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Fine Tuning of PEDOT electronic properties using solvents

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Abstract

Non-destructive method of Spectroscopic Ellipsometry (SE) from IR to FUV was applied to study PEDOT/PSS thin films deposited by spin coating from aqueous dispersions of the material with different N,N-Dimethylformamide (DMF) volume percent. In our work we used the Tauc-Lorentz model to describe the dielectric function of PEDOT/PSS:DMF films in the Vis-FUV energy region. First, the spectrum analysis showed that the thickness and the fundamental band gap E_g of the film is being decreased with the increase of DMF content in the dispersion. Taking into account that the heating temperature is below the boiling point of DMF we assume that DMF molecules are incorporated in the film volume and act as dopants. Further more, this means that carrier concentration is being increased and thus we have higher electrical conductivity. The existence of DMF molecules in the film proved from FTIR SE, which can probe the bonding structure of the materials. The results showed lowering of peak intensity assigned to PEDOT/PSS and appearing of peaks assigned to DMF in the imaginary part of spectrum. In conclusion, SE is a potential tool for the evaluation of electronic properties for conductive polymers.

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1. Introduction

Over the last 5 years the organic electronic materials are becoming more and more competitive to the inorganic ones. Numbers of applications from organic materials have been such as flexible organic light-emitting diodes (OLEDs) and flexible organic photovoltaic cells (OPVs). [1-4] A wide used organic electronic material is the PEDOT (poly(3,4-ethylenedioxythiophene) stabilized with PSS (poly 4-styrenesulfonic acid) in water dispersion is a transparent conductive polymeric material that is widely used as anode buffer layer in FEDs and is expected to be used in the future as an anode in its own right and replace the inorganic, brittle and expensive ITO. [5-8]. Furthermore, it was found[9] that the addition of a polar solvent can enhance the conductivity up to 2-3 orders of magnitude

In this work, we have studied the effects of the addition of N,N-Dimethylformamide (DMF) in the polymer solution on the optical properties in the growth of spin-coated PEDOT:PSS thin films by the use of Spectroscopic Ellipsometry (SE) from the IR to FUV energy region.

2. Experimental

The PEDOT:PSS dispersion, was supplied by Sigma Aldrich (483095, 1.3 wt % dispersion in H₂O, conductive grade) and was modified with

four different concentrations of N,N-Dimethylformamide (DMF) (4, 8, 12 and 16%v/v). Thin films of PEDOT:PSS:DMF were spin coated on Si(100) wafers in two stages process (Stage I: 600rpm for 15sec, Stage II: 5000rpm for 30sec) followed by heating at 100°C for 10 minutes to remove the solvent.

The Vis-FUV spectra were carried out by means of a phase modulated ellipsometer (PME) of Jobin-Yvon/Horiba at an angle of incidence of 70°, over the range 1.5–6.5 eV, with a step of 10 meV. The unit is consisted by two photomultiplier detectors; one for the Vis-UV range (1.5–4.0 eV) and one for the UV-FUV range (4.0–6.5 eV). The light source was a proper Xe lamp 150 W, having high intensity at FUV, and the whole energy spectrum was acquired using a special designed monochromator (M200 model). All the optical and polarized components of the system were suitable for the FUV.

The IR measurements were performed in the range of 900-4000 cm⁻¹, using a Jovin Yvon Fourier Transform IR Phase Modulated Ellipsometer adapted to the UHV deposition chamber using BaF₂ windows. The IR beam is produced by a commercial IR spectrometer (BOMEM-MB100) which includes a thermal source of SiC bars and a Michelson interferometer and is focused on the sample through an optical system of reflectors and

lenses. A grid analyzer and a photo-elastic modulator, which modulates the IR beam polarization with a frequency of 37 kHz, define the polarization of the incident beam. After its reflection on the sample, the polarization of the IR beam is detected by a grid analyzer and then is focused on the detection head through a suitable optical system.

3. Results and Discussion

The effect of DMF content in the PEDOT:PSS:DMF thin films was first studied by Spectroscopic Ellipsometry in the Vis-UV region. The measured quantity by SE is the pseudodielectric function $\langle \epsilon(\omega) \rangle = \langle \epsilon_1(\omega) \rangle + i \langle \epsilon_2(\omega) \rangle$, which has information on the system consisted of the substrate and thin film and depicted in Figure 1.

