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Plasma Polymerization in Mixture System of Tetramethyltin and Ammonia Gas

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SUMMARY

Plasma polymerization in a mixture system of tetramethyltin (TMT) and ammonia (NH_3) gas was investigated by elemental analysis, IR spectroscopy, and ESCA in comparison with that in a mixture system of tetramethylsilane (TMS) and NH_3 gas. NH_3 gas contributed to the formation of polymers containing much tin, less carbon and hydrogen, and negligible nitrogen element. IR and ESCA spectra showed acceleration in dehydrogenation and /or dealkylation of carbon chains and in oxidation of tin element by NH_3 gas. While, plasma polymerization in the TMS/NH_3 mixture system showed incorporation of nitrogen residues as amido and amino groups as well as dehydrogenation and dealkylation. This descrepancy in chemical structure between polymerizations in the TMT/NH_3 and the TMS/NH_3 system might result from Sn-N bonds susceptible to moisture to form oxidized Sn.

INTRODUCTION

Plasma polymerization is an unique polymer-forming process which proceeds radically not in chain reactions but in stepwise reactions by repetition of the fragmentation of monomers and the recombination of activated fragments. Polymers plasma-polymerized, therefore, contain essentially all the elements present in a plasma, for example in plasma polymerization in the mixture system of tetramethylsilane (TMS) and nitrogen gas, or TMS and ammonia gas(CHEN 1981, INAGAKI et al. 1983a, b).

Sn and Si element lie directly below carbon in the Periodic Table. The structure and reactivity of organometallics containing these elements are similar to those of the corresponding carbons (NEGISHI 1980). The Sn-C bonds, although weaker in bond energy than Si-C and C-C bonds, does not react in chemistry with free radicals. In this sense plasma polymerization in the mixture system of TMT and NH_3 gas was compared with that in the mixture system of TMS and NH_3 gas.

EXPERIMENTAL

Plasma polymerization was carried out using capacitive coupling of 20 kHz audio frequency. The details of this reaction system and experimental procedures for the polymerization have been reported previously (INAGAKI et al. 1983c). TMT and NH_3 gas as monomers were obtained from Ventron Co. and Matheson respectively.

The C, H, and N contents of the polymers were determined using a Yanagimoto CHN corder MT-2. The Sn and Si contents were determined on the basis that the residual products, when heated in oxygen atmosphere at 850°C until the residues reached a constant weight, were assumed to be SnO_2 and SiO_2, respectively.

IR and ESCA spectra for the polymer films were recorded with a Nihon Bunko spectrometer A-3 and a Shimadzu electronmeter ESCA 750. The complex C_{1s} and Sn_{3d} spectra were resolved on the basis of the assumption of a gaussian distribution using a Shimadzu data system ESCAPAC 760.

RESULTS AND DISCUSSION

Preliminary experiments showed that plasma-polymerized polymers varied in their apparance from filmy to powder-like by changing operating conditions. Filmy polymers could be formed under narrowly limited operating conditions which were TMT flow rates of less than 6 cm^3(STP)/min, af current of less than 35 mA, and pressures of less than 20 Pa. All the plasma polymerizations in this study, thus, were carried out at a TMT flow rate of 4 cm^3(STP)/min, an af current of 28 mA, and a pressure of 16 Pa.

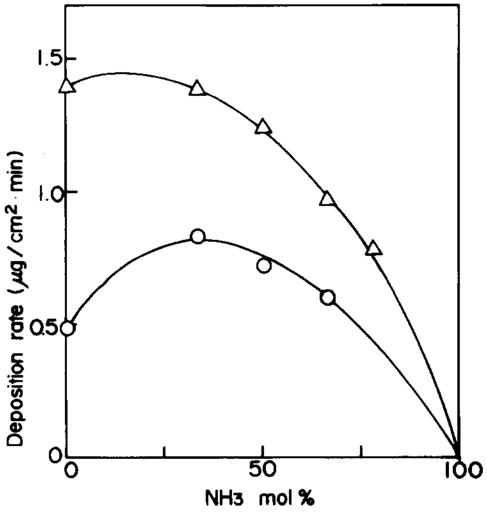

Fig. 1 Polymer deposition rate in plasma polymerization in TMT/NH$_3$ and TMS/NH$_3$ mixture system as a function of NH$_3$ concentration; △, TMT/NH$_3$; ○, TMS/NH$_3$.

Polymer deposition rate

Plasma polymerization in TMT/NH$_3$ mixture system yielded colorless, transparent filmy polymers. Figure 1 shows the polymer deposition rate as a function of the NH$_3$ concentration in the TMT/NH$_3$ mixture. The polymer deposition rate increased as increasing the NH$_3$ concentration, maximized at ca. 30 mol%, and then decreased. If NH$_3$ gas mixed with TMT played only as a diluent the polymer deposition rate should decrease linearly as increasing the NH$_3$ concentration. This acceleration in the polymer deposition rate by mixing NH$_3$ gas indicates some interaction between TMT and NH$_3$ gas in a discharge state. Such acceleration has been also observed in the TMS/NH$_3$ mixture system as shown in Figure 1 (INAGAKI et al. 1983b).

