Interactions in metal–polymer–metal interfaces

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Interfacial layers in metal–polymer–metal structures have been investigated. Analysis by X-ray photoelectron spectroscopy (X.p.s.) at room temperature of the changes in various core electron spectra associated with the polymer film and the overlayers shows that there is formation of metal oxide–carbide species in the polymer–metal interface in the system obtained by deposition of metal on poly(phenylene vinylene) (PPV) polymer. In contrast, for the system in which metal is deposited on the PPV precursor, no complex species are observed after the transformation of precursor into PPV by heat treatment. This difference can be explained by the side-reactions of the under-products generated during the pyrolysis of the precursor into the polymer. Finally, the role of the interfacial complex species in the origin and in the mechanism of the rectifying contacts observed in the metal–polymer–metal structures is also discussed.

INTRODUCTION

Polymers with a π-conjugated backbone are anticipated to have a variety of practical applications. The first electronic device of a field-effect transistor (FET) with a conjugated polymer as an active new component, reported by Tsumura et al.[1], showed that conducting polymers are very promising materials for electronic devices.

However, in contrast to the development of inorganic materials, the processing and characterization of electroactive polymeric materials have not as yet been satisfactorily established. Although many studies on the electrical properties of polymers have been reported, the role of the polymer–metal contact in the transport mechanism and its nature are still insufficiently understood. For example, both the relative roles and the nature of the polymer and the metal in the interface have been studied, but they are still a matter for discussion[2,3]. In our previous work on the metal–poly(p-phenylene) (PPP)–metal structures[4], using both electrical measurements and X-ray photoelectron spectroscopy (X.p.s.) analysis, we were able to study the nature of the polymer–metal contact of each system and could establish that a chemical reaction between carbon, oxygen and metal occurred at the interface to form a metal–oxygen–carbon (M–O–C) complex, presumably responsible for the observed electrical a.c. behaviour of these devices.

In the present paper, we have carried out a similar study on the interfacial layers between metal (Cr and Al) and poly(p-phenylene vinylene) (PPV) thin films.

Particular attention has been given to those layers between the metal and the precursor which need a supplementary heat treatment to be transformed into a PPV film. The choice of PPV as active component in this kind of device is made for many reasons: PPV can be obtained via a hydrosoluble precursor; it is highly resistant to oxidation; it has a high thermal decomposition temperature (up to 500°C under ambient atmosphere)[5]; PPV of highly oriented chains resulting from the drawing of its precursor during pyrolysis[6] has excellent mechanical properties (comparable to those of polyethylene for oriented PPV)[7]; it can be considered as the copolymer of benzene and acetylene monomers, so that its electronic properties are intermediate between those of PPP and polyacetylene (PA)[8]; and it can also be p- or n-doped into a metallic regime comparable to that of PA[9].

EXPERIMENTAL

The PPV was synthesized by the method of Wessling and Zimmerman[10], which is briefly described here.

First, the sulfonium monomer is obtained by reaction of dihalogeno p-xylene with a sulfide. In the preparation of PPV for this study, the sulfide used was tetrahydrothiophene[11]:
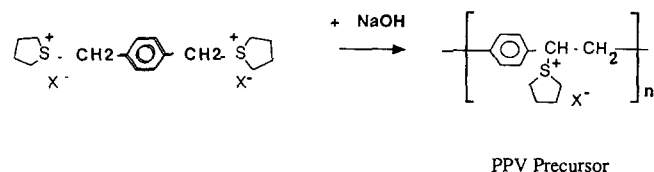

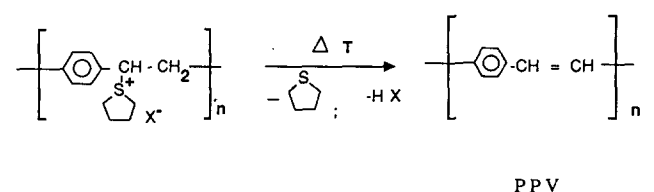(X = Br or Cl)   Sulfonium Monomer

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The polymerization reaction is carried out with sodium hydroxide, as shown by:

$$\text{⟨S⟩}^+ \cdot CH2 \text{-⟨O⟩-} CH2 \cdot \text{⟨S⟩}^+ \quad + \text{ NaOH} \quad \longrightarrow \quad \left[\text{-⟨O⟩-} \underset{\text{⟨S⟩}^+ \ X^-}{CH \cdot CH_2} \right]_n$$

$$X^- \qquad\qquad X^-$$

<div align="center">PPV Precursor</div>

The solution of reaction is then submitted to dialysis in order to eliminate all the under-products or non-reactant residues as well as the low-molecular-weight products ($< 10^4$ Da). The obtained polymer, a hydrosoluble polyelectrolyte of polysulfonium, is the precursor of PPV. The casting of the precursor allows the production of PPV films of different shape and thickness.

