A new four-point probe design to measure conductivity in polymeric thin films

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Un nou disseny de sonda de quatre punts per mesurar la conductivitat en capes primes polimèriques.

Un nuevo diseño de sonda de cuatro puntos para medir la conductividad en capas delgadas poliméricas

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RESUMEN

En el desarrollo de nuevas aplicaciones de polímeros conductores, la medida de forma precisa de la conductividad es todavía un reto, especialmente para muestras muy delgadas como los obtenidos por CVD. Este estudio muestra el diseño de una sonda de cuatro puntas innovadora, para la caracterización de la conductividad de capas delgadas de polypirrole sintetizadas por polimerización por plasma. El sistema asegura la distancia mínima posible entre los electrodos, junto con una gran relación longitud vs espaciamiento entre los electrodos para mejorar la respuesta eléctrica. La sonda de cuatro puntas ha sido fabricada en una placa de circuito impreso, que ofrece algunas ventajas común mejor calidad en la deposición del polymer, el bajo costo o la repetibilidad en las medidas.

Palabras clave: Capas delgadas, polipirrol, conductividad, polimerización asistida por plasma.

SUMMARY

In the development of new conducting polymers applications, the conductivity measurement is still a challenge, specially for extremely thin samples as the ones obtained by CVD. This study shows the design of a novel four-point probe for conductivity characterization of polypirrole thin films synthesized by plasma enhanced polymerization.. The system possesses the minimal distance possible among electrodes, together with a high ratio of electrode length to spacing to enhance the electrical response. The four-point probe has been fabricated in a printed circuit board, which offers some advantages such as non-damaging samples, low cost or repeatability in the analysis measurements.

Key words: Thin films, polypyrrole, conductivity, plasma polymerization

RESUM

En el desenvolupament de noves aplicacions de polímers conductors, la mesura de forma acurada de la conductivitat és encara un repte, especialment per a mostres molt primes com els obtinguts per CVD. Aquest estudi mostra el disseny d'una sonda de quatre puntes innovadora, per a la caracterització de la conductivitat de capes primes de polypirrole sintetitzades per polimerització per plasma. El sistema assegura la distància mínima possible entre els elèctrodes, juntament amb una gran relació longitud vs espaiament entre els elèctrodes per millorar la resposta elèctrica. La sonda de quatre puntes ha estat fabricada en una placa de circuit imprès, que ofereix alguns avantatges comuna millor qualitat en la deposició del polymer, el baix cost o la repetibilitat en les mesures.

Mots clau: Capes Primes, Polipirrole, Conductivitat, Polimerització assistida per plasma

The four-point probe technique is the most commonly used to measure resistivity in semiconductors. The set-up consists of four-point collinear probes, where a constant current is applied in the two outer probes and the voltage drop is measured in the inner probes. Then, the surface or sheet conductivity is given by equation 1, where CF is the correction factor based on the ratio of the probe to wafer diameter and on the ratio of wafer thickness to probe separation.

$$\sigma = \left(\frac{V}{I}\right) * CF \qquad (1)$$

Electrical measurements in the micro/nanoscale have gained an increasing attention in the development of different kind of devices. As the Moore's law predicts there has been a continuously reduction in the size of these electrical components. Because of that, nanotechnology has to overcome the difficulties related to working at such a small scale. Different attempts have been performed to measure conductivity in several types of materials. Conducting Atomic Force Microscopy (C-AFM) has been used in the study of ITO films [1] or in DNA conductivity [2]. Nevertheless, one of the problems associated to this kind of technique is the parasitic capacitance associated in these measurements. This unwanted effect can be avoided by using the four-point probe technique. Due to the fact that the current between the inner probes is practically zero, the contact resistance can be neglected. This method is particularly useful for measuring very small samples because the dimensions of the samples and the spacing of the contacts are insignificant. Furthermore, when the sample thickness is much thinner than the probe spacing, the correction factor becomes a constant, π/Ln2. Consequently, this technique can be used for flat, arbitrarily shaped samples [3]. According to this, several research groups have designed different four-point probe arrays. Keller et al have reported the fabrication of a microscopic four-point probe with a spacing of about 15 μm among the probes by a micromachining process [4]. Ju et al have managed to reduce the separation among electrodes to 1 μm by modifying an AFM probe using a focused ion beam system (FIB) [5]. Similar electrode spacing can be constructed using microfabrication of these probes by photolithography [6]. However, for all these systems there are some drawbacks that need to be improved. One of the key factors in the resistance measurements is the contact between the sample and the probe. For instance, achieving a proper ohmic contact in the junction is highly important in the development of diodes [7]. On the other hand, an excessive force in the contact pressure can lead to an irreversible damage in the probe or, even, in the sample, especially for polymers. In our study, an insight in the electrical characterization of polymeric thin films is presented. In order to solve the problems discussed previously, we have performed the conductivity measurements on printed circuit boards on which the probes have been incorporated. Moreover, different kinds of geometry and configuration have been tested. As a result, a new printed circuit board, which combines the advantages of the different probes, has been designed. Consequently, to develop a four-point probe incorporated in a printed circuit board enables to work without any risk of damaging the sample during the analysis. In addition, a printed circuit board fabrication is a very cheap and easy method to manufacture these arrays. These reasons make these arrays excellent candidates for resistivity measurements studies in thin films.

