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Ohmic contacts between sulfonated polyaniline and metals

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Abstract We have compared the resistivity, ρ , of sulfonated polyaniline (SPAN) prepared via three different synthetic routes: electrochemical synthesis with a supporting electrolyte (camphorsulfonic acid), $\rho = 340 \Omega\cdot\text{m}$; electrochemical synthesis without a supporting electrolyte, $\rho = 530 \Omega\cdot\text{m}$, and; chemical synthesis, $\rho = 166 \Omega\cdot\text{m}$. Independent of the metal contact (Al, Au, Cu), SPAN forms ohmic contacts with the metal and the contact resistance $r_c \sim 5 \Omega$ does not correlate with the metal's work function.

Keywords Sulfonated polyaniline · Ohmic contacts · Organic electronics

Introduction

Conjugated polymers constitute a class of materials that present interesting properties in both the doped and the undoped forms, associating the mechanical advantages of polymers with some electronic or optical properties of semiconductors required for device application. Several devices based on conjugated polymers and molecules have been reported, e.g., light-emitting diodes [1], transistors [2], photodetectors [3], high rectification ratio diodes [4], switches [5], and electronic memories [6], some of these achieving a performance compatible with commercial viability.

As also is the case with inorganic semiconductor devices, ohmic contacts are necessary in organic semiconductors to avoid excessive energy dissipation and/or injection current-controlled charge transport. Considering that, in several nominally undoped conjugated polymer films, the charge transport is injection-limited (at least for small thickness values [7]) and dependent on

the choice of electrode metal, ohmic contacts associated to one-directional charge transport limiting interfaces (rectifying contacts) permit the construction of high rectification devices [4]. Furthermore, low contact resistance (r_c) interfaces are necessary in multilayer organic devices or even in connecting paths.

Intensive research on polyanilines (PANI) and their derivatives has been carried out in the last decade [8]. Among the PANI derivatives, special interest has been devoted to sulfonated polyaniline (SPAN). Yue and Epstein [9] reported the synthesis of SPAN with 50% of the PANI phenyl rings sulfonated by the treatment of PANI with concentrated sulfuric acid. The properties of SPAN are different from those of PANI, mainly in the following aspects: high solubility in aqueous alkaline solutions, the property of self-doping, and the fact that the conductivity does not change upon treatment with aqueous solutions at $\text{pH} \leq 7$ [10, 11, 12]. A different approach to obtain SPAN is the electrochemical copolymerization of aniline with metanilic [13, 14, 15, 16, 17] or orthanilic acid [18, 19] (*meta*- or *ortho*-aminobenzenesulfonic acid) in several electrolytes.

During electrochemical polymerization, the presence of foreign anions could lead to side reactions or influence the morphological or conductive properties of the polymer, through, for example, migration inside the film during current versus voltage $I(V)$ measurements. Formation of the polymer in the absence of a supporting electrolyte should, therefore, yield a material with more reproducible and well-defined properties. A self-doped polymer can be produced by reaction of monomeric units in the absence of a supporting electrolyte, using the monomer itself as electrolyte [19].

In this contribution we demonstrate that sulfonated polyaniline (SPAN) obtained either by electrochemical polymerization (with and without a supporting electrolyte) or by chemical synthesis exhibits a low resistance ohmic contact with Au, Al, and Cu, three of the most commonly used metals in electronics. SPAN has the additional advantage that it presents good adhesion

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onto these metals and better thermal stability than conventional polyaniline [20].

Materials and methods

The electrochemical formation of SPAN films was carried out by cycling the potential between -0.10 and 0.90 V (versus Ag/AgCl/KCl), for the solution containing the supporting electrolyte camphorsulfonic acid (CSA) and -0.10 and 1.0 V for the solution without a supporting electrolyte. In both cases, the upper limit was 1.1 V for the first cycle. A platinum wire was used as counter electrode and the used scan rate was 50 mV/s. The electrolyte solution was 0.1 mol/L CSA + 0.1 mol/L metanilic acid + 0.01 mol/L aniline (denoted in the sequence as SPAN-CSA) or 0.1 mol/L metanilic acid + 0.01 mol/L aniline (denoted in the sequence as SPAN-WSE). All resulting SPAN films, deposited on gold working electrodes, presented good adherence and homogeneity. The occurrence of sulfonation was verified using FTIR (Fourier transform infrared spectroscopy), through the presence of peaks at 1312 and 1034 cm^{-1} , corresponding to the C-N and S-O stretching bands, respectively [15].