Elemental composition of the formed polymers

TABLE 1 shows elemental composition of the polymers prepared from the TMT/NH$_3$ mixture. The incorporation of oxygen element into the polymers formed is not to be surprised because polymers plasma-polymerized contain always more and less oxygen element. The elemental composition of the polymers formed, as shown in TABLE 1, varied significantly by mixing NH$_3$ gas. The carbon and hydrogen contents decreased with in-

TABLE 1. Elemental composition of polymers prepared from TMT/NH_3 and TMS/NH_3 mixtures

Mixture system	NH_3 concentration	Empirical formula of polymers
TMT/NH_3	0 mol%	$C_{3.5}H_{7.4}N_{0.1}O_{3.4}Sn$
	33	$C_{2.5}H_{6.3}N_{0.1}O_{2.5}Sn$
	50	$C_{2.5}H_{5.8}N_{0.2}O_{3.0}Sn$
	67	$C_{2.1}H_{4.8}N_{0.2}O_{2.6}Sn$
TMS/NH_3	0	$C_{3.1}H_{6.2}N_{0.1}O_{0.4}Si$
	33	$C_{2.9}H_{6.8}N_{0.9}O_{0.4}Si$
	50	$C_{2.1}H_{5.6}N_{0.9}O_{0.5}Si$
	67	$C_{1.6}H_{4.2}N_{1.1}O_{0.5}Si$

creasing the NH_3 concentration in the mixture. Surprisingly, the polymers had negligible nitrogen even when the NH_3 concentration reached at 67 mol %. We believe that molecules introduced into a discharge state are subjected to fragmentation to give activated fragments and then, these fragments recombine to give large molecules. Therefore, polymer formation in plasma polymerization would proceed by the stepwise repetition of the fragmentation and the recombination. Plasma polymerization in the TMS/NH_3 mixture system is a good example, and yields nitrogen-containing polymers (TABLE 1). The amount of nitrogen element incorporated into the silicon polymers depends on the starting composition of the mixture. Such dependence of polymers plasma-polymerized in elemental composition on starting gas composition has been frequently observed in some other systems (CHEN et al. 1981, INAGAKI et al. 1982a, b). In this sense plasma polymerization in the TMT /NH_3 system is a special case, and this singularity may be due to the nature of tin compounds.

IR and ESCA spectra of the formed polymers

On the spectra of the polymers from TMT strong absorptions appeared at 3400 (OH), 2970 (CH_3), 2920 (CH_2), 1620 (C=C), 1450 1370 (CH_3, CH_2), 1180 (Sn-CH_3), 1110, 1060 (Sn-O-C), 760 (Sn-O-Sn), 570 (Sn-O), and 520 cm^{-1} (Sn-C), which indicate that these polymers consist of CH_3, CH_2, Sn-CH_3, Sn-O-C, Sn-O-Sn, and Sn-OH groups. The polymers from the TMT/NH_3 mixture showed IR spectra different from the former, and variable with the NH_3 concentration in the TMT/NH_3 mixture. The polymers formed from a TMT/NH_3 mixture of 1/2 molar ratio showed weak absorptions at 2970, 2920, 1450, 1370, and 1180 cm^{-1} which are related to CH_3, CH_2, and Sn-CH_3 groups, and intense absorptions at 3400 and 770 cm^{-1}. And no absorptions due to Sn-O-C groups at 1110 and 1060 cm^{-1} and a new absorption at 840 cm^{-1} appeared. This new absorption assigned as Sn-N groups disappeared when stored in air for 0.5 - 1 h. No absorption related to nitrogen residues except the Sn-N groups could be observed although NH_3 gas of 33 mol% was introduced into plasma. For the polymers from the TMT/NH_3 mixture containing concentrated NH_3 gas (67 mol%) the absorptions related to CH_3, CH_2, and Sn-CH_3 groups became less intense and the absorptions due to Sn-O-Sn groups became more intense.

The Sn3d core level spectra, which are not represented here for the sake of brevity, had a main peak at 486.7 - 487.0 for $Sn3d_{5/2}$ (Sn-O) and at 495.3 eV for $Sn3d_{3/2}$ (Sn-O), and a small peak at 484.9 - 485.1 eV (Sn-C). The relative peak area of the Sn-O feature increased from 84 to 96 % by addition of

NH_3 gas of 67 mol%. The C_{1s} core level spectra were composed of a main component due to aliphatic carbon groups at 285.0 eV and two small components due to carbonized carbon (at 283.9 eV) and C-O groups (at 286.8 - 287.0 eV). The main peak at 285.0 eV decreased from 95 to 83 % in relative peak area by addition of NH_3 gas and the carbonized carbon groups increased from 9 to 14 %. These ESCA spectra also indicate accelerated dehydrogenation and oxidation of Sn residues by NH_3 gas.

From these results investigated by IR and ESCA it is not doubt that NH_3 gas assists dehydrogenation and oxidation of TMT to yield polymers containing much Sn element but less nitrogen element. This assistance, especially less formation of nitrogen residues, is substantially different from that in the TMS/NH_3 mixture system. Plasma polymerization in the TMS/NH_3 mixture system, as listed in TABLE 1, yielded polymers containing much Si and nitrogen elements. These polymers showed strong absorptions at 3300 and 740 cm^{-1} due to NH groups in their IR spectra (INAGAKI et al. 1983b). Such difference between plasma polymerizations in the TMT/NH_3 and the TMS/NH_3 mixture system may be due to the chemical nature of Sn and Si atoms. Sn-N bonds are easier to rupture than Si-N bonds and to subject to hydrolysis (NEGISHI 1980).

$$\rightarrow Sn-N< \quad + \quad H_2O \longrightarrow \ >NH \quad + \quad \rightarrow SnOH \longrightarrow \ \rightarrow Sn-O-Sn\leftarrow$$

Since Sn-N bonds could be observed on IR spectra of the polymers prepared from the TMT/NH_3 mixture it can be assumed that accelerated oxidation of Sn element and less formation of nitrogen residues might result from the easy cleavage of Sn-N bonds by moisture.

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