The pyrolysis of these films under an inert atmosphere in the temperature range 180–280°C gives rise to the elimination of sulfide and halogen acid, and leads to the final product of PPV:

$$\left[\text{-⟨O⟩-} \underset{\text{⟨S⟩}^+ \ X^-}{CH \cdot CH_2} \right]_n \quad \xrightarrow[- \text{⟨S⟩} \ ; \ -HX]{\Delta \ T} \quad \left[\text{-⟨O⟩-} CH = CH \text{-} \right]_n$$

<div align="center">PPV</div>

It is noteworthy that the use of tetrahydrothiophene in this synthesis has the advantage of lowering the pyrolysis temperature and minimizing the side-reactions[11].

Characterizations of the thin films obtained by optical methods (u.v.-vis.) and surface analysis were performed on probe samples to ensure the quality of the films. Metal–PPV–metal structures were obtained by casting the PPV precursor film on a glass substrate containing a predeposited chromium electrode; this is found to give the most satisfactory results (with no destruction of the electrode). After an annealing treatment of the system at 200°C for 3 h in a high vacuum furnace, the PPV film was formed. The system was cooled down to room temperature and a subsequent metallization step was carried out to obtain the top electrode. Aluminium and chromium were used in this experiment, the thickness of the metallic electrodes was about 100 nm to ensure low contact resistance conditions. All evaporation procedures were performed under high vacuum conditions ($< 10^{-6}$ torr). The active area of the samples was 2×2 mm^2 and their thickness varied from 0.5 to 1 μm.

The electrical measurements were performed in a vacuum of 10^{-3} torr in the temperature range 77–420 K. The current was measured using a high-impedance input electrometer (Keithley 617) coupled to a computer. The X.p.s. measurements were performed on a Leybold LH 12 analyser (CNRS-Université de Nantes) using a Mg Kα X-ray source in a UHV system, the pressure of the chamber being kept in the 10^{-9} torr range during the experiments. Binding energy data were referenced to the Au $4f_{7/2}$ line (84 eV) from a gold plate attached to the sample holder.

RESULTS AND DISCUSSION

Identification of complex species in interfacial layers

The metal–polymer interfaces were analysed using the X.p.s. technique to study the chemical bondings in these regions and compare them with those in PPV films. For

this purpose, thin films of PPV were deposited on stainless steel substrates with or without metallic electrodes, the preparation parameters being kept identical as in the metal–PPV–metal device fabrication technique. In order to reach the interfacial layer, successive removals of the metallic overlayer were performed by Ar$^+$ bombardment of the sample surface. The accelerating voltage of the ion beam was kept at 1 kV to avoid possible damage of the analysed surface (previous tests performed on both polymer and metallic surfaces did not show any change in the shape and the peak position of the carbon or the metal X.p.s. lines before and after erosion). The spectra of the core level of carbon, oxygen and metal were recorded after each erosion and the process was repeated until the whole interfacial layer had been analysed. This layer is defined as that where both carbon and metal spectra are observed. When approaching the polymer side, the intensity of the metal spectrum gradually decreased while that of the carbon line increased and became constant inside the polymer films. This was used to estimate the thickness of the interfacial layer in our experiment.

