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Characterization of organic ultra-thin film adhesion on flexible substrate using scratch test technique

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ABSTRACT

The mechanical properties of interfaces and more precisely the adhesion are of great importance for the understanding of the reliability of thin film devices. Organic thin film transistors (OTFT) on flexible substrate are a new class of electronic components. Since these devices are flexible and intended for different fields of application like sensors and displays, they will undergo a lot of mechanical and thermal stress during their useful life. Moreover, interfaces play an important role in the electrical stability of these transistors. In this context, the adhesion of two organic submicron thin films, semi conducting and dielectric respectively, deposited on polymeric substrate were investigated by scratch test method. This study demonstrates the feasibility and selectivity of the scratch test as a tool for assessing the adhesion and the damage behaviour of ultra-thin organic film on flexible plastic substrate. The semi-crystalline substrate presents a brittle cracking damage from a given strain, whereas when covered by the semi-conducting thin film, the sample exhibits a more ductile behaviour. Moreover, this technique has proven to be sensitive enough to highlight the effects of a plasma treatment prior to deposition.

1. Introduction

Interdisciplinary research efforts have led to the rapid development of Organic Thin Film Transistors (OTFTs) [1] with performances close to those of a-Si TFTs [2]. OTFTs are made of submicronic organic and inorganic layers deposited on a flexible substrate. Various materials [3,4] and designs [5] have been investigated to improve the electrical functionality and stability of these devices. In a "top gate–bottom contacts" design, the semiconducting layer is deposited on the plastic substrate after the patterning of source and drain contacts. Then the dielectric layer is deposited, on top of which a gate contact is fabricated. These transistors show now good stability in ambient air [6]. The electrical and optical properties of these organic semiconductors have been extensively studied [7,8], but their mechanical behaviour is not yet well understood. Since these transistors are flexible, they will undergo a lot of mechanical strains and stresses during their useful life. So the investigation of their reliability under mechanical stress is of great importance. Interfaces play a crucial role on the electrical functionality of devices and consequently the study of the mechanical properties of interfaces is essential.

Many adhesion test techniques have been developed to measure adhesion energy at the interface, among which peel and pull-off tests are two widely used methods to test adhesion of thin films and coatings. The peel test is used in a variety of configurations, in which a thin strip is pulled away at an angle from the underlying substrate. Although the peel test offers simple test geometry for measuring adhesion strength [9,10], in the case of submicronic organic active layers of OTFT, the coating may tear due to the high stresses at the contact with the mechanical grips [11]. Moreover it is difficult to initiate the delamination with film thickness below 1 μm.

The pull-test allows a quantitative adhesion measurement, in which strain or energy can be extracted [12]. But it still suffers from several problems like the adhesive compatibility [13]. Indeed, pull-off test is performed by fixing, with an adhesive, a loading fixture to the surface of the film. Failure occurs along the weakest interface within the system which is often the adhesive/film interface because, in the present case, coatings have a poor adhesion to different types of adhesives.

Others specific adhesion test techniques have been developed like cross section indentation [14], four point bending [15], tensile loading [16] or blister adhesion test [17,18]. However, these methods require coating thickness of about several hundred μm, a rigid substrate and difficult sample preparations.

Thus, a brief literature overview indicates adhesion measurements are hard to implement for OTFT technology. In the submicron thickness range analyses of coating damage is challenging, considering many relevant material properties such as toughness are unknown. Numerous papers deal with adhesion properties determined by scratch test of various materials such as hard coatings or polymers [19–22]. However,

