The Korean Journal of Ceramics, 4 [3] 222 - 226 (1998)

Synthesis and Properties of CuN_x Thin Film for Cu/Ceramics Bonding

Sang Ok Chwa, Keun Soo Kim and Kwang Ho Kim

Department of Inorganic Materials Engineering,
Pusan National University, Pusan 609-735, Korea

(Received June 5, 1998)

Cu_3N film was deposited on silicon oxide substrate by r.f. reactive sputtering technique. Synthesis and properties of copper nitride film were investigated for its possible application to Cu metallization as adhesive interlayer between copper and SiO_2. Cu_3N film was synthesized at the substrate temperature ranging from 100℃ to 200℃ and at nitrogen gas ratio above $X_{N_2}=0.4$. Cu_3N, CuN_x, and FGM-structured Cu/CuN_x films prepared in this work passed Scotch-tape test and showed improved adhesion property to silicon oxide substrate compared with Cu film. Electrical resistivity of copper nitride film had a dependency on its lattice constant and was ranged from 10^{-7} to 10^{-1} Ωcm. Copper nitride film was, however, unstable when it was annealed at the temperature above 400℃.

Key words : Copper nitride film, Reactive sputtering, Adhesion property, Silicon oxide substrate, Electrical resistivity

I. Introduction

Copper is one of promising materials for metallization in micro magnetic devices[1,2] and in ultralarge scale integrated (ULSI) circuits due to its low resistivity and high electromigration resistance.[3-5] In spite of its merits, the application of copper metallization has been obstructed because copper has a poor adhesion property to ceramic substrate such as SiO_2.[3]

Recently, an interesting material, Cu_3N was synthesized in nitrogen plasma by sputtering technique[6] and was investigated on its possible applications for recording media.[7-9] However, other properties of the copper nitride film are not well-known yet and its application as a bonding promoter for the copper metallization has never been reported. The present work was, therefore, undertaken to investigate the bonding characteristics of copper nitride film to SiO_2 substrate and to try a successful copper metallization using the copper nitride film.

II. Experimental Procedures

Copper nitride films were prepared on SiO_2(4000 Å)/Si wafer by reactive magnetron sputtering technique. Copper target(99.99%, CERAC) of 2 inches in diameter and 1/8 inch in thickness was sputtered in the plasma of gas mixture composed of nitrogen and argon. The distance between the substrate and the target was 50 mm and the chamber was pre-evacuated to less than 1×10^{-6} torr pressure before film deposition. Pre-sputter etching of target was carried out to obtain a clean surface of target. Flow rates of high purity (99.999%) Ar and N_2 gases were separately controlled by mass flow controllers and the chamber pressure was monitored by a Pirani gauge. The surface temperature of substrate was monitored by a thermocouple and was controlled in the range from room temperature to 400℃ for the deposition. The sputtering process was proceeded at chamber pressure of 10 mtorr under r.f. power of 30 watt.

Phase and crystallinity of the deposited film was analyzed by the X-ray diffractometer (Rikaku) using CuKα radiation. Film thickness was measured by stylus (Tencor, α-step). Scanning electron microscopy (SEM) was used to determine thickness of the film and to observe fracture cross-sectional morphology of the deposited layer. Optical microscopy (OM) was used to observe the surface morphology of the film. Auger electron spectroscopy (AES) was used to determine the depth distribution of Cu, N, Si, and O in the deposited layer. Auger spectra were collected by using a Perkin-Elmer 600 AES with 1 μA electron beam accelerated to 10 kV.

Adhesion property of copper nitride film to SiO_2 substrate was tested in accordance with standards of both D 3330 (Method for Peel Adhesion of Pressure-Sensitive Tape of 180 Angle) and D3359-87 (Test Method for Measuring Adhesion by Tape Test) of American Society for Testing Materials(ASTM).[10,11] For the tape test, half inch wide, semi-transparent and pressure-sensitive tape (3M) was attached on the deposited area of 4×4 mm². In order to attach the pressure-sensitive tape to film with uniform attaching force, the tape was suppressed with a constant pressure of 10 bars by using a press instead of rubbing by a pencil with an eraser described in ASTM standards. The attached tape was removed by seizing a free end and pulling it off rapidly back on itself at as close to angle of 180° as possible. Fig. 1 shows a schematic illustration of the Scotch-tape method for adhesion test.

