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Dielectric Behaviour of PVP 360 and PVA for Thin Flexible Transistors Application

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***Abstract**: Despite important progress in the field of the thin flexible transistor (TFT)-based electronics, a major challenge still exist for organic TFTs to decrease the operating voltage, which is related to the properties of the dielectric and semiconductor layers from the OTFTs structure. In this paper, we present the electrical behavior of two biocompatible polymers, polyvinylpyrrolidone (PVP 360) and polyvinyl alcohol (PVA), regarding the application as insulating layer in thin-film transistors. The PVA and PVP 360 thin films were deposited onto epoxy resin copper double-sided layer and polyethylene terephthalate/Indium tin oxide (PET/ITO) substrates by sol-gel method, spin-coating technique. Two sol concentrations (1 and 5 wt. %) were prepared and the contact angle onto the used substrates was measured using a digital microscope camera. The obtained films have been characterized by scanning electron microscopy (SEM) and dielectrical behaviour. For electrical measurements, the metal-insulating-metal (MIM) structure was realized by cooper electrodes deposition at room temperature, onto the top of thin films, by magnetron sputtering method. The current (I) - applied voltage (from -5 to +5 V) curves were measured in air at room temperature (RT), using the Picoammeter homemade device. PVA and PVP 360 thin films showed low leakage currents with values within ± 2 nA for ±5 V range.*

***Keywords**: dielectric polymers, thin film transistors, PVA thin films, PVP360 thin films*

1. Introduction

Polymer thin film technology have been studied over the last decades because of their potential application in easily processable, low-cost, flexible and large area electronic devices that include thin film transistor, coatings, organic light emitting diodes, photovoltaic cells, sensors, switching devices, nanogenerators, memristors [1-4]. The dielectric layer is one of the most important items that determine the device performance due to the effect on the charge carrier conducting channel. The electrical characteristics of the application are associated with the physicochemical interaction that takes place between the dielectric layer and the substrate of TFTs. One of the critical factors is surface energy, so the engineering of it can be the essential part to improve the electrical properties of electronic devices [2]. Usually, polymer thin films are responsible for different physical phenomena that change with type of solvent, film thickness, confinement and surface interaction effects [4]. Dielectric polymers such as polyimide (PI) [5], polyethylene phenol (PEP) [5, 6], polynorbornene [7], polyvinylpyrrolidone [2], poly(methyl methacrylate) (PMMA) [8] and poly(4-vinyl phenol) [9] has received an increasing interest as gate dielectric material due to: high dielectric constants, bio-degradability, flexibility, low cost and non-toxicity. In this paper we focused on two dielectric polymers used as dielectric gate in thin film transistors: PVA and PVP 360. This two polymers were chosen because the electrical properties and surface tension of polymers solution can be modified using different dopants [10] and solvents [11] (water and ethanol). PVA is a non toxic polar soluble polymer which has a capability of strong film forming, with high mechanical strength, high dielectric perimitivitty, good charge storage capacity. In case of PVA, charge defects and carrier traps can lead to weakening the contact between the polymer layer and cooper contacts. PVA also is considered one of the most used and studied polymer in dielectric

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gate material for OTFTs due to its versatility [12].

PVP is an amorphous and water soluble polar polymer due to the existence of double bond in pyrrolidine ring, and hydroxil groups existing in the structure [13].

Nowadays flexible transparent electrodes play an important role in the next generation of transparent flexible electronics [14]. The uses of polymers in TFT structure for flexible and transparent electrodes is very important for the application in many devices as: optoelectronic, touch screens, portable solar cells, organic light emitting diodes (OLEDs), fuel cell electrode, sensors and transparent heaters [14].

In addition insulators polymers are poor conductors of electrical current and typically have a high resistivity in the range of 10^9 to 10^{20} ohm·cm [15]. To measure the electrical resistivity of a thin layer usually a known potential is applied to the sample and the resulting current is measured. The response regarding the values of the current is within the ranges of nano- or picoamperes. The electrical resistivity of an insulator is determined by measuring resistance, then converting it to resistivity by taking geometric considerations into account [15].

