JOURNAL OF MATERIALS SCIENCE 12 (1977) 1411–1415

Time-dependent properties of organic thin films deposited by glow discharge

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Sample capacitors were constructed with dielectrics obtained from completely fluorinated carbons which were polymerized in a plasma glow discharge. The rate of degradation of the capacitor properties depends on the size of the monomer molecule selected, the discharge frequency used during the deposition of the film, the vacuum anneal immediately after deposition, the temperature, the applied electric field, and the air or vacuum environment during life tests. The diversity of the results is explained by plasma acitvation of the carbon–carbon bond in the monomers and the formation of the films from the radicals thus produced.

1. Introduction

Depositing thin films is of interest for various industrial applications. The methods of evaporation, sputtering, galvanic deposition, and pyrolyse are already used for many different products, but deposition of gases by stimulation from an electron beam, ultra violet light, or glow discharge are still under investigation. Of the latter three, the method of glow discharge seems to be the most promising one for early industrial application. There are numerous publications which cover the properties of films deposited in a glow discharge of organic gases [1–4], but none describes the properties of these films with respect to humidity. Obviously, such data is of importance when the films are used as dielectrics or for coating electronic elements. Some results of properties dependent on moisture are reported in this paper.

2. Preparation of samples

The apparatus for depositing the polymer films was similar to the one described in [5]. The insulating probe substrate had been evaporated with an aluminium electrode and was placed on one of the discharge electrodes. Then the apparatus was closed, evacuated with an oil diffusion pump, flushed with the monomer gas, evacuated again, and then kept under a pressure of 200 N m^{-2} during the deposition process. The two electrodes were connected to the current generator, which operated at 0.17 to 10 MHz, the discharge current density being 0.2 A m^{-2}. Unfortunately, it was not possible in this apparatus to evaporate the other aluminium electrode on the samples, so they were kept in vacuum and transferred to the evaporation chamber just before the metallization process. The electric properties of the capacitors as produced were measured under different environmental conditions described below.

To limit the scope of the investigation only completely fluorinated carbons were selected as monomers, which, because of their similar molecular structure to tetrafluoroethylene, were expected to form polymer films with dielectric properties comparable with polytetrafluoroethylene (teflon).

Samples in a range of 0.02 to 3 μm thickness and 0.1 to 10 cm^2 area were investigated, but most samples were typically 0.3 μm thick and 0.5 cm^2 large.

3. Results

The films obtained from the materials listed in Table I were yellow, unperforated, withstood an electric field of 300 V (μm)$^{-1}$, sublimed at about 350° C, and could not be dissolved in organic solvents (this is not true for hydrocarbon monomers: for example styrene after polymerization in glow discharge can be dissolved in acetone). However, they could be "etched" in a glow discharge with oxygen, and X-ray investigation showed them to be completely amorphous. These latter two properties indicate that the polymers differed chemically from teflon foil.

The deposition rate on a plane substrate – small in size compared to the distance of the elctrodes – was measured with respect to its angle with the electrodes: at 0.17 MHz there was a cosine dependence though at 10 MHz there was almost no dependence on angle. If the substrate was kept parallel to the electrodes and the current density constant, the deposition rate at 10 MHz was found to be lower than at 0.17 MHz. Under fixed geometric conditions and fixed frequency, the deposition rate was proportional to the molecular mass of the gases listed in Table I, which are of structural formula C_xF_{2x}.

It is of theoretical interest to add that no polymer film of perfluoropentane was obtained under the same experimental conditions. This result is consistent with findings of Bradley [6] who treated perfluoroacetone in a glow discharge and proved by gas chromatogram that fragments of CF_4, C_2F_6 and C_3F_8 were present among others, but he did not get a film. Materials of the structural formula C_xF_{2x+2} did not polymerize.

The change of capacity of the samples in different relative humidity proved to be dependent on the dielectric volume, only and not directly on the length of edge, the thickness, or the capacitive area. No swelling could be observed under an interference microscope, so the polar nature of the water was thought to be the cause for the increase in capacity. As a bulk property moisture absorption has the same effect as changing the dielectric constant after absorption. Let ϵ_1 and C_1 be the effective dielectric constant and the capacity for a dry sample of area F and thickness d and ϵ_2, C_2 the values after absorption, then the ratio

$$\frac{C_2 - C_1}{C_1} = \frac{\epsilon_2 \epsilon_0 F/d - \epsilon_1 \epsilon_0 F/d}{\epsilon_1 \epsilon_0 F/d} = \frac{\epsilon_2 - \epsilon_1}{\epsilon_1}$$

does not depend on the size of the sample. Therefore, if ΔC is the change of the capacitance C due to a 1% change of relative humidity at constant temperature, the ratio

$$\beta_c = \frac{\Delta C}{C} \quad \text{per 1\% r.h.}$$

is a measure to describe the dielectric's property to absorb moisture. By definition β_c is positive for an increase of capacitance with increasing relative humidity. β_c was determined by capacity measurements on a General Radio capacitance bridge at 100 kHz, the accuracy of C and loss tangent being better than 3% each. The values recorded in Tables I and II are the means of ten samples. Loss tangents were taken after vacuum drying. As vapour dissipation or vapour absorption lasts between 1 h and 1 day for films deposited at a discharge frequency of 0.17 and 10 MHz, respectively, this time had to lapse before measurements under equilibrium conditions could be made for β_c.

