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Conformal, Conducting Poly(3,4-ethylenedioxythiophene) Thin Films Deposited Using Bromine as the Oxidant in a Completely Dry Oxidative Chemical Vapor Deposition Process

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Poly(3,4-ethylenedioxythiophene) (PEDOT) thin films were obtained through oxidative chemical vapor deposition (oCVD) by using a new oxidant—bromine. The use of bromine eliminates any post processing rinsing step required with other oxidants like iron chloride and hence makes the process completely dry. Film properties are further compared with the PEDOT films deposited using iron chloride as the oxidant. Accelerated aging experiments show longer retention of electrical conductivity for the PEDOT films obtained using bromine as the oxidant. Conductivities as high as 380 S/cm were obtained for PEDOT films deposited using bromine as the oxidant at 80 °C, which is significantly higher than that for PEDOT films deposited using iron chloride as the oxidant at the same temperature. Cross-sectional SEM of the PEDOT films deposited using bromine on silicon trench wafers demonstrates high conformal deposition of the films. All the results show the possibility of depositing highly conducting, conformal PEDOT films on any substrate including silicon, glass, paper, and plastic.

Introduction

Since their discovery in 1970,[1] extensive research on conducting polymers has been motivated by potential applications for flexible electronic devices including light emitting diodes (LEDs), transistors, biosensors, biomedical devices, chemical sensors, solar cells, electrodes, microwave absorbing materials, new types of memory devices, nanoswitches, optical modulators and valves, imaging materials, polymer electronic interconnects, nanoelectronic and optical devices, and nonlinear optical devices.[2−9] Conducting polymers show negligible conductivity in the neutral state. Conductivity results from the formation of charge carriers upon oxidation or reduction of their conjugated backbone.[10,11] Difficulties with traditional methods of synthesis and film formation for conducting polymers, many of which are insoluble, motivate the development of alternate approaches, such as chemical vapor deposition (CVD).

The vapor deposition of both the oxidant and the monomer is termed the oxidative chemical vapor deposition (oCVD) method for growing conducting polymer thin films.[12,13] Deposition of the poly(3,4-ethylenedioxythiophene) (PEDOT) films by oCVD using $FeCl_3$ has been described in detail in the literature.[12] With this method smooth PEDOT films with conductivities as > 1000 S/cm have been obtained.[13] But one of the drawback of using iron chloride as the oxidant for the polymerization of EDOT is that it is not a completely dry process. Post processing of the oCVD PEDOT films deposited using iron chloride by methanol is required to remove the unreacted iron chloride, the reaction byproduct Fe(II)Cl_2, and any oligomers or short chains formed during the polymerization process as they become a contaminant during device fabrication.[12] In an attempt to make the process completely dry, halogens are used as the replacement for iron chloride as the oxidant for the oCVD process in our experiments. Halogens have been widely used by researchers as a dopant for making conducting polymers.[14−28] Mathai et al.[14] studied the effect

