Polymer Bulletin 11, 541–544 (1984)

Polymer Bulletin
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Films

Moisture Sensor Device of Plasma-Films Doped with Methylbromide

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SUMMARY

Films plasma-polymerized from the tetramethylsilane/ammonia gas mixture were sensitive in electrical resistance to moisture. A linear relationship between the logarithm of the electrical resistance and the relative humidity was observed. This susceptibility in the electrical resistance to moisture was improved by doping of methylbromide. This improvements by the doping treatment may be as results of quaternization of amino groups and of hydrolysis of methylbromide. The improved device could detect relative humidity from 20 to 90 % where the electrical resistance varied from 10^7 to 10^4 Ω. The response time was less than twenty-five seconds, and the hysteresis in cyclic changing of the relative humidity was negligible.

INTRODUCTION

In plasma-polymerization the starting materials introduced into plasma are subjected more or less to fragmentation to form polymers. Therefore, when two different materials were simultaneously introduced into plasma formed polymers are mixtures of these ingredients. In plasma-polymerization of tetramethylsilane/ammonia gas (TMS/NH_3) mixture polymers containing nitrogen as well as silicon elements were formed, and the concentration of the nitrogen residues could be controlled by mixing ratio of TMS and NH_3 (INAGAKI a 1983). The surface properties of these polymers varied from hydrophobic to hydrophilic depending on the nitrogen concentration. Such hydrophilic surfaces became sensitive to moisture, and the electrical resistance decreased with increase in the relative humidity (INAGAKI b 1983). This invesitgation focusses on practical application of the plasma-films prepared from the TMS/NH_3 mixture to a moisture sensor device. To improve the susceptibility to moisture doping of methylbromide is discussed.

EXPERIMENTAL

The apparatus made of Pyrex glass (35 mm i. d., 400 mm long) and the experimental procedures performed in this study for plasma-polymerization are the same as reported elsewhere (INAGAKI a 1983). The glow discharge was initiated at a pressure of 1.3 Pa at a constant rf power (13.56 MHz) of 25 W, and continued for a given duration. TMS (NMR grade) and NH_3 gas (99.99%) were purchased from Tokyo Kasei Kogyo Co., and

Matheson, respectively.

Plasma-polymerized films were doped with methylbromide vapor in an autoclave at 70°C at 2 x 10^5 Pa for 48 h.

On a glass plate on which a pair of comb electrodes of InO_2 (0.3 μm thick) had been already fasted by vacuum evaporation technique plasma-polymerized polymers deposited, which was used as a moisture sensor device. The dimension of the comb was 70 μm wide, 20 mm long, and 130 μm separate between two combs; and a number of the comb was 100. The device was connected with a resistor of 100 kΩ in series, and a field of 20 V at 120 Hz was applied. From the potential between both ends of the resistor the electrical resistance of the device was estimate as a function of the relative humidity. The film thickness was determined by interferometry.

Infrared and ESCA (N_{1s}) spectra for the plasma-films were recorded with a Nihon Bunko spectrometer A-3 and a Shimadzu electronmeter ESCA 750, respectively.

RESULTS AND DISCUSSION

The electrical resistance of plasma-films prepared from the TMS/NH_3 mixture, as shown in Fig. 1, was functions of the composition of the mixture as well as the relative humidity. The electrical resistance decreased with increasing the NH_3 concentration in the mixture. A previous investigation by infrared spectroscopy and ESCA pointed out that such decreases in electrical resistance were due to incorporation of nitrogen groups into the plasma-films (INAGAKI a 1983). For all the plasma-films prepared from the TMS/NH_3 mixtures a logarithm of the electrical resistance decreased linearly with increasing the relative humidity. Especially, the plasma-films from the TMS/NH_3 mixture of a 1/2 molar ratio showed electrical resistance of less than 10^8 Ω at fairly low relative humidities (1.8 x 10^7 Ω at 30 RH%) and wide response ranges of the relative humidity from 30 to 90 %, which indicates an availability of the plasma-films for moisture sensor devices.

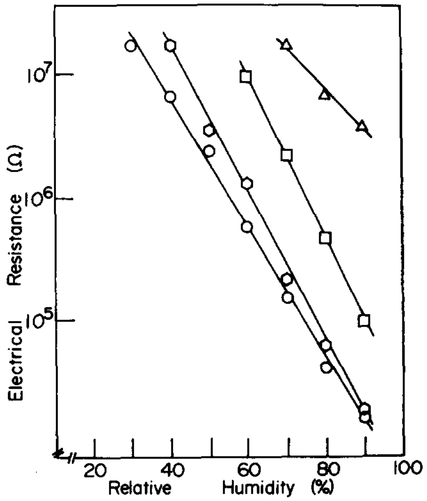

Fig. 1 Electrical Resistance of Plasma-films prepared from TMS/NH_3 Mixture of 1/0 (△), 2/1 (□), 1/1 (⬡), and 1/2 (○) molar ratio as a function of Relative Humidity.

Altermations in chemical composition and physical properties of formed polymers by changing operating conditions are frequently observed in plasma-polymerization even if identical starting material was used (INAGAKI c 1983).

