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Thin film metallization by magnetron sputtering from highly pure molybdenum targets

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Abstract

Both vacuum and powder metallurgy methods of preparation of molybdenum for magnetron-sputtering targets were studied. It is found that a combination of multiple-electron-beam melting and electric arc vacuum melting is an optimal metallurgical method to obtain highly pure molybdenum polycrystalline ingots for massive magnetron targets. Highly sensitive methods of analysis were used to characterize the molybdenum target. The specific resistivity of deposited thin molybdenum films was found to be strongly dependent on both the sputtering conditions and the initial target purity.

1. Introduction

Aluminium and polycrystalline silicon have been used effectively for many years as low resistance interconnections in microelectronic devices. However, these materials cannot be applied in devices with elements of submicron dimensions because of electrical leakage and film degradation at high temperatures. This problem can be solved by using thin films of refractory metals for metallization. A low concentration of alkaline metals (potassium, sodium), radioactive metals (thorium, uranium) and light elements (carbon, oxygen, nitrogen, hydrogen) is required as well as chemical and structural homogeneity of the deposited thin films. This is the main reason for the demand for high purity refractory metals in microelectronic applications. Unfortunately, only very limited information on the preparation of high purity molybdenum for magnetron sputtering can be found in the literature [1].

As a rule, commercial molybdenum sheets produced by standard powder metallurgy are of limited use for the preparation of thin metallic films of good electrophysical quality because of their high concentration of gaseous and metallic impurities. Light metal impurities, characterized by high vapour pressure at the melting temperature of molybdenum, can be removed during vacuum melting, annealing and/or chemical purification. Radioactive metal impurities in molybdenum can be extracted by chemical methods. The basic method of controlled reduction of gaseous impurities (carbon, oxygen, nitrogen, hydrogen) in refractory metals is high temperature vacuum melting. During this procedure the dissolved atoms of gaseous impurities diffuse to the liquid metal surface and then desorb from it. The main mechanisms of oxygen desorption depend on the nature of the metal. On the basis of the principles of "evaporation deoxidation", the high temperature behaviour of oxygen in liquid molybdenum in vacuum is characterized by a high excess of the metal oxide vapour pressure over the metal vapour pressure. Therefore dissolved and then chemisorbed oxygen desorbs either oxygen molecules or metal (carbon) oxides.

Another situation exists for carbon atoms which are strongly bound to the metal and cannot desorb independently. The basis of carbon evolution into vacuum is the interaction of carbon and oxygen on the metal surface and further desorption in the form of gaseous CO.

We have accomplished a complex study which allows us to establish the kinetic connection between the behaviour of the mean concentrations of carbon and oxygen in molybdenum and other refractory metals. We studied theoretically and experimentally the dependence of this connection on the initial concentrations of these impurities, on temperature, on the gaseous phase and on the "diffusional transparency" of the liquid metal [2–4]. The optimal conditions of vacuum refining were determined and the possibility was demonstrated of preparing molybdenum and other refractory metals with extremely low concentrations of carbon and oxygen (about 10^{-6} at.%). Therefore in this paper the relationship between the purity of the initial molybdenum targets used for magnetron sputtering and the

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sputtering conditions was examined for the preparation of thin molybdenum films with optimal specific resistivity.

2. Experimental procedure

Two metallurgical procedures were used to prepare magnetron targets from molybdenum of high purity [5]. Procedure 1 consisted of multiple-electron-beam melting (EBM) of compacted powder feedstocks at a melting rate of about 0.5 kg min^{-1} in a vacuum of 1×10^{-6} Torr. The mean EBM power was 100 kW at an accelerating voltage of 25 kV and an emission current of 4 A. Two types of water-cooled copper crystallizers were used: cylindrical and rectangular. Cylindrical crystallizers were used to prepare ingots 80–140 mm in diameter and 1300 mm long. Rectangular crystallizers were used to prepare "flat" ingots of dimensions $35 \times 100 \times 1300$ mm^3. Procedure 2 consisted of duplex processes, *i.e.* multiple-electron-beam melting and electric arc vacuum melting. The melting rate of multiple EBM was the same as in procedure 1 but the rate of arc melting of ingots 200 mm in diameter and 300 mm long was about 2.5 kg min^{-1}. The liquid molybdenum in the crystallizer of the electric arc vacuum set-up was intensively stirred by the electromagnetic field of the solenoid. Thus EBM was used for vacuum purification of the liquid metal from gaseous and metallic impurities, while electric arc vacuum melting was used to prepare ingots which had a cross-sectional macrostructure with a mean grain size of about 2 mm. Analysis of the impurity concentration in the molybdenum target before sputtering was carried out by means of highly sensitive analytical methods: fast neutron and deuteron activation, spark mass spectrometry, atomic absorption, combustion, etc.

