Analysis of Build-up Process of CA Multilayers on the Basis of IR Spectroscopic and Ellipsometric Data

Norihisa MINO[*], Kazufumi OGAWA[*], and Motoyoshi HATADA[**]

Oriented multilayers were prepared form a chlorosilyl-type surfactant of 18-nonadecenyltrichlorosilane ($CH_2=CH(CH_2)_{17}SiCl_3$:V-NTS) by repeated cycles of a chemical adsorption (CA) process and an electron beam irradiation process in an active gas atmosphere. The thickness of CA multilayers measured by ellipsometer increased with increasing number of CA-EB cycles, n, and leveled off above certain number of n. Change of thickness of the multilayers was studied by infrared spectroscopic analysis. It assume that film material was lost by radiation-damage during EB process. On the basis of the assumption, the decrement of the CA film thickness was calculated at every EB process and the calculated curve of the CA film thickness was fit to the thickness curve measured at the number of CA-EB cycles.

KEY WORDS: Chemical absorption / Multilayer / IR / Ellipsometry

INTRODUCTION

We reported in our previous papers[1,2] that thin organic multilayers were prepared on silicon wafers by repeated cycles of two processes one, a chemical adsorption (CA) process of long aliphatic compounds having a trichlorosilane group on one end and an unsaturated vinyl group on the other end, such as 18-nonadecenyltrichlorosilane ($CH_2=CH(CH_2)_{17}SiCl_3$: V-NTS) , and the other, an electron beam irradiation (EB) process. This technique provides a method to prepare ultra-thin organic multilayers in practically larger quantity with reasonably higher speed than conventional Langmuir-Blodgett (LB)[3,4] technique. In our previous study[1], it was found that the thickness increased almost linearly with increasing cycles of process, but later study[2] revealed that the increment of the thickness of the multilayer by one cycle of process seems to decrease after 15 cycles. Two mechanisms are considered to be a candidate of this observed build-up curve; one is that the amount of film substance deposited at the CA process decreases at higher n, and the other is that the amount of the film substance does not decrease, but the loss of the film substance by radiation chemical damage at EB process in the previously built-up layers decreases the increment of the total film thickness. In this report, detailed analysis was made on the build-up process of the CA multilayers based on our past experimental data to obtain clear image of structure of the CA multilayers, and to find optimum condition for preparing CA multilayers.

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* 美濃規央, 小川一文：Central Research Laboratories, Matsushita Electric Industrial Co., Ltd.
  3-1-1, Yagumo-Nakamachi, Moriguchi, Osaka 570, Japan
**畑田元義：Japan Atomic Research Institute, Osaka Research Laboratory, 25-1, Mii-Minamimachi,
  Neyagawa, Osaka 572, Japan

EXPERIMENT

All experimental details were reported elsewhere, and only brief summary of the experiments which are necessary to the following discussions are described.

Substrates

Substrates used were silicon wafers of semiconductor grade (Osaka Titanium Co., Ltd.) on which surface aluminum and after the subsequent silicon dioxide were sputtered (SiO_2 (t = 10 nm) /Al (t = 200 nm) /Si). They were cleaned by acetone dipping followed by radio frequency plasma cleaning. The substrates were very useful for an infrared spectroscopic measurement of the multilayers.

Materials

CA multilayers were made from 18-nonadecenyltrichlorosilane ($CH_2=CH(CH_2)_{17}SiCl_3$: V-NTS). The V-NTS was synthesized and characterized by NMR, IR, and mass spectrometry. The detail assignments were reported in our previous paper[5,6]. The purity of V-NTS measured by gas chromatography was 89.4%.

