Reactively sputtered amorphous MoN film as a diffusion barrier for copper metallization

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The barrier capability of amorphous MoN thin film was investigated against Cu diffusion. The MoN layers were reactively sputtered of 50 nm by using a different nitrogen flow rates. The phase identification was evaluated by X-ray diffractometer (XRD), four probe method and scanning electron microscope (SEM). Results indicate that the amorphous 50 nm MoN layer act as a good diffusion barrier upto 600 ˚C for cooper metallization.

(Received December 18, 2010; accepted January 26, 2011)

Keywords: Reactive d. c. sputtering, Diffusion barrier, Copper metallization

1. Introduction

Copper is an attractive material for interconnection metallization in such ultra large scale integration (ULSI) devices owing to its low resistivity, high reliability against electromigration, and feasibility of physical vapor deposition (PVD) [1]. However, copper diffuses readily into the Si and SiO_2 layers, and is oxidized easily, which causes degradation of electrical performance of device. To prevent the copper diffusion and corrosion, the insertion of effective diffusion barrier and capping layers is most important aspects of Cu interconnect technology [2-8].

A large number of refractory metals such as Ti, Ta, Mo, Cr, Co, W, Pd, and Nb and their alloys either in polycrystalline or amorphous phase have been investigated for their diffusion properties in terms of their higher thermal stability and low resistivity [8-10].

A few reports on the investigation of Mo and its alloys have been reported in the literature.

In this work, MoN films are deposited by reactive d.c. magnetron sputtering from a Mo target. The variation of deposition rate and crystalline and amorphous microstructure formation is studied. In addition, the thermal stability of amorphous MoN barrier layer is investigated by using Cu/MoN(50nm)/Si structure and vacuum annealing from 300 ºC to 700 ºC for 30 minute.

2. Experimental details

N-type (100)-oriented Si wafers and glass substrates were used for this study. These substrates were cleaned by standard cleaning process (RCA).

MoN thin films were prepared by reactive d.c. magnetron sputtering technique by sputtering Mo target (99.99% purity) with Ar gas mixed with N_2 in predetermined ratios. The background pressure in the chamber was less than 5.5×10^{-6} torr prior to deposition. The nitrogen gas flow was varied between from 0 to 20 sccm. During depositions, the sputtering power, argon gas flow and total gas (Ar + N_2) pressure were kept constant at 80 W, 40 sccm and 3×10^{-2} torr, respectively; the substrate holder was placed at 40 mm far from the target. The thicknesses of the films were measured using the stylus Profiler (AMBIOS XP-1). Thin film X-ray diffraction (XRD) spectra of MoN recorded using a Panalytical's X'Pert Pro diffractometer operating in the θ-2θ Bragg configuration using Cu Kα radiation. Data were collected at a scan rate of 0.075 θ min^{-1} and sampling interval of 0.002 °θ. The voltage was set at 45 kV with a 40 mA flux.

To test the thermal stability of the MoN barriers, copper films of 100 nm in thickness were sputtered over the 50 nm thick MoN layers. The Cu/MoN/Si samples were then annealed in a Vacuum furnace for 30 min. Interfacial behavior and phase formation of the samples after annealing were characterized by JEOL JSM - 6390 LV (INCA from Oxford instruments) Scanning Electron Microscope (SEM) and XRD, respectively. Variation in sheet resistance of samples, before and after annealing, was measured with a four-point probe method.

3. Results and discussion

3.1 Material characteristics of sputtered MoN thin films

a) Deposition rate:

The deposition rate of MoN coating was evaluated for different nitrogen partial pressure, as shown in Fig. 1. The deposition rate decrease with increases the nitrogen gas flow rate, this behavior may be explained based on the occurrence of the so called target poisoning by the reactive gas [11].