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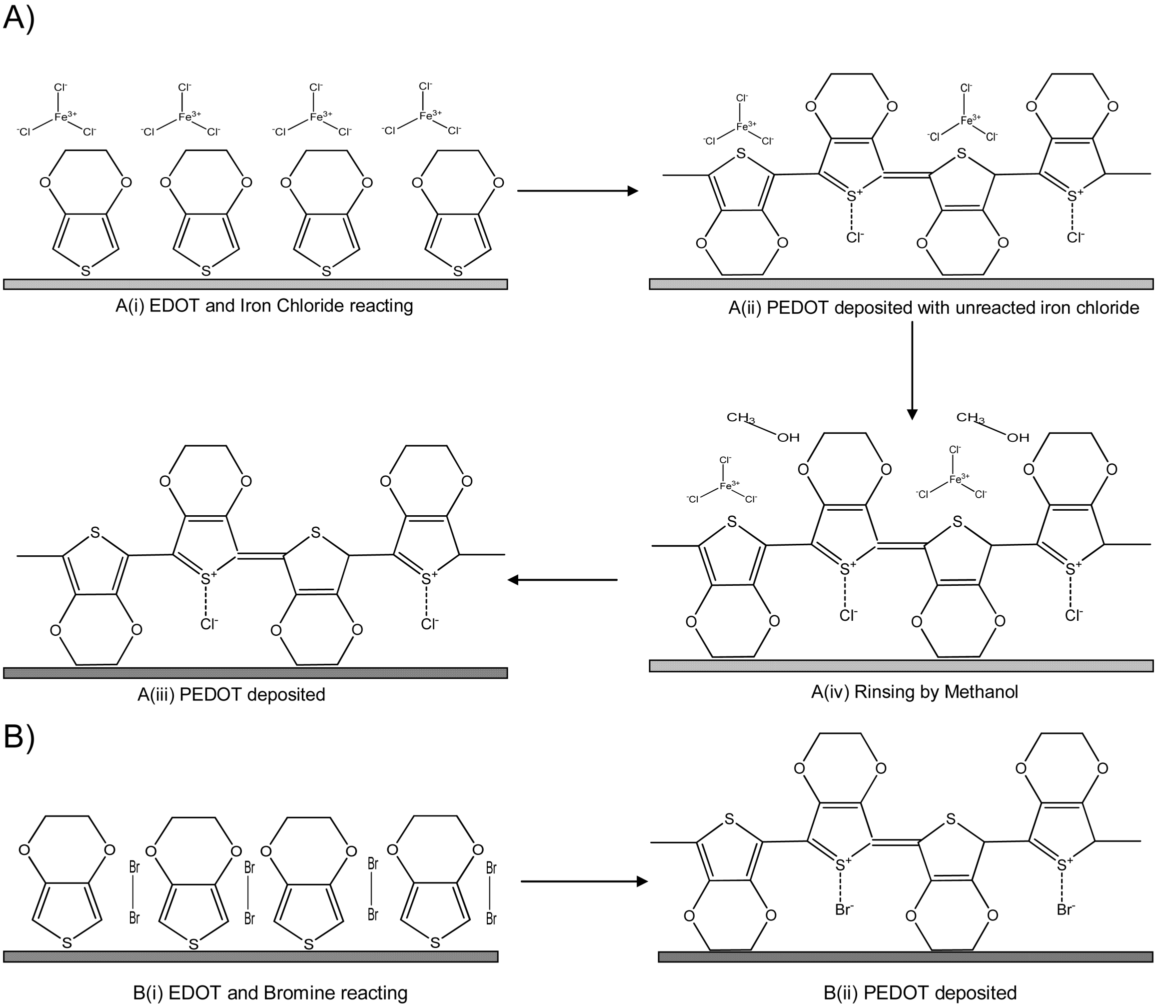

A(i) EDOT and Iron Chloride reacting

A(ii) PEDOT deposited with unreacted iron chloride

A(iii) PEDOT deposited

A(iv) Rinsing by Methanol

B(i) EDOT and Bromine reacting

B(ii) PEDOT deposited

Figure 1. Steps in oCVD process of depositing PEDOT thin films using (A) iron chloride and (B) bromine as the oxidants. No post processing step was required in the case of bromine as the oxidant.

of iodine doping on the band gap of aniline thin films. Gal et al.[15] compared the electrical conductivity of poly(2-ethynylthiophene) and poly(2-ethynylfuran) doped with iodine, bromine, and iron chloride. In most of the cases, doping of the polymers was done by dipping the polymer film in the bromine/iodine (or any other dopant) solution or by exposing to halogen vapor for sufficient time.

In the current work, a completely dry process utilizing bromine as the oxidant as well as the dopant is successfully demonstrated to deposit conductive PEDOT films with enhanced stability. In this paper, the notation Cl-PEDOT will refer to films deposited using iron chloride as the oxidant while Br-PEDOT will denote films deposited using bromine as the oxidant. Differences in the series of processing steps for the two oxidants are shown in Figure 1. By avoiding the rinsing step, we made it possible to deposit oCVD PEDOT film in a completely dry manner. A few of the advantages of making the process completely dry include the possibility of using solvent-sensitive substrates such as paper, overcoming the effects of rinsing on the underlying films in case of multilayer structure, avoiding exposure of the films to air while rinsing. In essence, it is now possible to carry out oCVD PEDOT deposition on any substrate in roll-to-roll or cluster tool processes.

