STRUCTURAL ANALYSIS OF COPPER PHTHALOCYANINE THIN FILMS FABRICATED BY PLASMA-ACTIVATED EVAPORATION

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ABSTRACT

Copper Phthalocyanine (CuPc) thin films were fabricated on the silicon wafers by plasma activated evaporation method and structural analysis were carried out with various spectroscopies. The CuPc films had dense and smooth morphology and they also showed good mechanical properties and chemical resistance. The main molecular structure of the CuPc, which is the conjugated aromatic heterocyclic ring structure, was maintained even in the plasma process. However, metal-ligand (Cu-N) bands were deformed by the plasma process and the structure became amorphous especially at higher process pressures. Oxygen impurities were incorporated in the film and carboxyl functional groups were formed at the peripheral benzene ring. The structure and morphology of the films were dependent on the process pressure but relatively irrespective of the RF power.

Keywords : copper phthalocyanine, plasma activated evaporation, structure, analysis

INTRODUCTION

Phthalocyanine (Pc) is an organic compound with a wide scope of technological applications such as rectifier, transistor, photovoltaic cell, gas sensor, catalyst, and electrochromic display[1]. Copper phthalocyanine (CuPc, $C_{32}H_{16}N_8Cu$), of which the central hydrogen atoms are replaced by a copper atom, is a very stable compound and shows high sensitivity to the electrophilic gases such as NO and Cl[2]. CuPc thin films are usually prepared either by vacuum evaporation[3-5] or by casting of Pc-containing polymer binders[6,7]. Langmuir-Blodgett (LB) method was also examined using Pcs with attached chains[8]. The films prepared by the vacuum evaporation or the LB method show poor mechanical and adhesion properties and those prepared by casting method contains pinholes especially when they are thin. When polymer films are fabricated by plasma processes, they generally exhibit good mechanical and chemical properties due to the highly-branched and cross-linked structure. In this study, CuPc films were fabricated by plasma-activated evaporation method under various process conditions and structural analysis were carried out with various spectroscopies.
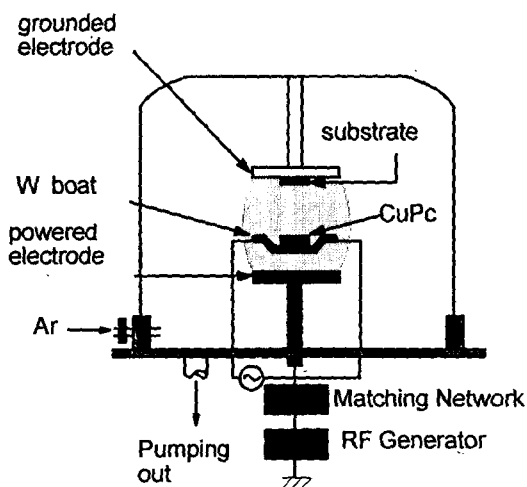
Fig. 1. Schematic diagram of the plasma activated evaporation system.

EXPERIMENTAL

A schematic diagram of the plasma activated evaporation system is shown in Fig. 1. The reaction chamber is consisted of a Pyrex glass bell jar and a capacitively coupled electrodes (10cm diameter and 4cm spacing) connected to a 13.56 MHz RF generator. CuPc powder (Aldrich, β-form) was pressed to form a disk of 5mm diameter and 3mm thickness as an evaporation source. The source was placed in a tungsten boat and evaporated by heating the boat to 580℃. CuPc films with a thickness of 600nm were deposited on p-type (100) Si wafers by plasma activated evaporation under the following conditions: deposition pressure 20~300mTorr and RF power 10~50W. We also prepared CuPc thin films by vacuum evaporation at the pressure of 7×10^{-6} Torr for the purpose of comparison.

Film morphology was observed with a scanning electron microscopy (SEM). Crystalline structure was analyzed with x-ray dif-

fraction using Cu Kα monochromatic source. Compositions and bonding properties of the films were analyzed with an Auger electron spectroscopy (AES, with 5kV electron beam) and an x-ray photoelectron spectroscopy (XPS, with Al Kα x-ray). Infrared (IR) spectra were obtained with a FTIR spectrometer (Bomem DA8). Raman spectra were obtained using 514.5nm excitation laser beam.