For chemical synthesis, the PANI emeraldine base was sulfonated by dissolving it in fuming sulfuric acid as described previously [9]. The SPAN precipitate was dissolved in aqueous NH_4OH solution 0.1 mol/L (10 mg/mL). After filtering, the solution was spin coated onto the metallic substrate. The spin-coated films spontaneously released the weak base NH_3 to produce films of SPAN in the self-doped emeraldine salt form. These films required no further doping. They were maintained at 60 °C during 1 hour in order to remove remaining water. FTIR data showed absorption bands at 820 and 870 cm^{-1} , indicative of 1,2,4- trisubstitution, and 1080 , 700 and 620 cm^{-1} , which are the absorptions of the sulfonic groups [10]. In the sequence, these films will be denoted as SPAN-CHE.

Devices for electrical measurements were prepared in a sandwich structure. The bottom metallic contact was evaporated onto a glass substrate, followed by SPAN deposition through one of the above-cited methods. In the sequence, the upper metallic contact was evaporated onto the SPAN film to complete the device. For the cases of SPAN obtained by the electrochemical methods, gold was used as bottom contact and aluminium as upper contact. For SPAN obtained chemically, aluminium was used as bottom contact and copper as upper contact.

The $I(V)$ curves were measured by changing the applied voltage stepwise (steps of 0.05 V) at a rate of 0.05 V/s. The SPAN film thickness was determined using a surface profiler. The device area was of 1 mm^2 .

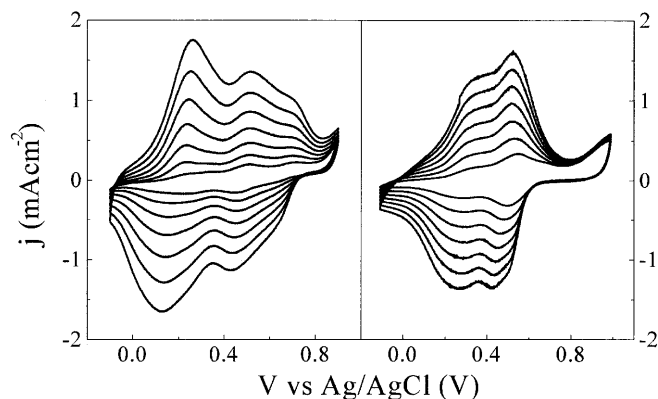


Fig. 1 Successive cyclic voltammograms recorded every 10^{th} cycle of a Au electrode in: 0.1 mol/L CSA + 0.1 mol/L metanilic acid + 0.01 mol/L aniline (left); and 0.1 mol/L metanilic acid + 0.01 mol/L aniline (right). Scan rate: 50 mV/s

Results

In Fig. 1 we present the cyclic voltammograms of the SPAN-CSA (left) and SPAN-WSE (right) film growth.

Fig. 2 relates film thickness as a function of the number of growth cycles for the electro-synthesis of SPAN-CSA and SPAN-WSE.

In Fig. 3 the $I(V)$ curves obtained from Au/SPAN-CSA/Al devices with different SPAN-CSA film thickness, can be seen. Several devices with film thickness t ranging from 46 to 235 nm were investigated, but only some examples are shown in the Fig. 3, to avoid data overlap and loss of clarity. The linear $I(V)$ dependence of Au/SPAN-CSA/Al indicates ohmic behaviour of this device in the investigated voltage range, independent of polarity. This result indicates that both Au and Al (which have quite different work functions, approximately 5.1 eV and 4.3 eV, respectively [20]), form ohmic contact with SPAN-CSA. From these data, the resistance $R = \left(\frac{\partial I}{\partial V}\right)^{-1}$ can be calculated. Qualitatively similar results were obtained for SPAN-WSE and SPAN-CHE. In Fig. 4 we present the $R(t)$ data for the devices: Au/SPAN-CSA/Al, Au/SPAN-WSE/Al, and Al/SPAN-CHE/Cu.

