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Cu/Mo Nanostructured Alloy Thin Films

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The synthesis of nanostructured materials was pioneered by the inert gas condensation and compaction technique. We investigate magnetron sputtering as an alternative processing route in comparison with thermal evaporation. We have studied the elaboration process and alloy formation by annealing as a function of molybdenum content. The sputtered material was investigated by means of X-ray diffraction, scanning electron microscopy, electron dispersion spectroscopy, atomic force microscopy and Vickers hardness tester. The results indicate that Cu/Mo alloys are semi-hard nanostructures with colors that change from black to yellow-golden when the Mo content increases. Hard nanostructured composite alloys were obtained at 500 °C only at high Mo content. The yellow-golden alloys can be considered as molybdenum bronzes and can be used for integrated circuits (IC), electrical contacts, metallic resistors and high voltage sockets.

Introduction There has been a growing interest in the synthesis of materials with nanoscale microstructures because of potential structural, magnetic and electronic applications [1, 2]. The common synthesis techniques are: chemical vapor deposition, chemical precipitation, sol-gel processing, gas-phase condensation, physical evaporation and sputtering [3, 4]. Sputtering seems to yield certain advantages with respect to the others techniques, such as, for instance, the possibility to prepare refractory materials and quaternary alloys. To date, sputtering has mainly been used to produce thin films with grain sizes in the micrometer scale. Recently, it has been reported that sputtering can produce nanoscale particles at low and high gas pressures [5, 6].

Copper and its alloys have good electrical and thermal conductivity, good resistance to corrosion, special colors and ease of fabrication. Therefore, they are used more often than any other metal. The properties of copper and its alloys greatly depend on the amount of the alloying elements and even on small additions of impurities, hence the method of producing the copper alloys is very important and decisive for the final application. In this paper, we report on the synthesis of Cu/Mo alloy thin films by dc magnetron sputtering technique at low gas pressure.

Experimental A Cook Vacuum Mag. III magnetron dc sputtering system was used for the elaboration of the Mo films. Copper thin foils ($\approx 400 \mu\text{m}$) were used as substrate, previously degreased in trichlor-isopropanol, then cleaned in a 20% nitric acid solution, rinsed with deionized water and dried in an argon gas flux. Pure molybdenum (99.99%) with a thickness of 1/8 of inch and 2 inches of diameter was used as

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target. The Mo films were grown under argon atmosphere at a working pressure of 5×10^{-3} Torr.

The thickness was varied by means of different deposition times, from 15 to 120 min, with a Mo target power of 25 W, at room temperature. The magnetron target was water-cooled during the whole deposition process. The film thickness was measured with a Sloan Dektak profilometer (20 to 180 nm) on the step produced at the substrate copper foil and support during deposition with an estimated accuracy of $\pm 5\%$. The layer thickness was proportional to the deposition time with a linear regression coefficient of 0.9847. For growing the alloy the samples were annealed in a pure hydrogen gas (99.98%) at 400 and 500 °C for 2 h. The phase formation was determined by X-ray diffraction technique. The crystallite sizes were determined in the as-deposited samples by analyzing the line broadening of the Bragg reflections using the Scherrer formula.

The global and phase compositions were determined by electron dispersion Spectroscopy (EDS) at 20 keV. Grain size and roughness were measured by atomic force microscopy (AFM) at a contact force of 10 nN. The surface morphology, segregation and precipitated particles were analyzed by scanning electron microscopy. Vickers microhardness measurements were made at 10 g load applied for 20 s.

Results and Discussion The XRD patterns of the as-deposited samples are shown in Fig. 1. The molybdenum crystallite sizes were determined by analyzing the (1, 1, 0) peak broadening. The crystallite size increases from 8.1 to 12.4 nm; as increases the deposition time (from 15 to 120 min), i.e., as increases the Mo content (from 6 to 37 at%Mo) and the thickness of the Mo layer (from 20 to 1800 nm). The results are summarized in Table 1. Figure 2 shows the XRD patterns observed after a 400 °C/2h annealing treatment. Alloying is evidenced by the fact that the Bragg reflections of the Cu substrate can be considered as a superposition of two peaks with different widths and different intensities. The narrow one originates from the Cu substrate foil, the broad one is due to the Mo/Cu alloy crystallites, formed by the annealing treatment. This effect is best

