

Nitrogen partial pressure influence on physical properties of DC magnetron sputtered copper nitride films

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Dc magnetron sputtering technique was employed for preparation of copper nitride films on glass substrates by sputtering of copper target at a substrate temperature of 423 K under various nitrogen partial pressures in the range 1×10^{-4} – 5×10^{-3} mbar. The dependence of cathode potential on the nitrogen partial pressure was explained in terms of nitridation of copper target and secondary electron emission. The deposition rate of the films was correlated with the nitrogen partial pressure. The effect of nitrogen partial pressure on the structural, mechanical, electrical and optical properties of copper nitride films was systematically investigated. The single phase films of copper nitride with electrical resistivity of $5 \times 10^{-2} \Omega \text{ cm}$, microhardness of 4.1 GPa under optical bandgap of 1.85 eV were obtained at nitrogen partial pressure of 1×10^{-3} mbar.

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1. Introduction

In recent years much attention has been focused on the covalent metal nitrides for applications in microelectronic devices. Among these, copper nitride (Cu_3N) is a stable material at room temperature and starts to decompose into copper at a temperature of about 573 K. The low decomposition temperature with discriminating optical properties made it useful for generating microscopic copper metal spots on Cu_3N films by local laser heating [1]. Maya obtained Cu_3N films by dc sputtering to explore the feasibility to generate microscopic copper metal lines on maskless laser writing [2,3]. A density over Mb/cm^2 in $1 \mu\text{m} \times 1 \mu\text{m}$ dot array has been realized using electron irradiation [4] where the write rate of 3.3 Mb/s can be achieved [5]. Various thin film deposition techniques such as ion assisted vapor deposition [1], dc and rf sputtering [2,3,6 - 11] and pulsed laser deposition [12] were employed for preparation of Cu_3N films. Among the sputtering techniques, dc reactive magnetron sputtering has advantage of proper control on the chemical composition, high deposition rates and low substrate heating during the deposition of the films. It provides films of uniform thickness on large area substrates and good control of the physical properties. The physical properties of the dc magnetron sputtered films critically depends on the sputter process parameters such as nitrogen partial pressure, sputtering pressure, substrate temperature and substrate bias voltage apart from the sputtering power. In this investigation an attempt is made in the deposition of Cu_3N films by dc reactive magnetron sputtering under various nitrogen partial pressures. The influence of the nitrogen partial pressures on the structural, electrical and optical properties has been investigated.

2. Experimental

Cu_3N films were grown on glass substrates by using dc reactive magnetron sputtering technique. The sputtering system is capable of creating an ultimate vacuum of 3×10^{-6} mbar. A circular planar magnetron of 100 mm diameter was used as the magnetron cathode. The magnetron target assembly was mounted on the top plate of the sputter chamber such that the sputtering could be done by sputter down configuration. A continuously variable dc power supply of 750 V and 3 A was used as power source for sputtering. 100 mm diameter and 3 mm thick copper (99.99% pure) was used as sputter target. Pure argon was used as sputter gas and nitrogen as reactive gas. The flow rates of both argon and nitrogen gases were controlled individually by Tylan mass flow controllers. Before deposition of each film, the target was sputtered in pure argon atmosphere for 15 min to remove impurities if any on the surface of the target. Cu_3N thin films were deposited at a substrate temperature of 423 K, sputtering pressure of 5×10^{-2} mbar under various nitrogen partial pressures in the range 1×10^{-4} - 5×10^{-3} mbar. The deposited films were characterized by studying the crystallographic structure, mechanical, electrical and optical properties. Thickness of the films was measured by optical interference method. The crystallographic structure of the films was analyzed by (Seifert Model 3003 T) X-ray diffractometer using copper K_α radiation with wavelength of 0.15405 nm. The X-ray diffraction profiles of the films were taken in 2θ with the range 20° - 80° . The lattice parameter (a) of the films was calculated from the interplanar spacing (d) and corresponding Miller indices using the relation

$$d = a / (h^2 + k^2 + l^2)^{1/2} \quad (1)$$

where h , k and l are the Miller indices. The microhardness of the films was measured using Nano-Indenter XP system. Quartz was used as a reference sample whose hardness was about 10 GPa. It was measured at a constant depth of 50 nm and measured at 20 points on each film and the average value of hardness was taken. The electrical resistivity was determined by employing the van der Pauw method [13]. The sheet resistance (ρ_s) of the films was calculated using the equation

