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THE EFFECT OF RF PLASMA TREATMENT ON THE SURFACE ACTIVATION OF POLYCARBONATE SUBSTRATE

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Abstract

In the present study the effect of Ar and Ar/O_2 RF plasma treatment of the surface of the polycarbonate (PC) substrates has been studied. Changes in the surface free energy of the polymer substrates were followed in dependence of the plasma treatment condition (plasma power and plasma treatment time). The polar γ_s^p and dispersion γ_s^d components of the polymer surface free energy were determined on the basis of the theory of Owens, Wendt, Kaelble and Uy. It was found that γ_s^p increase rapidly within the first 1-3 minutes at higher RF power, while γ_s^d changes slightly after all plasma gases treatments. The Ar/O_2 plasma treatment at higher RF power also led to pronounced improvement of the adhesion of thin ZnO film, plasma deposited on the modified PC substrate.

1. Introduction

In recent years, optical polymers like polycarbonate have substituted glass products in many optical applications where low weights, chemical inertness, high impact resistance, flexible formability as well as relatively low cost are of major importance. The depositing of thin films on polymer substrates is becoming increasingly important for an application in flat-panel displays, transparent electrodes, thin layer transistors, solar cells, sensors and other optoelectronic devices. However, the desirable bulk properties of polymers are often compromised by their unfavourable surface characteristics, such as low hardness, low resistance to abrasion and scratching, and low surface energy, which generally leads to low wettability and poor adhesion [1].

Low pressure, soft plasma treatment has been successfully used as a dry process to alter the surface properties of polymers. (for review see [2]). The effect of plasma treatment depends on a variety of parameters such as the kind of plasma (DC, radio frequency (RF) or microwave (MW)), the discharge power density, the pressure and flow rate of the gas or gas mixture, as well as the treatment time [3-5]. Typically, a reactive plasma (H_2O or O_2) is used to add a polar functional group (hydroxyl, carboxyl, ether, carbonyl etc.), which can dramatically increase the surface free energy of the polymer [2, 6].

In the present paper the effect of Ar and Ar/O_2 RF plasma treatment on the free surface energy of the polycarbonate substrates has been studied in dependence of the plasma treatment condition (plasma power and plasma treatment time). The influence of plasma treatments on the adhesion of thin ZnO films, plasma deposited on the modified PC substrates has been also followed.

2. Experimental

All samples of commercial PC substrates of optical quality, used widely in polymer optics were carefully cleaned before plasma treatment with iso-propanol. The gas plasma was excited by a 13.56 MHz RF generator in a GENUS 8720 plasma enhanced chemical vapor deposition facility. RF power was varied within 500- 2000W range and treatment time – between 1- 30 min. The working pressure of 150 mTorr was kept constant for all treatments.

The surface energy was calculated as sum of dispersive energy and the polar energy on the basis of the Owens - Wendt and Kaelble-Uy theory. The wetting angles of bidistilled water and methylene iodide were measured by the sessile drop method proposed by Bickerman. The theory and the method are described in details in our previous paper [7, 8].

The ZnO films with thickness of about 500 nm were plasma deposited by an oxidation of Zinc acetylacetonate hydrate in the same vacuum cycle immediately after plasma treating. Adhesion of ZnO films on substrates was evaluated with adhesive tape (3M Scotch Magic Type 810) according to ASTM D3359-97 [8].

3. Results

On the basis of the contact angle data, the polar γ_s^p and dispersion γ_s^d components of the surface energy of 1.2 and 40.2 mJ m^{-2} respectively were determined for untreated PC. These values agree well with literature data. The low values of the polar components indicate the hydrophobic nature of PC substrates. Fig. 1 (a, b) shows the changes in γ_s^p after Ar and 3:1 Ar/O plasma treatment at indicated RF powers. It is seen that γ_s^p is altered after all plasma treatment. The polar component increase rapidly within the first 1-3 minutes at higher RF power. The partial replacement of Ar with O_2 gas leads to the relatively greatest enhancement of the polar component of the free surface energy up to 35 mJ m^{-2} which indicates the most hydrophilic and wettable surface. It is seen that at lower RF power of 500 W γ_s^p could not be enhanced > 20 mJ m^{-2} even at prolonged treatment. Most probably the ion flux increases with

RF power and this feature enhances the efficiency of plasma treatment. Under the condition of RF power of 1000- 2000 W high ion flux helps in saving the plasma treatment time an as a result γ_s^p increases most rapidly in first 1-3 minutes. The polar force component arises from the orientation of permanent electric dipoles, which includes dipole-dipole interactions, dipole-induced dipole interactions, hydrogen bonds, π-bonds, charge transfer interactions, etc. It has been shown that the surface energy of the PC substrate is increased by enhancement of the number of the polar functional group such as C=O, C-O and C-H [9]. The C=O bond has the largest dipole moment and is the most effective in increasing the surface energy. However, these bonds could be broken by other ions impinged the surface which is most probably the reason for the γ_s^p decrease with plasma treatment time at higher RF power.