Experiments

Substrates used in the experiments were glass and silicon. Two different sets of experiments were done using iron chloride

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(Fe(III)Cl_3) (97%, Aldrich) and bromine (Br_2) (reagent grade, Aldrich) as the oxidants. For the Cl-PEDOT films, iron chloride was thermally evaporated by resistive heating a crucible within the reaction chamber, as previously described.[12] For the Br-PEDOT films, bromine was delivered as a vapor through a side port of the same chamber. Since bromine is very volatile, no heating of the source jar or delivery lines was required. For both types of films, vapor phase EDOT monomer (3,4-ethylenedioxythiophene, Aldrich) as 3 sccm was delivered into the reactor from a side port. Source jar and feed lines were heated to 150 °C. The chamber pressure was maintained at 150 mtorr. All the chemicals were used as obtained from the vendors. Experiments were performed at a substrate temperature of 80 °C so as to result in reasonably conducting films at reasonable deposition rates for both of the oxidants. This temperature is not an optimized substrate temperature for either the bromine or the iron chloride doped PEDOT film deposition processes. The rest of the deposition process for Br-PEDOT remained similar to the oCVD process using iron chloride as the oxidant. Prior to each deposition, the reactor chamber was baked at 120 °C for several hours to reduce any contamination. Both films were grown to a total thickness of 40 nm. Deposition time for Cl-EPDOT films was 20 min and for Br-PEDOT films was 40 min. Further details of the oCVD process and reaction chamber are published elsewhere.[12] After deposition, films deposited using iron chloride were rinsed with methanol whereas films deposited using bromine were used as is for characterization.

Fourier transform infrared(FTIR) measurements were performed on a Nexus 870, Thermo Electron Corp. Composition of the films was estimated using X-ray photoelectron spectroscopy (XPS) (Surface Science Instruments (SSI) model SSX-100) utilizing monochromated Aluminum K-α X-rays (1486.6 eV) to strike a sample surface. Conformality studies and roughness studies were performed using scanning electron microscopy (SEM) (JEOL JSM- 6060) and atomic force microscopy (AFM) (Digital Instruments, D 3100s-1). The thicknesses and conductivity of the films deposited on glass were measured using a KLA Tencor P-16 surface profilometer and with a four-point probe (Model Keithley SCS-4200), respectively. Conductivity values were calculated using the sheet resistivity measured by the four-point probe and thickness measured by the profilometer.

Results and Discussions

Characterization of the unrinsed (e.g., "all dry") Br-PEDOT and methanol-rinsed Cl-PEDOT films revealed several similarities between the films but also revealed several clear differences.

Chemical Bonding. The similarity in the FTIR spectra of the Br-PEDOT and Cl-PEDOT (Figure 2) clearly confirms the formation of doped PEDOT when using bromine as the oxidant. The intensity of the C=C peak at 1520 cm^{-1} is higher for the Br-PEDOT than for the Cl-PEDOT. This increased intensity reflects a higher degree of conjugation, which in turn is expected to result in higher conductivity.[12,29−31]This result is in line with the observed conductivities of Br-PEDOT (380 ± 8 S/cm), and Cl-PEDOT (40 ± 1 S/cm). Conductivities of the oCVD PEDOT film obtained for this study were similar to those reported previously.[12]

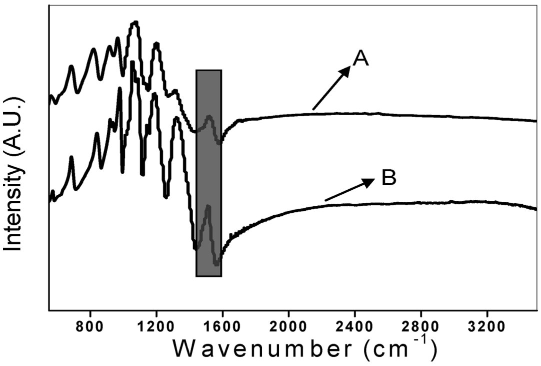

Figure 2. Fourier transform IR (FTIR) spectra of PEDOT deposited using (A) iron chloride and (B) bromine as the oxidants. Shaded rectangle highlights an absorption region associated with conjugation in oCVD PEDOT.