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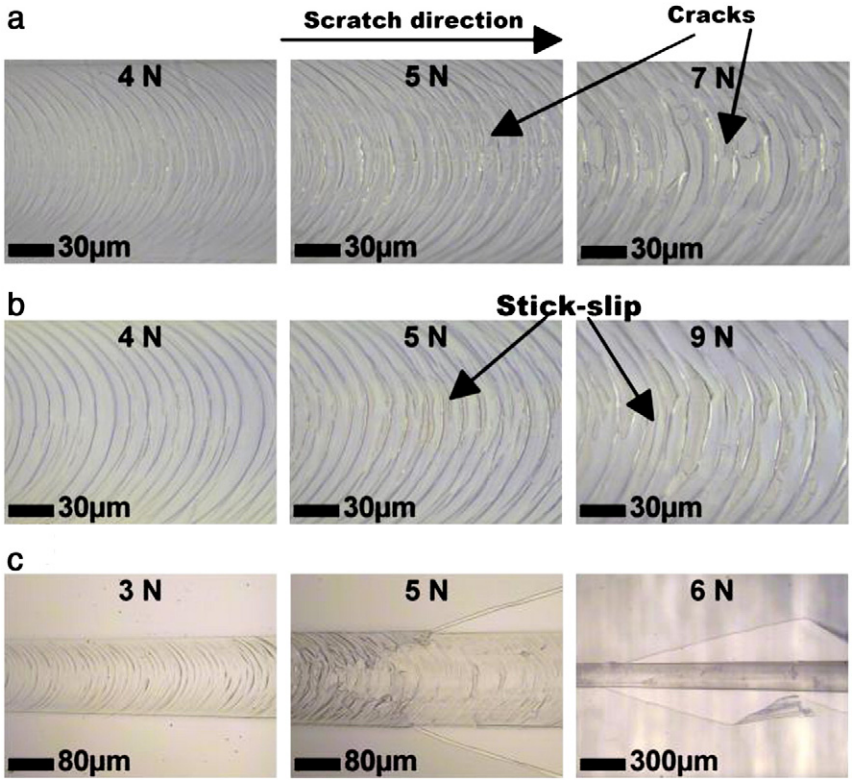

Fig. 1. Main part of the scratch track on PEN (a), P1/PEN (b) and P2/PEN (c) observed by optical microscopy.

few adhesion data are available for thin polymer coating deposited on polymeric substrate [23], and none concerns submicronic electronic polymer coatings deposited on polymeric substrate. The present paper focuses on adhesion evaluation using a scratch test which requires limited preparation to induce and quantify interface failure. Moreover the scratch test method is a useful tool because it is sensitive to several parameters (internal stresses, thickness, elastic properties…). The purpose of this study is to verify and investigate the feasibility and sensitivity of this method on two submicron amorphous polymeric layers of OTFT deposited on semi crystalline substrate.

2. Experimental

In the present study one type of specimen has been used for simplicity. It consists of a single thin layer deposited on a 125 µm thick Teonex® Poly Ethylen Naphtalat (PEN) semi crystalline polymeric substrate. The substrate was obtained by a lamination process inducing anisotropic properties. The Young's Modulus was specified by DuPont-TeijinFilms™ at 5060 and 6240 MPa for directions parallel and perpendicular to the lamination direction, respectively. Two thin films were considered. The first coating, called P1, is a 200 nm thick triarylamine amorphous semiconducting polymer [24]. The second, denoted as P2, is an 800 nm thick perfluoropolymer dielectric layer [25]. The films were deposited on PEN by spin coating, using a SCS 6800 spin coater, at room temperature at 3000 rpm during 35 s for P1 and 2000 rpm during 25 s for P2. The substrate size in the deposition process was 10×10 cm^2. Two deposition conditions were studied, with and without Plasma Treatment (PT) prior to coating deposition. The plasma treatment, performed with an RIE Oxford Instrument Plasmalab apparatus, consists of a rapid reactive ion etch using O_2 and SF_6 gases, in order to improve the wettability of PEN surface [26]. Both layers present a glass transition temperature above 100 °C preventing any change of structure during measurements. The layer thicknesses have been defined to optimise the electrical performances of the OTFT [27].

The adhesion properties were evaluated using a CSM Micro Scratch instrument scratch tester. The procedure was similar to that detailed elsewhere [19]. The scratch indenter was a diamond Rockwell C stylus with a spherical tip having a radius of 200 µm. The indenter was chosen in order to operate in the optimum accuracy range of the experimental apparatus in terms of load and sensor sensitivity. For the 5 mm scratch length the applied load was progressively increased from 0 N to 10 N at a rate of 50 N/min. This intermediate scratch speed was used to optimise the sensitivity to elastic, plastic and fracture contributions, since polymer materials are sensitive to time dependant effects and as reported by Barletta et al. plasticity tends to decrease and fracture contribution to increase when scratch speed is increased [28]. Five measurements were performed at room temperature for each sample perpendicularly to the substrate lamination direction and an average value of the critical load is obtained. After the test a critical load (Lc) where a particular failure mode occurred was determined by post-mortem observation of the scratch track using an optical microscope. The error on the Lc determination is due to two main contributions. A major contribution is due to statistical errors, and the position accuracy of the sample under the microscope of 1 µm induces an error of some mN. Since statistical errors represent the major contribution the scattering given below corresponds to the standard deviation. In addition Acoustic Emission signals were recorded during the test by a sensor attached to the load arm.

