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ELECTRICAL AND OPTICAL PROPERTIES OF COPPER NITRIDE THIN FILMS PREPARED BY REACTIVE DC MAGNETRON SPUTTERING*

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Copper nitride films were deposited by reactive DC magnetron sputtering onto glass and other substrates in nitrogen atmosphere. Thickness, deposition rate, refractive index and optical band gap energy were determined from reflection and transmission spectroscopy depending on the deposition pressure and power. The crystallographic nature of films was investigated by x-ray diffraction. The films were further characterized by photoelectron spectroscopy (XPS) and multiple internal reflection (MIR) infrared spectroscopy, where the presence of Cu_3N nanocrystalline structure was confirmed. Considerable changes of DC conductivity and activation energy of the films before and after annealing at 500 °C were found.

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1 Introduction

Technologically important binary nitrides BN, AlN, Si_3N_4, WN, TiN known as hard and stable compounds are rather well characterized. On the other hand covalent metal nitrides as Sn_3N_4, Cu_3N and Ni_3N are less known but potentially important because of their semiconductor properties and an ability to release nitrogen at higher temperature [1, 2]. They can be locally metalized by a laser beam [3] which could be utilized in electronic industry, printing technology or in other fields.

Cu_3N has a cubic anti-ReO_3 type crystal structure with a lattice constant of 3.815 Å. Cu atoms do not occupy perfectly the sites in (111) plane, so the crystal structure has many vacant interstitial sites that can be filled by contaminants with remarkable changes of the electrical and

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optical properties [4]. The metastable phase of Cu_4N was described by Blucher *et al.* [5], and epitaxial films were prepared on different substrates by rf sputtering [4, 6].

Chemically prepared Cu_3N (reacting CuF_2 with NH_4F) has the density 5.84 g/cm^3 and a dark green color. Thermal decomposition of Cu_3N occurs gradually above 350 °C. For the films [2, 7] it occurs in maximum extent at about 465 °C. Electrical, optical and mechanical characteristic of sputtered Cu_3N films were studied in [8, 9].

However, the properties of copper nitride films, considering their thermal instability and sensitivity to contaminants, are not fully understood. In this study, the electrical and optical properties of sputtered copper nitride films were studied as a function of nitrogen pressure and discharge power.

2 Experimental

Copper nitride films were deposited using a laboratory-made DC magnetron sputtering system, with a water cooled Cu target 100 mm in diameter, 2 mm thick and nominally 99.9% pure. The target-to-substrate spacing was 80 mm and the sputtering chamber was evacuated by oil pumps with a background pressure of 2.10^{-3} Pa. Deposition was conducted in pure nitrogen flow up to 0.6 cm^3/s, maintaining constant pressure (from 0.85 to 4.5 Pa), discharge voltage (280 to 400 V) and discharge current (from 0.35 up to 2.5 A), Table I. No external heating was applied to the holder with different substrates (Silicon wafers, glass, Al foil and some thinner films on polypropylene foils). Before deposition the target was sputter cleaned to remove oxides and contaminants.

Table I. Process and material parameters of deposited copper nitrides.

Sample	N_2 pressure [Pa]	N_2 flow [cm^3/s]	Power [W]	Dep. time [min]	Energy [kWs]	Thickness [nm]	Dep. rate [nm/s/kW]
1	0.85	0.42	125	10	75	230	3.1
2	1.5	0.45	140	9	75	270	3.6
3	2.3	0.47	105	12	75	205	2.7
4	2.3	0.47	210	6	75	160	2.1
5	2.3	0.47	315	4	75	140	1.9
6	3.5	0.54	113	11	75	120	1.6
7	4.5	0.58	300	6	110	155	1.4
8	4.5	0.58	625	4	150	355	2.4
9	4.5	0.58	1000	2	120	320	2.7

The amount of deposited nitride was established (*ex situ*) by weighting the coated specimens on a microbalance and locally measuring the thickness by profile-meter Dektak 3030, Veeco Instruments Inc. and also by interference of light in visible region. The reflection spectra at two different angles of incident light (18° and 40°) were used to determine the refractive index n of the nitride films [10] and then the spectra at small incident angle (18°) for local thickness determination. Reflection spectra, as well as the absorption ones were measured by a Pye Unicam spectrophotometer 8800 with reflectance accessories.

