Adsorption and Desorption Properties of Cationic Polyethylene Film Gels to an Anionic Compound

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An investigation was undertaken on the adsorption and desorption properties of DMAEMA grafted (PE-g-PDMAEMA) PE films using indigocarmine (IC) as an anionic organic compound at different pH values and 25 °C. The amount of IC anions adsorbed onto PE-g-PDMAEMA films had the maximum at about pH 3. This is due to an increase in the protonation of dimethylamino groups with a decrease in the pH value. However, the adsorbed amount decreased below pH 3, since the ionic strength increased by the addition of HCl to adjust the initial pH value. It was found from analysis according to Langmuir adsorption isotherm equation that IC anions were electrostatically bonded to protonated dimethylamino groups in the 1:1 stoichiometry. The desorption of IC anions from PE-g-PDMAEMA films had the maximum at the initial pH value of 11.0. The cyclic process of adsorption at the initial pH value of 3.0 and desorption at the initial pH of 11.0 was alternately repeated without any appreciable fatigue of the PE-g-PDMAEMA film. It was made clear that the PE-g-PDMAEMA films were used as a repeatedly regenerative weakly basic ion-exchange membrane for adsorption and desorption of IC anions.
Key words: polyethylene, photografting, 2-(dimethylamino)ethyl methacrylate, adsorption, desorption

1. INTRODUCTION

It is possible to prepare functional membranes with practical mechanical strength by photografting various monomers throughout the bulk of polyethylene (PE) films [1,2]. PE films grafted with ionic monomers could absorb a considerable amount of water and possessed reasonable mechanical properties in the swollen state [1-3].

The grafted PE films have been shown to have promise for various membrane separation techniques such as uphill transport [4-8] and selective separation [7]. The pH [4-6] and electric potential [7,8] differences across the grafted PE films were applied to the source of the driving force.

In addition, membrane separation of anionic or cationic compounds by adsorption and desorption with ion exchange membranes is a potentially attractive process for the removal of undesirable ions, purification of waste water, and concentration or recovery of valuable materials with low energy and operating cost. However, few studies have been reported on the equilibrium isotherms for adsorption of anionic and cationic compounds on weakly basic or weakly acidic ion-exchange membranes. Here, weakly basic or weakly acidic polyelectrolytes

play an important role in the membrane separation by adsorption and desorption because the positively charged or negatively charged functional groups can be changed reversibly and rapidly in the response to a pH change of the surrounding solution.

In this study, an investigation was undertaken on adsorption and desorption properties of PDMAEMA-grafted PE (PE-g-PDMAEMA) films using indigocarmine (IC) as a model anionic compound (strong electrolyte) at different pH values and 25 °C. In addition, the reusabilities of PE-g-PDMAEMA film were examined by alternately repeating the cyclic process of adsorption and desorption experiments.

2. EXPERIMENTAL
2.1 Photografting

A film of PE (thickness, 30 μm; density 0.924 g/cm^3) supplied from Tamapoly Co. Ltd., (Japan) was used as a polymeric substrate. The photografting of DMAEMA onto PE films was carried out by the same method described previously [2].

2.2 Ion exchange capacity

PE-g-PDMAEMA films equilibrated in a 1.0

2. EXPERIMENTAL

Granular films, $270 \sim 300$nm in thickness, of Co_x-$(SiO_2)_{1-x}$ were deposited on substrates of glass (Samples #3~#12) and rock-salt crystal (Sample #5') by rf-diode co-sputtering under 10mTorr (0.133Pa) of Ar pressure. We used as target a SiO_2 glass disk (74mmϕ) on which Co sheets (10×10mm²) were placed. Composition of Co in films were varied by changing the number of the Co sheets. A film sample deposited on the glass substrates ($26 \times 76 \times 1.1$mm³) was cut into several pieces, 5×5mm² in area, which were annealed at temperatures T_a=500, 600, 700, 900°C, for 3 hours in a mixed gas of H_2/N_2 (=1/9). On these samples, thickness was measured by using a styrus machine and chemical composition x of Co by inductively coupled plasma (ICP) method, from which volume fraction f of Co particles was calculated assuming that the constituent materials, Co and SiO_2, have densities equal to those reported for bulk samples [10,11].

Magnetic measurement was performed with a vibration sample magnetometer applying magnetic field up to 15kOe (1.19×10^6A·m⁻¹), and Faraday effect measurement by a polarization modulation method in wavelength range of λ=400-900nm, applying magnetic field up to 15kOe(1.19×10^6A·m⁻¹). Size and dispersion of the Co particles were observed by transmitted electron microscope (TEM) on the films deposited on the rock salt substrate.

