Ion – beam assisted process in the physical deposition of organic thin layers

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Abstract. A novel method was developed for physical deposition of thin polyimide layers by applying an argon plasma assisted process. The influence was investigated of the plasma on the combined molecular flux of the two thermally evaporated precursors – oxydianiline and pyromellitic dianhydride. The effects observed on the properties of the deposited films are explained with the increased energy of the precursor molecules resulting from the ion-molecular collisions. As could be expected, molecules with higher energy possess higher mobility and thus determine the modification of the films structure and their electrical properties.

1. Introduction

Polyimides (PI) are polymers with various applications thanks to their inherently good mechanical properties, high chemical resistance, low dielectric constant and high thermal stability. These polymers are, therefore, suitable as materials for insulating or protective layers and optical coatings [1, 2]. Physical evaporation of organic PI molecules is feasible at relatively low temperatures of deposition due to the thermal instability of the organic molecules. As a result, the thin organic layers formed have structural defects or micropores and cracks. To overcome this disadvantage, the use of electron assisted deposition (EAD) of PI precursors - oxydianiline(ODA) and pyromellitic dianhydride (PMDA) - was described by us in a previous paper [3]. This study was related to energy-stimulated processes based on the electron-treatment of the molecular flow of the PI precursors in the gas phase. The results obtained stimulated the development of an experimental technique for deposition of thin PI layers by applying a low-energy argon plasma assisted process. The aim of the present paper is to reveal the effects related to such as in view of the possibilities of applying this new type of process for production of thin PI layers.

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2. Experimental

2.1. Sample preparation
The PI layers were formed by vacuum co-deposition of the precursors ODA and PMDA from two independent heated vessel sources (figure 1) on a static substrate. The deposition rate was 0.2 – 0.4 nm/sec. The base pressure was $4 \times 10^{-2}$ Pa. The evaporation temperatures were 120 - 145$^\circ$C for PMDA and 100 - 110$^\circ$C for ODA. The layers were grown using Ar plasma assisted treatment processes: the molecular fluxes of the evaporated precursors cross the Ar plasma. Part of the ionized Ar molecules and electrons collide with the organic molecules of the precursors and act on the growing deposited layers. The plasma source was water-cooled in order to prevent excessive heating of the substrates. The processes parameters were as follows: cathode current 21 A; anode current 1.4 A; anode voltage 100 V. The layers obtained were transformed into PI by a 5-min microwave (MW) treatment (2.45 GHz, 700 W) followed by a 15-min thermal treatment at 300$^\circ$C in air [4].

2.2. Methods of investigation
The film microhardness (Mhd) was determined by the Knoop prism method known to be sensitive for measurements of thin films. The load value was 1.25 mPa for all samples studied.

The surface morphology of the layers was characterized by scanning electron microscopy (SEM), Philips 515. The FTIR spectra (PI on KBr substrate) were recorded by a Bruker interferometer in the range of 4400 - 450 cm$^{-1}$ with a resolution of 2 cm$^{-1}$.

2.2.1. Electrical measurements. The layers investigated were deposited on soda-lime glass substrates with previously prepared bottom Au electrodes. Aluminium top electrodes were then evaporated in vacuum perpendicularly to the Au electrodes. The resulting Au / PI / Al sandwich structures (figure 2) were again thermally treated at 200$^\circ$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 a computer controlled Keithley 617 electrometer. The conductivity ($\sigma$) was determined as the slope of the linear regression of the Ohmic part of the I-U curves.

3. Results and discussion
The FTIR spectroscopy investigation results are shown in figures 3 and 4. According to the kinetic theory of collisions, the reaction rate of depends mainly on the energy factor, i.e. the number of collisions between the particles of the reagents. These collisions are called effective and chemical interaction takes place only between the particles taking part in them. The reaction rate depends also on the so-called factor of orientation (a possible space volume factor) between the reagents. It expresses the probability for the appropriate spatial orientation needed for the accomplishment of effective collisions between them. In figure 3 the typical bands of PI are observed prior to and after the thermal treatment of the vacuum deposited layer (the band at 1384 cm$^{-1}$) and the ratio of the band areas at 1384 cm$^{-1}$ and 1500 cm$^{-1}$ is used for assessing the degree of imidization $\delta$ [5]. In this case $\delta = 0.89$ following the thermal treatment.
Applying treatment in Ar plasma with raising the current to $I_a=0.60$ A leads to $\delta$ gradually rising to 0.99. In this case, a process of imidization is observed even in the PI layer that was not thermally treated. Therefore, the application of PAD facilitates the imidization process.

