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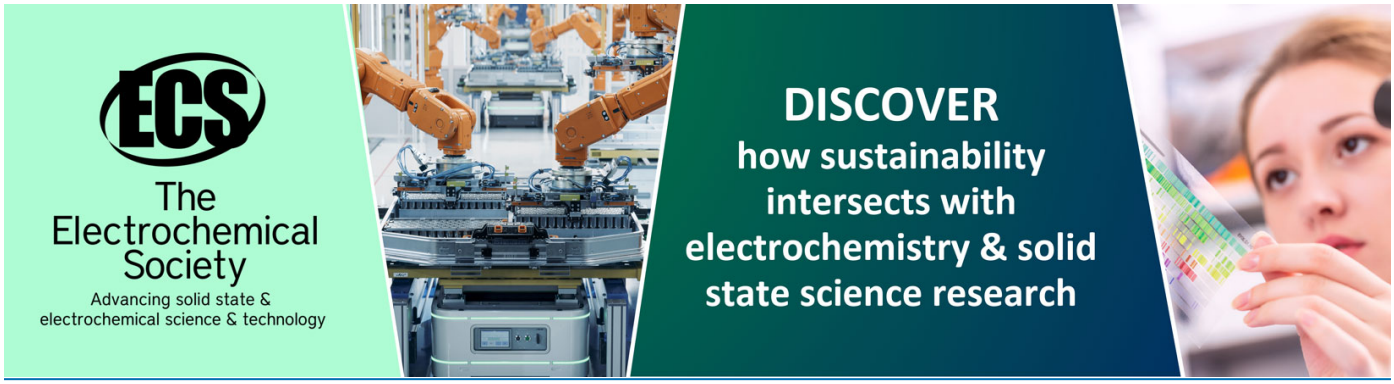

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A nitriding process of very thin molybdenum films in an expanding microwave plasma at low temperature

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Abstract. A transfer of nitrogen of about 20 at % is detected in very thin molybdenum films of about 200 nm thick coated on Si (100) wafers heated at 673 K and exposed to ternary (Ar-N_2-H_2) plasma. The nitrogen diffusion goes with a noticeable decrease of the remaining oxide layers in the whole film thickness. On the contrary, pure N_2 gas exposure leads to a slight diffusion of nitrogen into the first molybdenum layers up to a depth of about 40 nm, only and an enhancement of oxygen amount also. Hydrogen species contained in the plasma reduce the oxide layers which act as nitrogen diffusion barrier. The nitrogen diffusion decrease with increasing distance of the workpiece surface from the centre of the discharge as well as the occurrence of nitrogen diffusion in molybdenum layers at room temperature highlight the role of $NH_{x<3}$ active species of the plasma on the reactivity of the surface. The morphology of the nitrided surface consists of slightly smaller grains compared with those corresponding to untreated molybdenum films ranging in size from 30 to 50 nm wide. In contrast to substrates heated at 873 K, the tetragonal Mo_2N structure has not been detected in molybdenum films heated at 673 K.

Introduction

In addition to attractive physical and chemical properties of transition metal nitrides such as high hardness, melting point and electrical conductivity, good chemical stability, a growing scientific and technological interest is focused on their catalytic properties. Mo_2N and W_2N compounds are catalytically active for NO reduction in presence of hydrogen. The NO conversion on Mo_2N is equal to 89 % at 723 K and remains constant for 10 h. Besides, the catalytic properties of Mo_2N can be compared to those of noble metals for hydroprocessing, H_2-D_2 exchange reactions and so on…[1-2]. Moreover, since metal nitrides exhibit a good corrosion resistance, a very thin layer forms a good diffusion barrier preventing the metal film from oxidizing [3]. A thermochemical process including expanding plasma activated by microwave discharge has been successfully developed for metal nitriding [4, 5]. The method consists of producing gaseous species and carrying them out along the discharge up to the workpiece surface. Since the density of electrons in the discharge is strongly reduced by inelastic collisions occurring between electrons and molecules, high dilutions of molecular gas in Ar gas are realized. So, this method allows selecting active gaseous species such as $NH_{x<3}$ simple radicals since, they are mainly detected in (Ar-N_2) gas mixtures with low N_2 as H_2 is injected within the discharge [6]. The purpose of this work is to carry out measurements on the transfer of nitrogen into very thin molybdenum layers heated at low temperature and exposed to various (Ar-N_2-

H_2) gas mixtures. Correlations with plasma parameters such as the electron density and the presence of active gaseous species in the plasma such as $NH_{x<3}$ radicals are sketched. The crystallographic structure and the morphology of the nitrided film are also investigated and compared to those obtain at higher temperature. Such experimental conditions are suitable for metal films coated on substrates which could be damaged by using high temperature.