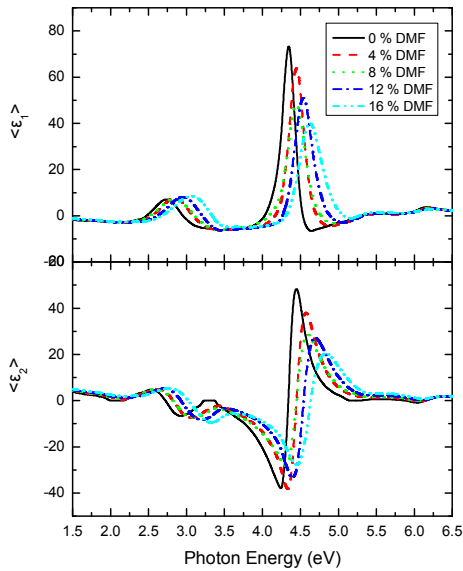


Figure1: The real (top) and the imaginary (bottom) part of the pseudodielectric function for PEDOT:PSS films on Si wafers.

The spectrum of the pseudodielectric function is divided into two regions: the multiple reflection regions from 1.5 to 5 eV and the absorption region from 5 to 6.5 eV. The first region is useful for the spectrum analysis in order to calculate the thin film thickness, whereas the second region is useful for the determination of the optical and electronic properties. From the horizontal shift of spectrums in the multiple reflections region is clear that there is thickness variation as the DMF content is being varied. For the data analysis we used the 3-layer model: air/PEDOT:PSS:DMF layer/Si and the layer's dielectric function is being described with 2

Tauc-Lorentz oscillators[10]. The imaginary part of the dielectric function is given by

$$\epsilon_2(E) = \begin{cases} \frac{AE_0C(E-E_g)^2}{(E^2-E_0^2)^2+C^2E^2} \frac{1}{E} & E > E_g \\ 0 & E \leq E_g \end{cases} \quad (1)$$

and the real part is $\epsilon_1(E)$ calculated from the Kramers-Kronig integration [10]. The five fitting parameters are: the non-dispersive term ϵ_∞ , the fundamental band gap energy E_g , the amplitude A, the Lorentz resonant energy E_0 , namely Penn gap, and the broadening term C.

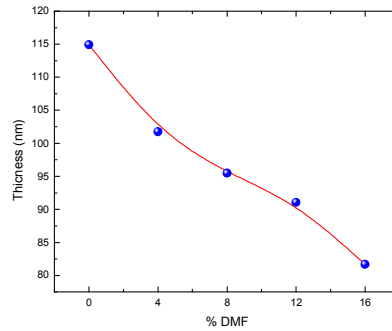


Figure 2: Thin film thickness dependence from the DMF content

Using the afore mentioned data analysis PEDOT:PSS:DMF thickness and optical-electronic properties can be calculated. Figure 2 shows the decrease of the thickness as the DMF content is being increased. In general when polar molecules dispersed in dispersion tend to separate the existing particles and reduce its cohesion. This means that under spinning process most of the material is being lost due to centrifugal force and the rest is being adhered on the substrate. This phenomenon explains the reduction of the layer thickness as the DMF content is being increased.

Apart from thickness, the optical and the electronic properties also affected by the DMF addition. Figure 3 shows the variation of E_g , E_1 and E_2 as a function of the DMF volume percent. As it is observed the energy gap E_g is being decreased. Due to the dependence of E_g to the electrical conductivity σ , this results means that the conductivity is being increased and agrees with the results from the literature[9]. Furthermore, there is no significant variation on the two Penn Gap E_1 and E_2 . These energies depend on several materials parameters like the composition and the structure. From this result it is obvious that

DMF molecules affect only the band structure of the PEDOT:PSS and not the composition or the bonding structure.

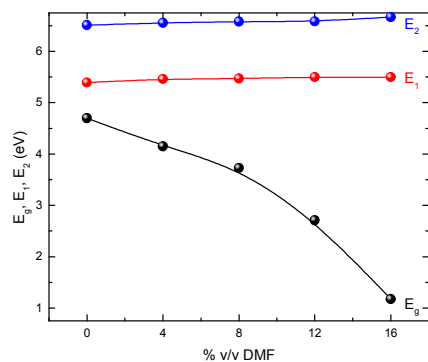


Figure 3: Band Gap Energy E_g and Penn Gap E_1 , E_2 dependence from the DMF content

