ON THE STRUCTURE AND DIELECTRIC BEHAVIOR OF PLASMA POLYMERIZED TETRAFLUOROETHYLENE FILMS

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ABSTRACT

Plasma polymerized film using hydrogen as a carrier gas is more highly crosslinked than that polymerized using argon. The former shows higher tanδ than the latter. Heat treatment in vacuum decreases tanδ. Radicals are considered polyene type in the two kinds of films.

1. INTRODUCTION

Plasma polymerization is considered to be a good method to make flawless thin films, and is being studied widely with a view to applying it for electronic device industry. Because a conventionally polymerized film which has fluorine atoms in its structure generally shows good chemical and electrical properties, plasma polymerized thin films containing fluorine atoms were chosen as an object of our study.

2. EXPERIMENTAL

The apparatus shown in Fig. 1 was used for experiments. Argon or hydrogen gas was used as a carrier gas, which was introduced from the top of a bell-jar. The carrier gas was ionized to create a glow discharge by an RF power of 13.56 MHz supplied through a capacitive coupling. Polymerization was effected by introducing tetrafluoroethylene gas into the "tail-flame" of the glow discharge. The flow rates of argon and hydrogen were each adjusted to 13 ml/min, while that of tetrafluoroethylene was set to 8 ml/min. The pressure inside the
bell-jar was then about 53 Pa. The total polymerization period
was varied from 10 minutes to 1 hour. The substrates on which
the thin films were polymerized consisted of glass plates
(Corning 7059) for the thickness and dielectric measurements,
KBr crystals for IR measurements, cloven KBr crystal for ESR
measurements and aluminium foil for ESCA measurements.

3. RESULTS

From now on, the terms Cg-H$_2$ and
Cg-Ar are used to stand for the
experimental conditions in which
hydrogen and argon were used as
carrier gases, respectively.

The deposition rates of
plasma–polymerized films for Cg-H$_2$
and Cg-Ar are shown in Fig. 2 as a
function of the discharge power,
which can be explained as follows.
The rate of radical formation from
monomer molecules is closely
related to the electron
temperature in the plasma. If
only polymerization were
dominant, and ablation were
negligible, the deposition rate
would have a positive correlation
with the electron temperature,
which increases with increase in
the mean free path of electrons.
Because the mean free path of
electrons is longer in hydrogen
than in argon, the deposition rate
can be higher for Cg-H$_2$ than for
Cg-Ar.

However, ablation due to F radicals emitted from C$_2$F$_4$
molecules cannot be neglected in the actual polymerization
reaction. With Cg-H$_2$, emitted F radicals react with H,
creating HF, which is then discharged from the discharge
chamber. When the discharge power increases and more F
radicals are emitted than can react with H, ablation begins to
occur to a higher degree for Cg-H$_2$ than for Cg-Ar, because
electrons have higher temperatures for Cg-H$_2$. However, with
Cg-Ar, ablation takes place from a low discharge power,
although its degree is lower than with Cg-H$_2$. Thus the
deposition rates depend on the discharge power as shown in
Fig. 2.

The ESR spectra for both Cg-H$_2$ and Cg-Ar were symmetrical
singlet signals similar to those of polyenyl radicals, which
appear in polyethylene irradiated by $\gamma$-rays at high doses. (7)
Table I shows relative spin densities (R.S.D.) and maximum
slope widths ($\Delta H_{msl}$) obtained from ESR spectra. The R.S.D.
values are normalized by the spin densities observed with
virgin samples measured within 15 minutes after polymeri-
zation, during which the samples were kept in argon at
1.4x10$^6$ Pa except for a short period needed for handling. If
Table I. R.S.D. and ΔHmsl of PPTFE (100 W).

<table>
<thead>
<tr>
<th>Sample</th>
<th>R.S.D. Virgin</th>
<th>R.S.D. After H.T.</th>
<th>ΔHmsl(G) Virgin</th>
<th>ΔHmsl(G) After H.T.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cg-H₂</td>
<td>1.0</td>
<td>0.80</td>
<td>22.0</td>
<td>23.9</td>
</tr>
<tr>
<td>Cg-Ar</td>
<td>1.0</td>
<td>0.78</td>
<td>44.0</td>
<td>44.6</td>
</tr>
</tbody>
</table>

Hydrogen appears in the structure of PPTFE for Cg-H₂, radicals in this sample are considered to be similar to the following radical, which exists in plasma-polymerized vinyl fluoride:

-\(\text{CHF}^+\text{CH}-(\text{CH}=\text{CH})\text{n-CHF-}\). (2)

Considering that ΔHmsl of PPTFE for Cg-H₂ is 20–22 G and that of plasma-polymerized vinyl fluoride is 15.7 G, it can be assumed that radicals in PPTFE for Cg-H₂ contain F, which has a large coupling constant in conjugate double bonds. Radicals contained in PPTFE for Cg-Ar are assumed to be those of the polyene type, which contain no hydrogen. The reason for the bigger value of ΔHmsl for Cg-Ar is probably the large coupling constant of F and the abundance of low-molecular-weight molecules compared to PPTFE of Cg-H₂. Heat treatment in vacuum at 150°C for 1 hour decreases R.S.D. both for Cg-H₂ and for Cg-Ar, as shown in Table I. This is probably due to the progression of crosslinking and polymerization through the aid of residual free radicals.

