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PARAMETER STUDY ON PLASMA-POLYMERIZATION OF LANTHANIDE DIPHTHALOCYANINE FILMS FOR ELECTROCHEMICAL DEVICES

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ABSTRACT

Lanthanide diphthalocyanines have interesting properties on electrochemical and chemical redox reactions. It is however, difficult to use because of thier short device life. Plasma-polymerization attends to improvement thier device life. Yb-diphthalocyanine ($YbPc_2$) polymer film was deposited in a parallel plate electrodes-type RF plasma reactor. $YbPc_2$ was sublimed into the argon plasma, and polymer film was obtained on a substrate. Radio frequency was constant of 13.56MHz. Pressure of argon gas, sublimation rate of $YbPc_2$ and RF power were variable parameters depending on film quality. Surface of polymer films include a lot of sub-micron order lumps. It was indicated that size of lumps depends on polymerization degree controled by parameters. Size of lumps and polymerization degree are increased with RF power. However, by the high RF power over 40W, polymerization degree is decreased with RF power and surface of film is rough. In condition of RF power is high, polymerization will compete with etching of film. We obtained good films for electrochromic display with RF power of 20W, argon gas pressure of 8.0 Pa and sublimationrate of 1.2×10^{-5} mol/min, and good films for gas sensor with RF power of 30W, argon gas pressure of 10.6Pa and sublimation rate of 1.2×10^{-5} mol/min.

INTRODUCTION

Lanthanide diphthalocyanines have semiconductive properties and electorchemical activities such as electrochromic display[1] and gas sensors. However, vacuum-deposited film is weak in cycle life due to film decadance. Cycle life can be improved by polymerization of film. Osada and Mizumoto prepared copper phthalocyanine polymer film using plasma polymerization[2] and we also have reported Yb-diphthalocyanine polymerfilm by plasma polymerization method[3]. Plasma polymerization also have given us a new complex; iodized polymeric Yb-diphthalocyanine film in stable[4], it shows favorable propaties as high conductive semiconductor and high speed electrochromic display[5]. Reproduction of film preparation is required for expanding of use. We suggest relations between conditions of

filmx preparation and film properties. We obtained good films for electrochromic display with RF power of 20W, argon gas pressure of 8.0Pa and sublimationrate of 1.2×10^{-5} mol/min, and good films for gas sensor with RF power of 30W, argon gas pressure of 10.6Pa and sublimation rate of 1.2×10^{-5} mol/min.

EXPERIMENTAL

Yb-diphthalocyanine($YbPc_2$) was used for monomer material which was synthesized according to Moskalev et.al. method.[6] Plasma polymerization was carried out in parallel plate electrode type plasma reactor schematically illustrated in Fig. 1. $YbPc_2$ was sublimated from boat placed on bottom electrode. Substrate was placed surface of upper-electrode. Argon gas was used as carrior gas. Film deposition was carried out with followed steps: the argon plasma was generated in 2.6 ~10.6x Pa after the chamber was evacuatedto 1×10^{-3} Pa. The substrate was then bombarded with the plasma for 5 min. Next, $YbPc_2$ was sublimated from the tungsten boat to the Ar plasma where the $YbPc_2$ underwent polymerization reactions. Then, the plasma-polymerized $YbPc_2$ was deposited on the substrate. Sublimation rate is a one of parameters for preparation. The sublimation rate is contant of 1.2×10^{-5} mol/min in this research.

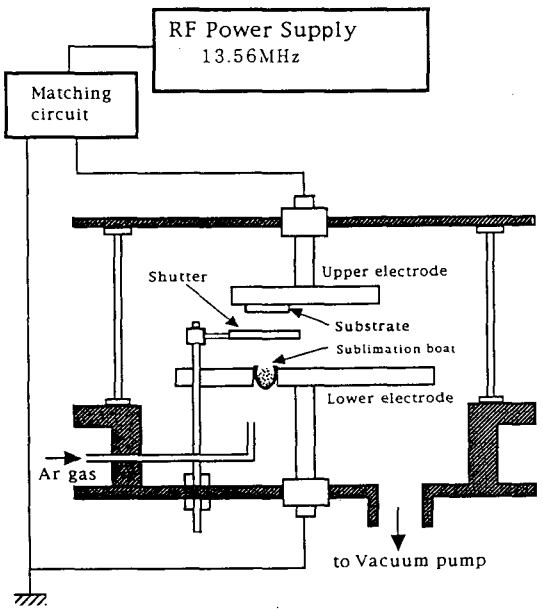

Fig. 1 Schematic illustration of C-coupling plasma reactor.