2. Experimental set-up

The nitriding treatments are carried out in expanding plasma activated by microwave discharge. The reactor consists of a fused silica tube where a microwave discharge is produced using a power supply SAIREM GMP 12 kE operating up to 1200 W. The plasma is expanded out of the discharge centre into the stainless steel vessel up to the workpiece substrate put on a heating holder which can move relatively to the discharge centre along the vertical axis. The experiments are all carried out at a total pressure of 0.13 kPa using an Alcatel roots blower pump. More details are given in reference [5]. The surface temperature is calibrated with a two colours pyrometer (IRCON mirage). Molybdenum thin films of about 200 nm thick are deposited on Si (100) wafers in an electron beam evaporator. Molybdenum pellets, 99.95% pure are evaporated in Ar gas at a pressure of 0.5 Pa on a Si (100) substrate heated at 400°C and polarized at - 400 V. Such experimental conditions allow reducing oxygen in the ingot and providing a good adhesion of molybdenum films on Si substrates.

The molybdenum films are heated at 673 K and exposed to pure N_2 gas and (Ar-25%N_2-30%H_2), (Ar-8%N_2-10%H_2) and (Ar-30%N_2-12%H_2) ternary gas mixtures. The gas contents are expressed as a percentage of total volume of gas. The experiments are conducted at a microwave power of 400 W for 40 or 15 min. One sample is exposed to (Ar-25%N_2-30%H_2) at room temperature. The elemental depth profiles of the nitrided molybdenum films are recorded by secondary neutral mass spectrometry (SNMS) in a secondary ion mass spectrometer LAB from VG Instruments. The sputtering is carried out using Ar^+ primary ions beam with energy of 8 keV. The size of the as-formed craters is of (500 x 500) μm^2. The sputtered neutrals are ionized by a thermionic filament [7]. The yield of ionization can be assumed as a constant and reference samples are used to conduct quantitative measurements. The crystallographic structure is investigated by X-ray diffraction (XRD) in a theta-2 theta SIEMENS D5000 diffractometer using CuKα radiation and sol-X energy dispersive detector. The configuration of the system is the classical Bragg-Brentano geometry. Atomic force microscopy (AFM) measurements of the morphology of the surface are performed by means of a Digital Instrument Nanoscope II operating in constant force mode. The signal is fitted by subtracting a “polynomial plane” which consists of a surface whose cross section is a second order polynomial in one axis and a horizontal line in the other axis.

3. Results and discussion

Mo, Si, N, C, and O depth profiles recorded in SNMS from molybdenum films exposed to pure nitrogen gas and (Ar-25%N_2-30%H_2) gas mixture are displayed on figure 1. A large nitrogen transfer occurs up to the Mo-Si interface in the molybdenum film exposed to ternary plasma during 15 min compared to the untreated surface and the one exposed to pure nitrogen gas (Figure 1 (b),(a) and (c)).

As seen in figure 1(b), the nitrogen concentration slightly decreases from the surface up to the Mo-Si interface. The nitrogen concentration in the molybdenum layers increases with increasing treatment duration since the nitrogen concentration is constant and equal to about 20 at.% in the whole film thickness (Figure 1(d)). Moreover, a noticeable decrease of remaining oxides and carbides is also seen, almost no oxygen is detected compared to the untreated molybdenum film and the one nitrided during 15 min. In contrast to these results, pure N_2 gas exposures under the same experimental conditions lead to a slight nitrogen transfer into the molybdenum layers up to a depth of 40 nm, only (Figure 1(c)). Moreover, an amazing strong increase of oxygen content is detected in the first molybdenum layers. At a depth larger than 40 nm, the oxygen concentration is similar to the one corresponding to the untreated substrate. It is worth noting that the sputtering effect of impinging energetic ions which plays a great role in most of plasma treatments is rather low in our process, since the mean electron energy values range between 0.5 and 0.7 eV in (Ar-N_2-H_2) gas mixtures, so the reduction of oxide layers is mainly due to the reducing properties of hydrogen species [5]. Moreover, the addition of hydrogen in the nitriding gas mixture prevents the molybdenum film from oxidizing during the nitriding process.

