

Molybdenum as an Alternative Metal: Thin Film Properties

V. Founta,^{1,2} T. Witters,¹ S. Mertens,¹ K. Vanstreels,¹ J. Meersschaet,¹ P. Van Marcke,¹ M. Korytov,¹
A. Franquet,¹ C. J. Wilson,¹ Z. Tőkei,¹ S. Van Elshocht,¹ and C. Adelman¹

¹ Imec, 3001 Leuven, Belgium

² Department of Materials Engineering, KU Leuven, 3001 Leuven, Belgium

Abstract—The structural and electrical properties of Mo thin films have been studied to assess the potential of Mo as an alternative to Cu or W metallization. The adhesion energy with dense low- κ dielectrics was above 5 J/m², suggesting that Mo can be integrated without the need for an adhesion liner. The Mo resistivity was lower than W in the entire thickness range between 3 and 50 nm and lower than Cu sandwiched between 1.5 nm TaN barriers for total a stack thickness below 8 nm. Mo thus appears promising as an interconnect metal, especially a potential replacement for W.

Keywords—Molybdenum; alternative metals; thin films; resistivity; adhesion

I. INTRODUCTION

Molybdenum (Mo) has recently received increasing interest as a potential conductor metal to replace W or Cu in logic or memory interconnects [1,2]. Mo offers low bulk resistivity (5.3 $\mu\Omega\text{cm}$) and high melting temperature (~ 2900 K), which can be considered as a proxy for electromigration performance. Furthermore, Mo possesses a short mean free path of the charge carriers (~ 11 nm), significantly shorter than those of W (~ 16 nm) and Cu (~ 40 nm) [2]. This suggests that the resistivity of Mo should increase less strongly with line or via width/area than W and Cu.

A first step towards the assessment of Mo as an interconnect metal is the study of the properties of thin films with thicknesses in the nm range. Especially the thickness dependence of the Mo resistivity in the relevant thickness range has not been well established and in many cases, rather high Mo thin film resistivities have been reported [3,4], presumably due to poor crystallinity of the films. In this paper, we discuss the properties of Mo thin films deposited by PVD with thicknesses in the range between 3 and 50 nm. We show that these Mo films are promising for conductor applications, especially to replace W.

II. EXPERIMENTAL DETAILS

All Mo films were grown by PVD on 300 mm SiO₂(100 nm)/Si wafers using a Canon Anelva tool. Mo film thicknesses were determined by a combination of x-ray reflectance and Rutherford backscattering spectrometry. Resistivities were determined from 4-point sheet resistances in combination with the film thickness corrected for the thickness of the surface

oxide, which was assumed to be insulating. Adhesion energies were determined by the 4-point bending method.

III. RESULTS

Fig. 1 shows x-ray diffraction (XRD) patterns (2θ - ω and grazing incidence) of Mo films with thicknesses as indicated. The 2θ - ω patterns in Fig. 1a were consistent with bcc Mo and indicate that films thicker than ~ 10 nm show a strong (110) (fiber) texture, typical for bcc metals. The grazing incidence XRD patterns in Fig. 1b indicated the presence of a minority component with random orientation, whose volume was rather independent of the film thickness. This suggests that the Mo films grew initially with a random orientation close to the interface with SiO₂, followed by the development of a (110) texture for thicker films. The grain size of a 10 nm thick Mo film was determined by the linear intercept length method using dark-field transmission electron microscopy (TEM) and was found to be 18 nm. This confirms the rather high degree of crystallinity observed by XRD. The AFM rms surface

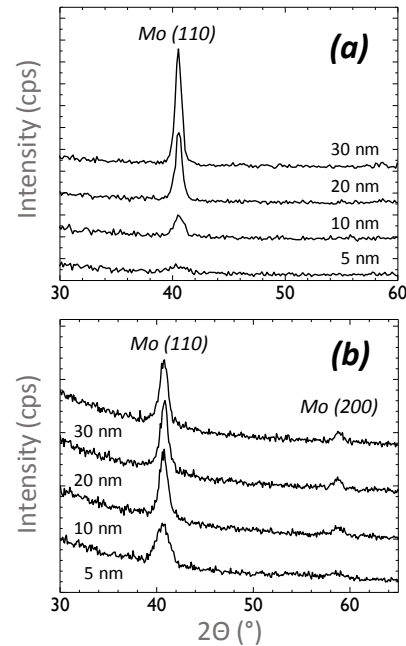


Fig. 1. (a) 2θ - ω and (b) grazing incidence XRD pattern of Mo films with thicknesses as indicated. The data are offset for clarity.

