

PLASMA POLYMERIZED ORGANOSILANES AS A PROTECTIVE COATING ON METAL*

SUN Qiushi (孙求实) and HOU Xiaohua (侯晓淮)

(*Institute of Chemistry, Academia Sinica, Beijing 100080*)

ABSTRACT

Polymer-metal oxane bonds (M-O-Si) can be created in the form of tight networks by silane plasma polymerization directly on the metal (e.g. copper) substrates. In this paper the structure and properties of the plasma-deposited organosilane polymers, the corrosion performance of such coating system on copper substrates were investigated.

INTRODUCTION

Plasma polymer of organosilane compounds have been widely studied. A large number of these studies deal mainly with the characterization, structure, and properties of polymer films, and reaction mechanisms of plasma polymerization of organosilicon compounds^[1]. Plasma organosilane polymers have been used as intermediate oxygen etch resistance layers in resist lithography^[2-4]. Gas permeability studies and applications of plasma-polymerized organosilane films as a gas separation membrane have been of much interest to researchers^[5]. This work aims to the study of depositing a thin organosilane plasma film on copper substrates as an effective corrosion-resistant coating.

EXPERIMENTAL

Materials

Cyclooctamethylsiloxane (D₄) monomer was obtained from Beijing Chemical Factory and H59-1 sheet copper was used as substrate.

The apparatus for plasma polymerization was a bell jar-type reaction chamber which was connected with monomer inlet, pressure gauge, vacuum system, and matching network for inductive coupling of a 13.56 MHz radio frequency (rf) source.

* This project is supported by the Science Fund of the Chinese Academy of Sciences.

Received March 6, 1995

A copper sheet was put on the low-electrode as the substrate. The reaction system was evacuated to 10–20 Pa. The surface of copper sheet was exposed to air plasma for 5 minutes, then the monomer gas was introduced into the reaction chamber at 20 Pa. The rf power was tuned on, and the plasma polymerization was conducted under different power level.

X-ray photoelectron spectroscopy (XPS) was used for element analysis of plasma deposited polymer films. The photoelectron spectrometer (PERKIN ELMER PHI 5300) was used with an X-ray source Mg K α (1253.7 eV). Fourier transform infrared (FTIR) spectra of plasma deposited polymer on a NaCl plate were recorded on a BRUKER IES 13V spectrophotometer. The SEM photography of the surface morphology of the plasma deposited polymer film was taken with HITACHI S-530.

The coated sheet was immersed in FeCl₃ solution for 2 hours at 25°C the Fe³⁺ concentration of the used solution was determined at 400 nm by a spectrophotometer, thereafter. Corrosion performance was evaluated by the Fe³⁺ concentration difference. The tested samples were examined visually for failure such as film lifting, peeling, adhesion loss, or blistering.

Table 1 Element compositions for plasma deposited D₄ polymer from XPS

Power (Watt)	O	C	N	Si
	%			
20	31.52	44.52	0.41	23.35
30	29.00	44.80	0.09	25.46
40	34.09	40.89	0.00	25.02
50	44.55	30.39	0.21	24.85

Deposition time 8 min

RESULTS AND DISCUSSION

1. Characterization of silane plasma polymers

The XPS spectra of a representative plasma-polymerized D₄ film on copper substrate are shown in Fig.1. It was found that the oxygen content of surface of plasma-polymerized D₄ film is significantly increased. Elemental compositions from XPS for plasma D₄ polymer deposited under different power levels are listed in Table 1. The increment of oxygen content were explicated as follows: i) the carbon content was reduced during the polymer deposition, ii) extra oxygen was incorporated into the polymer film and surface from the residual water or air in the vacuum chamber and possibly from adsorbed oxygen after the deposited film was exposed to air. This point was also proved by nitrogen incorporation into the polymer film and surface.

The XPS spectra of plasma-polymerized silane polymer show that each peak is a combination of two or more component peaks. This result agrees with that obtained from FTIR analysis described in the following. The chemical structure and possible bonds in the plasma polymer films were also characterized by means of IR spectroscopy. The FTIR spectrum of a typical D₄ plasma polymer is shown in Fig.2. According to the literature^[6], the peaks can be assigned as follows: 802cm⁻¹ (Si—CH₂ asymmetric rocking), 845cm⁻¹ (Si—CH₂ symmetric rocking), 1080–1090cm⁻¹ (Si—O—Si, Si—O—R stretching), 1261 cm⁻¹ (Si—CH₃ symmetric deformation), 2965 cm⁻¹ (CH₃ stretching). The bonding environments surrounding Si atoms are essentially Si—O—Si, Si—O—R, Si—CH₃ and Si—CH₂.

