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Deposition of polyimide layers by applying argon plasma

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A new method for physical deposition of thin polyimide layers was developed by applying argon plasma assisting process. The study included both the impact on the individual precursors (oxydianiline (ODA) and pyromellitic dianhydride (PMDA)) and that on the combined molecular flux of both precursors. SEM study showed considerable changes in the structures of the condensed precursors. It was established that the plasma assisted deposition leaded to an increase in the layer thickening with remarkable changes in their surface morphology. As a consequence the measured microhardness of the polyimide layers increased more than two times. The results from FTIR analyses confirmed the formation of closed anhydride rings of PMDA, which is an indication that in this way the "soft" plasma treating contributes to the proceeding of the imidization process. The observed effects were explained by the increased energy of the precursor molecules as a results of the interaction with the plasma.

Keywords: Ar plasma, polyimide, evaporation

INTRODUCTION

Polyimides have evolved in the past 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]. Different methods such as spin-coating, dipping, roll to roll, vapor deposition polymerization, ionized cluster beam deposition and the recently developed method - glow discharge have been used for obtain PI coating [2]. Danev and Spasova have prepared thin PI layers by physical vapor deposition of precursors [3] and studied their properties [4] in view of their applicability in optics and electronics. It was found that the prepared films exhibited specific surface defects due to the low thermal energy of the deposited precursor molecules [4]. By adding extra energy during their deposition it can be expected the improving the film quality.

In this paper we investigate the effect of plasma assisted deposition of the precursor molecule flux on the properties of obtained PI layers. Our assumption was that the influence of the plasma flux would result an increase of the precursor molecule mobility. This would lead to a considerable reduction of the number of surface defects in the layers and probably to a greater film density.

EXPERIMENTAL

Sample preparation

The 500 nm thick PI layers 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 vessels sources (Fig.1). The pressure was ≤ $5x10^{-4}$ Pa. The evaporation temperatures were 120 - 145°C for PMDA and 100 - 110°C for ODA, and they were strictly controlled at all steps of vacuum deposition. The deposition rates were 0.2 – 0.38 $nm.sec^{-1}$, controlled by quartz oscillators. The layers were grown by argon plasma assisted processes. The ion beam was irradiated perpendicular to the vapor flux as it can be seen in Fig. 1. The plasma conditions were: cathode current – 22 A; anode current – 0,6 A; anode DC voltage – 120 V at constant Ar flux.

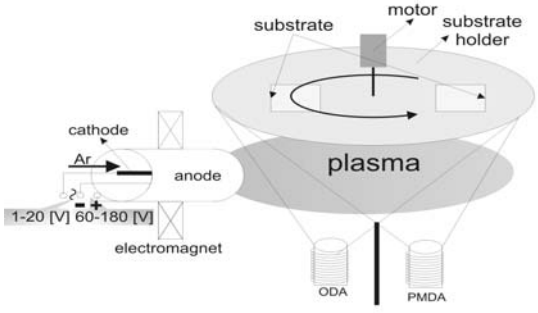

Fig. 1. Detailed scheme of the experimental set up.

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In our past work we have found that for complete transforming of deposited co-precursors into polyimide, the films had to be treated for 5 min in microwave oven followed by thermal treatment for 15 min at 300°C in air environment [5].

Methods of investigation

The surface morphology of the films was studied by means of scanning electron microscope (SEM), Philips 515. The FTIR spectra of PI on KBr substrate were recorded by a Bruker interferometer in the range of 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 sensitive for measuring the hardness of the thin films. The polar and dispersion surface free energy of films were determined on the basis of the theory of Owens, Wendt, Kaeble and Uy according to procedure explained in details elsewhere [9].

