PLASMA INDUCED CHANGES ON THE SURFACE FEATURES OF A POLYIMIDE AND THEIR ROLE IN INTERFACIAL ADHESION

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Abstract: *Optoelectronic and electronic devices have known an outstanding development once the polymers have been introduced in these fields. Circuit elements are often made by combining insulators with conductors, so plastics are often interfaced with metals. The present paper investigates the role of plasma treatment in optimization of compatibility of a polyimide with several metals used in electronic circuits design. Plasma produced changes in surface topography and wettability are discussed. Atomic force microscopy (AFM) scans are employed to analyze some surface texture parameters that can be improved for higher polymer/metal interfacial compatibility. Surface energy components are used for assessment of the work of adhesion of the pristine and modified sample surface with several metals. The reported data have are paramount for fabrication of circuits with high reliability.*

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Keywords: *polyimide, plasma, morphology, adhesion.*

1. Introduction

Polymers are widely recognized as high engineering plastics and they are encountered in numerous applications, ranging from electronic products, membranes, aircraft equipments and biomedical devices [Zia,2017]. Among the technical uses of the these materials, a special attention was drawn towards the field of micro/nano-electronics [Nilagiri,2018]. Depending on their physico-chemical properties, polymers can be employed as semi-conductors or insulators [Lai, 1989]. In the latter case, the polymer dielectric has the role to attenuate the interference of the signals passing through the conductor metal lines from the electrical circuit. For this purpose, the polymer must fulfill certain important criteria, particularly low dielectric constant, roughened morphology and good interfacial wetting.

Among the engineering polymers, polyimides (PIs) are often used for manufacturing electronic circuits owing to their mechanical and thermal resistance, combined with excellent film forming abilities [Ghosh,1996]. However, conventional PIs display strong charge transfer complex (CTC), which is known to decrease solubility and to increase absorption properties [Watari,2012]. Moreover, CTC interactions are contributing to the augmentation of the dielectric constant [Mathews,2007]. So, the solution for this issue is to introduce in the polymer synthesis cycloaliphatic monomers that reduce the CTCs, while improving the polymer solubility, optical and dielectric performance [Mathews,2006].

During PI implementation in the electrical circuit, it is of paramount importance to investigate their morphological and wettability properties. Higher surface roughness and polarity are key factors for attaining good interfacial adhesion of PI with the neighboring metal conductors. To enhance these properties, plasma treatment of the PI film surface is frequently applied [Nakamura, 1996; Lee, 2009].

In this paper, a semi-aromatic PI film is prepared and subjected to plasma treatment for testing its adhesion with some metals and metal alloys. The topography changes were examined using atomic force microscopy experiments. The PI/metal interfacial compatibility is evaluated using surface tension concepts. The reported data have are essential for proper design of circuits with upgraded reliability.

2. Materials

The semi-aromatic PI is the result of the polycondensation reaction in solution of 5-(2,5-Dioxotetrahydrofurfuryl)-3- methyl-3-cyclohexene- 1,2-dicarboxylic acid anhydride (EPICLON) and 1,4-bis(p-aminophenoxy)benzene. Details of the preparation procedure are previously reported [Hulubei,2007]. To visualize the flexibility of this polymer, molecular modeling is done with Chem 3D Ultra 8 (demo version) for 6 structural units (SUs). The chemical structure of the PI sample and its simulated conformation are illustrated in Figure 1.

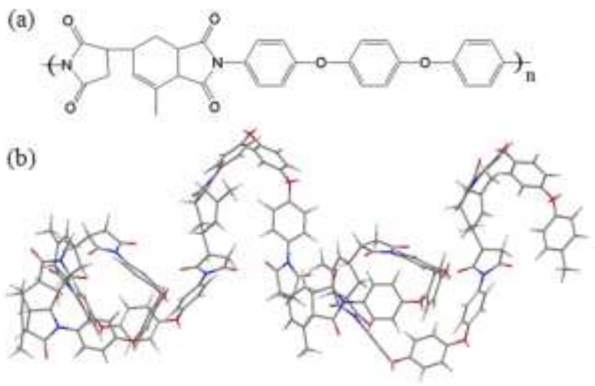

Figure 1: *The chemical structure (a) and molecular modeled conformation of 6 SUs at minimized energy (b) of the studied PI structure.*

Plasma treatment of the PI film is performed using air as working gas and high frequency system. An electric field intensity of 3000 V/cm was set together with a 0.6 mbarr pressure and 100 W power. The sample was placed between the electrodes and exposed in the glow discharge for 10 minutes.

