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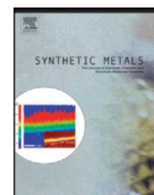

Interface effect of oxygen doping in polythiophene

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ABSTRACT

Long-time evolution of the electrical characteristics for two-terminal and transistor of poly(3-hexylthiophene) film with various gate dielectric interfaces are measured. The oxygen doping is found to depend sensitively on the amount of hydroxyl groups of the interface and irreversible after long time in vacuum except for quartz. For a given interface, dip-coated film always has a higher doping level and slower de-doping than spin-coated films because of higher porosity. With careful control of the oxygen level transistor with mobility of 0.12 cm^2/V s and on–off ratio of 29,000 are obtained for dip-coated film on glass substrate.

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1. Introduction

Solution-processed conjugated polymers have been considered as promising semiconductor materials for a wide range of applications including driving transistors for plat-panel display and smart card on plastic substrate. So far poly(3-hexylthiophene) (P3HT) and some other thiophene-based polymers have the highest carrier mobility over 0.1 cm^2/V s [1,2]. One of the major difficulty of polythiophene is their susceptibility to oxygen p-doping which causes a large leakage current and a poor on–off ratio in the transistor. High on–off ratio has been reported for P3HT transistors fabricated on silicon wafer with thermal oxide as the gate dielectric [3,4]. However for most applications glass or plastic substrates are required due to transparency, flexibility, and cost considerations. Despite of the large amount of effort the on–off ratio of the polymer transistors on non-silicon substrate remain low and highly unreproducible [5–8]. Because of the physical rather than chemical nature of the interaction between oxygen molecules and P3HT [9], in principle the doping caused by partial electron transfer is reversible when the oxygen molecules are removed [10]. However so far there is no report on the reversibility and the time scales of such doping and de-doping processes. The dramatic difference between polymer transistors on Si wafer and other substrate suggests the strong influence of the interface between the active polymer layer and the gate dielectric. Furthermore, the field-effect channel is confined in a hole accumulation region only a few monolayers thick [11] where the polymer chain forms a lamellar ordered structure of 40–60 Å thick by self-assembly [12]. The off-current is therefore expected to be very sensitive to the physical and chemical conditions at the interface [13,14]. In addition to the interface effect, the off-current also depends strongly on the polymer film deposition methods including spin coating and dip coating, implying the oxygen doping is also determined by the polymer film morphology.

In this work we perform a systematic comparison of two-terminal and transistors of P3HT on various surface including quartz, glass, SiO_2 grown by plasma-enhanced chemical vapor deposition (CVD), SiO_2 modified by self-assembled monolayer (SAM), and the insulating polymer polyvinylphenol (PVP) and octadecyltrichlorosilane (OTS). The off-current is monitored up to 400 min in vacuum to check the reversibility of the initial doping. For a given interface spin-coated and dip-coated P3HT films are compared in order to see the effect of polymer morphology.

It turns out that oxygen doping is more serious for interface with more polar hydroxyl groups. Only the doping in quartz, with lowest hydroxyl groups, is reversible under vacuum. Spin-coated films exhibits lower doping level and better reversibility under vacuum annealing than dip-coated film. With careful control of the oxygen level transistor with mobility of 0.12 cm^2/V s and on–off ratio of 29,000 are obtained for dip-coated film.

2. Experimental

Regio-regular P3HT with head-to-tail fraction greater than 98.5% and molecular weight Mw of 84,000 is purchased from Aldrich. 0.2 μm-filtered solutions of P3HT in high-purity chloroform from Merck are made with concentrations of 0.5 mg/ml for dip coating and 5 mg/ml for spin coating. Prior to filtration the solutions

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are heated to 50 °C for at least 10 min in order to increase their solubility and attain the homogeneity of the films.

Five types of channel surface are used to study the oxygen doping and its reversibility of oxygen doping: quartz, glass, CVD silicon oxide, spin-coated PVP films on glass, and OTS treated glass surface. P3HT are spin coated and dip coated either inside or outside the glove boxes. For the reversibility study the drain current at fixed voltage bias is recorded during a long period in a vacuum chamber with heating control, and the samples are not packaged in order to expose the P3HT film to the environment. The samples for transistor characteristics measurement is always packaged to maintain a fix condition during measurement. For samples made in air the packaging is also in air. For transistors made in glove box the packaging is also in the glove box. For two-terminal devices gold source/drain electrodes with channel length of 50 μm and channel width of 2 mm are thermally evaporated using a shadow mask. The organic polymer dielectric PVP is spin coated in iso-propanol solution on glass. The organic layer of OTS is spin coated in 0.1 wt% toluene solution on glass.

