HYDROPHILIC MODIFICATION OF POLYIMIDE SUBSTRATE USING OXYGEN PLASMA-TREATMENT FOR ADHESION ENHANCEMENT OF MWCNTS/EPOXY FILMS

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Abstract

Flexible strain sensors based on MWCNTs/epoxy nanocomposite coated on a polyimide (Kapton HN) substrate are often preferred due to their outstanding properties. Nevertheless, polyimide has a poor adhesion with different classes of materials, such as ceramic, polymers and metals, caused by its hydrophobic nature and low specific surface energy. Generally, the physicochemical properties at the substrate interface are decisive for the performance of strain sensors. To enhance the adhesion to substrate, oxygen plasma cleaning is proposed as an adhesion improvement technique. For this, different exposure times were investigated; 2 min, 4 min, 5 min and 10 min. The PI surface wettability was investigated by static contact-angle measurements using two different liquids; water and n-hexane. Results demonstrate that the contact angle of water decreases with increasing the oxygen plasma treated time to reach a completely hydrophilic surface with a contact angle of 12.6° after 4 min. The effect of plasma treatment on thin film nanocomposite performance was evaluated using DC measurements. To understand the phenomena behind the increased conductivity by plasma cleaning, the chemical groups introduced by the treatment were examined using Raman spectroscopy measurements. The results show the formation of more carbonyl groups with the elimination of hydrocarbon impurities after 4 min of exposure to plasma which increase the electrical resistance.

Keywords: Adhesion, contact angle, Raman spectroscopy, electrical characterization, strain sensor

1. INTRODUCTION

Adhesion in microelectronics and MEMS devices has a cardinal importance for the durability and performance of devices. Consequently, adequate adhesion of thin film to substrate is needed. In the last decade, polyimide substrate is widespread in microelectronic applications results of their desirable bulk properties in term of flexibility, high thermal stability, low moisture absorption, good mechanical properties and good processability [1]. However, polyimides have unfavourable surface characteristics caused from hydrophobic nature, low surface energy and poor chemical reactivity which leads to poor adhesion to other materials [2-3]. Many works illustrate that enhanced adhesion at the interface are linked to the composition and processing conditions. Dauskardt et al. found that interfacial impurity content, morphology and adjoining microstructures are the keys interfacial parameters [4]. In fact, adhesion promoter techniques are usually used to remove contaminations and to modify the surface morphology.

Recently, interest in plasma cleaning process for surface modification of polyimide has increased because of its possibility to change the surface characteristic by cleaning surface from contaminations, roughening the surfaces and introducing functional groups. The degree of these effects vary depending on parameters such as the type of plasma (direct current, radio frequency or microwave), the power, the pressure, the used gas mixture (Ar, He, N_2 or O_2) and the treatment time [5-7].

In this study, multiwalled carbon nanotubes (MWCNTs)/epoxy nanocomposite films were coated on the top of polyimide substrate treated using oxygen plasma under different exposure time to determine the influence of the film/substrate interface on the overall conduction properties and to predict the optimal treatment time to get better adhesion and ensuring a good stress transfer at the interface which in turn has effect on both the electrical properties of films and the sensitivity of prepared strain sensor. The effect of plasma through the time

is characterized using several techniques to determine the phenomena behind the changes of films electrical resistances. Contact angle measurements are performed to provide information about the wettability of the surface and surface polarity through the time. In addition, Raman spectroscopy is used to determine chemical compositions and functional groups created at the interface by the treatment.

2. EXPERIMENTAL

2.1. Fabrication process of conductive polymer nanocomposite film

Many methods have been described in the literature for fabrication of CNTs polymer nanocomposite including direct mixture of polymer and CNTs, in-situ polymerization, and melt mixing [8-9]. In this study, direct mixing methods is chosen due to the simplicity and efficiency to distribute uniformly the fibers inside the polymer matrix. The process is done as following MWCNTs purchased from Southwest Nano Technology with high level of purity was added to epoxy resin with two different amounts 0.3 wt.% and 0.75 wt.%. The epoxy resin employed in this study is from R&G Faserverbundwerkstoffec composite technology, GmbH, Germany which is a bisphenol A/F resin diluted with a difunctional butanediol diglycidyl ether. Because of the high surface energy that induce agglomerations, it was necessary firstly to apply an ultrasound energy using a horn sonicator (Bandelin GM 3200, Sonication Temperature: 25 C˚, Sonication Power: 15W, Duty Cycle: 50 %) to enhance distribution of nanotubes within the polymer and remove agglomeration of tubes. Then, the dispersion was mixed for 100 min at 80°C with magnetic stirrer followed by addition of hardener and mixing for 10 min. At the end, degassing process is done in vaccum oven in order to remove bubbles. Prior the film deposition, surface modifications of polyimide are carried out to give uniform deposition of thin film and to improve interfacial bonding between the film and substrate. To this aim, Polyimide (Kapton HN) obtained from DuPont is exposed to oxygen plasma treatment as it is shown in **Figure 1**. The oxidation is done using an oxygen radical source which is an RF plasma generated from an RF power of 13.56 MHz applied to the top electrode coil to induce plasma. The surface treatment experiments of PI films were performed on a working pressure of 39 mTorr. The treatment time was varied from 2 min up to10 min. For the deposition of thin film, screen printing method was used after recovering substrate by an isolation foil. At the end, films were kept in the oven to be cured.

