INFLUENCE OF PREPARATION CONDITIONS ON VACUUM DEPOSITED POLYIMIDE LAYER PROPERTIES AND APPLICABILITY

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Conditions for fabrication of PI films with reproducible composition, uniform and smooth surface, without mechanical and chemical defects have been established. It was demonstrated that the values of conductivity – differences between $7.0x10^{-14}$ and $4.0x10^{-1}$ $ohm^{-1}m^{-1}$, or dielectric constant in a wide range-2.2-3.2, by simultaneously keeping the attractive properties of the PI films or PI matrix, offer a combination of parameters, which are in some cases unique This investigation is a new attempt to confirm that composites represent a promising key to broadening the prospects for obtaining novel materials in the nanotechnology area.

Keywords: polyimide films, vacuum deposition, porosity, conductivity

1. INTRODUCTION

The superb properties of the polyimide (PI) films, like high thermal stability, low dielectric constant**,** high chemical resistance, high optical transmittance have led to their wide spread application as insulator, barrier layer or capsulation film [1]. In the last decade there are many convincing investigations [2,3], confirming the attractivity and functionality of PI films for preparation of nanocomposite layers consisting of a matrix and "guest"- particles, dispersed in the matrix. Composites are a promising key to broadening the prospects for obtaining novel materials in the nanotechnology area [3].

One of the widely used methods for PI layer preparation is physical vapor deposition (PVD) of precursors, like diamines and dianhydriedes [4] followed by thermal treatment. Simultaneously, the especially designed experimental set up [5,6] permits regulation of the evaporation time for each precursor, as well as the layer preparation with a wide spreading of the films' architecture in the presence of controlled residual atmosphere. Thus, controlled preparation of some composites consisting of a PI matrix and embedded nano-sized particles of metal, chromophore or dielectric [2] is made possible. We are deeply convinced that the formation of PI layer is in itself a technological challenge due to the significant problems stemming from the discrepancies between the organic nature of the molecules and the principles of PVD.

The aim of the paper is to discuss the possibilities for controlled preparation of PI films with desired properties - reproducible compositions without mechanical defects, low dielectric constant, high electrical resistance, respectively and high transmittance.

2. EXPERIMENTAL

2.1. Sample preparation

Vacuum deposited polyimide (VDP) films have been prepared on soda-lime-glass plates at a pressure of < $7x10^{-4}$ Pa. The precursors used (4, 4'- oxidianiline-ODA and pyromellitic dianhydride - PMDA), as well as the chromophore used – copper phthalocyanine (CuPc) were evaporated from three independent thermally-heated Knudsen type sources at deposition rates from 0.2 to 2 A/sec. [4-6] In the case of the carbon particles [4] the latter were obtained by means of a quasi arc erosion and evaporation of the spectroscopic carbon electrode. Upon preparing the porous films, the precursors condensed on the substrates in the presence of an Ar atmosphere at a vacuum of 4.10^{-2} Pa kept by a mass flow controller. The alternating deposition of the ultra-thin films of the precursors was carried out with especially designed device [5].

The co-deposited precursors were transformed into PI by a two - step treatment at strictly controlled temperatures (1 hour at 170^{o}C + 1 hour at 250^{o}C). Also, as could be expected for layers prepared in the presence of Ar, at thermal treatment the incorporated Ar should be desorbed from the layers and free volumes could be formed.

2.2 Methods of investigation:

a/ Electron microscopy - the surface morphology of the PI films was followed on a Scanning Electron Microscope (SEM), Philips 515.

b/ Fourier Transform Infrared Spectroscopy (FTIR): FTIR spectra (PI on KBr substrate) were recorded on a Perkin Elmer 1600 spectrometer in the range 3600-450 cm^{-1}; resolution 4 cm^{-1}, interval 0.2 [4]. From the spectra the existence of PI, chemical defects, degree of imidization were detected.

c/ Electrical measurements: The preparation of PI films on a Si wafer for electrical measurements has already been described earlier [4,6,7]. Current-voltage (I-V) characteristics were measured in DC (Direct Current) mode at room temperature in a vacuum of 1 Pa by computer controlled Keithley 617 electrometer. The conductivity (σ) was calculated using the Equation (1):

$$\sigma = \frac{\Sigma.d}{S} \quad (1),$$

where **S** is the sample area and **d** is the layer thickness. The conductance Σ was determined by the slope of the linear regression of the I-V characteristics.

d) The optical spectra were measured on a Carry 5E, Variant, Spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Surface morphology of the PI films

In the Fig. 1 SEM micrographs of films obtained after thermal treatment of co-evaporated precursors of PI and PI/CuPc composite are presented.