RESULTS AND DISCUSSION

Surface morphology of the deposited CuPc films was examined with SEM. The CuPc films deposited by vacuum evaporation (hereafter referred as e-CuPc films) are porous and show villi-shape crystallites with a diameter of about 100nm, whereas the CuPc films deposited by plasma-activated evaporation (hereafter referred as pe-CuPc films) are much denser than e-CuPc films and shows very smooth surface morphology, as shown in Fig. 2. The morphology of pe-CuPc films was irrespective of the RF power used in this research, 10~50W. However, process pressure caused some changes in film morphology and crystal structure. The films fabricated in low pressure plasma (20~100mTorr) had columnar grains with diameters of 500~1000nm and showed x-ray diffraction pattern with sharp peaks at 15.6°, 24.0°, 25.0°, 26.7°and 27.6°of 2θ. With increasing pressure, the collisional cross-section increases and so does the dissociation probability of the evaporated CuPc molecules, which causes more cross-linking and branching between the molecules in the film, resulting in a denser structure. The pe-CuPc films fabricated at 300mTorr did not exhibit a sharp X-ray dif-

fraction pattern.

It was found from a scratching test that pe-CuPc films were much harder than e-CuPc films. In an adhesion test using a 3M tape, most of e-CuPc films were peeled off whereas the pe-CuPc films remained intact on the substrate. The CuPc films were immersed in 60% concentrated sulfuric acid and the chemical resistance of the films were examined. The e-CuPc films were dissolved in about 10 seconds, whereas the pe-CuPc films lasted for about 40 seconds. Conductivity of the pe-CuPc films was about 2 orders of magnitude lower than that of e-CuPc films. The electrical properties of the pe-CuPc films had been reported elsewhere[9, 10].

AES spectra of e-CuPc and pe-CuPc films are shown in Fig. 3(a). Oxygen is not detected in e-CuPc films, meaning that its content
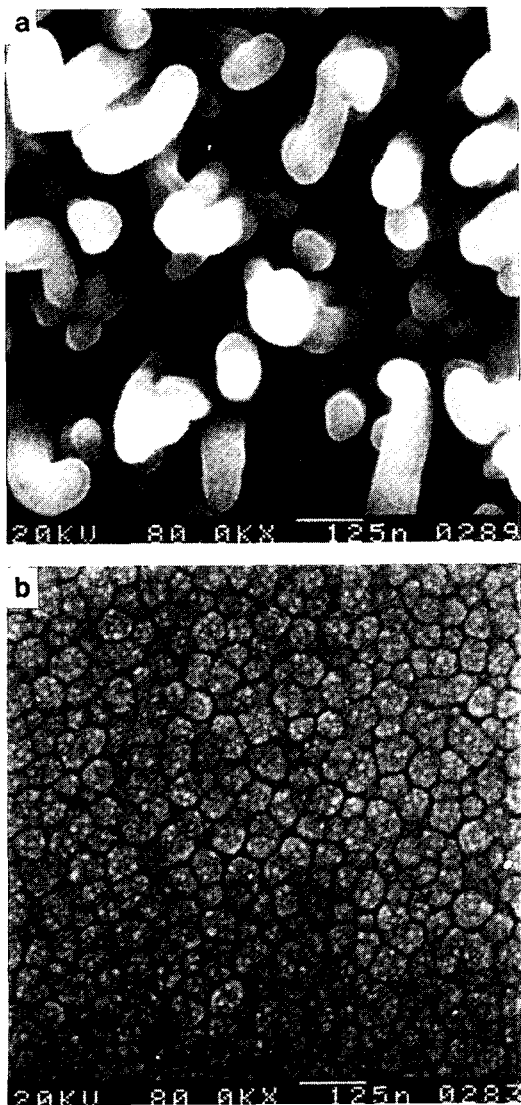

