High-speed atmospheric atomic layer deposition of ultra thin amorphous TiO₂ blocking layers at 100 °C for inverted bulk heterojunction solar cells

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ABSTRACT

Ultrafast, spatial atmospheric atomic layer deposition, which does not involve vacuum steps and is compatible with roll-to-roll processing, is used to grow high quality TiO₂ blocking layers for organic solar cells. Dense, uniform thin TiO₂ films are grown at temperatures as low as 100 °C in only 37 s (~20 nm/min growth rate). Incorporation of these films in P3HT-PCBM-based solar cells shows performances comparable with cells made using TiO₂ films deposited with much longer processing times and/or higher temperatures. Copyright © 2013 John Wiley & Sons, Ltd.

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KEYWORDS

blocking/selective/barrier layers; bulk heterojunction polymer solar cells; compatible with roll-to-roll processing; spatial atmospheric atomic layer deposition (ALD); thin film deposition; printing of oxides

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1. INTRODUCTION

Organic and dye-sensitized solar cells are two very promising technologies to replace costly silicon-based solar cells. Bulk heterojunction organic solar cells rely on an intimate blend between two organic semiconductors, typically a polymer and a fullerene derivative. Efficiencies for this type of cell have seen a continuous increase since the first report back in 1995 [1], with values of 10% being reached [2]. A key factor in the rapid increase in efficiency for bulk heterojunction solar cells has been the introduction of blocking or selective layers. The intimate mixing of the two organic semiconductors at the nanoscale maximizes exciton dissociation and provides percolation paths for the charges towards the electrodes, but it also allows charge

recombination when holes and electrons come together at the same electrode. By introducing a selective *p*-type or *n*-type blocking layer, shunting and reverse currents are minimized, thus enhancing the fill factor of the cells and the overall efficiency obtained [3,4]. Apart from having charge selectivity, inorganic blocking layers can provide the additional benefit of extending the lifetime of bulk heterojunction solar cells both in conventional and inverted cells. In the former, the TiO₂ layer prevents undesired reaction in the interface between the organic blend and the top contact [5], and in the latter, UV filtering provided by a TiO₂ layer has also been proved to extend cell life [6]. TiO₂-blocking layers can also be used as optical spacers in conventional cells [7]. Finally, their incorporation in organic cells is interesting from a theoretical point of view, for example, for studying

the effect of TiO_2 crystal structure on the bonding of the organic semiconductors and on the efficiency and stability of the cells [8].

From the viewpoint of properties and processing, the blocking layers must have no cracks or pinholes, and they must be able to be grown by a low temperature, fast, and cost-effective route, which is compatible with high throughput roll-to-roll (R2R) processing. Currently, used processing techniques include thermal evaporation, pulsed layer deposition, sputtering, spray pyrolysis, thermal decomposition, chemical bath deposition, sol-gel, and atomic layer deposition (ALD) [3,4]. Of all the different possibilities, ALD has great promise because it is capable of producing high quality conformal thin films at low temperatures and in a single step. It has been used successfully in bulk heterojunction cells [9–11] as well as in other types of solar cells [12]. However, conventional ALD has low deposition rates and requires vacuum processing, thus limiting its industrial use, although it is well-suited to batch processing of ultrathin layers, for example, in the microelectronic industry [13,14].

For ALD to be widely used in photovoltaics (PVs), vacuum-free processing is highly desirable, and for flexible PVs, R2R compatibility is also required. Indeed, in recent years, progressive development of vacuum-free ALD technologies has taken place with novel systems capable of working in the open atmosphere being developed [15] and successfully applied to deposit Al_2O_3 passivation layers on Si cells [16]. The next desirable technological step should be to use designs compatible with R2R processing to demonstrate the potential of vacuum-free ALD in the deposition of solar cell active layers, which is the approach of this study.