In this paper, we have investigated PVA and PVP 360 solutions for preparing thin films by spin coating method, one of the most commonly used sol-gel method to obtain its, for the simple and low-cost process. In order to evaluate the hydrophilic behavior of the as prepared solution, the contact angle was measured using a digital microscope between the cooper layer and the solution drops. We fabricated a MIM device, represented by Cu top-electrode/PVA (or PVP-360) films/Cu (or ITO) layer substrate, to study the dielectric properties of the obtained polymeric thin films and to calculate their surface electrical resistivity.

2. Materials and methods

2.1. Precursor solution preparation

PVA with a molecular weight of 80000-90000 (99% hydrolyzed) and PVP-360 with a molecular weight of 360000 were purchased from Sigma-Aldrich. 1 and 5 wt. % PVA and PVP360 (abbreviated PV and PP, respectively, in this paper) precursors were prepared by dissolving the polymer particles in water (**H**) and absolute alcohol (**A**). These aqueous and alcoholic solutions were ultrasonically processed for 1 h, before to be aged at 60^{o}C under magnetic stirring until it was completely homogeneous. The prepared solutions are presented in Table 1.

Table 1. The PVA and PVP-360 solutions in water or alcohol prepared for thin film deposition and corresponding values of contact angle

Solution sample		**Polymer weight percent/ Contact angle**		
	1%	5%	1%	5%
Water (H)	PAH1/59°	PAH5/58°	PPH1/58°	PPH5/49°
Alcohol (A)	PAA1/49°	PAA5/44°	PPA1/45°	PPA5/30°

A digital microscope (1600x) was used in order to measure the surface tension of PVA and PVP-360 solutions.

2.2. Film fabrication and characterization

For the film deposition, printed circuits boards (PCB) plates were used as substrates. These substrates were then prepared with a cooper double sided deposited and a micron thick cooper wire stacked on both sides in order to have the contact between the thin film layer and the top-cooper electrodes (Figure 1).

To observe the flexibility of the thin films, we also deposited a solution of PPA5 on polyethylene terephthalate (PET) substrate. The both solutions were spin-coated 2000 rot/min for 20s, two layers, and annealed for 2h at 120^{o}C in an oven, in order to eliminate the water and alcohol. The thickness of the layer was measured by scanning electron microscopy using a SEM FEI QUANTA 200 microscope, at Dunărea de Jos University of Galați (UDJG). For all the investigations, a beam accelerating voltage of 20 kV was applied.

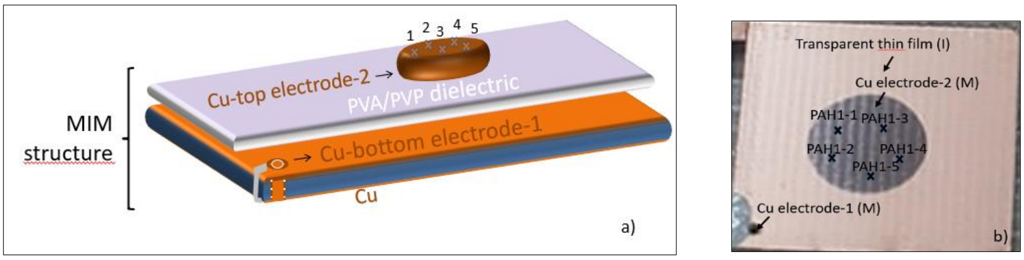

Figure 1. Schematic representation of MIM structure layer by layer (a) and the digital photo image on the top of the MIM structure (b) used for I-V measurements

2.3. Metal-insulator-metal device fabrication and electrical characterization

To measure the electrical characteristics of the PVA and PVP-360 films, a MIM device structure was fabricated. The MIM device is a multilayer structure, represented by Metal Cu top-electrode/PVA or PVP-360 Insulator films /Metal Cu or ITO bottom-electrode (Figure 1). As bottom electrode (Cu electrode-1) we used the cooper layer of the PCB substrate. The 25 nm-thick circular cooper top-electrode (Cu electrode-2) was deposited by direct magnetron sputtering onto polymer thin film (Figure 1), through a shadow metal mask, during 20 min at the argon flow of Q = 2cm^3/min at $2\cdot10^{-2}$ mbar; the distance between target and PCB substrate was 50 mm and the discharge voltage and current were 420V and 120mA, respectively. The current-voltage (I-V) characteristics of the MIM capacitor were measured using a Picoammeter home-made device (Figure 2a) in visible light under ambient conditions.

