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Ion beam assisted physical deposition of polyimide♣

D. DIMOV*, E. SPASSOVA, J. ASSA, G. DANEV
Central Laboratory of Photoprocesses, Bulgarian Academy of Sciences, Acad. G.Bonchev St., bl. 109, 1113 Sofia, Bulgaria

Polyimide layers prepared by condensation of treated with an Ar plasma vapour flux of precursors - oxydianiline – ODA and pyromellitic dianhydride – PMDA, are studied. An influence on the structure of the so prepared layers, and as a consequence a change of their properties is expected. Through SEM analysis, considerable changes in the structures of the condensed precursors are shown. It is established that the ion assisted deposition leads to an increase in the layer thickening, with remarkable changes in their surface morphology. As a consequence of the thickening, the measured microhardness of the polyimide layers increases by more than 40 percent. 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. The FTIR analyses are interpreted as confirmation of the breaking of the chemical bonds, and in this way the "soft" plasma treating contributes to the imidization process.

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Keywords: Polyimide, Ion beam, Physical deposition, Ar plasma

1. Introduction

Polyimides have evolved in recent decades, to emerge as attractive materials in a wide variety of industrial and research applications. Due to the considerable range of characteristics displayed by polyimide (PI) materials, their potential applications appear unlimited [1]. For obtaining PI coatings, different methods such as spin-coating, dipping, roll to roll, vapour deposition polymerization, and the recently developed method [2] of glow discharge ionized cluster beam deposition, have been used. We have prepared thin PI layers by physical vapour deposition of precursors [3], and studied their properties [4] in view of their applicability in optics and electronics. The quality of these polymer films depends on and suffers very often from the low energy of the deposited precursor molecules, which leads to the formation of specific surface defects This was one reason to investigate the influence of the additional energy - ion beam (plasma) assisted deposition of the precursor molecule flux on some properties of the PI. Our assumption was that the influence of the plasma flux would result in an increase in the precursor molecule mobility. This would lead to a considerable reduction in the number of surface defects in the layers, and probably to a greater film density. The aim of this work was to study the influence of the irradiated Ar plasma on the molecular flux of the precursors and the following changes in the properties of the resulting PI films.

Because of the activated molecules as a result of the plasma treatment, it was expected that better ordered and thickened layers would be obtained, as well as an enhanced imidization process of the precursors to the PI.

2. Experimental

2.1 Sample preparation

The PI layers (500 nm thick) were formed on static soda-lime glass substrates by vacuum co-deposition of the precursors (oxydianiline – ODA and pyromellitic dianhydride – PMDA), from two independent thermally heated Knudsen-type vessel sources (Fig.1). The pressure was $\leq 5 \times 10^{-4}$ Pa. The evaporation temperatures were 120 - 145°C for PMDA and 100 - 110°C for ODA, and were strictly controlled at all steps of vacuum deposition. The evaporation rates were 2 – 3.8 A/sec, controlled by quartz oscillators.

The layers were built up by argon plasma assisted processes. As seen in Fig. 1, the ion beam was irradiated perpendicular to the vapour flux.

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The ion beam conditions were: cathode current – 23 A; anode current – 1.4 A; anode DC voltage – 100 V, at a constant Ar flux. The obtained layers were transformed into PI by a two-step treatment – 5 min microwave (MW) treatment (2.45 GHz, 700W) followed by a 15-min thermal treatment at 300°C, in air environment [5].

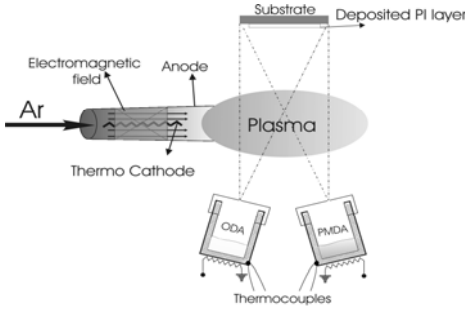

Fig.1. Detailed scheme of the experimental set- up.

2.2 Methods of investigation

The surface morphology of the films was studied using a scanning electron microscope (SEM), Philips 515. The FTIR spectra (PI on KBr substrate) were recorded with a Bruker interferometer, in the range 4400–450 cm^{-1} with a resolution of 2 cm^{-1}. The film microhardness (Mhd) was determined by the Knoop prism method, known to be a sensitive one for measuring the hardness of thin films.