This alternations is considered to be related to how the starting materials interacted with electrons generated by discharge. The energy level of electrons may be a key to determine the interactions with the starting materials, and changing operating conditions such as the rf power, the monomer flow rate, etc. would shift the energy level of electrons (YANAGIHARA 1982). A W/FM parameter, where W, F, and M are the rf input power, the flow rate and the molecular weight of the monomers, respectively, is frequently used to summarize effects of these operating conditions (YASUDA 1981). This parameter means an apparent input power per mass of the monomers, and is semi-quantitatively related to the energy level of electrons. Fig. 2 shows typical influences of the W/FM values on the electrical resistance of the formed polymers. The operation at a higher W/FM value of 1800 MJ/kg rather than at that of 550 MJ/kg was favourable to form polymers with low electrical resistance and high sensitivity of the electrical resistance in changing the relative humidity.

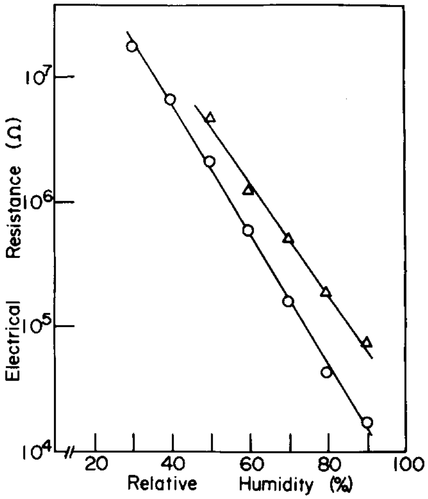

Fig. 2 Electrical Resistance of Plasma-films prepared from the TMS/NH_3 Mixture (1/2 molar ratio) at W/FM Values of 550 (△) and 1800 MJ/kg (○) as a Function of Relative Humidity.

To improve the moisture sensitivity these films were doped with methylbromide. Effects of the doping treatment is illustrated in Fig. 3. The doping treatment made the electrical resistance for the polymers prepared from the TMS/NH_3 mixture of a 1/2 molar ratio at a W/FM value of 1800 MJ/kg one order less and also the ranges respondent to moisture changes wide. For such moisture sensor devices there was almost linear relationship between the logarithm of the electrical resistance and the relative humidity from 20 to 90 %. Such increased sensitivity may be due to the formation of quaternary nitrogen groups which is as results of interactions of methylbromide with nitrogen residues such as amino groups. Actually the infrared spectra for the doped polymers showed new but not strong absorptions at 3190 and 1400 cm^{-1} which can be assigned to CH streching and deformation in N^+-CH_3 groups, respectively, and the ESCA (N_{1s}) spectra showed N^+ features at 401.9 eV. However, similar improvements of the moisture sensitivity by the methylbromide-doping treatment could be observed for the polymer films prepared from TMS which never contain nitrogen residues (Fig. 3), indicating contribution of H^+ and/or Br^- ions which were products in hydrolysis of methylbromide with water.

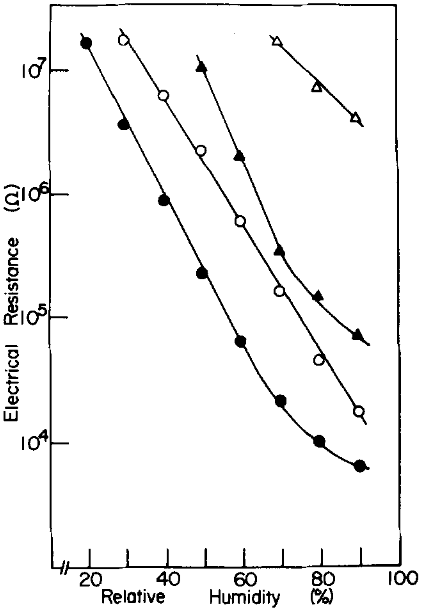

Fig. 3 Electrical resistance of Plasma-films prepared from TMS (△ , ▲) or TMS/NH_3 (1/2 molar ratio) (○ , ●) as a Function of Relative Humidity, △ and ○ undoped, and ▲ and ● doped with CH_3Br.

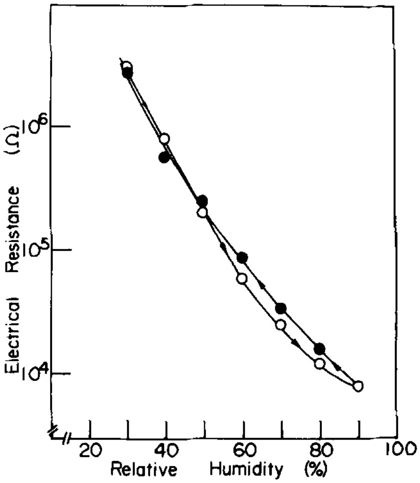

Fig. 4 Hysteresis of the Electrical Resistance for Plasma-films from TMS/NH_3 91/2) Mixture doped with CH_3Br.

Finally, the hysteresis of the electrical resistance, when the relative humidity changed cyclically from 20 to 90 %, was examined. Fig. 4 shows negligible hysteresis for the moisture sensor devices composed of plasma-films doped with methylbromide. The response time depended on the thickness of the plasma-films. For 0.82 µm thick the response time was less than twenty-five seconds.

ACKNOWLEDGMENT

The authors acknowledge Professor T. Yamamoto and Mr. H. Shimizu, Research Institute of Electronics, Shizuoka University, for advice on the measurements of electrical resistance; and also Dr. M. Niinomi and Mr. K. Yanagihara, Tokyo Research Laboratoty, Japan Synthetic Rubber Co. Ltd., for assistance of ESCA measurements.

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Accepted April 2, 1984