Polymerization degree was measured using viscosities of dimethylformamide (DMF) solutions. Surfaces of films were observed using SEM. Film structure is assigned from Vis and IR spectra. Electrochemical activity was estimated redox current peak value of cyclicvoltamometry. Electrolyte of 1.0M KCl aq. and reference electrode of Ag/AgCl were used.

RESULTS AND DISCUSSION

SEM photographs are shown in Fig. 2. Plasma polymerized films have lumps on surfaces. Diameter of lumps grow with RF power, but in the condition of large RF power, diameter of lumps are conversely decreased. Half width of peak at 680nm of UV spectra are increased with RF power, but peak absorbance is decrease with RF power as shown in Fig. 3. Vis-spectrum of DMF solution of polymer prepared by 40W of RF power shows mixture spectrum of $YbPc_2$ and mono-type of YbPcCl with approxymately ratio of 1:2. IR spectra of vacuum-deposited film and polymer films are shown in Fig. 4. absorption peaks at 725, 1115 and 1325cm^{-1} are assigned to diphthalo-cyanine sandwitch structure. Strong peak at 1452cm^{-1} is obserbed in

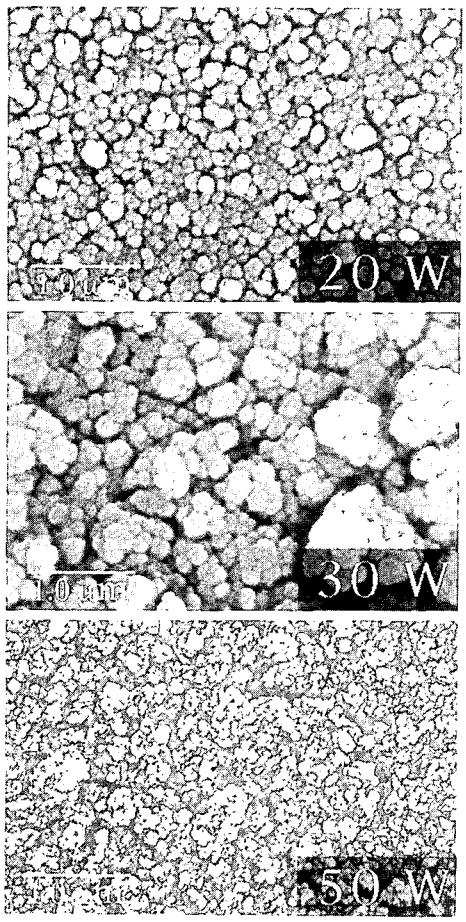

Fig. 2 SEM photographs of polymer films prepared in RF power of 20W, 40W and 50W.

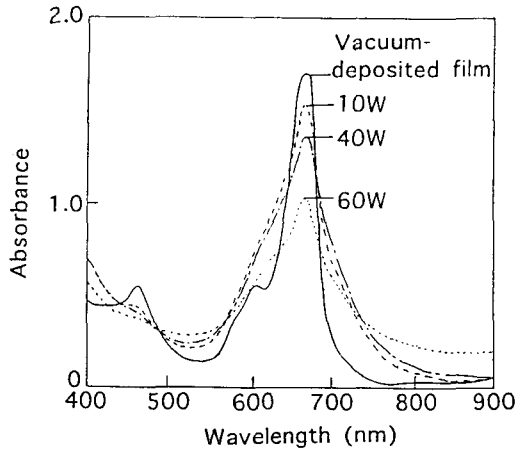

Fig. 3 Vis-spectra of polymer films. Film thickness are 0.15 μm of constant.

