasmas are well confined above the targets. The target disks with pure W (99.99%) and pure Cu (99.99%) have a diameter of 10 cm and a thickness of 0.6 cm, respectively. The three target surfaces are 30° tilted from the substrate surface direction and the target surface center is faced to the half radius of the substrate, as shown in Fig. 1. The distance from the target center to the substrate half radius is 9.0 cm. The substrates have 10 cm x 10 cm surface area and are vacuum transferred on a rotating holder. The base vacuum in the deposition chamber is better than 1 x 10^{-7} Pa by using a turbomolecular pump (ATP900, ALCATEL). A cold cathode / pirani gauge (ACC 1009, ALCATEL) is used to measure the vacuum in the range of $10^{-7} - 10^{5}$ Pa. The working gas is argon and it is introduced into the vacuum chamber at a fixed flow rate of 30 standard cubic centimetre per minute (sccm). The substrates are pure Fe (200 μ thick) and are ultrasonically degreased in acetone before mounting on the substrate holder. Prior to any deposition, the target surface is sputter-cleaned for 3-5 min while the substrate is protected by a movable shield. The deposition is carried out without extra heating or cooling of the substrate. Thus effective substrate temperature depends on the deposition conditions. The target power is changed from 100 W to 650 W using power supplies of constant power type. The Ar gas pressure is varied from 0.2 Pa to 2.5 Pa by controlling the the pumping speed (throttling) and keeping the gas flow rate constant. The deposition time is chosen according to the desired coating thickness of W (400 nm) and Cu (200 nm). The cross-section, film thickness, surface morphology including the grain size are measured by scanning electron microscopy (SEM) (Hitachi: S-4200). Deposition rates are estimated from the mean thickness measurements taken

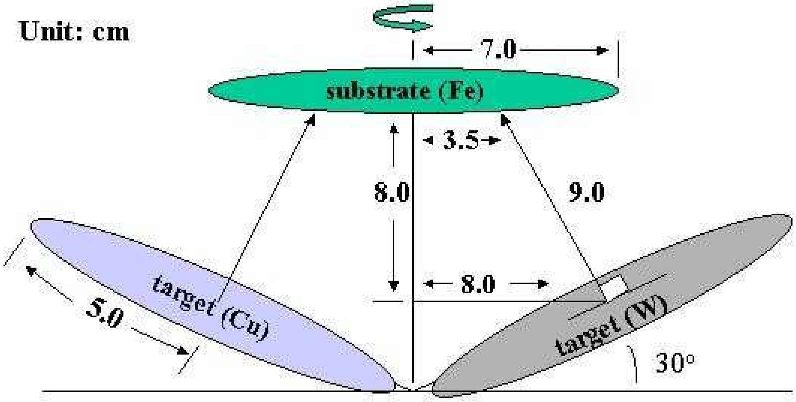

Figure 1. Schematic drawing of the geometrical position of the target and the substrate

from cross- sectional SEM micrographs with known deposition time. The crystalline structure is measured by x-ray diffraction (XRD). The surface areal density and the layer depth profile are determined by Rutherford backscattering spectroscopy (RBS) using a 2.0 MeV $^4He^+$ ion beam of a Van de Graaff accelerator.