Assuming that $R = 2r_c + R_f$, where R_f is the resistance of the polymer film ($R_f = \rho \frac{t}{A}$, where ρ is the polymer resistivity and A is the device area, perpendicular to current flow), the extrapolation of $R(t \rightarrow 0)$ leads to $r_c \cong 4.5$ Ω/mm^2 for Au/SPAN-CSA/Al, less than recently reported for Cu/PEDOT(PSS) [4], [PEDOT(PSS): poly(3,4-ethylenedioxythiophene)/polystyrenesulfonate]. The independence of R on the voltage polarity permits us to consider the r_c -values of Au/SPAN-CSA and Al/SPAN-CSA as being nearly the same. Furthermore, we calculate $\rho = A \frac{\partial R}{\partial t} \cong 340 \Omega \cdot \text{m}$.

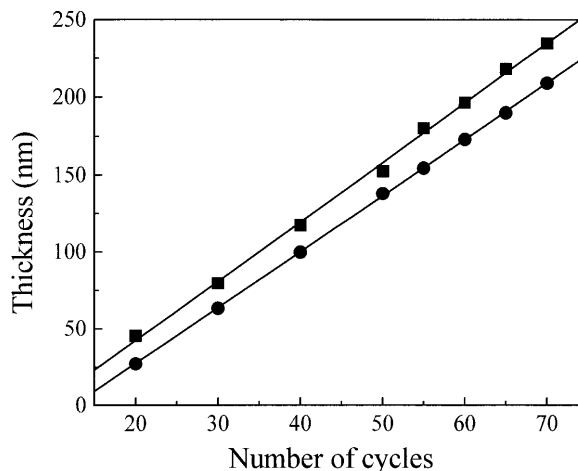


Fig. 2 Film thickness as a function of number of cycles for SPAN obtained electrochemically under the set of conditions described in Fig. 1. (squares: SPAN-CSA; circles: SPAN-WSE; continuous lines are linear fits to each set of data)

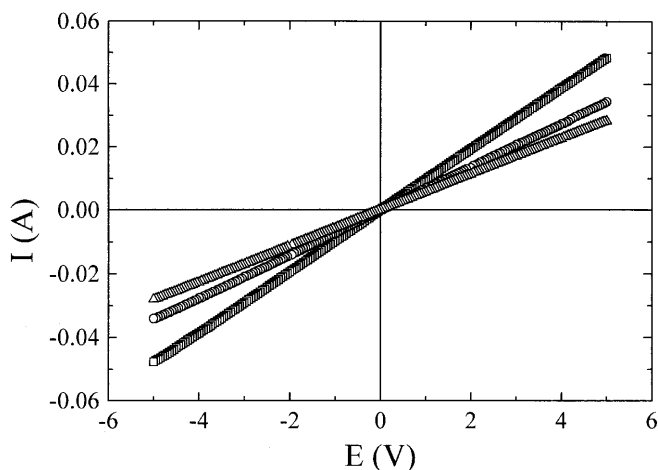


Fig. 3 $I(V)$ characteristics of Au/SPAN-CSA/Al devices for devices with different SPAN-CSA film thickness. (squares: 45.5 nm; circles: 152.5 nm; triangles: 234.7 nm)

The values of r_c and ρ determined using devices prepared with SPAN-CSA, SPAN-WSE, and SPAN-CHE are listed in Table 1.

Discussion

From the cyclic voltammograms presented in Fig. 1, it can be seen that, in the SPAN film growth process, the oxidation peak of the SPAN-WSE is displaced to a higher potential than that for SPAN-CSA. This observation is due to the contribution of the supporting electrolyte in the case of SPAN-CSA. Furthermore, by analyzing Fig. 2, it is possible to verify that the SPAN-CSA film growth is more efficient (larger film thickness values are achieved) than the SPAN-WSE film growth.