Scanning Electron Microscopy (SEM) was performed using a CARL ZEISS-Ultra 55 apparatus and elemental analyses were carried out by Energy-Dispersive X ray (EDX) using an OXFORD INCA system.

3. Results and discussion

Taking into account the load range, the tip geometry, material properties and layer thicknesses, the mean penetration depth at 10 N is about 40 µm for all specimens studied in the following. In addition, due to the viscoplastic nature of materials a pile up is formed ahead of the tip and on the edges of the track.

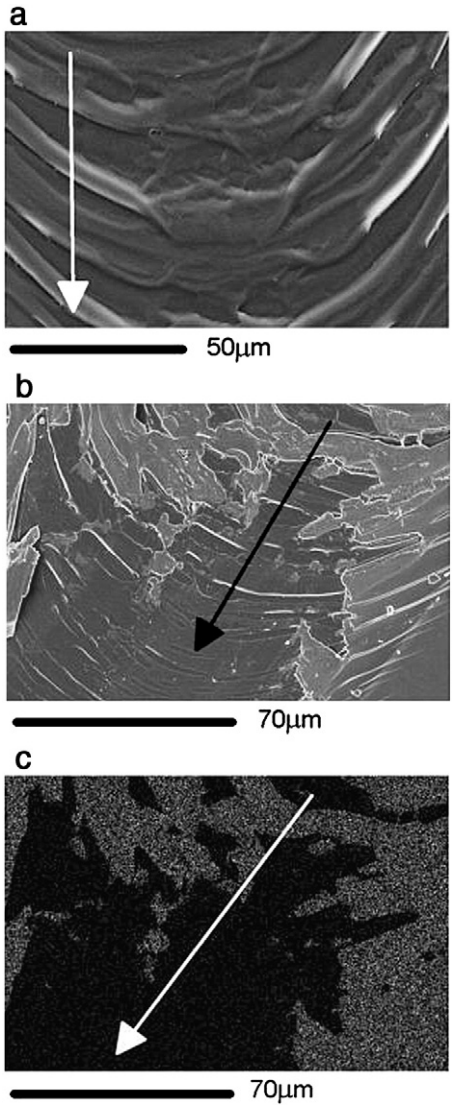

Fig. 2. SEM micrographs of P1 (a) and P2 (b) on PEN in the scratch track and corresponding F Kα EDX cartography of P2 on PEN (c). Arrows indicate the scratch direction.

The damage sequences of specimen PEN, P1 layer on PEN and P2 layer on PEN are shown in Fig. 1. For all materials tested, there is only a small amount of deformation observed under low load and stress level. This includes fully recoverable elastic deformation, time dependant viscoelastic deformation, and a small amount of non-recoverable plastic deformation resulting from compressive indentation, tentatively termed "mar" [29].

The damage sequence observed for the PEN substrate, at room temperature, is presented in Fig. 1-a. At the early stage of the scratch, only mar deformation is observed up to about 1.7 N. Progressively forward semi circular features occurred in the scratch track as seen at 4 N. Actually, plastic deformation in front of the scratch tool produced a pile up of polymer which offers a resistance to the advancing indenter. This material is submitted to compressive stresses, and at the same time the material under the indenter is in a strong tensile state [30,31]. Hence, the observed damage is due to the compressive stresses ahead of indenter and the plastic flow around it, as indicated by the parabolic morphology [32,33]. At higher load, microcracking occurs in the track transversally to the scratch direction, as shown at 5 N and which is more visible at 7 N, indicating a brittle behaviour [34]. This is very likely due to the semi crystalline nature of this polymer [35]. The mean load at which the cracks appear is 4.3 ± 0.3 N.