3. Results and discussion

The samples with the layered structure: W (400 nm) - Cu (200 nm) - W(400 nm) were deposited on Fe substrates with variable target powers and working pressures. In order to investigate the effects of the target power on the film characteristics, the power is changed from 200 W to 650 W for tungsten and from 100 W to 300 W for copper while keeping the working pressure constant at 1.0 Pa. Fig. 2 displays the evolution of the target bias voltage V and current I as a function of the input power. With the same power, the electric currents at the W target are always larger than the Cu target and conversely, W target bias voltages are smaller than Cu target bias voltages. Fig. 3 indicates that the deposition rates of both W and Cu increase linearly with the increasing target power for a constant gas pressure of 1.0 Pa. For target powers fixed 500 W for tungsten and 250 W for copper, the Ar pressure is changed from 0.2 Pa to 2.5 Pa. Thus Fig. 4 displays the evolution of target bias voltage V and current I against Ar pressure. The difference of the deposition rates between W and Cu is increasing very fast when increasing pressure above 1 Pa, as shown in Fig. 5. A maximum deposition rate for respectively W and Cu is reached when increasing working pressure at fixed target powers. From Fig. 5, the maximum deposition rate of W is 1.3 nm.s^{-1}, with the target power of 500 W, when the Ar gas pressure is 2.0 Pa. The maximum deposition rate of Cu is 1.0 nm.s^{-1}, with the target power of 250 W, when the Ar gas pressure is 1.0 Pa. Beyond this maximum, deposition rates will decrease. This behaviour results from the monotonic decreasing target bias voltage while target current continuously increases as pressure is increasing (Fig. 4). This means that while more positive ions impinge on the target, less metallic atoms and ions reach the substrate due to lower bias voltage leading to less efficient sputtering. Moreover, the excess Ar gas pressure induces shorter mean free path of Ar^+ ions with more frequent collisions, which induces a lower kinetic energy when they impinge on the target. As a result, it contributes to less sputtered atoms. At high working pressure, the sputtered metallic atoms also have more collisions and can be scattered off, which also account for lowering the deposition rate. Fig. 6 shows a cross-sectional view of the W-Cu-W coating grown at power of 500 W (for tungsten), 250 W (for copper), and at pressure of 1.0 Pa. The thickness of W-Cu-W multilayer are 370 nm, 186 nm and 370 nm, respectively. It exhibits a good interlayer contact and a dense structure. W layers display a columnar structure. The surface morphology of the tungsten and copper films, as observed by SEM top view micrographs, are shown in Figs. 7-8. Both copper and tungsten surfaces exhibit grained structure. Fine grain sizes and dense structure occur at low pressures and high target powers. The tungsten grains are in the shape of small rice grains. This grain shape remains unchanged whatever the