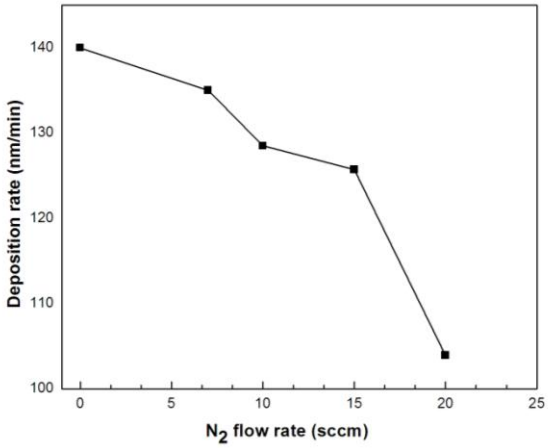

Fig. 1. Deposition rate versus N_2 flow rate.

b) Structure:

Fig. 2 shows the XRD profiles of 50-nm thick MoN films which were prepared by sputtering deposition on a glass substrate using various (Ar + N_2) flow ratios. With a zero nitrogen flow Mo (110) phase at angle 40.58˚ was observed. γ-Mo_2N (111), β-Mo_2N(200) and β-Mo_2N(220) phases were formed when the film was prepared with a low 7 sccm flow rate of nitrogen. The XRD intensity of the peaks increases at the 10 sccm nitrogen flow rate and γ-Mo_2N (111) transformed into Mo_3N_2 (111) phase. Although peaks corresponding to crystalline MoN were observed with increasing nitrogen upto 15 sccm flow rate and shift towards the lower angle. Subsequent to 15 sccm of nitrogen flow rate the intensity of MoN peak start decrease which indicates that the amorphousization starts. The XRD profile changes with increasing the nitrogen gas flow are indicates of a film structural transition from crystalline to amorphous structure in the as-deposited MoN films. It is evident that the MoN films structure is very sensitive to the nitrogen gas flow ratios. Information about the phase in the as-deposited films observed by the XRD is given in Table 1. The grain size (D) of alloy films was calculated by using Scherrer formula:

$$D = \frac{0.89\lambda}{\beta_{1/2}\cos\theta}$$

where λ, θ and $\beta_{1/2}$ are the X-ray wavelength (1. 54056 Å), Bragg diffraction angle and full width at half maximum (FWHM), respectively.

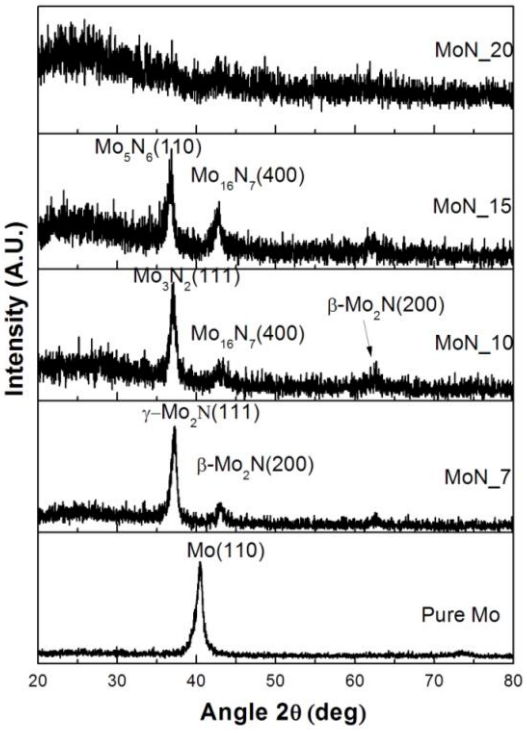

Fig. 2. XRD spectra of MoN deposited at various N_2 flow rates.

Table.1. Micro-structural observations of as-deposited MoN thin films.

Samples Name	**Nitrogen flow (sccm)**	**2θ (deg)**	**FWHM (2θ deg)**	**Grain Size (A˚)**	**d-spacing (A˚)**	**Phase**
Pure Mo	0	40.498	0.576	146.146	2.225	Mo(110)
MoN_7	7	37.226	0.6298	132.848	2.4154	γ-Mo_2N(111)
		43.073	0.6298	135.742	2.1001	β-Mo_2N(200)
		62.584	1.536	59.8689	1.4835	β-Mo_2N(220)
MoN_10	10	37.056	0.551	150.659	2.4260	Mo_3N_2(111)
		42.973	1.536	54.993	2.1029	$Mo_{16}N_7$(400)
		62.584	1.536	59.868	1.4835	β-Mo_2N(220)
MoN_15	15	36.766	0.6298	131.573	2.4455	Mo_5N_6(110)
MoN_20	20	42.668	0.960	88.1672	2.1173	$Mo_{16}N_7$(400) Amorphous structure

c) Resistivity:

Fig. 3 shows the resistivity of reactively sputtered MoN films as a function of nitrogen flow rates. In this figure, pure Mo (110) film with a resistivity of 3.028×10^{-7} Ω-cm is observed without any nitrogen flow. The resistivity of MoN films increase slightly between nitrogen flow of 7 to 15 sccm and then increases dramatically for exceeding 15 sccm flow rate. Fig. 2 shows the XRD spectra of MoN films deposited at different nitrogen flow rates. It is known that crystallographic structure of MoN film is affected by nitrogen flow during the reactive sputtering. The same phenomena observed in TaN [12, 13]. At the nitrogen flow rate of 20 sccm, the XRD spectrum shows an amorphous structure. Hence the resistivity of MoN increased dramatically above this point may be due to the amorphous phase.

