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SOME OPTICAL AND ELECTRICAL PROPERTIES OF THIN FILMS DEPOSITED BY THE PLASMA POLYMERIZATION METHOD[1])

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Polymeric thin film deposition by the plasma polymerization method of different monomers has been investigated. The volt-ampere characteristics of Al-polymer-Al (Au) system, frequency dependences of capacity (resistance), relaxation effects and semipermeability properties of the above systems have been measured.

О НЕКОТОРЫХ ОПТИЧЕСКИХ И ЭЛЕКТРИЧЕСКИХ СВОЙСТВАХ ТОНКИХ ПЛЕНОК, НАНОСИМЫХ МЕТОДОМ ПОЛИМЕРИЗАЦИИ В ПЛАЗМЕ

В работе приведены результаты исследований тонких полимерных пленок методом полимеризации различных мономеров в плазме. Измерены вольтамперные характеристики систем Al–полимер–Al, частотные зависимости емкости (сопротивления), эффекты релаксации и свойства магнитной полупроницаемости указанных систем.

I. INTRODUCTION

In the non-isothermic, especially high frequency plasma a great deal of monomers may be polymerized [1, 2, 3]. In the plasma, moreover, even such monomers do form polymers, which by usual chemical methods cannot be polymerized at all [1]. The most commonly used ones appear evidently as thin films up to the 2 μm of thicknesses. The polymerization usually takes place at a pressure from 5 to 600 Pa, the monomer vapours are diluted by inert gar or hydrogen [4, 5], where the ratio of partial pressures of monomer and the buffer gas may affect the deposition rate of the polymeric films. The real plasma polymerization is produced either in the so-called barrel arrangement with inductive and/or capacitive coupling of a high frequency energy source, or in the bell-jar system with the plasma internal

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electrodes and the use of capacitive coupling of a high frequency source. For each monomer there may be found optimum conditions of polymerization [4, 5]. Also, it is possible to copolymerize several monomers or prepare comined polymer — metal composite thin films, too [6]. Meanwhile, there exists some practical experience as to the plasma polymerization of volatile monomers having a vapour tension at standard conditions above 10^{-1} Pa. The physical properties of thin deposited polymer films depend to a certain extent on a number of external parameters and experimental production conditions.

II. METHOD

Plasma polymerization of different monomers is carried out in a bell-jar reaction (Fig. 1) under a throug-Flow regime. As a substrate there were used glass, glass with a deposited al film and polished Si. High frequency plasma was capacitively generated between two circular electrodes at a power output of (40—80) W (27 MHz). Argon was used as diluting gas. The total pressure (monomer + buffer gas) ranged between (10—30) Pa. Polymer films were formed using toluene, allylamine, benzene, benzonitrile, pyridine, octamethyltetrasiloxane (OMTS) and 3-etoxopropylaminosilane (aminosilane).

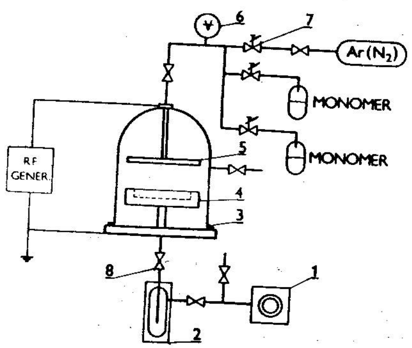

Fig. 1. A schematic drawing of the experimental arrangement for the study of plasma polymerization. 1 – oil pump, 2 – cold trap, 3 – bell-jar glass vessel, 4 – lower electrode with substrate, 5 – upper electrode, 6 – Pirani vacuum gauge, 7 – variable needle valves, 8 – valves.