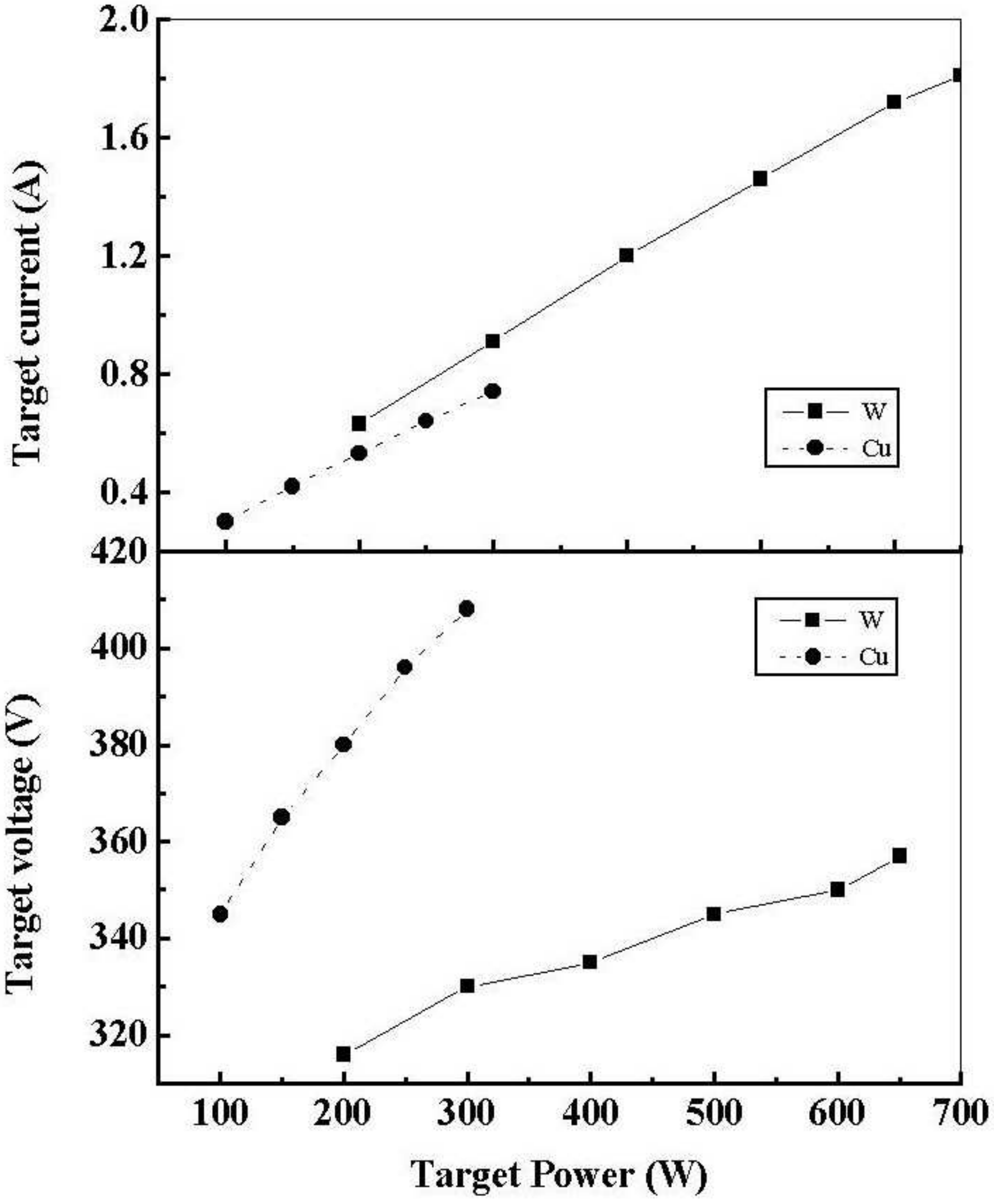

Figure 2. Variation of the target voltage and current with the target power for W and Cu sputtering (Ar pressure: 1.0 Pa)

deposition parameters are, while the grain size decreases from 250 nm to 150 nm when increasing target power or reducing Ar pressure. Fig. 7 shows the SEM micrographs of the W surface with different power, at fixed Ar pressure and the same film thickness.

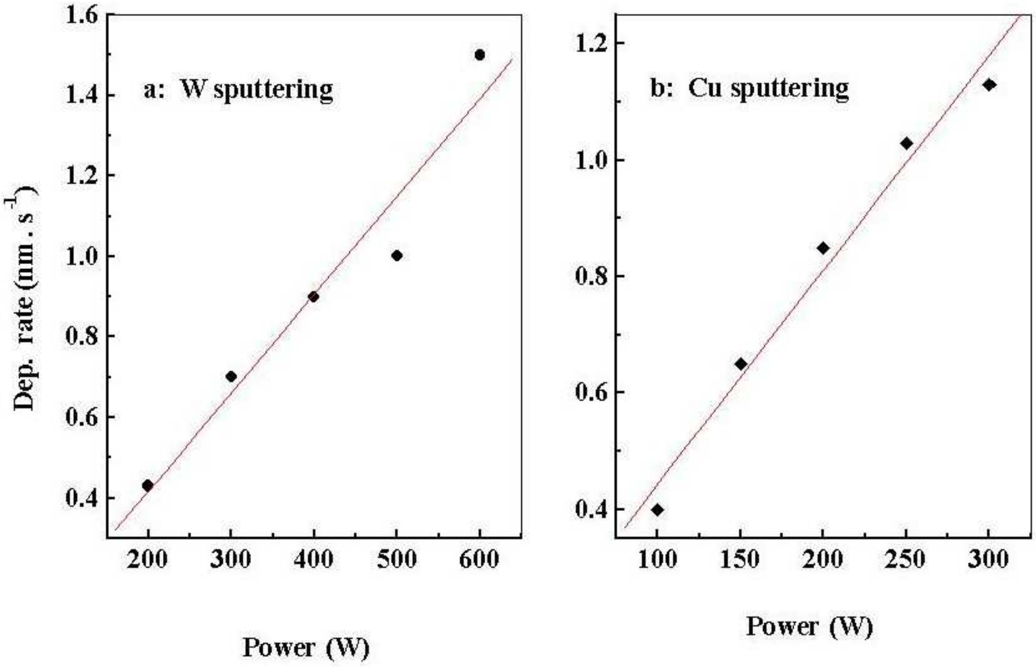

Figure 3. Variation of the deposition rate of W and Cu with the target power (Ar pressure: 1.0 Pa)

Copper grains also have the smallest size at low pressure or high power (Fig. 8b). Moreover, Cu porous structure appears at high pressure ($>$ 2.0 Pa) or low power ($<$ 250 W) (Fig. 8a). Beyond these conditions, the Cu film structure becomes dense without porosity. The change of the grain size mainly results from tuning depositing atom kinetic energies rather than varying deposition time. The high depositing atom kinetic energy (resulting from low working pressure) is beneficial to form a great number of grain cores, and thus reducing size. The XRD patterns (Fig. 9) show the typical diffraction peaks of Fe, Cu and W. Unfortunately, we can not find any apparent difference in the Cu layer, using XRD, when varying deposition conditions. On the contrary, the structure of tungsten evolves from β-W to α-W, also when increasing target power and decreasing Ar gas pressure, as can be deduced from Fig. 9. XRD pattern of β-W displays an unambiguous (200) peak at $\theta = 35.5°$, while other XRD peaks are usually mixed with α-W and/or Cu. However, we can determine if the film structure is a single phase or a mixed phase from the intensity and broadening of the peaks. When the Ar pressure is 1.0 Pa and the target power is below 300W, the β-W phase is obtained, as shown in Fig. 9a. With powers greater than 300 W, the β-W phase transfers completely into α-W, as seen in Fig. 9b. However, Fig. 9c indicates that, if the Ar pressure is increased more than 2.0 Pa in spite of the high target power, the β-W phase appears again, mixed with α-W phase. Therefore the W phase formation is sensitive to a combination of the