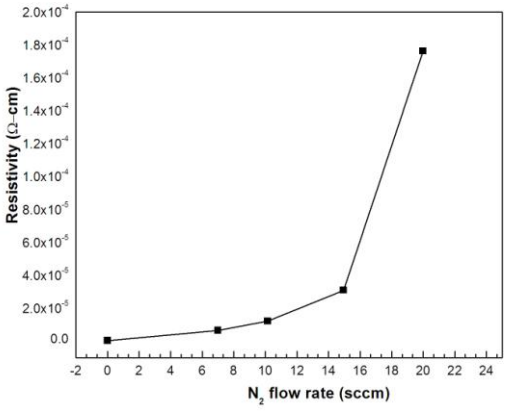

Fig. 3. Resistivity of reactively sputtered MoN films as a function of Nitrogen flow rates.

3.2. Thermal stability of Cu/MoN/Si structure

Amorphous 50 nm MoN film use a diffusion barrier between the Cu layer and Si substrate to compare the barrier properties. Single crystalline materials are expected to function as the best diffusion barriers because at low temperatures bulk diffusion is extremely small, and there are no grain boundaries for fast diffusion. However, deposition of single crystalline thin films can not yet be technologically realized. Consequently, the preferred microstructure of thin films for diffusion barrier applications is amorphous as it eliminates the fast diffusion paths along the grain boundaries. Fig. 4 shows the XRD from the Cu/MoN/Si systems before and after annealing for 30 minute. The spectra of the sample annealed at 300, 400, 500 and 600 ˚C are similar to that of the as-deposited. At 700 ˚C, diffraction peaks of Cu_3Si appear. The difference of the sheet resistance between the annealed and as-deposited samples, divided by the sheet resistance of as-deposited samples, is called the variation percentage of sheet resistance (ΔRs/Rs %) [14]. It is well known that Cu diffuses fast in Si and form CuSi compounds at a temperature as low as 200 ˚C, and the formation of Cu-Si compounds results in the increase of sheet resistance of Cu films.

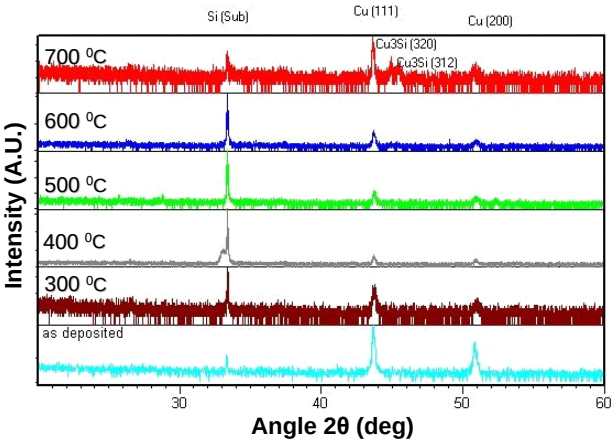

Fig. 4. XRD pattern of Cu/MoN/Si structure annealed at various temperatures.

Fig. 5 presents the variation percentage of sheet resistance versus annealing temperature for the Cu/MoN/Si samples. It is shown that the sheet resistance of the Cu/MoN/Si structure remains constant upto 600 ˚C for 30 min. However, a drastic increase in sheet resistance is found after annealing above 600 ˚C. This is attributed to the formation of high resistive Cu_3Si precipitates according to the XRD analysis.

