High Temperature Stable Polymer Layers-Obtaining by Vacuum Deposition Methods

Velichka Jordanova Strijkova, Rumen Hristov Kazakov, Jacob Jossif Assa, Erinche Michilova Spassova and Gencho Vasilev Danev

Abstract – **It has been established that despite the use of the same precursors 4,4'-oxydianiline and pyromellitic dianhydride in the application of the different variations of evaporation plans in vacuum developed by us, the accomplishment of a desired modification of the structure, composition and properties of the layers is made possible. Layers with different electrophysical and micromechanical properties have been obtained. Conditions and technical means for the realization of the processes of polycondensation and imidization ensuring the electric characteristics with the values typical of a dielectrics have been established and successfully implemented.**

Keywords – **Polyimide, Thin layers, Vacuum deposition**

I. Introduction

High – temperature polymers represent a large class of organic materials mainly built from aromatic molecules. Polyimides (PIs) are their typical representatives [1,2]. Their low solubility creates serious problems in the production of thin layers (thickness less than 1000 nm). The problem is almost unsurmountable when the limit of 100 nm must be overcome. Various research teams have been studying and developing for over 20 years the vacuum methods for the deposition of such layers based on the thermal evaporation of their precursors [3, 4]. Aromatic PI materials have been widely investigated for the past decade because of their excellent dielectric, thermal, adhesive and dimensional stability and are mainly used in the aerospace and electronic industries in the form of films and mouldings [5]. By the creation of an intimate mixture of the precursors deposited on a substrate a solid – phase reaction is achieved by means of thermal influence and polycondensation until the obtaining of the PI [6-7]. Our studies show that this alternative for the production of thin PI layers requires the solution of a number of problems both research and technical ones.

The aim of the paper is to show that despite the use of the same precursors ODA (4,4'-oxydianiline) and PMDA (pyromellitic dianhydride) in the application of the different types of their evaporation in vacuum developed by us, obtaining of the layers with desired modification of the structure, composition and properties is made possible.

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II. Experimental

A. Sample Preparation

Type 1: The thin PI layers were formed by vacuum co-deposition of the initial precursors PMDA and ODA and a ratio in the flux of 1:1 for ODA : PMDA. They were evaporated from two independent thermally heated Knudsen-type vessel sources. The deposition rate of 0.2-0.4 nm/s was controlled by quartz oscillators. The deposited layers were transformed into PI by a two-step thermal treatment in air (Fig.1).

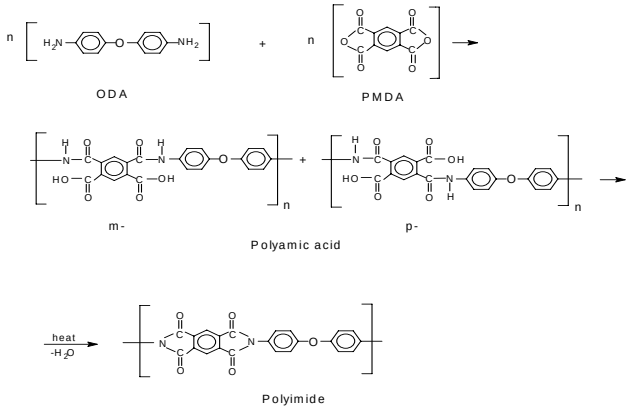


Fig.1 Reaction of ODA with PMDA to form PI

Two types of samples were investigated: 1- precursors condensed on the linearly moving (LM) substrates and 2- precursors condensed on planetary rotating (PR) substrates (Fig.2). The formation of PI layers in LM substrates at a movement velocity of 5 mm s^{-1}, is effectuated by a layer-by- layer growth of the films.