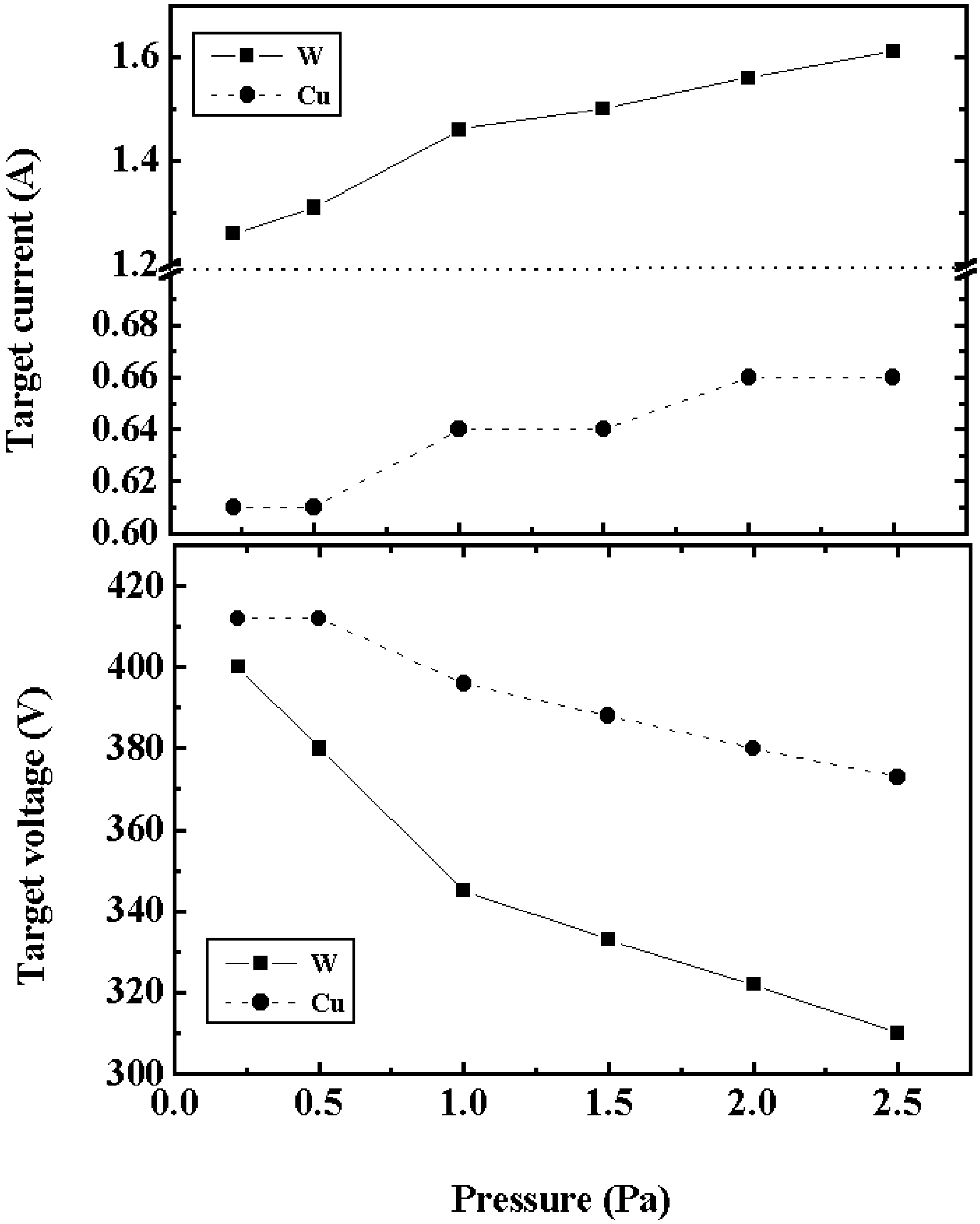

Figure 4. Variation of the target voltage and current for W and Cu sputtering with the Ar gas pressure in a fixed target power (tungsten: 500 W; copper: 250 W).

