Sputter-deposited amorphous-like tungsten

N. Radic*, A. Tonejc, J. Ivkov, P. Dubček, S. Bernstorff, Z. Medunić

"Rudjer Bošković Institute, Bijenička 54, HR-10000 Zagreb, Croatia
"Faculty of Sciences, Bijenička 34, HR-10000 Zagreb, Croatia
"Institute of Physics, Bijenička 46, HR-10000 Zagreb, Croatia
"Sincrotrone Trieste, SS 14 km 163,5, I-34012 Basovizza, Trieste, Italy

Abstract

Thin tungsten films were prepared by sputtering of pure tungsten in a cylindrical magnetron device. The XRD-patterns of tungsten films deposited at 3.5 Pa argon pressure regularly exhibited only a very broad signal centered at 2θ ≈ 40°—a distinctive mark of amorphous metals and alloys. The grain size of such amorphous-like tungsten material was estimated to be approximately 2 nm, while SAXS measurements yield a radius of gyration of 1.4 nm. Its thermal coefficient of the electric resistivity at room temperature was negative—a characteristic feature of amorphous metals and alloys. Thermal stability of the amorphous-like tungsten films was investigated by isochronal heating up to 720 °C in vacuum, with continuous monitoring of electric resistivity. The obtained results indicate that amorphous-like tungsten is thermally stable up to 450 °C.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Magnetron sputtering; Tungsten films; Amorphous phase

1. Introduction

Tungsten is a metal of choice for some applications in microelectronic and optoelectronic devices. Its superior properties makes it suitable for gate contacts and interconnects in ULSI/VLSI devices, diffusion barriers in Al–W based technology, absorption layer for masks in X-ray lithography, and alternating layer in X-ray mirrors.

Tungsten films are often deposited by one or the other version of the chemical vapour deposition (CVD) process, the WF₆ being usually a source of tungsten and H₂ [1], Si [2], GeH₄ [3] and SiH₄ [4] were used as a reducing agents. Sometimes, W(CO)₆ is used instead of WF₆ [5]. Depending upon the deposition parameters, different modifications of metallic tungsten are obtained: thermodynamically stable α-W with the bcc crystal structure, metastable β-W form with A15-like crystal lattice, and even amorphous tungsten films were obtained [2,3].

Another extensively used method of tungsten films formation is d.c. or r.f. magnetron sputtering [6–11]. The sputter-deposited films tend to have high residual stress, which changes from strongly compressive to tensile with increasing working gas pressure. Simultaneously, the phase composition of tungsten films changes from predominantly α-W form to β-W phase modification. The formation and stabilization of β-W in case of sputter-deposited tungsten films is attributed to the incorporation of oxygen in the film [8,10,11], while in the CVD produced films, the observed β-W phase seems to be stabilized by various impurities: oxygen/fluorine [1], silicon [2,4], germanium [3], or carbon [5].

If the deposition conditions (either in CVD or sputtering processes) are beyond those of β-W formation, an amorphous tungsten phase is formed [3,4,10]. The characteristics of CVD prepared amorphous-like tungsten films have recently been examined in some more details [4].

Here we present the results on structure, oxygen content, electrical properties and thermal stability of amorphous-like tungsten films prepared by magnetron sputtering.

2. Experimental

Thin tungsten films were prepared in a sputtering system with two cylindrical magnetrons, and equipped with a diffusion pump and auxiliary titanium sublimation
pump [12]. The base pressure in the system was approximately $10^{-4}$ Pa. Working gas (argon, 5 N) pressure was varied in the range of 0.7–3.5 Pa, and the partial pressure of spectroscopically pure oxygen was varied in a 0–8% range with a total pressure kept constant at 1.4 Pa. A d.c. magnetron discharge operated in a continuous gas flow. Pure tungsten was used as cylindrical targets, and the average current density at the cathodes was 3.3 mA/cm$^2$. Substrates were discs of approximately 1 cm diameter made of sapphire, fused silica and monocrystalline silicon, and mounted onto a rotating holder in order to achieve lateral homogeneity of the films. The deposition rate was approximately 0.2 nm/s, and the final film thicknesses were in the 150–200 nm range.

