

In Situ Investigations of the Electrodeposition and Electrochromic Properties of Poly(3,4-ethylenedioxythiophene) Ultrathin Films by Electrochemical–Surface Plasmon Spectroscopy

Chuanjun Xia and Rigoberto C. Advincula*

Department of Chemistry, The University of Alabama at Birmingham,
Birmingham, Alabama 35294-1240

Akira Baba and Wolfgang Knoll*

Max-Planck-Institute for Polymer Research, Ackermannweg 10, D-55128, Mainz, Germany

Received November 6, 2001. In Final Form: February 7, 2002

The electropolymerization and optical properties of poly(3,4-ethylenedioxythiophene) (PEDOT) was investigated in detail by a combined electrochemistry and surface plasmon spectroscopy setup. The *simultaneous* electrochemical–surface plasmon spectroscopy (EC-SPS) technique allowed for characterization of the changing dielectric constant and thickness of an electrodeposited PEDOT film at various stages of the electrodeposition process in situ. Surface plasmon spectroscopy (SPS) was used to investigate the electrochromic properties of PEDOT upon doping and dedoping and its effect on reflectivity at two laser wavelengths. The SPS curves change dramatically when the polymer film was switched to different electrochromic states upon doping and dedoping revealing important property changes on the film dielectric constants and electrochromic behavior. The SPS characterization was found to be consistent with previously observed changes in the bulk absorption (transmission) properties of PEDOT. The importance of this work is in the use of *attenuated total reflection* phenomena to characterize electrochromism in ultrathin conjugated polymer films.

Introduction

Ever since the introduction of poly(3,4-ethylenedioxythiophene) (PEDOT), a new polythiophene derivative developed and commercialized by scientists at the Bayer AG research laboratories in Germany in the late 1980s,¹ it has attracted a lot of research interest. A comprehensive review has been reported recently by Groenendaal et al.² This low band gap (ca. 1.6–1.7 V) polythiophene derivative³ is highly stable in its doped state and reaches a conductivity as high as 200 S cm⁻¹. When switched from its dedoped state to the doped state, a significant color change occurs from deep dark blue to transparent sky blue. Due to its interesting electronic properties, it has been seeking applications as antistatic coatings,⁴ hole-injecting layers for organic light-emitting diodes,⁵ sensors,⁶ photodiodes,⁷ and electrochromic windows.⁸ The polymer can be synthesized electrochemically by oxidative polymerization⁹ from aqueous or nonaqueous solutions. Electropolymerized films have been studied extensively in

order to understand the intrinsic properties of the polymer. Various techniques, such as in situ UV–vis spectroscopy, Fourier Transform Infrared (FT-IR) spectroscopy,¹⁰ atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS),¹¹ and electrochemical quartz crystal microbalance (E-QCM)¹² studies, have been applied to investigate the film formation, the structure and volume changes, and the ion transport upon doping and dedoping. For actual display device applications, the requirements for ultrathin film formation necessitate a detailed characterization of not only the electrical properties but also the optical and dielectric constants of the material.

Surface plasmon spectroscopy (SPS) is a technique of high sensitivity for the characterization of ultrathin films at the nanometer thickness scale.¹³ The resonance angle and the shape of the spectrum are well correlated to the film thickness and its dielectric constants, i.e., refractive index. Combined with other techniques it becomes a powerful tool for probing optical and dielectric properties simultaneously with field effects (electrical, optical, etc.) and external film environment changes (solution and subphase conditions, temperature and pressure changes, etc.) By monitoring the angular-reflectivity changes by SPS simultaneously with electropolymerization, we are

* To whom correspondence should be addressed.

(1) Bayer AG, Eur. Patent 339340, 1988.

(2) Groenendaal, L.; Jonas, F.; Freitag, D.; Pielartzig, H.; Reynolds, R. *Adv. Mater.* **2000**, *12*, 481.

(3) Pei, Q.; Zuccarello, G.; Ahlskog, M.; Ingnas, O. *Polymer* **1994**, *35*, 1347.

(4) Heywang, G.; Jonas, F. *Adv. Mater.* **1992**, *4*, 116.

(5) (a) Granstrom, M.; Berggren, M.; Ingnas, O. *Science* **1995**, *267*, 1479. (b) Bharathan, J. M.; Yang, Y. *Appl. Phys. Lett.* **1998**, *84*, 3207.

(c) Cao, Y.; Yu, G.; Zhang, C.; Menon, R.; Heeger, A. J. *Synth. Met.* **1997**, *87*, 171.

(6) (a) Yamato, H.; Ohwa, M.; Wernet, W. *J. Electroanal. Chem.* **1995**, *397*, 163. (b) Babacka, J. *Anal. Chem.* **1999**, *71*, 4932.