Preparation of CA Monolayers

The CA monolayers for multilayers were prepared in a grove box filled with dry nitrogen by a chemical adsorption (CA) technique according to the method reported by Sagiv[7,8] using a CA solution of V-NTS (concentration of ca. 10 mmol/L) dissolved in a mixture solvent of 80 wt% n-hexadecane, 12 wt% CCl_4, and 8 wt% $CHCl_3$. The substrates were immersed in the CA solution at 30℃ for 1 hour in a dry nitrogen atmosphere. The nitrogen gas was obtained by vaporization of liquid nitrogen and passed through a 0.2 μm filter and a dryer to remove possible contamination of dust particles and moisture. The substrate covered with the CA monolayer was washed by dehydrated chloroform and followed by washing with water which had been purified by ultrafiltration of deionized water in order to stabilize the CA monolayer. The chlorosilane functional groups of V-NTS enables covalent bonds of the molecules to surfaces rich in hydroxyl groups. Thus CA V-NTS monolayers, similar to the Langmuir-Blodgett (LB) films in organization and packing but anchored to the surface of solid substrates via oxygen atom by cross-linked siloxane network, can be fabricated with good orientation and order of molecular structure. All solvents of reagent grade were purchased from Aldrich Chemical Co., Inc. and used without purification.

Preparation of CA Multilayers

After the formation of the CA monolayers, in order to convert the outer vinyl groups of the V-NTS monolayer to hydrophilic groups on which the second CA monolayer is to be formed, electron beam (EB) irradiation was carried out on the substrate covered with the CA monolayer in a nitrogen, helium and oxygen atmosphere using an electron accelerator of a transformer type (Nissin High Voltage Co., Ltd.). Concentrations of oxygen contained as impurity in nitrogen and helium atmosphere were controlled between 50 ppm and 200 ppm, below 20 ppm, respectively. The above two steps, chemically adsorption step and EB irradiation step, were alternately repeated to build up CA multilayers. Details of the process

was previously reported elsewhere[1,2]. The irradiation chamber was made of stainless steel and was equipped with an irradiation window of aluminum foil, thickness of 15 μm at the top, through which the electrons penetrated. The acceleration voltage was 300 keV, and the dose rate was 200 Gy/s at 50 μ A beam current. The irradiation was carried out at dose of 20 kGy for each EB irradiation process. The temperature of the CA multilayers did not exceed 30℃ during the irradiation. The characteristic of the CA multilayers was previously reported by elsewhere[9].

IR Measurements

An FTIR spectrophotometer (FTIR-4300, Shimadzu Co.; resolution 2 cm^{-1}, MCT (merecury-cadmium-tellurium) detector, multiple external reflection attachment) was used to elucidate the quality of the monolayer and multilayers. The reflection IR spectra of the CA multilayers were taken on SiO_2/Al/glass substrates. The angle of incidence was 73 degree and the number of external reflections was seven. The details of the measurement was reported previously[10]. Accumulation of five hundred interferograms was necessary to obtain spectra of high S/N ratio. A plate without CA films was used as a reference. The assignments of the absorption bands were made in reference to the reports by Hayashi[11] and Kimura[12].

Thickness Measurements

Thickness measurements were carried out by using an ellipsometer (Automatic Ellipsometer AEP-100, Shimadzu Co.) on the CA multilayers on the silicon substrate. The helium neon laser light (632.8 nm) was used as the light source. The angle of incidence was 70 degrees.

Since the refractive index used for calculation of the CA multilayers thickness was not known, it was assumed to be 1.450. The index value was obtained from the thickness measurement of CA multilayers of 40 layers and other study[13], and below 40 layers we could not measure the index values.

RESULTS AND DISCUSSION

Figure 1 shows film thickness as measured by ellipsometry using measured refractive index of 1.450 for the film substance at every CA process up to 5th cycle in nitrogen, helium and oxygen atmosphere at a dose of 50 kGy for each EB process. A film thickness of the CA V-NTS monolayer was decided to 2.2 nm by using the refractive index. It was already established in the previous studies that (1) at the first CA cycle on silicon wafer, V-NTS adsorbed on the wafer by forming Si-O bond with OH group exist on the silicon oxide layer of the wafer, (2) at the first and later EB cycles, double bond at the terminal of hydrocarbon chain was converted to COH, COOH, NH, or NH_2 group by the reaction with O_2 or N_2 excited by the irradiation, (3) at subsequent CA cycles, trichlorosilane group of V-NTS reacted with these functional groups to form additional layer on the previously formed layer. The formation of these functional groups (2) are confirmed in infrared spectra of monolayers after the first EB cycle in helium, nitrogen, and oxygen atmospheres (see Figure 2). The absorptions due to COH, COOH groups were clearly observed after EB process in oxygen