III. Results and discussion

1. Synthesis of Cu_3N film with deposition variables

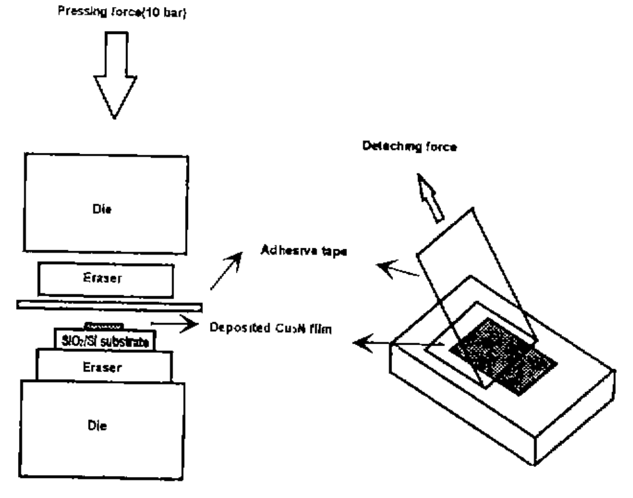

Fig. 1. Schematic illustration of our Scotch-tape method for adhesion test.

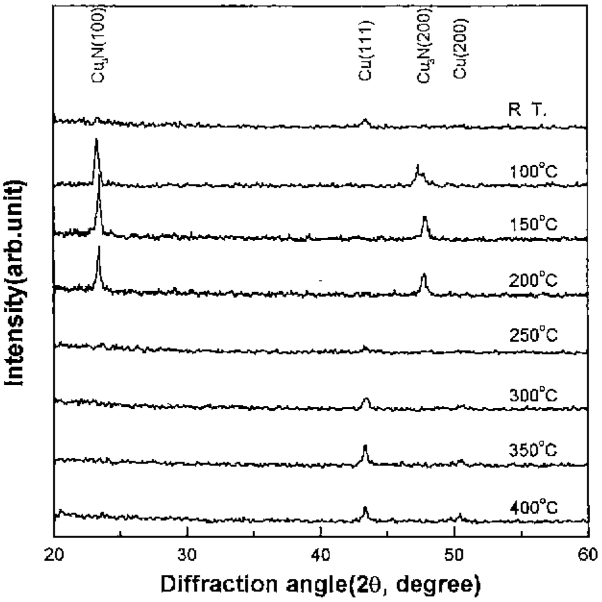

Fig. 2. X-ray diffraction patterns of films deposited at various substrate temperatures (deposition pressure, 10 mTorr; r.f. power, 30W; $X_{N_2}=0.5$).

Fig. 2 shows X-ray diffraction patterns of films deposited at various substrate temperatures. Nitrogen gas ratio in sputtering gas mixture was fixed at $X_{N_2}=0.5$. At room temperature metallic Cu peak was appeared, but at substrate temperatures in the range of 100-200°C Cu_3N films were deposited. Further increase of substrate temperature above 250°C, metallic Cu peaks appeared again. From our experimental results it was found that optimum temperature range to synthesize Cu_3N was from 100°C to 200°C. At the low substrate temperature like room temperature thermal energy to synthesize copper nitride is considered to be insufficient, whereas at high substrate temperature thermal decomposition of synthesized copper nitride is known to occur.[12,13] T. Maruyama et al.[7] have reported that at high substrate temperature around 300°C, re-evaporation of atomic nitrogen in the copper nitride film occurred. Fig. 3 shows X-ray diffraction patterns of films deposited at various nitrogen gas ratios. Substrate temperature was fixed at 150°C and nitrogen gas ratio, X_{N_2} was changed from zero to one. At pure argon atmosphere of $X_{N_2}=0.0$, metallic copper was deposited. At $X_{N_2}=0.2$, any diffraction peaks corresponding to either metallic copper or copper nitride phase did not appear. At nitrogen gas ratios above $X_{N_2}=0.4$, however, crystalline copper nitride films with [100] preferred orientation were deposited.

