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Electrical Properties of Polymer Films Prepared from Mixture of Tetramethylsilane and Oxygen by Glow Discharge Polymerization

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SUMMARY

The electrical properties of polymer films prepared from tetramethylsilane (TMS) and the mixture of TMS and oxygen by glow discharge polymerization were investigated in connection with the chemical structure of the polymers.

The polymer films showed two different electrical properties which depended on the strength of electrical field. Under the electrical field of less than 10^4 V/cm, the polymers showed ohmic behaviour, and their resistivity was approximately 10^{14} $\Omega\cdot$cm being independent of the chemical structure of the polymers. Under the electrical field of above 10^4 V/cm, non-ohmic behaviour was observed, and the current increased exponentially with increasing of the applied field. To explain this enhanced current the contribution of the Poole-Frenkel emission was assumed. The dielectric breakdown of the polymer films (1000 - 5000 angstroms) occured at the electrical field as high as 3 MV/cm. This indicates that these thin films may be deposited on substrates without pinhole.

INTRODUCTION

Thin films prepared by glow discharge polymerization of organic or organometallic compounds have been taken interest in since this polymerization technique has unique advantages: the chemical composition of the formed polymers can be easily controlled by mixing of two different monomers; the formed polymers are deposited as thin, highly-crosslinked films; the thickness of the deposited films can be also controlled by changing the operational conditions (Yasuda. 1981).

Our previous investigation showed that alterations in the chemical composition of the polymers prepared from TMS were accomplished by mixing of inorganic gases such as argon, nitrogen, oxygen and tetrafluoromethane (Chen, et al. 1981). Further, this alteration reflected some physical properties including surface energy, surface hardness and thermostability. Especially in the system of the TMS/O_2 mixture the chemical structure of the formed polymers strongly depended on the composition of the starting mixture. The siloxane-like polymers were formed when a little of oxygen was mixed with TMS, and the quartz-like polymers when much of oxygen was mixed were formed.

This study focusses on electrical properties of the polymer films prepared from the TMS/O_2 mixture in connection with

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alterations the chemical structure of the formed polymers.

EXPERIMENTAL

The apparatus and procedures for the preparation of the polymer films by glow discharge polymerization were basically the same as described elsewhere (Inagaki, et al. 1981). A tubular reactor (35 mm inner diameter, 400 mm long) was used, and the glow discharge was drived by an inductive coupling of r.f. power (13.56 MHz) with the coil placed out of the reactor. The polymerization was performed under following operational conditions: the r.f. power, 25 W; the pressure in the reaction chamber before discharge, 5.3 Pa (4.0×10^{-2} Torr); the flow rate of the monomer gas, 0.264 cm^3(STP)/min. These conditions are the same as used previously (Chen, et al. 1981).

Two special specimens were provided for the measurement of electrical resistivity. For the measurement of the surface resistivity, the polymer films were deposited on the quartz plates (13 X 20 X 2 mm), and then on these films a pair of parallel electrodes which were 2 mm apart from each other was fastened by the vacuum evaporation coating of aluminum, silver or gold. For the measurement of the volume resistivities the specimens having sandwich structure were prepared. An electrode of aluminum, silver or gold was deposited on the quartz plates by the vacuum evaporation, the polymer films were successively deposited on the quartz plates by the glow discharge polymerization, and then the upper electrode of aluminum, silver or gold was fastened deposited on the polymer films by the vacuum evaporation. The specimens, therefore, were consist of the structure of quartz plate/metal electrode/polymer films/ metal electrode. The thickness of these deposited polymer films was in the range from 1000 to 6000 angstroms that was determined by interferometry.

These specimens were placed under vacuum (less than 1×10^{-3} Pa), and the current, when a suitable level of d.c. voltage was applied between the electrodes, was measured at temperatures from -80 to 95 °C using a pico-ammeter (Takeda Riken TR 8641).

RESULTS AND DISCUSSION

The polymer films prepared from the mixture of TMS/O_2 by the glow discharge polymerization showed electrically different behaviours depending on a magnitude of applied d.c. voltages. Under the applied voltage of up to approximately 1×10^4 V/cm the polymer films showed ohmic behaviour. Under the applied field of more than approximately 1×10^4 V/cm the polymers showed non-ohmic behaviour. Accordingly, the electrical behaviours were discussed separately.

(a) I-V characteristics at the low-applied voltages

When the polymer films prepared from the TMS/O_2 mixture were placed in the field of d.c. voltage up to 10^4 V/cm, the observed current increased linearly with increasing the applied voltage. The slope of the plot of current vs. voltage means resistivities of the polymers. The results are listed in Table I as a function of the composition of the TMS/O_2 mixture.

Table I
Surface and volume resistivities of the polymer films formed from TMS/O_2 mixture by glow discharge polymerization

TMS/O2 ratio	Empirical formula of polymers	Resistivity	
		Surface(Ω/sq)	Volume(Ω·cm)
1/0	$C_{3.7}H_{8.2}N_{0.2}O_{1.1}Si$	1.8×10^{14}	2.5×10^{14}
3/1	$C_{2.8}H_{5.9}N_{0.3}O_{1.6}Si$	2.1×10^{14}	5.4×10^{14}
3/2	$C_{1.1}H_{2.5}N_{0.2}O_{2.2}Si$	3.2×10^{14}	8.8×10^{14}
1/1	$C_{0.4}H_{0.8}N_{0.1}O_{1.8}Si$	2.4×10^{14}	1.9×10^{15}
1/1.8		1.4×10^{13}	7.1×10^{14}

The chemical composition of the polymers formed from the TMS/O_2 mixture, as described in the previous paper, was altered by the ratio of the TMS/O_2 mixture (Chen, et al. 1981). With increasing of the concentration of oxygen in the mixture, the quantities of CH_2 and CH_3 groups in the formed polymers decreased and became rich in Si-O-Si groups.