atmosphere by the reaction of the terminal unsaturated group with oxygen, and were slightly observed after EB process in the other two gases with oxygen exist as impurities, while those due to NH and NH_2 groups were observed only for the monolayer when the irradiation was carried out in nitrogen atmosphere. The adsorption (3) of V-NTS on the layer by the reaction with these groups was confirmed by the increase of the bands due to CH_2 group and SiO group which will be discussed later.
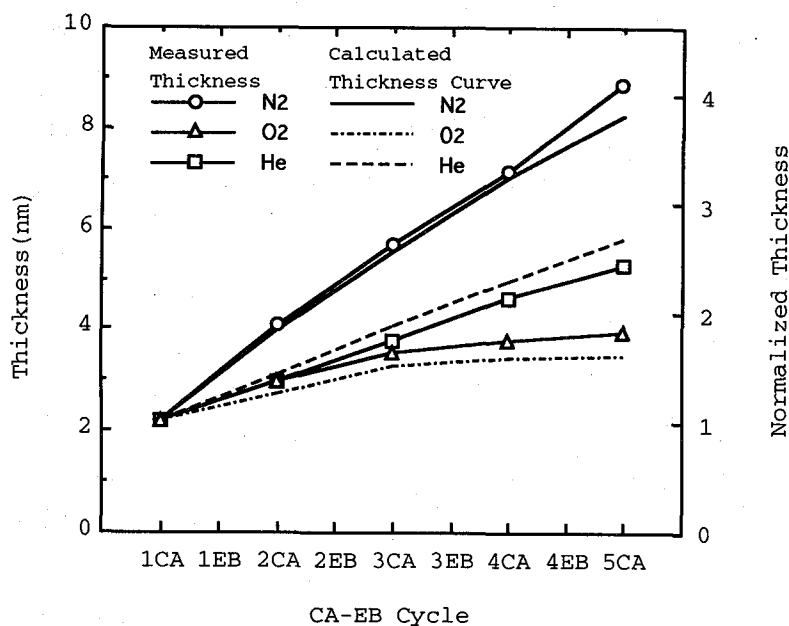

Figure 1. Changes of thickness of the CA V-NTS multilayers which were prepared by CA process and EB irradiation process of 50 kGy in nitrogen (O), helium (□) and oxygen (△) atmosphere, and calculated curves for the multilayers obtained with the experimental value (N_2: $\alpha = 0.2$, $\delta = 0.1$, He: $\alpha = 0.538$, $\delta = 0.059$, and O_2: $\alpha = 0.754$, $\delta = 0.666$, $\epsilon = 0.5$).
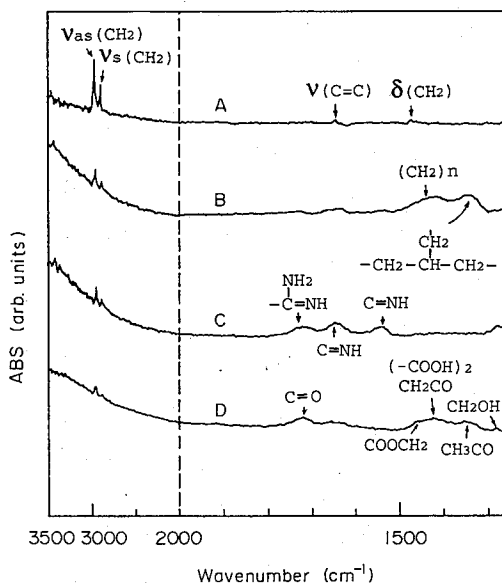
Figure 2. IR spectra of CA V-NTS monolayers at EB irradiation of 50 kGy in various gas atmospheres. (A) As deposited, (B) helium, (C) nitrogen and (D) oxygen.