Molybdenum films were deposited on Si(100) wafers (10–20 Ω cm) with or without a thin film (about 0.3 μm) of silicon dioxide at room temperature. The substrates were cleaned chemically prior to loading into the magnetron-sputtering apparatus. Special care was taken to exclude such contaminants as oxygen, carbon and alkaline metals from the apparatus environment. The sputtering chamber pressure was about 10^{-6} Torr prior to sputtering on the substrates; the magnetron targets were trained for 40 min in vacuum. During sputtering, the chamber was filled with argon of high purity to a pressure of about 10^{-3} Torr. The relative atomic purity concentration in argon was less than 3×10^{-6}. Before sputtering, heating of the silicon wafers to 250–300 °C was carried out. It has been found that such a procedure is sufficient to produce a clean surface. The deposition rate is practically proportional to the sputtering power at a constant pressure in the sputtering chamber. The sputtering rate and layer thickness were controlled with a and microprocessor and profilometer respectively. Then the as-deposited films were annealed in vacuum. The resistivity of the films was measured using a standard four-point resistivity probe.

3. Results and discussion

The specific resistivity of metals is an integral characteristic of their purity. Generally speaking, the film properties are affected not only by the deposition process as a whole but also the initial quality of the sputtering targets. The idea of the complex vacuum metallurgy process which was used for the preparation of highly pure molybdenum is mainly to decrease the contents of gaseous impurities to extremely low values [6]. Thus the concentration of the gaseous and most important metal impurities in the prepared molybdenum targets is as follows (at. ppm): 0.1 C, 0.5 O, 0.05 N, 0.6 K+Na, 20 W, 2 Nb, 2 Ta; the total concentration of 24 other elements analyzed is 17 ppm. The specific resistivity of massive specimens of EBM molybdenum is 5.2–5.6 μΩ cm. To study the influence of the metallurgical procedure used for the preparation of targets on the specific resistivity of thin molybdenum films, we sputter targets prepared both by the standard powder metallurgy (PM) procedure and by vacuum EBM. The content of gas-forming elements (carbon, oxygen, nitrogen) in the PM specimens is at least 100 times greater than in the EBM molybdenum specimens. It should be mentioned that after prolonged vacuum annealing the concentration of gaseous impurities is still very high. The specific resistivities of molybdenum films 0.15–1.0 μm thick deposited from PM and EBM targets under the same sputtering conditions are 20–35 and 7 μΩ cm respectively. Thus these experiments show that the initial purity of the target material has a very strong influence on the specific resistivity of thin molybdenum films.

After sputtering, the magnetron targets of both types (cylindrical and rectangular) had an erosion path about 10 mm deep and 20 mm wide (Fig. 1) and the further sputtering process was unstable. The quantity of sputtered material was about 15%–20% depending on the target construction. This also shows that the design of the targets and magnetrons used was not optimal.

We also study the effect of substrate heating on the specific resistivity. When molybdenum films are deposited on unheated substrates, their specific resistivity increases by 50%–150% and the scatter of the specific resistivity increases by 30%–40%. This can be accounted for by the influence of gaseous impurities adsorbed on the substrate surface. We find confirmation of this fact in the lowering of the specific resistivity of molybdenum films deposited on unheated substrates with a sublayer of titanium or vanadium (a few hundredths of an

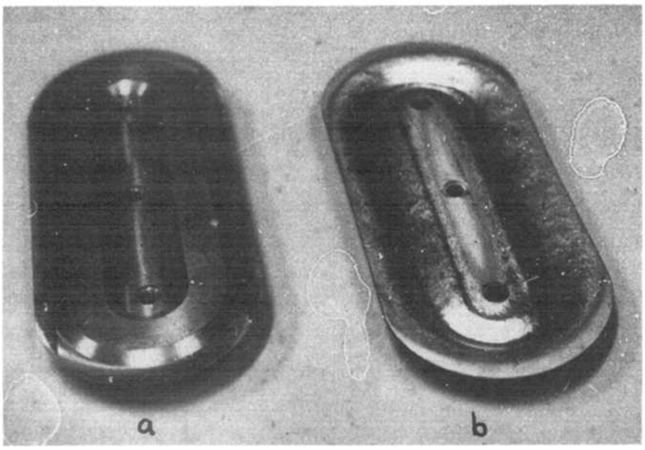

Fig. 1. Two types of magnetron targets before (a) and after (b) sputtering.