3. Results and discussion

SEM micrographs of the studied layers are presented in Fig. 2. The changes in the pictures (2-b,d,f) could be perceived and explained as results of the reordered and increased thickening of the layers prepared by "soft" plasma treated precursors. The molecules are condensed, with a higher energy ,and the films are built up with higher densities. Therefore the surfaces are smoother – Fig 2-b,d, in comparison with those in Fig. 2-a,c. In the case of Fig 2-e,f, we observe the influence of the additional processes – thermal and MW treatment. Both surfaces of the PI layers with (Fig. 2 f) and without Ar plasma assisted deposition (Fig. 2 e) are smooth and defect free.

The SEM investigation of the cross sections indicates a thickening of the layer volume, as well as a change in the manner of fracture of the layer (Fig. 2 h) for the plasma treated films. The first effect is confirmed by the measured 30-40 percent higher Mhd of the layers, obtained by plasma assisted deposition.

The FTIR spectroscopy investigation results are shown in Figs. 3-6. The band at 1621 cm^{-1} (Fig. 3), which is related to the stretching vibration of the C-C bonds from the aromatic rings, shows a high degree of thickening at ODA in the Ar plasma assisted deposition, since it is single with a slightly implied shoulder to the left, in contrast to the ODA spectrum in normal conditions, where two bands are fixed.

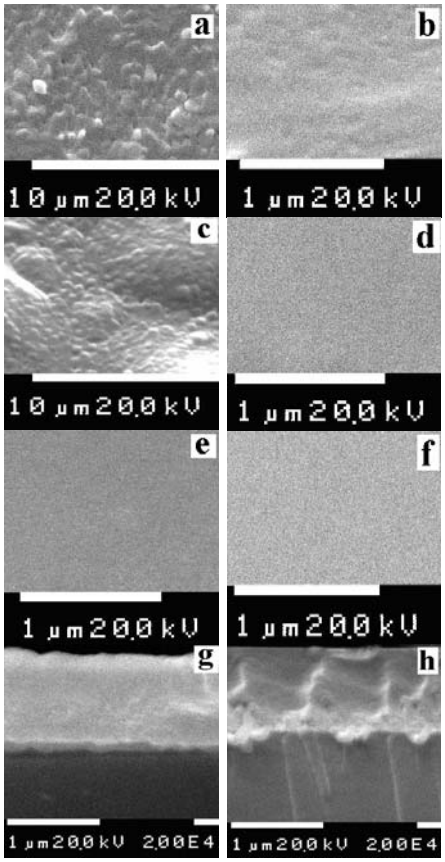

Fig.2. SEM micrographs of PMDA (a,b), ODA (c,d), PI (e,f)layers and PI cross section (g,h);(a,c,e,g) obtained without Ar plasma;(b,d,f,h) – obtained with Ar plasma assisted deposition.

This indicates an availability of more than one state in the arrangement of the layer obtain under normal conditions. The same conclusions are valid for the band centred at 827 cm-1. The bands for ODA obtained under normal conditions in the range 1400 to 1300 cm-1 and 1190 to 1000 cm-1 allow for the assumption that the molecules display a large spatial volume and are not fixed in one plane. Because of this, their capacity for vibration in the different planes is greater than the one in the ODA layers obtained in an Ar plasma [6,7].

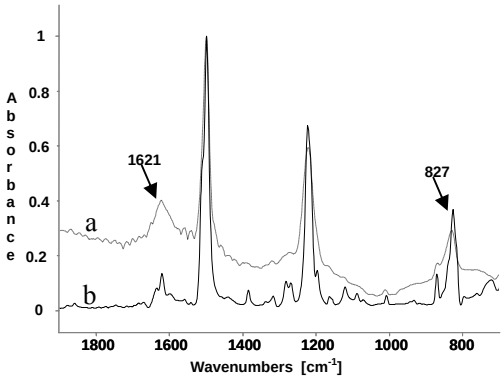

Fig.3. FTIR spectra of ODA films, 500 nm thick: (a) obtained with Ar plasma assisted deposition; (b) obtained without Ar plasma assisted deposition.

From the spectra presented in Fig. 4 (PMDA), the following interpretations can be proposed. The differences in the areas and peaks in the range 1800-1700 cm^{-1} confirm the changes in the carbonyl group. The spectra in the range 1300-1100 cm^{-1} register the deformation vibrations of the acid, ester and anhydride, and out of the plane vibrations of the carbonyl group at 950 – 750 cm^{-1}. In a PMDA layer deposited in a normal atmosphere, there is an opening of the benzene ring (hydrolysis to pyromellitic acid) which is confirmed by both main bands in the carbonyl range – peaks at 1731 cm^{-1} (for the anhydride) and 1696 cm^{-1} for the acid. Also, in a PMDA layer formed in plasma assisted deposition this band is single, greatly broadened and centred at 1717 cm^{-1} where the anhydride vibrations overlap. The bands at 1406 and 1385 cm^{-1} confirm the deformation vibrations of the C-O-H group from the acid. The complex bands at 1259, 1278 and 1304 cm^{-1} characterize the deformation vibrations of the O-C bonds which are related to the acid, ester and anhydride bonds. A typical band for the carboxyl group in the field of the out of the plane vibrations is 950 - 905 cm^{-1}. It can be concluded that for the PMDA deposited in the presence of an Ar plasma, a greater part of the molecules form closed rings (anhydride) as compared to the PMDA deposited under standard conditions. This means that a drying process is taking place simultaneously [8].