A new head design is used, which delivers the different precursors simultaneously over the surface to be coated. The precursors are separated in space rather than in time (as opposed to conventional ALD, which has a sequence of pulse-purge steps) [17–19], thus allowing orders of magnitude faster deposition rates and low precursor wastage [15]. Figure 1 shows a schematic of our atmospheric atomic layer deposition system (AALD) head and deposition process, and a picture of the actual system. Nitrogen is bubbled through a volatile precursor (here, TiCl_4) and through water, and the two flows are distributed through the head. A third N_2 flow prevents reaction of the precursors above the sample. The sample is scanned back and forth under the head, and thus, the pulse sequence of conventional ALD is replicated.

In this work, AALD was used to deposit high quality TiO_2 films to act as hole blocking layers in inverted bulk heterojunction solar cells. The AALD film performance was compared with TiO_2 films often used as blocking layer [20,21]. The results show that very thin AALD amorphous TiO_2 films made at temperatures as low as 100°C in just a few seconds give similar efficiencies to the spray pyrolysed films made at 450°C and significant longer fabrication time due to a necessary curing time and slow cooling rate after film deposition (over 3 h when cooling

Figure 1. a) 3D scheme of the AALD head. The carrier gasses containing the metal precursor and oxidizer, are distributed in parallel flows over the substrate to be coated, kept apart by inert gas flows; b) Side view representation of the AALD coating process. As the sample is scanned under the head, it encounters two flows carrying the metal precursor. Thus, for each AALD cycle (back and forth oscillation of the sample), four conventional ALD cycles are replicated, as labeled in the scheme; c) Picture of the actual system. The system can be viewed as a low temperature oxide printer, with potential for implementing in R2R processing.

at $2.5^\circ\text{C}/\text{min}$). Our work is the first example of a spatial or atmospheric ALD system being applied to the fabrication of an active functional layer in the solar cell and is a clear proof of the huge technological potential of the AALD approach for bulk heterojunction and other types of PV cells where low temperature grown oxide layers are required (e.g., plastic solar cells).

2. EXPERIMENTAL

2.1. AALD film deposition

All films were deposited on clean glass/ITO substrates (Prazisions Glas & Optik GmbH, Im Busch 14, D-58640 Iserlohn Germany, 14 mm × 14 mm × 0.7 mm). For the AALD depositions, films were grown using TiCl_4 (Sigma-Aldrich) and H_2O as the metal and oxidizing precursors, respectively. Depositions were carried out at 100 and 350 °C using metal, oxidizing and inert gasses carrier flow rates of 200, 300, and 1500 ml min⁻¹, respectively. Bubbling rates through TiCl_4 and H_2O were 25 and 50 ml min⁻¹, respectively. The sample was scanned under the head at 50 mm s⁻¹, and there was only minimal time (a fraction of a second) imposed by the mechanics to reverse the sense of scanning. This time is taken into account by the software and in the data we report. ITO glass slides were coated in batches of four. Films grown by spray pyrolysis were deposited as in Weickert *et al.* [22].

2.2. Film characterization

X-ray diffraction (XRD) measurements were performed using a Bruker D8 theta/theta XRD system with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and a LynxEye position sensitive detector. Scanning electron micrographs were obtained using a LEO VP-1530 field emission scanning electron microscope (SEM). Atomic force microscopy (AFM) measurements were taken in a Veeco Dimension 3100 AFM system using TappingMode™. AFM data was treated with the WsXM software [23]. The cross-sectional transmission electron microscopy (TEM) samples were prepared through a conventional process including cutting, grinding, polishing, and final ion milling thinning step. The TEM analysis was conducted using a FEI Technai G2 F20 microscope under 200 kV with a point-to-point resolution of 0.12 nm.