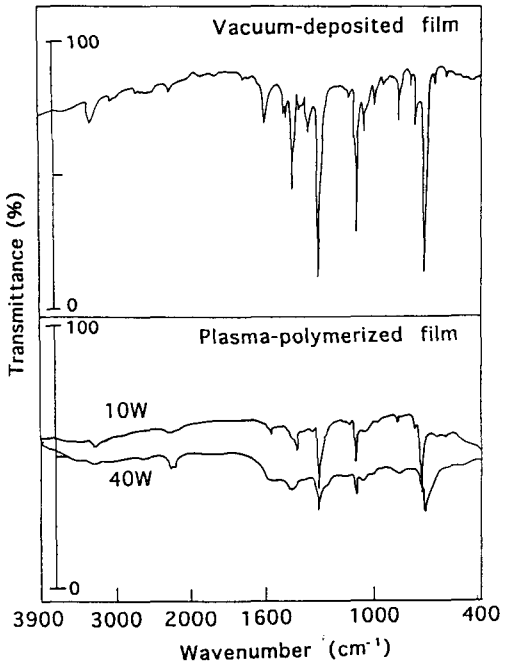

Fig. 4 IR spectra of vacuum-deposited film and polymer films.

spectrum of vacuum-deposited film. It is reported by M.M' Sadak et. al. that this peak will be shifted by substitutions at phenyl site of phthalocyanine. Absorption peak of 1452 cm^{-1} of polymer films are weak compared with vacuum-deposited film. $YbPc_2$ molecules will bind each other at phenyl site of phthalocyanine ligands. Base absorption of IR spectra of polymer films are larger than vacuum-deposited film considered to increasing of impurities such as production from broken phthalocyanine rings. Accordingly, it is suggested that polymerization competes with etching of film in the condition of RF power is high.

Polymerization degree dependence on RF power is shown in Fig. 5. Polymerization is increased with RF power till 35W. Mean diameter of lumps are also increased with RF

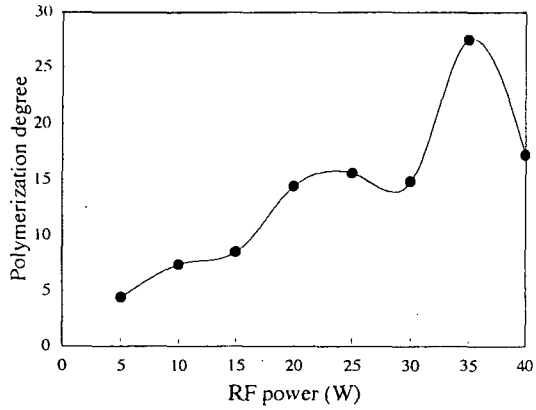

Fig. 5 Polymerization degree as a function of RF power. Ar gas pressure is 10.6Pa.

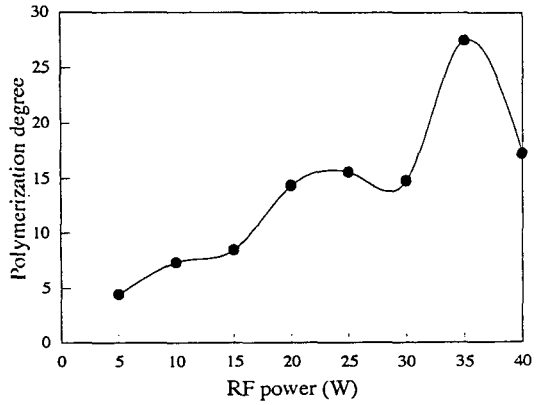

Fig. 6 Lumps diameter as a function of RF power. Ar gas pressure is 10.6Pa.

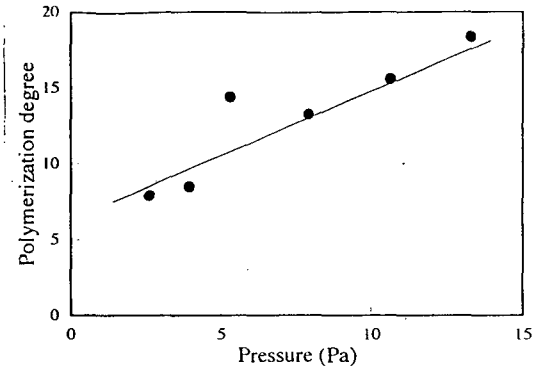

Fig. 7 Polymerization degree as a function of Ar gas pressure. RF power is 20W

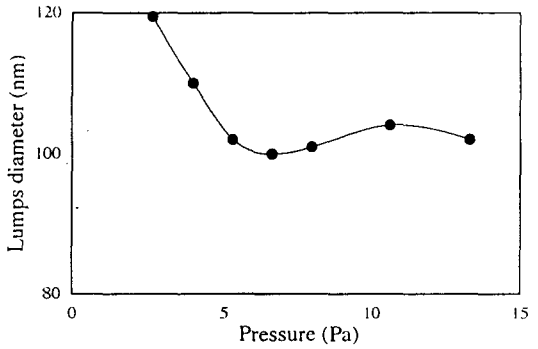

Fig. 8 Lumps diameter as a function of Ar gas pressure. RF power is 20W

power as shown in Fig. 6. Polymerization degree is increased with Ar gas pressure as shown in Fig. 7. However, mean diameter of lumps are decreased with Ar gas pressure till 5.3Pa and they are almost changeless till 13.3 Pa as shown in Fig. 8. Ar gas pressure will mainly affect to polymerization degree. Other word, polymerization degree is controlled easy the Ar gas pressure range between 5.3 and 13.3 Pa.