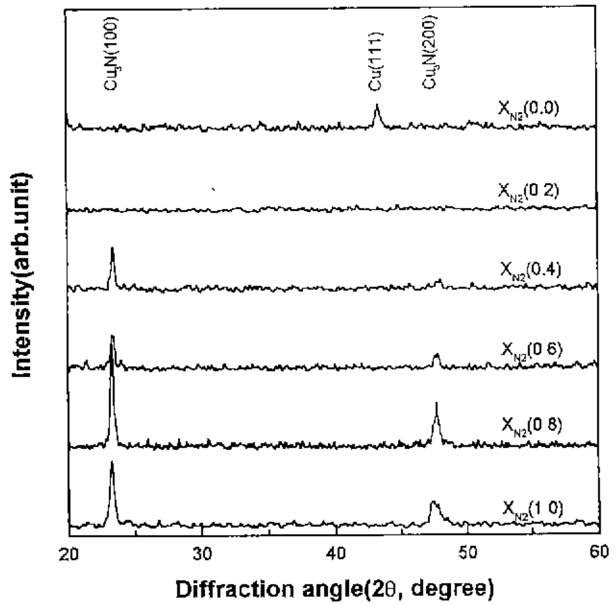

Fig. 3. X-ray diffraction patterns of films deposited at various nitrogen gas ratios (deposition temperature, 150°C; deposition pressure, 10 mTorr; r.f. power, 30W).

2. *Adhesion properties of copper nitride film*

Table I shows the tape test results of films deposited on SiO_2 with various substrate temperatures and nitrogen gas ratios. The thickness of copper nitride films for tape test was in the range of 1800-2500Å. All Cu_3N films deposited at substrate temperatures in the range of 100-200°C did not peel off from substrate and passed the

Table I. Tape test Results of Films Deposited on SiO_2 with Various Substrate Temperatures and Nitrogen Gas Ratios

Sample	Result	Sample	Result
$T_{R.T.}N_{0.5}$	×	$T_{400}N_{0.5}$	×
$T_{100}N_{0.5}$	○	$T_{150}N_{0.0}$	×
$T_{150}N_{0.5}$	○	$T_{150}N_{0.2}$	○
$T_{200}N_{0.5}$	○	$T_{150}N_{0.4}$	○
$T_{250}N_{0.5}$	○	$T_{150}N_{0.6}$	○
$T_{300}N_{0.5}$	×	$T_{150}N_{0.8}$	○
$T_{350}N_{0.5}$	×	$T_{150}N_{1.0}$	○

where, T: substrate temperature (°C), N: nitrogen gas ratio (X_{N_2}) in sputtering gas, ×: peeled off, ○: passed.