For transistors SiO_2 gate dielectric with 300 nm thickness is deposited by CVD over glass substrates with Cr gate. Au source/drain contacts are thermally evaporated on top of the CVD oxide surface and the drain/source electrodes of 5 μm channel length and 200 μm width are made using the standard photolithographic lift-off process. All the samples are treated by O_2 plasma to obtain a hydrophilic surface and reduce the SiO_2 surface roughness. As in our previous report, the root mean square (RMS) value of SiO_2 surface roughness is reduced to 1 nm [5]. Prior to deposition of the P3HT, hexamethyldisilazane (HMDS) SAM is deposited to convert the hydrophilic surface to hydrophobic surface, upon which P3HT is ready to self-assemble into microcrystalline structures. HMDS is either spin coated or dip coated followed by annealing at 70 °C for 5 min to form a monolayer. P3HT films are deposited on HMDS by either spin coating or dip coating. The two-terminal and transistor characteristics of all samples are measured by a high impedance HP 4157 parameter analyzer. The morphology of the spin- or dip-coated P3HT films are studied by the atomic force microscope (AFM).

3. Results and discussion

Long-time current measurements of two-terminal devices with various interfaces are performed in vacuum for the spin-coated P3HT films as shown in Fig. 1(a) and for dip-coated P3HT films as shown in Fig. 1(b). From 0 to 30 min the samples are exposed to air. In this period the drain currents of the devices with all interfaces increase with the air exposure time due to the oxygen doping. After 30 min the air is pumped out that the chamber is in a vacuum of 10^{-3} Torr. Fig. 1(a) shows that P3HT/quartz interface exhibits a good reversibility of oxygen doping as the current drops quickly due to de-doping. On the other hand P3HT/CVD oxide interface is difficult to de-dope and the current remains nearly constant. Both quartz and the CVD oxide are made of silicon dioxide. One difference is that the CVD oxide surface is full of the hydroxyl (OH) group while the quartz surface is not. The results in Fig. 1(a) implies that oxygen molecules in the quartz surface can be pumped out in vacuum while they are trapped by the OH group at the interface in CVD oxide interface. One possibility is that the strong dipole of the OH group attract the oxygen molecules by a induced dipole moment. The reversibility of P3HT/glass interface is only slightly higher than the CVD oxide interface apparently also due to the presence of OH groups. The reversibility is improved when the glass is covered by the organic dielectric PVP and OTS with and without OH groups, respectively. The oxygen trapping in PVP is not as serious as in glass and CVD oxide probably because of the lower density of OH groups and smoother surface. Note oxygen doping should be present in both the bulk and the interface and