(7) Arias, A. C.; Granstrom, M.; Petritsch, K.; Friend, R. H. *Synth. Met.* **1999**, *102*, 953.

(8) (a) Gustafsson, J. C.; Liedberg, B.; Ingnas, O. *Solid State Ionics* **1994**, *69*, 145. (b) Sotzing, G. A.; Reddinger, J. L.; Reynolds, J. R.; Steel, P. J. *Synth. Met.* **1997**, *84*, 199.

(9) (a) Sakmeche, N.; Aaron, J. J.; Fall, M.; Aeiya, S.; Jouini, M.; Lacroix, J. C.; Lacaze, P. C. *J. Chem. Soc. Chem. Commun.* **1996**, 2723. (b) Lima, A.; Schottland, P.; Sadki, S.; Chevrot, C. *Synth. Met.* **1998**, *93*, 33. (c) Sakmeche, N.; Aeiya, S.; Aaron, J. J.; Jouini, M.; Lacroix, J. C.; Lacaze, P. C. *Langmuir* **1999**, *15*, 2566.

(10) Kvarnstrom, C.; Neugebauer, H.; Blomquist, S.; Ahonen, H. J.; Kankare, J.; Ivaska, A. *Electrochim. Acta* **1999**, *44*, 2739.

(11) Xing, K. Z.; Fahlman, M.; Chen, X. W.; Ingnas, O.; Salaneck, W. R. *Synth. Met.* **1997**, *89*, 161.

(12) Paik, W.; Yeo, I. H.; Suh, H.; Kim, Y.; Song, E. *Electrochim. Acta* **2000**, *45*, 3833.

(13) Knoll, W. *Annu. Rev. Phys. Chem.* **1998**, *49*, 569.

able to obtain information about the film formation and the optical properties as it changes in situ. The use of electropolymerization to form films of conjugated and conducting polymers on conducting substrates has been reported by numerous groups.¹⁴ The combination of SPS with other electrochemical methods for in situ characterization of electrode/electrolyte interfaces has been documented.¹⁵ Attempts to combine SPS with the electropolymerization of conjugated polymers have recently been described in detail by our group.^{16,27} We had first investigated the electrochemical process of polyaniline film formation and its properties on a gold electrode surfaces using electrochemistry–surface plasmon spectroscopy (EC-SPS) and surface plasmon field enhanced light scattering (SPFELS).

In this paper, we report detailed investigations of the electropolymerization and ultrathin film formation of PEDOT and its electrochromic properties on a conducting Au surface. The electropolymerization and optical properties were studied by the combined technique of EC-SPS. The simultaneous electrochemistry–surface plasmon spectroscopy technique allowed us to characterize the dielectric constant and thickness of an electrodeposited PEDOT film during electrodeposition in situ. SPS at two different wavelengths was also used to study the electrochromic properties of PEDOT upon doping and dedoping. The SPS curves change dramatically when the polymer was switched to a different electrochromic state, correlating with the changes in the dielectric constant. This property was found to be consistent with bulk film absorption (transmission) characteristics.

Experimental Section

Chemicals. 3,4-Ethylenedioxythiophene (EDOT), anhydrous acetonitrile (ACN), lithium perchlorate, and tetrabutylammonium hexafluorophosphate were purchased from Aldrich and used as received.

Electrochemistry. All potentiostatic and cyclic voltammetry experiments were performed using a one-compartment, three-electrode electrochemical cell driven by an EG&G PAR system (model 263A). Vacuum-evaporated gold films on LaSFN9 glass substrates were used as working electrode; the counter electrode was a platinum wire and an Ag/Ag⁺ nonaqueous electrode was used as reference. All the potentials reported in this paper were made according to this electrode reference. All solutions were carefully purged by dry nitrogen before the electrochemical measurements to ensure anhydrous conditions.

Electrochemistry Surface Plasmon Spectroscopy (EC-SPS) Setup. The setup for the excitation of surface plasmons in the Kretschmann configuration combined with an electrochemical cell is shown in Figure 1. Details of this setup have been previously described.¹⁷ Surface plasmons are excited at the metal–dielectric interface, upon total internal reflection of a polarized laser light. We used two laser wavelengths, $\lambda = 632.8$ nm and $\lambda = 1152$ nm, to investigate the films. The electropolymerization and electrochromic processes on gold were detected by monitoring reflectivity changes as a function of time at a fixed incidence angle, θ . Angular measurements were