working gas pressure and the input power. α-W phase is a stable body centred cubic (BCC) (a = 0.316 nm) structure with the largest density of 19.3 gcm^{-3}. β-W structure is a metastable phase with primitive cubic (PC) lattice (a =0.505 nm) and lower density

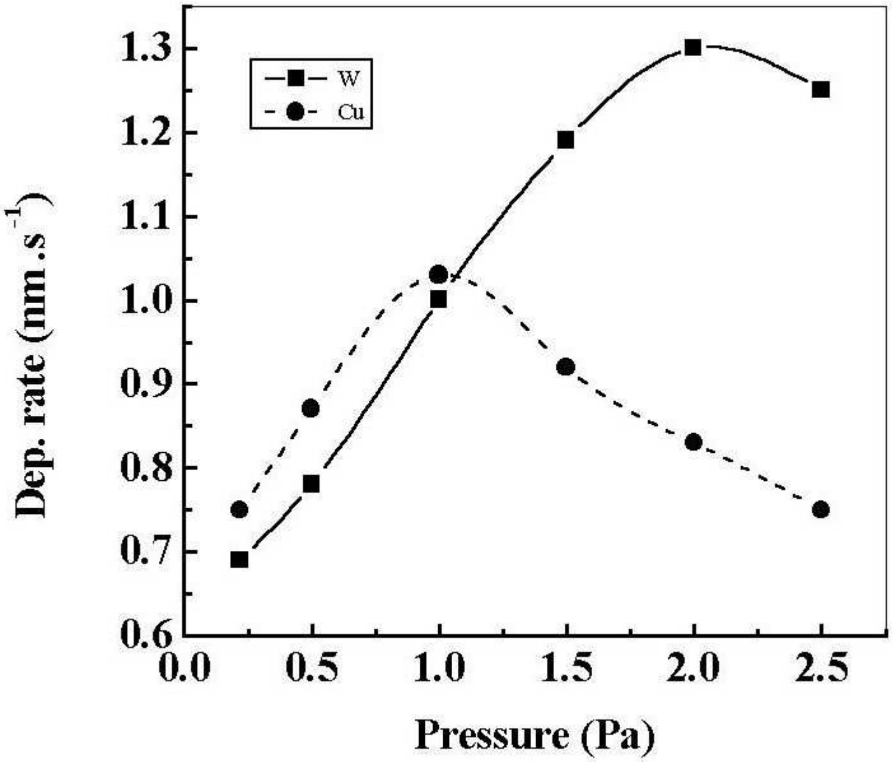

Figure 5. Correlation of the deposition rates of W and Cu with Ar gas pressure in a fixed target power (tungsten: 500 W; copper: 250 W).

is 14.6 g.cm^{-3} [2]. Therefore, the formation of α-W rather than β-W is also consistent with a dense W coating. Furthermore, the surface areal density is determined from RBS measurements. The RBS spectra show that the depth profiles of the elements have a broadened tail which implies an inter-diffusion between the metallic layers. Fig. 10 gives a typical RBS spectrum of W-Cu-W layers together with the simulated spectrum. We can see the intermixed zone between W and Cu or W and Fe layers, which is expected to be beneficial for film and interlayer adhesion. The film thickness is deduced by the corresponding RBS peaks using the standard bulk density: ρ_{W} = 19.3 gcm^{-3}, ρ_{Cu} =8.95 gcm^{-3} , and they are compared with the results from SEM. The W- thickness estimated from both SEM and RBS are nearly identical within the experimental error for most of the samples, except for the samples with the target power below than 300 W (pressure: 1.0 Pa) or Ar pressure more than 2.0 Pa (target power: 500 W), which