2.3. Device fabrication

Poly-3-hexylthiophene (P3HT, Merck) and phenyl-C61-butyric acid methyl ester (PCBM [6], Nano-C) were dissolved in chlorobenzene at 20 mg/ml, and a blend solution was prepared by mixing the components at a 1:1 volume ratio. The TiO_2 layers were annealed at 150 °C in air for 5 min to remove adsorbed humidity and then the blend was spin cast at 600 rpm for 1 min and resulting films were covered with a Petri dish and slowly dried. The films were then annealed at 105 °C for 3 min. Poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) was spray-deposited from a 1:10 diluted solution in isopropanol onto the organic blend layers as described elsewhere [22]. Subsequently, samples were annealed at 105 °C for 5 min. Approximately 100 nm of Ag were sputtered through a shadow mask as top contacts using an Emitech K575 sputter coater at 10 mA and an Ar pressure of 1×10^{-2} mbar. The illuminated active area was 0.125 cm². After fabrication,

cells were annealed at 140 °C for 5 min in ambient air. The cells were not encapsulated.

2.4. Solar cell testing

Current-voltage characteristics were acquired with a Keithley 2400 SourceMeter using a LabView program. Cells were illuminated with a LOT Oriel LS0106 solar simulator through a shadow mask exposing only the active cell area, and light intensity was adjusted to 100 mW/cm². The intensity was calibrated using a Fraunhofer institute certified Si reference cell equipped with a KG5 filter.

3. RESULTS AND DISCUSSION

Table I summarizes the deposition parameters for the different AALD and spray pyrolysed samples. For AALD, five different samples were made using 10, 20, 30, 40, and 50 AALD cycles at 100 °C. As indicated in the table, the deposition times are very short, the longest AALD deposition taking only 2.5 min (80 cycles at 350 °C). The thinnest films (10 cycles) were grown in only 18 s. For spray pyrolysed films, curing was undertaken at 450 °C for 15 min, and cooling rate was long compared with almost immediate cooling for AALD. Hence, overall growth times were up to ~600 times faster for AALD films.

Atmospheric atomic layer deposition films deposited at 100 °C resulted in amorphous TiO_2 , as shown by lack of crystalline peaks in XRD (Figure S1) or lattice fringes in TEM (Figure 2 aii and aiii). This is consistent with previous reports for conventional ALD using the same precursors and temperatures [24]. Deposition at 350 °C led to either amorphous or crystalline films depending on the number of cycles. Films of ~25 nm thickness (80 cycles – sample S350-80) are crystalline as indicated by the clear anatase (101) peak at ~25° in XRD (Figure S1) and distinct lattice fringes in TEM (Figure 2 biii), in agreement with conventional ALD results [24]. However, thinner films deposited at 350 °C (40 cycles – sample S350-40), from both XRD and TEM (data not shown), have a more amorphous character due to the high stresses present in extremely thin films [24]. The spray pyrolysed films cured at 450 °C are clearly crystalline (Figure S1).

High continuity, conformality, and crack-free films were obtained in all cases as observed in the cross-sectional images in Figure 2. The roughness values (measured from AFM) for all the films were similar and all fairly low (~4 nm, see Table I). The different films were used to fabricate inverted bulk heterojunction solar cells using P3HT and PCBM as organic semiconductors. The cells were all made simultaneously to minimize any variation from cell to cell, so that only the effect of the different TiO_2 layers could be observed. In all cases, the cells had to be illuminated under UV light (using the solar lamp) for 3 min to photodope the TiO_2 layers, and fill existing defect/trap states [6,25,26]. Figure 3a shows dark current density (J) versus voltage (V) curves for the cells, all of

Table I. Growth parameters and characteristic values of the different TiO₂ films and performances of the best as-prepared P3HT-PCBM solar cells for each different TiO₂ blocking layer, as calculated from J-V curves measured under simulated solar illumination.