Figure 3 shows ESCA C1s spectra of PPTFE. Each spectrum was deconvoluted into several component peaks using a mini-computer. Table II lists the heights of the component peaks divided by the maximum height of the spectrum. The value of F1s/C1s is lower in PPTFE for Cg-H₂ than for Cg-Ar. This indicates that PPTFE for Cg-H₂ is more highly crosslinked than that for Cg-Ar. The reason for the F1s/C1s value being greater than 2 for Cg-Ar is perhaps due to the creation of aluminum fluoride on the surface of the aluminum foil. (3)

Figure 4 shows the IR spectra of the PPTFE. The spectrum for Cg-H₂ has weak absorption at 2900 cm⁻¹ owing to C-H stretching. This confirms that hydrogen is captured in the structure of PPTFE for Cg-H₂, which agrees with the results of ESR measurement. The wide
Table II. ESCA results of PPTFE (100 W).

<table>
<thead>
<tr>
<th></th>
<th>*CF3-</th>
<th>-CF2-CF2-</th>
<th>-CF2-C-</th>
<th>-CF-C-</th>
<th>-CF-CF2-</th>
<th>-C-C-</th>
<th>F1s/C1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cg-H2</td>
<td>0.05</td>
<td>0.15</td>
<td>0.27</td>
<td></td>
<td>1.00</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Cg-Ar</td>
<td>0.05</td>
<td>0.46</td>
<td>0.73</td>
<td>0.86</td>
<td>0.05</td>
<td>2.2</td>
<td></td>
</tr>
</tbody>
</table>

absorption band at 1240 cm\(^{-1}\) that can be seen in the spectrum for Cg-Ar is considered to be C-F stretching. In PPTFE for Cg-H\(_2\), this absorption band moves toward lower wave number. It is said that C-F bonds scattered in the hydrocarbon chain usually show absorption at the lower side of the wave number.\(^{(6)}\) This may be the case in the present spectrum for Cg-H\(_2\). Furthermore, the wide absorption from 1600 cm\(^{-1}\) to 1800 cm\(^{-1}\) arises from the combined effect of the absorption at 1700 cm\(^{-1}\) due to C=O stretching and that at 1600 cm\(^{-1}\) due to C=C stretching.

Figure 5 shows the temperature dependence of the dielectric loss tangent (\(\tan\delta\)) of PPTFE, and Fig. 6 shows the frequency dependence. Heat treatment in vacuum at 150°C for 1 hour decreases the values of \(\tan\delta\) both for Cg-H\(_2\) and for Cg-Ar. This is ascribed to the decrease in the number of free radicals resulting from crosslinking during heat treatment.\(^{(5,6)}\) The PPTFE film for Cg-H\(_2\) has higher values of \(\tan\delta\) than that for Cg-Ar. The amount of free radicals in the polymerized film is considered to increase with the emission of F atoms during polymerization. Because electrons are assumed to have higher temperatures in the case of Cg-H\(_2\), PPTFE for Cg-H\(_2\) has more free radicals, which seems to be the reason for the higher \(\tan\delta\) value.
The PPTFE film for Cg-H$_2$ has a tanδ peak at about -80°C, which is now called $\gamma_p$ peak. The relation between the temperature $T$ at which $\gamma_p$ peak exists and its frequency $f_m$ is shown in Fig. 7 for three different discharge powers. Similar relation of $\gamma$ peak of a conventionally polymerized tetrafluoroethylene film is also shown in the same figure for comparison. (7) Assuming that $f_m$ and $T$ satisfy the relation,

$$f_m = A \exp\left(-\Delta H/RT\right),$$

the activation energy $\Delta H$ is calculated as shown in Table III.

The $\gamma_p$ peak of PPTFE seems to correspond to the $\gamma$ peak of conventional PTFE and be ascribable to motion of side chains. Carbonyl groups which appeared in Fig. 4 may cause it. The reason why the temperature of the $\gamma_p$ peak is lower than that of $\gamma$ peak is probably because the plasma polymerized film has more free volume inside the film. The $\gamma_p$ peak moves toward a higher temperature with increase in the discharge power. This is probably because the film becomes more highly crosslinked as the discharge power becomes bigger. On heat treatment, the $\gamma_p$ peak moves to a lower temperature and $\Delta H$ becomes smaller. This indicates that dipoles associated with the $\gamma_p$ peak are made more mobile by heat treatment. The free volume in which dipoles can rotate is thought to be created by the evaporation of molecules of smaller molecular weight. (6)

The increase in tanδ at high frequencies shown in Fig. 6(a) is thought to be attributable to the same absorption as the $\gamma_p$ peak. The increase at low frequencies can be attributed to motion of long molecular chains. Disappearance of the increase at low frequencies by heat treatment seems to
Table III. Activation energy of PPTFE for Cg-H₂ (kcal/mol).

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>ΔH before H.T.</th>
<th>ΔH after H.T.</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>10.7</td>
<td>5.2</td>
</tr>
<tr>
<td>100</td>
<td>15.2</td>
<td>8.6</td>
</tr>
<tr>
<td>150</td>
<td>16.5</td>
<td>10.7</td>
</tr>
</tbody>
</table>

Fig. 7. Reciprocal temperature dependence of log fm for PPTFE. White and black symbols are before and after heat treatment in vacuum, respectively. Solid line indicates the relation of conventionally polymerized tetrafluoroethylene [after Ref.(7)].

indicate that long molecular chains become immobile with the progression of crosslinking and polymerization. The absence of the γ peak in PPTFE for Cg-Ar in Figs. 5 and 6(b) is perhaps because the corresponding peak exists at an even lower temperature, since the degree of crosslinking is lower and the relaxation time is shorter than in PPTFE for Cg-H₂. The tan δ peak seen at about 0°C for samples before heat treatment is probably due to the effect of ice.

ACKNOWLEDGMENT

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REFERENCES