2.4. Picoammeter device and electrical characterization

The I-V characteristic curves for the evaluation of the polymer thin films electrical behavior were recorded using a home-made device including a voltage source that can apply voltage from -40 V to +40V and measure the current that passes through the thin film, within 1pA-1000nA range (Figure 2a).

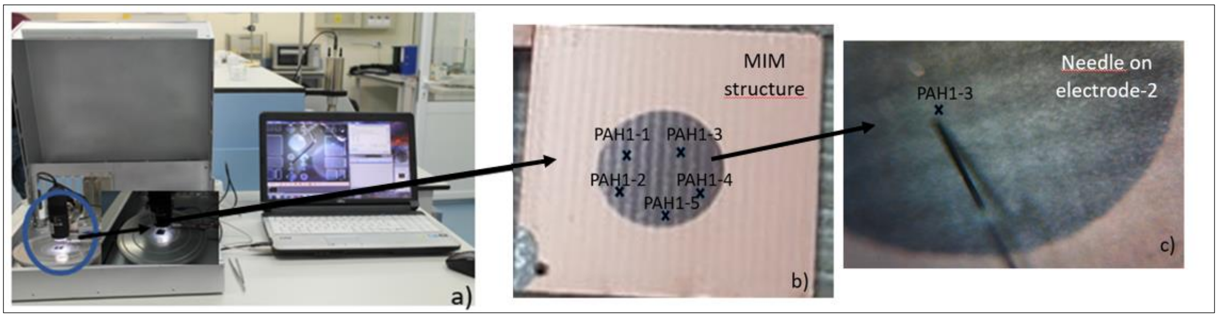

Figure 2. Picoammeter device (a), MIM structure (b) and flexible needle on the top Cu electrode (c)

Surface resistivity, the resistance to leakage current along the surface of an insulating material, was calculated based on the Ohms' low (equation 1), according to the equation (2):

$$I = \frac{U}{R} \qquad (1)$$

I= current intensity
U=voltage applied
R=resistance of circuit

$$\rho = R\frac{A}{\ell}, \qquad (2)$$

ρ - is the electrical resistance
l-is the thickness of the polymer layer
A- is the cross-sectional area of 2nd electrode

3. Results and discussions

The measured contact angle for PVA and PVP-360 solutions showed values below 90°, confirming their hydrophilic behavior in contact with the cooper layer surface (Figure 3). The films prepared with ethanolic solutions showed in the first minutes increased hydrophilic behavior, when comparing with the corresponding aqueous solutions (Figure 3). The drops of polymer solutions were let to dry in air atmosphere for 6 h, when they formed homogenous and transparent film as presented in the Figure 3.