Capacity changes are also dependent on (a) the discharge frequency during the deposition of the films, (b) vacuum heat treatment immediately after deposition, (c) temperature, electric field, and air or vacuum environment during subsequent life tests. So these factors were taken into account when planning the experiments to measure β_c. Table I shows the results for different monomers at two discharge frequencies shortly after the samples were produced. Obviously, the higher dis-

TABLE I Properties of polymer films.

Monomer	Discharge frequency (MHz)	$\beta_c \times 10^6$/1% rel. hum.	tan δ (100 kHz) $\times 10^3$	$\sigma \times 10^5$ (N cm^{-1})
perfluorocyclobutane	0.5	500*	1.9*	20†
	10	400†		
hexafluoropropylene	0.5	600*	2.0*	20†
	10	400†		
perfluoromethyldecalin	0.5	600*	2.8*	25†
	10	400†		
perfluorobutylene	0.5	2200*	3.6*	30†
	10	600†	3.0*	

* Measured when the sample was in a vacuum chamber immediately after fabrication

† Measured after equilibrium had been reached under room conditions.

TABLE II Properties of films prepared from hexafluoropropylene at a discharge frequency of 0.17 MHz, after various test conditions.

Vacuum heat treatment	Test conditions			Results at end of test	
	Temp. (°C)	Applied electric field V (μm)$^{-1}$	Time in air environment (h)	$\beta_c \times 10^6$/1% rel. hum.	tan δ (100 kHz) $\times 10^3$
none	20	0	1	650	4
180° C, 0.5 h	20	0	1	400	2
none	100	0	1000	1600	10
180° C, 0.5 h	100	0	1000	1000	2.8
none	100	100	1000	1700	10
none	100	0	5000	1700	14
none	100	100	5000	2300	30

charge frequency gives the better results for all monomers. Surface tension, obtained from spreading drops of liquids with known surface tension, and loss tangent are also given and are correlated with β_c.

As described in [4] and [7], vacuum annealing improves the long term stability of dielectric properties of such films. Annealing at 100° C has no effect. The minimum temperature necessary to show an effect is about 150° C and a few minutes treatment is sufficient. Further improvement is impossible unless the temperature is raised, but above 250° C no further improvement is possible, and again a few minutes treatment is sufficient. This result is very similar to that for teflon foil [8]. Keeping the samples in vacuum at room temperature only delays the degradation to be described now.

Table II shows the life test results for films prepared from hexafluoropropylene at 0.17 MHz as a representative example. tan δ and β_c increase under all test conditions. As a rule for all monomers of Table I, β_c changes more in any subsequent long term test for higher initial values of β_c. So the trends as indicated for hexafluoropropylene in Table II are typical for all monomers listed in Table I, and by choosing 0.17 MHz as the discharge frequency the trends are more obvious than for higher discharge frequencies. In summary, if the films are used on a product, which makes use of their dielectric properties, a final hermetic coating of the product is recommended.

4. Discussion

To interpret the diversity of the results, we must first have a theoretical outline for the formation of the films. In a d.c. discharge the film grows on the cathode, so the importance of electron bombardment can be dismissed [9]. Positive ions migrate to the cathode where they are involved with film growth. When an alternating electric field is applied between two electrodes, the film grows during a half cycle on one electrode and during the next half cycle on the opposite electrode. For some monomers the deposition rate can be increased by cooling the electrodes [9], and the yield can be more than two polymerized molecules per ion [5]. This indicates that adsorbed molecules on the electrode surface can take part in film growth.

Hydrocarbon monomers in a glow discharge break into fragments, some of which lead to a polymer deposit, making analysis difficult [6]. In our case analysis was simplified because there were only valence bonds between carbon–carbon atoms and carbon–fluorine atoms in the materials investigated. The binding energy for the fluorine atoms is higher than the one between carbon atoms so that the latter bonds should have been activated first. In order to explain that no film could be produced from perfluoropentane and related materials of formula C_xF_{2x+2} which have a simple chain of carbon atoms, it must be assumed that either a carbon ring or a carbon–carbon double bond is activated because either one or the other is present in the materials with C_xF_{2x} (Table I). By activating one such molecule at that valence bond, a radical with two unsaturated valence bonds is created. These radicals unite to form the polymer chain. Clearly, for different monomer molecules with equal activation energy the deposited mass is proportional to the molecular mass. As the activation energy to open a carbon ring is about the same as for a carbon–carbon double valence bond, the deposited mass was found to be simply proportional to the molecular mass, for the materials of Table I.