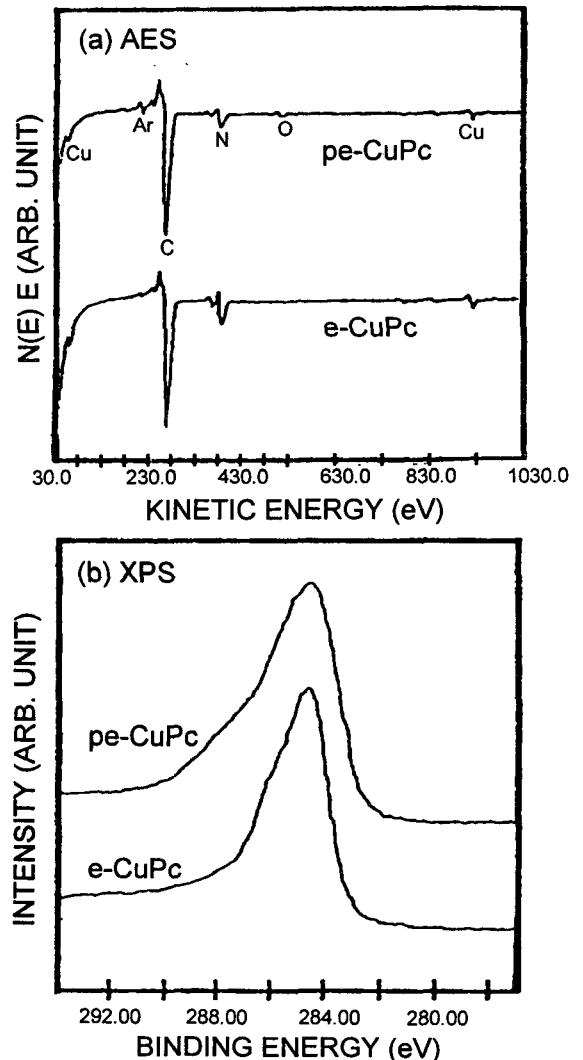Fig. 2. SEM surface morphologies of (a) e-CuPc and (b) pe-CuPe film

Fig. 3. (a) Auger electron spectra and (b) XPS Cls photoelectron peaks of e-CuPc and pe-CuPe films.

is less than the AES detection limit (~0.1at %). Whereas pe-CuPc thin film contains about 1% of oxygen which is originated from those contained in β-CuPc powder source. It is reasonable to induce that oxygen molecules contained in the CuPc powder were pumped out during vacuum evaporation while in the plasma process they were reacted with CuPc molecules activated by high energy electrons and incorporated in the film. Fig. 3(b) shows C1s photoelectron peaks of e-CuPc and pe-CuPc films. The C1s peak of e-CuPc film has an asymmetric shape, and is generally considered to be resolved to C^a1s (284.8eV, associated with aromatic hydrocarbon), $C1^b s$ (286.2eV, associated with carbon atoms binding with two nitrogen atoms) and satellite peak (287.9eV) of C1s. The C1s peak of pe-CuPc film has a more asymmetric shape with an extra shoulder at the vicinity of 288 eV. Clark[15] showed a general trend of core-level binding energy by means of spectroscopic analysis and theoretical calculation on pure polymer and low-molecular-weight molecule model. According to his suggestion, C1s photoelectron peak shifts to the higher binding energy by 1.5eV per C-O bond. Therefore the binding energy shoulder of C1s photoelectron peak is considered to be originated from carbon atoms bonded with oxygen impurity which had been incorporated in the pe-CuPc film.

IR spectral data provide important information concerning the bonding characteristics. IR spectra of e-CuPc and pe-CuPc films were analyzed in the wavenumber range of $450 \sim 4000 cm^{-1}$. There were not so much differences between e-CuPc and pe-CuPc films in the position of most absorption bands. This indicates that the main molecular structure of CuPc film, which is the conjugated aromatic heterocyclic ring structure, was maintained even in the plasma activated process. There, however, were some differences in the IR spectra between the two. Generally, absorption bands were broader in pe-CuPc films than in e-CuPc films. In the pe-CuPc IR spectra additional absorption bands were observed at 1668 and $1727 cm^{-1}$ which were absent in e-CuPc film as well as in CuPc powder. In conventional CuPc polymers functional groups such as carboxylic acid, imide and amide at the peripheral benzene rings show absorption bands at the frequencies of $1600 \sim 18000 cm^{-1}$ [11,12]. From the previous analysis with AES and XPS it was found that oxygen atoms were incorporated in pe-CuPc film and bonded with carbon atoms. Thus those additional bands were considered to come from carboxyl functional groups formed at the peripheral benzene rings. Fig. 4 shows the IR spectra of pe-CuPc films deposited at various deposition pressures in the wavenumber range of 450-$900 cm^{-1}$. The absorption bands appeared at 505, 573, 637, 870 and $900 cm^{-1}$ came from metal-ligand (Cu-N) vibration and the other peaks came mainly from C-H vibration[13]. As shown in the figure, the absorption intensities, especially for the metal-ligand vibration peaks, decreased as the process pressure increased, indicating that the Cu-N bonds in the pe-CuPc film were greatly deformed by the plasma process.