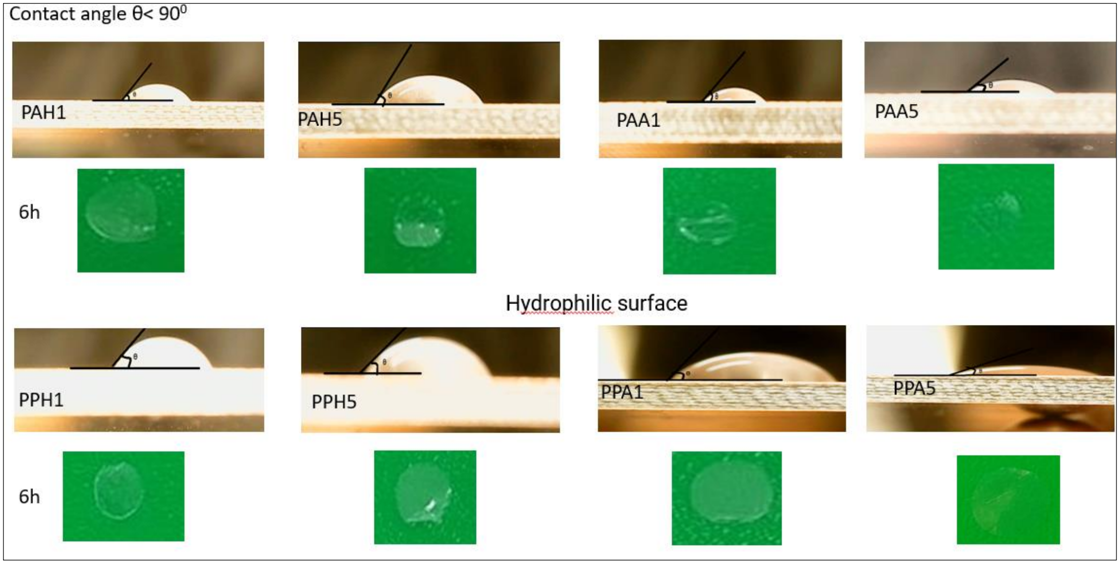

Figure 3. Measurements of contact angle for PVA and PVP-360 solution with 1 and 5 wt. % concentration (Table 1) and (below) the corresponding digital images of the resulting disc films after 6 h of air drying

The measurements showed that the polymer concentration does not change so much the contact angle value (Table 1). The most important difference in the values of contact angle is due to the solvent type. As the polymer concentration increases, the contact angle decreases. The drop from aqueous solutions has a larger contact angle than the drop from alcoholic solutions. Higher polymer concentration, lower contact angle values, so better wettability of copper contact surface, for both aqueous and alcoholic solutions. The effect is more obvious for alcoholic-based solutions (PAA and PPA, Table 1), that show good hydrophilic behavior.

The SEM images of the lateral cross section of the PCB substrates after spin-deposition of the organic PAH5 thin film is presented in Figure 4. One can observe a smooth polymer film surface (Figure 4a). The phase contrast image, clearly highlight (in red) the polymeric layer, as having a thickness that range between 260-400nm. Most likely, this variation in thickness is due to the roughness of the cleaned copper layer, on which the polymer film was deposited. It is also observed that a polymer layer (in red) was deposited at the same time, with different thickness, on the fracture surface of the Cu layer in the PCB substrate (Figure 4b). The digital image (Figure 4c) of PVP 360 thin layer deposited on PET/ITO substrate shows that the transparency percent is very high, over 90%.

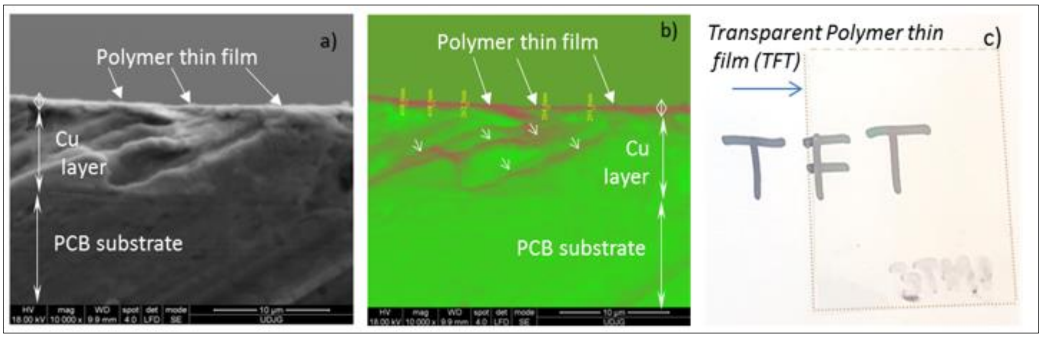

Figure 4. SEM cross-section image of PPH5 polymer thin film on the top of copper layer of PCB substrate (a) and the same image highlighting (in red) the polymer deposition, as thin film (for thickness measurement) and on the breaking surface of the copper layer (b). Digital photo image of the transparent PPH5 thin film deposited on the (PET/ITO) substrate (c)

The electric behavior of PVA and PVP-360 thin films are presented in Figure 5. A TFTs requirement to be used in electronic devices is that the dielectric leakage current should be under 1nA/mm^2 at electric fields of 3MV/cm [16]. All the obtained MIM structure samples including thin films based on aqueous and alcoholic solution have similar electrical behavior. The I-V curves showed the leakage current through the dielectric films around 10^{-9}A (nA range), providing the basic requirement for a dielectric behavior. Because for the same polymer film type, PPA or PAH, the I-V curves measured in different (1 to 5) points (marked with "x" in Figure 2b present similar shape for the two used concentration values (1 and 5%), we choose to present in the paper the curves for only one concentration for each of the two types polymers. It was observed that for the PVA polymer film, the leakage current increases until 2nA in the range of about ±0.5 V applied voltage, and it remains constant up to values of ±5V (Figure 5a). For PVP-360 polymer films, the I-V curves measured in two points, (PPH5-2 and PPH5-3) show different shape, i.e. the leakage current increases until 2nA for applied voltage within ±1V range and remains constant up to values of ±5V (Figure 5b). The different behavior can be assumed to the existence of polar groups from the structure of polymers which can lead to charge storage due to the dipolar moments from the structure in case of PVP. Better I-V curves and electrical properties in the case of films deposited from alcoholic solution of PVP can be also explained by better wettability of alcoholic solution and consequently better contact between the thin films and the copper electrodes.