Influence of polymerization degree and mean diameter of lumps to electrochemical reaction was observed. Changes of electrochemical current depending on polymerization degree and mean diameter of lumps are shown in Fig. 9 and Fig. 10, respectively. Electrochemical current is decreased with polymeriza-tion degree. It is considered that polymer strtucture-bindings between $YbPc_2$ molecule sites-disturbs ion conduction into the lumps. On the other hand, electrochemical current shows tendency to increase with mean diameter of lumps. In the case of film which has large diameter of lumps, it has wide crevices between lumps that causes easy ion conduction through the film. Filling density of $YbPc_2$ sites is known by distance between

$YbPc_2$ site measured using X-ray analysis. The mean distance of $YbPc_2$ sites in the film have about 20 of polymerization degree and 100nm of lumps is about 1.286pm, that is 0.03 pm larger than vacuum-deposited film.

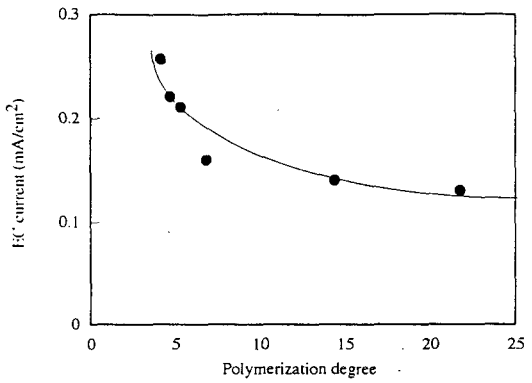

Fig. 9 Electrochemical current depending on polymerization degree.

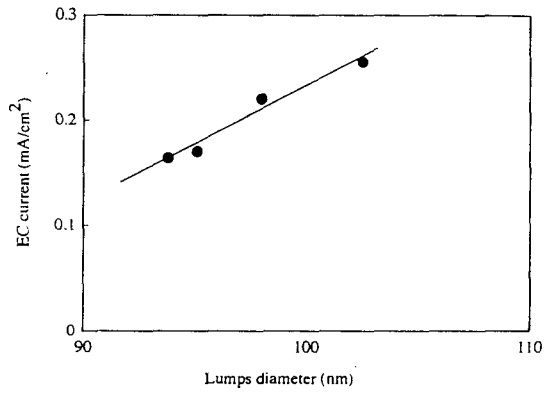

Fig. 10 Electrochemical current depending on polymerization degree of films are about 20.

CONCLUSIONS

Plasma polymerized film has bindings between $YbPc_2$ site and it contains 100nm order lumps. In the range of RF power less than 40W, polymerization degree and mean diameter of lumps is increased with RF power. Polymerization degree is also increased with Ar gas pressure, however, mean diameter of lumps are decreased with Ar gas pressure till 5.3Pa and they are almost changeless till 13.3Pa. Polymerization may occure in plasma balk and lumps may grow at near substrate.

In general, parameters for preparation of film are strongly depended on apparatus. Moreover, in the case of plasma polymerization, polymerization degree and film structure as size of lumps affect to function for electrochemical devices. Electrochemical current is decreased with polymerization degree and it shows tendency to increase with mean diameter of lumps. The polymer film suited to electrochemical device should have 2~25 of polymerization degree and about 100nm of mean diameter of lumps, they can be prepared with condition of 3~40W of RF power and 5.3~13.3Pa of Ar gas pressure. For example, application to electrochromic display, ion conduction due to lumps is essential than poly-merization degree, then film could prepared condition of RF power of 20W, argon gas pressure of 8.0Pa. In the case of gas sensor, because of diffusion materials in gas state, polymerization degree could be increased, then we can prepare the film with condition of RF power of 30W, argon gas pressure of 10.6Pa.

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