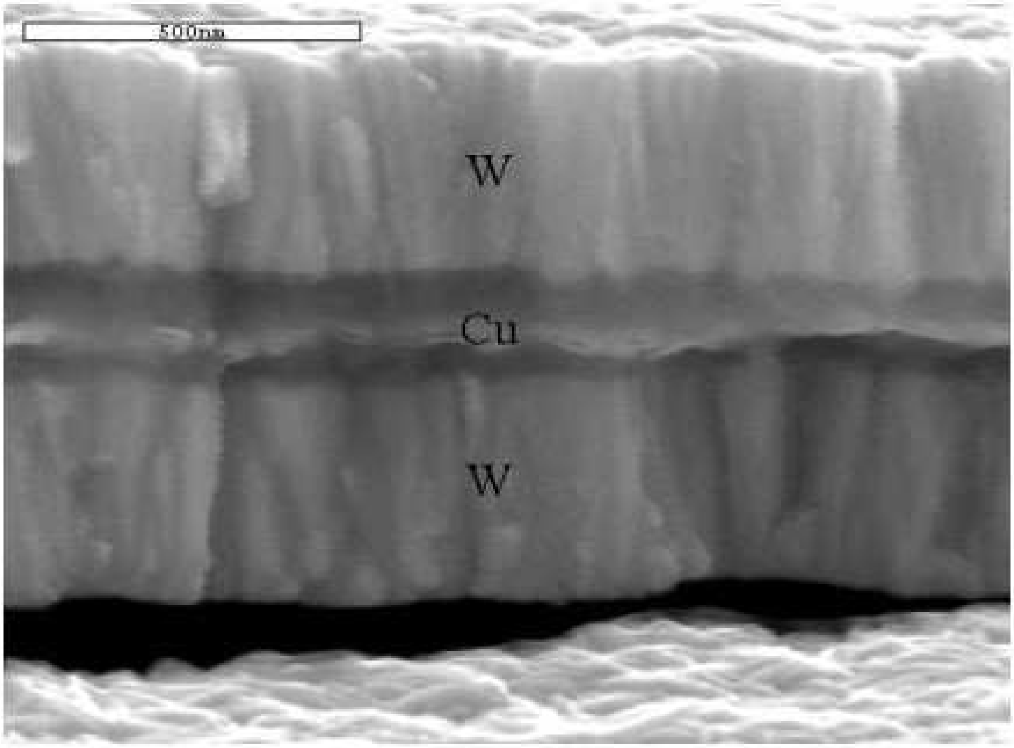

Figure 6. The SEM photograph of a cross-section structure of a W-Cu- W multilayer coating (target power: W:500 W; Cu:250 W , Pressure: 1.0 Pa)

are thinner than the estimated by SEM, indicating that a lower density than bulk. This indicates that the areal density of the W layer with fine grain size and α-W phase is very near the bulk density. In summary, RBS, XRD and SEM results are in agreement among each other. While the Cu layer is capped between two W layers, so its thickness is difficult to be calculated from RBS simulation. In addition, how the film stress and interfacial adhesion change when changing deposition parameters will be an important topics for ongoing experiments. Preliminary scratch tests show that the film adhesion is also improved when increasing target power from 200 W to 600 W or when decreasing working pressure from 2.0 Pa to 0.2 Pa, which is contrary to the results reported in Ref. [2]. This also means that dense layers lead to the best adhesion.

4. Conclusion

Dense W - Cu - W multilayer deposition parameters have been studied in a multitarget magnetron plasma reactor. Deposition rates are shown to scale linearly with input power. But after reaching a maximum when increasing working pressure, they fall down due to the effects of collisions, which reduce kinetic energy of Ar^+ ions and increase

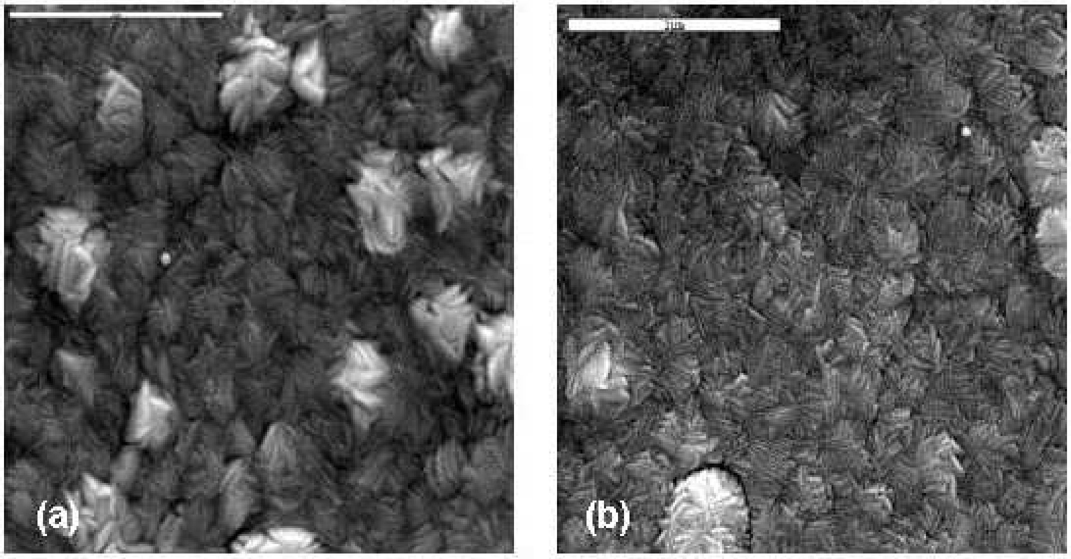

Figure 7. Comparison of the SEM photographs of W surface morphology with different target power ((a) 400 W; (b) 700W, in the same Ar pressure: 0.2 Pa, both film thickness is about 320 nm)