In the sandwich Al–polymer–Al system (Al deposited on glass) voltampere characteristics were measured for different kinds and thicknesses of polymeric films. Further, capacity frequency characteristics of the above system were determined and the permittivity and loss angle relative values evaluated. Thin film thicknesses and parameters measurements were executed applying the ellipsometric and interferometric methods. For the ellipsometric parameters evaluation the absorption coefficient was assumed to equal zero. The above assumption was verified on a series of samples with different polymer deposition thicknesses. Indices of refraction (r) were obtained within an accuracy of ± 0.01 and the

thicknesses ± 2 nm from the ellipsometric and ± 5 nm from the interferometric data, respectively. Measurements were taken from thicknesses of 20—400 nm for films whose parameters are given in Table 1. The Al electrodes were vacuum deposited on glass substrates, the sandwich sample surface was 7.85×10^{-5} m^2.

III. RESULTS

The voltampere characteristics were measured in the 0—30 V d.c. voltage range, the corresponding leakage current then within $10^{-12} - 10^{-2}$ A. Considering the above characteristics in nonlinear coorinate systems the Schottky conductance character of thin films has been proved and the height of the potential barrier of the Al–polymer (Φ_0) has been determined. (See Table 1.) The typical VA characteristics for various aminosilane film thicknesses are illustrated in Fig. 2.

Table 1

Monomer	Φ_0 [eV]	ε_r	v_d [nm min^{-1}]	n
toluene	0.57 ± 0.5	5.2 ± 0.9	9.5	1.60
allylamine	0.54 ± 0.02	3.5 ± 0.7	17.5	1.59
benzene	0.55 ± 0.02	7.6 ± 2.0	4.6	—
aminosilane	6.8 ± 0.4	31 ± 7	31.0	1.54
OMTS	0.56 ± 0.10	3.6 ± 2.0	13.0	1.45
pyridine	0.60 ± 0.02	*	15.0	—
benzonitrile			5.4	1.62

* The relative permittivity depends on thickness (see Fig. 4).

If the polymeric thin films are exposed to electric field strengths, the relaxation effects that take place are characterized by a current decrease with time at a constant voltage. The relative permitivity ε_r was evaluated from the measured capacity frequency characteristic of the system. The capacity of the sandwich system is rather independent of frequency and within the layer thickness interval considered it ranges from 10—100 nF. The alternating leakage resistance markedly decreases with increasing frequency, being somewhere between 10^7—10^2 Ω. The deposition rate v_d was calculated from the deposition time and the measured layer thicknesses by the Tolansky interferometric method. The capacity measurements were carried out together with those of the alternating leakage current taken from the interval of 10^{-2}—10^{-7} A. The dependence $R = R(f)$ decreases relatively rapidly with growing frequency, in the coordinates with log $R = F(\log f)$ it is nearly linear with the line slope in the interval -0.8 to -1.4. The frequency dependence of capacity for several samples are demonstrated in Fig. 3.

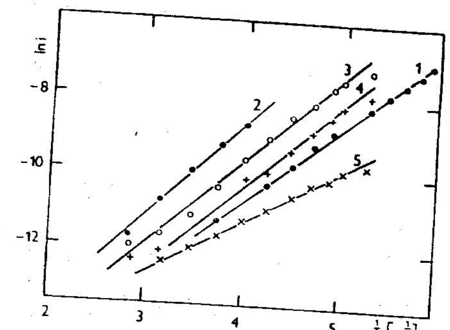

Fig. 2. Voltampere characteristics of OMTS thin polymeric films. (Numbering of the VA characteristics denotes the successive measurements obtained with the same sample).

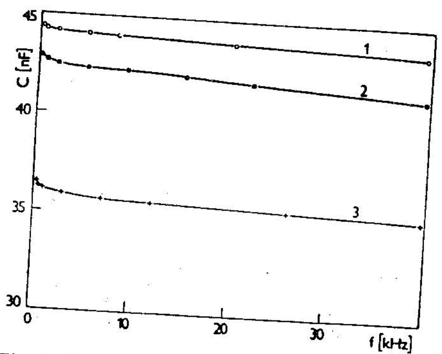

Fig. 3. Dependence of capacity of an Al-polymer–Al sandwich system on frequency. 1 – aminosilane, 2 – pyridine, 3 – toluene.