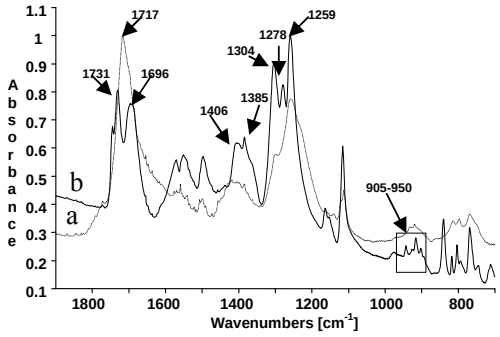

Fig.4. FTIR spectra of PMDA films, 500 nm thick: (a) obtained with Ar plasma assisted deposition; (b) obtained without Ar plasma assisted deposition.

The FTIR spectra in Fig. 5 (PI) are normalized at 1500 cm^{-1} [3,4]. By applying treatment in an Ar plasma when the PI layers are formed, the processes of formation of a new phase or destruction are not established. A process of initial imidization is observed (a band at 1384 cm^{-1} emerges in the thermally untreated layer obtained in the presence of the Ar plasma, while under normal conditions such a band is absent). In the untreated layer deposited under standard conditions [3,4] the quantity of the polyamide acid is greater. On the contrary, in the Ar plasma treated flux, the PI is formed more easily because the precursor molecules react more actively and at a greater rate.

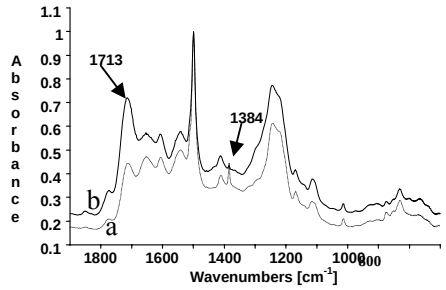

Fig. 5. FTIR spectra of PI films, 500 nm thick, untreated after deposition: (a) obtained with Ar plasma; (b) obtained without Ar plasma assisted deposition.

The FTIR spectra presented in Fig.6 categorically corroborate the fact that the imidization in the PI obtained by Ar plasma assisted deposition is facilitated (the spectra are normalized at 1500 cm^{-1}). In this case, the molecules would react more easily and at a greater rate, due to the additional energy which they have gained in the deposition in the presence of Ar plasma assisted evaporation. Moreover, as the energy for breaking the bonds in the precursor molecules is sufficient that it is feasible that other properties such as the conductivity could be influenced over broad limits.

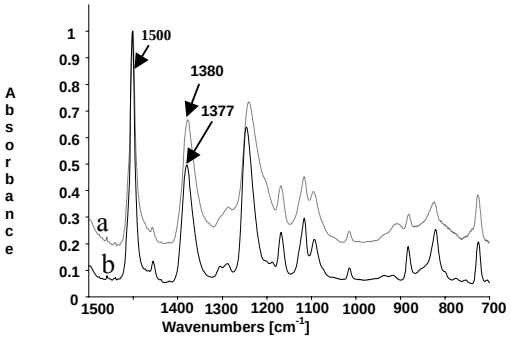

Fig.6. FTIR spectra of PI films, 500 nm thick, treated after deposition (5 min. MW and 15 min. thermal treatment): (a) obtained with an Ar plasma; (b) obtained without Ar plasma assisted deposition.

4. Conclusions

A new mode of physical deposition of polyimide thin films employing ion beam (plasma) assisted deposition has been developed. The impact of the Ar plasma on the precursor molecular flux provokes an increase in the kinetic energy of the molecules. In this way, the plasma treatment leads to an activation of the precursor molecules, and so to an enhancement of the imidization process, with changes in the structure (thickening of the layers), as well as influencing the film properties (an increase in the Mhd). The proposed method allows the changing of the investigated parameters of vacuum deposited polyimide films, in the direction desired by us.

Acknowledgements

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*Corresponding author: dean@clf.bas.bg