Atomic force microscopy (AFM) was used to investigate the surface morphology of the samples before and after the plasma treatment. Scanning probe microscope Solver Pro-M from NT-MDT (Zelenograd, Russia) was operated in tapping mode, in atmospheric conditions, with a NSG 10 cantilever also from NT-MDT (Zelenograd, Russia), having the resonance frequency of 254 kHz, using a set point of 8 V, feedback gain of 0.575, scan velocity of 15.69 μm/s, with a step of 19 nm, over areas of 5x5 and 1x1 μm^2. Image Analysis 3.5.0.19892 software from NT-DMT was employed to obtain the AFM images, the height histograms, bearing area curves, and the height, hybrid, shape and functional texture parameters, namely arithmetical mean height (average roughness) of the surface (Sa), surface area ratio (Sdr), kurtosis of height distribution (Sku), skewness of height distribution (Ssk), peak material volume (Vmp), core material volume (Vmc), core void volume (Vvc), pit void volume (Vvv).

Surface wettability of the pristine and plasma irradiated films was assessed from contact angle data as presented in a previous study [Ioan,2007].

3. Results and discussion

3.1 Morphological analysis

The PIs containing EPICLON in their structure are known to lead to films characterized by low surface roughness [Cosutchi,2008; Stoica,2013;Stoica,2017]. When investigating the surface of the PI films before the plasma treatment by means of AFM technique (Figure 2), morphological features evenly distributed over the entire scanning area were observed, having the appearance of a real network. As seen in Table 1, indeed, the value of the average roughness of around 1 nm was very small. This aspect could be explained based on the particularity of the polymer chains that lead to molecular ordering and cluster, which occur during thermal imidization and drying processes.

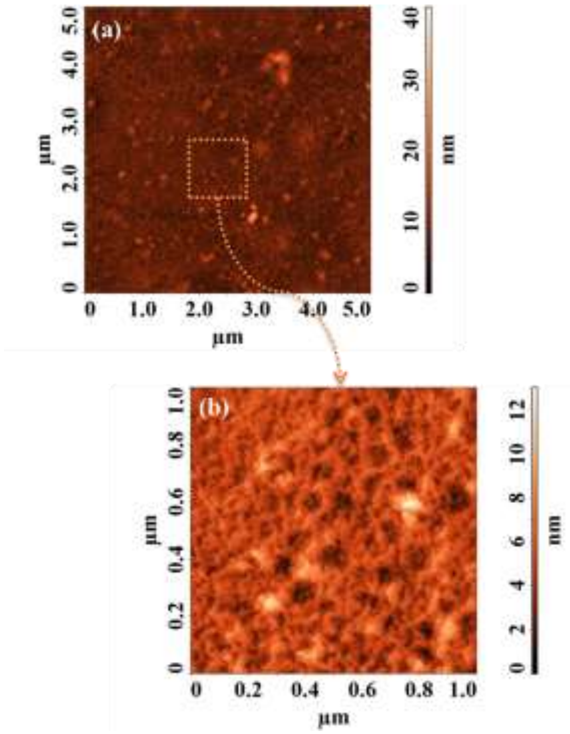

Figure 2: *AFM morphology images of the studied PI film collected over 5x5 µm^2 (a) and 1x1 µm^2 (b) scanning area.*

Plasma treatment has the advantage of preserving the bulk properties, while the surface properties can be rightly adjusted for the pursued applications. In our case, after the plasma irradiation, the polymer surface was visible chemically modified, leading to the occurrence of different morphological characteristics, in granular form (as observed in Figure 3). These grains well-repartitioned upon the surface favor the enhancement of the roughness and complexity of morphology, suggested by the hybrid parameter surface area ratio from Table 1, phenomenon which remains constant in time, as found in experiments performed at significant time intervals. Also, the increase of the surface area ratio suggests the increase of the ability to adhesive junctions.