$$\rho_s = (\pi / \ln 2) f [(R_1 + R_2) / 2] \quad (2)$$

where f is the van der Pauw correction factor, which depends on the position of electrical contacts on the film surface. The value of van der Pauw correction factor can be obtained from the relation

$$f = 1 - (\ln 2 / 2) [(R_1 - R_2) / (R_1 + R_2)]^2 \quad (3)$$

The electrical resistivity (ρ) of the films has been determined from the relation

$$\rho = \rho_s \times t \quad (4)$$

where t is the film thickness. The optical transmittance (T) and reflectance (R) were recorded using Hitachi U – 3400 UV-Vis- NIR double beam spectrometer in the wavelength range 300 –1500 nm. The optical absorption coefficient (α) has been calculated from the optical data using the relation

$$\alpha = (1/t) [\ln T / (1-R)^2] \quad (5)$$

The dependence of α on the photon energy ($h\nu$) was fitted to the relation for direct transition between the top of the valance band and the bottom of the conduction band using the relation

$$\alpha h\nu = A (h\nu - E_g)^{1/2} \quad (6)$$

where E_g is the optical band gap of the film and A the absorption edge width parameter.

The refractive index (n) of the films was evaluated from the interference pattern of optical transmittance data using the Swanepoel's envelope [14] technique employing the relation

$$n(\lambda) = [N + (N^2 - n_0^2 n_1^2)^{1/2}]^{1/2} \quad (7)$$

and

$$N = 2 n_0 n_1 [(T_M - T_m) / T_M T_m] + (n_0^2 + n_1^2) / 2$$

where T_M and T_m are the transmittance maximum and minimum, respectively.

3. Results and discussion

In the reactive sputtering the deposition of Cu_3N films can be understood by studying the current – voltage

characteristics of copper target under various nitrogen partial pressures. The variation of copper cathode potential on the nitrogen partial pressure is shown in Fig. 1. At any constant cathode current, initially the cathode potential shows a gradual decrease with the increase of nitrogen partial pressure. After reaching a critical nitrogen partial pressure the cathode potential starts to increase with the increase of nitrogen partial pressure. At a constant cathode current of 150 mA the cathode potential decreased from 360 V to 346 V with the increase of nitrogen partial pressure from 1×10^{-4} mbar to 8×10^{-4} mbar, respectively. The decrease of cathode potential was due to the start of the building up of nitride layer on the target surface. Since the nitrides and oxides have higher secondary electron emission coefficient than that of the pure metal of copper, the total number of electrons as well as ionization increased there by decrease in the cathode potential to maintain the same cathode current. At higher nitrogen partial pressures the formation of nitride layer on the surface of the copper target increased thereby decreasing the electrical conductivity of the sputter target. Hence higher cathode potential is necessary to break up this barrier on the copper [15]. Such a change of cathode potential was also noticed in the reactive sputtering of pure metal targets like titanium [16], aluminum [17] and zinc [18] in the presence of reactive gas of oxygen.

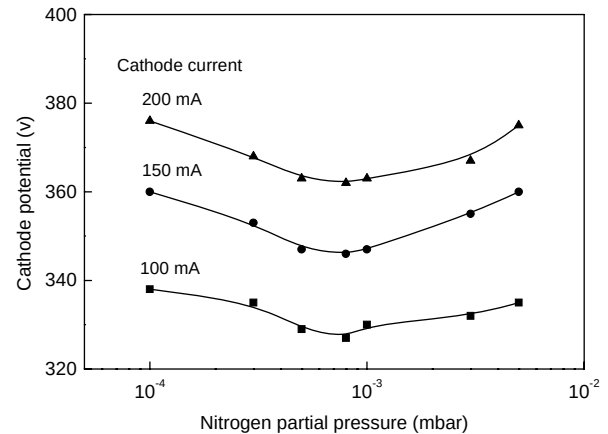


Fig. 1. Dependence of copper cathode potential on the nitrogen partial pressure.