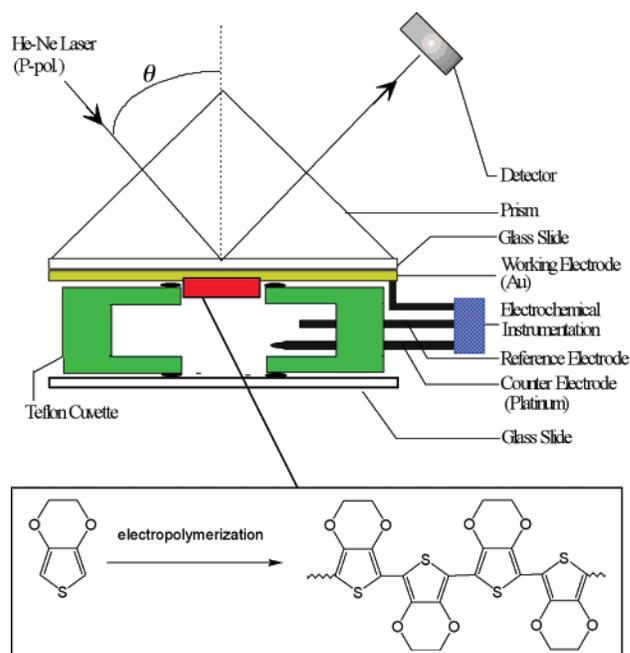


Figure 1. Electrochemistry–surface plasmon spectroscopy (EC-SPS) setup for in situ investigation of the electropolymerization and electrochromism of EDOT to PEDOT.

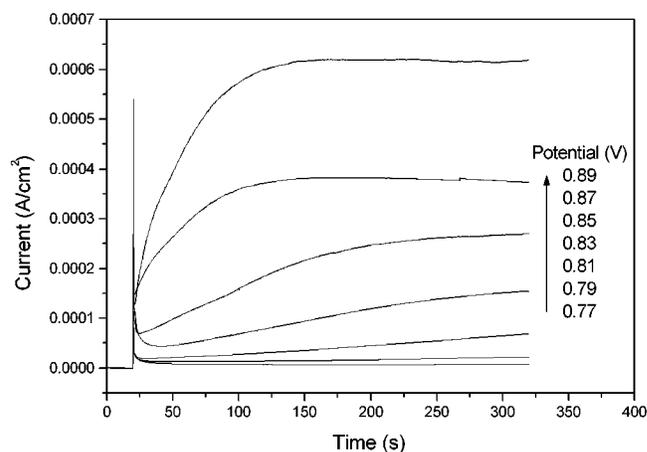


Figure 2. Potentiostatic experiments on the electropolymerization of EDOT to PEDOT.

performed by scanning an incident angle range while holding the potential of the working electrode at a constant value.

Results and Discussion

Electropolymerization of EDOT under Potentiostatic Conditions. The electropolymerization of EDOT in the potentiostatic mode at different potentials was performed in order to find suitable conditions for the SPS measurement. The potential was held constant at 0.5 V before polarizing the electrode to the desired potential in order to minimize the double layer current. The chronoamperometric curves recorded between 0.77 and 0.89 V are shown in Figure 2. The electropolymerization process under constant potential involves three successive steps:¹⁸ nucleation, polymer growth on the electrode, and diffusion of the electroactive species within the deposited film. The deposition of the PEDOT film on the gold electrode occurs when the potential is greater than 0.79 V. Higher bias potentials shortened the nucleation process,

(14) (a) *Handbook of Organic Conductive Molecules and Polymers, Conductive Polymers: Transport, Photophysics and Applications*; Nalwa, H. S., Ed.; John Wiley & Sons: New York, 1997; Vol. 4. (b) Skotheim, T. *Handbook of Conducting Polymers*; Pomerantz, M., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998; p 277. (c) Reynolds, J. R. *CHEMTECH* **1988**, *18*, 440.

(15) (a) Chinowsky, T. M.; Saban, S. B.; Yee, S. S. *Sens. Actuators, B* **1996**, *35–36*, 37. (b) Badia, A.; Arnold, S.; Schermann, V.; Zizlsperger, M.; Mack, J.; Jung, G.; Knoll, W. *Sens. Actuators, B* **1999**, *54*, 145. (c) Iwasaki, Y.; Horiuchi, T.; Morita, M.; Niwa, O. *Electroanalysis* **1997**, *9* 1239.

(16) Baba, A.; Advincula, R. C.; Knoll, W. *J. Phys. Chem. B* **2002**, *106*, 1581.

(17) Aust, E. F.; Ito, S.; Sawondny, M.; Knoll, W. *Trends Polym. Sci.* **1994**, *2*, 9.

(18) (a) Li, F.; Albery, W. J. *Electrochem. Acta* **1992**, *37*, 393. (b) Hillman, A. R.; Mallen, E. F. *J. Electroanal. Chem.* **1987**, *220*, 351.