It should be noted that in contrast to the polar component, the dispersion component changes slightly after all plasma gases treatments. Dispersion forces are related to the internal electron motions, independent of the dipole moments. Thus the incorporation of polar functional group to a polymer surface should not have much effect on γ_s^d, which is consistent with the results obtained.

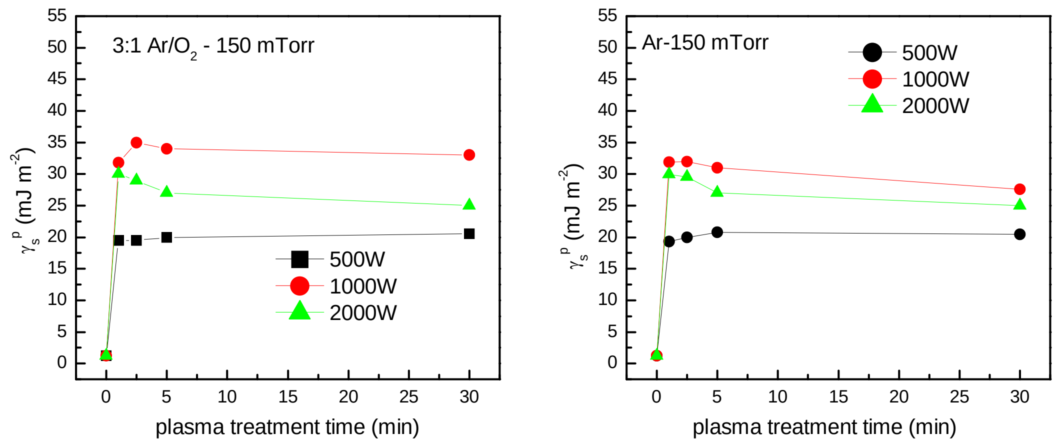

Fig. 1. The polar γ_s^p component of the free surface energy of PC treated in Ar and 3:1 Ar/O_2 plasma vs treatment time at indicated RF power.

The effects of plasma treatments on the adhesion of thin ZnO film are shown in Table 1. It is seen that most effective in improving film adhesion is Ar/O2 mixture at RF power of 1000 and 2000 W. The pure Ar plasma is less effective one. These results are unexpected from the point of enhanced surface energy of PC, obtained after these plasma treatments. The adhesion improvement usually is related to the formation of an interfacial region between the underlying polymer and the film. There is strong evidence that upon film plasma deposition the interphase contains a cross-linked region followed by a region over which the film is covalently bonded to polymer substrate [2]. Formation of such an interphase may be attributed to the synergistic effects on the polymer surface of charged particles, energetic photons and chemically species generated in the plasma environment during plasma treatment and during initial stage of the film growth. The effects of all these factors depend strongly on the distinct experimental conditions used.

Table 1. Adhesion of 500 nm thick Zn O films deposited on PC substrates, plasma treated for 1 min with inducated gases

Plasma treatment	Adhesion			
	0 W	500 W	1000 W	2000 W
untreated	2A	-	-	-
Ar	-	2A	3A	3A
3:1 Ar/O_2	-	2A	5A	5A

5A – no peeling or removal of the film occurs at all; 4A – trace peeling or removal along incisions; 3A – jagged removal along incisions occurs up to 1.6 mm; 2A – jagged removal along incisions occurs up to 3.2 mm; 1A – most of the area of the X under the tape is removed; 0A - removal of the film beyond the area of X ocurrs

Conclusion

On the basis of contact angle data it is shown that the polar component of the surface free energy of the polycarbonate surface increases after all RF plasma treatments, while the dispersion component changes slightly. The obtained polar character of the surface is mainly due to enhanced amount of the polar groups and it reaches its maximum after short plasma treating with 3:1 Ar/O_2 gas mixture at higher RF power. This plasma treatment also leads to the pronounced improvement of the adhesion of ZnO films to the PC substrates.

Acknowledgments

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