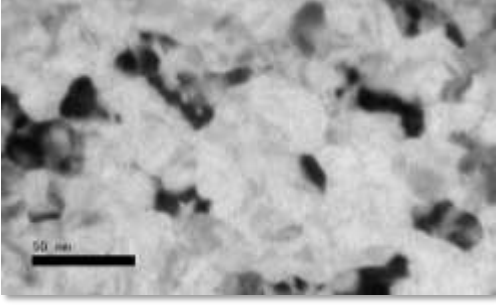


Fig. 2. Dark-field TEM image of a 10 nm thick Mo film.

roughness (not shown) was below 0.5 nm even for a 30 nm thick film, indicating little roughening during deposition.

The thickness dependence of the resistivity of as deposited PVD Mo thin films is shown in Fig. 3. For reference, data are also shown for Cu sandwiched between 1.5 nm of TaN, W, as well as several Pt-group metals. Mo showed resistivities that were lower than those of W over the entire thickness range and comparable to TaN/Cu/TaN below a total stack thickness of 8 nm. Resistivities were about 30% higher than those of Ru around 10 nm. The thickness dependence of the resistivity was similar to that of W and much weaker than that of Cu. The resistivity of Mo increased however more rapidly with decreasing thickness than the Pt-group metals. These results are qualitatively consistent with the respective mean free paths of the charge carriers, which are shortest for the Pt-group metals (~6 nm for Ru; 7 nm for Ir [2]) and longest in Cu.

Adhesion between Mo and dielectrics was found to be strong. Measured adhesion energies on SiO₂ and on dense OSG low- κ dielectric with $\kappa = 3.0$ are shown in Tab. I. On both dielectrics, adhesion energies were above 5 J/m². Annealing at 800°C did not affect the adhesion energy on SiO₂. A thin TiN liner increased the adhesion further. The results suggest however that the Mo adhesion might be sufficiently strong for truly barrierless integration in interconnects, in contrast to *e.g.*

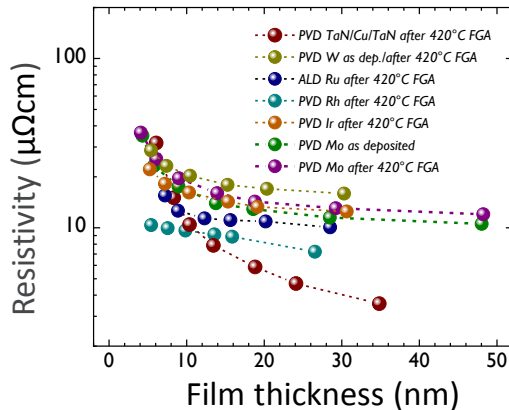


Fig. 3. Resistivity of PVD Mo (both as deposited and after annealing in forming gas at 420°C) as a function of film thickness. For comparison, data are also shown for TaN/Cu/TaN, W, and several Pt-group metals.

TABLE I. ADHESION ENERGIES OF PVD MO ON DIFFERENT DIELECTRICS, LINERS, AND FOR DIFFERENT POST-DEPOSITION ANNEALING (PDA) CONDITIONS

Dielectric	Liner	PDA	Adhesion energy (J/m ²)
SiO ₂	none	none	6.9 ± 0.5
SiO ₂	none	800°C, 30 s	6.6 ± 0.7
SiO ₂	0.3 nm TiN	none	10.1 ± 3.7
Low κ	none	none	5.1 ± 0.5
Low κ	0.3 nm TiN	none	5.7 ± 0.3

Ru, which typically requires an adhesion liner [5].

Annealing of the Mo films at 420°C in forming gas, *i.e.* H₂/N₂ (FGA), increased the resistivity by about 25% as shown in Fig. 3. This is in contrast to Pt-group metals, which showed recrystallization and a decrease of the resistivity upon annealing. The increase in resistivity could be linked to the incorporation of N in the film, as evidenced by secondary-ion mass spectrometry (not shown). The XRD pattern after annealing (not shown) indicated a slight reduction of crystallinity but showed no signs of the MoN_x phases expected to form at higher temperatures [6]. This indicates that a N₂-containing ambient cannot be considered as “inert” for the annealing of Mo even at temperatures as low as 420°C.

IV. CONCLUSION

In conclusion, we have studied the properties of PVD Mo thin films for the prospective use of Mo as a conductor metal in logic or memory interconnects. The Mo resistivity was about 30% higher than that of Ru but outperformed W over the entire studied thickness range. Due to the good adhesion with SiO₂ and low- κ dielectrics, Mo has the potential for true barrierless integration. The main remaining challenge for the dual damascene integration of Mo in scaled interconnect lines and vias lies in the development of a Mo deposition process that is capable of filling narrow lines with a material quality and crystallinity similar to those demonstrated here for PVD.

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