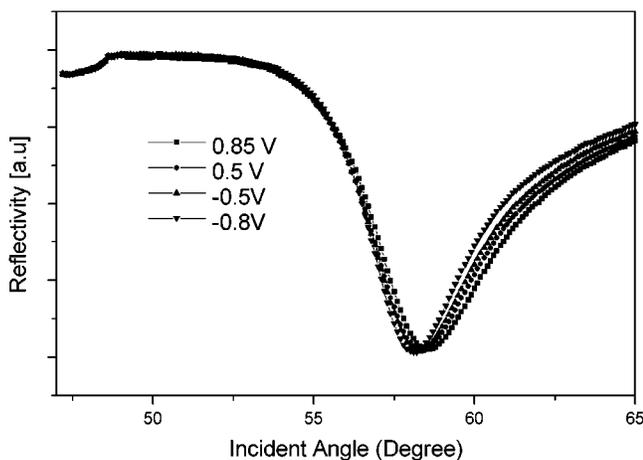
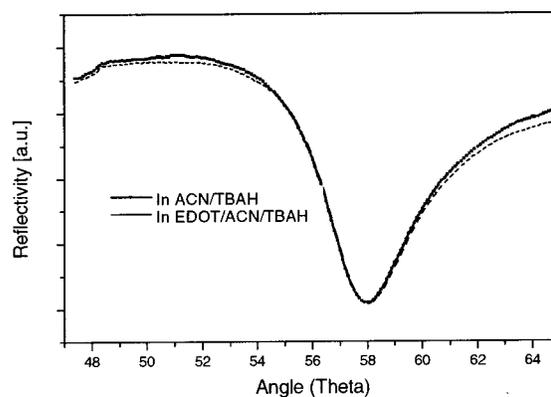


Figure 3. SPS reflectivity changes of gold film in electrolyte solution under different potentials. The electrolyte solution contains 0.1 M tetrabutylhexafluorophosphate in acetonitrile.

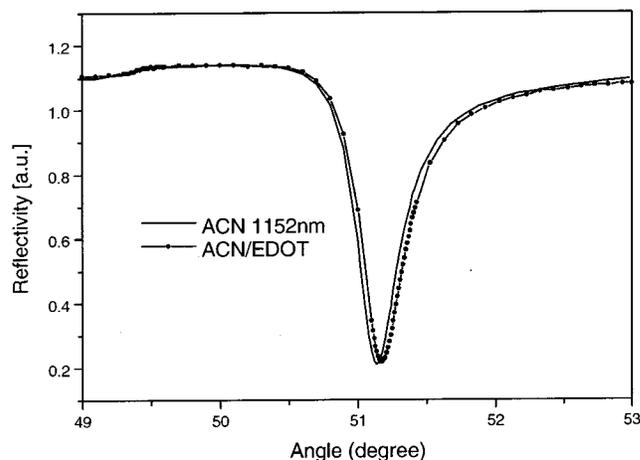
and an intensity plateau was obtained after a certain time of polarization.

The initial stage of the electropolymerization indicates that the polymerization was a combination of instantaneous two-dimensional (IN2D) and instantaneous three-dimensional (IN3D) nucleation mechanisms. It has been reported previously that the IN2D mechanism was the predominant process in the initial stages of the electrodeposition.¹⁹ In addition, the decrease of the monomer concentration and polarization potential favors the IN2D mechanism, which results in a compact, amorphous, and smooth film on the substrate. Previous scanning electron microscopy (SEM) studies²⁰ have shown that PEDOT films prepared on platinum substrates at lower switching potentials gave dense amorphous films, while porous crystalline films were formed with higher potentials. However, a uniform and smooth film is required for SPS characterization. On the basis of this knowledge and the chronoamperometric curves ($I-t$), a relatively low monomer concentration, i.e., 10 mmol/L, and a relatively low potential, 0.85 V, were chosen for the preparation of PEDOT films for the SPS characterization.

SPS Change of the Gold Substrate in the Potential Window. The first question that needs to be answered is whether the SPS resonance of the gold substrate undergoes significant changes within the potential window of interest. The angular measurements of the gold film in 0.1 M tetrabutylammonium hexafluorophosphate monomer free electrolyte solution under different potentials are shown in Figure 3. No redox reactions are expected in this potential range in the electrolyte solution, and only a slight drift of the resonance angle was observed. The resonance angle increased with potential in the double-layer region. This phenomenon is probably due to the adsorption of anions on the electrode surface and change of the electron density in the vicinity of the gold surface, as has been observed by others.²¹ Therefore, a local refractive index change near the gold surface induced the resonance angle shift. However, compared with the change due the deposition of the PEDOT film and its dielectric constant changes, this should not cause significant errors in qualitative or semiquantitative studies, as will be shown later in this study.



(a)



(b)

Figure 4. SPS reflectivity curves of gold film in 10 mM EDOT solution in 0.1 M TBAH/acetonitrile with two wavelengths: (a) 632.8 nm and (b) 1152 nm.