The structure of the tungsten films was investigated by the Philips 1820 vertical goniometer with a monochromatized Cu Kα-radiation, in a Bragg–Brentano geometry.

SAXS measurements were performed at the ELETTRA synchrotron radiation source, Trieste (Italy), at the SAXS beamline, using a X-ray beam energy of 8 keV ($\lambda=0.154$ nm). Grazing incidence measurements were taken at different, fixed grazing angles on the sample, using a 2D CCD detector ($1024\times1024$ pixels) at a fixed position. The scattering was also measured with the beam entering the film perpendicularly to the surface (SAXS).

The oxygen content of the films was determined by nuclear reaction $^{16}$O(D,p)$^{17}$O, with 0.85 MeV deuterons. Mylar foil was placed in front of silicon detector in order to suppress detection of deuteron particles. For quantitative determination a reference standard of anodically oxidized tantalum was used [13].

The film resistivity was measured by the four probe method and by the standard a.c. technique. Thermal stability was examined by continuous monitoring of the electric resistivity variation during isochronal heating at the 4 K/min rate in vacuum better than $10^{-2}$ Pa. The structure of the film was checked by the XRD method at selected temperatures, in order to examine the degree of phase transformation.

3. Results and discussion

3.1. Structure and oxygen content of tungsten films

The structure of the prepared films follows a well-established sequence corresponding to the variation of the working gas pressure: stable $\alpha$-W phase at 0.7 Pa, a set of mixed-phases films with the increase of working gas pressure, predominantly $\beta$-W phase with the A15-like structure at 2.8 Pa, and an amorphous-like tungsten film obtained when the argon pressure is held at 3.5 Pa. The grain size in amorphous-like tungsten films can be estimated from the XRD patterns to be approximately 2 nm. The transition from $\beta$-W to amorphous-like tungsten occurs when the oxygen content in the films increases from approximately 13 to 17 at.%. In order to examine the effects of oxygen content in tungsten films upon their phase composition, pure oxygen was added into argon up to 8% partial pressure of 1.4 Pa total pressure. The tungsten films prepared at that pressure with pure argon regularly consist of almost pure $\alpha$-W phase. The XRD patterns of thus prepared films are shown in Fig. 1, while the corresponding oxygen content is given in Fig. 2. As seen, the film phase composition changes from pure $\alpha$-W up to 2.5% $O_2$ to completely amorphous-like above 3.0% $O_2$ partial pressure. Only in a narrow transitory range of 2.5–3.0% $O_2$, which corresponds to 14–16 at.% of oxygen in the film, a small fraction of $\beta$-W phase is observed. These results indicate that it is not only the total oxygen content in the tungsten film which determines the formation of different phases, but the way the oxygen
Fig. 2. Oxygen content (in at.%) as a function of oxygen partial pressure in working gas (argon), for a series of tungsten films deposited onto mono-Si at room temperature (cf. Fig. 1). The shaded area corresponds to the transitory range of pressure for which the $\beta$-W phase is observed.

It was recently shown [14] that oxygen, either in its molecular or atomic form, does not readily chemically react with fresh tungsten surface at room temperature. However, a tungsten surface adsorbs oxygen [14–16], presumably dissociatively [14]. Those adsorbed oxygen atoms might be either desorbed, thrust into the depth of the film, or simply buried by the incoming sputtered tungsten atoms. The relative probabilities of those processes obviously depend upon the incoming particle energy. If the incoming tungsten atoms are so slow that they can not push adsorbed oxygen atoms into the supporting layer of growing film, the single or several oxygen atoms might be simply buried under the new layer of the film. Thus, formed regions inhibit tungsten grains growth and effectively promote amorphous-like film structure. If not interstitially embedded, the observed oxygen must be situated in the grain boundaries, voids or as small oxygen aggregates embedded into the film. Those structural features were investigated by the SAXS and GISAXS methods.