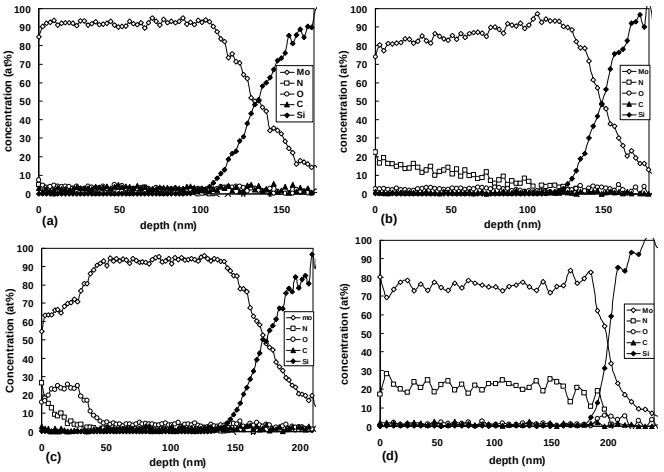

Figure 1. SNMS depth profiles of Mo films at 673 K at 9.5 cm from the discharge centre exposed to (Ar-25%N_2-30%H_2) during 15 min (b), to pure N_2 gas during 15 min (c), to (Ar-25%N_2-30%H_2) during 40 min (d) compared to the untreated surface (a)

As seen in figure 2(a) and (b), a 40 min treatment in (Ar-8%N_2-10%H_2) and (Ar-30%N_2-12%H_2) plasma leads to similar results than those previously described for (Ar-25%N_2-30%H_2) plasma.

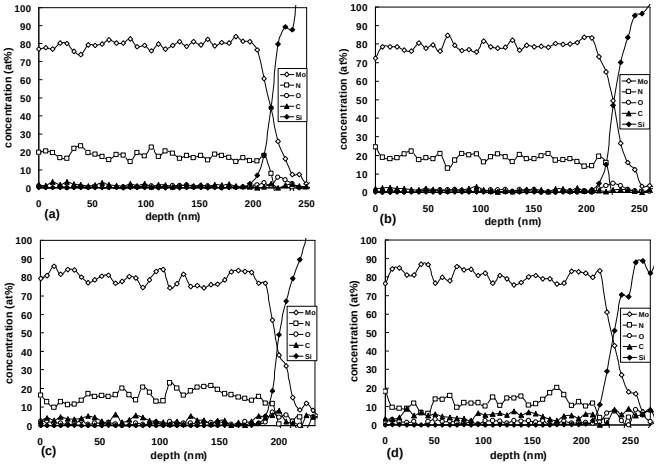

Figure 2. SNMS depth profiles of molybdenum films nitrided at 673 K at 9.5 cm from the discharge centre during 40 min in (Ar-8%N_2-10%H_2) plasma (a), in (Ar-30%N_2-12%H_2) plasma (b), at 15 cm from the discharge centre in (Ar-25%N_2-30%H_2) plasma (c) and at room temperature at 9.5 cm from the discharge centre (d)

The nitrogen transfer decreases with increasing distance from the centre of the discharge (Figure 2(c)). This behaviour could be correlated to $NH_{x<3}$ species remaining close to the centre of the discharge because of their high reactivity. The results reported in Figure 2(d) display nitrogen diffusion and large oxygen and carbon amount in the whole film thickness at room temperature. A similar trend has already been detected by SIMS investigations [9]. As indicated in figure 3, such behaviour could be due to porous films. However, exothermic reactions occurring between impinging species such as atomic H, $NH_{x<3}$ radicals and the surface could promote the nitrogen diffusion into the molybdenum film. Further investigations could confirm such trends. It is worth noting that the heats of formation of Mo_2N and MoC at room temperature are equal to -34 and -18.24 kJmole^{-1}, respectively whereas those of MoO_2 and MoO_3 are equal to -544 and -755 kJmole^{-1}, respectively [8].

