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Corrosion Protection of Plasma-Polymerized Cyclohexane Films Deposited on Copper

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Abstract

The corrosion failure of electronic devices has been a major reliability concern lately. This failure is an ongoing concern because of miniaturization of integrated circuits (IC) and the increased use of polymers in electronic packaging. Recently, plasma-polymerized cyclohexane films were considered as a possible candidate for a interlayer dielectric for multilever metallization of ultra large scale integrated (ULSI) semiconductor devices. In this paper the protective ability of above films as a function of deposition temperature and RF power in an 3.5 wt.% NaCl solution were examined by polarization measurement. The film was characterized by FTIR spectroscopy and contact angle measurement. The protective efficiency of the film increased with increasing deposition temperature and RF power, which induced the higher degree of cross-linking and hydrophobicity of the films.

Keywords : *Corrosion, Plasma enhanced chemical vapor deposition (PECVD), Cyclohexane film*

1. INTRODUCTION

Continuing improvement in microprocessor performance historically involves a decrease in the device sizes. This allows greater device speed, an increase in device packing density and an increase in the number of functions that can reside on a single chip. However, the trend of miniaturization of integrated circuits (IC) chips requires the replacement for new materials in microelectronic devices because higher packing density and narrower pathway results in propagation delay, crosstalk noise and power dissipation. In recent years, copper is in a stage of replacing aluminum as the interconnecting metal in advanced microelectronic devices due to its lower bulk resistivity and a variety of interlayer dielectrics with low-k constant have been developed[1,4]. On the other hand, copper dose not form self-passivating oxide relative to aluminum and the resistance to corrosion decreases in humid and oxygen-containing environments[5]. Furthermore, plasma-polymerized thin films as interlayer dielectrics have a high tendency to absorb water in the presence of moisture and can act as a corrosive media. This situation results in galvanic corrosion between metallized conducting lines, and electromigra-

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tion (EM) under humid condition[6]. To inhibit effectively the multilevel interconnections from corrosion-induced malfunction, it is necessary to examine corrosion problem resulting from a new-developed interlayer dielectric in microelectronic devices.

In this paper plasma-polymerized cyclohexane films were considered as a possible candidate for a interlayer dielectric for multilevel metallization of ULSI semiconductor devices.

2. EXPERIMENTAL

2. 1 Film deposition

Plasma polymerization was carried out in a vacuum chamber made of stainless steel. Polymer-like thin films were deposited on disk-shaped copper specimens (99.99% copper) by the plasma-enhanced chemical vapor deposition (PECVD). After cleaning the sample using acetone, isopropanol and distilled water, the substrates were *in-situ* pre-treated with Ar plasma to give an oxygen-free surface and a buffer layer for enhancing film adhesion. The deposition lasted up to 2 hours, depending on the RF power and deposition temperatures. The general deposition pressure was $2\sim4\times10^{-1}$ Torr and the deposition temperature was 298 K and 373 K, respectively. The typical conditions of the PECVD process applied in this study are 30W and 50W of RF power, 20 sccm of Ar carrier gas, and 20 sccm of H_2 bubbler gas. Cyclohexane monomer was used as an organic precursor. The as-grown plasma polymerized thin films were ex-situ characterized with Fourier transform infrared reflection (FT-IR) spectroscopy.

In order to evaluate the wettability of the surface film, contact angle measurements were carried out on the coated surfaces by the sessile drop method with a microscopic goniometer.

2. 2 Electrochemical test

Polarization measurements of the electrodes, both bare and covered with cyclohexane films, were carried out potentiodynamically in a 3.5 wt.% NaCl solution open to air at room temperature. For each materials and electrolyte combination, the corrosion sample was allowed to absorb water in the electrolyte for 3 hours. After immersion of the specimen in the solution, the potential of the electrode was swept at a rate of 0.166 mV/s from the initial potential of -250 mV vs. E_{corr} to the final potential of 1000 mV vs. E_{corr}. All potentials recorded in this paper were referred to the saturated calomel electrode (SCE), and the counter electrode was a high-purity graphite rod.

3. RESULTS AND DISCUSSION

3. 1 Potentiodynamic polarization measurements and protective efficiency

Fig. 1 shows typical potentiodynamic polarization curve of copper in a 3.5 wt.% NaCl solution. This polarization behavior of copper has long been studied by many authors[7]. In the potential range examined, the polarization curve generally has three distinct regions: the active dissolution region (apparent Tafel region), the active-passive transition region and the limiting current region. Especially, a linear E/log i relation with Tafel slope of about 60 mV/decade was obtained. This slope value indicates that the dissolution process is determined by the rate of