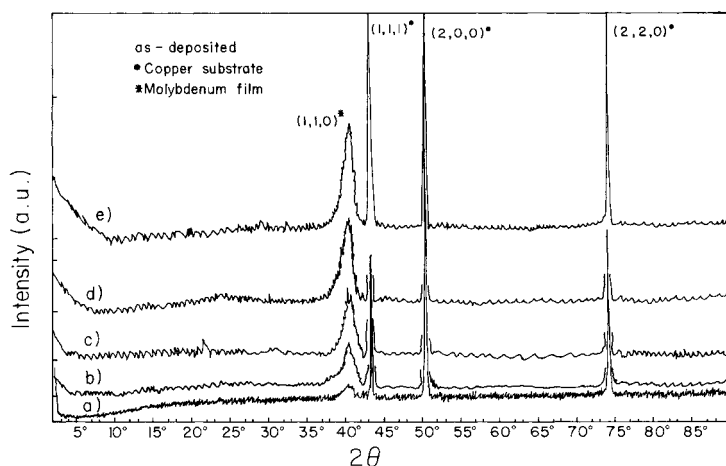


Fig. 1. X-ray diffraction patterns of the as-deposited samples. The Mo peak broadening is due to the small grain size

Table 1
Summary of experimental data

deposition time (min)	15	30	45	60	120
layer thickness (nm $\pm 5\%$)	20	78	540	960	1800
as-deposited XRD grain size (nm $\pm 10\%$)	8.1	8.5	9.4	11.2	12.4
as-deposited Mo	6.29	9.58	19.4	23.30	37.20
composition (at% $\pm 1\%$ Cu)	93.71	90.42	80.60	76.70	62.80
as-deposited surface roughness ($\text{\AA} \pm 5\%$)	45	45	49	52	60
sample color (annealed at 500 °C)	black	grey	brown	yellow	yellow golden
composition of granular precipitates (at% $\pm 1\%$)	molybdenum: 76.75 copper: 23.43				
composition of segregates at boundaries (at% $\pm 1\%$)	molybdenum: 5.4 copper: 94.60				
surface roughness of annealed sample ($\text{\AA} \pm 5\%$)	243	248	255	262	275

visible at the (1, 1, 1), (2, 0, 0) and (2, 2, 0) peaks in the samples named d and e in Fig. 2. Notice that the (1, 1, 0) peak of molybdenum cannot be observed (disappeared) because it is in solid solution with the copper matrix. The samples a, b and c in Fig. 2 show diffraction peaks broader than those of the as-deposited samples due to the alloying process but with a small Mo content. A tentative lattice parameter can be intended considering that the alloy is cubic. From the peak position, we obtained 2θ values of 43.11° and 50.20° corresponding to the (1, 1, 1) and (2, 0, 0) copper peaks, respectively. The tentative lattice parameter was $a = 3.6323 \text{ \AA}$, what is larger than that of copper ($a = 3.6150 \text{ \AA}$) and molybdenum ($a = 3.1472 \text{ \AA}$). Consequently, this result suggests that molybdenum atoms are incorporated in the copper lattice, increasing the lattice parameter from 3.6150 to 3.6323 \AA due to the alloying process. This molybdenum bronze has not been reported in the JCPDS, International Center for Diffraction Data.

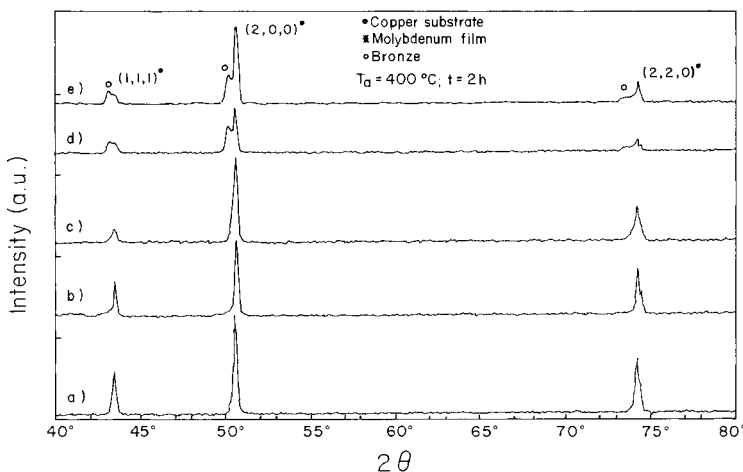


Fig. 2. X-ray diffraction patterns of the annealed samples at 400 °C/2h. Alloying is evidenced by the superposition of the peaks