Before they have been exposed to plasma, molybdenum films have been cut from substrates of various roughness. The corresponding surfaces exhibit small and rather round grains ranging in size from about 30 to 50 nm (Figure 3(a) and (c)). The former consists of agglomerates. The roughness is equal

to about 15.2 and 4.3 nm, respectively. (Ar-8%N_2-10%H_2), (Ar-25%N_2-30%H_2) ternary plasma as well as pure N_2 gas exposures lead to a slight increase of roughness equal to about 15.8, 15.5 (not shown here) and 5,4 nm, respectively and a slight decrease of grain size.

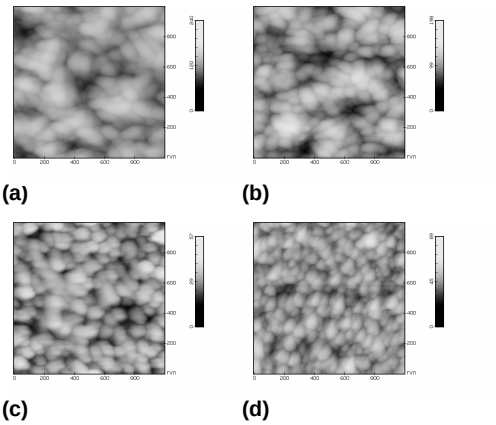

Figure 3. Surface morphology investigated by AFM of molybdenum films heated at 673 K and exposed to (Ar-8%N_2-10%H_2) plasma (b), to pure N_2 gas (d) and compared to the corresponding untreated substrates (a) and (c), respectively.

Previous investigations performed on nitrided molybdenum films heated at 873 K and exposed to ternary plasma have shown that a large nitrogen diffusion occurs in molybdenum films with diffusion coefficients ranging between 5 x 10^{-10} and 5 x 10^{-9} cm^2s^{-1}. The formation of grains of nanometer size of Mo_2N tetragonal structure is also reported [5]. This structure has not been detected in molybdenum films heated at 673 K. Investigations are currently carried out to evidence a possible formation of non-stoichiometric Mo-N phases.

4. Conclusion

The nitriding process using expanding microwave plasma with (Ar-N_2-H_2) ternary gas mixtures promotes the transfer of nitrogen up to Mo-Si interface in molybdenum film heated at low temperature and even at room temperature compared to pure N_2 gas exposure which leads to a slight nitrogen diffusion. Hydrogen species contained in the plasma allow reducing oxide and carbide species which act as diffusion barrier. The role of active $NH_{x<3}$ species has been also evidenced, however further works will lead to a better understanding of the influence of such species. In the same way, the possible formation of non-stoichiometric Mo-N phases will be investigated.

5. Acknowledgement

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6. References

[1] Shi C, Zhu A M, Yang X F and Au C T 2004 *Appl. Catalysis A* **276** 223
[2] Nagai M, 2007*Appl. Catalysis A.* **322** 178
[3] Shiota T, Imamura T, and Hasuo S 1991 *J. Appl. Phys.* **70** 6958
[4] Jauberteau I, Jauberteau J L, Cahoreau M and Aubreton J 2001 *Trends in Vacuum Science and Technology* **4** J. Menon (Trivandrum, India : Research Trends) 77
[5] Jauberteau I, Jauberteau J L, Goudeau P, Soulestin B, Marteau M, Cahoreau M and Aubreton J 2009 *Surf.Coat.Tech.* **203** 1127
[6] Jauberteau J L, Jauberteau I, and Aubreton J 2002 *J. Phys .D : Appl. Phys* **35** 665
[7] Czerwiec T, He H, Weber S, Dong C, and Michel H 2006 *Surf. Coat. Tech* **200** 5289
[8] Perry R H, Green D W 1984 *Chemical Engineers Handbook 6th edition* (Mc Grow-Hill, New-York 3)
[9] Jauberteau I, Jauberteau J L, Cahoreau M and Aubreton J 2005 *J. Phys .D : Appl. Phys* **38** 3654