Microstructure of the as-deposited films was studied by x-ray diffraction with $\theta - 2\theta$ scans using Philips PW 1820 powder diffractometer with CuK_α, $\lambda = 0.1542$ nm radiation operating at

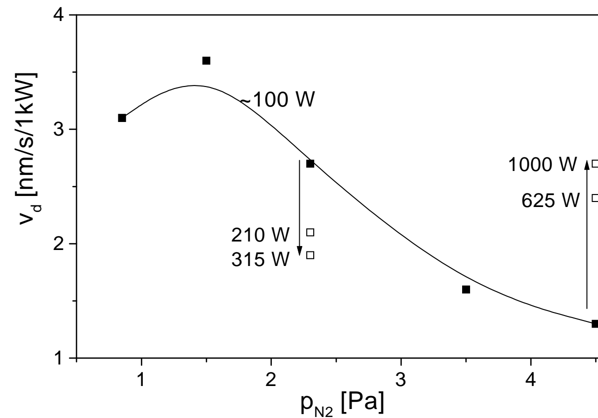

Fig. 1. Pressure dependence of the normalized deposition rate with the approximation curve for 100 W of discharge power (solid symbols). Open symbols and arrows indicate a change of the deposition rate with the power.

1.6 kW (40 kV, 40 mA) with accuracy 0.015°of 2θ. In order to collimate the beam a set of slits and masks were used. The CuK_α radiation was attenuated by a Ni foil filter between the x-ray source and the sample. We used a 0.5° divergence slit and a 2 mm brass mask, to limit the size of the x-ray beam on the sample. In front of the detector there was a 0.2 mm antiscatter slit and a 0.5° divergence slit followed by a Ge-crystal monochromator. This arrangement eliminates any K_β that has passed through the Ni-filter and also reduces fluorescence effects from the sample.

Chemical composition of the films was studied by multiple attenuated total reflection (ATR) IR technique (also called MIR IR - multiple internal reflection) by spectrophotometer Perkin Elmer using 45° TlJ/TlBr crystal (KRS-5) in MIR accessory and two samples were tested also by x-ray photoelectron spectroscopy (XPS) Microlab 310-F system with a non-monochromated MgK_α (1254 eV) x-ray source.

DC resistivity of the films was measured by a two electrode method in vacuum within the temperature scale, from 25 to 170 °C, to determine the activation energy of conduction, E_σ. The electrodes were deposited onto the nitride film by vacuum evaporation of Al, positioned parallel, with 8 mm distance and 75 mm long.

3 Results and discussion

The color of as-prepared films was dark reddish-brown (influenced by interference namely in the thinner case) and their thickness varied between 0.12 and 0.36 μm (Table I). Calculated deposition rate is normalized to 1 kW of discharge power (Fig. 1). However, it is not fully independent of deposition power as shown by the arrows. At 100 W of the discharge power deposition rate decreases with nitrogen pressure above 2 Pa. Below 1.5 Pa the nitridation is limited, deposition rate achieves a maximum around 1.5 Pa because of increasing incorporation of nitrogen into the film.