The SAXS intensities, measured on amorphous-like tungsten, are shown in Fig. 3, where the substrate contribution has been subtracted. No anisotropy in the scattering has been observed, and therefore the integral intensity is shown. Using the Guinier fit, we obtained $R_g = 1.42$ nm for the radius of gyration. A significant depletion of intensities at very small angles is a result of particle–particle correlation. The SAXS data from $\alpha$-W and $\beta$-W are displayed for comparison. While the $\beta$-W displays similar scattering, with the radius of gyration slightly smaller ($R_g = 1.26$ nm), much lower scattering intensity and considerably smaller particle sizes ($R_g = 0.83$ nm) are found for $\alpha$-W.

GISAXS contour patterns (logarithmic) for amorphous-like tungsten are shown in Fig. 4. Apart from the broadened Yoneda peak at $q_s = 0.6/\text{nm}$, the scattering is of flattened particle type for the critical grazing angle value, i.e. minimum penetration depth, Fig. 4a. A more complex pattern for $\alpha_W = \alpha_{\text{CRIT}} + 0.6^\circ$ (Fig. 4b) suggests a considerable variation of the particle sizes deeper within the film.

From the above results, the amorphous-like tungsten films might be conceived as composed of nanosized grains of pure tungsten (with only a small amount of interstitial oxygen) separated by oxygen-stuffed voids and grain boundaries.

3.2. Thermal stability of amorphous-like tungsten

Thermal stability of amorphous-like tungsten was investigated up to $720^\circ$C, and the typical results are shown in Fig. 5. The temperature coefficient of the electric resistivity at room temperature was negative for all $\alpha$-W samples ($-1\times10^{-4}/\text{K}$), thus corroborating its amorphous-like nature. The electric resistivity drops sharply at approximately $300^\circ$C, and the XRD-analysis of the samples after a completed thermal cycle confirms a full transformation to the stable $\alpha$-W phase, with the electric resistivity reduced to approximately 40% of the initial value. Sequential up–down heating cycles showed that the amorphous-like tungsten film on fused silica substrate remains amorphous at least up to $440^\circ$C, while the crystallization was completed at $720^\circ$C (Fig. 6). The observed decrease of electric resistivity at approximately $300^\circ$C is probably due to some kind of
Fig. 4. 2-D GISAXS contours (logarithm of intensity) of amorphous-like tungsten for the grazing angle equal to critical angle, and 0.6° above the critical angle, (a) and (b), respectively. Axes values are given in $q=2\pi S$.

structural relaxation, which is reversible in its initial stage.

The above results indicate a considerable thermal stability of the amorphous-like tungsten phase. A similar thermal stability was observed in amorphous-like osmium films deposited from OsO$_4$ by plasma deposition process [17].

4. Conclusions

Thin films of amorphous-like tungsten were prepared by the magnetron sputtering technique, either by increase of the working gas (argon) pressure, or by a controlled addition of pure oxygen into discharge atmosphere. The results of XRD, SAXS and GISAXS examination suggest that such films consist of nanosized particles of pure tungsten with oxygen-stuffed voids or grain boundaries in between. The amorphous-like tungsten films are thermally rather stable, staying amorphous up to 440 °C and completely transforming into $\alpha$-W phase at 720 °C. That makes them suitable for anti-diffusion barriers even at elevated temperatures.

Fig. 5. Relative variation of the electrical resistivity upon isochronal heating (4 K/min) of the amorphous-like tungsten films deposited onto sapphire and fused silica substrates, respectively.

Fig. 6. The XRD patterns corresponding to the thermal transformation of the amorphous-like tungsten film deposited onto fused silica upon heating up to the selected temperatures.
Acknowledgments

The authors thank Mr A. Pavlešin for technical assistance.

References