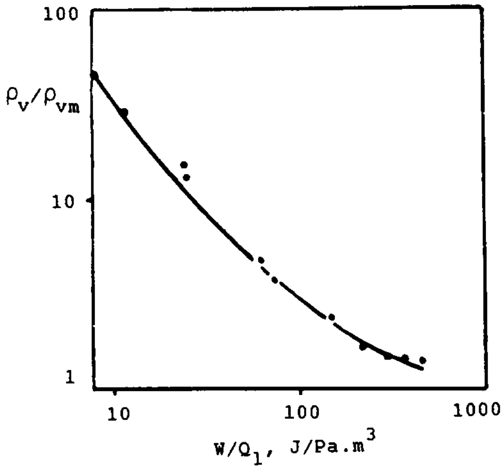

Fig. 2. Dependence of the film resistivity on the ratio of the sputtering power W and the air leakage Q_l; ρ_{vm}, specific resistivity of the massive target; ρ_v, specific resistivity of the deposited film.

ångström thick). These metals were sputtered from other targets in the same sputtering chamber and probably react with the gases adsorbed on the substrate surface. We suppose that the presence of additional very thin layers should not have a strong effect on resistivity measurements.

To elucidate the influence of gaseous impurities in the specific electrical resistivity of molybdenum films, the sputtering power (deposition rate) was varied and an air leakage (1×10^{-5}, 4×10^{-5} and 4×10^{-4} Pa m^3 s^{-1}) was introduced during sputtering. The experiments confirmed that the specific electrical resistivity of the films depends strongly on the deposition rate and the presence of reactive gases in the deposition region (Fig. 2). The ratio of the film resistivity (ρ_v) to the target resistivity (ρ_{vm}) is a characteristic of the procedure (film) quality: the higher the ratio, the less clean is the procedure (film). In other words, the specific resistivity of the film depends on the ratio of the quantities of sputtered (deposited) atoms and interstitials dissolved in the molybdenum film.

We have obtained the dependence of the specific resistivity on the interstitials dissolved in the deposited film (Fig. 3). To analyse this dependence, the atomic concentration C_i of interstitials from reactive gases can be written as

$$C_i = \left(1 + \frac{\nu_m S}{n\nu_g S}\right)^{-1} \tag{1}$$

where ν_m and ν_g are the specific rates of metal deposition and of the condensation of molecules of n-atom reactive gases in the molybdenum film respectively; S is the deposition area.

The rate of dissolution of reactive gases in the deposited molybdenum film is much higher than the rate of gas exchange in the deposition region of the magnetron-sputtering units, *e.g.*, for the air leakage Q_l we have

$$Q_l = \nu_g S \tag{2}$$

Here we have assumed the rate of dissolution of reactive gases in the film to be constant. Because the quantity of metal atoms, $\nu_m S$, which is sputtered in unit time is nearly proportional to the sputtering power W, we have

$$\nu_m S = kW \tag{3}$$

where k is the coefficient of proportionality. This coefficient changes slowly with the electrical sputter parameters and is determined by the dependence of the sputtering coefficient of molybdenum on the energy of the sputtering ions and the geometry of the sputtering unit. Considering eqns. (1)–(3), we have

$$C_l = \left(1 + \frac{kW}{nQ_l}\right)^{-1} \tag{4}$$

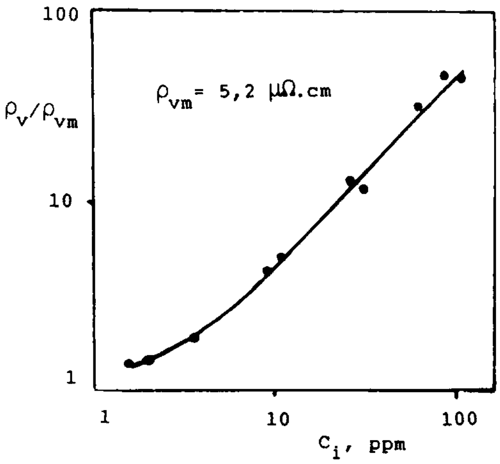

Fig. 3. Dependence of the resistivity ratio on the interstitial concentration in the deposited molybdenum film.

This equation describes the dependence of the interstitial concentration in the film on the ratio of the sputtering power to the reactive gas flow into the deposition region. This dependence allows one to present the curves of Fig. 2 as the dependence of the specific resistivity on the atomic concentration of interstitials in the film (Fig. 3). The air leakage influence becomes very strong as the atomic concentration of interstitials in the film becomes higher than about 10^{-3} at.%.

4. Conclusions

We have demonstrated the possibility of preparing molybdenum with concentrations of carbon and oxygen which are on the level of the sensitivity limit of current analytical methods. Multiple- (double- or triple-) electron-beam melting and electric arc vacuum melting are the optimal methods for the preparation of high purity polycrystalline molybdenum targets for magnetron sputtering. The preparation method of the massive targets and the conditions of sputtering have a strong effect on the electrophysical properties of deposited molybdenum thin films. By indicating a way to evaluate the interstitial concentration in the deposited film, this approach allows one to determine regimes of sputtering providing the preparation of high purity metallic layers with optimal electrical resistivity. The difference in specific resistivity between molybdenum targets and deposited thin films depends entirely on the sputtering conditions.

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