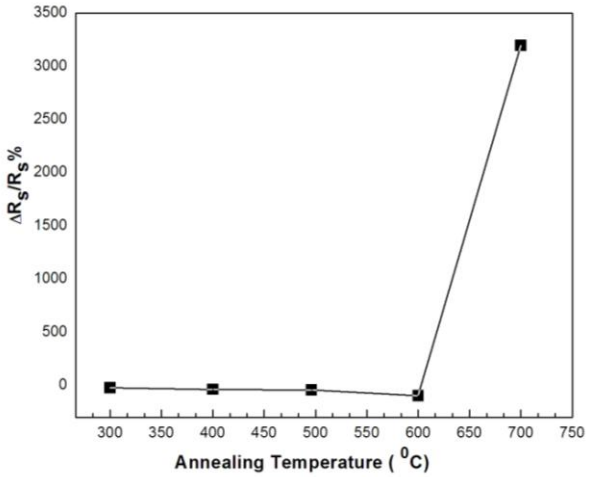

Fig. 5. Variation percentage of sheet resistance against annealing temperature for the Cu/MoN/Si samples.

As deposited surface morphology of Cu/MoN/Si structure using SEM micrographs is shown in Fig. 6a. The top copper film is continuous even after annealing of the structure at 600 ˚C is given in Fig. 6b. The micrograph in Fig. 6c shows tiny white particles on the surface. The deterioration in the top copper film is clearly visible at 700

˚C annealing, means that the MoN barrier layer failed at this temperature.

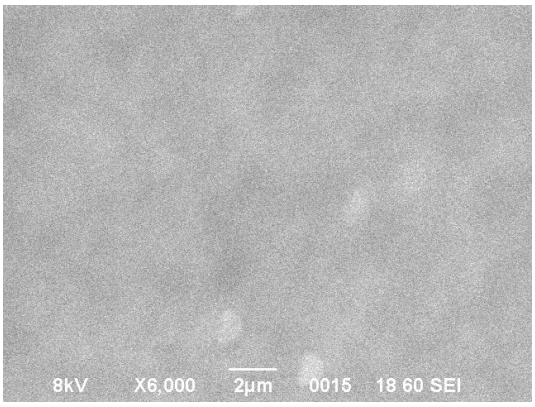

Fig. 6a. SEM image of Cu/MoN/Si as deposited structure.

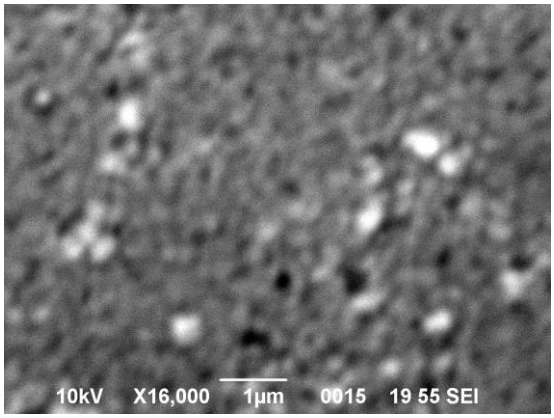

Fig. 6b. SEM surface morphology of Cu/MoN/Si structure, 600 ºC annealed samples for 30 min.

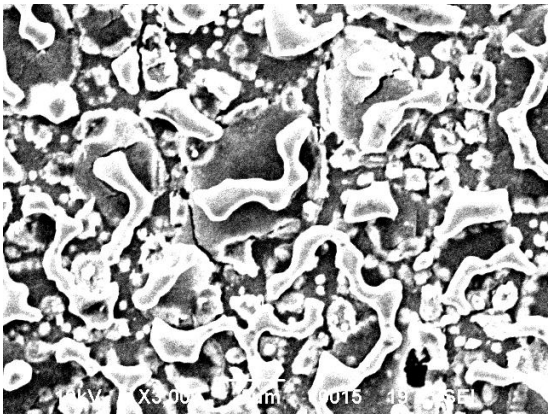

Fig. 6c. SEM surface morphology of Cu/MoN/Si structure, 700 ºC annealed samples for 30 min detorated film clearly observed.

4. Conclusion

Amorphous MoN thin films prepared by sputtering Mo target using argon and nitrogen mixed gas. It was found that the structures of the MoN films were sensitive to the nitrogen gas flow ratio during sputtering and complete amorphous phase were observed with high nitrogen flow rates.

The thermal stability of amorphous MoN thin film against Cu diffusion was evaluated for the application in the copper interconnection technology. It was observed that the MoN act as a diffusion barrier up to 600 ˚C. The annealing at higher temperature resulted in appearance of high resistive copper silicide phase.

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