RESULTS AND DISCUSSION

SEM micrographs of the studied films are presented in Fig. 2 and Fig. 3. The surfaces of PMDA and ODA precursors films obtained in Ar plasma (Fig. 2-b, d) a smoother than those of the films obtained without plasma (Fig. 2-a, c). Both

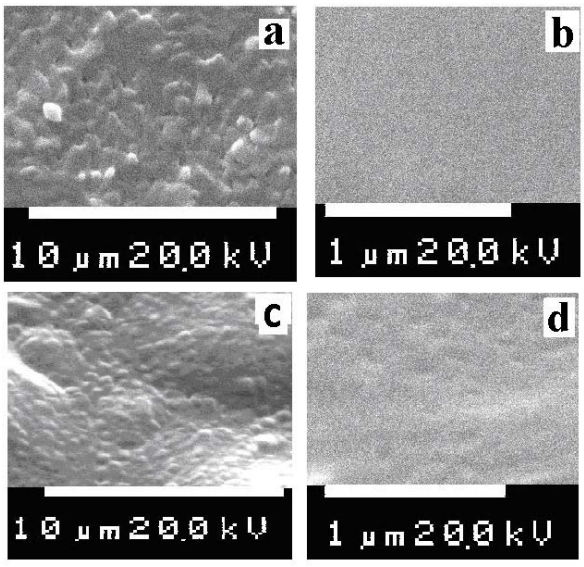

Fig. 2. Top-view SEM images of as-deposited films of PMDA (a, b), ODA (c, d), obtained without (a, c) and with Ar plasma assisted deposition (b, d).

surfaces of the PI layers without (Fig. 3a) and with Ar plasma assisted deposition (Fig. 3b) are smooth and defectless. The SEM investigation of the cross sections indicates a thickening and better ordering of the layer volume as well as a change in

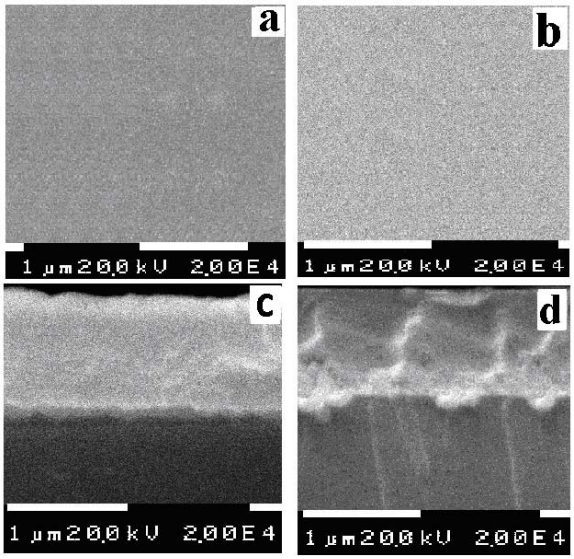

Fig. 3. Top view (a, b) and cross-sectional view (c, d) SEM images of PI films obtained without (a, c) and with Ar plasma assisted deposition (b, d).

fracturing of the plasma treated films (Fig. 3d). The observed changes in the film structure (Fig. 2b, d and Fig. 3d) could be explained as results from the reordered and increased thickening of the layers prepared by "soft" plasma treated precursors. Most probably the precursor molecules condense on substrate with higher energy and the films are grown up with higher density. It is also possible a polymerization process of precursors to take place.

Table 1 shows results from microhardness measurement of the layers obtained without and with plasma assisted evaporation. It can be seen two times higher microhardness of the layers, obtained by plasma assisted deposition which is consistent with the result of SEM study.

Table 1. Microhardness Mhd of PI layers obtained without and with Ar plasma during their deposition

PI layer obtained:	Mhd [GPa]
without Ar plasma	0.577
with Ar plasma	1.343

The results of FTIR spectroscopy investigations are shown in Fig 4. The band at 1621 cm^{-1} (Fig. 4a,b) which is related to the stretching vibration of the C-C bonds from the aromatic rings shows a high degree of thickening of ODA in the Ar plasma assisted deposition, since it is single with a slightly implied shoulder to the left by contrast to the spectrum of ODA obtained at normal conditions, where two bands are fixed. This indicates an availability of more than one state in the

arrangement of the layer obtained by normal conditions. The same conclusions are valid also for the band centered at 827 cm^{-1}. The bands for ODA obtained under normal conditions in the range of 1400 to 1300 cm^{-1} and 1190 to 1000 cm^{-1} lead to the assumption that the molecules display a great spatial volume and are not fixed in one plane, because their capacity for vibration in the different planes is greater than that of ODA layers obtained in Ar plasma [6, 7].