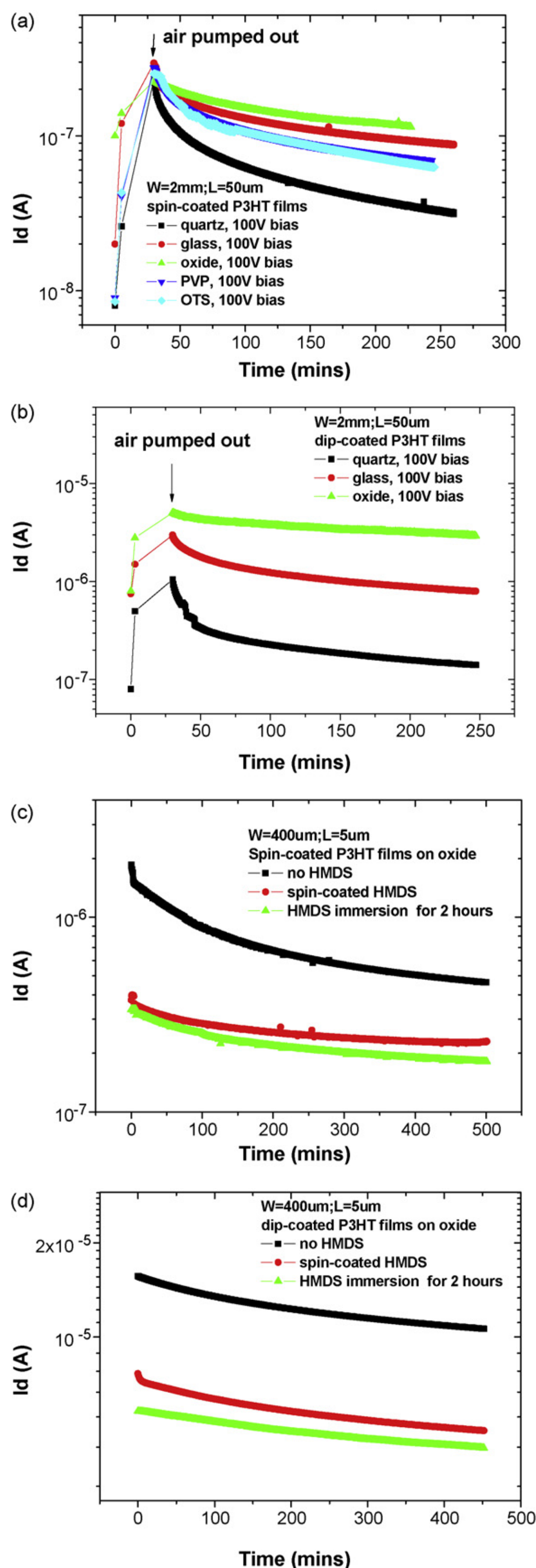

Fig. 1. Drain current I_d of two-terminal devices as a function of vacuum time for various polymer–dielectric interface are shown in (a) for the spin-coated P3HT films and (b) for dip-coated P3HT films. The results for CVD oxide interface with or without the self-assembled monolayer of HMDS are shown in (c) for spin coating and (d) for dip coating.

only the oxygen trapping near the interface depends on the type of the dielectric. The surface trapping has the predominant effect on the conductivity since the current density is higher near the interface. Fig. 1(b) shows the results for dip-coated P3HT films. The order of reversibility of devices with three interfaces are the same as in Fig. 1(a) for spin coating. The overall current is much larger because of the enhanced hole mobility. After air exposure of 30 min the dip-coated film on CVD oxide shows a much high current than quartz, implying the OH group not only limit the oxygen removal in vacuum but also enhance the oxygen adsorption in air. While the quartz devices still shows a rapid de-doping in dip-coated film, the CVD oxide samples becomes even more irreversible than spin-coated ones and the current changes little after 250 min in vacuum. The results above suggests that CVD oxide commonly used for gate dielectric on glass and plastic substrate is in fact a poor choice for the off-current because of the difficult oxygen de-doping and easy doping during dip coating. One way to improve this is to modify by the oxide surface by SAM. HMDS is the most widely used molecule for the modification. Below we study the reversibility of transistors with CVD oxide as gate dielectric with different HMDS conditions. The devices have 5 μm channel length and 400 μm channel width. In Fig. 1(c) it is shown that the doping level for devices without HMDS have a much higher doping level than devices with HMDS for spin-coated P3HT. Whether HMDS is spin coated or dip coated does not make much difference. The results for dip-coated P3HT transistors are shown in Fig. 1(d). The general behaviors are the same as the spin-coated transistors but the overall current is higher due to higher mobility as the two-terminal devices. The effect of HMDS is therefore to block the attraction of the bare polar oxide surface to oxygen. Unfortunately once the doping is formed the reversibility is poor even with HMDS as shown in Fig. 1(c) and (d). This suggests that in order to make a P3HT transistor with high on–off ratio on