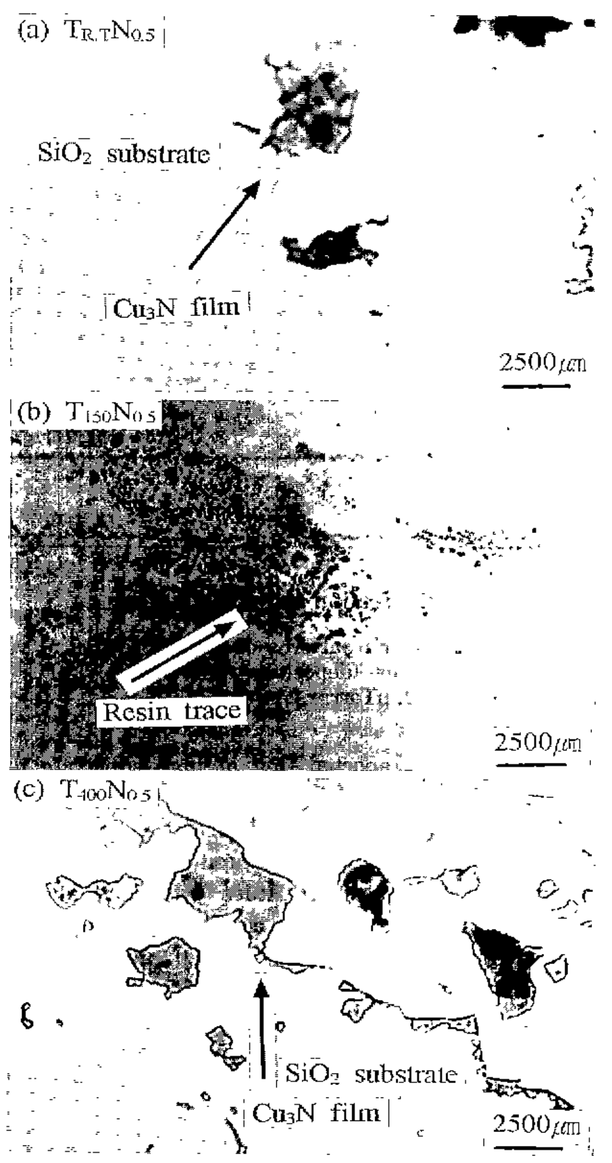

Fig. 4. Optical micrographs of film surface after tape test for the films deposited at (a) room temperature, (b) 150°C and (c) 400°C.

tape test, whereas Cu films got easily removed from the substrate by the tape and showed poor adhesion property. Fig. 4 shows optical micrographs of film surface after tape test. The copper films deposited both at room temperature and at 400°C peeled off from SiO_2 substrate after performing tape test. On the other hand, copper nitride film deposited at 150°C remained as it had been and rather left the resin trace on its surface, detached from the adhesive tape. This reflects the fact that the adhesion force of copper nitride film to SiO_2 substrate at least exceeds maximum adhesion capability of the tape.

For an adhesive copper metallization to SiO_2 using a copper nitride film, FGM (functionally graded materials) structured films were deposited on SiO_2 substrate. Double layer Cu/CuN_X film was prepared on SiO_2 substrate by changing the nitrogen gas ratio of plasma gas mixture during the sputtering process. Fig. 5 shows a cross-sectional SEM micrograph of the prepared $Cu/CuN_X/SiO_2$ layer. In Fig. 5, morphological distinction between Cu and CuN_X layers are drawn without clear interface. Fig. 6 also shows Auger depth profile for the $Cu/CuN_X/SiO_2$ layer. Nitrogen content in the CuN_X layer was found to be about 8 at.% by our AES analysis, which indicated a copper nitride phase of Cu excess from stoichiometric Cu_3N. Small nitrogen incorporation in Cu layer in Fig. 6 was caused by the retained nitrogen gas in chamber during the process. The nitrogen content in Cu layer is, however, believed to be largely suppressed by controlling the process. Our FGM structured film of Fig. 5 showed good adhesion properties to SiO_2 and passed the tape test. In our experiments, all FGM structured films using copper nitride interlayer passed the tape test regardless of thickness of the copper nitride interlayer.

Fig. 5. Fracture cross-sectional morphology of the prepared $Cu/CuN_X/SiO_2$ layer by SEM.

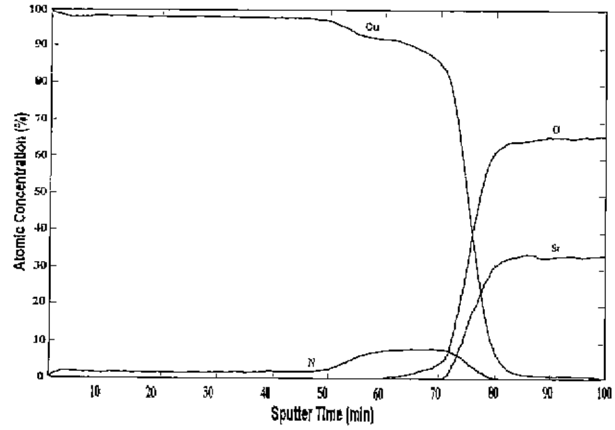

Fig. 6. Auger depth profile for the $Cu/CuN_X/SiO_2$ layer.