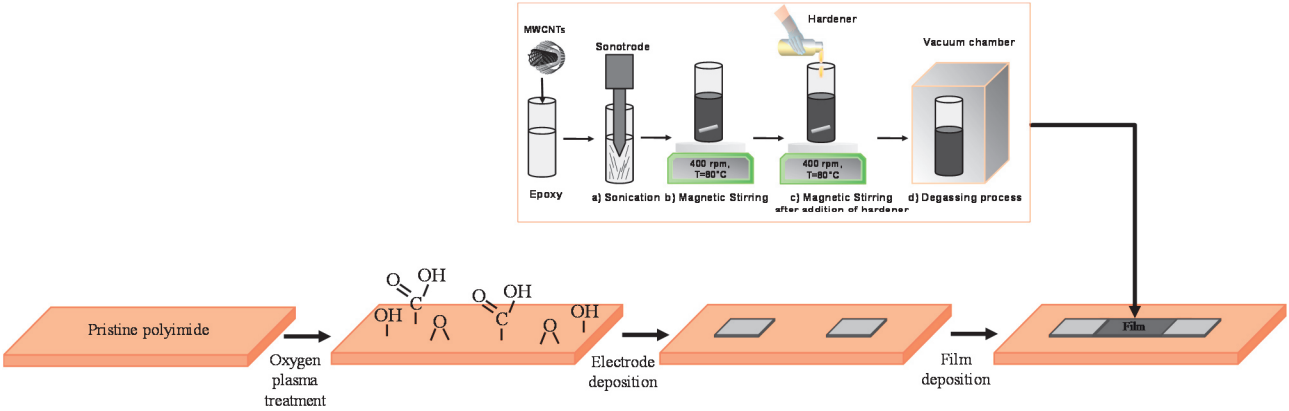

Figure 1 Shema of the thin film preparation process

2.2. Characterization techniques

The surface properties such as wettability, surface energy, adhesion work and polarity of pristine and treated substrates were investigated using several characterization techniques. Contact angle measurements of two types of liquids (water and n-Hexane) were performed under atmospheric conditions at room temperature by the sessile drop technique using contact angle system OCA from DataPhysics Instruments GmbH, Germany in order to determine the influence of the plasma treatment on the hydrophilicity. The process is done as

following, PI sample is mounted in front of microscope video camera on a sample holder. A drop of 5µl was set onto the substrate using a syringe containing the wetting liquids using a motorized platform. An image was taken for the drop to obtain the contact angle by fitting a tangent to both sides of the drop. Six measurements on the top of the substrates are made and averaged. Based on the measured contact angle, the surface free energy of the treated PI substrates is calculated using Owens-Wendt, Rabel and Kaelble methods. Additionally, the composition structure of treated substrates was analyzed using Raman spectroscopy Xplora plus microscope. An Ar+ laser beam was used giving an infrared light of 785 nm with an incident power of 58.5 mW at the sample, served as the excitation source. A 100x magnification objective lens is used for collection of scattered radiation. The Raman spectra in the wave number region were deconvoluted from 300 to 2000 cm^{-1}.

After deposition of thin conductive composite, the electrical resistance was measured using 4 wires measurement set up. These measurements are done using Keithley 2602A sourcemeter connected to a host computer, the I-V characteristics were measured by applying a DC voltage from -5 to 5 V and the resulting currents were recorded and then resistance of the film was obtained.

