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Full Length Research Paper

Influence of hydrogen plasma on properties of transparent PEDT/PSS thin films

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Poly (3, 4-ethylene dioxy thiophene)/ poly (styrene sulfonic acid) conductive polymer was deposited on glass substrates through Dip-coating method. These films were subjected to hydrogen plasma in order to evaluate the probability of resistivity reduction. Their electro-optical behavior and structure were studied before and after this process. Hydrogenation at a substrate temperature of 80°C for 30 min reduced the electrical resistance around 22.3%, without considerable decrease in optical transmittance. Van der Pauw measurements showed that the hydrogenation process had increased the mobility of samples (approx. by 84.8%). SEM micrographs displayed the reduction in domain sizes and elimination of void spaces among them. Hence increase in the conductivity can be essentially attributed to deactivation of 'dangling bonds' associated with the structural defects in PEDT/PSS films.

Key words: PEDT/PSS conductive polymer, transparent conducting thin films, hydrogen plasma, hydrogenation process, dangling bonds, electrical passivation of structural defects.

INTRODUCTION

Interest in PEDT/PSS as a semiconducting and electro-active polymer has grown over the last several years. In water, PEDT/PSS forms a dispersion of the oxidized polymer PEDT and the polyanionic PSS. This dispersion is commercially available from Bayer under the trade name Baytron P. It is a low bandgap material, with the gap in the visible near-infrared transition region (1.5 eV $\pi+\pi^*$ energy level).

So far, existing applications of Baytron P include anti-static layers, e.g., for photographic films or hole injection layers in organic light emitting diodes (Pielartzik et al., 1999). These applications are possible due to the very good film forming properties of the material. Increase of conductivity of the PEDT/PSS sample provides various uses such as an electromagnetic radiation shielding and a better electrical transport layer. Over the last decade, great progress has been made in efforts to synthesize higher conductivity versions of PEDT/PSS; however, their conductivities are still low for such applications. An important contribution to the structural characterization of PEDT was presented by Inganäs and co-workers (Aasmundtveit et al., 1999). They prepared thin PEDT films that were subsequently studied with grazing incidence X-ray diffraction using synchrotron radiation. From these studies they concluded that the material is very anisotropic and that there is a limited crystalline order in these thin films.

Amorphous structure suggests a high concentration of trapping centers created by structural defects in the PEDT/PSS films. Defect passivation in polycrystalline and amorphous silicon layers by means of hydrogenation is a well-known technique for optimum performance of solar cells (Pankove, 1978; Pankove, 1991). Influence of hydrogen plasma on different TCO's like ITO (Keshmiri et al., 2002); ZnO and IZO (Raniero et al., 2006) has already been investigated. These studies confirm the hydrogen role in passivation of 'dangling bonds' exist in films. The aim of this work is to study the influence of hydrogen plasma during different exposition times and substrate temperatures on electrical conductivity of the PEDT/PSS films. Moreover, effect of hydrogen plasma for optimum exposition time and temperature on optical transmittance and structure of the samples has been investigated.

This paper is organized as follows. Details of the expe-

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rimental model which have been used are presented in section 2 and the results are interpreted in section 3.

EXPERIMENTAL DETAILS

Our PEDT/PSS films have polycrystalline structure with very small crystallite sizes. Henes these films contain a high density of structural defects such as grain boundaries, interstitial atoms and vacancies. A great many electrically active dangling bonds might be expected in these films. With their small size, hydrogen can readily diffuse into the bulk of the film and passivate these dangling bonds. This will result in a considerable increase in carrier mobility and hence electrical conductivity of the film.

The PEDT/PSS (Baytron P) was purchased from Bayer A.G. Baytron P was an aqueous dispersion of the conductive polymer, PEDT/PSS. The weight ratio of PEDT to PSS was 1:1.6, and the mixture was diluted with H_2O. Films were prepared by casting the solution on glass substrates through Dip-coating technique with different speeds between 300 and up to 500 millimeter per minute. The samples were dried in a vacuum oven at 100°C for 20 min. A four probe method was used for measuring DC conductivity and in order to eliminate the photovoltaic effect measurements were carried out in a dark environment. The optimum speed for lowest resistance was found to be 450 mm/min. Therefore most layers were prepared for the hydrogenation process under the condition of 450 mm/min speed and 20 min annealing at 100°C. Atomic-hydrogen plasma was produced by a setup schematically shown in Figure 1.