The refractive index n, was calculated from the shift of interference pattern extremes of the

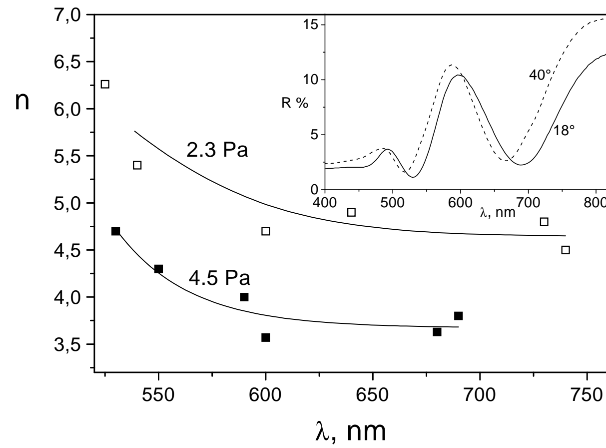

Fig. 2. Wavelength dependence of the refractive index of copper nitride films deposited on glass at two different pressures. The inset illustrates the shift of reflection spectra at different angle of incident light (for sample 4).

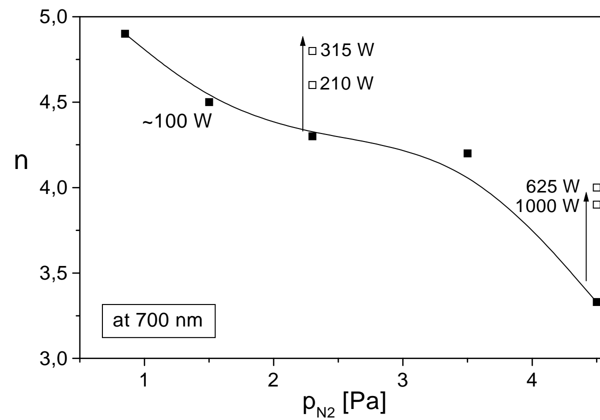

Fig. 3. Nitrogen pressure dependence of refractive index at 700 nm of the films prepared at 100 W of discharge power (the curve) and at higher power (the arrows).

reflection spectra of nitride films deposited on glass and Si substrates by changing the angle of incident light, Fig. 2. The points calculated from the shifts of the extremes are connected with the cubic spline approximation curve. The index increases rapidly below 600 nm due to strong absorption of nitride films. The pressure and discharge power dependence of the index around 700 nm is shown in Fig. 3, where the experimental points responding to films prepared at 100 W are connected by an approximation curve. (The arrows and open symbols indicate a change of the index with the deposition power.) The values of R in the inset of Fig. 2 are just relative reflectance (measured values). So the values of R are rather low, considering the high refractive

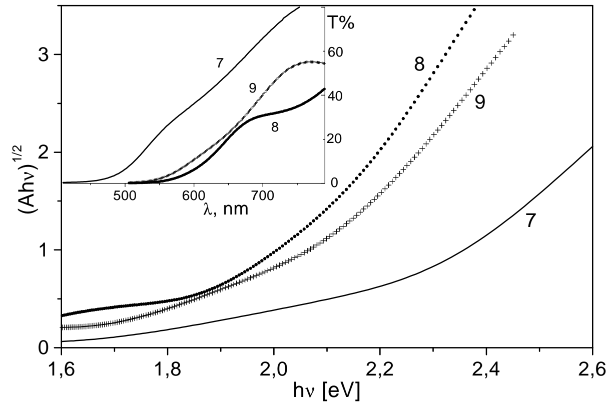

Fig. 4. A plot of $Ah\nu^{1/2}$ vs. photon energy, for band gap energy determination. Inset: Transmission spectra of sample set (7, 8, 9) on glass.

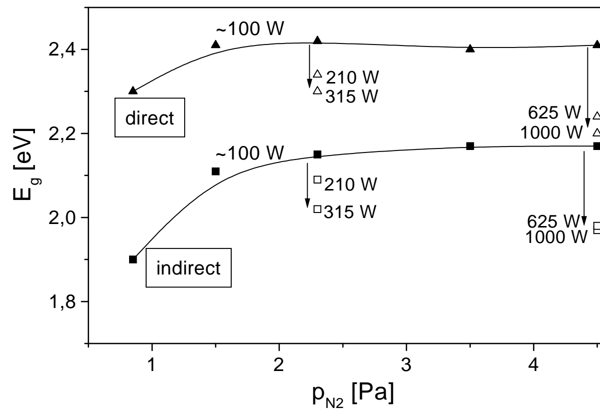

Fig. 5. Optical band gap energies of nitride films prepared at 100 W, for direct and indirect transitions (solid symbols and curves) vs deposition pressure of nitrogen. Open symbols and arrows indicate the gap change with the deposition power.

index of the film. Absolute values would be approximately 2.3 times higher.