The spectrum of uncovered PPV film consists of the C(1s) line which is located at 284.5 eV with a full width at half maximum ($FWHM$) of 1.5 eV (*Figure 1a*, curve f); this line is characteristic of carbon atoms in phenyl rings. Traces of oxygen are also found at the surface of the film with the O(1s) line located at 532.5 eV. However, its intensity is very weak compared to that of the C(1s) line; the contamination affects only a few atomic layers near
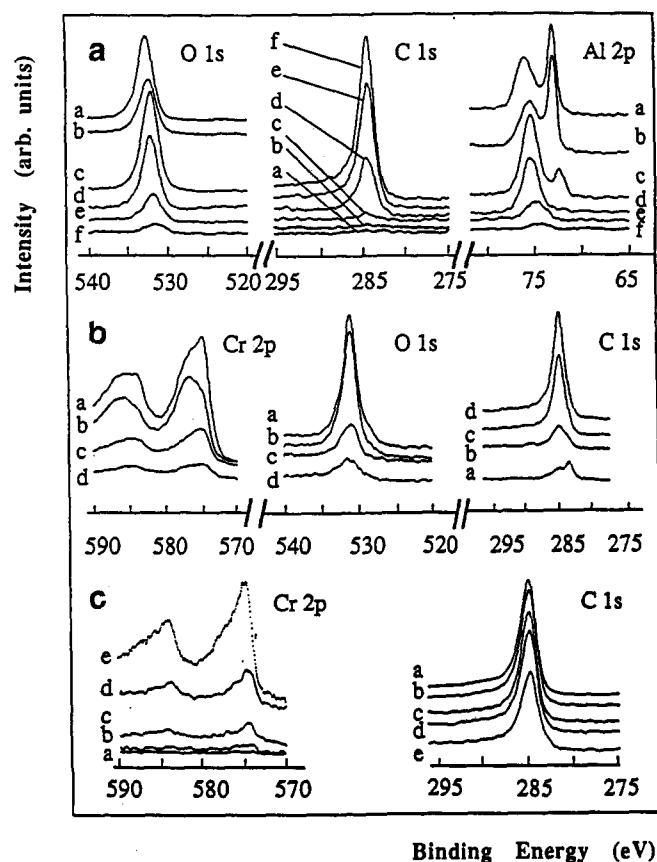

Figure 1 X-ray photoelectron spectroscopy spectra of PPV films: (a) in the interfacial layer PPV-Al with successive removals of the Al layer (curves a–f); (b) in the interfacial layer PPV–Cr with successive removals of the Cr layer (curves a–d); (c) in the interfacial layer Cr–PPV with successive removals of the Cr layer (curves a–e)

the surface since this line disappeared after cleaning of the film by ion bombardment as described before. It should be noted that the samples were stored *in vacuo* before X.p.s. analyses and furthermore handling of the samples during transfer into the analysis chamber was limited to only a few minutes. This result is very similar to studies reported on neutral PPV thin films in which the presence of a slight oxidation of the film surface was also mentioned[12].

For the PPV–Al interface, we observe a significant presence of oxygen judging by the intensity of the O(1s) line (*Figure 1a*). This line grows in intensity further from the polymer surface. It has a peak position at 531.6 eV which gradually shifts to O(1s) in Al_xO_y (532.6 eV) in the outermost layer. In the intermediate layers, Al_2O_3 is also observed with the peak at 532 eV (curves c and d). Simultaneously, aluminium is also detected in the interfacial layer. The Al(2p) spectra show an evolution in lineshape and in peak position throughout the interface. Near the surface of the polymer film, the Al(2p) peak is located at 74.6 eV. It then shifts to 75 eV which corresponds to Al(2p) of Al_2O_3 while another component also grows at 72.7 eV (curves c) indicating that clean Al is formed[13]. As for the C(1s) line, its position seems to be unchanged compared to that of pristine PPV surface (284.5 eV). A small shoulder at 284 eV is, however, observed in the curves b and c which may reflect a change of carbon bindings in some parts of the interfacial layer.

For the Cr–PPV interfaces, the spectra of O(1s), Cr(2p) and C(1s) corresponding to the top contact of PPV–Cr interface are shown in *Figure 1b*. As in the case of the PPV–Al interface, a growth of oxygen species with a peak position of the O(1s) line situated at 531 eV having a small shoulder at 530.5 eV (curve d) is observed when approaching the polymer surface. On the other hand, the Cr(2p) spectra show important changes in lineshape from clean chromium (curve a). The peak position of this line shifts from 574 eV (curve a) to 576.6 eV (curve c) and finally to 574 eV (curve d) just beyond the PPV film with an increase in linewidth. It is evident that chromium oxide Cr_2O_3 is present in the layer as shown by the peak by 576.6 eV[12]. As in the case of the 576 eV peak, it would correspond to some intermediate chromium oxide compound[14]. The C(1s) spectra show very different features to those observed in the PPV–Al interface. Although the main peak near the polymer side is located at 284.5 eV, another component is seen at 283.3 eV in the outermost layer. This new peak corresponds to that of carbon bindings observed in metal–carbon complex systems[15,16].

