A reduction–nitridation process of molybdenum films in expanding microwave plasma: Crystal structure of molybdenum nitrides

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ABSTRACT

This work reports the structure of molybdenum nitride phases crystallizing in molybdenum films coated on Si (100) substrates, and exposed to (Ar–N_2–H_2) gas mixtures with various gas contents in an expanding microwave plasma reactor. Compared with the numerous data found in literature, the formation of βMo_2N and γMo_2N phases strongly oriented in the [204] and [220] crystalline directions, respectively is unexpected. The βMo_2N phase is synthesized in molybdenum films exposed to pure N_2 plasma for 1 h whereas the molybdenum films exposed to (Ar–33%N_2–1%H_2) plasma for only 30 min consists almost entirely of γMo_2N phase. The Mo_2N crystallites about 30 nm wide display a columnar morphology in the growth direction after processing in (Ar–33%N_2–1%H_2) plasma. In contrast with most processes where energetic ions improve the nitrogen transfer into the surface layers of the metal film, the expanding plasma process promotes the chemical reactions on the surface of the material. The remaining oxides are reduced by hydrogen species such as NH_x radicals produced in (Ar–N_2–H_2) plasma. The reactions are exothermic and could involve the formation of intermediates such as hydrogen molybdenum bronze H_xMoO_3 that would promote the crystallization of the high temperature γMo_2N phase to the detriment of the low temperature βMo_2N phase during the reduction–nitridation process.

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1. Introduction

Transition metal nitrides have been widely investigated for their very interesting physical and chemical properties. Their very good catalytic properties compared with those of noble metals are due to the presence of nitrogen atoms in interstitial lattice sites of the metal which are active for adsorption and catalytic reactions [1–7]. Molybdenum nitrides have been especially applied to a large range of reactions such as CO hydrogenation, NO dissociation, NH_3 synthesis, and hydroprocessing. They are very active during hydrodenitrogenation and their properties can be compared with more traditionally used catalysts as sulfided Ni–Mo and Co–Mo. Besides catalytic properties, transition metal nitrides have been found to have extreme hardness, thermal integrity, high melting point, low solubility in non-ferrous metals such as copper, good chemical resistance, metallic-like appearance that make them very attractive for numerous applications such as hard coatings, corrosion and abrasion resistant layers, decorative coatings, barriers of diffusion, and gate electrodes. Transition metal nitrides are promising to replace traditional materials in deep submicron integrated circuits in which the number of transistors grows continuously [8–11]. Moreover, owing to their good electronic conductivity

and their moderately high specific area, the molybdenum nitrides can be used in electrodes for thin film capacitors [12,13].

The solubility of nitrogen in molybdenum metal is rather low [14, 15]. The use of NH_3 instead of N_2 as reactive gas makes the reaction difficult to control and often leads to a mixture of phases. Moreover the NH_3 decomposition is endothermic so the use of N_2–H_2 gas mixture circumvents the problem of heat transfer. A thermodynamic analysis of the formation of group VI nitrides and especially Mo_2N from Mo or MoO_3 and N_2, N_2–H_2 or NH_3 has been published [16]. The Gibbs free energy corresponding to the reaction between Mo and N_2 is equal to -40.15 kJ mol^{-1} at 300 K [14]. Three MoN phases are identified on the phase diagram [14]. The high temperature γMo_2N phase of face centred cubic structure of NaCl type (Fm3m space group) consists of nitrogen atoms randomly distributed in half of the total octahedral sites of the structure. The low temperature βMo_2N phase of tetragonal structure is a distorted face centred cubic lattice with an ordered arrangement of nitrogen atoms similar to the nitrogen martensite $Fe_{16}N_2$ where the c-parameter is doubled compared with γMo_2N. These two phases exist over a wide range of stoichiometry $Mo_2N_{1+/-x}$. The transition between them depends on the stoichiometry and lies in the temperature range from 673 to 1123 K [17]. The third δMoN phase is stoichiometric and crystallizes in an ordered hexagonal structure with three different structure types; WC, NiAs and distorted NiAs [6,7]. In the same way these authors report a γMo_2N phase of Pm3m space