The band gap energy E_g was derived from the absorption spectra of nitrides coated on glass using the Tauc plot for indirect (Fig. 4) an also direct transitions in crystalline semiconductors [11],

$$(A(\nu)h\nu)^m = \text{const}(h\nu - E_g),$$

where $h\nu$ is the photon energy, A is the absorbance and $m = 1/2$ and 2 for the indirect and direct transitions, respectively. Band gap energies found at different pressure and deposition power (in Fig. 5, where the points are obtained from Tauc plots, responding to 100 W of deposition power are connected with the spline approximation curve) are generally higher in comparison

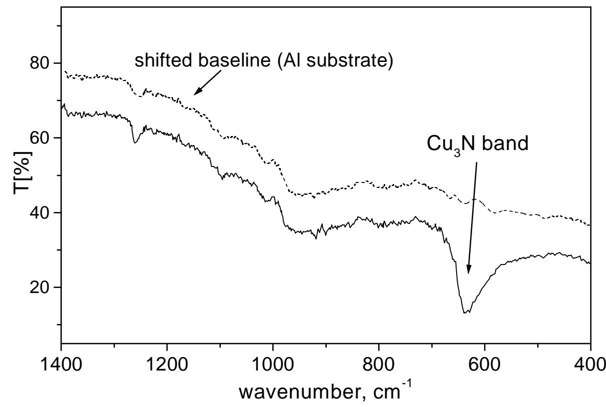

Fig. 6. IR transmission spectra of copper nitride film on Al substrate (sample 4) taken by MIR technique with KRS-5 crystal. (T is transmitance.)

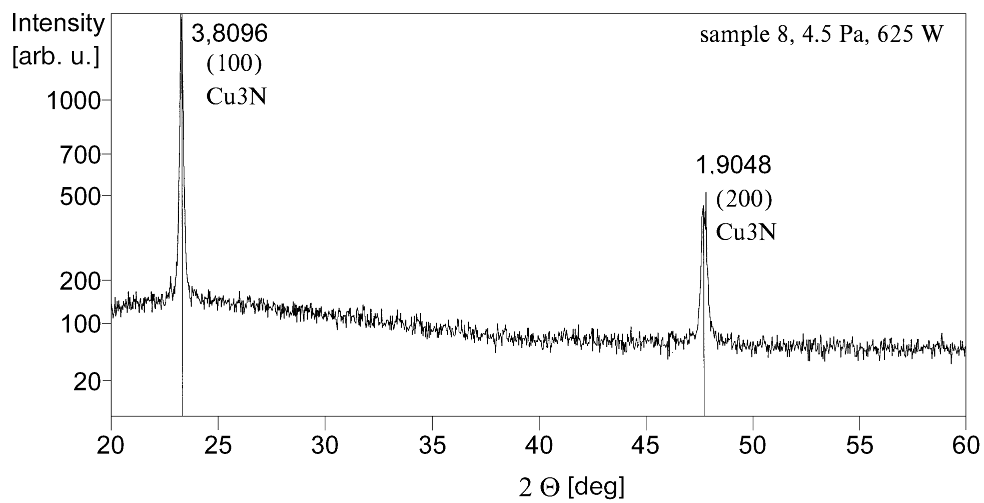

Fig. 7. XRD pattern of copper nitride film (355 nm) on glass.

with values reported for the Cu_3N phase (in [4] just for direct and in [9] for the indirect transitions). Higher E_g can be caused by a presence of other phases than Cu_3N, amorphous phases and impurities.

