Thin Solid Films 536 (2013) 211–215

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Surface morphology, optical properties and conductivity changes of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) by using additives☆

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ARTICLE INFO

Article history:
Received 20 October 2012
Received in revised form 26 March 2013
Accepted 27 March 2013
Available online 10 April 2013

Keywords:
Optical properties
Conductivity
Surface morphology
Conducting polymers
Spectroscopic ellipsometry
Organic electronics

ABSTRACT

The optical properties and electrical conductivity of highly conducting poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS) are reported as a function of the processing additive conditions. The addition of dimethyl sulfoxide (DMSO) increases the conductivity and modifies the dielectric response as observed from the ellipsometric studies. Also the surface roughness and morphology change with the composition of PEDOT:PSS:DMSO and film deposition conditions. The real part of the dielectric function becomes negative in highly conducting samples, indicating the presence of delocalized charge carriers. The real and imaginary parts of the refractive index were determined as a function of wavelength. The results are consistent with the increase in conductivity upon the addition of DMSO.

1. Introduction

The highly conducting poly(3,4-ethylenedioxythiophene):poly (styrenesulfonate) PEDOT:PSS (with a brand name PH1000, Clevios Heraeus Co.) has the potential to be used as a viable alternative to the usual transparent conducting oxides like indium-tin oxide (ITO), doped zinc oxide, etc. in electronics [1–4]. Although the optical transparency of the earlier versions of PEDOT:PSS is rather close to that of ITO, the relatively high resistance has remained an obstacle in these optoelectronic applications. Earlier studies have shown that chemical processing of PEDOT:PSS plays a major role in changing its morphology and conductivity [5–11]. By mixing PEDOT:PSS with various solvents like dimethyl sulfoxide (DMSO) and also by annealing at higher temperatures the conductivity varies by several orders of magnitude [12,13]. Since PEDOT:PSS is a rather complex system, as shown in the schematic diagram in Fig. 1, the PEDOT rich parts of the chains tend to diffuse more towards the core and the PSS rich portions form a shell like structure in these gel particles of wide range of sizes from micro to nano scale [14,15]. In usual aqueous PEDOT:PSS solution the chains tend to form compact coils that pack randomly upon drying in solid state films. In this case, the nanomorphology always plays a significant role in the bulk charge transport, hence a wide range of values of surface resistance in transparent electrode application has been reported [16]. However, it has been observed from small angle X-ray scattering and charge transport studies that in the presence of additives the compact coils transform to more elongated ones so that the localized electronic states get partially delocalized to enhance the transport mobility of charge carriers [17,18]. In this case the barriers will be lowered in the elongated conformation of chains facilitating charge transport. The effect of these morphological modifications can be observed especially in the low temperature charge transport properties and frequency dependent conductivity.

In this work a systematic study has been carried out to investigate the effect of the addition of DMSO on morphology, optical absorption and conductivity of PEDOT:PSS thin films. For the spin-coated layers, the thickness and surface roughness have been determined from atomic force microscope (AFM) measurements for various DMSO concentrations. The optical properties of the pristine PEDOT:PSS as well as mixed with DMSO were studied using spectroscopic ellipsometry and real and imaginary part of their dielectric functions were determined. Using the complex dielectric function, the absorption coefficient, and the complex refractive index were calculated. The results were compared with a less conducting form of PEDOT:PSS (brand name PH510, Clevios Heraeus Co.) for a better understanding of the influence of free charge carriers on their optical properties. Finally the conductivity values have been measured by using four probe technique in all PEDOT:PSS (PH1000) samples. The effect of thickness and surface roughness of the samples on the optical and electrical properties is also investigated in this study.

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http://dx.doi.org/10.1016/j.tsf.2013.03.124

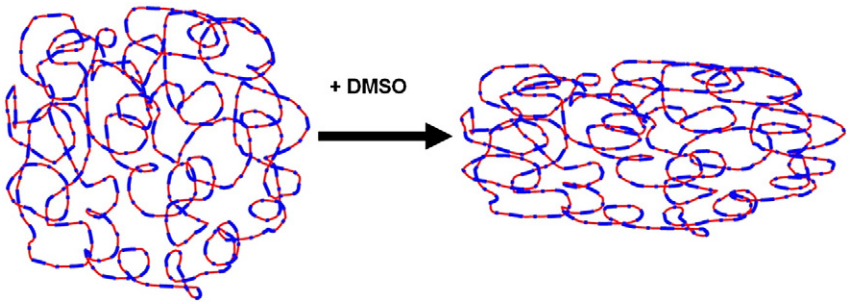

Fig. 1. The PSS (red) is sparingly covered by short PEDOT segments (blue) creating spherical nanostructure. After adding DMSO the coil structure elongates into an ellipsoidal form.

2. Experiment

In this work, an aqueous solution of PEDOT:PSS (brand names PH1000 and PH510, Clevios Heraeus Co.) was used. The pristine PEDOT:PSS (PH1000 and PH510) solutions were compared with solutions with 5%, 10%, 15% and 20% v/v concentrations of dimethyl sulfoxide (≥99.5%, Sigma Aldrich) in PEDOT:PSS:DMSO solution. These solutions were deposited by spin coating using P6700 spincoater (Speciality Coating Systems, Co.) on a 15 × 15 mm^2 glass substrate from Menzel Gläser. The glass substrates were precleaned by sequential sonication in acetone (99.8%, NORMAPUR), isopropanol (99.9%, NORMAPUR) and de-ionized water. Before spin coating, the solutions were filtered using Whatman Puradisc AS25 filters. For the thickness variation two different spin coating programs were used, allowing us to obtain two thicknesses — approx. 50 nm (high rpm — 2000 rpm, 1 s + 4000 rpm, 1 s + 6000 rpm, 60 s) and 120 nm (low rpm — 1500 rpm, 40 s + 2000 rpm, 20 s). The thickness and surface morphology of the films were characterized by atomic force microscope (Digital Instruments Dimension 3100, Veeco Metrology group) working in the tapping mode. Ellipsometric characterization was done using Woollam M-2000 (rotating compensator) ellipsometer which spans an energy range of 0.73 to 6.5 eV. The linear four probe technique was applied to measure the conductivity by using Keithley 2400 sourcemeter.