Doping bands were observed at 1513, 1319, 1195, 1090, 1060, 980, and 849 cm^{-1}, as expected for Cl-PEDOT.[32−34] The doping induced bands are observed to be shifted to lower wavenumbers in the Br-PEDOT film.[35] This shift to lower wavenumbers reflects the reduced bonding strength associated with substitution by the larger and heavier bromine atom (covalent radii of 0.1142 nm and ionic radii 0.196 nm versus a covalent radii of 0.099 nm and an ionic radii 0.181 nm for chlorine).[36]

Elemental Composition. The XPS survey scans of both Cl-PEDOT(Figure 3a) and Br-PEDOT (Figure 3b) films showed the presence of the characteristic elements C, O, and S. The position of the C, O, and S peaks in both the Cl-PEDOT and Br-PEDOT were identical and match well with the previous reports.[37,38] For Cl-PEDOT, the high resolution scan for chlorine reveals a spin-split doublet Cl $2p_{1/2}$ and Cl $2p_{3/2}$ having a 1.6 eV energy splitting, as shown in the inset in Figure 3a. No bromine was detected in the Cl-PEDOT films.

For Br-PEDOT, the high resolution scan for bromine revealed a spin-split doublet Br $3d_{3/2}$ and Br $3d_{5/2}$ having a 0.9 eV energy splitting,[39] as shown in the inset in Figure 3b. Additionally, a high resolution scan for chlorine in the Br-PEDOT film confirmed the absence of chlorine. This was done to ensure that there was no cross-contamination by chlorine in the Br-PEDOT films as

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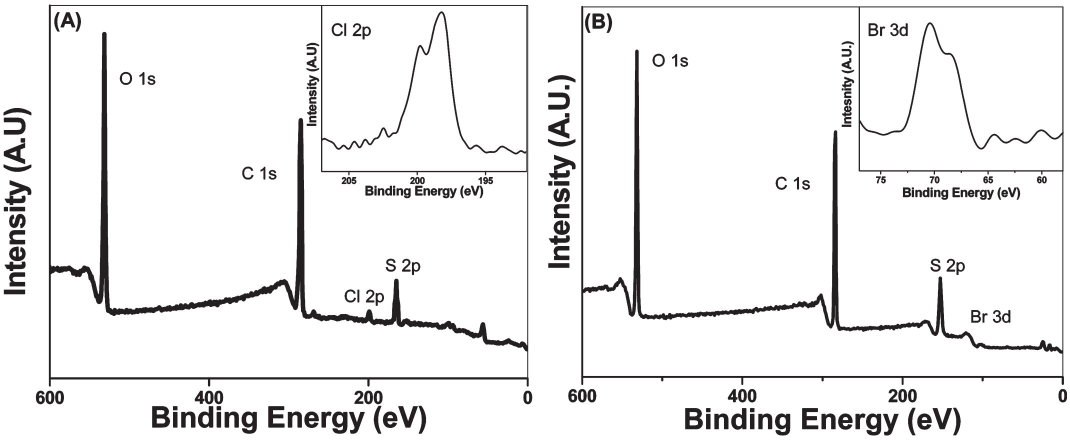
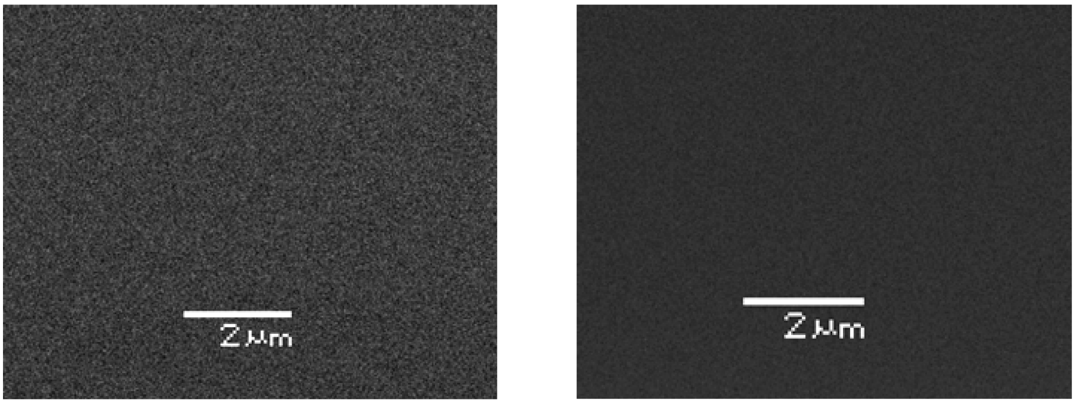