The relative permittivity depends on the polymeric thin film thickness — see Fig. 4. To measure the humidity of gases and vapours we may utilize the condenser capacity change (Al–polymer–Au), whose component is the in the plasma deposited dielectric film. Most of the plasma polymerized monomers used exhibit the capacity change dependent on humidity, only in the case of benzonitrile the capacity of the sandwich system remains practically unchanged. The sensitivity of the capacity measuring element to the humidity increases with a decreasing polymer dielectric thickness. In Fig. 5 there are shown the measured capacity dependences on the dewing point for cases of poly-allylamine and poly-aminosilane.

The classical hygrometric elements with oxide films are less resistant to mechanical disturbances and the unfavourable influences of eventual corrosive gases.

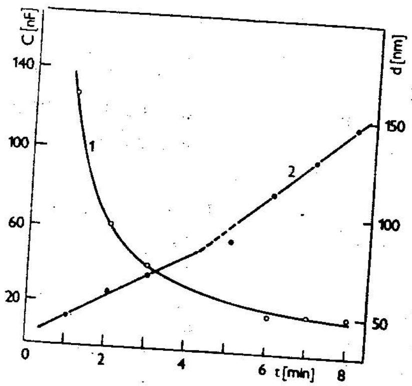

Fig. 4. Capacity and thickness dependences of Al-polypyridine-Al systems on deposition time. $1 - C = f(t), 2 - d = f(t)$.

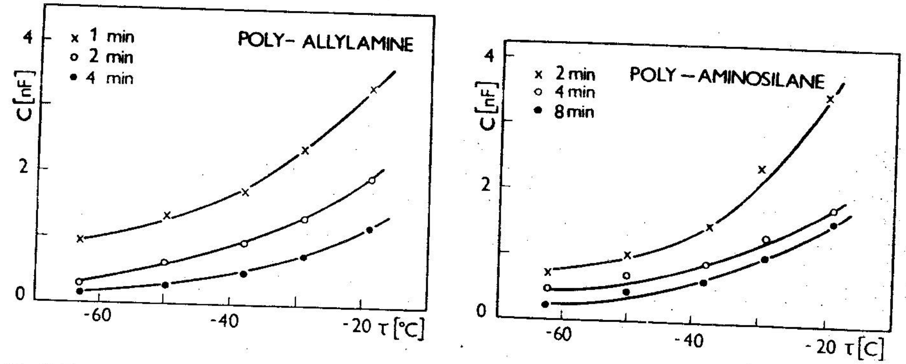

Fig. 5. Dependence of capacity of an Al–polymer–Au system on the air humidity for different deposition times of the polymeric layer.

Therefore the plasma polymers were used as semi-permeable membranes. The oxide hygrometric elements provided with protective layers produced by the plasma polymerization method do not change their sensitivity to humidity. This fact has made it possible to use the above layers for determining humidity even in a very contaminated medium.

IV. SUMMARY

Thin poly-(toluene, allylamine, benzene, aminosilane, OMTS, pyridine, benzonitrile) films were prepared by the plasma polymerization method. The voltampere characteristics of the Al–polymer–Al system and the frequency dependences of capacity and resistance of the above systems were measured as well.

Thin films produced by the plasma polymerization method of different monomers exhibit some interesting electrical and optical properties. From the measured voltampere characteristics of Al–polymer–Al sandwich systems where the relaxation effects on exposing the film to the electric field are markedly pronounced the Schottky conduction character has been proved. A very interesting property of the Al–polymer–Au sandwich system is the dependence of the capacity system on the humidity of the close environment. Also, the semipermeability properties of the above films and their stability with respect to aggressive gases make the protection of the classical hygrometric elements possible.

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