The plasma source consisted of a glass tube with a tungsten filament, heated by a 6 V (ac) power supply, as the electron source. This filament was placed between two metal rings. The lower ring (anode) and the upper ring (cathode) were connected to the accelerating DC power supply. A second DC supply was used for adjusting the hydrogen ion energy. Sample was placed on top of the plasma source, beneath a resistance heater which was used for heating the sample during the hydrogenation process. The whole set-up was placed inside a vacuum coating unit (Edwards E306-A). High purity (99.99%) hydrogen gas was fed into the system from the lower end of the plasma source.

Film transparency spectra were recorded before and after the hydrogenation process by a single beam spectrophotometer (Agilent model 8453). The experimental data were collected in the ultraviolet-visible and near-infrared ranges (λ = 260 - 1100 nm) with a step width of 1 nm.

From the transmittance spectra the absorption index α(λ), thickness and the optical bandgap (*Eg*) of the films were calculated using the Swanepoel method (Swanepoel, 1980).

The role of hydrogen on electrical properties such as free carrier concentration (*n*) and Hall mobility (μ_H) were studied through the Hall effect measurements using the Van der Pauw geometry at a constant magnetic field of 0.5 T. The influence of plasma on the surface morphology of the films was analyzed using a scanning electron microscope (SEM).

RESULTS

Measurements showed that the PEDT/PSS films had resistances in the range of 0.42 - 0.46 (MΩ), the lowest resistance being for films prepared at 450 mm/min speed (Figure 2). In the range of 300 up to 400 mm/min, the reduction of resistance is low. A minimum resistance (420 KΩ) exists at 450 mm/min and for higher speeds, it increases again. Higher resistances below 450 mm/min could be ascribed to thicker layers.

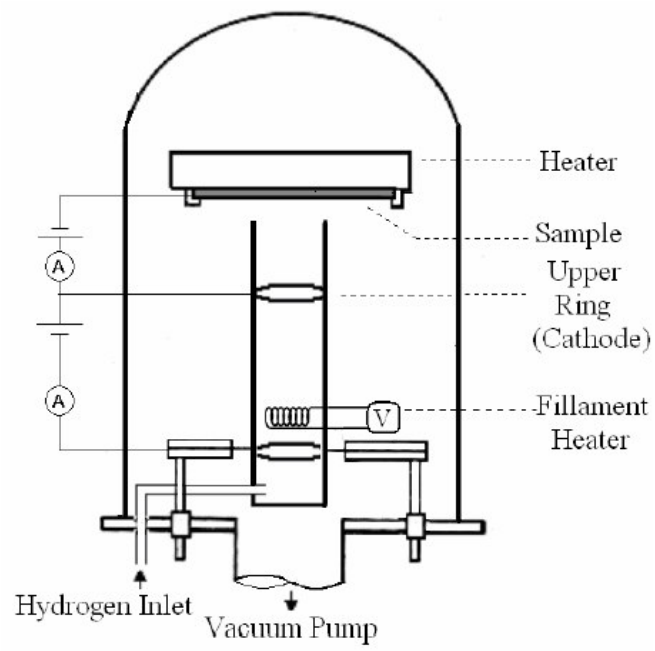

Figure 1. Configuration of the plasma source.