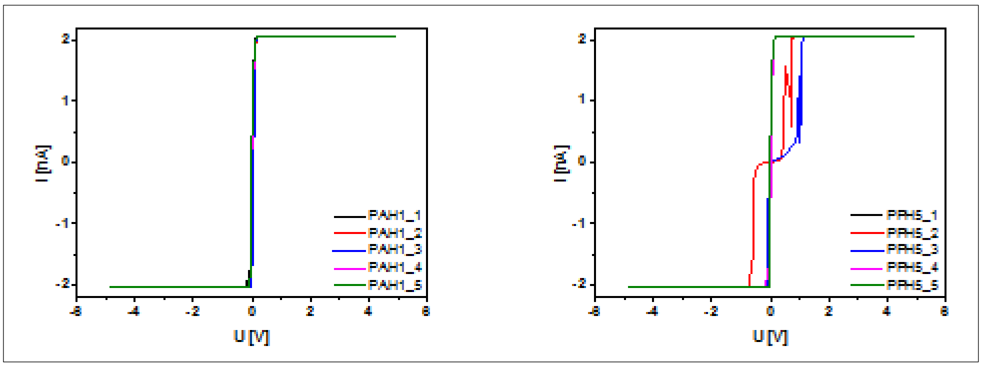

Figure 5. The I-V characteristics of 1% PVA (a) and 5% PVP (b) thin films, in the range of ±5V

Some I-V curves show noises, which can be associated with the presence of polarizable organic molecules, when the current passes through the layer also the chain mobility of polymers can increase the dielectric response [17, 18]. This behavior can also occur due to a non-homogenous deposition of top-copper electrode and not very good contacts of both, top and bottom, Cu electrodes with the polymer film. In order to calculate the electrical resistivity, the values of intensity for applied voltage from -1V to +1V were used. The calculated values for the surface resistivity in different points (1, 2 and 3) of the PVP-360 polymer insulator layer are presented in Table 2.

Table 2. Electrical resistivity, measured in different surface points, of PVP-360 (5wt.%) thin films

Sample name	**I (A)** **10^{-9}**	**U (V)** **10^{-3}**	**R (Ω)** **10^{3}**	**l(m)** **10^{-9}**	**ρ(Ω·cm)** **10^{11}**	**ρ_m(Ω·cm)** **(average)**
PPH5-1	2.039	249	122	400	7.7	$6.3 \cdot 10^{11}$
PPH5-2	2.038	256	182	400	3.46	
PPH5-3	2.037	248	120	400	7.74	

4. Conclusions

PVA and PVP-360 alcoholic and aqueous solutions were prepared and transparent thin films were spin-coating deposited with a thickness of around 400 nm. The I-V curves show dielectric behavior with leakage current values around 10^{-9} A, providing the basic requirement for a dielectric behavior. It can be assumed that the noise that appears in the electrical measurements is due to the high roughness of the

Cu layer on which the polymer film was deposited, the inhomogeneity of top-copper electrode and not very good contacts of electrodes with the polymer film. There is no significant difference regarding the electrical properties due the polymer concentration. Better I-V curves and electrical properties in the case of films deposed from alcoholic solution can be explain by better wettability of alcoholic solution and consequently better contact between the thin films and the copper electrodes. The average value of electrical resistivity is around $6.3 \cdot 10^{11}$ $\Omega \cdot$cm for PVP-360 and one can conclude that polymer films can be used as transparent and flexible dielectric layer in OFETs. Further investigation regarding the polymer concentration and the influence of thickness layer and electrodes will be realized in an advanced study.

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