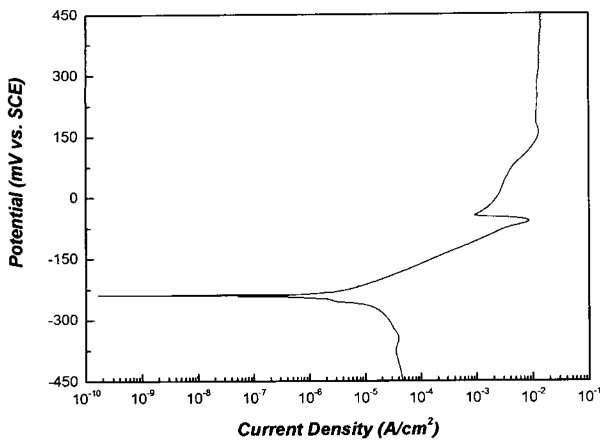

Fig. 1. Polarization curve of copper in a 3.5wt.% NaCl solution

diffusion of soluble species for the electrode surface into bulk solution[8]. Table 1 shows corrosion properties of copper obtained from polarization test. Fig. 2 shows potentiodynamic polarization curves of the copper covered with cyclohexane films as a function of deposition temperature and RF power. The cathodic process was obviously suppressed by covering the surface with the cyclohexane film to a great extent, indicating that oxygen diffusion was arrested with the barrier layer. This reaction is related to the limiting diffusion current density. The anodic process of copper dissolution was also inhibited in the presence of the film, suggesting that the tightly-interconnected cyclohexane film suppressed diffusion of aggressive anions, like chloride ions, to the surface. Corrosion properties of coated specimens obtained from potentiodynamic data are shown in Table 2. The protective efficiency, P_i (%) of the film was determined from the polarization curves by equation (1),

Table 1. Corrosion properties of copper obtained from polarization curve

E_{corr} (mV)	i_{corr} (μA/cm^2)
-240.5	6.502

$$P_i(\%) = 100(1 - i_{corr}/i^{\circ}_{corr}) \quad (1)$$

where iocorr and i_{corr} refer to the corrosion current densities obtained by the presence and absence of the film, respectively[9-10]. Fig. 3 shows the protective efficiency calculated from Tables 1 and 2. The protective efficiency of films increased with increasing deposition temperature and RF power. The highest protective efficiency was 85.26% at 100℃-50W.

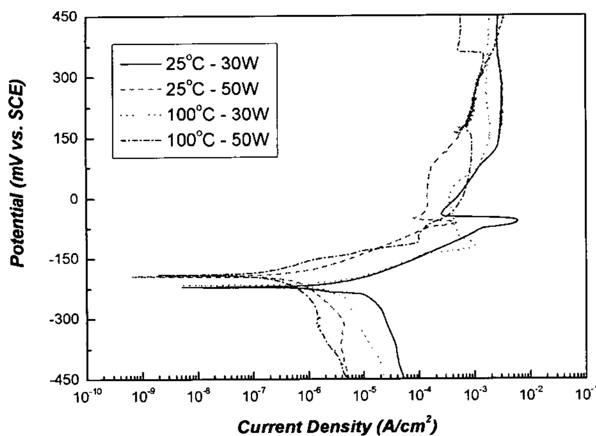

Fig. 2. Polarization curves of the copper coated with cyclohexane films as a function of deposition temperature and RF power.

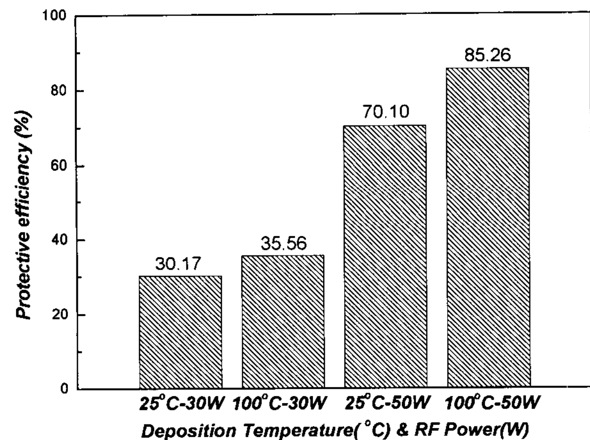

Fig. 3. Protective efficiency of the copper coated with cyclohexane films as a function of deposition temperature and RF power.

Table 2. Corrosion properties of copper coated with cyclohexane films obtained from polarization curve

	E_{corr} (mV)	i_{corr} ($\mu A/cm^2$)
25℃-30W	-221.3	4.539
25℃-50W	-195.4	1.944
100℃-30W	-219.7	4.189
100℃-50W	-191.5	0.958

3. 2 FT-IR spectroscopy

Fig. 4 shows the FT-IR spectra of plasma polymerized cyclohexane films. In the case of general liquid cyclohexane, Two strong absorption peaks appear at 2910 and 1450 cm^{-1}. The absorption peak at 2910 cm^{-1} can be assigned to the aliphatic C-H stretching mode of methyl group. And the methyl group can also assign the absorption peak at 1450 cm^{-1} to the CH_2 bending mode. C-H stretching peak of polymers increases with increasing deposition temperature and RF power, as shown in Fig. 4(a)-(d). This result indicates that cyclohexane molecular is ionized by the plasma effect. Also, cyclohexane films have the higher degree of cross-linking because cyclohexane molecular produces richer radical with increasing deposition temperature and RF power.