To carry out the measurements a polypyrrole (PPy) thin film has been deposited over the electrodes. Our research group has a broad experience in the synthesis and deposition of polymers by plasma enhanced chemical vapor deposition (PECVD) [8-10]. This technique enables an absolute control in the deposition rate by adjusting the base and the operating chamber pressure. In addition, by working without any solvent, any undesirable reaction is prevented. Nevertheless, PECVD yields the reduced form of polypyrrole and requires an oxidation process to obtain the conducting form after its synthesis, which is not needed in the chemical or electrochemical method [11]. An exposure to the iodine vapour in an iodine-saturated chamber stimulates the oxidation process, which distributes positive charge on the backbone of the polymer and generates electroconductivity of the polymer[12].

The PPy thin films were deposited in a homemade reactor previously described [13]. The vacuum chamber was evacuated to a base pressure of 0.04 mbar, and the working pressure was set at 0.07 mbar. The polymerization time was fixed at 40 minutes for all the samples. The experiments were carried out at a power of 20 W, with a frequency of 15 Hz and a duty cycle of 90%. Finally, samples were left in an iodine chamber for 30 minutes to carry out the doping process. Different kinds of electrodes (Figure 1) were polymerized by PECVD. Afterwards, the resistance measurements were performed using a SOLARTRON 1260 impedance analyzer. The probe geometry can be classified into four-point probe, two-point probe and interdigital probe. Moreover, there are different models concerning the area and the separation among probes. The purpose is to study the correlation between these parameters and the resistance to determine which are the most critical factors for designing the new probe.

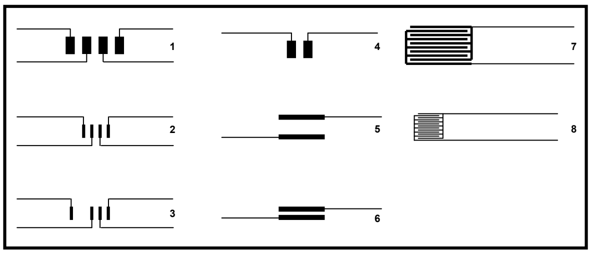

Figure 1. Schematic representation of the different probes used for the resistivity measurements. The four-point probes correspond to numbers 1, 2 and 3, and are named 4Pa, 4Pb and 4Pc respectively. The two-point probes correspond to numbers 4, 5 and 6, and are named 2Pa, 2Pb and 2Pc respectively. The interdigital probes correspond to number 7 and 8, and are named IPa and IPb respectively.

The eight probes, divided into three groups, employed in the experiments are described as follows. There were three different kinds of four-point probes, 4Pa, 4Pb and 4Pc. The 4Pa electrodes had a active area of 2.00 x 1.00 mm and an electrode spacing of 0.90 mm. In 4Pb, the electrodes area measured 1.30 x 0.25 mm and the spacing 1.00 mm. The 4Pc had the same electrode area as that of the 4Pb, but the spacing among probes was changed. The three closer electrodes were separated by 0.44 mm and the external one by 2.00 mm. Moreover, there were three different types of two-point probes, 2Pa, 2Pb and 2Pc. The 2Pa had an electrode geometry that measured 1.30 mm in length and 0.25 mm in width, and the distance between the probes was 0.90 mm. The 2Pb consisted of two 5.00 x 0.125 mm electrodes separated by 1.40 mm. In the 2Pc, the electrode area was the same as that of 2Pb and the separation between probes was reduced to 0.20 mm. At last, two different interdigital probes were tested: IPa and IPb. IPa was composed by 10 electrodes each with an area of 10.00 x 0.23 mm and separated by 0.315 mm. While IPb had 14 electrodes with an area of 5.00 x 0.135 mm and separated by 0.19 mm. The probe resistance measurement of all the systems was performed before the plasma polymerization in order to acquire a reference value for further experiments. The resistance was practically the same for all eight probes, at around 10^8 Ω. After the polypyrrole deposition on the probes, the resistance remained 10^8 Ω for 4Pa, 4Pb, 4Pc, 2Pa and 2Pb. A possible explanation for this might be that the probe layout is incorrect. Thus, despite having a conducting polymer, no electrical signal flows through the probes. In contrast, a change in resistance values has been observed in 2Pc, IPa and IPb, which were 10^7 Ω, $9{\cdot}10^5$ Ω and 10^5 Ω respectively. The main difference respect the other samples is the distance among probes. The lowest resistance corresponds to the probe with the shortest spacing among electrodes, the IPb. These results could be explained taking in account that charge transport in conducting polymer is ruled by the probability of hopping transport, which is the phenomenon of charge carriers passing from one molecule to another [14]. Due to the fact that PPy has been deposited in the nanometer range, the probability of hopping is lower since there are fewer possible pathways among molecules. Therefore, it seems logical that a larger spacing among probes makes the charge transport more difficult. In addition, the IPa probe shows a lower resistance that the 2Pc probe despite having a larger distance among electrodes. It should be noted that probes with a different configuration have been used. The interdigital possesses a bigger electrode surface area, which could enhance the electron transfer between the electrodes, comparing with 2Pc probe. Therefore, one of our interests would be to optimize the probe area. It is possible to hypothesise that the electrode area probe should be enlarged to improve the electron transfer process. Based on this, we postulate that a probe with an enlarged area and minimal probe spacing will improve the electron transfer process.

