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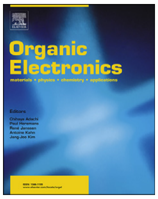

Plasma deposition of organic polymer films for solar cell applications

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ABSTRACT

The use of plasma deposited organic thin films as the interlayer component in organic solar cells applications is demonstrated for the first time. Up to 20% increase in solar cell device performance was observed when an interlayer deposited from the vapour of 4-methylthiazole was used. This work demonstrates the potential of plasma deposition of organic films to be integrated in fabrication of organic solar cells with superior properties.

1. Introduction

Controlling and tuning the properties of interfaces in semiconducting devices is essential to achieve high performance and stability [1–5]. The physical as well as electronic contact between electrode materials and the active semiconducting components of devices must be appropriately aligned. Interlayer materials are often used to achieve the desired outcome by changing the physical properties of surfaces [5]. Properties including surface roughness, surface energy (i.e. hydrophobicity and hydrophilicity) and workfunction can be tuned to attain intimate physical and electronic contact between various device layers [6,7]. In organic solar cells, interlayers can also selectively block charges [3,8] and affect the molecular order of the thin films [9] resulting in improved device performance. There are several types of interlayers currently in use in organic solar cells [1,10]. One of the more interesting example is the use of polyethylenimine (PEI) as workfunction modifying interlayers in organic electronic devices [11]. The workfunction of a number of metal oxides and metals can be changed by applying a thin layer of the polymer on the surface. This resulted in better electronic contact between the electrode material and the active semiconducting materials. This work inspired us to examine thin polymer layers deposited by plasma deposition for application in interface modification.

Plasma deposition of organic films has become a hot topic of investigation to produce functional coatings for a variety of applications including antibaterial films and nanocapsules for drug delivery [12–14]. Plasma deposition is an attractive process because it is solvent-free, the process is independent of substrate and generates smooth pinhole-free films with good adhesion properties (Fig. 1a) [15]. It is important to note here that plasma deposition of organic materials is significantly different to most deposition techniques (e.g. spin coating, splutter coating, chemical vapour deposition, etc.) because chemical reaction occurs in the plasma leading to chemical bonding and crosslinking of precursor molecules to form polymeric films. There are only a few studies in the literature that used plasma deposited polymeric materials for electronic applications [16–21]. The majority of these studies were focused on the conducting properties of doped films. Investigations into semiconducting properties of plasma deposited organic films has been rare [19]. For this reason, we were encouraged to explore the possibility of generating organic films by plasma deposition in semiconducting device applications. The use of plasma as a deposition method in organic semiconducting devices have the added advantage of process simplification. This is because the deposition process can be blended with one of the most commonly applied process in the fabrication of organic electronic devices which is the oxygen plasma cleaning of the inorganic device substrate. It is envisaged that the device fabrication process will be simplified if

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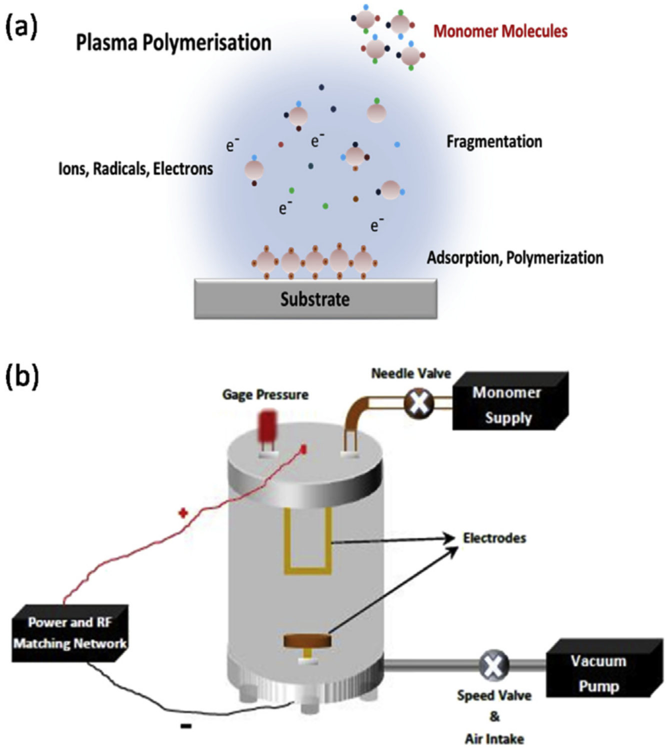

Fig. 1. (a) Illustration of the plasma deposition process and (b) representation of the plasma deposition experiment setup.

the interlayer film can be deposited directly after the oxygen plasma cleaning in the same plasma chamber. Furthermore, organic films deposited from plasma typically have strong bonding to the substrate which is expected to benefit device performance.