Sample	T / °C	Cycles	Deposition time (min/s)	Thickness / nm	Roughness (RMS)/nm	J _{sc} / mA · cm ⁻²	V _{oc} /V	FF (%)	Eff. (%)	R _s / Ω · cm ²	R _{sh} / Ω · cm ²
S100-50	100	50	1'34"	30 ^a	3.8(0.2)	-6.73	0.55	50.2	1.89	31.7	520
S100-40	100	40	1'15"	24 ^b	4.1(0.4)	-7.11	0.53	48.8	1.88	19.7	528
S100-30	100	30	56"	18 ^b	3.9(0.2)	-7.04	0.53	46.7	1.85	18.0	500
S100-20	100	20	37"	12 ^b	4.0(0.1)	-7.17	0.53	51.0	1.99	10.2	505
S100-10	100	10	18"	6 ^b	4.5(0.1)	-7.06	0.53	47.5	1.80	27.6	492
S350-80	350	80	2'30"	30 ^a	5.0(0.5)	-6.91	0.53	56.8	2.11	1.7	627
S350-40	350	40	1'15"	15 ^b	4.0(0.1)	-6.98	0.51	44.6	1.62	13.8	388
S450-sp	450	Spray	15' (168) ^c	30 ^a	3.4(0.2)	-6.57	0.52	57.7	1.99	2.3	647

^aEstimated from SEM images.

^bBack extrapolated using SEM images of thicker films together with knowledge of growth rate.

^cTime in brackets includes the cooling step required to avoid the formation of cracks (see experimental section).

them showing a high rectification with almost no leakage current. The logarithmic plot of the dark current (inset to Figure 3a) reveals a lower reverse current for the cells incorporating amorphous AALD TiO₂ (S100-50 to S100-20). These results are a clear indication of the high blocking quality of all the AALD TiO₂ films, even when deposited at 100 °C.

Figure 3b shows the current density versus voltage curves under illumination obtained for the best as-fabricated cells, namely those incorporating TiO₂ deposited by AALD: 100 °C, 20 cycles and 350 °C, 80 cycles, as well as the cell incorporating TiO₂ by spray pyrolysis. The efficiency parameters obtained for all the cells are very similar, in the range $\eta = 2\%$ (Table I). A closer look at the current versus voltage plots (Figure 3) and at the values in Table I shows small differences between the different cells, such as in fill factor (with 16% difference between the best and worse cell, see Table I) and the slope of the curves in the first quadrant (positive current and positive voltage). Conversely, open circuit voltage (V_{oc}), which is mainly a function of the combination of the particular organic donors and acceptors used, and short circuit current density (J_{sc}) are very similar for all cells (8% and 10% difference, respectively). The slopes in the first quadrant and, in particular, at the intersection of the voltage axis, are used to calculate the series resistance of each cell [22].

Figure 4a shows the R_s value for the cells incorporating the different films, as listed in Table I. As expected, the cells incorporating crystalline TiO₂ films (Sprayed and S350-80) showed the smallest series resistance values whereas cells incorporating amorphous TiO₂ layers had an order of magnitude higher R_s values. Unsurprisingly, AALD cells grown with more cycles, thus incorporating thicker TiO₂ films, were more resistive and showed the higher R_s values and lower slopes in the dark J versus V curve (Figure 4a) as well as lower forward current (Figure 3a inset).

The shunt resistance values (Table S1) calculated from light J versus V plots [22] (Figure 4a) is high, with similar values for all the cells tested. As for the fill factor, the cells incorporating the thinnest AALD layers for each temperature (S100-10 and S350-40, with thicknesses of ~6 nm and 15 nm, respectively) were lower than for the other cells, indicating a few shunt pathways presumably owing to incomplete coverage at these low film thicknesses, consistent with the lower shunt obtained for these cells. Figure 4b summarizes the average efficiency values obtained for the different cells studied versus blocking fabrication time, measured immediately after they were produced. The plot emphasizes that AALD is capable of producing comparable quality films with spray pyrolysis in around two orders of magnitude shorter times and at much lower temperature (100 °C vs. 450 °C). Thus, bulk heterojunction cells incorporating only ~12 nm amorphous TiO₂ deposited at 100 °C in just 37 s showed the same efficiencies as cells incorporating ~30 nm crystalline TiO₂ films made in an overall processing time of ~10,000 s by spray pyrolysis at 450 °C.

Figure 2. ai) SEM cross section of sample S100-50; aii-iii) TEM images of sample S100-20; b) SEM cross section of sample S250-80; bii-iii) TEM images of sample S350-80. c) SEM cross section of sample S450-sp.