Table 1. Resistance measurements of the different probes

	4Pa	4Pb	4Pc	2Pa	2Pb	2Pc	IPa	IPb
R [Ω]	10^8	10^8	10^8	10^8	10^8	10^7	$9{\cdot}10^5$	10^5

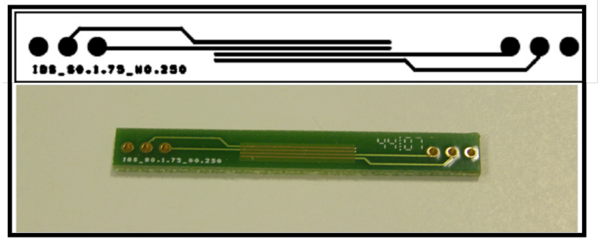

Figure 2. Scheme and picture of the four-point probe design.

Comparing all the results discussed above, we concluded that the interdigital probe presents the most interesting characteristics related to spacing electrodes and electrode configuration. The goal of this work is to combine these optimal features with the four-point probe geometry to make profit from the advantages discussed previously. As a result, we have designed a new four-point probe in a printed circuit board which is shown in Figure 2. The length of the probe is 15 mm and the width 0.25 mm, the distance among probes has been fixed at 0.285 mm (the minimal distance that can be achieved in the circuit print board design for this configuration). A final experiment was carried out using the new probe. A 190 nm thick PPy film was deposited on it. Then, to study the voltage behaviour of the sample, a current range was applied. It was observed a correlation between voltage and current from 20 nA to 2 μA (a region of this trend can be observed in Figure 3), resulting in a 0.1 S/cm electrical conductivity. To study the deposition of PPy some AFM topography images were taken (XE-100, Park System). Figure 4 compares the probe topography before and after the plasma polymerization. A clear difference is observed after the modification between the two images. Furthermore, the modified image presents the typical features of PPy thin films, as it was investigated previously [13]. The mountain-shaped structures can be attributed to the nucleation-growth step in the PPy polymerization. Hence, it can be suggested that the probes, which are made of copper, do not interfere with the PPy deposition process.

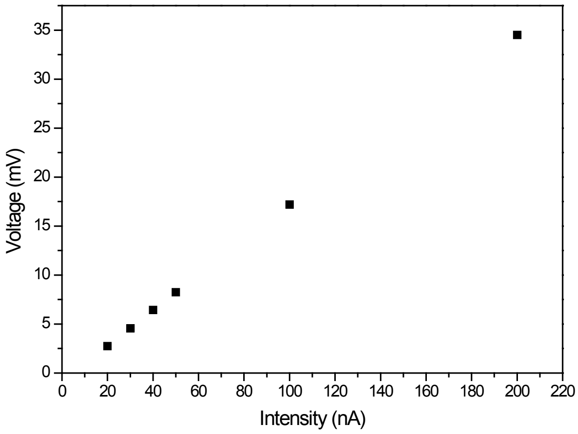

Figure 3. Voltage Vs Current graph of a PPy thin film measured with the new four-point probe.

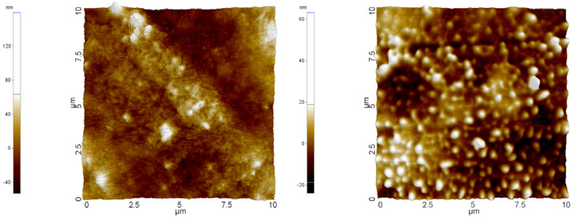

Figure 4. AFM images of the bare probe surface (left side) and the probe after PECVD polymerization (right side).

This study has shown the importance of the shape and the distribution of electrodes in a probe array, leading to the design of a novel four-point probe. The system possesses the minimal distance possible among electrodes, together with a high ratio of electrode length to spacing to enhance the electrical response. The four-point probe has been fabricated in a printed circuit board, which offers some advantages such as non-damaging samples, low cost or repeatability in the analysis measurements.

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