The incorporation of DMF molecules in the PEDOT:PSS volume can be found with FTIRSE. The potential of this technique is that can be used with all kind of materials. Especially, the second derivative of the spectrum can enhance the characteristic vibration energies and eliminate the contribution from the substrate. PEDOT and PSS has been studied before with FTIR spectroscopy[11,12] where the main vibrations are at 1512, 1454, 1394, 1370 and 1168 cm^{-1} from the stretching of C=C and C-C in the thiophene ring. Further vibrations from the C-S bond in the thiophene ring can be seen at 930, 830, 727 and 697 cm^{-1} . Vibrations at 1183, 1144-1128, 1093-1076 and 1052-1047 cm^{-1} are assigned to stretching in the alkylendioxy group. The PSS vibrations appear the at 1184 cm^{-1} for the asymmetric stretching of the SO_3 -group and at 1042 cm^{-1} for the symmetric-stretching of the sulfonic group. At 1130 cm^{-1} and 1011 cm^{-1} are for in-plane skeleton vibrations and in-plane bending vibrations, respectively, of the benzene ring. The DMF peaks that reported in the literature[13] are CH_3 symmetric stretching mode at 2930 cm^{-1} , C-H stretching mode at 2857 cm^{-1} , C=O stretching mode at 1676 cm^{-1} , C-N stretching mode at 1507 cm^{-1} , CH_3 asymmetric deformation mode at 1439 cm^{-1} , CH_3 umbrella mode at 1406 cm^{-1} , N-C-H bending mode at 1388 cm^{-1} , C-N asymmetric stretching at 1257 cm^{-1} and CH_3 rocking mode at 1093 and 1063 cm^{-1} .

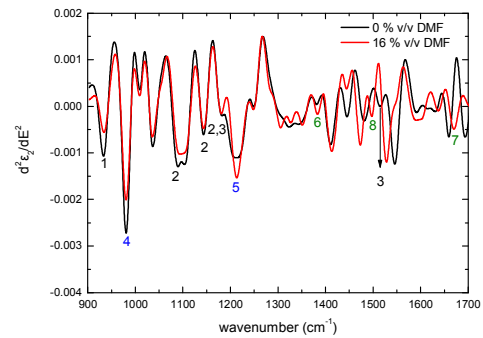


Figure 4: The second derivative of the imaginary part of the pseudodielectric function. The numbers in black correspond to PEDOT, blue to PSS and in green to DMF vibrations.

Figure 4 shows the second derivative of the imaginary part of the pseudodielectric function for 0 and 16% v/v DMF samples. The correspond to the sample with 0%v/v DMF shows most of the vibrations correspond to PEDOT:PSS like: (1)→ C-S bond from the thiophene ring, (2)→ the alkylendioxy group, (3)→ C=C bond from PEDOT and (4)→ phenyl ring with SO_2 and (5)→ O=S=O from PSS. The same vibrations appear also in the spectrum of sample with 16%v/v DMF. Additionally to them three extra vibrations correspond to DMF appear: (6)→ N- CH_3 , (7)→ -C=O and (8)→C-N. This means that DMF molecules are dispersed in the volume of PEDOT:PSS their polar feature results affects the electron transport and thus the decrease of band gap energy E_g . The explanation to that is laid on the high boiling point of DMF (153°C) compared to the water, which means that the heating at 100 °C is sufficient to remove the water but not the DMF molecules from the solvent.

4. Conclusions

Spectroscopic Ellipsometry from IR to FUV energy region was applied to PEDOT:PSS spin coated thin polymer films formed with DMF additions in the PEDOT:PSS dispersion.

In the range from 1.5 to 6.5eV the spectrum analysis showed that the DMF molecules reduce the cohesion of the PEDOT:PSS dispersion and thus more quantity from the material is being lost due to the centrifugal force during spinning. Furthermore, there is significant reduction of the band gap energy E_g which means that the layer is becoming more conductive as the DMF %v/v is being

increased. On the other hand, the main absorptions of PEDOT:PSS at $\sim 5.5\text{eV}$ and $\sim 6.5\text{eV}$ do not seem to be affected by the DMF molecules. So the polar solvent can reduce the fundamental band gap or in other words enhance the electrical conductivity of PEDOT:PSS without significant changes the polymer structure.

The existence of DMF molecules in the volume of PEDOT:PSS layer is expected by the fact that the heating after the spinning process is below the boiling point of DMF. FTIRSE showed the vibrations correspond to the characteristic bonds of N-CH₃, C-N and C=O.

Finalizing, the use of Spectroscopic Ellipsometry in combination with the appropriate model for the description of the dielectric function can evaluate the optical and the electronic properties of the modified PEDOT:PSS material with DMF and explain the mechanisms that enhance the electrical conductivity.

Acknowledgements

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