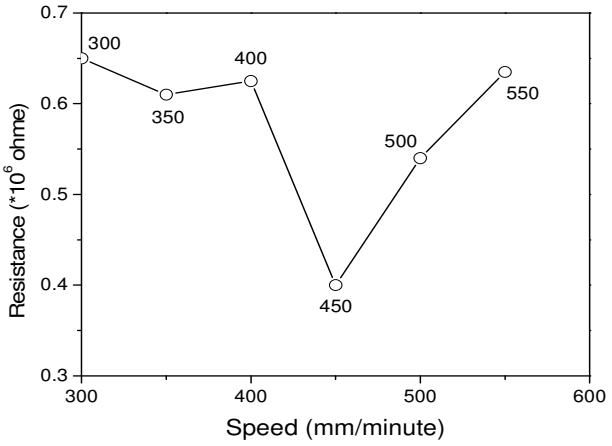

Figure 2. The electrical resistance versus dipping speeds.

Higher resistances below 450 mm/min could be ascribed to thicker layers. Optical transmittance of a layer which is prepared with 450 mm/min speed is quite high in the visible range Figure 6a. Transmittance at the beginning of the range is around 90% and near the end is about 80%. There is an absorption edge below 320 nm. With the use of transmittance spectra, the film thickness (220 nm) and optical bandgap (*Eg* = 1.16 eV) were calculated using the Swanepoel method (Figure 3). One PEDT/PSS film was hydrogenated at a substrate temperature Tsub = 60°C for 45 min. The sample was allowed to cool down and its resistance was measured. Then the hydrogenation step was repeated for a similar

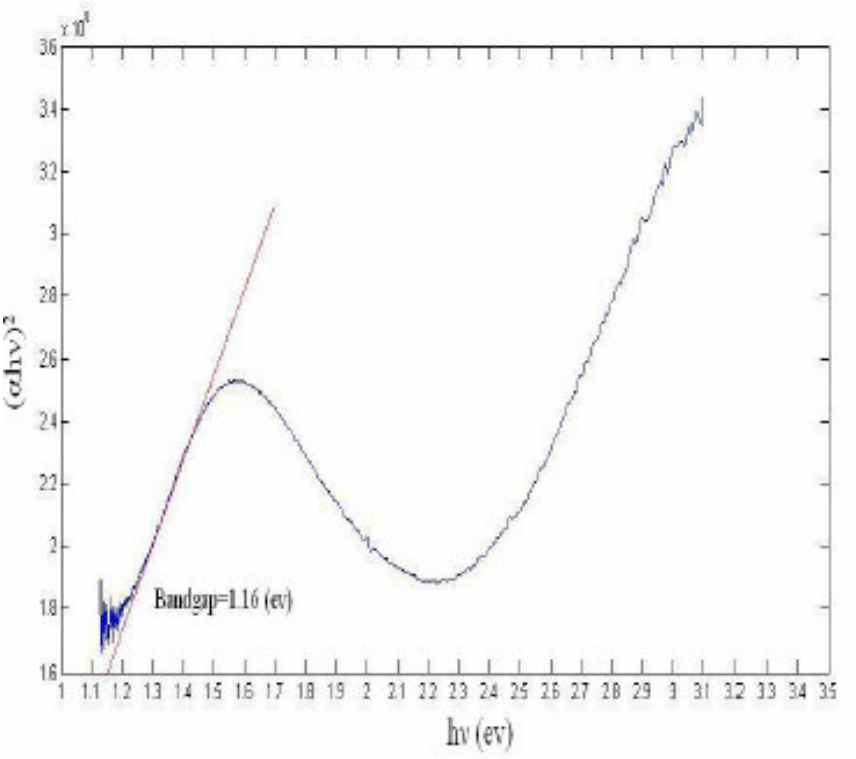

Figure 3. Optical bandgap of the PEDT/PSS film.

