Study of the effect of DMSO concentration on the thickness of the PSS insulating barrier in PEDOT:PSS thin films

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One of the most used secondary dopants in thin film processing of PEDOT:PSS is dimethyl sulfoxide (DMSO). In this work, we present results that explain, from the point of view of impedance spectroscopy, the mechanism of the increase in the conductivity observed on films based on PEDOT:PSS. The results obtained with this technique, combined with others such as AFM, and Raman and UV–vis–NIR spectroscopies, clearly show that there is a thinning of the insulating barrier of PSS surrounding conductive grains of PEDOT. It is shown that the thickness of the insulating barrier is related strongly and inversely with the onset frequency of AC conductivity. However, this is not the only existing effect, because for values beyond the optimal concentration of DMSO, we observe a decrease in the conductivity related with an increase of the separation of the PEDOT grains. The AC measurements and the AFM images also show the clear interplay between the increase of the PEDOT average grain size and the separation between them.

1. Introduction

Currently, one of the most promising conductive polymers is poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate), abbreviated as PEDOT:PSS. The reason for its technological and industrial importance lies in its ease of processing, high stability and transparency compared with some other polymeric materials. This issue has been partially resolved with the so-called secondary doping, which consists of combining two or more components to form a connected whole without a change in chemical structure of these components. In this case, it has been partially resolved with the so-called secondary doping (i.e., increasing the conductivity by adding a variety of compounds in the aqueous dispersion of PEDOT:PSS) [4–17], UV radiation [18], films prepared under different drying conditions [19], etc., thus increasing the conductivity by several orders of magnitude. Despite the large number of publications related with the mechanism of conductivity enhancement caused by secondary doping, there is still controversy about the responsible mechanism of this enhancement and several explanations have been proposed [9–17] such as the secondary doping produces a conformational change of PEDOT chains in the films [12] or that their effect is to induce the segregation of the excess PSS [13–17].

In this paper, we present a study of the effects of dimethyl sulfoxide (DMSO) loading on the electrical and optical properties of PEDOT:PSS thin films. The films have been prepared under different baking temperatures, atmospheres and different concentrations of the secondary doping in order to study how the conductivity depends on these variables. We have found that the films baked in air, for a given doping concentration, showed the maximum conductivities, in contrast with previous reports [19]. These films have been characterized by using several techniques such as AFM, and Raman, UV–vis–NIR and impedance spectroscopies (IS). Our results show that the mechanism responsible for the increase in the conductivity is related with the partial phase separation of the excess PSS. Therefore the insulation of conducting PEDOT:PSS domains is reduced [13–17]. In addition, Nardes et al. [17] have shown that this enhancement in the conductivity is due to a transition from 3D variable range hopping (3D-VRH) to quasi-1D VRH.

As is well known, impedance spectroscopy (IS) is a technique that allows to obtain information about the material under study...