To see how the plasma irradiation influences the aspect of the texture height distribution, the height histograms were represented for each sample (as noted in the Figure 4) and shape parameters kurtosis and skewness of height distribution were calculated. The resulted values are illustrated in the Table 1.

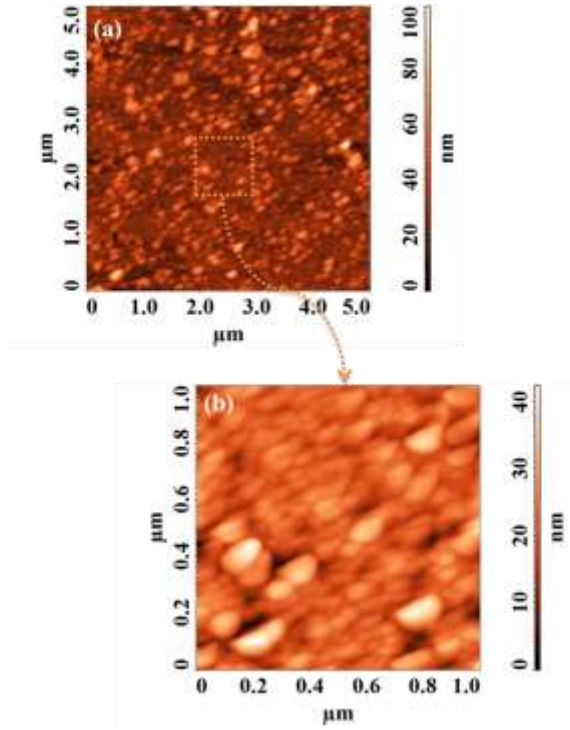

Figure 3: *AFM morphology images of the studied plasma treated PI film collected over 5x5 µm^2 (a) and 1x1 µm^2 (b) scanning area.*

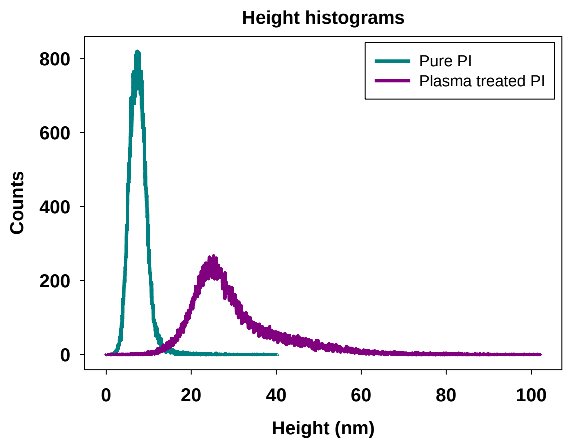

Figure 4: *AFM height histograms obtained for pure and plasma treated PI films, collected over 5x5 µm^2 scanning area.*

Table 1: *Height, hybrid and shape parameters calculated based on AFM images and height histograms obtained for PI before and after plasma treatment.*

Sample	Height, hybrid and shape parameters on 5x5 μm²			
	Sa	Sdr	Sku	Ssk
Pure PI	1.6	1.065	13.176	1.648
Plasma treated PI	7.8	5.409	6.041	1.463

Sa: arithmetical mean height (average roughness) of the surface (nm); Sdr: surface area ratio (%); Sku: kurtosis of height distribution; Ssk: skewness of height distribution

According to these data, the height distribution of the pure PI is narrow, while in the case of the plasma treated sample it is much wider, indicating a bumpy morphology. In both cases the material is situated below the mean plane. Also after the plasma irradiation the decrease of the kurtosis indicated an improve the contact of the rough surface with different metal layers, according to Belhadjamor et al. [Belhadjamor,2020].

The bearing area curves (also called the Abbot-Firestone curves) were represented for pure and plasma treated PI films (Figure 5) starting from the AFM Height images from Figures 2 and 3. These curves are helpful in estimating the functional volume parameters (Table 2) that are used to evaluate the tribological performance of the surfaces.

