# Ion-Assisted Processes – a Novel Tool for Accomplishing of Physical Deposition of Organic Layers

Deyan Sabtchev Dimov, Ivaylo Cankov Jivkov, Erinche Michilova Spassova, Jacob Jossif Assa, Peter Doncheff Dineff and Gencho Vasilev Danev

*Abstract* - **Polyimide layers prepared by condensation of polyimide precursors - oxydianiline and pyromellitic dianhydride treated with an Ar plasma vapour flux are studied. Through SEM analysis, optical and FTIR spectroscopy an impact on the properties of the so- prepared organic layers is registered. It is established that the ion assisted deposition leads to an increase in the layer thickening. The conductivity of the studied layers increases with approximately 4 orders of magnitude. This effect is discussed as a consequence of the free radical formation as well as the broken longer polymer chains. The results obtained confirm our suggestion that ion assisted deposition leads to an increase in the energy of the irradiated precursor molecules, and in this way the "soft" plasma treating contributes to the imidization process.**

*Keywords* – **Polyimide, Ion beam, Physical deposition, Ar plasma**

## I. INTRODUCTION

Polyimide (PI) is one of the polymer materials of the highest heat-resisting rank. It is of good thermal properties, electricity performance, mechanical properties, radiation-resisting performance, solvent-resisting performance, and so on. A PI material is of prospects for widespread application in fields such as aerospace, automobile industry, microelectronics, large scale integrated circuits, semiconductor material production, panel display, etc. PI thin films constitute the fundamental branch of the PI application [1-3].

Traditional film preparation methods are mainly focused on casting, spin-coating, and Langmuir-Blodgett dip coating. However, those methods have a lot of limitations in the preparation of polymer nanometer thin films. In the recent years, evaporation assisted techniques have a wide range of applications in many fields, such as non-linear optics, luminescent devices, electronics, various sensors. Such is the case with the MAPLE technology (the matrix-assisted pulsed laser evaporation). This method has applications in the deposition of polymer and organic thin films [4-6]. At low laser fluence the chemical bonds can be broken, resulting in decomposition of the films.

On the contrary, at high laser fluence, protection of the structure of the PI thin films and an obvious decrease in the decomposition is observed.

D. Dimov, I. Jivkov, E. Spassova, J.Assa, G. Danev are a Central Laboratory of Photoprocesses, Bulgarian Academy of Sciences, "Acad. G. Bonchev" St., bl. 109, 1113 Sofia, Bulgaria, e-mail: dean@clf.bas.bg

P. Dineff is Technical University, "Kl. Ohridski" blv.,# 8, 1797 Sofia, Bulgaria

The high laser fluence is more suitable for the deposition of polymer and organic thin films than the low laser fluence [7,8]. Other authors have studied the application of the low-energy ion – assisted growth of titanium nitride layers [9], in the formation of polymer films [10] and etc. The use of vacuum deposition of organic materials suffers from serious limitations due to:

- the molecular weight of the precursors;
- the insufficient thermal stability of the organic materials.

That is why it is necessary an effectuation of the evaporation at temperatures up to 150 $^{o}$C and hence the low energy condition of the condensing molecules is incumbent this affecting the adhesion and thickness of the layers.

The aim of the present study is to present a model and an experimental technique for evaporation of organic substances assisted with low-energy ions. The study was carried out in order to forward a possibility for obtaining PI thin layers by simultaneous evaporation of the PI precursors (4, 4'- oxidianiline (ODA) and pyromellitic dianhydride (PMDA)) and implementation of ion fluxes of low–energy state allows for the increase of precursor molecule energy state.

## II. EXPERIMENTAL

### *A. Sample preparation*

The PI layers (300 - 1000 nm thick) were formed on soda - lime glass substrates by vacuum co-deposition of the precursors ODA and PMDA from two independent thermally heated Knudsen-type vessel sources – experimental set-up (Fig.1). The evaporation rate is 2 – 3,8 A/sec for ODA and PMDA respectively on static substrate. The base pressure was 4x10-2 Pa. The evaporation temperatures were 120 - 145° C for PMDA and 100 - 110°C for ODA. The layers were built up by means of assisted Ar ion plasma treatment processes: cathode current – 21 A; anode current – 1,4 A; anode voltage – 100 V. The obtained layers were transformed into PI by a two-step treatment – 5 min microwave (MW) treatment (2,45 GHz, 700W) followed by 15 min at 300°C, in air [11].

### *B. Methods of investigation*

The optical spectra were recorded on a Cary 5E spectrophotometer in the range 400 - 800 nm. FTIR spectra

(PI on KBr substrate) were recorded with a Bruker spectrometer, in the range of 4400–450 $cm^{-1}$ with a resolution of 2 $cm^{-1}$. The surface morphology of the films was followed on a scanning electron microscope (SEM), Philips 515. The film microhardness (Mhd) was determined by the Knoop prism method [12] known to be sensitive for measurements of thin films. The load value was 1.25 mPa for all samples studied.