The variation of deposition rate of Cu_3N films with the nitrogen partial pressure is shown in Fig. 2. The deposition rate of the films remains constant of about 20 nm / min up to nitrogen partial pressure of 5×10^{-4} mbar, thereafter gradually decreases with the increase of nitrogen partial pressure and reaches a value of 12 nm/min at 5×10^{-3} mbar. This indicates that the nitrogen partial pressure at which cathode potential starts the decrease related to the one at which deposition rate drops. The decrease in the deposition rate is the result of the nitridation of target and the resultant low sputtering yield of the nitride. The decrease of deposition rate with the increase of nitrogen partial pressure was also noticed in rf magnetron sputtered Cu_3N films [8].

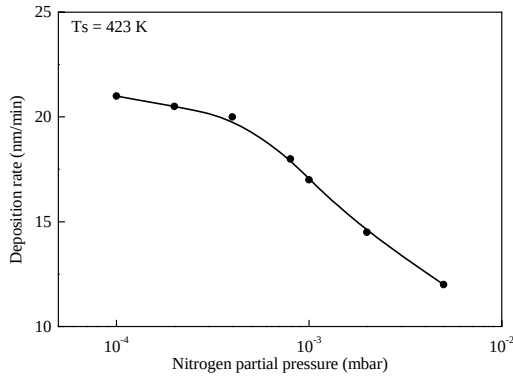


Fig. 2. Variation of deposition rate of copper nitride films with the nitrogen partial pressure.

The X-ray diffraction patterns of the films formed at various nitrogen partial pressures are shown in Fig. 3. The films formed at low nitrogen partial pressure of 5×10^{-4} mbar contained the peaks at $2\theta = 23.30^\circ$, 41.55° and 43.15° . The peaks observed at 23.30° and 41.55° related to the (100) and (111) orientation of copper nitride. The peak at 43.15° belongs to the unreacted copper. It indicates that the films formed at low nitrogen partial pressures resulted the mixed phase of copper and copper nitride. When the nitrogen partial pressure increased to 1×10^{-3} mbar single phase films of copper nitride were formed. For further increase of the nitrogen partial pressure the intensity of the peaks increase. This indicates that the crystallinity of the films increase with the increase of nitrogen partial pressure from 5×10^{-4} mbar to 5×10^{-3} mbar respectively. Nosaka et. al [8] obtained the single phase copper nitride films at nitrogen partial pressure of $> 3 \times 10^{-4}$ mbar in reactive rf magnetron sputtering where the sputtering was done at the total nitrogen and argon pressure was 8×10^{-3} mbar. Pierson [10] obtained single phase copper nitride films at nitrogen partial pressure of 1×10^{-3} mbar by rf magnetron sputtering. The grain size of the films evaluated from the (111) peak of copper nitride increased from 12 nm to 20 nm with the increase of nitrogen partial pressure. The lattice parameter of the films formed at nitrogen partial pressure of 1×10^{-3} mbar was 0.3818 nm which is in good agreement with the standard JCPDS data [19].

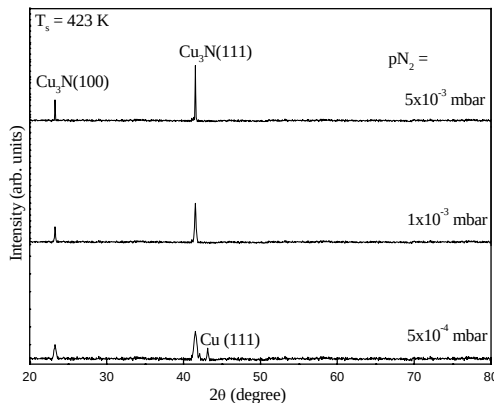


Fig. 3. X-ray diffraction patterns of copper nitride films.

The variation of microhardness of copper nitride films with the nitrogen partial pressure is shown in Fig. 4. This shows that the microhardness of the films is highly influenced by the nitrogen partial pressure. The microhardness of the films increased from 3.0 GPa to 4.3 GPa with the increase of nitrogen partial pressure from 1×10^{-4} mbar to 5×10^{-3} mbar, respectively. The microhardness of pure copper was 1.7 GPa. The low hardness at low nitrogen partial pressures was due to the formation of mixed phase of Cu and Cu_3N . The increase of hardness with the increase of nitrogen partial pressure was due to the formation of single phase Cu_3N . The microhardness observed at nitrogen partial pressure of 1×10^{-3} mbar was 4.1 GPa. It is in agreement with the value of 4.25 GPa achieved in rf magnetron sputtered films [10]. High microhardness of about 8 GPa was reported in the Cu_3N films prepared by rf plasma chemical reactor with low pressure supersonic single jet system [20].