Irradiation at nitrogen atmosphere

It is noticed in Fig. 1 that the film thickness increased almost linearly with the number of cycles, but careful examination of increment revealed that the increment of the normalized thickness at the second cycle is 1.8. This means that 0.2 of the original thickness was lost at the irradiation on the assumption that the thickness increase is 1.0 as in the first CA process. This assumption is supported from changes of infrared absorption of CH_2 and SiO groups at CA and EB processes which are summarized in Table 1, where it is noted that the absorption due to CH_2 increased at every CA process and decreased at every EB process, and that the absorption due to SiO increased at every CA process and remained constant at the subsequent EB process.

$I \nu_{as}(CH_2)$

	CA-EB Cycle								
	1		2		3		4		5
	CA	EB	CA	EB	CA	EB	CA	EB	CA
N_2	1.000	0.569	1.077	0.585	1.200	0.544	1.323	0.615	1.508
O_2	1.000	0.754	1.108	0.769	0.892	0.800	0.861	0.800	0.831
He	1.000	0.538	0.584	0.369	0.677	0.554	0.892	0.615	0.923

I ν (SiO)

		CA-EB Cycle							
		1		2		3		4	5
		CA	EB	CA	EB	CA	EB	CA	EB	CA
N_2		1.00	0.00	1.30	0.00	0.90	0.00	1.30	0.00	1.00
O_2		1.00	0.00	1.20	0.00	0.95	0.00	1.15	0.00	1.20
He		1.00	0.00	0.50	0.00	0.55	0.00	0.50	0.00	0.55

Table 1. Amounts of infrared absorption intensity changes of ν as (CH_2) and ν (SiO) of CA V-NTS multilayers at each CA and EB process in nitrogen, helium and oxygen atmosphere.

The increment of absorption due to CH_2 group at the second CA cycle is larger than 1 and increased gradually with increasing cycle of CA process. This would mean that the thickness inclement of the film be increased with increasing number of the cycles, but this may not be the case. The gradual increase of the absorption increment may be come from the increase of molar extinction coefficient due to gradual increase of the tilt angle of the hydrocarbon chain.
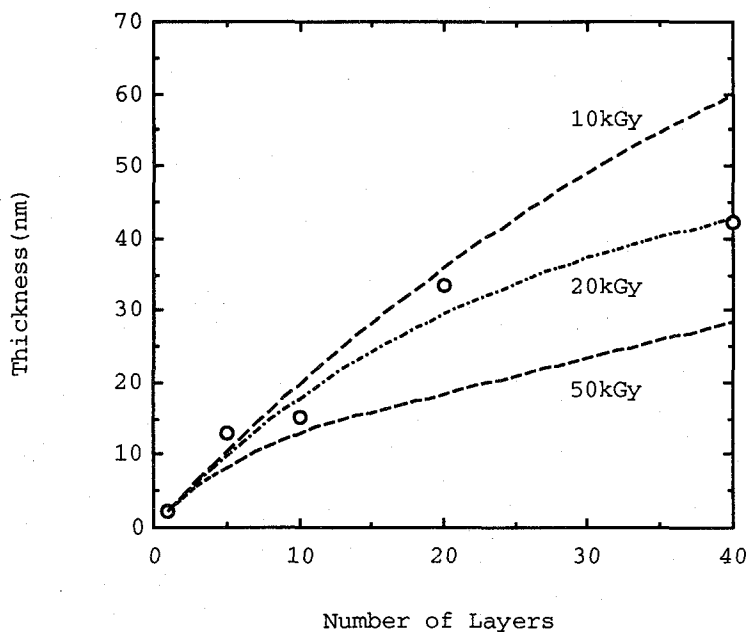

Figure 3. Changes of the thickness (O) of the CA V-NTS multilayer prepared by CA process and EB irradiation process of 20 kGy and calculated thickness curve for the multilayers was obtained with the experimental values (50 kGy: $\alpha = 0.2$ and $\delta = 0.1$, 20 kGy: $\alpha = 0.08$ and $\delta = 0.04$ and 10 kGy: $\alpha = 0.04$ and $\delta = 0.02$ and) as a function of the number of layers.