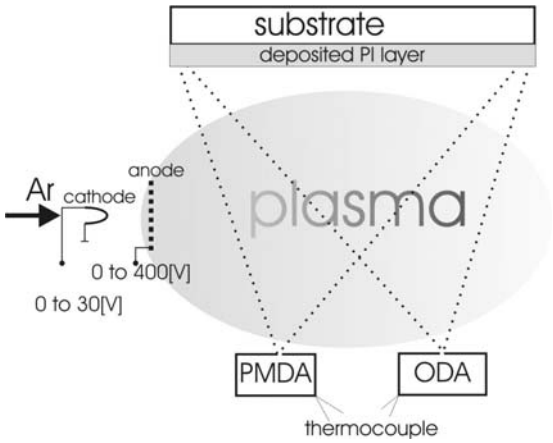



Fig.1. A detailed scheme of the system for Ion Assisted Deposition (IAD)

*C. Electrical measurements*

The investigated layers were obtained on soda – lime glass substrates with previously prepared bottom Au electrodes. Al top electrodes were then vacuum evaporated perpendicular to the Au electrodes. The resulting Au / PI / Al sandwich structures (Fig.2.) were again thermally treated at 200°C for 4 hrs to make the metal / polymer contacts more effective. Current-voltage (I-V) characteristics were measured in the DC (Direct Current) mode at room temperature in a vacuum of 1 Pa by computer controlled Keithley 617 electrometer. The conductivity was determined as the slope of the linear regression of the ohmic part of the I-V curves.

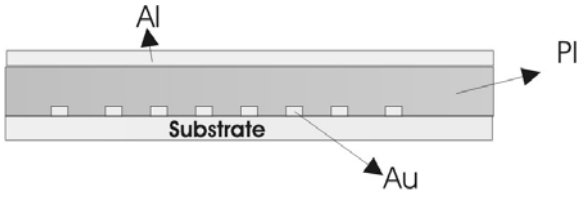
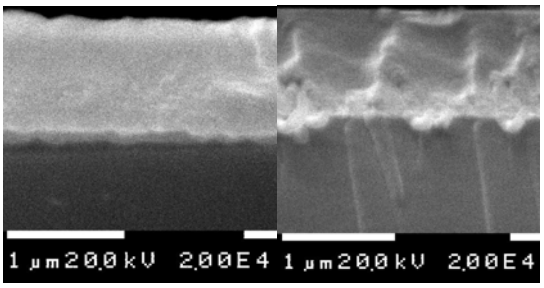



Fig.2. Scheme for current – voltage (I-V) measurement

## III. RESULTS AND DISCUSSION

The electron microscopy investigation of the cross sections demonstrate a thickening of the layer volume and a change in the manner of fracturing of the layer (Fig.3 b) as compared with the case of standard way of formation of the layer (Fig.3a). These results are also confirmed by the measured values of Mhd. The microhardness value of the layers, obtained with Ar plasma treatment is by 30 – 40% higher.




a/ b/

Fig.3. SEM micrographs of a cross section of PI layers obtained: a/ without Ar plasma treatment; b/ – with Ar plasma treatment respectively

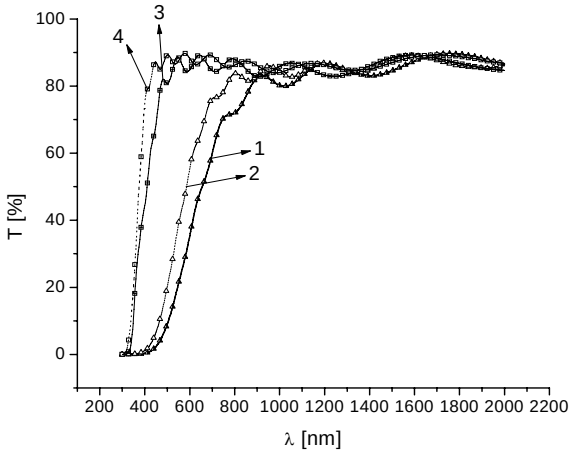



Fig.4. Optical spectra of thin (1200 nm) PI layers: 1 and 2 – PI obtained with assisted action with Ar plasma; 3 and 4 – PI, without assisted action; 1 and 3 – treated after vacuum deposition 5 min MW, followed by 15 min at 300°C, in the air [11]; 2 and 4 untreated after vacuum deposition.