Figure 3. XPS survey scan of oCVD PEDOT deposited using (A) iron chloride and (B) bromine as the oxidants showing characteristic elements. The inset shows the high resolution scan for chlorine and bromine in Figure 3(A) and Figure 3(B), respectively.



(A) (B)

Figure 4. SEM images of oCVD PEDOT deposited using (A) iron chloride and (B) bromine as the oxidants. AFM measurements give the roughness of PEDOT films as (A).

both Br-PEDOT and Cl-PEDOT depositions were carried out in the same reactor. The absence of chlorine validates the hypothesis that bromine is the dopant species in Br-PEDOT. The ratio of Cl/S was 0.22 in the Cl-PEDOT films, and for Br-PEDOT the ratio of Br/S was 0.21.

Conformality. Electrical properties of the conducting polymers are strongly dependent on their film morphology and orientation of the chains.[40−43] The morphology of the oCVD films deposited using iron chloride has been studied before, and very smooth films were obtained. Im et al. have used $CuCl_2$ as the oxidant for depositing PEDOT through oCVD but obtained porous films because of the weaker oxidizing strength of $CuCl_2$.[29] Bromine is a strong oxidizing agent, so smooth dense PEDOT films were anticipated. Indeed, oCVD PEDOT films deposited using bromine as the oxidant appeared smooth in SEM as shown in Figure 4 a. AFM was conducted to compare the roughness of the films deposited using iron chloride and bromine as oxidants. Films deposited using iron chloride have roughness of ~5 nm whereas roughness of films deposited using bromine as the oxidant had roughness ~4.5 nm, slightly better than its counterpart.

Trenches (8 μm deep × 2 μm wide) in silicon were used to examine the conformal coverage of oCVD PEDOT grown with bromine as the oxidant. Figure 5 demonstrates the cross-sectional SEM image of the Br-PEDOT on the standard trenches. The cross-sectional image clearly shows the conformal deposition of the Br-PEDOT. Uniform deposition can be seen at both the side walls and the bottom of the trench. Conformal deposition is possible only in the CVD process and very difficult to achieve in any other solution phase process. In the work previously done by our group,[29] conformality studies were done for PEDOT films deposited by spin-casting and polymerizing a mixture of EDOT and $FeCl_3$ solution in methanol and were compared with oCVD PEDOT films grown with $CuCl_2$, $FeCl_3$ as the oxidants. In case of PEDOT films obtained by spin-casting, the solution was trapped at the bottom of the trench with depleted side walls and the top of the trench.

In case of oCVD PEDOT with $FeCl_3$ because of the directional deposition of $FeCl_3$ through the crucible, most of the deposition was on the entrance of the trench. Best conformality was reported for oCVD PEDOT films with $CuCl_2$ as the oxidant because of the volatility of Cl_2.[29]

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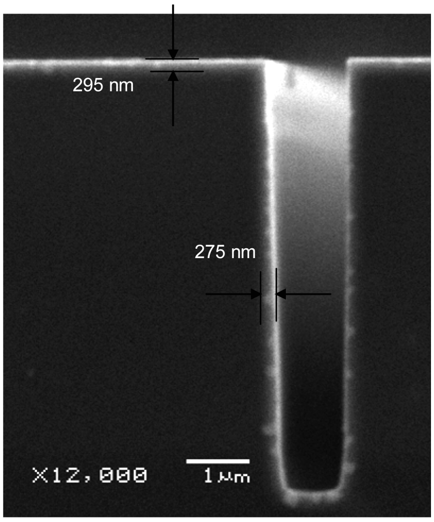

Figure 5. Cross-sectional SEM image of the oCVD PEDOT film deposited using bromine as the oxidant demonstrating high conformality of the deposition.