3. Results and discussion

PEDOT:PSS (PH1000) thin films were prepared by using four different concentrations of DMSO. The concentration was varied in the PEDOT:PSS (PH1000):DMSO solution and the samples were compared with a pristine sample. For each solution two samples were prepared according to low and high spin coating speeds. This procedure allowed us to obtain samples with controlled thicknesses. The thickness, surface roughness and conductivity values are listed in Table 1. The thinner samples around 50 nm and thicker ones around 120 nm are studied to find out the influence of thickness and roughness on the physical properties. To our surprise, the surface roughness hardly varies by a factor of two by changing the sample preparation conditions. However, the trend indicates that roughness slightly increases upon increasing the concentration of DMSO and also on thicker samples; yet a roughness of 1–3 nm in a sample of 50–120 nm is only in the marginal level. The influence of DMSO on the PEDOT:PSS (PH1000) surface morphology as functions of a concentration as well as a function of thickness is presented in Fig. 2. Layers without and with very low concentration of DMSO shows relatively smoother surface with roughness from granular structure of PEDOT:PSS. With an increasing concentration of DMSO a noticeable increase of the roughness of the films can be observed. This is due to the fact that small grains of the PEDOT:PSS (PH1000) are formed. The optical properties were obtained by fitting spectroscopic ellipsometric measurements in the NIR–VIS–UV range (energies between 0.73 and 6 eV). The complex reflectance ratio $\rho = \frac{r_p}{r_s} = \tan\psi e^{i\Delta}$ was measured. In the equation ρ is the ratio of the complex reflection coefficients, r_p and r_s are the complex Fresnel reflection coefficients for p- and s-polarized light, respectively, tan ψ represents the absolute value of the ratio and Δ describes the phase difference between p- and s-polarized light. The dielectric functions of the PEDOT:PSS were fitted with the known thickness and the assumption of a negligible roughness (i.e. that the roughness is much smaller than the wavelength). For fitting procedures, a Drude-ansatz was used with a generic oscillator. Then, after obtaining a reasonable mean square error, a direct inversion procedure was employed to obtain $\varepsilon_1(\omega), \varepsilon_2(\omega)$. The values are accurate at the same level than the thickness values, which were measured by profiling on 4 spots with an average deviation of 3–5%. All data presented represent the true dielectric function, not the pseudodielectric. The comparison between pristine PEDOT:PSS (PH1000) and with DMSO (10 and 20% v/v) is presented in Fig. 3. The real part of the dielectric function (ε_1) is plotted as a function of energy. The negative values detected below 2 eV confirm the Drude model and let us assume that the charged carriers, contributing to the Drude term, are highly delocalized. Upon the addition of DMSO the appearance of the new broad peak with a maximum around 1.7 eV indicates a shift in the oscillator strength from the Drude tail towards a DMSO related interband transition, as the conductivity increases. These highly delocalized carriers indicate the possibility of a plasma edge around 1.4 eV for pristine PEDOT:PSS. The shift of the plasma edge with the increase of DMSO concentration to 0.76 eV would on the first sight indicate a reduction of the number of charge carriers. However, what can be seen in the imaginary part (ε_2) of the dielectric as a function, presented in the inset of the Fig. 3, is that with the increasing concentration of DMSO the absorption broadens, which implies that the damping coefficient in the Drude term increases – not surprisingly – in the mixed phase. The total number of electrons, however increases, as can be immediately determined by the sum rule for the dielectric function [19]. By using a numerical Kramers–Kronig transform we checked that the slight shift in the spectra at 2 eV is consistent with that observed in the real part of the dielectric function. The obtained imaginary and real parts of dielectric function were used to calculate real (Re(RI)) and imaginary part (Im(RI)) of the refractive index. The Re(RI) values plotted as a function of energy for pristine PEDOT:PSS and mixed with 10 and 20% v/v DMSO is presented in Fig. 4A. For all samples it can be

Table 1
The measured root mean square (RMS/nm) roughness and conductivity (σ/S cm^{-1}) values of the different PEDOT:PSS and PEDOT:PSS:DMSO layers.

PEDOT:PSS composition			RMS roughness	σ/S cm^{-1}
Pure PEDOT:PSS	A	45 nm	1.49 nm	0.549
	B	115 nm	1.44 nm	0.689
PEDOT:PSS:DMSO (5% v/v)	C	50 nm	1.64 nm	454
	D	120 nm	1.94 nm	563
PEDOT:PSS:DMSO (10% v/v)	E	50 nm	1.97 nm	402
	F	100 nm	2.43 nm	966
PEDOT:PSS:DMSO (15% v/v)	G	40 nm	1.87 nm	531
	H	120 nm	2.32 nm	866
PEDOT:PSS:DMSO (20% v/v)	I	40 nm	2.25 nm	575
	J	90 nm	2.72 nm	732