Table 1 Contact angle of water and n -hexane droplet for different treated substrates and the obtained surface energies

Treatment Time (min)	Contact angle (°)		Surface energy (mN/m)		
	Water	n_hexane	γ	γ_s^d	γ_s^p
0	74.73 +/- 3.37	9.53 +/- 0.58	30.74	18.18	12.56
2	26.22 +/- 0.2	8.13 +/- 0.87	66	18.25	47.75
4	12.60 +/- 0.73	9.23 +/- 1.22	71.98	18.19	53.79
5	22.53 +/- 0.85	9.30 +/- 1.10	67.99	18.19	49.8
10	21.97 +/- 2.46	9.83 +/- 0.80	68.27	18.16	50.11

3. RESULTS AND DISCUSSION

Table 1 gives the measured contact angles on pristine polyimide and treated polyimide. It is seen clearly the fast change on the surface wettability. After 4 min of exposure to plasma, the water contact angle is reduced from 74.73° to 12.6° indicating the improved level of liquid spreading on the top of polyimide. Based on the contact angle measurements, the surface energies are calculated. According to Fowkes, the total surface energy (γ) can be described as the sum of contributions from dispersive interactions (γ^d) and polar interactions (γ^p).

$$\gamma = \gamma^p + \gamma^d \tag{1}$$

Owens and Wendt and Kaelble proposed a geometric-mean approach to predict the solid surface energy, which is written as following:

$$(\gamma_s^d \gamma_l^d)^{1/2} + (\gamma_s^p \gamma_l^p)^{1/2} = \frac{1}{2}\gamma_l(1+\cos(\theta)) \tag{2}$$

where γ_l is the surface energy of the liquid in equilibrium with the liquid vapor. γ_s is the surface energy of the solid and ‘‘d’’ and ‘‘p’’ correspond to the dispersive and polar components, respectively. θ is the contact angle between the liquid and the solid. Using two liquids, the two surfaces components are determined by solving Equation 2.

Table 1 shows the calculated surface energies of the different surfaces; the total surface energy is increased approximately to two times after 2 min of plasma exposure from 30.74 mN/m for pristine polyimide to 66 mN/m. This enhancement in the total surface energy is result of increased polar interactions. This indicates that oxygen plasma treatment yields to higher polarity of the surfaces due to the formation of reactive chemical groups on the surfaces making it become more hydrophilic.

Interestingly, additional exposure time above 4 min is followed by a little decrease in the film wettability caused by removing of hydrophilic groups from the surface by the excessive micro etching. To determine the functional groups formed on the polyimide surfaces, Raman spectroscopy is used as shown in **Figure 2**. IR spectrum of treated films contain peaks near 1796,1720,1620,1520, 1385, 1169, 1125, 855, 725 and 350 cm^{-1} assigned to C=O (in phase), C=O (out of phase), COO^{-1}, C-N, and $(OC)_2NC$ vibration bands.

Around 1420 cm^{-1}, the peaks intensity was sharply reduced for the substrate treated for 4 min in comparison to the others treated substrates. This band correspond to hydrocarbon chains formed by impurities. In addition, the graph show that the surface functional groups are improved with oxygen plasma cleaning and more carbonyl group are formed as it is shown in the region 850cm^{-1} and 600 cm^{-1} especially at 4 min. The increase of number of polar groups such as CO, COOH and COO- on the plasma treated polymer surfaces was detected, making the surfaces more hydrophilic compared to the untreated polymer surface.