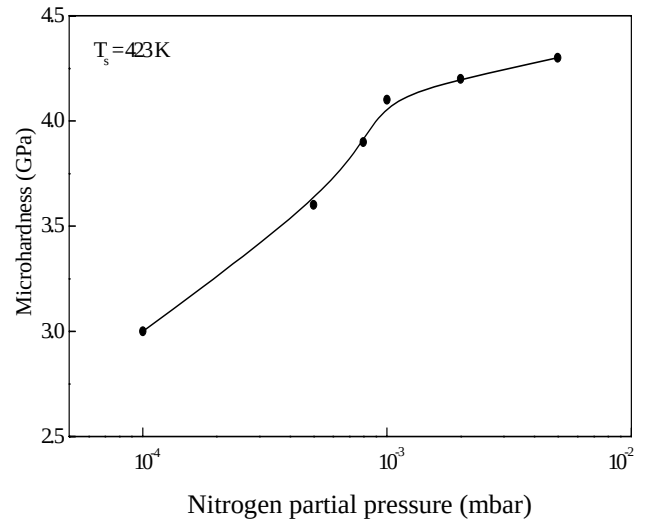


Fig. 4. Variation of microhardness of copper nitride films with the nitrogen partial pressure.

The electrical resistivity of Cu_3N films formed at different nitrogen partial pressures is shown in Fig. 5. The electrical resistivity of the films formed at low nitrogen partial pressure of 1×10^{-4} mbar was $1.6 \times 10^{-3} \Omega\text{cm}$. When the nitrogen partial pressure increased to 1×10^{-3} mbar the electrical resistivity increased to $5 \times 10^{-2} \Omega\text{cm}$, where as those formed at higher pressure of 5×10^{-3} mbar the electrical resistivity reached a saturation value of $6.8 \times 10^{-2} \Omega\text{cm}$. The low electrical resistivity at lower nitrogen partial pressure was due to the presence of mixed phase of copper along with the copper nitride. A sharp increase in the electrical resistivity at nitrogen partial pressure of 1×10^{-3} mbar reveals the optimum nitrogen partial pressure to produce single phase films of Cu_3N . The electrical resistivity achieved in the nitrogen partial pressure is in good agreement with the rf magnetron sputtered films [21,22].

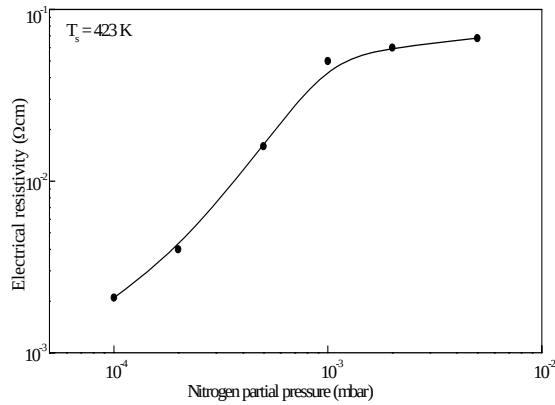


Fig. 5. Dependence of electrical resistivity of copper nitride films on the nitrogen partial pressure.

The optical transmittance spectra of Cu_3N films formed at different nitrogen partial pressures are shown in Fig. 6. The optical transmittance of the films increased with the increase of nitrogen partial pressure. The low optical transmittance in the case of the films formed at low nitrogen partial pressure was due to the presence of copper phase along with Cu_3N . The unreacted copper acts as scattering centers for light hence decrease in the optical transmittance. At high nitrogen partial pressures the higher optical transmittance was due to the decrease of scattering centers because of formation of single phase Cu_3N films. The optical absorption edge of the films shifted towards lower wavelength side with the increase of nitrogen partial pressure. The optical band gap evaluated from the $(\alpha h\nu)^2$ versus photon energy plots increased from 1.50 eV to 1.89 eV with the increase of nitrogen partial pressure from 5×10^{-4} mbar to 5×10^{-3} mbar. The optical band gap of the films formed at nitrogen partial pressure of 1×10^{-3} mbar was 1.85 eV. It is in good agreement with the reported value of rf reactive magnetron sputtered films [21]. It was also noticed that the optical band gap of the films increased from 1.30 eV to 1.76 eV with the increase of nitrogen partial pressure in rf reactive sputtered Cu_3N films [9].