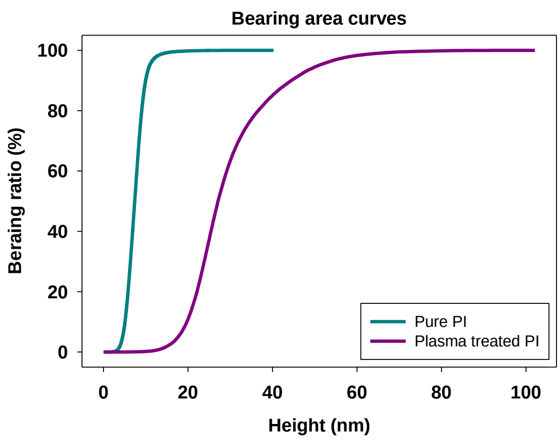

Figure 5: *AFM bearing area curves obtained for pure and plasma treated PI films, collected over 5x5 μm² scanning area.*

Table 2: *Functional volume parameters calculated based on AFM images and bearing area curves obtained for PI before and after plasma treatment*

Sample	Functional volume parameters on 5x5 μm²			
	Vmp	Vmc	Vvc	Vvv
Pure PI	0.099	1.322	1.742	0.148
Plasma treated PI	0.892	7.424	14.909	0.625

Vmp: peak material volume (nm^3/nm^2); Vmc: core material volume (nm^3/nm^2); Vvc: core void volume (nm^3/nm^2); Vvv: pit void volume (nm^3/nm^2)

It can be seen that all the functional volume parameters are improved after plasma treatment, showing a low wear assessment, important in technical control of manufacturing of the components for electric devices.

3.2 Interfacial adhesion

In an electrical circuit, the PI film is found in continuous contact with the wire conductors. The role of the PI is mainly to insulate the metal lines and to ensure high speed of the signal through circuit. In addition to this, the polymer must have good interfacial compatibility to the inorganic phase. Work of adhesion (W_A) was determined using the following relation:

$$W_A = 2\left(\gamma_p^{disp} \cdot \gamma_m^{disp}\right)^{1/2} + 2\left(\gamma_p^{+} \cdot \gamma_m^{-}\right)^{1/2} + + 2\left(\gamma_p^{-} \cdot \gamma_m^{+}\right)^{1/2} \quad (1)$$

where γ denotes the surface tension, the subscripts "p" and "m" refer to the polymer and metal, while the superscript "-" and "+" are indicating the electron-donor and electron-acceptor parameters of the polar surface tension corresponding to each phase.

The adhesion of the samples with some metals and metal alloys was estimated. Figure 5 presents the obtained data regarding W_A parameter. For the untreated PI film, the highest adhesion was achieved for Cr and Al and lowest for TiAlCrN alloy. It can be remarked that upon plasma exposure the adhesion of the PI to all the considered inorganic phases is enhanced. This ensures an adequate compatibility of the polymer to the metal layer as demanded in electronic applications.

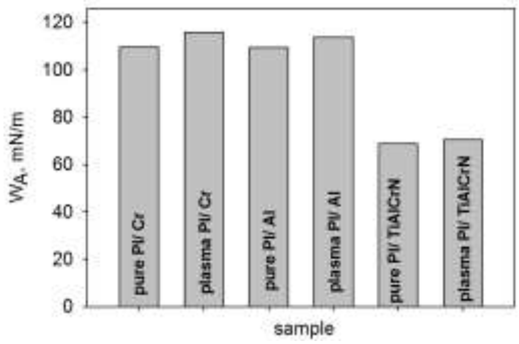

Figure 5: *The impact of the plasma exposure of PI films on the adhesion to Cr, Al and TiAlCrN.*

4. Conclusions

A semi-aromatic PI resulted from the polycondensation reaction was processed in the form of film. The surface properties were investigated before and after plasma treatment, in order to improve the sample adhesion to metal layers as demanded in electronic applications. According to the AFM data, the complexity of the morphology was changed after the irradiation, and with it there was a significant increase in roughness. The evaluation of the shape parameters indicated an improvement of the rough surface contact with different inorganic layers, such as metal or alloys. Also important in technical control of manufacturing, the functional volume parameters were improved after the plasma treatment, showing a low wear assessment.

The polymer interfacial compatibility to the inorganic phase was evaluated through the work of adhesion, finding that the highest adhesion is achieved for Cr and Al and lowest for TiAlCrN alloy and that this phenomenon is amplified by the plasma treatment. This offers a guarantee that the compatibility of the polymer to metal layer is suitable, as requested in electronic applications.

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