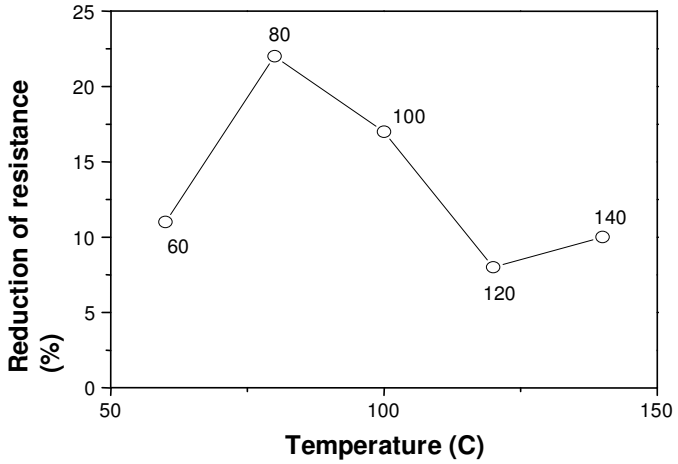

Figure 4. Influence of substrate temperature during hydrogenation process on reduction of resistance.

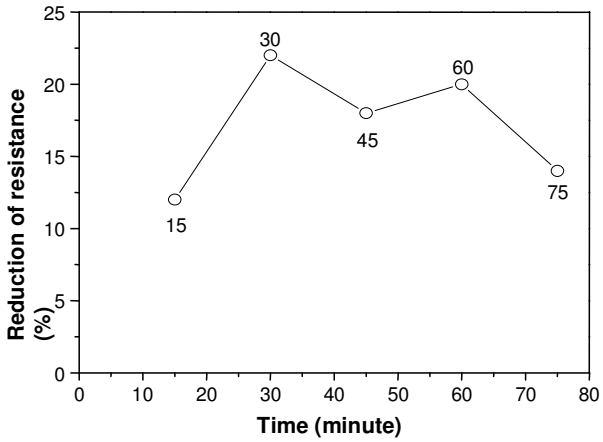

Figure 5. Influence of substrate temperature during hydrogenation process on reduction of resistance.

sample, but at Tsub = 80°C. This process was repeated for five different substrate temperatures. Figure 4 shows the results. As seen in Figure 4, R is reduced by about 21% after hydrogenation at Tsub = 80°C. We believe that the increase in resistance for Tsub > 80°C is due to the low thermal stability of polymers which is thus their drawback for possible high temperature applications. We have also observed a similar increase in the resistance of the films when heated in vacuum at temperatures of 140°C and above. In order to study the effect of hydrogenation time, another PEDT/PSS sample was hydrogenated for 15 min. The substrate temperature was fixed at 80°C. Then the hydrogenation step was repeated for a similar sample in a 15 min interval.

This process was repeated for five different hydrogen-nation times. The results are plotted in Figure 5. As the

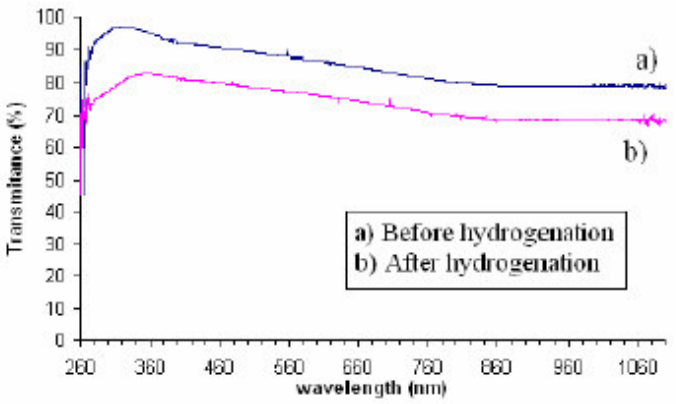

Figure 6. Optical transmission spectra of the PEDT/PSS film before and after hydrogenation.