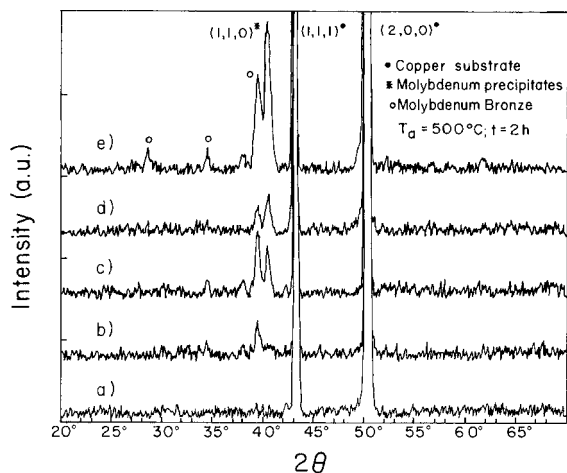


Fig. 3. Extra-diffraction peaks in the samples annealed at 500 °C/2h, due to segregation and the particle precipitation process

When the annealing temperature was increased to 500 °C, Fig. 3, extra-diffraction peaks were observed. These were in agreement with those for molybdenum rich particles with embedded copper (molybdenum bronze) and with the broader copper peak

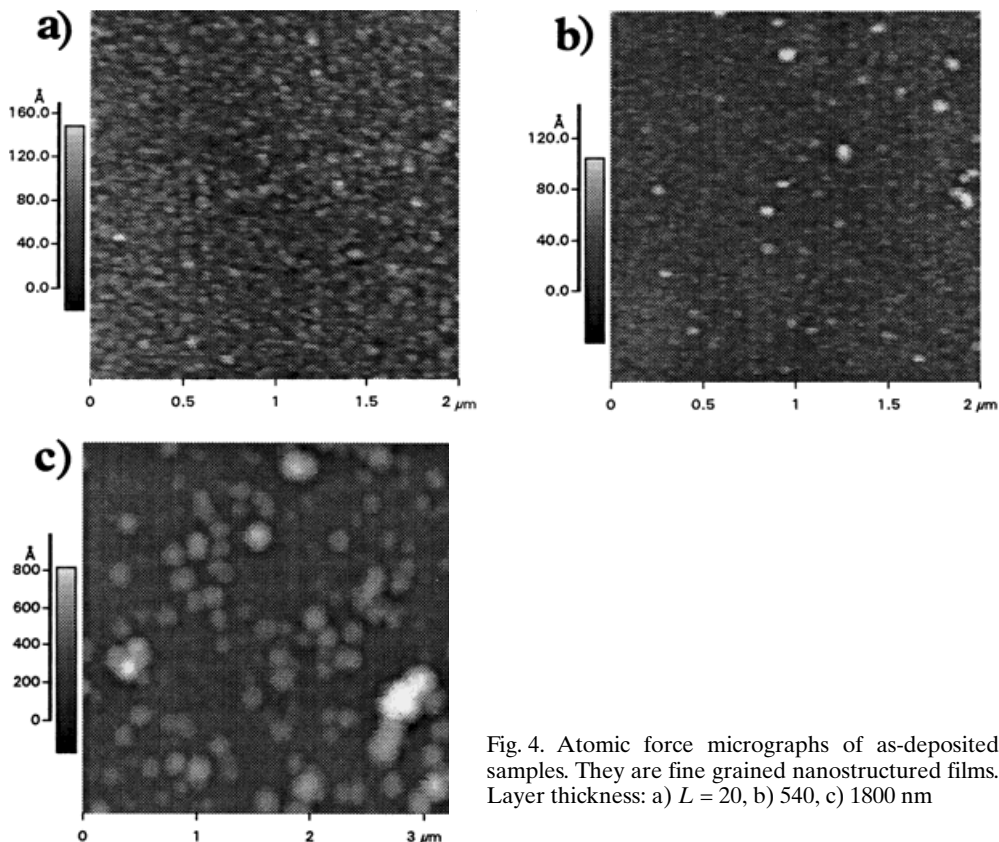


Fig. 4. Atomic force micrographs of as-deposited samples. They are fine grained nanostructured films. Layer thickness: a) $L = 20$, b) 540, c) 1800 nm

due to embedded molybdenum as segregated particle as seen in the electron microscopy picture. This set of samples can be considered as composite alloyed films of Cu/Mo. The color of the alloyed samples changes from black to yellow-golden with increasing Mo content.