The presence of the Cu_3N phase in our copper nitride films was confirmed by IR and XRD spectroscopy. An absorption band around 640 cm^{-1} was clearly found in the IR spectra of all films except those of samples 1 and 7 (Fig. 6). It is in agreement with and very close to a value of 643 cm^{-1} of Cu_3N single band reported by L. Maya [1]. In the spectrum of sample 7 the band was small, and there was no band observed in sample 1.

The XRD patterns (Fig. 7) clearly exhibited (100) and (200) peaks of Cu_3N structure reported

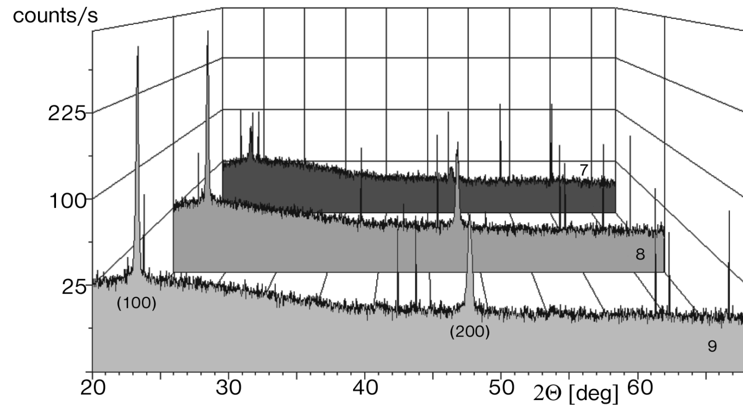

Fig. 8. XRD pattern of copper nitride films (samples 7, 8, 9) on glass.

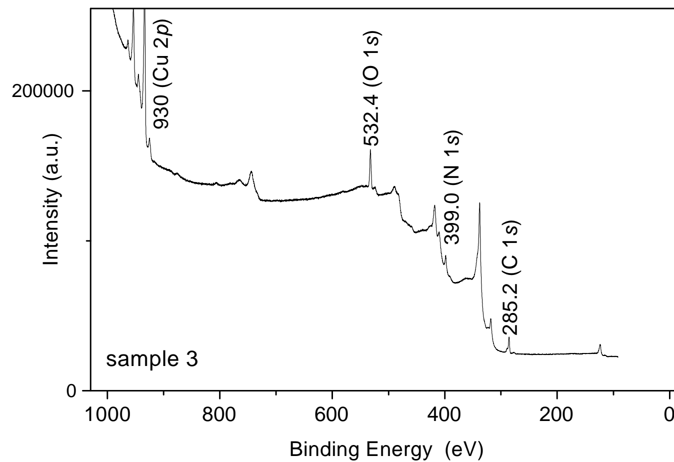

Fig. 9. XPS spectrum of copper nitride on glass (sample 3)

in [4, 7] (d-spacing 3.815 Å. and 1.905 Å., resp.). The narrow singular peaks would indicate highly textured films. However, the peak 100 lies on a much broader peak (up to 35°) that is relatively higher in the case of films prepared at lower pressures and powers. This may imply that the crystallinity of the films is far from perfect that could be expected when the growth occurred on an amorphous glass substrate at low deposition temperatures. Films are composed of crystallites in nanometer scale. High pressure and high deposition rate cause a higher temperature of substrate and cleaner process so the films of samples 8 and 9 are more ordered (Fig. 8).

The XPS spectrum of sample 3 (Fig. 9) on glass substrate indicates, except Cu, a low content of N and also a considerable presence of O, and C. The spectrum is taken from a very thin surface layer (about 6 nm) of the nitride. This can be caused by the instability of copper nitride or by contamination of films by pump oils and residual oxygen.