The surface resistivities of the polymers from the TMS/O_2 mixture were in the order of 10^{14} Ω/sq. There was no remarkable change in the resistivities even when the polymers composition was altered. However, the volume resistivity showed the tendency of slight increase with increasing the concentration of oxygen in the mixture. This volume resistivity is comparable to that of silicon oil and polysiloxanes and is slightly lower than that of quartz (10^{14} - 10^{17} Ω·cm)(Mark, et al. 1966).

(b) I-V characteristics at the high-applied voltages

When the applied d.c. field was increased from 10^4 to 10^6 V/cm, the observed currents increased exponentially with the applied voltages as shown in Figure 1. This surprisingly high electrical conduction for the thin films may be due to either of the tunneling current, the space-charge-limited current, the Schottky emission and the Poole-Frenkel emission current (Gregor. 1968). If the current was controlled by the Schottky or the Poole-Frenkel emission the current can be expressed by the following equations (Lamb. 1967).

$$J = A\, T^2 \exp[(\beta_s E^{1/2} - \Phi)/kT] \qquad (1)$$

for the Schottky emission,

$$J = A\, E \exp[(\beta_{pf} E^{1/2} - \Phi)/kT] \qquad (2)$$

for the Poole-Frenkel emission, where J: current density, A: constant, T: temperature (°K), $\beta_s = (e^3/4\pi\varepsilon\varepsilon_0)^{1/2}$, E: applied field, Φ: activation energy for conduction, k: Boltzmann constant, $\beta_{pf} = (e^3/\pi\varepsilon\varepsilon_0)^{1/2} = 2\beta_s$, ε: dielectric constant of the polymer film, ε_0: permittivity of free space. Consequently,

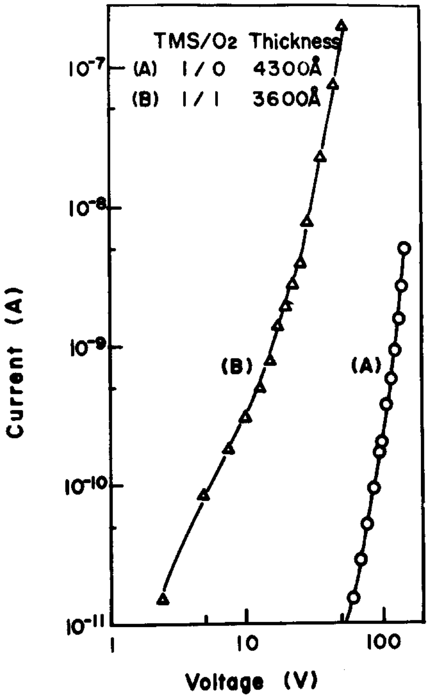

Fig. 1: I-V characteristic of polymer films formed from TMS/O_2 mixtures by glow discharge polymerization

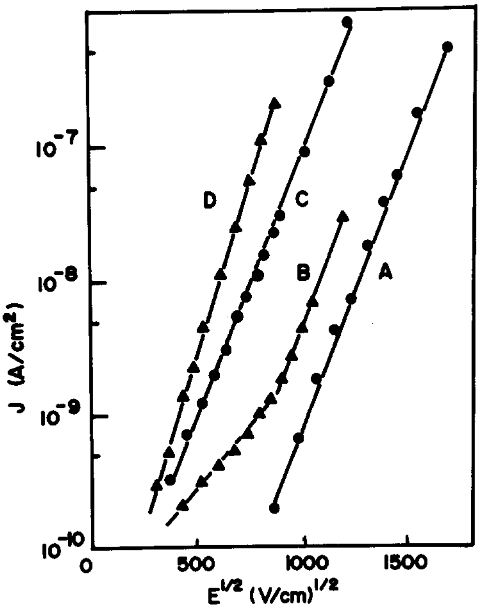

Fig. 2: Schottky plot for polymer films formed from TMS/O_2 mixtures by glow discharge polymerization: A, TMS/O_2 = 1/0; B, 3/1; C, 1/1; D, 1/2.6

the log (current) should be proportion to $E^{1/2}$ for the two conduction mechanisms.

All the polymer films prepared from the TMS/O_2 mixture, as seen in Figure 2, showed the relationship of log (J) - $E^{1/2}$, indicating that the current was controlled by either of the Schottky or the Poole-Frenkel emission. Instead of the symmetrical electrodes, the asymmetrical electrodes, i.e., Au/ polymer films/Al and Ag/polymer films/Al, were used, but there was no influence on the conductive characteristics. The apparent activation energy for the conduction from -20 to 90 °C was determined to be approximately 0.9 eV. This value was fairly lower than half of the optical gap (approximately 4 eV) of the polymer films. From these results it can be speculated that such conduction may be controlled by the Poole-Frenkel emission.

When the electrical field above 10^6 V/cm was applied the current was suddenly stopped, and the structure of the metal electrode/polymer films/metal electrode was broken down by arcing between the electrodes. The strength of the electrical field in which the dielectric breakdown was triggered increased linearly with the thickness of the polymer films, and the strength was estimated to be 3.1 MV/cm and 2.8 MV/cm for the polymer films prepared from TMS and the TMS/O_2 mixture (1/1 mixing ratio), respectively. These magnitudes of the electrical field at which the dielectric breakdown initiated are comparable to that of quartz (4 - 7 MV/cm). This high resistance against the dielectric breakdown is a remarkable feature of the polymer films prepared by the glow discharge polimerization. The glow discharge polymerization technique can yield polymers as a film without pinhole. These experimental evidences suggest a capability that these polymer films may be an excellent insulator. However, prior to application of these polymer films as an insulator dielectric loss should be examined.

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