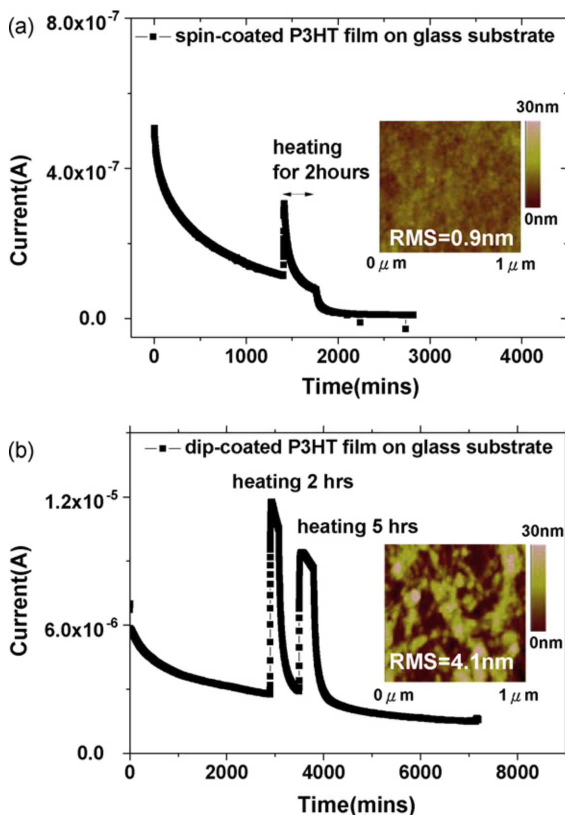

Fig. 2. The effects of heat treatment in vacuum and AFM images of P3HT surfaces are shown in (a) for spin-coated P3HT films and (b) for dip-coated P3HT films.

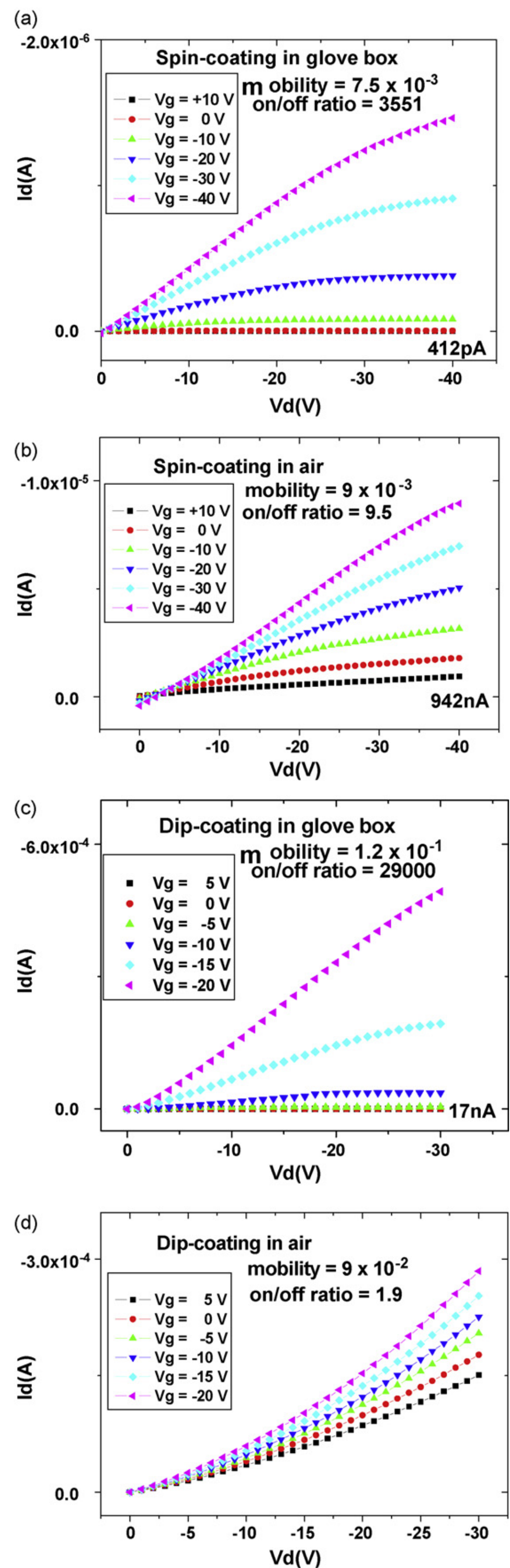

Fig. 3. The electrical characteristics of (a) a spin-coated transistor in glove box, (b) a spin-coated transistor in air, (c) a dip-coated transistor in glove box and (d) a dip-coated transistor in air. The gate dielectric of all samples are CVD oxide modified by HMDS monolayer.