As it is seen from the picture of Fig. 1a the surface of the PI films is smooth, without noticeable peculiar defects or granular structure. We suggest that the formation of the interstitial product – polyamic acid and in the second step (thermal treatment) – PI determine the losses of surface relief and morphological details.

a b c

Fig. 1. SEM micrographs of VD layers : a/ 500 nm thick PI layer, thermally treated 60 min at 170° C and 60 min at 250° C; PI/CuPc composite layers, thermally treated 1h at 200° C: b/ CuPc ≤ 25 %; c/ CuPc = 50 %

In Figs. 1b and 1c SEM micrographs of PI/CuPc composite films are presented. The incorporation of the "guest" over the critical concentration (25%), drastically influenced the surface structure turning into a coarse one of the ripple type. It can be pointed here that the conditions of the temperature treatment of the co- or separately deposited ODA, PMDA and CuPc precursors should be determined very carefully. For under critical concentration the influence of CuPc on the layer morphology is negligible. But, as we shall show further the variation in composition offers a way to producing desired changes of the electric conductivity as well as the optical transparency.

3.2. FTIR spectroscopy

The FTIR spectra for the films formed by ODA : PMDA = 52:48 (spectrum A); spectrum B - excess of PMDA and spectrum C - excess of ODA are presented in Fig.2. As we have already discussed in detail [4, 8], the spectra are typical of bulk PI. The spectra A and C show pronounced shoulders around 1780, 1720 and 1380 cm^{-1} (after deconvolution, the positions of these shoulders were estimated to be 1793, 1709 and 1399 cm^{-1}, respectively) characteristic of isoimide groups. Our data - the presence of the 1793 and 1709 cm^{-1} bands indicate that an excess of ODA causes formation of isoimide groups. The films with excess of PMDA are without impurities like izo-imides. These results confirm the investigations made by others [8] who found that only doses with excess of PMDA produce high quality films.

From the FTIR spectra of the composite PI/CuPc/PI ("sandwich" type) layers in the major peaks of the PI matrix we have established [2] an increase of the amount of unreacted anhydride (1863 cm^{-1} and 1778 cm^{-1}) which suggests that the imidization processes (1380 cm^{-1}) are hampered.

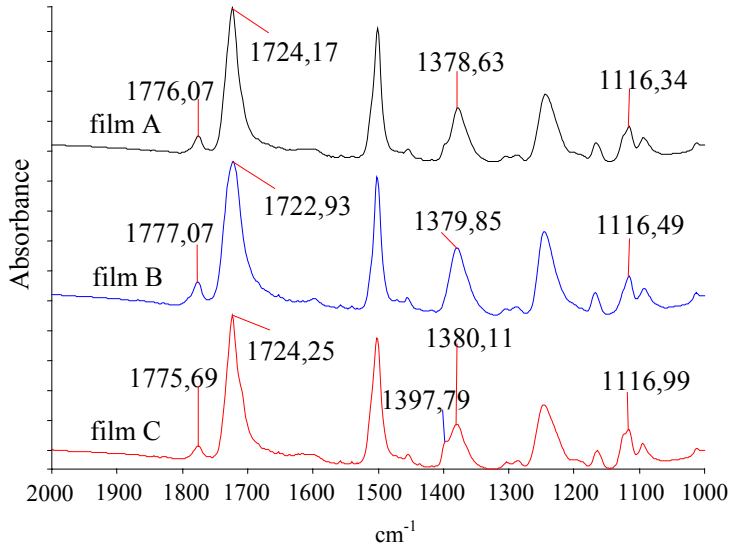

Fig. 2. FTIR spectra of thermally treated PI films: **A** (ODA: PMDA = 52:48), **B** (ODA: PMDA = 40: 60), **C** (ODA: PMDA= 60:40).

Thus, taking into account the results from SEM and FTIR spectroscopy, it could be summarized that the optimal concentrations of the CuPc are probably from 5 to 15% [2]. Their impact on the PI matrix properties is being minimal.

3.3. Electrical conductivity

The calculated σ from the measured I-U characteristic are summarized in Table 1. It can be seen that the conductivity of the investigated layers (obtained in an Ar atmosphere) decreases more than six orders of magnitude (from $1.9\text{x}10^{-8}$ $\text{ohm}^{-1}\text{m}^{-1}$ to $7.0\text{x}10^{-14}$ $\text{ohm}^{-1}\text{m}^{-1}$). This would imply an improvement of the dielectric properties of the PI layers with an increasing Ar concentration being established. The latter, according to our assumption is a consequence of the gas cavities formed in the volume. The porosity of the produced films depends on the balance between the inert gas pressure [6], the deposition rate, temperature and duration of their imminent thermal treatment.

Alternative ways to change σ of the PI films are the controlled doping of the latter or the use of the PI as a matrix in PI/C or PI/CuPc composites [2, 7]. In this case the films have another composition – mix of PI and C or CuPc. In Table 1 the summarized data from the electrical measurements of PI and PI/C composite films and the values of the dielectric constant of PI/CuPc are presented. In this case, the reason for the increased σ is the possibility to form conductive chains of C particles.