For the PPV–Cr interface corresponding to the bottom contact of the metal–PPV–metal structures, the main features of the spectra are shown in *Figure 1c*. The most interesting observation concerns the positions of both Cr(2p) and C(1s) peaks which remains unchanged throughout the interface. On the other hand, oxygen is almost absent and the Cr(2p) line shows no shoulder at 576.6 eV which is attributed to chromium oxide. Thus it appears that in this interface, chromium is found in the form of clusters embedded in the polymer matrix since its bindings and those of carbon are not modified.

Formation of complex species in interfacial layers

The X.p.s. data indicate that during metallization of PPV films at room temperature, Cr and Al (top electrodes) react with carbon in the presence of oxygen

while PPV deposited on the Cr layer (bottom electrode) has no reaction with it. The presence of oxygen in the interfacial layers is surprising at first sight. As we have already mentioned, the surface of as-deposited PPV thin films is sometimes found to be slightly oxidized but this oxidation is superficial. The recorded X.p.s. spectrum of the eroded surface permits the oxidized thickness to be evaluated as only a few atomic layers. In addition, it is unavoidable that all the metals used in this experiment could have been oxidized when exposed to air (X.p.s. spectra of as-deposited metallic layers show peaks corresponding to oxides). Nevertheless, with the first erosions performed on these layers, the oxide peaks disappear and are replaced by native metallic peaks. However, despite these facts, oxidation has already occurred on the outermost layers of the PPV–metal interface leading to the change in peak position of the aromatic carbon. Thus the presence of oxygen can be most readily explained by leaks in the vacuum chamber. Hence oxidation of the electrode as well as the polymer could occur during the deposition since the O(1s) line is observed throughout the interfaces. For the PPV–Cr interface, the intensity of this line is weaker, but in curve a of *Figure 1b* the characteristic satellite of chromium oxide (Cr_2O_3) can be seen in the Cr(2p) line, this proves that oxygen is effectively present in the layer. As for the PPV–Al interface, the oxidation there is much more important and it seems that many intermediate oxidation states are present as revealed by the continuous change of the O(1s) line from 531.6 to 532.6 eV.

By contrast, in the bottom contact (chromium–PPV interface), the O(1s) line intensity is practically negligible and neither the chromium nor the carbon lines have changed in position, so the polymer is preserved from chemical reaction. The absence of oxygen species may be explained by the side-reaction. In fact, the thin oxide layer formed on the bottom electrode is in contact with the precursor polymer solution in the preparation process. During the pyrolysis of the precursor, HCl generated from the reaction destroys this oxide layer, taking away the residual oxygen on the chromium electrode and giving rise on the surface of the Cr metal to chromium chloride which is insensitive to oxygen (from vacuum leaks during the metallization of the top electrode). However, since X.p.s. spectra also show no trace of the metallic oxide–PPV interaction, it is most likely that oxygen cannot diffuse through the compact PPV film into the bottom interfacial layer.

Furthermore, it is known that in amorphous semiconductors the formation of rectifying contacts is often linked to the presence of oxygen at the interface[17,18]. On the other hand, it is known that aluminium and to a lesser extent chromium are very reactive with oxygen in some polymers containing functional groups with oxygen[19]. For instance, Al breaks the carbonyl bonds at the surface of the polymer and forms the Al–O–C complex[15,20]. Similar reactions have been also observed in PPP that originally did not contain oxygen[4]; the mechanism of the complex formation in this polymer was explained by oxygen assistance. This mechanism involves the diffusion of metal into the polymer film and the combination of metal with the carbon of the polymer and residual oxygen. Since oxygen is effectively detected by X.p.s. analysis, we suppose that the chemical reactions between Al (and Cr) and the PPV films required oxygen which is introduced by the contamination. The role of
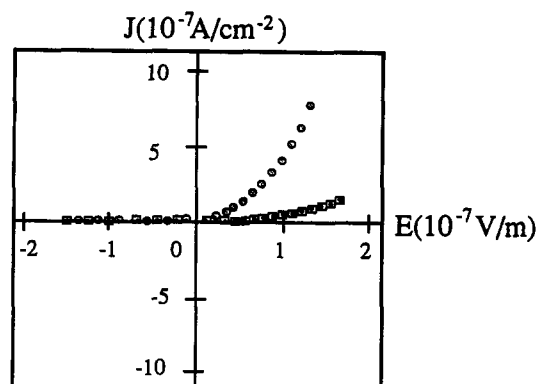
$J(10^{-7}A/cm^{-2})$