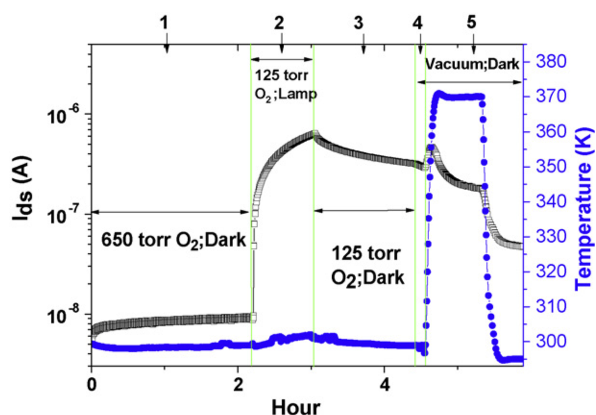

Fig. 4. Pure oxygen at 650 Torr is introduced in period 1. Lamp light is used to enhance the doping in period 2 where the pressure is reduced to 125 Torr. Light is off in period 3. Oxygen is pumped out in period 4. P3HT is de-doped by thermal treatment at 100 ◦ C in vacuum in period 5.

CVD oxide gate dielectric, the oxygen level of the whole fabrication process must be strictly controlled.

So far the vacuum processes and reversibility measurement are all in room temperature. It is well known that thermal annealing in vacuum reduces the oxygen doping level [10]. The de-doping process by annealing for spin- and dip-coated films are compared. We apply 2 h of heating to 100 ◦ C in the middle of the long-time vacuum process for spin-coated P3HT film. In Fig. 2(a) the current initially rises because of the elevated mobility at high temperature. At the end of the heat treatment the temperature goes back to room temperature. One can clearly see that the current becomes much smaller than what we would get by extrapolating the trend before the heating. In other words the heat treatment accelerated the oxygen out-diffusion for spin-coated films. On the other hand Fig. 2(b) shows the results for dip-coated film and the current always goes back to the original trend after the heating for both 2 and 5 h. So nothing is changed during the heating except for the elevated mobility. Despite of high mobility, dip-coated film therefore has the serious drawback of strong oxygen affinity and resistance to thermal de-doping. The origin of such oxygen-trapping tendency of dip-coated P3HT film is revealed by the surface morphology obtained by AFM images. Fig. 2 also shows the surfaces of P3HT films fabricated by (a) spin coating and (b) dip coating. The morphology of dip-coated P3HT films consists of porous structure and rod-like crystalline regions which gives its higher mobility. The RMS roughness is as high as 4.1 nm. The pores make it easy for the oxygen molecules to diffusive into the film and the large surface area of the porous structure keeps a high density of adsorbed oxygen. On the other hand the spin-coated P3HT shown in Fig. 2(a) is smooth with roughness only 0.9 nm. It is therefore much harder for the oxygen to penetrate and adsorb.

The characteristics of spin-coated and dip-coated transistors with HMDS modification fabricated in air or glove box are shown in Fig. 3(a)–(d). As the two-terminal devices the off-current of the transistors is very sensitive to the amount of oxygen in the environment and difficult to de-dope. For transistors made in air the on–off ratio is less than 10 as shown in Fig. 3(b) and (d). When fabricated in glove box, on/off ratio substantially increases regardless of spin coating or dip coating as shown in Fig. 3(a) and (c). Despite of the poor reversibility of dip-coated P3HT, good performances with the mobility of 0.12 cm^2/V s and on/off ratio of 29,000 is obtained as shown in Fig. 3(c) when the oxygen level of the glove box is kept below 1 ppm. The off-current is now limited by the leakage current of gate dielectric instead of the bulk doping.

So far all the samples are doped by exposing to air which contains moisture and other gases in addition to oxygen. In order to confirm that doping is indeed due to oxygen we perform experiments with pure oxygen for P3HT two-terminal device on glass as an example. The result is shown in Fig. 4. The current rises rapidly as oxygen doping is enhanced by lamp light and decreases as the oxygen is pumped out just like the case of air. Oxygen is therefore identified as the primary component in air which affects the polymer conductivity in all the results shown above.

4. Conclusions

In conclusion, the oxygen doping and reversibility for the high mobility polymer P3HT is shown to depend highly on the type of underlying dielectric layers, including quartz, glass, CVD silicon oxide, and organic dielectrics. Surface with high polarity appears to trap more oxygens. Dip-coated P3HT films shows higher mobility due to more self-assembly. But the assembly results in a porous structure which allows oxygen to penetrate and adsorb, resulting in a highly irreversible doping compared with spin-coated film. Despite of the high oxygen sensitivity, with strict control of oxygen level in the glove box the P3HT transistor on glass substrate shows mobility over 0.1 cm^2/V s and on–off ratio nearly 30,000 by dip coating. Such performance suggest the great potential of P3HT to be used for plastic electronics applications.

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