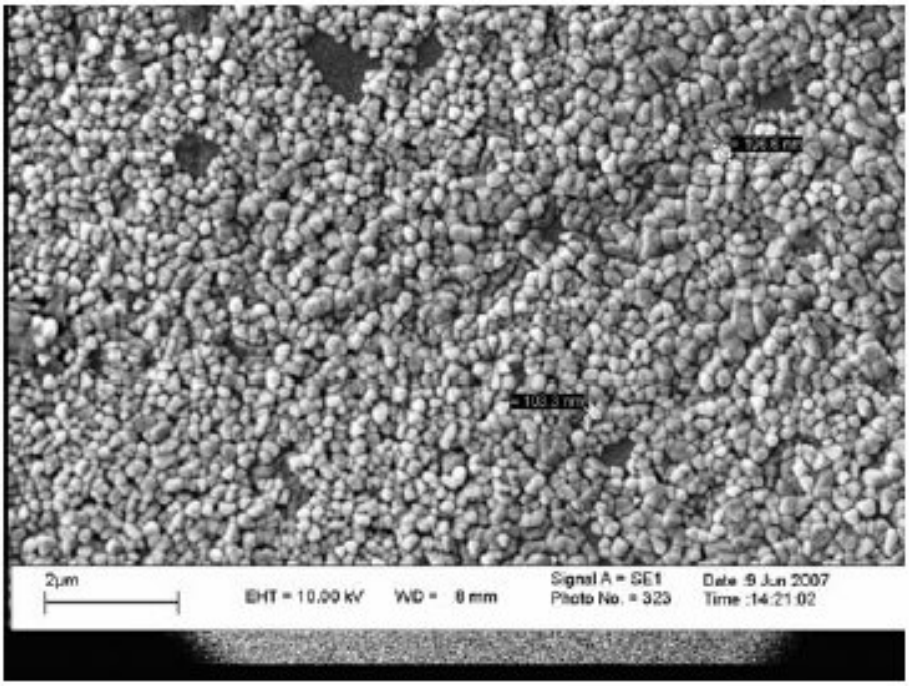

Figure 7. SEM micrograph before hydrogenation.

Figure shows, hydrogenation for 30 min produced the highest reduction of resistance (22.3%). For the sake of reaching an optimal hydrogenation condition, there should be a compromise between the substrate temperature and the exposition time. From our experiment the best condition is: hydrogenation at Tsub = 80°C for 30 min. The optical transmission spectra of the PEDT/PSS film before and after hydrogenation (to the optimal level for minimum resistance) are shown in Figure 6. It is seen that the transmission is reduced about 16.5% between 280 and 320 nm, however, during the visible range the reduction is only about 10%.

Van der Pauw measurements data before and after hydrogenation at optimum conditions show $n = 3.43 \times 10^{18}$ cm^{-3}, $\mu B = 3.16$ cm^2 V^{-1} s^{-1} and $n = 1.78 \times 10^{18}$ cm^{-3}, $\mu B = 5.84$ cm^2 V^{-1} s^{-1}, respectively. Thus the resistivity decrease arises essentially from an increase in mobility while the free carrier concentration reduces. This phenomenon is the well-known hydrogen induced dopant deactivation seen in a variety of commonly used semiconductors; atomic treatment typically causes reduction of the free carrier concentration by up to several orders of magnitude in materials as varied as Si, GaAs, InP and CdTe (Schubert, 1993).

SEM micrographs of the sample are shown in Figures 7 and 8. Before the hydrogenation the domain sizes are

