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Glow Discharge Polymerization of Tetramethylgermanium in Capacitive Coupling System at 20 kHz Frequency

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SUMMARY

Germanium-containing polymers were formed from tetramethylgermanium by glow discharge polymerization at 20 kHz frequency. The formed polymers that were filmy or powdery depending on operational conditions were mixtures of polymers consisting of CH_3, CH_2, $Ge\text{-}CH_3$, Ge-O-C and Ge-O-Ge groups, and germanium metal. Most Ge species present at the outermost layers of the films were oxided, and the Ge species at the inner layers existed still as Ge metal. There was no significant discrepancy in chemical structure between polymers formed at 20 kHz and at 13.56 MHz discharge frequency.

INTRODUCTION

Glow discharge polymerization is an unique polymer-forming process. Appearance and chemical structure of the polymers formed by this technique varry frequently by changing system factors such as the mode of electric discharge, the position of a monomer inlet, etc. as well as operational conditions to sustain glow discharge (YASUDA 1981). The mode of electric discharge of these factors, especially discharge frequency, is important because the discharge frequency number determines the mode of coupling, i. e., capacitive or inductive coupling (YASUDA 1981). When used the internal electrodes for the capacitive coupling reactions at the electrode surfaces participated in some monomer system, and the polymers formed were altered, compared with those formed in an inductive coupling system with no surface reactions (KAY 1979).

In this study glow discharge polymerization of tetramethylgermanium (TMG) is performed in a capacitive coupling system at 20 kHz discharge frequency with internal electrodes, and the polymers formed are examined by infrared spectroscopy and ESCA analysis to compare with the polymers prepared in discharge at 13.56 MHz frequency.

EXPERIMENTAL

TMG was purchased from Ventron Co., and used as a monomer without further purification.

The apparatus used for the glow discharge polymerization was a bell-jar-type chamber (400 mm diameter, 470 mm high) being the same as reported elsewhere (INAGAKI et al. submitted). The glow discharge was drived by a capacitive coupling of 20 kHz ultrasonic frequency (uf), and a magnetic enhancement was employed. The reaction system, firstly, was evacuated to approximately 0.013 Pa, and to eliminate water adsorbed on surfaces of the substrates, the surfaces were exposed to argon plasma for 20 min. The system, again, was evacuated to 0.013 Pa, and TMG gas adjusted at the fixed flow rate at the given pressure from 10 to 60 Pa was injected into the reaction chamber. The uf power was turned on, the glow discharge polymerization was continued at the constant current of the uf power for a suitable duration. The pressure changes in the system and the voltage level between the electrodes were continuously recorded through the polymerization process with a Pirani gauge and a digital multimeter, respectively.

The polymers deposited on a glass disk and scraped with a knife were provided for C, H, N and Ge analysis, and also for the preparation of KBr disks. The C, H and N content were determined using a CHN corder MT-2 (Yanagimoto Co.). The Ge content was determined from the basis that the residual product, when heated in oxygen atmosphere at 850°C until the residue reached to the constant weight, was assumed to be GeO_2. Infrared spectra were recorded with a Nihon Bunko spectrometer A-3.

The polymer films (approximately 0.1 μm thickness) deposited on silicon wafer (5 X 5 mm) were provided for the measurement of ESCA spectra. Before ESCA measurement a trace amount of Au was deposited on surfaces of the polymer films by vacuum deposition technique to calibrate the binding energy. The spectra were recorded with a Shimadzu electron spectrometer ESCA 750 employing Mg or Al $K_{\alpha 1,2}$ exciting radiation. The Au_{4f} core level at 84.0 eV was temporarily used for the calibration of the energy scale. The complex spectra were deconvoluted by use of a Shimadzu data system ESCAPAC 760. A Gaussian distribution was assumed, and resolved curves that were mostly fitted to the observed spectra were determined by variation of three parameters, i. e., the position and the hight of the peaks and the full width at half-maximum (FWHM). A FWHM value of all the resolved curves was less than 2 eV.

RESULTS

Colorless and transparent polymers were deposited from TMG by glow discharge polymerization at 20 kHz frequency. Appearance of these polymers depended strongly on the operational conditions: filmy polymers were formed only under the limited conditions such that the pressure in the reaction chamber was less than 26.6 Pa, the level of the uf current less than 50 mA, and the flow rate of TMG less than 8 cm^3(STP)/min; and under the other conditions powdery polymers were formed. The polymer deposition rate varried by changing the pressure in the reaction chamber as well as the flow rate of TMG rather than the level of the uf current. The rate increased linearly as raising the pressure in the reaction chamber and the TMG flow rate.

The polymers prepared from TMG were examined by elemental analysis. All the polymers consisted mainly of C, H and Ge atom with a small amount of N and O atom (TABLE 1).