group with ordered vacancies which can be distinguished from γMo_2N phase Fm3m space group by the presence of superstructure reflections. The Mo–N compounds exhibit superconducting transition at critical temperatures ranging between 12 and 15 K for δMoN and at temperatures as low as 4–5 K for γMo_2N [8,18,19]. Such values have been reported in other works [20,21]. Molybdenum nitride compounds also crystallize in Mo_2N of hexagonal structure [9] and $\beta Mo_{16}N_7$ of tetragonal structure [9,22]. Mo_3N_2 crystallises in a structure similar to γMo_2N with an excess of nitrogen in the lattice [9]. Amorphous structures are also reported in the literature as $Mo_{72}N_{28}$ [10], $Mo_{75}N_{25}$ [23] as well as compounds with N/Mo ratio larger than 1 as the gold coloured Mo_2N_3 phase [9,24]. The metastable stoichiometric γMoN phase of cubic structure has been predicted and could achieve superconducting temperature as high as 29 K [9,18,19]. Mo_5N_6 compound of hexagonal structure has also been reported [6,7].

Films of molybdenum nitrides can be made by various processes including reactions between molybdenum film or substrate and NH_3 gas [15,25], metal organic chemical vapour deposition (MOCVD) [9,24], atomic layer deposition (ALD) using metal precursors [8], DC, RF or magnetron reactive sputtering [10,11,18,26,27,28] electron cyclotron resonance [29] reactive cathodic arc evaporation [17], nitrogen plasma immersion implantation (PIII) [30,31], or pulsed laser irradiation [21,32].

In this work, the molybdenum films are processed in expanding $(Ar–N_2–H_2)$ plasma generated by a microwave discharge of 2.45 GHz. In such plasma, the electron and ion energy are rather low. In most plasma processes, the impinging energetic ions have a strong sputtering effect on the passive oxide or carbide layers which act as barrier of diffusion for nitrogen. In the expanding plasma process, the hydrogen species as NH_x radicals and/or H atoms produced in $(Ar–N_2–H_2)$ plasma are expected to reduce the remaining oxide layers that improve the transfer of nitrogen into the metal film compared with the molybdenum films processed in pure N_2 or $(Ar–N_2)$ plasma. Moreover our previous works have shown that hydrogen species also prevent the formation of MoO_2 oxides which takes place in molybdenum films exposed to pure N_2 plasma. The MoO_2 oxides are probably synthesized from oxygen and/or water desorption from the walls of the reactor in contact with the plasma [33,34]. So, since the diffusion of nitrogen as well as the composition has already been greatly reported in our previous papers, the present work is mainly focused on the crystallographic structure of molybdenum films of different thickness processed in $(Ar–N_2–H_2)$ gas mixtures of various compositions. Nevertheless the diffusion of nitrogen and the element composition are briefly reported in what follows as well as some comparisons of our results with those obtained by other processes. The main purpose of this work is to correlate the structure of molybdenum nitrides with the composition of plasma and especially with hydrogen species produced in $(Ar–N_2–H_2)$ plasma.

2. Experimental set-up

The reactor consists of a fused silica tube (external and internal diameter of 24 and 20 mm, respectively) passing through a surface wave launcher where a microwave discharge is produced using a power supply SAIREM GMP 12 kE operating up to 1.2 kW at a frequency of 2.45 GHz. The plasma is expanded out of the discharge centre into the stainless steel vessel up to the heating substrate holder which can move relative to the centre of the discharge along the vertical axis (Fig. 1). The temperature of the surface of the sample is calibrated with a two colour pyrometer (IRCON mirage). A turbomolecular pump maintains a base pressure of 10^{-5} Pa in the reactor and the total pressure of 0.13 kPa is kept constant using an Alcatel roots blower pump (70–700 $m^3\ h^{-1}$) with a corresponding gas drift velocity of about 20 ms^{-1}.

$(Ar–N_2–H_2)$ gas mixtures of various compositions are introduced in the fused silica tube.