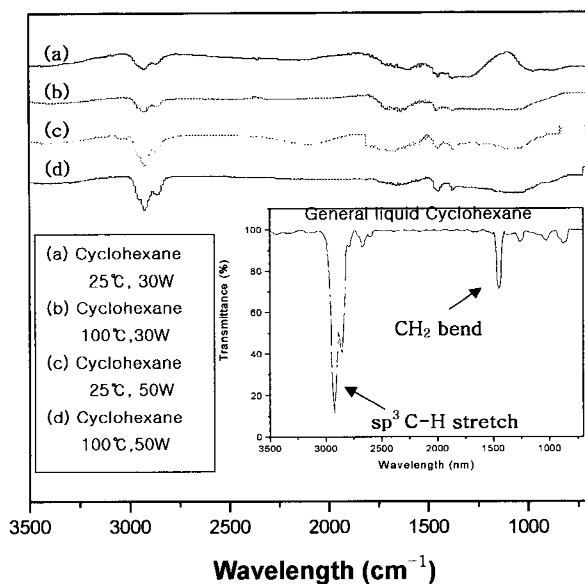

Fig. 4. FT-IR reflection spectra of the copper coated with cyclohexane films; (a) 25℃-30W, (b) 100℃- 30W, (c) 25℃- 50W, (d) 100℃- 50W.

3. 3 Contact angle measurements

Fig. 5 shows the contact angle with water of cyclohexane film as a function of deposition temperature and RF power. The contact angles increase with increasing deposition temperature and RF power, i.e., the plasma-polymerized cyclohexane film exhibits a higher hydrophobicity with increasing deposition temperature and RF power.

From the results of FT-IR analyses and contact angle measurements, cyclohexane films with increasing deposition temperature and RF power had the higher degree of cross-linking and hydrophobicity. The better corrosion protection for copper coated with cyclohexane films with increasing deposition temperature and RF power is based on the densely packed and tightly interconnected cyclohexane film because of the higher degree of cross-linking in the film.

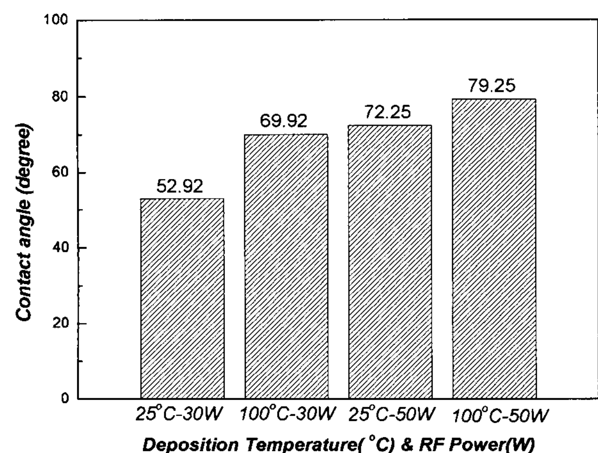

Fig. 5. Contact angle (θ) with water for the cyclohexane film as a function of deposition temperature and RF power.

4. CONCLUSIONS

1) The plasma-polymerized cyclohexane film in 3.5wt.% NaCl solution provided an increased corrosion resistance with increasing deposition temperature and RF power. The film barrier properties was ranked as follows: 100℃-50W > 25℃-50W > 100℃-30W > 25℃-30W

2) From the results of FT-IR analyses, cyclohexane films with increasing deposition temperature and RF power had the higher degree cross-linking density.

3) The contact angles increased with increasing deposition temperature and RF power. The protective ability of the film against corrosion in an aqueous solution is strongly dependent on the wettability of the film on the solid surface.

4) Better corrosion protection for copper coated with cyclohexane films with increasing deposition temperature and RF power is based on the densely packed and tightly interconnected cyclohexane film because of the higher degree of cross-linking and hydrophobicity of the films.

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REFERENCES

1. S. P. Murarka, Materials Science, Engineering, R19 (1997) 87.
2. W. W. Lee, P. S. Ho, MRS Bulletin, 22 (1997) 19
3. T. Homma, Thin Solid Films, 278 (1996) 28.
4. S. P. Murarka, I. V. Verner, R. J. Gutmann, Copper-Fundamental Mechanisms for Microelectronic Applications, John Wiley & Sons, INC. (2000) 22.
5. A. Kohn, M. Eizenberg, Y. Shacham-Diamand, Y. Sverdlov, Materials Science and Engineering, A302 (2001) 18.
6. J. S. Jeon, D. H. Jeon, Journal of Corrosion Science Society of Korea, 19 (1990) 33.
7. H. P. Lee, Ken Nobe, Journal of Electrochemical society, 133 (1986) 2035.
8. A. V. Benedetti, P. T. A. Sumodjo, K. Nobe, P. L. Cabot and W. G. Proud, Electrochimica Acta, 40 (1995) 2657.
9. D. Taneichi, R. Haneda, K. Aramaki, Corrosion Science, 43 (2001) 1589.
10. K. Nozawa, K. Aramaki, Corrosion Science, 41 (1999) 57.