Monolayer Formation of EDOT on Gold. Although theoretical work²² has predicted that thiophene would not interact with the gold surface, the formation of a self-assembled monolayer of thiophene on an Au(111) surface has been observed with scanning tunneling microscopy by Dishner et al.²³ From our observation of the SPS change, EDOT, a derivative of thiophene, is also observed to adsorb on the gold surface. Figure 4 shows the SPS curves, which were measured in acetonitrile solution before and after the immersion of the substrate in 10 mmol/L EDOT solution. Although there is almost no change as shown in Figure 4a when irradiated with a 632.8 nm laser, a small angle shift was observed when applying a long wavelength (1152 nm) laser. This small angular shift using 1152 nm light indicates that adsorption of EDOT on gold indeed occurred to form a condensed layer primarily through the attraction of the S atoms of thiophene on Au atoms of the substrate.²³ The difference of the refractive index, $\Delta n_{s-m} - \Delta n_s$, of the Au substrate–monolayer solution (Δn_{s-m}) and the Au solution (Δn_s) under these two different laser wavelengths explains the SPS behavior. Under 632.8 nm irradiation, the refractive index difference of the monolayer and the bulk solution is negligible. However, the difference at 1152 nm is sufficiently large to cause an observable change.²⁸

(19) Randriamahazaka, H.; Noel, V.; Chevrot, C. *J. Electroanal. Chem.* **1999**, *472*, 103.

(20) Niu, L.; Kvarnstrom, C.; Froberg, K.; Ivaska, A. *Synth. Met.* **2001**, *122*, 425.

(21) (a) Tadjeddine, A.; Kolb, D. M.; Kötzt, R. *Surf. Sci.* **1980**, *101*, 277. (b) Gordon, J. G.; Ernst, E. *Surf. Sci.* **1980**, *101*, 499.

(22) Elfeninat, F.; Fredricksson, C.; Sacher, E.; Selmani, A. J. *J. Chem. Phys.* **1995**, *102*, 6153.

(23) Dishner, M. H.; Hemminger, J. C.; Feher, F. J. *Langmuir* **1996**, *12*, 6176.

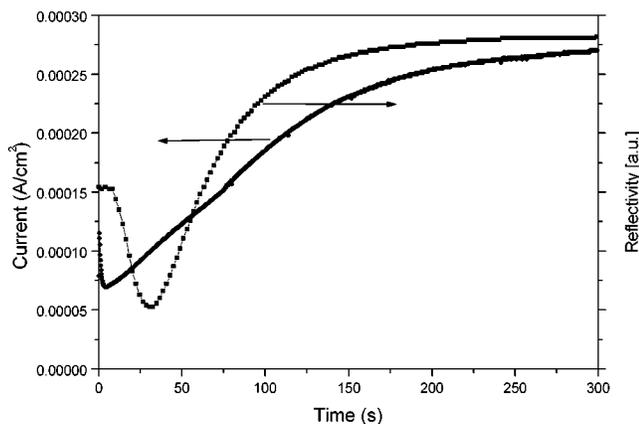
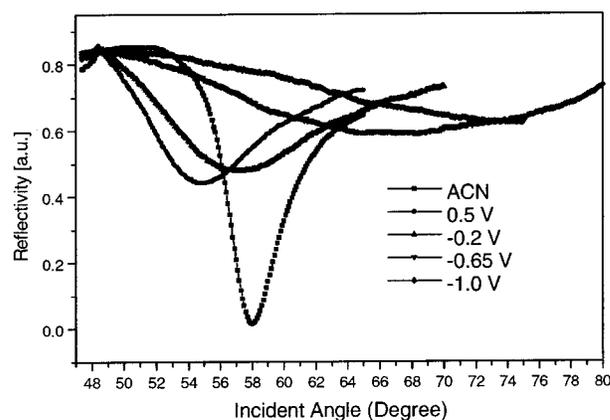


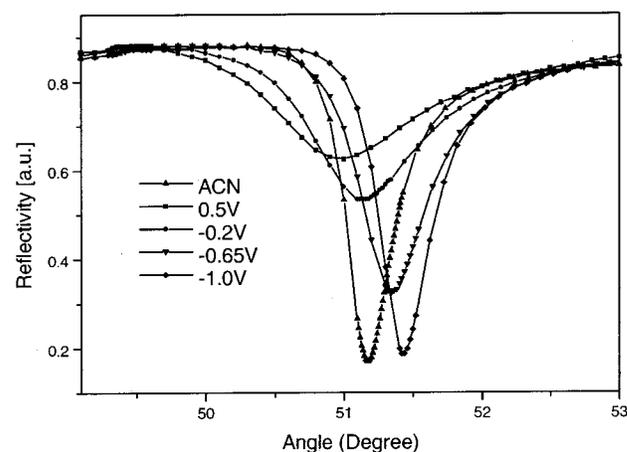
Figure 5. Simultaneous potentiostatic and SPS kinetic curve during the Electropolymerization to PEDOT. The reflectivity change was monitored at 57.5°.