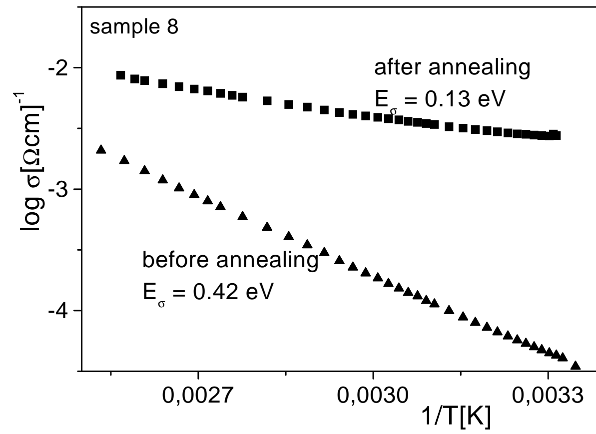

Fig. 10. Electrical conductivity of sample 8 before and after annealing, as a function of inverse temperature.

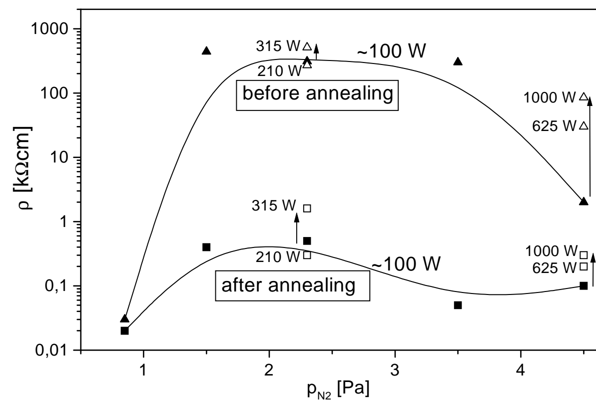

Fig. 11. DC resistivity of the films at 25 °C as a function of deposition pressure, before and after annealing (up to 500 °C). (Solid symbols and curves belong to 100 W of deposition power, open symbols and arrows to higher power.)

The nitride films were rather stable measuring the DC conductivity in the temperature range (25 °C - 170 °C). The plot of $\log \sigma(1/T)$ is almost linear (see the line in Fig. 10), so the activation energy of conduction (E_σ) can be calculated by the Arrhenius equation. The samples were annealed in an air furnace for 20 minutes at 500 °C to cause thermal decomposition of films and to release nitrogen. The changes of the conductivity and its activation energy after annealing were expressive. DC resistivity at the room temperature has fallen down by several orders of magnitude. The activation energy decreased also remarkably, however, it remained at a low positive value. It means the films did not change completely to a metal. Some films, prepared at lower pressures and higher power (sample 1, 4, 5) were a little destructed after annealing, by internal stress in the films.

The changes of DC resistivity (Fig. 11) at room temperature before and after annealing of the films show that from the point of view of insulator/conductor transformation and of internal stress, the optimal films are the ones prepared above 3 Pa. (The spline approximation curve in Fig. 11 connects the experimental points responding to deposition discharge power of 100 W. The arrows and open symbols indicate the resistivity of films prepared at higher powers than 100 W.)

4 Conclusion

Copper nitride films were deposited by DC magnetron sputtering in pure nitrogen onto glass, Si Al and polypropylene substrates without any external heating. The thickness, deposition rate, refractive index and optical band gap energy, determined by weighting and optical reflection and transmission spectroscopy, depend sensitively on the deposition pressure and power. Sufficient nitridation occurs in our conditions above 2 Pa. The films were characterized also by XRD, and MIR IR spectroscopy, where the presence of Cu_3N nanocrystalline structure was confirmed. X ray diffraction measurements showed a texture dominated (100) oriented grains. However, XPS pattern of one sample indicates the presence of oxygen, carbon and other phases. Considerable changes of DC conductivity and activation energy of the films before and after annealing at 500 °C were found. The best results (the highest conductivity changes and compact films without stress also after annealing) were achieved above 3 Pa. The conductivity is very sensitive to plasma discharge and gas flow conditions during preparation that must be further precisioned.

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