3. RESULTS and DISCUSSION

Table 1 shows composition, volume fraction f, and thickness of the samples.

Fig. 1 shows the saturation magnetization measured perpendicular to film plane plotted as a function of annealing temperatures T_a. The magnetization increases with increasing T_a, reaching to (and kept at) a value which is equal to that reported for bulk Co when $T_a \geq 700$°C. This is because the Co particles change from superparamagnetic to ferromagnetic by the annealing; magnetization hysterisis loops typical for ferromagnetic materials were obtained when $T_a \geq 700$°C, while those typical for superparamagnetic materials were obtained when $T_a \leq 600$°C. The Co-AlO_x films as deposited has saturation magnetization of magnitude almost equal to that of bulk sample, making a contrast with the Co-SiO_2 films. This may be related to the fact that SiO_2 has a lower heat of formation than AlO_x as mentioned in Introduction.

Fig. 2 shows TEM images for the sample #5' (x=0.23 , f=0.16) . The dark spots show the Co particles. They grow in size with increasing T_a, from 5 (as-deposited) to 130nm (T_a=900°C) in average. The grain size of Co in the present Co-SiO_2 granular films are much larger than those (4~15nm) observed in the Co-AlO_x granular films as deposited and annealed [6]. This may be also because AlO_x has a higher heat of formation.

Table I Various parameters and substrates of Co_x-$(SiO_2)_{1-x}$ granular

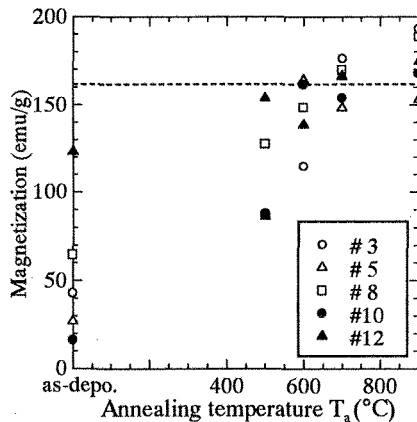| Sample	Composition x	Volume fraction f	Thickness (nm)	Substrate
#3	0.09	0.06	285	glass
#5	0.21	0.14	270	glass
#5'	0.23	0.16	280	rock-salt
#8	0.25	0.17	321	glass
#10	0.41	0.28	300	glass
#12	0.46	0.31	282	glass

Fig. 1 Magnetization versus annealing temperature T_a for granular Co_x-$(SiO_2)_{1-x}$ films.

Fig. 3 shows Faraday rotation spectra obtained for these Samples #5, 8, 12 annealed at various temperatures. In the figures spectra calculated for respective values of f of samples based on the Bruggeman's effective medium theory [5] are shown.

Sample #3 (x=0.09) as-deposited does not exhibited appreciable Faraday rotation (Fig. 3(a)). This agrees with the calculation, because the Co particles are very small in composition (x=0.09, f=0.06) and therefore in grain size. However, rotation increases prominently when annealed at T_a=500-

700°C, which slightly reduces when annealed at 900°C. In Fig. 3(b) Faraday rotation of Sample #8 having greater amount of Co (x=0.25) increases in magnitude when annealed at T_a=500-600°C. Again Faraday rotation decreases slightly when annealed at T_a=900°C. In Fig. 3(c) Faraday rotation of Sample #12 having much greater Co concentration (x=0.46) does not show a systematic change in magnitude and in sign with T_a. However, we can say that rotation at longer wavelength side (λ>600nm) increases when annealed at T_a=500-700°C, which as well slightly reduces when annealed at T_a=900°C. When annealed at T_a=600-900°C Faraday rotation at λ=700-800nm is much greater and opposite in sign as compared to the calculation. This makes a contrast with the observation that the Kerr rotation in the Co-AlOx system does not change in sign, though changes in magnitude [6]. This may be because Co
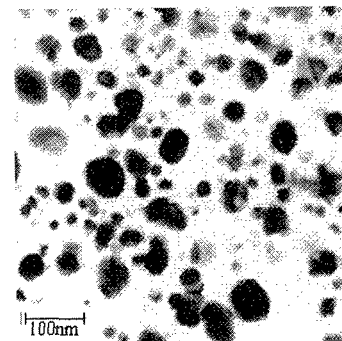
particles in the SiO_2 matrix are bigger in size and change more prominently by annealing than those in the AlO_x matrix. Any way, marked change introduced in the magneto-optical effect in the Co-SiO_2 system by annealing may be described to the weak localization of light similar as suggested in the Co-AlO_x system [6].
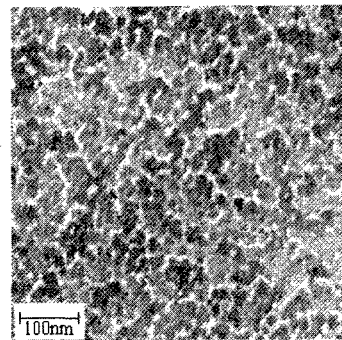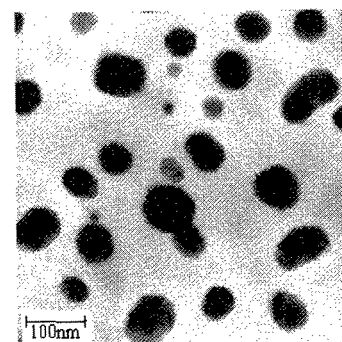