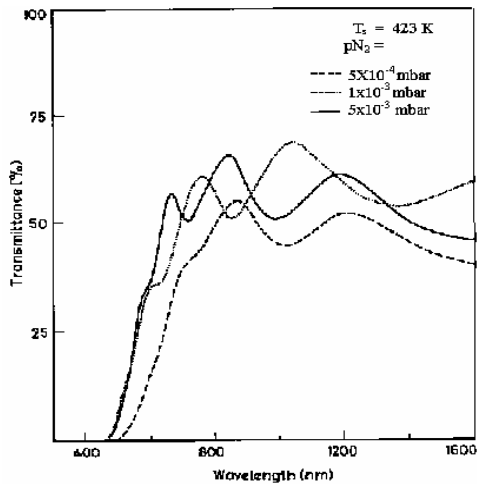


Fig. 6. Optical transmittance spectra of copper nitride film.

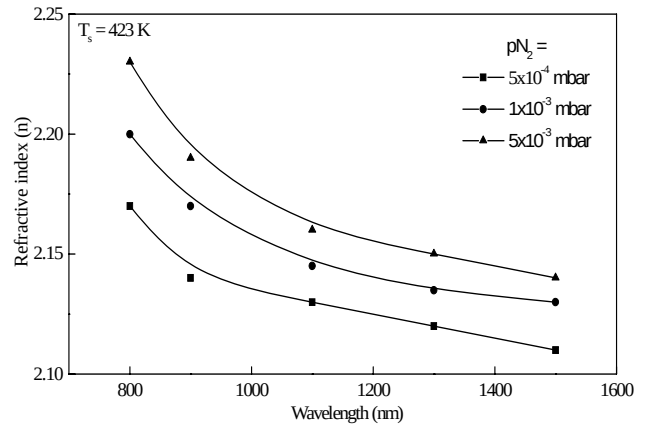


Fig. 7. Refractive index of copper nitride films.

The refractive index of the Cu_3N films was evaluated from the optical transmittance interference data employing Swanepoel's envelope method. Fig. 7 shows the wavelength dependence of refractive index of the Cu_3N films formed at different nitrogen partial pressures. It is seen from the figure that the refractive index decreases with the increase of wavelength. At a wavelength of 800 nm the refractive index increased from 2.17 to 2.23 with the increase of nitrogen partial pressure from 5×10^{-4} mbar to 5×10^{-3} mbar, respectively. The increase of refractive index with the increase of nitrogen partial pressure may be attributed to the increase in the packing density and crystallinity of the films [23].

4. Conclusions

Thin films of copper nitride were deposited on glass substrates by dc magnetron sputtering by sputtering of metal target of copper under various nitrogen partial pressures in the range 1×10^{-4} – 5×10^{-3} mbar. The dependence of cathode potential on the nitrogen partial pressure was related with the nitridation of copper target and secondary electron emission. The influence of nitrogen partial pressure on the structural, mechanical, electrical and optical properties was systematically studied. The films were polycrystalline in nature. The films formed at nitrogen partial pressures $< 1 \times 10^{-3}$ mbar were mixed phase of copper and copper nitride while those deposited at $\geq 1 \times 10^{-3}$ were single phase of copper nitride. The microhardness of the films increased from 3.0 GPa to 4.3 GPa with the increase of nitrogen partial pressure from 1×10^{-4} mbar to 5×10^{-3} mbar, respectively. The electrical resistivity of the single phase films of copper nitride was 5×10^{-2} Ωcm. The optical band gap of the films increased from 1.50 eV to 1.89 eV and the refractive index from 2.17 to 2.23 with increase of nitrogen partial pressure from 5×10^{-4} mbar to 5×10^{-3} mbar, respectively.

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