TABLE 1. Elemental Composition of Polymers prepared from Tetramethylgermanium by Glow Discharge Polymerization

Mode of Discharge	Flow Rate of TMG cm^3(STP)/min	Pressure before Discharge Pa	Discharge Current mA	Empirical Formular of Polymers
Capacitive	3	13.3	35	$C_{2.00}H_{3.06}N_{0.15}O_{0.32}Ge$
Coupling	3	26.6	35	$C_{1.70}H_{3.00}N_{0.14}O_{0.29}Ge$
at 20 kHz	8	13.3	35	$C_{1.47}H_{2.85}N_{0.07}O_{0.21}Ge$
Inductive	0.2	4.0	25*	$C_{3.30}H_{7.19}N_{0.08}O_{0.10}Ge$
Coupling at 13.56 MHz	1.7	4.0	25*	$C_{2.33}H_{5.50}N_{0.01}O_{0.10}Ge$

*: Discharge power in wattage.

The source of such N and O atom which were never contained in TMG may be residual air still remaining in the reaction chamber and/or atmospheric air introduced into the chamber after performing the polymerization. The polymers formed, as seen in TABLE 1, were different in elemental composition from TMG, and were characterized to be fairly low content of carbon and hydrogen. This indicates that some of methyl groups in TMG were splitt off by exposing plasma to form polymers. The C and the H content in the polymers formed varried by changing the operational conditions, and there was a tendency that these contents were lessened by raising the flow rate of TMG and the pressure in the reaction chamber.

On infrared spectra of the polymers formed from TMG, although the spectra are not represented here for the sake of brief, there appeared absorptions at 3400 (OH), 2980, 2920 (CH_3, CH_2), 2050 (Ge-H), 1640 (absorbed water), 1450, 1410, 1370 (CH_3, CH_2), 1240 (Ge-CH_3), 1035 (Ge-O-C), 820 (Ge-CH_3, Ge-O-Ge), 770 (Ge-CH_3, Ge-O-Ge), 670 (Ge-O-C) and 590 cm^{-1} (Ge-C). The presence of Ge-Ge groups in the polymers formed, which will appear at 230 cm^{-1}, is not excluded because of the limination of the spectrometer used. Even if operational conditions such as the TMG flow rate, the uf current and the pressure in the reaction chamber varried there was no essential change on these spectra although the intensity of the absorptions due to CH_3 and CH_2 groups became weak by increasing the TMG flow rate and the uf current. These spectra indicate that the polymers formed from TMG are composed of CH_3, CH_2, Ge-CH_3, Ge-O-C and Ge-O-Ge groups.

ESCA spectra showed detailed chemical structures of the polymers. Fig. 1 shows the C_{1s} and the Ge_{2p} core level spectra of the polymers prepared from TMG at a TMG flow rate of 5 cm^3(STP)/min at an uf current of 35 mA and at a pressure of 17.3 Pa in the reaction chamber. The C_{1s} core level spectra observed were deconvoluted into three peaks centred at 283.4, 284.5 and 286.4 eV. The position and the relative peak area of the each are listed in TABLE 2. These peaks deconvoluted can be assign-

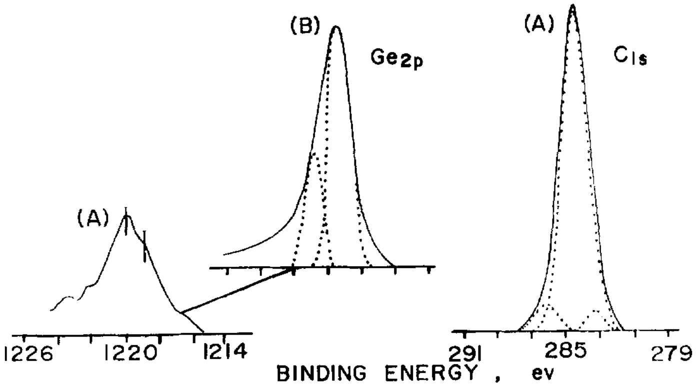

Fig. 1. ESCA (C_{1s} and Ge_{2p}) Spectra of Polymers prepared from TMG by Glow Discharge Polymerization, (A): Native, (B): Etched Surfaces.

TABLE 2. C_{1s} and Ge_{2p} Core Level Spectra of Polymers prepared from TMG by Glow Discharge Polymerization.