The failure events of the P1 layer deposited on the PEN substrate, shown in Fig. 1-b, present some differences. At low load, only mar deformation is observed up to about 1.8 N. For higher loads (see for instance at 4 N), the forward semi-circular feature is present, but with increasing load a stick–slip phenomenon is clearly visible in the bottom of the scratch track. A stick–slip phenomenon occurs when the indenter experiences change during the tip movement. Thus, formation and breakage adhesion between the tip and the coating occur repeatedly. Moreover this becomes more significant when the normal load increases [29,36]. In the present case, the strain energy release process appears by localised ductile tearing of superficial coating due to the interaction between the tangential load and the viscoelastic nature of the polymer; characterising the ductile behaviour of the system [36]. Nevertheless, it is worth noting that the forward semicircular feature occurs in both the coating and the substrate, since the layer still adheres to the substrate even for higher loads studied. In addition, no evidence of cutting mark or crack could be found for this specimen. The mean critical load, defined as the first appearance of the stick–slip phenomenon, is 5.1 ± 0.5 N. This behaviour is confirmed by a SEM observation presented in Fig. 2-a, showing the periodic tearing of superficial coating in the bottom of the scratch track. Although only semi conducting

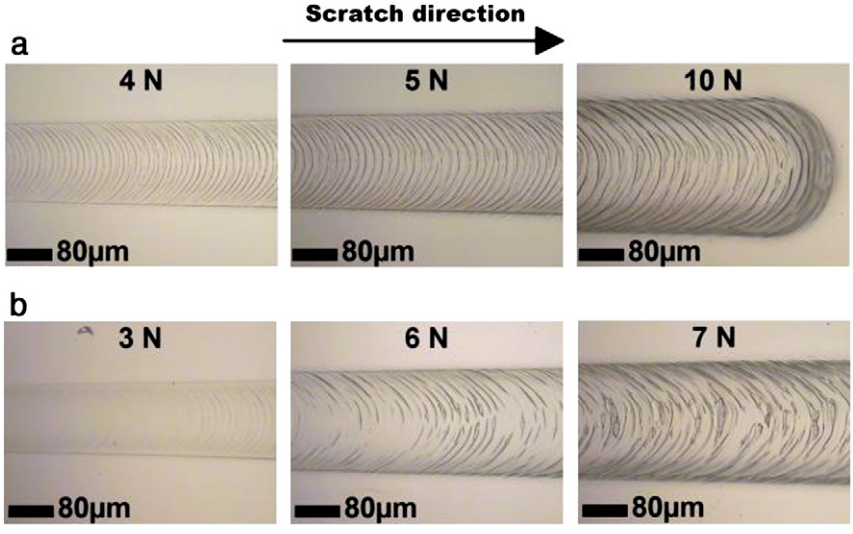

Fig. 3. Main part of the scratch track on P1 (a) and P2 (b) deposited on Plasma Treated PEN observed by optical microscopy.

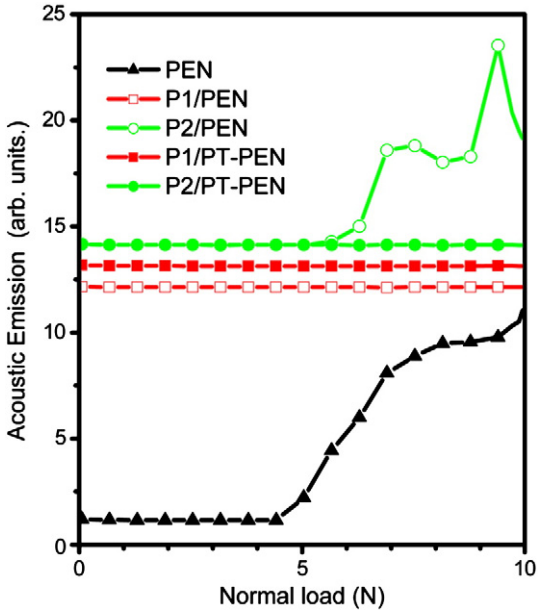

Fig. 4. Acoustic Emission recorded during a scratch measurement of PEN, P1/PEN, P2/PEN and P1/Plasma Treated PEN and P2/Plasma Treated PEN. For visualisation, curves were arbitrary shifted.

coating contains nitrogen and not the substrate, an EDX analysis was not relevant considering the resolution of the apparatus since N Kα energy is very close to the C one.