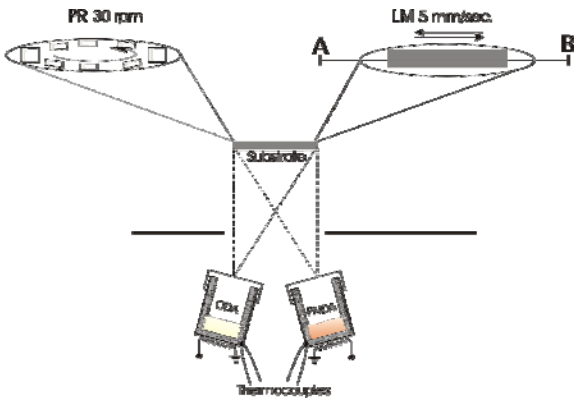


Fig.2. Experimental scheme for PI layers formation

In the PR substrates the spinning velocity of the substrates is 30 r.p.m. In this case the fluxes of both precursors are mixed and are simultaneously deposited on the substrate and the layer is growing discontinuously. In both cases the vacuum in the vacuum chambers is about 10^{-6} Torr.

Type 2: On PR substrates PI layers were obtained by assisted deposition of the precursors by means of a controlled introduction of an inert gas – Ar. The pressure in the vacuum chamber was about 10^{-4} Torr.

Type 3: Aiming at the attainment of a précised deposition of both PI precursors upon the substrate a system [8] of controllable consecutive evaporation from each of the two sources has been developed. The elaborated scheme represents an open system for automatic regulation of shutters over the evaporators designed to close in succession either of the sources of molecules of the separate precursors. The built – up of the PI chains is carried out after the scheme shown in Fig.3 [9].

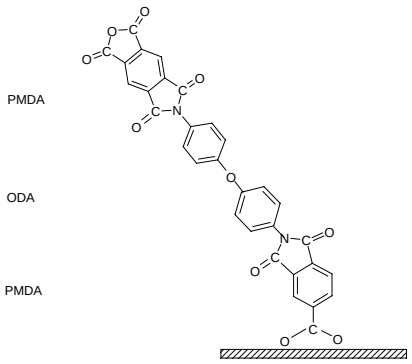


Fig.3. A model of the stack growth from ultra thin films, obtained in the consecutive depositions of the precursors.

B. Methods of investigation

Fourier transform infrared spectroscopy – FTIR spectra were recorded with a Perkin-Elmer 1600 spectrophotometer in the range of 2000-450 cm^{-1}, with a resolution 4 cm^{-1}.

The microhardness (Mhd) was determined by the Knoop prism method [10]. The load value was 1.25 mPa for all samples.

The surface morphology of the films was followed on the scanning electron microscopy (SEM) – Philips 515.

The electrical measurements were performed at room temperature, at a frequency of 1 Mhz with a Hewlett Packard Digital LCR meter 427B with an amplitude ranging from 0.2 to 1.0 V. The conductivity was determined using a Keithley electrometer 192 DMM at a current density - $4x10^{-7}$ A/cm^2.

The volt – ampere characteristics of the experimental samples of the sandwich type obtained on a conductive substrate and an upper Al electrode have been recorded (Fig.4).

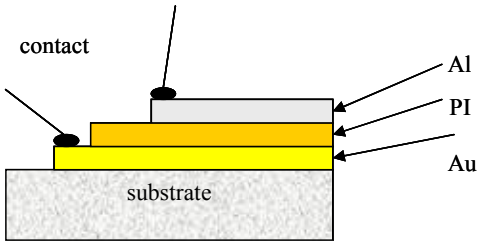


Fig.4 A scheme for measuring the electroconductivity of PI speciments of the sandwich type deposited on a conductive substrate.