SPS Change during Electropolymerization. The SPS change during the electropolymerization under potentiostatic conditions was monitored at an angle slightly lower than the resonance angle (Figure 5). As previously discussed, the electrodeposition through an IN2D mechanism was preferable under these conditions and gives a compact and smooth film. The reflectivity decreased first upon initial deposition of the PEDOT film, then increased as the polymerization proceeded, and finally reached saturation. The decrease of the SPS in the initial stage indicated that the resonance shifted to lower angles, which implied that the refractive index of the film (Δn) in the doping state is initially lower compared with the electrolyte solution. This was then followed by an increase of the SPS reflectivity after 30 s, which indicated that the dip of the SPS curve shifted to a higher angle than the initial dip. This is attributed mainly to the increase of the thickness of the film (Δd), which grows with the increasing conjugation length of the PEDOT film deposited onto Au substrate. The fact that the intensity is proportional to $\Delta n \times \Delta d$ indicates that both factors play a role in the observed reflectivity changes. At first, the dielectric constant at the interface is lower than the EDOT monomer electrolyte solution. Then as PEDOT film started to deposit, an increase in thickness as well as increase in refractive index accompanies the increasing polymer conjugation length.^{15,16} After 200 s, the SPS signal reached a plateau, which indicates that the film is too thick or the IN3D mechanism dominates the electrodeposition process, giving a rougher film. In fact, angular measurement of the formed film showed no resonance. Although the electrodeposition kinetics cannot be quantified from the SPS change at the fixed angle, the change of the reflectivity correlates with the mechanism of the film deposition process. This is assuming that the film is uniform and has the same dielectric constant all through out. Further experiments can be optimized to distinguish the contribution of Δn and Δd on each stage of the electropolymerization.^{15,16}

SPS Curves at Different Potentials. The electrochromic properties of PEDOT have been well studied by UV-vis spectroscopy.²⁴ The neutral polymer has an absorption peak at around $\lambda = 590$ nm. Upon oxidation, this absorption maximum decreases and the absorption at longer wavelengths in the near-infrared (NIR) region increases gradually. In this study, two laser wavelengths ($\lambda = 632.8$ and $\lambda = 1152$ nm) were intentionally chosen



(a)



(b)

Figure 6. SPS curves of ultrathin PEDOT films on gold under different potentials at two different wavelengths: (a) 632.8 nm and (b) 1152 nm.

in order to study the SPR response on the electrochromic behavior of the polymer.²⁸ From the absorption spectra, the extinction coefficient decreases at $\lambda = 632.8$ nm and increases at $\lambda = 1152$ nm upon doping. Figure 6 shows the SPS curves of the PEDOT film that was fabricated under constant potential (0.85 V) for 50 s. The angular measurements were performed under equilibrium conditions where the different potentials were held constant. Significant changes were induced during the doping and dedoping processes. Before analyzing these curves further, one needs to bear in mind that the SPS signal is really sensitive to changes on the film dielectric constant (complex dielectric constant, $\epsilon_r + i\epsilon_i$, real and imaginary respectively), thickness, and film structure. For both wavelengths, the resonance angle and shape of the curves changed from the oxidized state to its reduced state. At $\lambda = 632.8$ nm, the resonance angle shifted to larger values; at the same time the curves became broader, and the intensity at the minimum of the resonance increased. However, the resonance dip went deeper and became narrower at 1152 nm. As mentioned before, several factors can influence this change. For conducting polymer films, a volume change usually occurs during the doping and dedoping processes.²⁵ The film swells upon anion doping and shrinks upon dedoping. The bending beam method (BBM) was used to study the volume change of PEDOT

(25) (a) Yoshino, K.; Nakao, K.; Morita, S.; Onoda, M. *Jpn. J. Appl. Phys.* **1989**, *28*, L2027. (b) Murthy, N. S.; Shacklette, L. W.; Baughmann, R. H. *J. Chem. Phys.* **1987**, *87*, 2346. (c) Winokur, M.; Walmsley, P.; Smith, J.; Heeger, A. J. *Macromolecules* **1991**, *24*, 3812.

(24) Sotzing, G. A.; Reynolds, J. R.; Steel, P. J. *Adv. Mater.* **1997**, *9*, 795.