3. Thermal stability and resistivity of copper nitride film

Fig. 7 shows X-ray diffraction patterns of Cu_3N films annealed at various temperatures in Ar atmosphere. As-

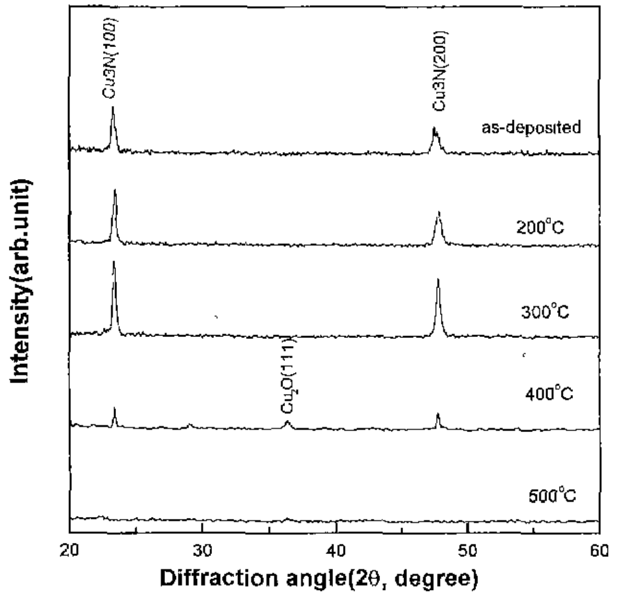

Fig. 7. X-ray diffraction patterns of Cu_3N films annealed at various temperatures in Ar atmosphere.

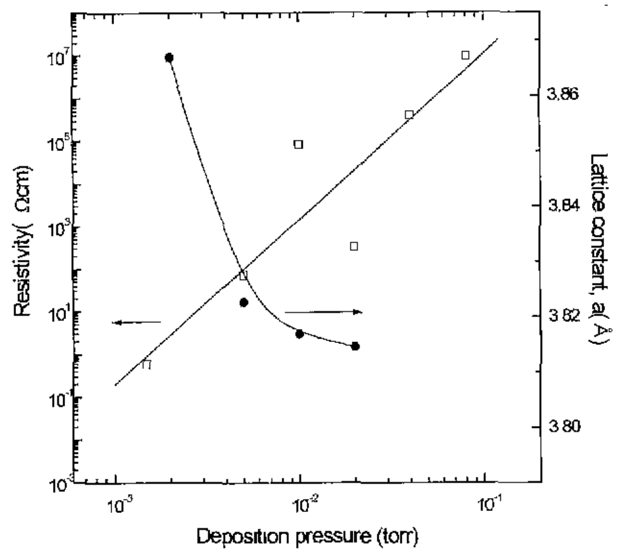

Fig. 8. Variation of both lattice constant of Cu_3N crystal and resistivity of copper nitride film as a function of deposition pressure.

deposited Cu_3N films were heated to various temperatures with heating rate of 5°C/min., held for 2 hours, and cooled down in furnace. Cu_3N film was found to be stable to 300°C, but degraded above the temperature of 400°C. As the Cu_3N film was heat-treated at temperatures above 400°C, intensity of diffraction peaks of Cu_3N largely diminished. Thermal unstability of Cu_3N film has been reported[12,13)] similar to our results. Small peak, corresponding to Cu_2O, appeared during heat-treatment at 400°C in Fig. 7 seemed to be caused by oxidation of Cu_3N due to oxygen adsorbed on the inner tube wall.

Fig. 8 shows variation of both lattice constant of Cu_3N crystal and resistivity of copper nitride film as a function of deposition pressure. As the deposition pressure decreased, lattice constant of copper nitride film increased. In addition, all copper nitride films prepared in this work had a little larger lattice constant than 3.815 A, that of stoichiometric Cu_3N crystal (JCPDS file no 2-1156). This implies that our films were Cu-rich nonstoichiometric compounds due to Cu interstitialcy. Because decrease of deposition pressure induces increase of the sputtering yield of target material, copper ions were oversupplied compared with nitrogen ions to the substrate with decreasing deposition pressure, and thus, Cu interstitialcy in copper nitride film. In Fig. 8, electrical resistivity of copper nitride film was changed with variation of deposition pressure, e.g., decreased with increase of lattice constant due to the decrease of deposition pressure. The electrical resistivity of copper nitride film is believed to do closely with lattice constant, that is, Cu interstitialcy since interstitial Cu atoms possibly produce donor electrons in the copper nitride film. As for the electrical property of Cu_3N, copper nitride has been reported to be insulator[6)] or semiconductor.[14)] Recently, T. Maruyama et al.[7)] reported that the electrical property of copper nitride film depended on its lattice constant and was ranged from insulator to semiconductor. Our results was well consistent with those of T. Maruyama and showed the electrical resistivity ranging from 10^{-7} to 10^{1} Ωcm.