Raman spectra of CuPc powder, e-CuPc and pe-CuPc films are shown in Fig. 5. The assignments of Raman spectra of vacuum evaporated CuPc film was suggested by Aro-
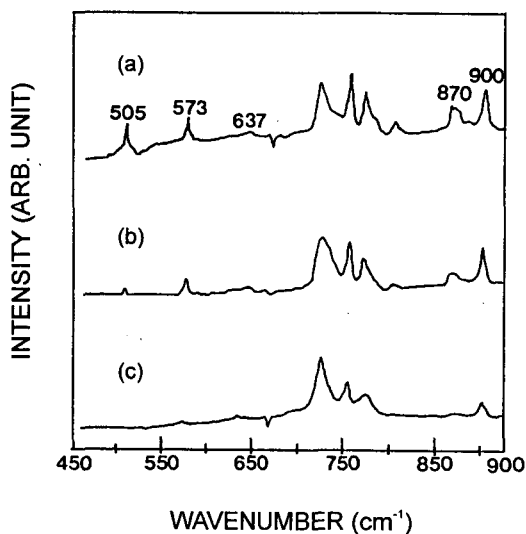
Fig. 4. IR absorption spectra in the region of 450-900cm^{-1} for pe-CuPc films deposited at various pressures : (a) 20mTor, (b) 100mTorr and (c) 300mTorr.
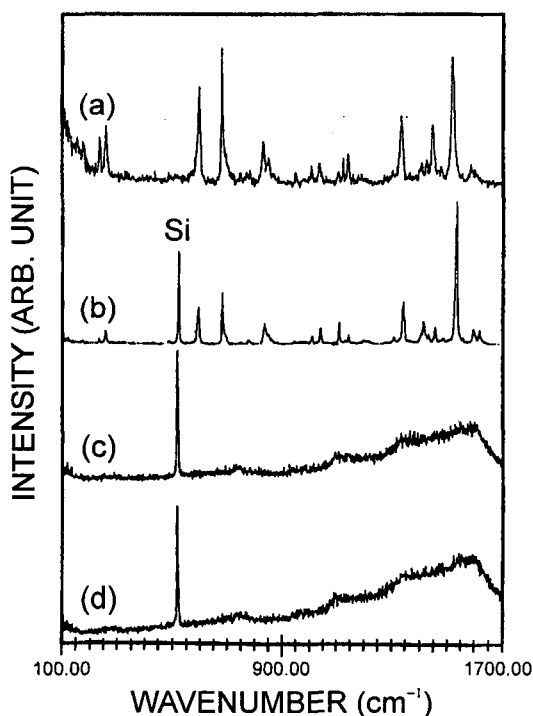

Fig. 5. Raman spectra of CuPcs : (a) CuPc powder, (b) e-CuPc film, (c) pe-CuPc film (RF power 10W) and (d) pe-CuPc film (RF power 50W)

ca[14]. Some additional peaks appeared in the spectra of CuPc powder in comparison with that of the e-CuPc film were considered to be originated from organic impurities. The peak appeared in the spectra of e-CuPc and pe-CuPc films at 520 cm^{-1} came from substrate silicon. Raman spectra of pe-CuPc films showed tiny and broad peaks at 840 and 1100cm^{-1} which were associated with C-H bending and benzene stretching vibration and at 1340cm^{-1} which was associated with C-H deformation vibration. Comparing with CuPc power as well as e-CuPc film, the general spectra of pe-CuPc films were greatly suppressed, indicating that the pe-CuPc films have random-oriented electric dipoles.

CONCLUSIONS

The CuPc films fabricated by plasma activated evaporation had dense and smooth morphologies and showed superior mechanical properties and chemical resistance to vacuum evaporated film. The main molecular structure of the CuPc, which is the conjugated aromatic heterocyclic ring structure, was maintained even in the plasma process. However, metal-ligand (Cu-N) bands were deformed by the plasma process and the structure became amorphous especially at higher process pressures. Oxygen impurities were incorporated in the CuPc film and carboxyl functional groups were formed at the peripheral benzene ring. The structure and morphology of pe-CuPc films were dependent on the process pressure but irrespective of the RF power in the range used in this research, 10~50W.

ACKNOWLEDGMENT

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