When the molecule of a compound contains chromophore groups forming a system of conjugated π-bonds in the UV spectrum a new absorption maximum emerges in the UV spectrum of the compound. This maximum is found at a greater wave length as compared to the bands of the individual chromophore groups (non-conjugated). This phenomenon is termed a batochromic effect. In the PI layer spectrum obtained in the application of Ar plasma assisted action (Fig.4) a strong batochromic effect as compared to the PI obtained without the assisted action implementation is observed. This fact could be due to the following reasons:

- the imidization of the PI layers obtained in Ar plasma is more efficient. Consequently the PI molecules are conjugated among themselves to a greater extent;
- the PI layer molecules obtained in Ar plasma are spatially better arranged (the layer is of a higher degree of arrangement). The electron transitions in such molecules are realized at lower energy;
- the chance for obtaining byproducts in the course of imidization in this case is smaller because the formation of

byproducts could be the cause for impairment of the conjugation in the molecules.

The FTIR spectra present a confirmation of these suggestions of ours and are shown in Fig.5.

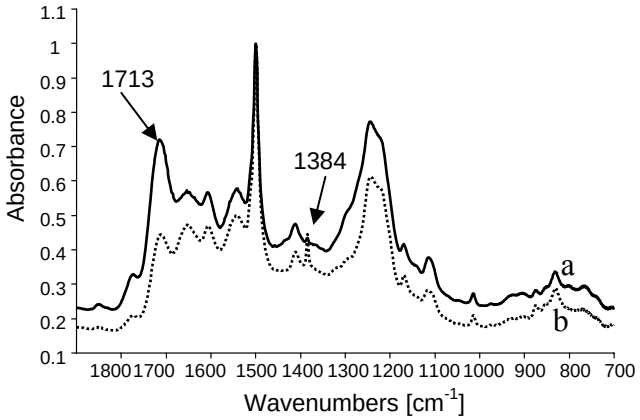



Fig.5. FTIR spectra of PI films, 500 nm thick, untreated after deposition, normalized at 1500 $cm^{-1}$: a/___without Ar plasma treatment; b/…….. with Ar plasma treatment.

The following conclusion can be drawn from the juxtaposition of both spectra: upon treatment in Ar plasma when the process of vacuum deposition of the two initial monomers ODA and PMDA is taking place and the PI layers are formed, processes of formation of a new phase or destruction do not occur. A process of initial imidization (a peak at 1384 $cm^{-1}$ is emerging) in the Ar plasma layer obtained (Fig.4.b/) and at the same time untreated thermally after vacuum deposition is observed. Upon standard conditions [13] of layer formation without treatment in plasma this band in the spectrum is missing. This effect is also confirmed by the bands at 1713 $cm^{-1}$. In the untreated layer evaporated under standard conditions [13,14] the polyamid acid is in a greater quantity.

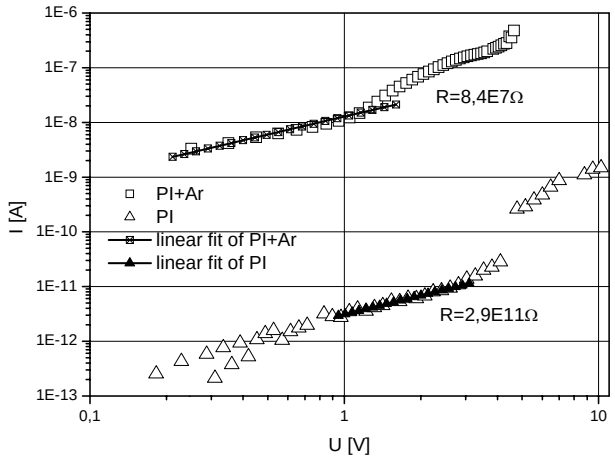



Fig. 6. Current-voltage characteristic of a 1200 nm thick polyimide layer, thermally treated after the deposition and obtained: a/ without assisted treatment in Ar plasma; b/ with assisted treatment in Ar plasma

Consequently in the PI layers, obtained in Ar plasma, the molecules react more easily and at a greater rate.

The results from the electrical measurements also come into confirmation of our assumptions (Fig.6.).

The current-voltage characteristics indicate to an impairment of the dielectric properties of the layers obtained with assisted treatment in Ar plasma. By linear regression of the experimental results from the ohmic parts of the I-V characteristics in Fig. 5 the resistance (R) is determined: R1= $8.39x10^{7}\pm0.45x10^{7}$ohm for PI, obtained in Ar plasma and R2= $2.66x10^{11}\pm0.5x10^{11}$ ohm for PI, obtained in standard conditions [13].

The conductivity of the obtained layers determined on the basis of these results is increased by 4 orders in magnitude. The lower R of the layers obtained in plasma could be due to the higher content of free radicals or short polymer chains. These results confirm our suggestion that ion assisted deposition leads to an increase in the energy of the irradiated precursor molecules, and enhances the thickening of the condensed polyimide films.

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