The AALD cells also showed good stability, giving an improvement in efficiency after 1 week as is often found [27–29]. The highest obtained efficiencies in this study thus were 2.26% for S100-20, 2.40% for S350-80, and 2.28% for S450-sp. Again, the three cells have comparable efficiencies and the values compare well with reported efficiencies for optimized inverted cells fabricated using the same materials (TiO_2 , P3HT, PCBM, and PEDOT: PSS), which have values between 2 and 3% [26,30–33]. Figure 4c (data in Table S1) compares the cells fabricated in this study, in terms of highest cell processing temperature, blocking layer thickness, and blocking layer fabrication time, with equivalent cells reported in the literature using TiO_2 layers made by scalable chemical growth methods. The ~12-nm-thick films of this study

are the thinnest reported. The continuity of the amorphous TiO_2 films deposited with our system allows for such extremely thin films to be used as blocking layer. This permits the deposition at temperatures compatible with plastic substrates and compensates for the higher resistivity of amorphous TiO_2 . Where a thicker blocking layer may be required, as for example, to maximize the electric field in the active region through the optical spacer effect of the blocking layer [7,34], the AALD system offers a high versatility in terms of material choice, deposition temperature, and light management strategy. For example, we have optimized the deposition of highly conducting, nanoparticulate Cu_2O AALD films [35], which are capable of enhancing light absorption in thin film $\text{ZnO}/\text{Cu}_2\text{O}$ cells because of light being scattered by the nanoparticles in the top AALD Cu_2O layer [36].

Figure 3. a) Dark current density versus voltage curves for the different samples. Inset: logarithmic plot of the dark J versus V curves. b) Current density versus voltage curves of the best as-fabricated samples for each deposition temperature, under one sun illumination (AM 1.5g, $100 \text{ mW}/\text{cm}^2$).

Figure 4. a) Series resistance (R_s , filled symbols) and Shunt resistance (R_{sh} , open symbols) values for each different set of cells (incorporating different TiO₂ blocking layers) calculated from J versus V curves under one sun illumination (100 mW/cm²). The arrow indicates the decrease of series resistance with decreasing TiO₂ thickness for the samples deposited at 100 °C, except the thinnest one, see text. b) Average efficiency obtained for the as-prepared different cells used in this study. The error bars indicate the highest-lowest values for each different cell; c) Best cell efficiency (for AALD, 1 week after cell preparation) compared with equivalent cells from the literature in terms of blocking layer fabrication time.

Comparing maximum cell efficiency after air annealing for 1 week versus TiO₂ film fabrication time for AALD and other low temperature processing routes (hence not including spray pyrolysis, but including sol-gel, electrodeposition and chemical bath deposition, which can be undertaken at ≤ 170 °C), shows that the cells incorporating AALD films have similar efficiencies while having several orders of magnitude lower growth times. This is so because no post-deposition annealing or aging time is required for the formation of the amorphous film, as opposed to other lower temperature methods (sol-gel, electrodeposition), which require an annealing step to yield a working amorphous TiO₂ blocking layer.

Together with the fast deposition (compatible with R2R), which do not require annealing or drying steps, the low processing temperature, and the scarce material usage, the reduced energy input required by the method (limited to substrate heating, and powering the motor and computer), makes AALD an effective way to decrease the cost associated with the processing of the blocking layer, thus reducing current estimations of the embedded energy in final devices and modules [37,38].

Finally, our AALD approach has also a high potential for other optoelectronic devices and in other applications such as food packaging industry (i.e., for the fast deposition of hydrophobic coatings).

4. CONCLUSION

In summary, spatial/atmospheric ALD has successfully been used for the first time for the deposition and implementation of functional components in organic solar cells. Both amorphous and crystalline TiO₂ films have been deposited to serve as blocking layers in bulk heterojunction solar cells. Ultra thin amorphous films grown at temperatures as low as 100 °C in only 37 s gave inverted cells with efficiencies comparable with reported values. Continuous, crack-free efficient functional films can thus be grown orders of magnitude faster and several hundreds of degrees lower than other rival chemical techniques.

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