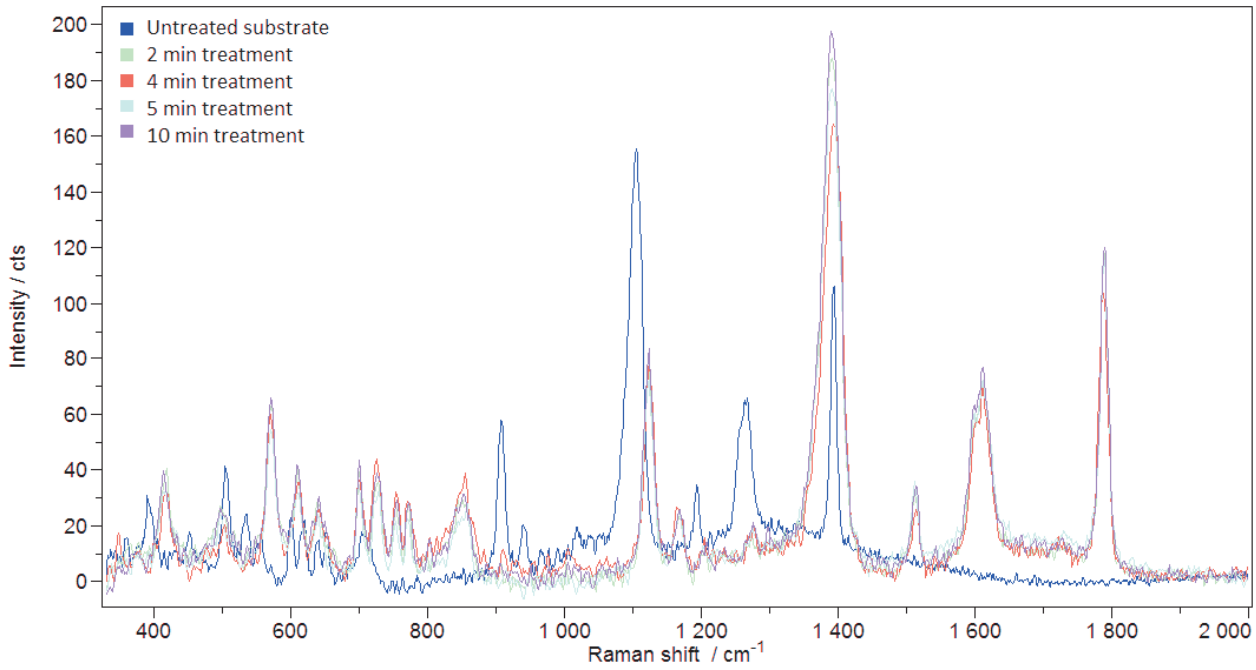

Figure 2 Raman spectrum for untrated substrate and the different treated surfaces

Figure 3 illustrates the electrical behavior of the MWCNTs/epoxy nanocomposite coated on different substrates. The results show the enhanced electrical conductivity at 4 min of exposure for both concentrations. This improvement in the surface electrical conductivity of is a sign of good cleaning of contaminations that inhibit the electrical property, uniform deposition of thin film obtained from the exposure to plasma and good quality of electrical transfer between MWCNTs achieved by the enhancement of substrate hydrophilicity and the improved bond between the substrate, carbon nanotubes (CNTs) fibers and the epoxy resin by the formation of carbonyl groups. Additionally, the graph shows the reduced electrical resistance at higher MWCNTs content due to the formation of more conductive paths inside the polymer matrix. However, in this case the change was by order of magnitude which imply that this concentration is above the percolation threshold.

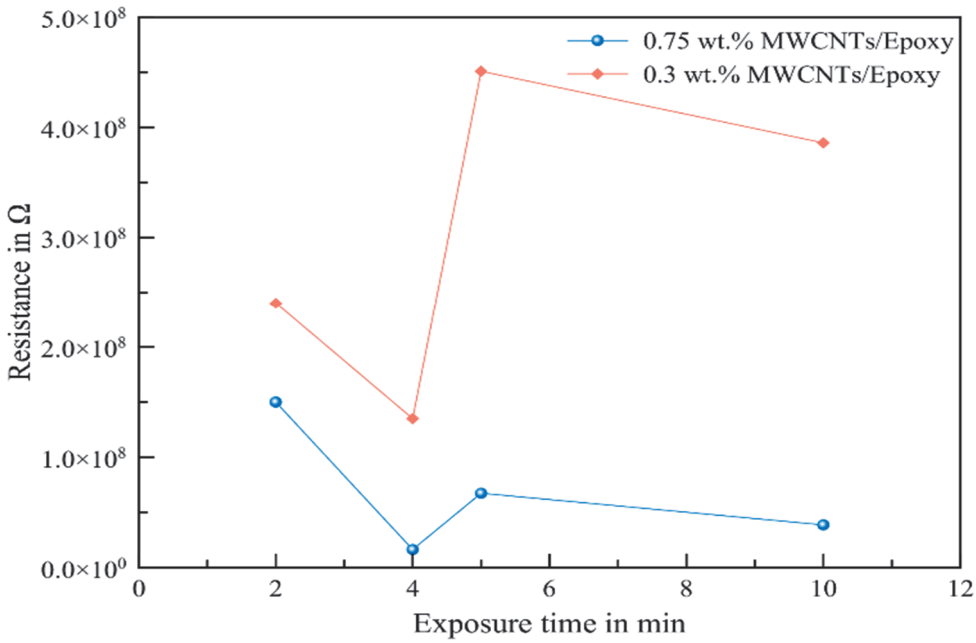

Figure 3 Variation of electrical resistance with exposure time for different MWCNTs concentrations

4. CONCLUSION:

The purpose of this work is to enhance the conductivity of nanocomposite thin film deposit on flexible polyimide substrate by improving the adhesion at the interface using oxygen plasma treatment. The effect of plasma treatment was investigated using contact angle measurement. The measured contact angle is dramatically reduced within the first minute of plasma cleaning to reach 12.6° after 4 min indicating the efficiency of the treatment to increase the hydrophilicity of the surface. Additionally, the total surface energy as well as the dispersion and polar components of the surface energy of the films were calculated from the measured contact angle. The polar component of surface energy of the polyimide is increased caused from the structural change that induce higher polarity due to the formation of carbonyl groups and deterioration of hydrocarbon group which was confirmed by the Raman spectroscopy measurement. The presence of functional groups promotes the interaction at the interface between the substrate and the thin film which in turn improve the electrical property in interface.

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