Physical deposition of thin polyimide layers by applying an argon plasma assisted process

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Abstract. A novel method for physical deposition of thin polyimide layers by applying an argon plasma assisted process has been developed. The influence of the plasma on the combined molecular flux of the two thermally evaporated precursors – 4,4’-oxydianiline and pyromellitic dianhydride was investigated. The process parameters were changed in the limits 0.4 – 2 A for the anode current and 80 – 170 V for the anode voltage. Their influence was studied using FTIR spectroscopy and electron microscopy techniques. It was proposed that the plasma flux crossing the molecular flows of the polyimide precursors enhances the imidization process by partly activating the precursor molecules in the gas phase.

1. Introduction
Polyimide (PI) is known to be a high performance aromatic polymer with outstanding mechanical and insulating properties, thermal and radiation stability [1]. This material is used in diversified areas such as space missions, nuclear, electronic and automotive industries [2]. For the last several decades, studies on the effects of high-energy radiation on polymer have become an important area of basic as well as applied research [3]. Several methods are available for the deposition of PI coatings on various substrates: from solution; vapour deposition polymerization (VDP) [4], ionized cluster beam deposition (ICBD) [5] and glow discharge induced VDP (GDVDP). The sputtering technique cannot be extended to the deposition of PI layers [6], because the ion bombardment of the target (a Kapton™ disk) is inapplicable for the ether and imide groups of the PI molecule. The chemical composition of the deposited film is different from the original PI. In the GDVDP method the evaporation of the monomers is not obtained by heating, but by the standard radio frequency magnetron sputtering equipment. In this paper we report a novel method for the physical deposition of thin PI layers by applying an argon (Ar) plasma assisted process in the deposition of the monomer vapours (obtained by heating) on a substrate taking place in a vacuum chamber. The aim of the paper is to describe the influence of the process parameters on the PI layer properties.

2. Experimental
The 500 nm PI layers were formed by vacuum co-deposition of the precursors 4,4’-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) from two independently heated vessel sources (Figure 1). The deposition rate was 0.2 – 0.4 nm/sec and base pressure $4 \times 10^{-2}$ Pa. The layers were grown using an Ar
plasma assisted process: the molecular fluxes of the evaporated precursors cross the Ar plasma. A part of the ionized Ar molecules and electrons collide with the precursor molecules and act on the growing deposited layers. In order to trace the influence of the assisted process we have studied PI layers, obtained at: a/ anode current (Ia) = 0.6 A and change of the anode potential difference (Ua) from 80 to 170 V; б/ Ua of 100 V and a shift in the Ia from 0.4 to 2 A. The obtained layers were transformed into PI by a thermal treatment 1h at 180°C followed by a 15 min at 300°C in air. The layers were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and by Transmission electron microscopy (TEM), JEM 2100. The FTIR spectra (PI deposited on KBr substrate) were recorded by a Bruker Tensor 27 spectrometer in the range of 4400 - 450 cm\(^{-1}\) with a resolution of 2 cm\(^{-1}\).

**Figure 1.** A detailed scheme of the system for plasma assisted deposition (PAD).

### 3. Results and discussion

The FTIR spectroscopy investigation results are shown in figures 2 and 3. The follow-up of the changes in the FTIR spectra shows that with the increase of Ua from 80 to 120 V (figure 2a, 2b, 2c) a gradual change of the band characterizing the imidization process (1376 cm\(^{-1}\)) is observed. Its intensity grows with the change of Ua and at Ua = 120 V (figure 2c) it is most intensive and most narrow. The same is also true in the band at 1241 cm\(^{-1}\), characterizing the molecular vibrations of the PI. At Ua = 170 V (figure 2d) the quality of the produced film is abruptly impaired. This is also corroborated by the non-characteristic bands for the PI in the long area of the stretching C-C vibrations at 1500 cm\(^{-1}\) for the aromatic ring, the range of the molecular vibrations as well as by the band typical of the degree of imidization (δ) at 1376 cm\(^{-1}\). A conclusion can be drawn that at Ia= 0.6 A and Ua = 120 V the obtained PI is of the best quality. Upon applying an plasma assisted deposition (PAD) process at Ia=0.4A (figure 3a) one could presume that the imidization process is facilitate as early as in the precursor deposition process. The band at 1378 cm\(^{-1}\) is shifted by 6 cm\(^{-1}\) to the lower frequencies as opposed to the PI obtained without PAD and δ is respectively greater. With the increase of Ia to 0.60A δ grows evenly and reaches maximum value (figure 3b). At Ia=1.0A (figure 3c) a shoulder at 1339 cm\(^{-1}\) on the imide band (1377 cm\(^{-1}\)) emerges. This could possibly mark the onset of destructive processes in the molecular fluxes of the evaporated PI precursors. The obtained PI should be containing low-molecular fragments which would impair its physical and chemical properties. At Ia=1.25 A (figure 3d), the shoulder at 1339 cm\(^{-1}\) on the imide band (1377 cm\(^{-1}\)) is clearly expressed, the band is slightly distorted which testified to a decrease of the effect of imidization and the formation of by-products as a consequence from the destruction of the precursors.

The entire PI spectrum is of low quality. With the increase of Ia above 1,25 A the massive deformation and splitting of the imide band and that characterizing the stretching vibrations of the aromatic ring (1500 cm\(^{-1}\)) was established. It supports our idea about the chemical alteration of the initial precursors under the influence of PAD leading to the PI of an impaired qualities and unclear composition.
Figure 2. PI layers with PAD and $I_a = 0.6\,\text{A}$: full linear - thermally treated; dashed lines - thermally untreated.

Figure 3. PI layers with PAD and $U_a = 100\,\text{V}$: full linear - thermally treated; dashed lines - thermally untreated.
The obtained results also show the effect of the $I_a$ on the properties of the produced layers is much stronger than that of the $U_a$. The PI layers obtained at $I_a = 0.4$ to $0.6$ A and $U_a = 100$ to $120$ V are of best quality which is also confirmed by the TEM micrographs (figure 4). Upon applying PAD the structure of the produced films is of finer granularity and is smoother.

![Figure 4. TEM micrographs of 50 nm VDP PI layers: a/ without PAD; b/ with PAD: $I_a = 0.6$; $U_a = 100$V](image)

4. Conclusions
The results from the research carried out show that the effect of $I_a$ on the properties of the obtained layers is much stronger than that of $U_a$. The PI layers obtained at $I_a = 0.4$ to $0.6$ A and $U_a = 100$ to $120$ V are of best quality and unchanged chemical composition. The observed effects on the properties of the deposited films are explained with the increased energy of the precursor molecules resulting from the ion-molecular collisions. 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. The presented new method, developed for the physical deposition of thin PI (PMDA/ODA) layers can probably be successfully used for the deposition of other polymeric films.

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