2. Results and discussion

To begin with, four organic precursors was selected for plasma deposition. These included thiophene, 4-methylthiazole, allylamine and heptylamine. Thiophene was chosen as one of the organic precursors because it was examined previously in conductivity measurements after doping [18,19]. However, in these cases, plasma deposition of thiophene produced films that were partially oxidised and highly crosslinked. 4-Methylthiazole was chosen as a nitrogen-containing analogue of thiophene while allylamine and heptylamine would potentially result in polymer structures similar to these proven to be beneficial as interlayers, as recently published [11].

To deposit plasma polymerised films, deposition was carried out in Continuous Wave (CW) mode. The samples were placed in the parallel plate plasma chamber (Fig. 1b, see SI for details on substrate preparation). The reactor was evacuated to 1×10^{-2} mbar and oxygen plasma was applied using power of 50 W at pressure of 1.1×10^{-1} mbar for 1 min. The reactor was then again evacuated to base pressure. Then, the precursors were introduced into the chamber with a selected flow rate by a needle valve. A radio frequency (13.56 MHz) generator was used to deliver RF power in the range of 1–50 W via the electrode in the reactor chamber in order to create low temperature plasma. A pulse generator (TTi) and a digital storage oscilloscope (Tektronix, TDS 2024) were added to the power generator circuit to provide the plasma in pulsed mode. In the plasma polymerisation process, the RF powers and the time of the polymerisation were carefully adjusted to achieve appropriate film thicknesses.

The precision in film thickness control (from 2 nm to >50 nm) is important in the application of these films in organic electronic devices. The sample thicknesses were measured by ellipsometry (see SI for experimental details). The deposition conditions were selected in a manner that plasma polymer film thickness increased linearly with deposition time for all precursors used. Fig. 2a shows a typical example of thickness growth vs time during deposition of thiophene (data for other monomers can be found in the SI, Figs. S2–S5). Once film thicknesses were determined, the photophysical properties and composition of the films were investigated. The UV–Vis absorption spectrum of the films were recorded (see SI for data on all films, Figs. S7–S10). For the thiophene and 4-methylthiazole samples, the absorption onset was at 400 nm (Figs. 2b and S8). This was a clear indication that there is a low degree of π-conjugation in the films as observed in previous studies with thiophene [19]. While this was obviously an undesirable outcome in terms of achieving semiconducting organic films, these materials can be used as thin interfacial components in solar cell devices [1,11]. It is important to note that plasma deposited films with thickness greater than 10 nm behave as electrically insulating films.

X-ray photoelectron spectroscopy (XPS) was used to examine their elemental composition of the plasma deposited films (Fig. 3). Table 1 shows the calculated elemental content of the films from the XPS data. It would be reasonable to expect that the ratio of elemental composition of the monomer precursor and that of the films to be similar if there was a high degree of structural retention. This is an important consideration for the thiophene and 4-methylthiazole films as high structural retention is related to the

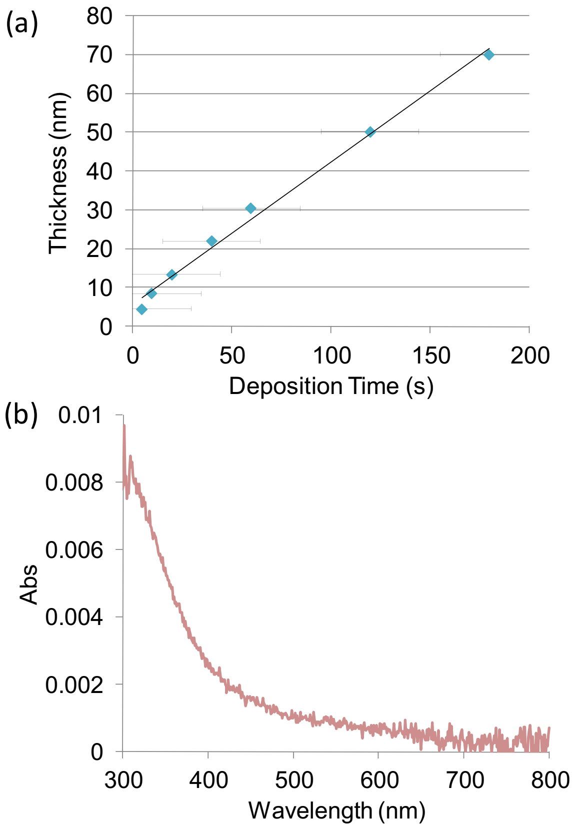

Fig. 2. (a) Plot showing the linear relationship between deposition time and film thickness for the thiophene deposition and (b) the UV–Vis absorption spectrum of the thiophene film (5 nm thick).