(a) As-deposited
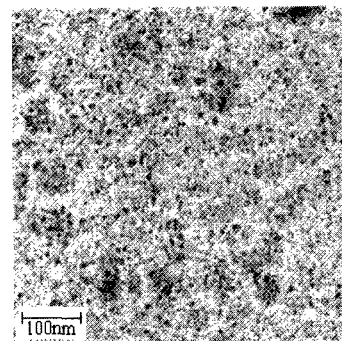
(b) T_a=500°C

(c) T_a= 600°C

(d) T_a=700°C

Fig. 2 TEM observation on granular Co_x-$(SiO_2)_{1-x}$ films, as deposited and annealed at various values of T_a.
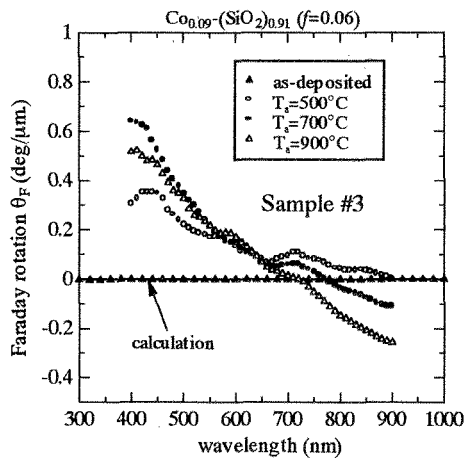
Fig. 3(b) Faraday rotation spectra for $Co_{0.25}$-$(SiO_2)_{0.75}$ (f=0.17) films, as deposited and annealed at various temperatures T_a.
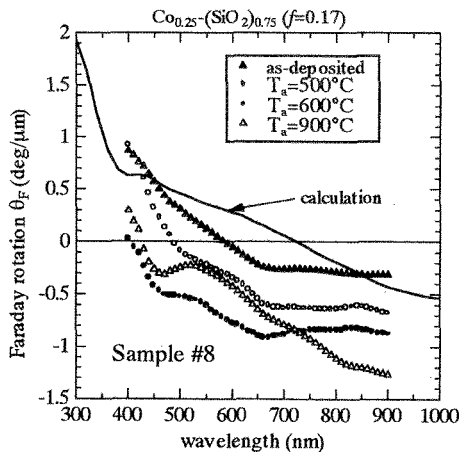

Fig. 3(a) Faraday rotation spectra for $Co_{0.09}$-$(SiO_2)_{0.91}$ (f=0.06) films, as deposited and annealed at various temperatures T_a.
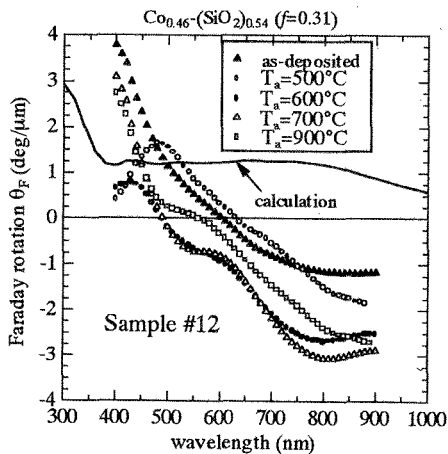

Fig. 3(c) Faraday rotation spectra for $Co_{0.25}$-$(SiO_2)_{0.75}$ (f=0.31) films, as deposited and annealed at various temperatures T_a.

4. CONCLUSIONS

Faraday rotation in Co_x-$(SiO_2)_{1-x}$ composite films varies sensitively on the Co concentration x, and increases in magnitude as the films are annealed at T_a=500-700°C, which is followed by a slight decrease when T_a is raised further to 900°C. Faraday rotation in the annealed Co-SiO₂ composite films exceeds the calculation, though in limited wavelength range. The marked enhancement of the Faraday rotation in the Co-SiO₂ granular film may be related to the weak localization of light in the granular structure similar as in the Co-AlO$_x$ granular films.

5. REFERENCES

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