　In order to decrease the amount of radiation damage on the film substance during EB cycle, the dose was decreased to 20 kGy and the building-up experiment was carried out up to 40 cycles, and the result is shown in Figure 3. The increase of the film thickness at the 5th CA process increased, as expected, up to 13 nm from 8.8 nm which had been obtained by the process carried out with 50 kGy EB cycle.

　However, as shown in Figure 3, results obtained by extended cycles of process up to 40 indicated that radiation-induced decomposition in the inner layers should be taken into consideration in addition to the decomposition of the surface layer. This idea that the radiation-induced decomposition occurred in the inner layers (protected by the surface layer from being exposed to atmosphere containing oxygen) in smaller degree compared to that on the surface layer was proposed from preliminary results (shown in Figure 4) that a monomolecular layer decomposed sensitively as the dose increased and disappeared at 200kGy, while an LB film of 25 layers decomposed similarly to the monolayer at first 200 kGy, and then decomposed gradually with dose[9].
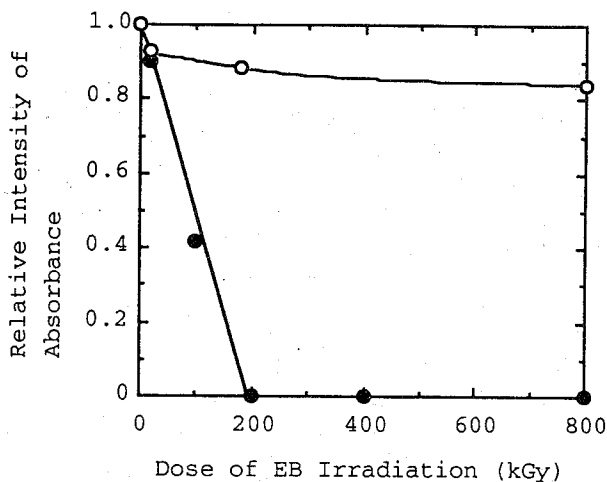

Figure 4. Changes of IR absorption intensities of ν as (CH_2) of CA V-NTS monolayer (●) and ADA LB film (○) of 25 layers as a function of the EB irradiation dose on the basis of the adsorption intensities before EB irradiation.

If we take a fraction that is decomposed in the surface layer is α, and that in the inner layers is δ, by one cycle of EB process, total thickness of the CA multilayer is expressed by:

$$D = T + \sum_{k=1}^{n-1} T (1 - \alpha)(1 - \delta)^k \qquad (1)$$

where n is number of cycles, T is a thickness of one V-NTS film.

The factor α is estimated as 0.08 from the corresponding value of 0.2 for EB dose of 50 kGy. The curve calculated using these parameter agrees well with the observed points as shown in Figure 4. These values give also a good fit to experimental results in Figure 1 in which the calculated curve obtained for parameters for 50 kGy, which are 0.2 and 0.1, respectively.