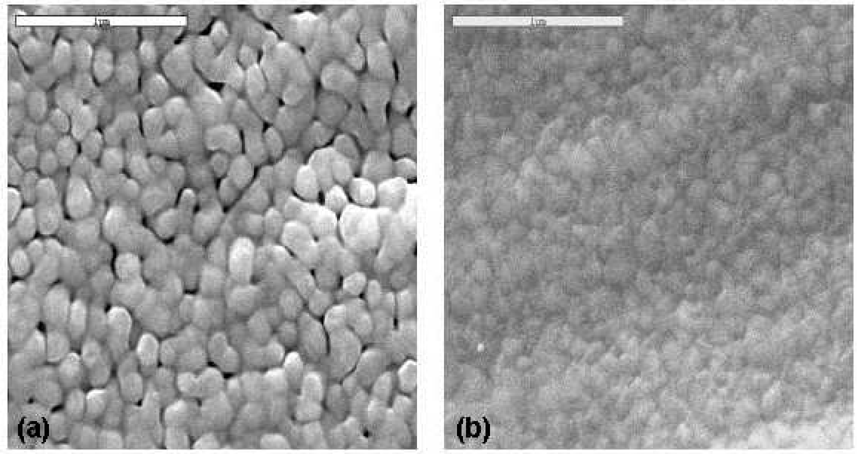

Figure 8. Comparison of the SEM photographs of Cu surface morphology with different Ar pressure ((a) 2.0 Pa; (b) 0.5 Pa, in the same target power: 250 W, both film thickness is about 200 nm)

scattering off the incoming W and Cu atoms. As observed by RBS, XRD and SEM, dense layers are obtained at low pressure and high power. Moreover good adhesion correlates very well with dense layers and fine grain structure.