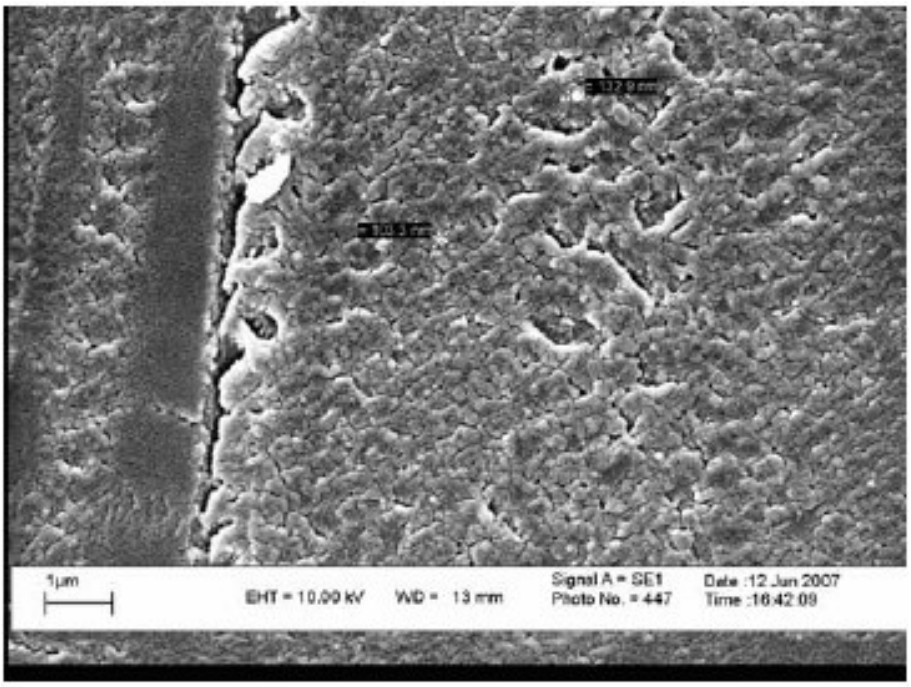

Figure 8. SEM micrograph after hydrogenation.

around 100 - 200 nm and they are reduced to 100 - 130 nm after hydrogenation. It is also seen that the voids between the domains are eliminated. Thus the improvement of the electronic quality of the sample could be attributed to the passivation of grain boundaries due to the plasma hydrogenation.

Conclusions

The data obtained reveal that the hydrogenation process was effective in reducing the electrical resistance of PEDT/PSS films. The hydrogenation at optimum conditions reduced the sample's resistance by 22.3% of its initial value without considerable reduction in optical transmission. We believe that the observed effect is analogous to the effect of atomic hydrogen in the case of amorphous silicon (Pankove, 1991; Poortmans et al., 1995; Keshmiri, 1995). Having a small size, hydrogen ions can readily diffuse into the bulk of a film and deactivate the 'dangling bonds' associated with the structural defects. This will result in the considerable increase in carrier mobility, and hence lifetime of electrons.

REFERENCES

Pielartzik H, Heuer H, Wehrmann R, Bieringer T, Kunststoffe AR (1999). Chemical vapour deposition of thin oxide thin films. Appl. Phys. Lett. 89: 135.

Aasmundtveit KE, Samuelsen EJ, Pettersson LAA, Inganäs O, Johansson T, Feiderhans R (1999). The surface and materials science of thin oxide. Synth. Met. 101: 561.

Pankove JI (1978). Applications and processing of transparent conducting oxides. Appl .Phys. Lett. p. 32.

Pankove JI (1991). "Hydrogen in semiconductors", Semiconductors and Semimetals 34, J. I.Pankove and N. M. Johnson, eds., Academic Press p.35.

Keshmiri SH, Rezaee-roknabadi M, Ashok S (2002). Thin Solid Films 413: 167-170.

Raniero L, Smith A, Pulcinelli SH (2006). ZnO-based transparent thin film transistor. Thin Solid Films 295-298.

Swanepoel RJ (1980). Applications and processing of transparent conducting oxides. J. Phys. E: Sci. Instrum. 16: 1214.

Schubert EF (1993). Doping in III–V Semiconductors, Cambridge University Press, Cambridge, p. 377.

Pankove JI (1991). in: J.I. Pankove, N.M. Johnson (Eds). Hydrogen in Semiconductors, Semi-conductors and Semimetals, Academic Press, San Diego, CA. p.33.

Poortmans J, Rosemeulen M, Kaniava A, Vanhellemont J, Elgamel H, Nijs J (1995), in: Ashok S, Chevallier J, Akasaki I, Johnson NM, Sopori BL (Eds). Defect and Impurity Engineered Semiconductors and Devices, Materials Research Society Symposium Proceeding, p.378, 399.

Keshmiri SH (1995). Fourth International Symposium on Advanced Materials, Islamabad, Pakistan, September 17-21, in: A. Ul Haq, F. Habibi, A.Q. Khan (Eds.), Advanced Materials-95, Dr. A.Q. Khan Research Laboratories, Pakistan, 1996, p. 459.