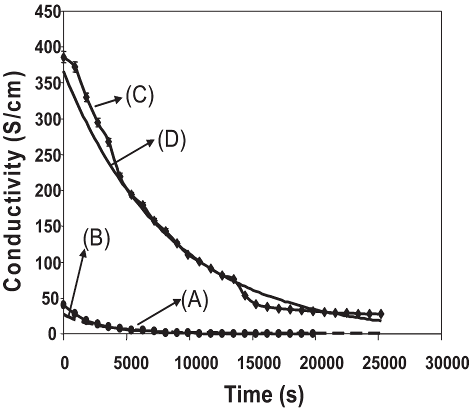

Figure 6. Results of accelerated aging experiments done on the oCVD PEDOT films at 100 °C. PEDOT Films were deposited using (A) iron chloride and (C) bromine as the oxidants. (B) and (D) are the exponential fits for (A) and (C), respectively.

In case of Br-PEDOT also, high conformality was observed because of the volatility of Br_2 as compared to $FeCl_3$. We believe that high volatility of the oxidant improves the conformality because of very low sticking coefficient.

Conductivity. Previously it has been shown that conductivity of the PEDOT films is a strong function of the conjugation length, dopant concentration, and orientation of the PEDOT chains.[12,15,37,44] Im et al.[12] showed that the substrate temperature affects the conjugation length of the deposited polymer, therefore affecting the conductivity. In our experiments we measured conductivity for both the films deposited at 80 °C. oCVD PEDOT films deposited using bromine showed conductivity of ~380 ± 8 S/cm, an order of magnitude more than that of oCVD PEDOT films deposited using iron chloride (~40 ± 1 S/cm). The difference in conductivity in our experiments can be explained in terms of the difference in the conjugation length because of the higher oxidizing strength of bromine in comparison to the iron chloride[45] as also reflected in the FTIR data (Figure 2).

Limited work has been reported on aging of PEDOT thin films.[46−50] On aging, the conductivity of the PEDOT decreases because of the polymer chain oxidation and counterion degradation. Guiseppielie et al.[16] observed that iodine-doped polyacetylene films become less conducting over time because of the iodination of the polymer bone. It is believed that stability of PEDOT films can be increased by reducing the oxidation potential of the polymer chains. The conductivity of Br-PEDOT and Cl-PEDOT films in air at 100 °C reveal that films having bromine as a dopant are more stable (Figure 6). Note this comparison is for films deposited at identical substrate temperature, as this parameter has often be correlated with the ultimate thermal stability of thin film. Note that the Br-PEDOT film had a higher value of initial conductivity, and it is unclear how, if at all, this property influences thermal stability. The conductivity of both types of PEDOT films decayed exponentially with annealing time ($R^2 > 0.95$). The corresponding life times at 100 °C are 2,300 ± 115 s and 10,160 ± 510 s. The observed ~5-fold increase in the stability for the Br-PEDOT is significant for electronic device applications. Hence apart from making the process completely dry, more stable oCVD PEDOT films were deposited by using bromine as the oxidant.

Conclusions

PEDOT thin films were obtained via the oCVD process using bromine as the oxidant. Use of bromine resulted in a completely dry process with no post processing required. Br-PEDOT films when compared with Cl-PEDOT films show enhanced properties in terms of conductivity, conformality of the deposition, and stability. Br-PEDOT films deposited at 80 °C showed conductivity of 380 ± 8 S/cm whereas Cl-PEDOT films showed conductivity of 40 ± 1 S/cm. The cross-sectional SEM image confirms the high conformality of the Br-PEDOT deposition. An XPS study confirms that PEDOT films deposited using bromine have the identical characteristic peak positions for C, O, S as those of Cl-PEDOT. XPS also confirms that Br-PEDOT is conducting solely because of bromine as the dopant and not any other contamination. Br-PEDOT retains electrical stability longer during accelerated aging experiments in air because bromine is less volatile and has a lower oxidation potential than chlorine. Enhanced stability will be critical in the application of PEDOT in device applications.

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