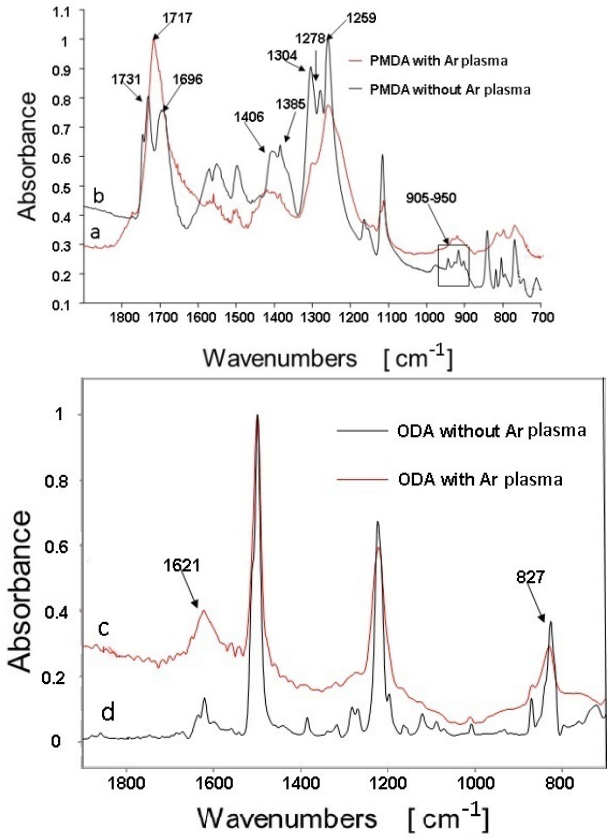

Fig. 4. FTIR spectra of 500 nm thick ODA and PMDA as-deposited films: a/ and c/ obtained with Ar plasma assisted deposition; b / and d/ obtained without Ar plasma assisted deposition.

From the spectra presented in Fig. 4 following interpretations can be proposed: The differences in the area and peaks within 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 groups and out of the plane vibrations of the carbonyl group at 950 –750 cm^{-1}. In PMDA layer deposited in a normal atmosphere there is 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 centered 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 cm^{-1}, 1278 cm^{-1} 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 of the carboxyl group in the field of the out of the plane vibrations is at 950 - 905 cm^{-1}. On the basis of the results obtained it can be concluded that greater part of the PMDA molecules deposited in the presence of Ar plasma are with a closed ring (anhydride) in comparison with the PMDA deposited at standard conditions. This means that a drying process takes place in plasma deposited PMDA films [8].

The FTIR spectra of PI layers shown in Fig.5 are normalized at 1500 cm^{-1} [3, 4]. It can be seen

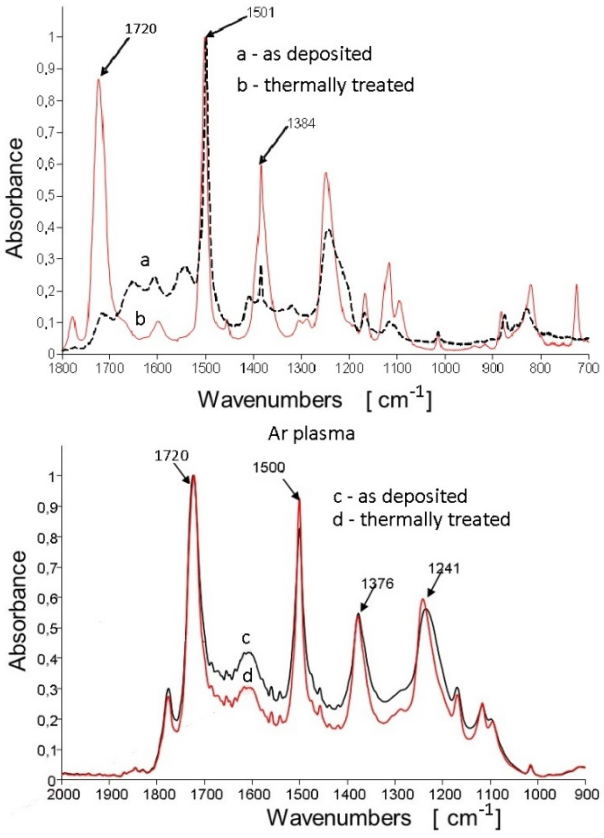

Fig. 5. FTIR spectra of 500 nm thick PI films a/ and c/ as-deposited; b/ and d/ thermally treated for 5 min. in MW oven and for 15 min. at 300°C in air; c/ and d/ are obtained with Ar plasma treatment.