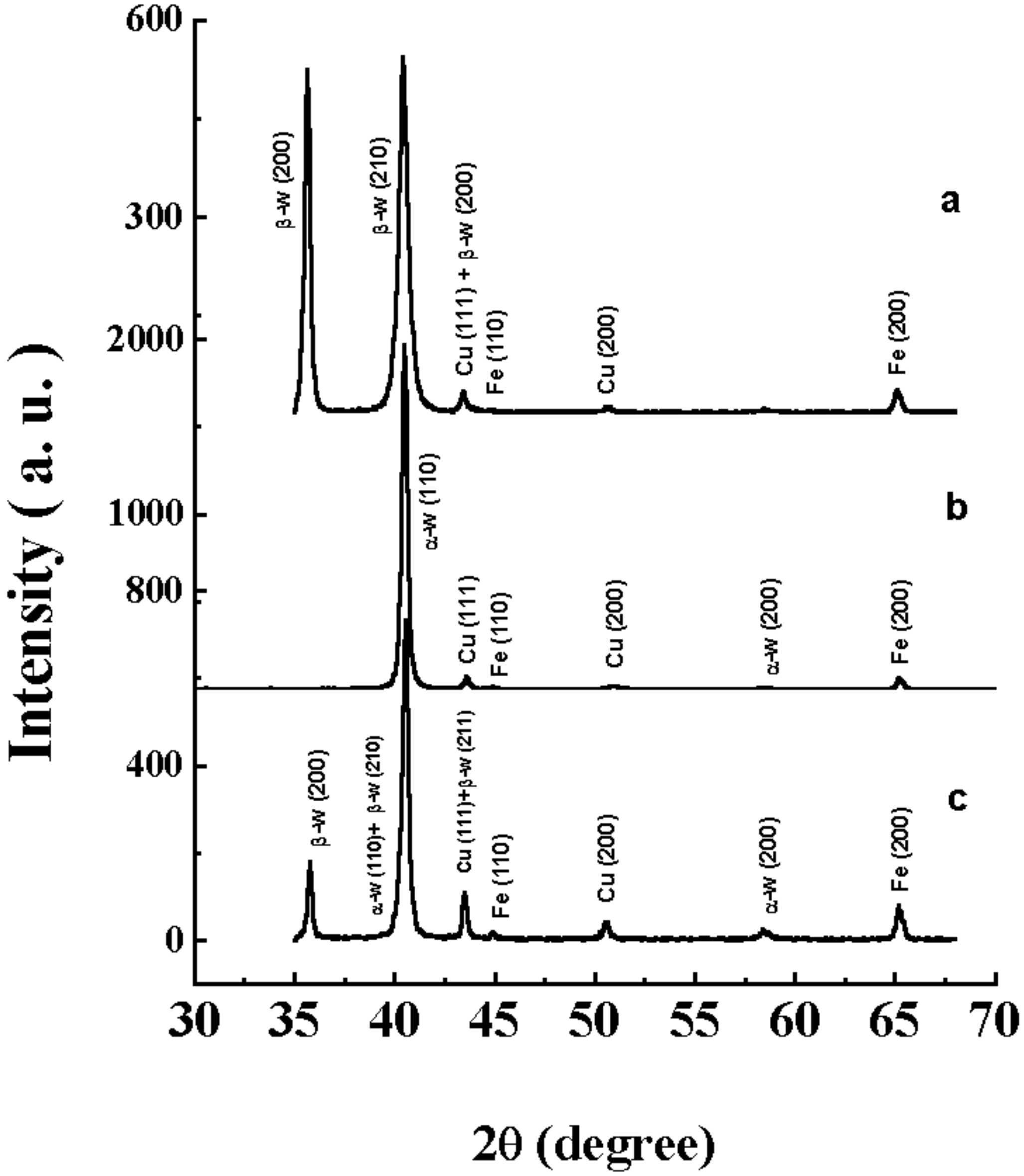

Figure 9. XRD patterns of the W-Cu-W films: a) power W:200,Cu:100 W, Pressure: 1.0 Pa; b) power: W:500,Cu:250 W, Pressure: 1.0 Pa; c) W:500, Cu:250 W, Pressure: 2.5 Pa

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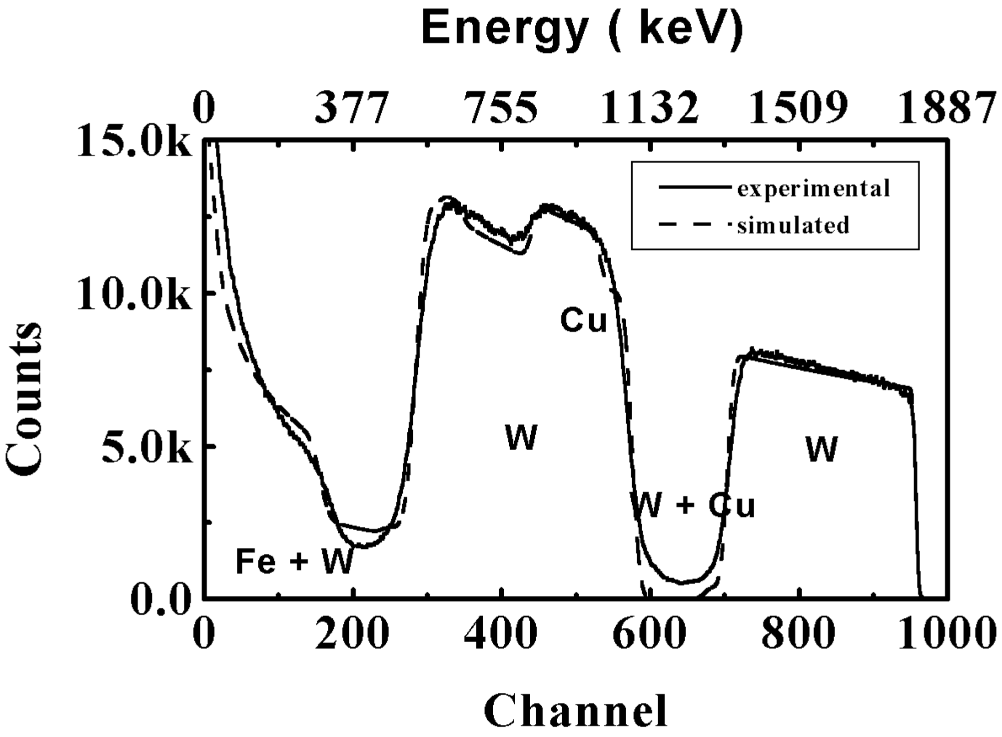

Figure 10. RBS spectrum of a W-Cu-W layered coating and the simulated spectrum (target power: W:500, Cu:250 W; Pressure: 1.0 Pa)

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