IV. Conclusions

In summary, Cu_3N film was successfully deposited in the substrate temperature range from 100°C to 200°C and at nitrogen gas ratio above $X_{N_2}=0.4$ by r.f. reactive sputtering technique and was found to be a possible bonding material as adhesive interlayer between copper and SiO_2. Our Cu_3N, CuN_x and FGM-structured Cu/CuN_x films passed Scotch-tape test and showed improved adhesion property to silicon oxide substrate compared with Cu film. Electrical resistivity of copper nitride film had a dependency on its lattice constant and was ranged from 10^{-7} to 10^{-1} Ωcm. Copper nitride film was, however, unstable when *it was annealed at the temperature above* 400°C.

Acknowledgment

This study was supported by the academic research fund of Ministry of Education, Republic of Korea (Advanced Materials, N-97-63)

References

1. C. P. Yue, C. Ryu, J. Lau, T. H. Lee and S. S. Wong, "A Physical Model for Planar Spiral Indictors on Silicon"; pp. 155 in *Proceedings of IEDM. Edited by* IEEE, San-Francisco, 1996.

2. W. B. Kuhn, A. Elshabini-Riad and F. W. Stepgenson, C "Entre-tapped Spiral Inductors for Monolithic Bandpass filters," *Electronics Letters,* **31**(8), 625-626 (1995)
3. S. P. Murarka, R. J. Gutmann, A. E. Kaloyeros and W. A. Lanford, "Advanced Multilayer Metallization Schemes with Copper as Interconnection Metal," *Thin Solid Films,* **236**, 257-266 (1993)
4. G. Minamihaba, T. Obara and T. Shimizu. "Double-level Cu Inlaid Interconnects with Simultaneously Filled via Plugs," *Jpn. J. Appl. Phys.,* **35**(2B), 1107-1110 (1996).
5. S. T. Hwang, I. Shim, K. O. Lee and H S. Choi, "Bisethylacetoacetato Cu(II) as a Novel Metal-organic Precursor for Cu film Production by Plsma-enhanced Chemical Vapor Deposition Metallization," *J. Mater. Res.,* **11**(5), 1051-1060 (1996).
6. S. Terada, H. Tanakd and K. Kubota, "Hetroepitaxal Growth of Cu_3N Thin Films," *J. of Crystal Growth,* **94**, 567-568 (1989).
7. T. Maruyama and T. Morishita, "Copper Nitride Thin Films Prepared by Radio-frequency Reactive Sputtering," *J. Appl. Phys.,* **78**(6), 4104-4107 (1995).
8. M. Asano, K. Umeda and A. Tasaki, "Cu_3N Thin Films for a new Light Recording Media," *Japn. J. Appl. Phys.,* **29**(10), 1985-1986 (1990).
9. T. Maruyama and T. Morishita, "Copper Nitride and Tin Nitride Thin Films for Write-once Optical Recording Media," *Appl. Phys. Lett.,* **69**(7), 890-891 (1996).
10. ASTM Designation: D3359-87, "Standard Test Methods for Measuring Adhesion by Tape Test".
11. ASTM Designation: D3330M-83, "Standard Test Methods for Peel Adhesion of Pressure-sensitive Tape at 180° Angle [metric]".
12. A. Baiker and M. Maciejewski, "Formation and Thermal Atability of Copper and Nickel Nitrides," *J. Chem. Soc., Faraday Trans.,* **80**(1), 2331-2341 (1984).

13 A. von Richthofen, R Dominick and R. Cremer, "Cu-N Films Grown by Reactive MSIP: Constition, Structure and Morphology," *Mikrochim. Acta.,* **125**, 172-177 (1997).

14. U. Hahn and W. Weber, "Electrical Structure and Chemical Bonding Mechanism of Cu_3N, Cu_3NPd and Related Cu(I) Compounds," *Phys. Rev. B,* **53**(9), 684-692 (1996).