Figure 2 *J–E* characteristics at room temperature of: (○) a Cr–PPV–Cr structure; (⊞) a Cr–PPV–Al structure

oxygen is to create radicals on the C atoms in the polymer to facilitate the formation of metallic carbide. Nevertheless, the exact nature of the compounds formed in the interfaces could not be investigated further because our attempts at characterization of the complex structures by optical spectroscopy (i.r. and Raman) failed. However, from the above results, it is obvious that metallic oxides are formed in the interfaces[4], and the displacements of the X.p.s. spectra, namely the C(1s) line, are consistent with the formation of a metal carbide[21] or a metallic oxide–carbide (M–O–C) complex[4].

Charge transfer behaviour of metal–PPV–metal devices

Typical dark current density *versus* applied electric field (*J–E*) characteristics of two devices, Cr–PPV–Cr and Cr–PPV–Al, at room temperature are shown in *Figure 2*. The characteristics are asymmetrical and show a rectifying behaviour. The forward bias corresponds to a negative voltage on the top electrode (Cr or Al). We can observe that both characteristics show a blocking contact with negative polarity of the top electrode; this part of the characteristics obviously corresponds to the bottom contact between chromium and the polymer. As for the top contacts, both Cr and Al form rectifying contacts to PPV films but their behaviours are apparently different, the rectifying ratio (forward current density/reverse current density) of the Cr–PPV contact is greater than that of the Al–PPV one. From the polarities of the biased structures, we suggest that the electrons are transferred from the top electrodes into the polymer which is p-type. The fact that *J–E* characteristics are asymmetrical for the symmetrical structure Cr–PPV–Cr is not surprising since this can be explained by the complex species in the metal–polymer interface.

Mechanisms of the rectifying contact

The M–O–C complexes identified above have been found to be responsible for the electrical a.c. behaviour of the metal–polymer–metal devices[16,19,22,23]. However, according to ref. 24 rectifying or ohmic contacts of semiconducting devices can be obtained by choosing metals with appropriate work functions with regard to that of semiconducting materials. In terms of energy band structure, the barrier height depends on the difference between the work function of the metal ψ_m and that of the semiconductor ψ_s. However, experiment shows, in many instances, that real surfaces behave quite differently and, in particular, the potential barrier is often found to be independent of the work function of the electrode

metal[25]. Furthermore, the studies of CH_x diodes with several metallic contact types[26] have underlined that the work function approach alone could not explain the behaviour of actual contacts. Finally, many workers proposed that the charge transfer occurred from metal to carbon atoms via oxygen atoms giving rise to the rectifying behaviour[19,22,23]. However, the metallic oxide seems not to play an essential role in the rectifying behaviour of the device and since the oxidation of Al is found to be much more important than that of Cr, the rectifying effect of Cr–PPV–Al system is lower than that of Cr–PPV–Cr (*Figure 2*). By contrast, the metallic carbide seems to play a principal role in the rectifying contacts. In fact, when carbon atoms of PPV do not react with Cr (at the bottom electrode) a blocking contact is observed. On the other hand, the displacement of the C(1s) line seems to be linked to the rectifying effect as observed in our samples and also in metal–polyacetelene contact[27]. In fact, the rectifying ratio is found to be greater in the PPV–Cr contact than in PPV–Al and the corresponding carbon line shifts are respectively 1.2 and 0.3 eV. Accordingly, the charge transfer is expected to occur directly from carbon atoms to metallic ones.

CONCLUSION

From the X.p.s. analyses of the interfaces formed between PPV thin films and metallic electrodes such as chromium or aluminium, we have shown that the chemical interactions between metal and polymer giving rise to a metallic oxide–carbide (M–O–C) complex are catalysed by oxygen. They occur only in the system obtained by deposition of metal on PPV polymer but not in that obtained by deposition of metal on the PPV precursor because of side-reactions during pyrolysis of the precursor. The electrical measurements performed on these devices show that the rectifying behaviour of metal–polymer–metal structures is in close relation with the formation of metal carbide in the interfacial layers.

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