III. RESULTS

The impact of thermal treatment was studied by the help of FTIR. The results from the spectral measurements are summed up in Fig. 5

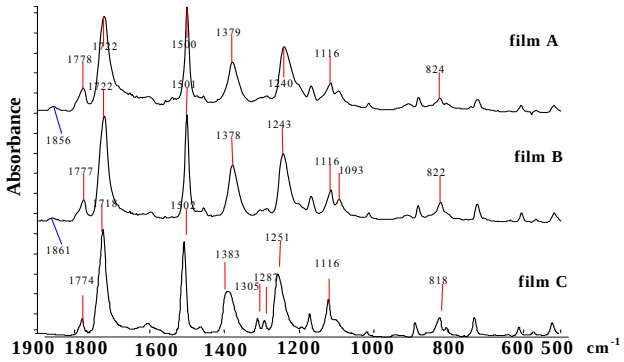


Fig. 5 FTIR spectra of PI (ODA: PMDA = 1:1), Thermally treated: **A** (6 h at 170° C), **B** (1 h at 170° C and 1 h at 250° C), **C** (1 h at170° C and 1 h at 350° C).

With the raising of the thermal treatment temperature the intensity of the carbonyl anhydride peak (1860 cm^{-1}) decreases and at a high temperature treatment (film C) the anhydride peak disappears. The peak (1380 cm^{-1}) which is an indication of an occurrence of imidization following thermal treatment was used as a measure for determining the degree of imidization (its area is normalized at the peak at 1500 cm^{-1}) (Table 1.)

TABLE 1. A DEPENDENCY OF THE IMIDIZATION DEGREE ON THE CONDITIONS OF THERMAL TREATMENT

Thermal treatment	Degree of imidization [%]
6h at 170^{O}C	36.8
1h 170^{O}C + 1h 250^{O}C	40.2
1h 170^{O}C + 1h 350^{O}C	63.4

The obtained results give us grounds for concluding that the PI matrix is of best quality upon thermal treatment for 1 hour at 170^{o}C + 1h 350^{o}C. At the same time the milder conditions of thermal treatment also allow for the occurrence of imidization processes but at a lower extent and with the formation of chemical defects in the matrix at a higher proportion. The prolonged thermal treatment – 6

hours at 170^0 C, is in no condition to make up for the treatment at 250 or 350^0 C. This is due to the incomplete imidization taking place under the milder conditions of thermal treatment which has its impact on the value of the measured microhardness (Table 2). After a thermal treatment for 6 hours at 170^0 C, the PI layer contains a significant quantity of non-reacted precursors which is not observed in the films treated at 350^0 C. The FTIR spectra of the latter do not display anhydride peaks.

The results from the electrical measurements (Table 3.) show that the obtained PI layers are of low values of the dielectric constant (ε) and are comparable with data on evaporated PI layers reported by other authors[4] as well as a PI obtained from a solution [11,12].

TABLE 2. SUMMARIZED RESULTS OF THE MEASURED MHD OF PI LAYERS OF A THICKNESS D = 800 NM

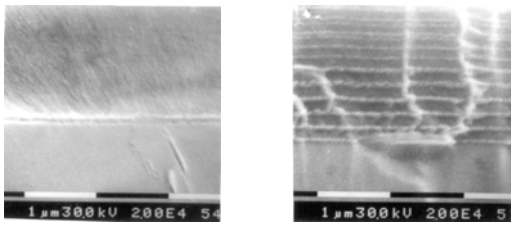
Thermal treatment	Mhd [kPa / mm^2]
without	34. 8
6 h 170o C	54. 4
1 h 170o C + 1 h 250o C	64. 5
1 h 170o C + 3 h 250o C	70. 5
1 h 170o C + 1 h 350o C	74. 6

It is obvious that the higher temperature of the second stage of the thermal treatment determines the lower value of the **ε.** This is explained with the higher degree of imidization and the greater purity of the layers with respect to the chemical defects shown by the infrared spectra.

TABLE 3: SUMMARIZED RESULTS CONCERNING THE RELATIONSHIP BETWEEN ε AND THE CONDITIONS OF THERMAL TREATMENT

d [μm]	Thermal treatment	ε
0.1	1 h 170^o C + 1 h 250^o C	3.0 - 3.2
0.1	1 h 170^o C + 1 h 350^o C	2.8
0.22	1 h 170^o C + 1 h 250^o C	3.1 – 3.3
0.22	1 h 170^o C + 1 h 350^o C	2.9

The electron microscopy studies on the surface morphology displayed an essential impact of the substrate movement type and the situation of the molecular fluxes on the morphology and properties of the deposited layers (Fig.6).