Table 1: Summarized results from the electrical measurements of the VD layers of different types

VD Layer type	Conductivity (σ), [$\text{ohm}^{-1}\text{m}^{-1}$]
PI,without Ar	$1.9\text{x}10^{-8}$
With Ar	$7.0\text{x}10^{-14}$
with 0.55 vol.% C	$2.0\text{x}10^{-5}$
with 1.4 vol.% C	$4.0\text{x}10^{-1}$

VD Layer type	Thickness (d) [nm]	Dielectric constant (ε)
PI	500	2.2
Composite PI/CuPc	600	3.2

It is obviously, that the "quest" could be influenced drastically the investigated parameters - ε decreased from 3.2-2.2.

3.4. Optical transparency and reflectivity

The embedded particles can provoke changes not only in the σ of the PI films, but also in their optical density, reflectance and transmittance. As it is seen from Fig. 3b, the increasing of the "guest" concentration, lead to the layer transmittance decreasing. The reflectance increases negligibly (Fig. 3a). The changes observed (the intensity of the peaks (Fig. 3) increases with the "guest" concentration) are probably related to the influence of the interference phenomena. We assume that changing the type of the embedded particles and their concentration and average size the optical properties

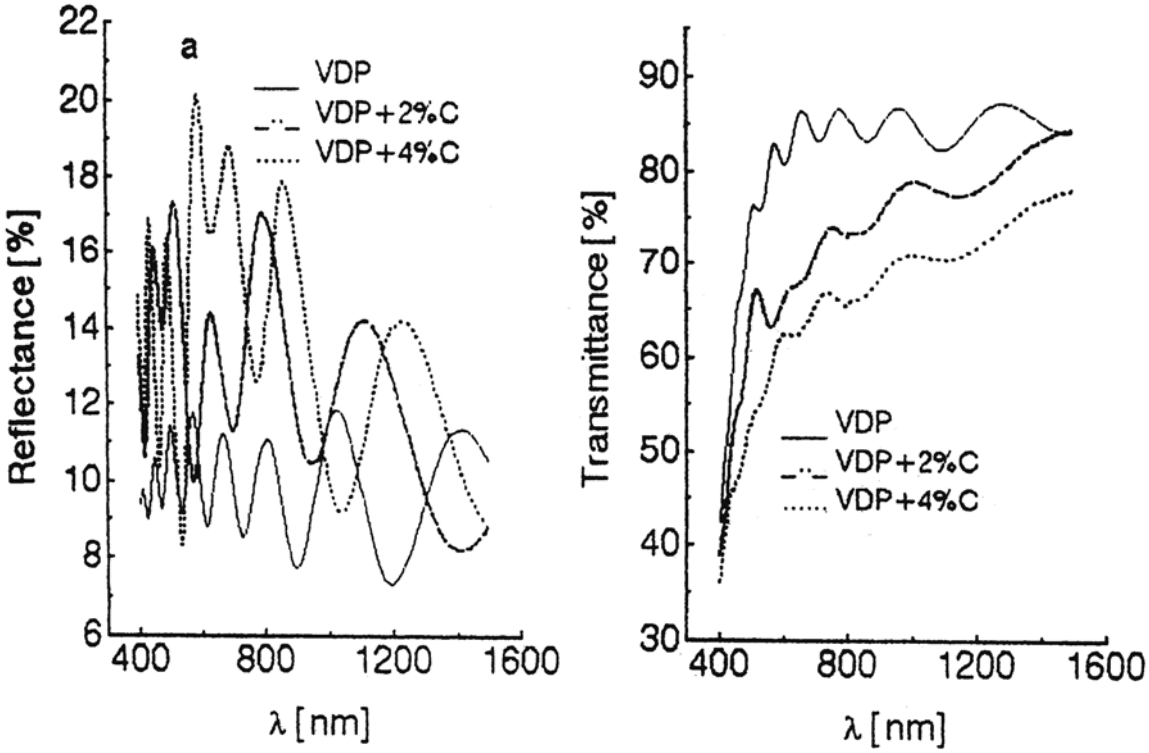

Fig. 3. Optical spectra of VD composite layers PI/C, 1000 nm thick: (a) reflectance; (b) transmittance

could be varied in a wide range. In the case of C – they increased the absorbance and simultaneously the σ, but incorporation of metal [7] increases the reflectance and σ. The method allows for practically unlimited combinations of type, concentration and sizes of embedded particles

4. CONCLUSION

The preparation conditions for PI films, as well as of composite films with reproducible composition, uniform and smooth surface, without mechanical (ripples, cracks) or chemical (izo-imides) defects have been established. They all constitute a precondition for fabrication of PI films with controlled composition, surface morphology and to a great extend determine their optical and electrical properties. The values of σ (differences between 7.0×10^{-14} and 4.0×10^{-1} $ohm^{-1}m^{-1}$), or ε in a wide

range (2.2-3.2), by simultaneously keeping the attractive properties of the PI (films or matrix), offer a combination of parameters, which in some cases are unique and unattainable for many substances or composites. Thus they can be attractive and preferred for application in electronics and optoelectronics, as coatings with changeable σ, prepared by condensation of the "guest" through a mask, barrier, capsulated or protected films with high transmittance in.

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