Figure 5 presents the volt-ampere (I/U) characteristics of PI layers obtained without (a) and with (b) assisted treatment in Ar plasma. The deviations from the linear dependency at the beginning of the graphs (a) and (b) are probably due to contact imperfections such as, e.g., contact barriers. In the section where Ohm law is observed, i.e. the ratio $U/I$ is linear, the resistance ($R$) of the material can be calculated from the equation $R = U/I$ and this result could be interpreted as ohmic conductivity. The dependencies $I(U)$ in the linear scale satisfy the equation of a straight line which in its most common type is expressed by the equation $U = A + B \cdot I$, where $A$ and $B$ are the respective coefficients of this equation.

The parameter $\sigma$ can be determined from the data obtained as well. For the $\sigma$ thus calculated, values of $1/2.911$ S for an untreated in Ar plasma PI and $1/8.47$ S for treated in Ar plasma PI are obtained.

It is well-known that the electrical characteristics of the PI layers are especially sensitive to the pre-history of the layer formation. Chemical and structural defects, unfinished imidization, inclusions of radicals or parts of molecules obtained in the bond cleavage, cracks, pores and uncontrollable adsorption of gases from the residual atmosphere – all these phenomena exert an influence on the electrical parameters of the layers under study.

If the assumption that PAD contributes to the imidization process and the production of layers with less chemical and structural defects is true, then the four-fold increase of $\sigma$ of the PI layers obtained in the case of PAD application in Ar plasma is probably due to the reduction of the free volumes in the PI matrix, i.e. a thickening of the layers is achieved. This assumption is confirmed also by the SEM micrographs of the plasma treated and plasma untreated PI precursors PMDA (SEM in figure 6, a and b) and ODA (SEM in figure 6, c and d).
Figure 6. SEM micrographs of PMDA (a, b), ODA (c, d); (a, c) obtained without Ar plasma; (b, d) – obtained with Ar plasma assisted deposition.

It is obvious that the ion treatment accounts for the production of layers of a smoother as well as more even and thicker surface structure [6]. As a consequence of the layer thickening, the value of the measured Mhd of the PI layers increases by more than 40 percent.

4. Conclusion
It can be assumed that the plasma flux crossing the molecular flows of the PI precursors enhances the imidization process by partly activating the precursor molecules in the gas phase. Their increased kinetic energy, as well as their chemical activation, not only assist the formation of defectless layers but also the solid-phase reaction of PI synthesis. Thus, the possibility arises of shortening the duration of the post deposition treatment of the layers obtained. The films exhibit higher micro-hardness and lower electric resistance (by a factor of 4). The results obtained contribute to the controllability of the processes and widen the potential of physical deposition of organic layers by introducing a low-energy action on the molecular organic flux to produce layers of desired properties, such as a lower resistance and increased density, as is our case.

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References
[1] Mittal K L 2003 Polyimides and Other High Temperature Polymers 2 (V.S.P. Intl Science) p 241
[2] Vora R H, Krishnan P S G, Veeramani S and Goh S H 2003 Polyimides and Other High Temperature Polymers 2 (V.S.P. Intl Science) p 3
[3] Dimov D, Spassova E, Karamancheva I, Zhivkov I and Danev G 2004 Electron-assisted deposition of thin organic layers Vacuum 76 223-6
[4] Dimov D, Georgiev A, Spassova E, Karamancheva I Shopov Y and Danev G 2007 Microwave assisted processes for producing thin layer materials in the field of nanotechnology J. Optoelectr. Adv. Mater. 9/2 494-7
[5] Spassova E 2003 Vacuum deposited polyimide thin films Vacuum 70 551-61
[6] Dimov D, Danev G, Assa J, Spassova E 2008 Ion beam assisted process in the physical deposition of polyimide Proc. 13th Int. School on Condensed Matter Phys. (Varna, Bulgaria)