The power of the electromagnetic wave absorbed by the plasma is mainly transferred to the electrons and then to other gaseous species by inelastic collisions. The conditions of propagation of the
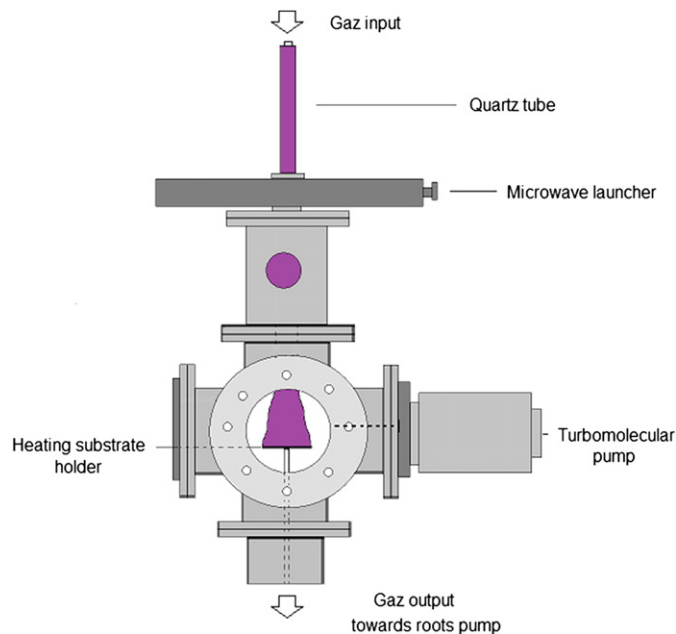

Fig. 1. Experimental set-up.

electromagnetic wave are satisfied when the density of electrons is above a critical value which depends on the plasma conditions (collisional or collisionless plasma) and on the microwave frequency. In pure Ar plasma, the electromagnetic wave frequency of 2.45 GHz is lower than the plasma frequency ω_p equal to 7.3 GHz at a microwave power of 400 W, at 2 cm from the discharge tube exit and for an electron density of $1.68 \times 10^{16}\ m^{-3}$. So, the real part of the relative permittivity is negative and the electromagnetic wave is reflected by the plasma [35]. The plasma is thus produced by a surface wave propagating into the reactor along the external surface of the expanding plasma. The reactive species which are mainly produced on the edge of the plasma diffuse towards the centre of the plasma and react at the surface of the material.

The electron density in pure N_2, $(Ar–33\%N_2)$ and $(Ar–33\%N_2–1\%H_2)$ plasma used in this study are almost similar. The values range between 0.03 and $0.15 \times 10^{16}\ m^{-3}$ in $(Ar–33\%N_2–1\%H_2)$ at 400 W. The electron energy ranges between 0.51 and 1.37 eV. The density and energy of the plasma are homogeneous above the surface of the metal film [36]. The density of NH_3 is equal to $5.77 \times 10^{20}\ m^{-3}$ and the density of NH_2, NH and N radicals ranges between 2.71 and $2.83 \times 10^{20}\ m^{-3}$, 2.48×10^{19} and $6.92 \times 10^{18}\ m^{-3}$, 1.04×10^{18} and $5.77 \times 10^{18}\ m^{-3}$, respectively, compared with the density of Ar equal to $2 \times 10^{22}\ m^{-3}$. The ion flux which mainly consists of Ar^+ ions impinging the surface is equal to about $6.9 \times 10^{18}\ m^2\ s^{-1}$. The ion energy at the sheath entrance is about 0.1 eV. So, the energy of the ion flux is too low to produce a sputtering effect on the surface and the heating effect can be probably disregarded.

Because of the geometry of the expanding plasma, it is expected to process surfaces of dimensions larger than those usually treated and equal to about 1 cm^2.

Molybdenum films 250, 500 nm and 1 μm thick are deposited on Si (100) wafers from pure molybdenum cylinder and pellets (99.95% pure) in an electron beam evaporator filled with Ar gas at a pressure of 0.5 Pa. The Si wafer is polarized at −400 V and heated up to 673 K to improve the adhesion of molybdenum films on silicon substrates. The samples (dimension of about 1 cm^2) are cut from the as-deposited molybdenum film — silicon wafer, heated at 873 K and exposed to pure N_2, $(Ar–33\%N_2)$ and $(Ar–33\%N_2–1\%H_2)$ at 400–500 W and at a distance of 12.5 cm from the centre of the discharge for 30 min or 1 h. The gas contents are expressed as a percentage of the