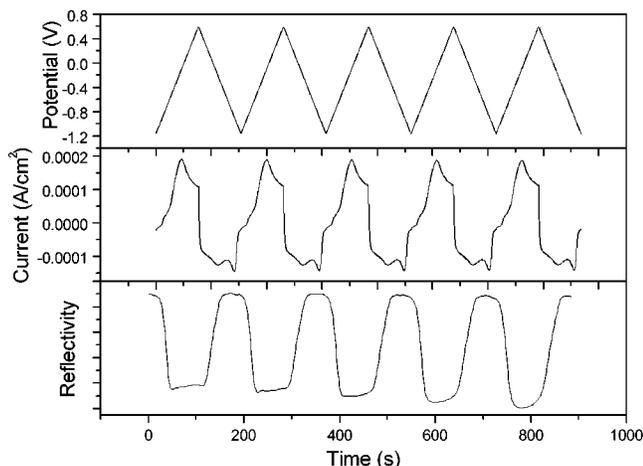


Figure 7. Electrochemical stability of PEDOT at 632.8 nm under reversible anodic and cathodic cycling: (a) potential change; (b) current change; (c) reflectivity change.

during the redox processes,²⁶ and it was found that the induced volume change was less than 1%. Therefore, the resonance angle shift can be attributed mainly to the change of the real part of the dielectric constant, ϵ_r , of the film. When the polymer was reduced from its oxidized state, the real part of the dielectric constant increased and shifted the resonance to a higher angle. At the same time, the imaginary part, $i\epsilon_i$ also changed. Since the imaginary part of the dielectric constant is related to the extinction coefficient at a particular wavelength, the opposite SPS behavior was observed at $\lambda = 632.8$ nm and $\lambda = 1152$ nm. At $\lambda = 632.8$ nm, the imaginary part, $i\epsilon_i$ of the dielectric constant increased upon dedoping of the polymer, while at $\lambda = 1152$ nm, there is an opposite change on this value. These SPS observations are quite interesting because it gives direct evidence of the electrochromic phenomena of PEDOT using a *total internal reflection* method. It can be very useful for the design and detection of the SPS-based sensors and biosensors combined with electrochromic properties of conducting polymers.

Stability of the Film. The PEDOT has a high electrochemical stability as can be seen by the reversibility with successive potential cycling of the polymer film in monomer free electrolyte solution (Figure 7). Almost no change can be seen in the cyclic voltammetry. Only the optical properties change slightly as detected by SPS during the potential cycling.

Again, this underlies the fact that the total internal reflection method is sensitive to the changes on the redox properties of the polymer film. The bottom curves of Figure 7 show the SPS changes at a fixed angle, in which the SPS intensity decreases upon doping and increases upon dedoping when illuminated at $\lambda = 632.8$ nm during repeated cycling. One may note that there is a slight drift of the SPS signal when the polymer goes to its oxidized state. Angular measurements using the $\lambda = 1152$ nm laser gave the same trend as shown in Figure 8. The SPS curves were taken under equilibrium when holding the potential back and forth at -1.0 V corresponding to the reduced form, but the SPS curve did not remain the same when going back to the oxidized form.

These observations indicate that the SPS reflectivity is highly sensitive to the redox process and its influence on the optical properties of the film.¹⁶ When the anions moved into the film to compensate the charge upon oxidation, they did not go to the same site each cycle, which influences

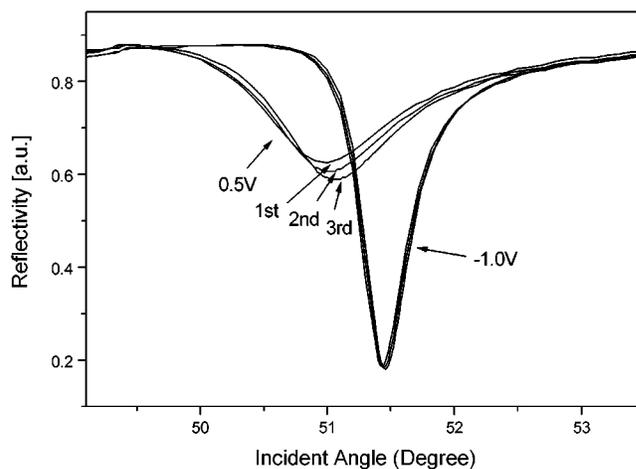


Figure 8. SPS curves under equilibrium (1152 nm) when holding the potential back and forth at 0.5 and -1.0 V.