Results for CA multilayers obtained in Helium and oxygen atmosphere

Calculated curve for CA multilayer prepared in helium atmosphere using parameters α, δ ($\alpha = 0.538$ and $\delta = 0.059$), which are estimated from IR data (see Figure 5) is also shown in Figure 1, where satisfactory fit with the experimental film thickness was shown. Increment of thickness at CA cycle estimated from the increment of IR absorption was roughly 0.5 normalized to the absorption of SiO at the first CA cycle as shown in Table 1. The smaller value compared to the data obtained in the other gaseous atmospheres may be resulted from that the amount of functional groups formed during EB cycle is small due to the low concentration of oxygen contained as impurity in the atmosphere.
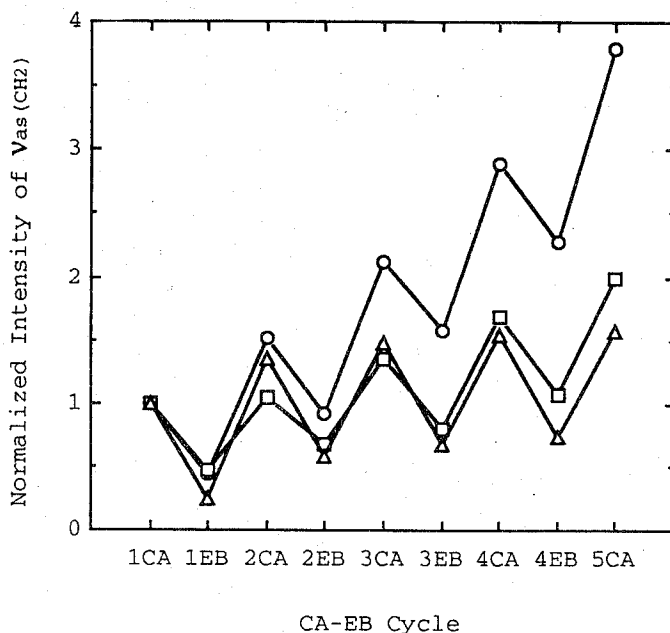

Figure 5. Changes of IR absorption intensities of ν as (CH_2) of CA V-NTS multilayers prepared with CA process and EB irradiation process of 50 kGy in nitrogen (◯), helium (▢) and oxygen (△) atmosphere.

However, for CA multilayer prepared in oxygen atmosphere, it was further necessary that the film thickness of the nth layer should satisfy the following requirements:

$$T (1 - \alpha)(1 - \delta)^n \rangle \varepsilon \tag{2}$$

where it means that the film thickness of one layer after irradiation of extremely large radiation dose will not decrease less than certain limit ε, which is a thickness of the film composed of SiO and carbon which will not undergo further decomposition by excessive irradiation. Satisfactory agreement between the calculated and the experimental data was obtained for $\alpha = 0.754$ and $\delta = 0.666$, which was estimated form IR data, and assuming value of $\varepsilon = 0.5$ nm. The value assumed for ε may be suitable for the thickness of skeletonized film composed of remaining carbon and silicon oxide. The extremely large value $\delta = 0.666$ is not surprising when one considers strong oxidizing effect of oxygen atmosphere during EB cycle.

Increment of thickness at CA cycle estimated from the increment of IR absorption was roughly 1 normalized to the absorption of SiO at the first CA cycle as shown in Table 1. The value is almost the same as that obtained in nitrogen atmospheres, indicating that the amount of functional groups formed during EB cycle is the same to that formed during EB cycle in nitrogen atmosphere.

The fact that the parameters estimated from IR data gave good fits to the experimental data may indicate that the hydrocarbon chain is not well oriented so that the absorption coefficient to polarized light is averaged out. Difference between bond angle of $(CH_2)_n$-C-N-Si and that of $(CH_2)_n$-C-O-Si may be responsible for the difference in build-up process in helium and oxygen atmospheres and in nitrogen atmosphere.

Predicted build-up curve for different build-up conditions

Predicted build-up curves obtained for 10 and 50 kGy at EB process are shown in Figure 1, where more linear build-up is expected by reducing the dose at EB process. However, decrease in the dose also may result in surface concentration of functional groups produced by the irradiation, which causes the decrease on the amount of surface material to be built-up on the subsequent CA cycles. Further experiment is necessary to obtain these parameters.

CONCLUSIONS

It is confirmed that the loss of film thickness by radiation-induced decomposition can not be excluded in the CA multilayer build-up process using electron beam. Thickness of the CA multilayer in which the properties of the layer is regarded as uniform for practical purpose depends on requirements for the practical use, dose on EB cycle, energy efficiency to produce functional groups on th surface layer and to decompose film substance, and concentration of active gases. On the contrary, this technique has possibility to manufacture thin film with gradual change of properties toward depth direction.

Development of more refined technique to prepare multilayer structure in molecular dimension is desirable to establish molecular device, and theory and technique to reveal oriented structure of thin layer by extensive use of polarized infrared spectroscopy developed

by Prof. Takenaka and his group will have important role in this field by more quantitative application of the theory and technique to our system.

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