that after thermal treating three imide bands are emerged at 1384 cm^{-1}, 1720 cm^{-1} and 1780 cm^{-1}. FTIR spectra do not indicate a new phase formation or destruction as a result of the applying Ar plasma treatment. Band at 1384 cm^{-1} emerges in the as-

deposited layer obtained in the presence of Ar plasma, while under normal conditions such band is absent, which is indication that the process of imidization takes place. In the as-deposited layer obtained at standard conditions without plasma the quantity of the polyamide acid is high [3, 4]. On the contrary our results show (Fig.5-c, d) that PI is formed more easily in the presence of Ar plasma because the precursor molecules react more actively and at a greater rate. FTIR spectra presented in Fig.5-c, d categorically corroborate the fact that imidization process takes place in the PI layers obtained by Ar plasma assisted process. The reason for the appearance of polyimide peaks in as deposited plasma treated films is not investigated in

Table 2. Contact angle, polar and dispersion component and overall free surface energy of PI layers deposited without and with Ar plasma.

PI layer obtained:	Contact angle		Polar component γ_s^p [mJ.m^{-2}]	Dispersion component γ_s^d [mJ.m^{-2}]	Surface energy [mJ.m^{-2}]
	H_2O	CH_2J_2			
without Ar plasma	93	31	0.26	43.8	44.1
with Ar plasma	73.6	16.0	4.55	45.36	49.91

details. Most probably the collisions between precursors, electrons and ions or the ultraviolet irradiation from the plasma influence strongly the imidization process.The influence of Ar plasma on the film surface energy is shown in Table 2. It is seen that the plasma treatment causes a small increase in the polar component of free energy. It can be expected that these changes in polar surface energy will be stable in time, because the layers are modified in the whole volume, not just at the surface. Obviously more detailed investigation is needed to confirm the assumption.

CONCLUSION

A new method of physical deposition of polyimide thin films employing plasma assisted deposition is developed. The impact of Ar plasma on the precursor molecular flux provokes an increasing in the kinetic energy of the molecules. In this way the plasma treating leads to an activation of the precursor molecules or some change of molecular structure of the precursors which results in an enhancement of the imidization process, in the thickening of the layers as well as in the increasing of microhardness. The results obtained show that the proposed method offers the possibility for changing the parameters of the vacuum deposited polyimide films in the direction desired by us.

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ОТЛАГАНЕ НА ПОЛИИМИДНИ СЛОЕВЕ ЧРЕЗ ПРИЛАГАНЕ НА АРГОНОВА ПЛАЗМА

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(Резюме)

Разработен е нов метод за физическо парно отлагане на тънки слоеве, чрез прилагане на плазмено асистиращи процеси. Изследването включва както въздействие върху индивидуалните прекурсори (оксидианилин (ОДА) и пиромелитов дианхидрид (PMDA)) така и върху двата мономера едновременно. Изследвано е влияние върху структурата на получените слоеве и промяна на свойствата им. Чрез SEM анализ, са показани значителни промени в структурата на кондензираните прекурсори. Установено е, че плазменото асистирано отлагане води до уплътняване на слоя, със забележителни промени в повърхностната им морфология. Наблюдавано е увеличаване на измерената микротвърдост с повече от 50 процента. Получените резултати от FTIR анализа потвърждават формирането на затворени анхидридни пръстени като по този начин плазмено асистиращо отлагане допринася за протичане на имидизационния процес. Наблюдаваните ефекти са обяснени с повишената енергия на прекурсорите, получена от взаимодействието с плазмата.