The surface morphology of the as-deposited samples was analyzed by atomic force microscopy. In Fig. 4a, b and c the micrographs corresponding to the samples a, c and d of Fig. 1 are shown. As can be seen, the samples are fine grained nanostructured films. The roughness varied from 45 to 60 Å. The results are indicate in Table 1.

After annealing at 500 °C, a considerable change in the microstructure was observed. In Fig. 5a, b a close view of segregation and precipitated particles by AFM is shown.

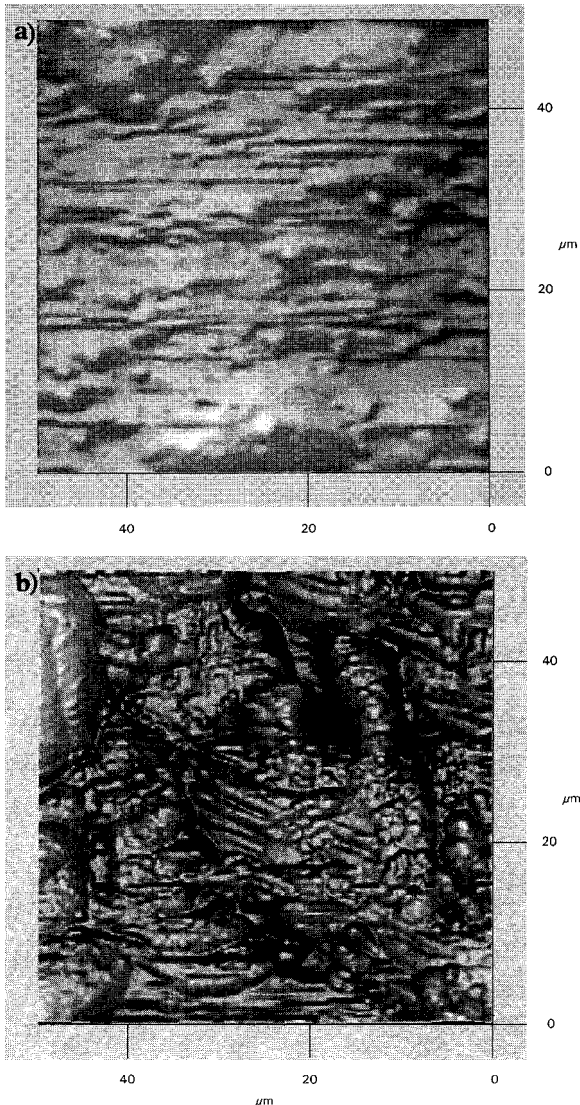


Fig. 5. Close view of annealed samples at 500 °C, showing particle precipitates and the segregation process by atomic force microscopy. Applied force 10 nN. Layer thickness: a) $L = 960$ and b) 1800 nm

The surface roughness has been increased from about 230 to 275 nm, due to considerable segregation in the grain boundaries of the copper substrate. The chemical composition of the samples was determined by EDS at 20 keV. As-deposited samples show a homogeneous composition that varied from 6.29 to 37.2 at%Mo with an oxygen composition that varied from 0.43 to 1.69 at%O, what means that the samples are practically oxygen free. For the samples annealed at 500 °C, many segregates in the grain boundaries of the copper substrate were observed by SEM. These segregates have a chemical composition of 5.4 at%Mo, therefore, they are copper rich alloys (see micrographs in Fig. 6). Some bright fine grained particles were observed, the composition of which was 76.57 at%Mo, therefore, they are molybdenum rich grains. Figure 6a, b show expanded surface views by SEM. It is clear that segregation and precipitates run over the whole surface with grain sizes around 500 to 700 nm. As can be seen, the particles and segregates are either separated from one another or clustered together, giving rise to a composite nanostructured alloy [7, 8].