Scratch results for the P2 coating deposited on the PEN substrate are reported in Fig. 1-c. The beginning of the damage sequence is the same as for the two previous specimens i.e. mar and subsequently parabolic deformation, but for increasing load a sudden and large delamination of the superficial coating is observed. This delamination spreads widely outside the scratch track. For this sample the critical load, defined as the lowest load inducing the delamination, is 4.2 ± 0.3 N.

In the area of critical load a SEM analysis has been performed (Fig. 2-b), and confirms optical observations showing a sudden damage of the coating. Moreover a F Kα cartography presented in Fig. 2-c indicates clearly that the perfluoropolymer coating is no longer detectable in the scratch track after the critical load. The shear stresses in the scratch subsurface region may be responsible for the delamination of the superficial coating [36].

It has to be noticed that we have checked on other specimens, not shown here, that the slight discrepancy of Young's Modulus measured on PEN substrate for both directions, i.e. parallel and perpendicular to the lamination direction, did not induce any variation either in the damage mode or in critical load for studied coatings.

In a second set of experiments, the effect of a plasma treatment (PT) on the substrate prior to coating deposition was investigated. The damage sequence of the P1 coating deposited on PEN substrate with PT is shown in Fig. 3-a. It is quite identical to the one obtained without PT (Fig. 1-b). Indeed, at low load only the groove of the indenter is observed up to about 1.5 N. The forward parabolic features are identified progressively and as the load increases a stick–slip phenomenon is observed at the bottom of the scratch track. The first apparition of a stick–slip phenomenon is detected for a critical load of about 4.2 ± 0.5 N; a slightly lower critical load than for the coating without PT. This indicates the weak influence of the pretreatment. Nevertheless, no brittle fracture was detected.

The failure sequence of P2 coating deposited on PEN substrate with PT is presented in Fig. 3-b. Contrary to the case of the P1 coating, the damage sequences with and without PT are different. With PT, the mar deformation is still observed up to about 1.5 N, followed by the forward parabolic feature. But as the load increases, the total delamination of the superficial coating is no longer present. Only a few localised and cohesive damages appear in the bottom of the scratch track as seen for instance at 6 N or 7 N. The lowest load at which this occurs is about 5.6 ± 0.2 N. The coating remains adhering to the substrate on the edge of the scratch track even at 10 N. For the P2 coating, the plasma treatment improves the adhesion of the thin film.

Acoustic Emissions (AE) recorded during tests are plotted for each specimen in Fig. 4. At low load, no AE signal is detected for any of the specimens. Then, the AE evolution depends on the failure mechanism. For PEN, the AE increases concomitantly with the apparition of cracks transversally to the scratch tracks confirming the brittle behaviour of this failure mode. For both P1 coatings, with and without PT, no evolution of the AE is detected all along the test, indicating a more ductile damage. Concerning the P2 coating deposited on PEN substrate, the AE increases simultaneously with the delamination observed by optical microscopy. But when the substrate is plasma treated prior to deposition the signal remains flat, showing the enhancement of the adhesion properties.

4. Conclusion

In the present paper, we have reported results concerning submicronic organic coatings deposited on a polymeric substrate. We stated that covering a semicrystalline polymer, which exhibits brittle behaviour, by a submicronic amorphous polymer could change drastically the damage behaviour. The scratch test method is a semi quantitative, sensitive and reproducible tool to characterise the adhesion of polymer coating on a polymer substrate even for thin layers of a few hundred nanometres. The scratch test was capable of highlighting clear differences between the mechanical behaviour of uncoated and coated substrates. But it also means that direct comparison between the critical load values of different systems is not possible: each critical load is related to different failure mechanisms. For direct quantification purpose, it is necessary to induce a unique failure mechanism, the use of a sharper tip would be therefore useful, because when the tip radius is smaller, the maximum stress is localised closer to the surface. In addition, the use of a higher scratch speed would have probably led to less ductile behaviours due to material viscoplastic properties [28].

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