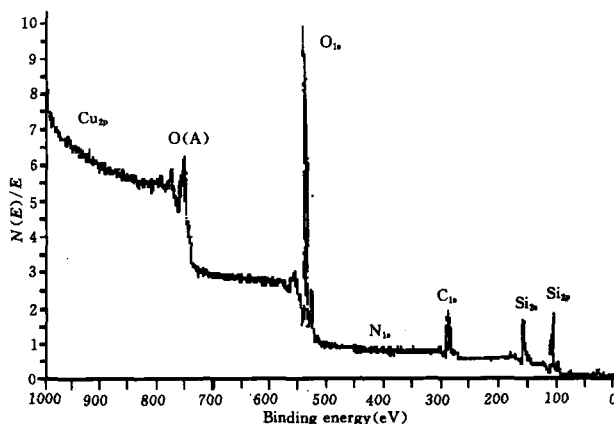


Fig.1 XPS spectrum of a plasma polymerized D₄ film on copper substrate. Plasma deposition conditions: power 10 W, deposition time 8 min

2. D₄ plasma polymer structure and deposition kinetics

When D₄ was polymerized in a glow discharge, the chemical structure and properties of the resulting polymers generally depend on the discharge conditions. Elemental compositions from XPS for D₄ plasma polymers deposited under different power levels are listed in Table 2. As shown the atomic ratio C/Si reduces when the discharge power increases. Polymers formed within this power range (20–50W) have atomic ratios of 1.91–1.22 which are lower than that of the starting monomers (2.0). The carbon content of films reduces when the deposition power increases. From a mechanistic viewpoint, this can be explained as follows: under the plasma conditions used, the contribution of silicon-containing segments to the polymer film is greater than the hydrocarbon segments. As a result, the plasma-deposited polymers have a smaller C/Si ratio than the monomers. The cleavage of the Si—C bond (305 kJ/mol) and C—H bond (414 kJ/mol) are the dominant reaction in D₄ plasma polymeriza-

tion. The stronger Si—O bond (464 kJ/mol) renders the Si—O—Si portion of the D₄ molecule difficult to decompose under plasma conditions. The decomposition of the alkyl portion of D₄ increases with the power level. The existence of Si—C and C—H bond cleavage and the formation of small, stable hydrocarbon molecules such as CH₄ and C₂H₄ result in a smaller contribution of hydrocarbon during the polymer deposition. As a result, this polymer contains relatively large amounts of silicon-containing moieties.

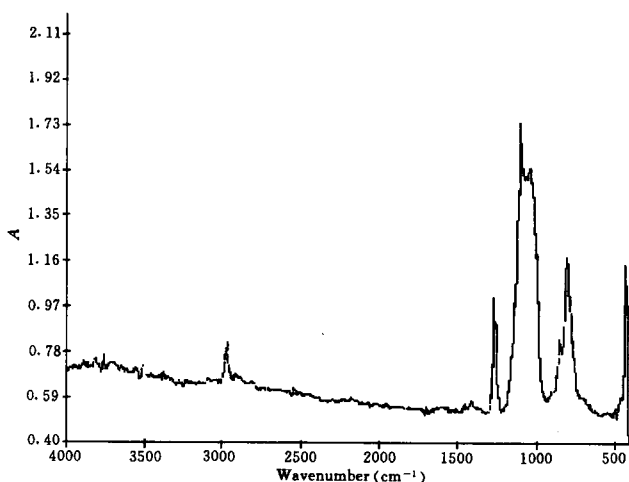


Fig.2 FTIR spectrum of D₄ plasma polymer. Plasma deposition conditions: power 10 W, deposition time 60 min

Table 2 Atomic ratios (C/Si) from XPS for plasma deposited D₄ polymer under different power levels

Power (Watt)	20	30	40	50
C/Si	1.907	1.760	1.634	1.223

The FTIR spectra of D₄ plasma polymer obtained under different power levels are shown in Fig.3. The areas of peaks of 2965cm⁻¹ (CH₃ stretching), 1261cm⁻¹ (Si—CH₃ symmetric deformation), 802cm⁻¹ (Si—CH₂ asymmetric rocking), and 845cm⁻¹ (Si—CH₂ symmetric rocking) reduce with the increase of discharge power. The area of peak of 1080—1090cm⁻¹ (Si—O—Si, Si—O—R stretching) increases when the discharge power increase. This agrees with that results obtained from XPS analysis described in the paragraph that precedes.

When the copper substrate was placed in the silane plasma gas for film depo-

sition, the polymer deposited on all surfaces exposed to the plasma gases. The surfaces of copper substrate were uniformly coated with a thin polymer film under 20 W discharge power, as is shown in Fig.4. After 2 min deposition (Fig.4b), the copper surface were covered with some island-like deposited polymer, as compared with Fig.4a. Perfect films were formed on the surfaces of substrates after 10 and 20 min deposition (Fig.4c and 4d). Defects can be seen in SEM micrograph after 60 min deposition (Fig.4e).