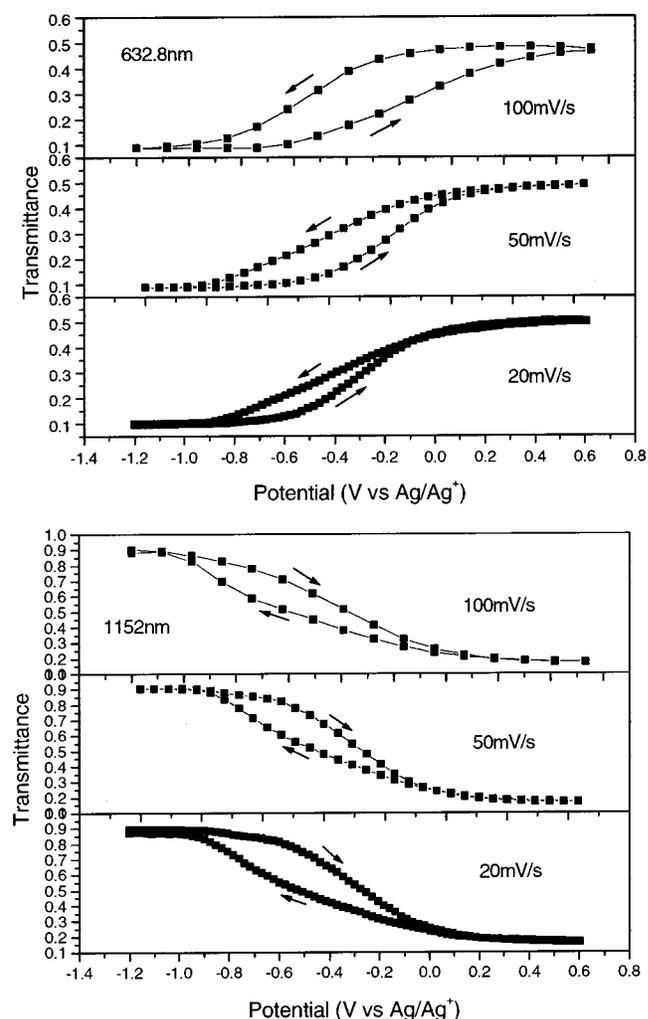


Figure 9. Transmittance change at two different wavelengths (632.8 and 1152 nm) during potential cycling between -1.2 and 0.6 V under different scan rates.

the local composition of the film and hence the refractive index variation. The internal film morphology can also change during the anion doping and dedoping process. Upon reduction, the anions were expelled from the film, even if there are some solvent molecules and electrolytes left in the film. The composition, and morphology of the film affects the film dielectric constants especially in the oxidized state. Hence, the observed changes in reflectivity

can reveal further insight into the doping and dedoping mechanism in these films.²⁷

Transmittance Changes at Two Wavelengths during Cycling. The transmittance change of the film was monitored at $\lambda = 632.8$ nm and $\lambda = 1152$ nm while cycling the potential from -1.2 to 0.6 V at different scan rates. The measurements were done by aligning the detector at the 180° position; two wavelength lasers were used as the light sources. The reference was taken before the film deposition. The film was fabricated potentiostatically on a transparent indium–tin oxide substrate. The results are shown in Figure 9. At $\lambda = 632.8$ nm, the film became more transparent upon oxidation, and the transmittance decreased upon reduction. On the contrary, the transmittance increased $\lambda = 1152$ nm upon oxidation and decreased upon reduction. However, all these cyclic spectrovoltammograms show a hysteresis, i.e., the trace of the reverse potential scans did not follow the corresponding trace of the forward scan. It can be seen that at $\lambda = 632.8$ nm the hysteresis increases with increase of the scan rate. On the other hand, this trend was not observed at $\lambda = 1152$ nm. By analyzing the absorption spectra, one can see that only the oxidized species absorbs at $\lambda = 1152$ nm, and both reduced and oxidized species have absorption at $\lambda = 632.8$ nm. This different type of hysteresis indicates that the redox process and relaxation mechanism can be probed differently at these two wavelengths. It is possible that the absorption or transmittance properties can be *selectively* monitored for one type of species with one wave-

(27) Baba, A.; Advincula, R. C.; Knoll, W. *ACS–Polym. Mater. Sci. Eng. Prepr.* **2001**, 85, 21.

length and another species with another wavelength.²⁸ Further studies are being made to understand these phenomena.

Conclusions

The electropolymerization and optical properties of poly-(3,4-ethylenedioxythiophene) were studied by a technique combining electrochemistry and surface plasmon spectroscopy. The simultaneous electrochemical–surface plasmon spectroscopy method allowed us to characterize the dielectric constant and thickness of an electrodeposited PEDOT film at several stages of the electrodeposition. SPS was also used to study the electrochromic properties of PEDOT upon doping and dedoping. Direct characterization of the electrochromic properties of this polymer was established through this reflectivity method at two laser wavelengths. The SPS curves change dramatically when the polymer was switched to different redox states and observed at two different wavelengths. The SPS characterization is also consistent with bulk absorption characterization.

Acknowledgment. C.X. acknowledges the summer research fellowship provided by MPI-P and R.C.A. acknowledges partial funding from NSF-CAREER, DMR 99-82010. A.B. acknowledges the Alexander von Humboldt Foundation for a postdoctoral fellowship.

LA0156661

(28) Peterlinz, K.; Georgiadis, R.; Herne, T.; Tarlov, M. *J. Am. Chem. Soc.* **1997**, 119, 3401.