These results cannot be attributed solely to the difference in resistivity and contact resistance values of

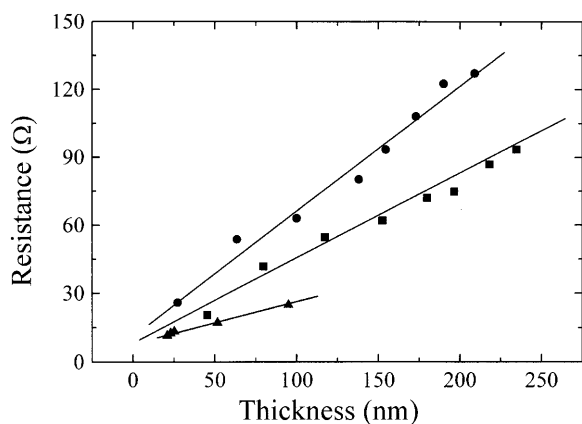


Fig. 4 Resistance of Au/SPAN-CSA/Al (squares), Au/SPAN-WSE/Al (circles), and Al/SPAN-CHE/Cu (triangles) devices as a function of SPAN-CSA film thickness. Continuous lines are linear fits to the experimental data

Table 1 Values of ρ and r_c determined using metal/SPAN/metal devices constructed with three different SPAN preparation routes, SPAN-CSA, SPAN-WSE, and SPAN-CHE

DEVICE	ρ [$\Omega\cdot\text{m}$]	r_c [Ω/mm^2]
Au/SPAN-CSA/Al	340	4.5
Au/SPAN-WSE/Al	530	5.7
Al/SPAN-CHE/Cu	166	4.2

SPAN-CSA and SPAN-WSE (see Table 1) that, in the case of SPAN-CSA, would permit higher currents to pass throughout the deposited film during the growth process. The oxidation peak is not gradually, but rather significantly displaced to higher potential values during the growth process.

The results summarized in Table 1 suggest, when comparing the electrochemical synthesis processes (SPAN-CSA and SPAN-WSE), that the CSA participate in the SPAN doping process, by adding an intermolecular doping contribution to the intramolecular doping of the sulfonic groups.

The SPAN-CHE films present lower resistivity than their electrochemically prepared counterparts. It is generally accepted that electrochemical synthesis severely limits the molecular weight of the synthesized polymer. In spite of the fact that conjugation length and molecular weight are not directly related, high molecular weight materials commonly present a higher conductivity. The resistivity values we have obtained in this work are lower than the value reported for SPAN pressed pellets (0.1 $\Omega\cdot\text{m}$) [9, 10, 11].

Some considerations about the choice of the electrode metal must be made. In the electrochemical synthesis Au was used as the bottom electrode due to its stability under the synthesis conditions. For SPAN-CHE, the Al bottom electrode was used because SPAN-CHE films deposited onto an Au substrate presented a high roughness and even showed discontinuities, frequently leading to short-circuits in the devices. Au evaporated on to thin polymer films presents difficulties, the occurrence of shorts also being frequent. For these reasons and to use a metal with a work function different from that of Al, which is commonly applied in electronic circuitry, Cu was selected.

In spite of the changes of the electrode materials combination used, the r_c value is nearly the same for the three SPAN synthesis routes (see Table 1), indicating that the potential barrier for charge injection does not correlate with the electrode metal's work function. A similar phenomenon was recently reported for phenylenevinylene oligomers [22]. A lowering of the energy levels of the organic layer was observed, presumably due to interface dipole layers such as to keep the hole injection barrier nearly constant and, therefore, at most only weakly sensitive to the work function of the metal or the ionization potential of the oligomer.

Poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate), PEDOT:PSS layers introduced be-

tween an electroluminescent polymer layer and ITO (indium-tin oxide) anode in organic light-emitting diodes, also present a similar effect [23, 24]. The introduction of the PEDOT:PSS layer implies a reduction of the potential barrier height at the anode/polymer interface and may improve hole injection, increasing device efficiency and reducing the turn-on voltage.

PEDOT:PSS and SPAN films seem to present quite similar properties concerning potential barrier height reduction at their interfaces with metals, probably due to a redistribution of charge density inside the film. By comparing both materials, it is important to stress that the contact resistance values found in this work for SPAN/metal interfaces are lower than the corresponding values for PEDOT:PSS [4], constituting an advantage in device applications. Furthermore, PEDOT:PSS is a blend of PEDOT and PSS whereas SPAN can be applied as a single-component material.

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