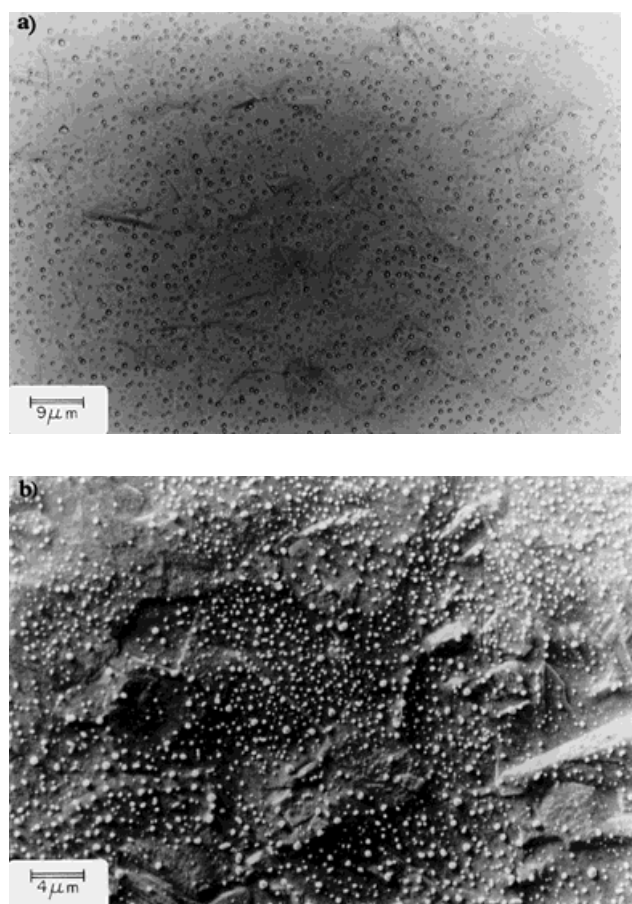


Fig. 6. Expanded SEM view of particle precipitates and the segregation process of the annealed samples. Layer thickness: a) $L = 20$ and b) 78 nm

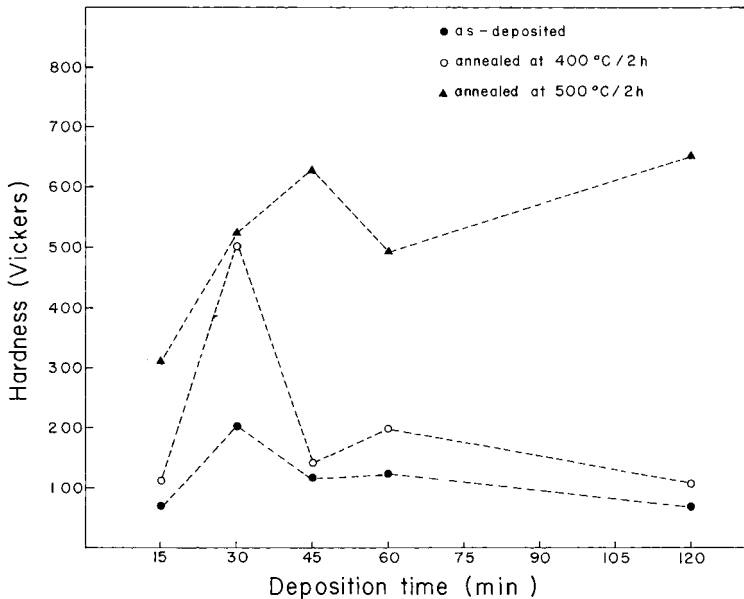


Fig. 7. Microhardness measurements performed on as-deposited and annealed samples. The hardness increases with the annealing temperature and the Mo content

Vickers microhardness measurements were made on as-deposited and annealed samples, using 10 g load applied for 20 s. The microhardness results are indicated in Fig. 7. The as-deposited samples are soft-ductile materials ($H_V \leq 200$ V), those annealed at 400 °C are semi-hard alloys and samples which are annealed at 500 °C can be considered as hard composite alloys. The hardness increases with the annealing temperature and the Mo content [9, 10].

Conclusions Nanocrystalline Cu/Mo samples were analyzed by XRD, EDS, SEM, AFM and Vickers microhardness measurements. The results indicated that Cu/Mo alloys are semi-hard nanostructures and hard composite alloys, with colors that change from black to yellow-golden when the Mo content and the annealing temperatures increase. The yellow-golden alloys are considered as molybdenum bronzes and can be used for integrated circuits, electrical contacts, resistors and high voltage sockets [11].

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