а/ б/

Fig. 6. Profiles of thermally treated PI layers deposited: a/ on a PR substrate in crossed molecular gaseous fluxes of the precursors; b/ on a LM substrate after the "shuttle" system in crossed molecular gas fluxes of the precursors.

The layers deposited on the PR substrate grow at a gradual pace while the ones on the LM substrate this is accomplished layer-by-layer. Most probably the adsorbed molecules (from the residual atmosphere in the vacuum chamber) between two successive layers in the LM substrate predetermine the observed stratified structure. Besides , the lower values measured for ε (Table 4.) give us grounds to conclude that structural defects of the "free volume" type in the case of the PR substrate bring about to the differences observed in the layers' electrical parameters.

TABLE 4: SUMMARIZED RESULTS FROM THE ELECTRIC MEASUREMENT OF 500 NM VACUUM DEPOSITED THERMALLY TREATED PI LAYERS

VD layer	capacity (C) [pF]	Dielectric constant (ε)
VDP layer on a PR substrate	9	3.2
VDP layer on a LM substrate	11	3.4

Our working hypothesis presumes an increase of porosity in the PI layers evaporated in Ar atmosphere (Type2) which would imminently lead to an improvement of the basic dielectric properties of the thin-layer matrix – an augmentation of the specific resistance and diminution of the ε value. The results from the performed electrical measurements confirmed our expectations. In Fig.7 the volt-ampere characteristics of thermally treated PI layers of identical thickness (280 nm) and monomer ratio (1:1) but obtained in differing residual gas atmosphere of the vacuum chamber are presented. It is obvious that the increase of the Ar content in the chamber leads to a decrease in the current and respectively to an augmentation of the resistance of the material. The estimated specific conductivity of the material ($5.8x10^{-6}$ $Ом^{-1}м^{-1}$ for a standard PI layer) reaches values of $2.2x10^{-11}Ом^{-1}м^{-1}$ for the Ar pressure $3x10^{-4}$ Torr., which testifies to an abrupt improvement of the dielectric characteristics owing to an increase of the free volumes in the layers thus formed. For a pressure of $3x10^{-5}$ Torr, the resistance $4.5x10^{-11}$ $Ом^{-1}м^{-1}$. Since the difference in the resistance of the layers obtained in both pressures of Ar is insignificant it can be assumed that a saturation of the layer is attained even at the lower level of pressure.

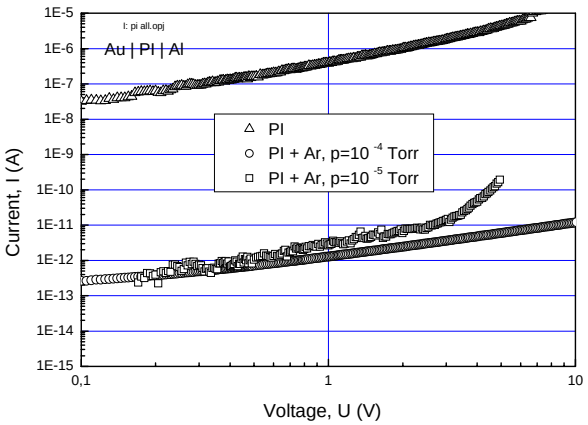


Fig.7. C/V characteristic of conventionally evaporated PI and a PI evaporated in the Ar atmosphere for two Ar concentrations.

IV. CONCLUSION

In the use of ODA and PMDA as initial precursors a "dry" method for the PI layer formation has been applied despite the manner of substrate movement, the type of evaporating apparatus developed by us and the differing gas atmosphere in the vacuum chamber. The implementation of this alternative way for the production of thin layers discloses attractive opportunities both for the improvement of the dielectric characteristics of the obtained layers and for overcoming the borderline thickness of 100 nm.

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