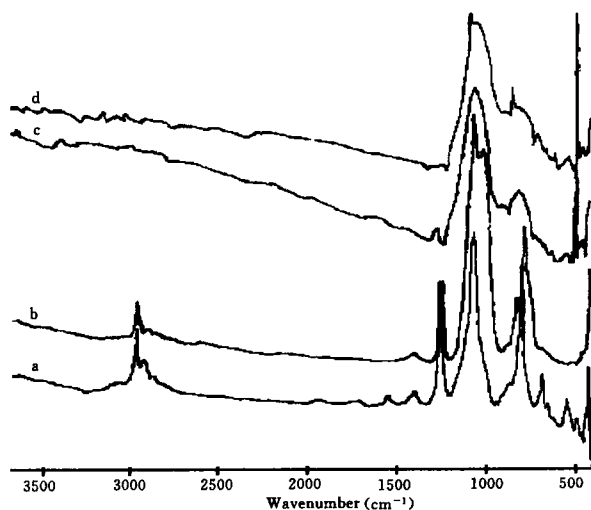


Fig.3 FTIR spectra of D₄ plasma polymers under different power levels (deposition time 60 min). a) Monomer; b) 10W discharge power; c) 30W; d) 40W

3. Corrosion resistance of coatings on metal substrates

When a metal substrate was cleaned with air plasma followed by a thin layer of plasma silane polymer deposit, the coated substrates showed good corrosion resistance. Samples were prepared and immersed in FeCl₃ solution for 2 hours at 25°C. The plasma-coated samples showed very little or no pitting on the surfaces, while severe corrosion appeared on the uncoated sample. The Fe³⁺ concentration difference of FeCl₃ solution under different deposition conditions are listed in Table 3. A better performance was found for samples with plasma polymers deposited at long discharge time under lower power levels, and short discharge time under higher power levels. The thickness of plasma polymer film increases with discharge time. As a result, corrosion resistance also increases with discharge time. Under higher power levels, the rate of cross-linking reaction increases with discharge time. The plasma polymers are relatively rigid due to their highly cross-linked nature. So little

defects were produced at long discharge time under higher power levels. As a result, corrosion resistance is dropped. This agrees with that results found from SEM micrograph mentioned above.

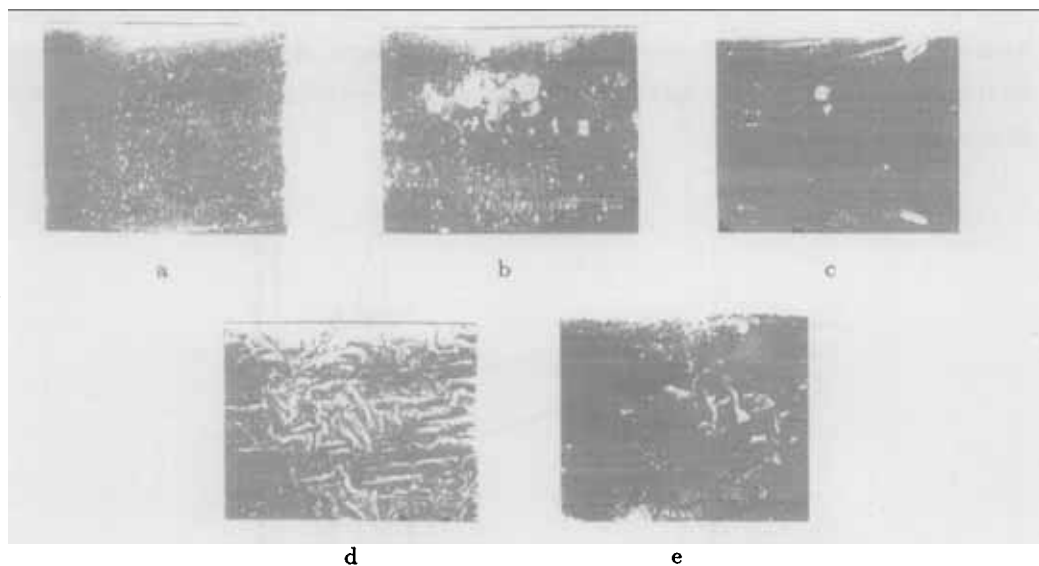


Fig.4 SEM micrographs of surfaces of copper substrates with and without deposition of plasma polymer of D₄. a) No plasma film deposition; b) 2 min deposition; c) 10 min deposition; d) 20 min deposition; e) 60 min deposition

Table 3 The Fe³⁺ concentration differences of FeCl₃ solution under different deposition condition

Time (min)	10W	20W	30W	40W	50W
0	24.23	24.23	24.23	24.23	24.23
2	17.19	15.33	12.71	9.26	7.99
4	12.95	9.26	6.70	7.47	5.29
6	10.01	6.70	5.92	5.39	4.86
8	6.96	4.86	4.06	5.39	4.06
10	6.70	3.52	4.06	6.70	6.44
20	5.39	3.25	3.79	9.26	11.74
30	5.39	3.25	5.12	10.51	12.71
60	5.39	3.25	6.44	14.15	16.27

Unit of concentration: 10⁻⁴ mol/L

CONCLUSIONS

XPS and IR analyses show that the plasma deposited silane polymers are essentially polyorganosiloxane in nature. The bonding environments surrounding

Si atoms are basically Si—O—Si, Si—O—R, Si—CH₃, and Si—CH₂. The polymer-metal interface bonding is believed to be a typical oxane linkage (M—O—Si). The elemental compositions of deposited silane plasma polymers vary with the discharge power. The atomic ratio C/Si of the polymer film reduces with the increase of discharge power. Corrosion performance of such-coated copper samples were found to be improved greatly.

Keywords:

Plasma polymers; Organosilanes; Protective coating

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