Mode of Discharge	Core level Spectra	Deconvoluted Component #1 centred at (eV)	Deconvoluted Component #2 centred at (eV)	Deconvoluted Component #3 centred at (eV)
Capacitive Coupling at 20 kHz	C_{1s}	283.4(7%)^{*1}	284.5(82%)	286.4(11%)
	Ge_{2p}		1218.8	1220
		1217.5(74%)^{*2}	1218.6(26%)	
Inductive Coupling at 13.56 MHz	C_{1s}	283.4(3%)	285.0(90%)	286.7(7%)
	Ge_{2p}		1218.8	1219.8
		1217.5(71%)^{*2}	1218.6(29%)	

*1: Relative peak area. *2: Etched by Ar plasma for 2 min.

ed to carbonized carbon; aliphatic carbon and C-Ge; and C-O groups in the order of increasing the binding energy (PERRY et al. 1972, MORGAN et al. 1973, DRAKE et al. 1975). The Ge_{2p} core level spectra, as seen in Fig. 1, showed a complex spectrum which had a peak.at 1220 eV with a sholder at 1218.8 eV. These can be assigned to GeO_2 and Ge-C groups (DRAKE et al. 1975). When this specimen was etched in vivo by argon plasma for 2 min using the equipment attached to the ESCA 760 spectrometer, the Ge_{2p} spectrum was altered, which was deconvoluted into two peaks centred at 1217.5 and 1218.6 eV. A thickness of the etched surface was approximately 100 Å. The two peaks can be assigned to Ge metal and Ge-C features. This indicates that the polymer films deposited have heterogeneous structures, that is, the outmost layers of the films (ca. less than 100 Å) is oxided, and the inner layers is still not oxided; and also that oxidation of the Ge species occured not during the polymerization process but after the polymerization. The existence of Ge metal in the films formed suggests that TMG was subjected to rupture of bonds between Ge and CH_3 groups in discharge to yield polymer films. This polymer-forming process is surely atomic polymerization proposed by Yasuda (YASUDA 1981).

DISCUSSION

Glow discharge polymerizations performed at 20 kHz in this study were compared with those at 13.56 MHz frequency, which have been reported in the previous paper (INAGAKI et al. submitted b). Influences of discharge frequency on glow discharge polymerizations should be searched using the identical reaction chamber because system factors such as a shape and a size of the reaction chamber might influence on glow discharge polymerizations. For the sake of practical difficults, however, the reaction chamber for operation at 20 kHz and at 13.56 MHz frequency were different each other. Discrepancies between the two glow discharge polymerizations, therefore, might result from the sum of alteration in discharge frequency and somewhat the system factors.

The elemental composition, as compared in TABLE 1, shows that the polymers prepared in discharge at 20 kHz frequency possess lower carbon and hydrogen content than those prepared at 13.56 MHz frequency. This indicates that the fragmentation of TMG occurs more vigorously to yield highly crosslinked polymers in the former system than in the latter system. This assumption can be recognized by the evidence that powdery polymers were easily formed at 20 kHz frequency, and that the formation of filmy polymers was limitted to under narrow operational conditions as described in the result part. On infrared and ESCA spectra, as seen in TABLE 2, there is no discrepancy between the two polymers.

Conclusively, glow discharge polymerizations of TMG at 20 kHz and at 13.56 MHz frequency yield the almost same polymers composing of chemical residues such as CH_3, CH_2, $Ge-CH_3$, Ge-O-C, Ge-O-Ge and Ge-Ge groups. An advantage of the bell-jar-type reaction system used in this study, compared with the tubular reaction system used in the previous study (INAGAKI et al. submitted b), is the uniformity in thickness of the films deposited. For example, the polymer deposition rate at a TMG flow rate of 5.0 cm^3(STP)/min was $0.35_7 \pm 0.005$ and $0.34_9 \pm 0.006$ $\mu g/cm^2 min$ at the right and the left side fo the disk surface, respectively. The rate at a TMG flow rate of 3.0 cm^3(STP)/min was $0.10_2 \pm 0.001$ and $0.10_4 \pm 0.001$ $\mu g/cm^2 min$. Such uniform polymer-coating is important for surface modification of materials such as membranes and optical lens of which physical properties are directly related to the thickness of the films coated.

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REFERENCES

1. DRAKE, J. E. and RIDDLE, C: Can. J. Chem., 53, 3602 (1975)
2. INAGAKI, N., CHEN, K. S. and OHNISHI, Y.: submitted to J. Appl. Polym. Sci.
3. INAGAKI, N. and MITSUUCHI, M.: submitted to J. Polym. Sci.
4. KAY, E. and DILKS, A.: J. Vac. Sci. Technol., 16, 428 (1979)
5. MORGAN, W. E. and Van WAZZER, J. R.: J. Phys. Chem., 77, 964 (1973)
6. PERRY, W. B. and JOLLY, W.: Chem. Phys. Lett., 17, 611 (1972)
7. YASUDA, H.: J. Polym. Sci., Macromol. Revs., 16, 199 (1981)

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