When polymerization is essentially via the whole molecule we can apply kinetic gas theory to the ions with mass m and radius r of the neutral monomer molecular without involving too great an error. The mean free path λ for molecule and/or ion and the average velocity v give a time of flight

$$t = \frac{\lambda}{v} = \frac{1}{4\pi\sqrt{2}Nr^2 \cdot 2\sqrt{(2/3\pi)}\sqrt{(3kT/m)}}$$

between two collisions at a particle concentration N. The discharge frequency whose half cycle equals the time of flight is

$$f = \frac{1}{2t} = \frac{8}{\sqrt{\pi}}Nr^2\sqrt{(kT/m)}$$

Inserting $N = 5.3 \times 10^{16}\ \mathrm{cm}^{-3}$ for a pressure of $200\ \mathrm{N\ m}^{-2}$, $r = (2 \text{ to } 5) \times 10^{-8}$ cm and $m = (150 \text{ to } 550) \times 1.66 \times 10^{-24}$ g for the materials of Table I, $k = 1.38 \times 10^{-16}\ \mathrm{g\,cm}^2\ \mathrm{sec}^{-2}$ per K; $T = 300$ K gives $f = 1.2$ to 4 MHz.

Below this frequency the time between two collisions determines the maximum amount of energy which an ion can obtain in the electric field. Above that frequency the maximum energy is reduced in two ways. First, the time between a directional change of the electric field limits the mean free path of the ions in the direction of the electric field, thereby limiting the maximum energy an ion can obtain. Second, as the mean free path of the electrons is greater, due to their smaller size, and as yet unaffected by the discharge frequency, the positive ion shield near the electrode surface expands with increasing discharge frequency which also lowers the energy of the ions which reach the electrode surface. At the higher discharge frequency the directional influence of the applied electric field is reduced resulting in a diffusion dominated arrival of the ions at the electrodes.

The insight into film growth from Williams and Hayes [9] is confirmed by the high frequency observations. The electrons do not stimulate the process since diffusion dominated deposition was observed at the higher frequency. The ions do not form the film themselves after neutralization, because at the same current density the mass deposition rate was less at the higher frequency. So it is concluded that the ions pass their energy on the electrode surface to adsorbed neutral gas molecules which then form the film.

The angle of the substrate with respect to the electrode surface has no effect on the ion density or ion velocity in the plasma, so that the contribution of a single ion to the film growth does not depend on angle. However the number of ions per unit area of the substrate decreases with increasing angle, resulting in a reduced deposition rate. At high discharge frequencies this effect is blurred by the diffusion at the substrate surface through the positive ion shield, but the reason why the dependence on angle is practically lost, is not yet known.

After these explanations of film growth, we proceed to the details of film properties. The dipole moment per carbon atom in the polymers from the materials of Table I is the same, and consequently the loss tangents of these products are of the same order of magnitude. Stoichiometric conditions and unintended impurities determine the length of the polymer chain, the ends of which are the locations of the major dipoles in the film. The existence of unsaturated valence bonds can be proven using electron spin resonance methods [6], and some of these bonds can be saturated by a vacuum anneal what gives a lower loss tangent and better results in long term tests. The longer the primary carbon chain of the activated monomer molecule, the less possibilities per unit volume there are to leave residual dipoles or to incorporate impurities. This conclusion is confirmed by the sequence of materials from low to higher $\tan\delta$, β_c, and σ (Table I). It also explains why $\tan\delta$ and β_c are so closely correlated in long term tests (Table II), however, this correlation does not exist when different discharge frequencies are applied for film deposition (Table I). Therefore it is proposed that an unknown impurity is present and the lower energy at 10 MHz is not enough to activate it.

6. Conclusion

Best quality polymer films are obtained by

(a) using dipole free monomers whose activated molecules give radicals which have as long a carbon chain as possible with unsaturated valence bonds at both ends of the chain

(b) applying only as much energy as is just needed to create the radicals; this can be done by taking the lowest electric field which sustains the glow discharge and by selecting a sufficiently high discharge frequency

(c) annealing for 15 min at 250° C vacuum immediately after film deposition.

Acknowledgements

The author is indebted to M. Kobale and H. Pachonik for helpful discussions during the progress of this work which was supported under the technological program of the Federal Department of Research and Technology of the F.R.G. The author alone is responsible for the contents.

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Received 27 October and accepted 17 Novemebr 1976.