

NiO_x via Flame Assisted CVD as a Route to Stable, Low Cost, Large Area, Hole Transport Layers for Perovskite Solar Cells

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Abstract

The advancement of perovskite photovoltaics continues to provide improved power conversion efficiencies, and steps have been made towards large scale production, though typically by wet chemical or vacuum based processing. However the widespread application of perovskite solar cells is, to date, still limited by the hygroscopic nature of the organic hole transport layer (HTL) which severely impacts long term stability. Additionally, the commonly reported materials, such as Spiro-MeOTAD and PTAA, carry a significant cost providing further motivation for an alternative material. Recent reports in the literature have demonstrated the use of nickel oxide to provide an effective hole transporting layer with significant benefit in terms of both air and thermal stability.

In this work we describe the use of a flame assisted CVD process for the production of NiO_x from nickel nitrate hexahydrate. This approach may be readily implemented on-line, combining continuous large area coating with a relatively low cost in terms of both installation and operation. It is envisaged that maximum benefit could be achieved when used sequentially alongside an on-line APCVD process depositing the FTO which would provide a substrate for an inverted cell stack.

Introduction

The hole transport layer (HTL) plays a critical role in perovskite cell performance. Conventional n-i-p structures typically employ organic semiconductors, such as 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD), poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA), or poly(3-hexylthiophene-2,5-diyl) (P3HT) which provide good initial efficiencies [1]. However these materials are expensive, which may limit large scale production and their permeability combined with the hygroscopic dopant may also contribute to

the long term air stability issues typically observed [2].

Photovoltaic cells are fabricated either with a planar or scaffold structure. The scaffold structure includes a mesoporous layer which is infiltrated by the perovskite absorber and aids transfer of the photogenerated electrons from the perovskite layer to the electrode and extraction into the circuit. The planar structure does not have a scaffold so after light absorption both charge generation as well as charge extraction occurs in the perovskite layer. The advantage of the planar structure is that it avoids the additional processing and annealing cycle required for the mesoporous layer and so facilitates the use of inverted p-i-n structures where the HTL is deposited directly on the TCO electrode. In this case poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is typically used, which also limits stability due to its acidity and hygroscopic nature [3].

Recently, low cost inorganic (HTL) materials have been investigated for inverted p-i-n structures, with NiO_x demonstrating good hole extraction properties and providing significant improvements in stability [2]. Such films are often produced by sol-gel processes, whilst reduced substrate temperatures and good performance have been reported for a solution based combustion method [4].

However, solution based processes could be a limitation to large area production, hence we investigate the feasibility of a flame assisted CVD (FACVD) method. Such an approach would be highly scalable, low cost and suitable for on-line integration. The application to inverted planar devices would allow the NiO_x to be applied continuously on-line, directly on the F:SnO₂ substrate.

Experimental

The films were deposited using an in-house FACVD system described previously and depicted schematically in

figure 1 [5]. This is an open environment process in which the substrate is passed under the coating head/burner to enable film deposition. The number of passes under the head determines the film thickness. Additional extraction ducts were positioned at each side of the linear burner head to extract any particulates that may be produced in the flame. A 0.05M (aq) nickel nitrate solution was prepared from nickel nitrate hexahydrate (99.999% Aldrich) and delivered as an aerosol via an ultrasonic nebuliser with a carrier gas flow of 2 l.min⁻¹. The precursor was added to the combustion gases (1 l.min⁻¹ propane / 20 l.min⁻¹ air) upstream of the burner head. Incremental additions of oxygen ranging from 0.1 to 0.6 l.min⁻¹ were added to the combustion mix. In order to simulate the envisaged online process, the float glass substrate was heated to 400°C and translated under the flame for 50 passes.

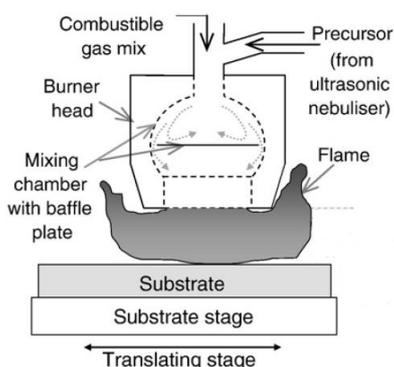


Figure 1: Schematic showing the FACVD apparatus [5].

Results and discussion

Initial tests, with a substrate temperature of 400 °C, resulted in a dark loose particulate film, with the dark colouration being indicative of a sub stoichiometric oxide. The addition of a small amount of oxygen (0.1 l.min⁻¹) to the air/propane mix resulted in the production of a clear adherent film. Weak X-ray diffraction maxima at 37.2° (111) and 43.3° (200) were observed, showing the production of NiO with some degree of crystallinity (JCPDS-47-1049). The broad peak round 22° relates to the glass substrate. Incremental increases in the additional

oxygen resulted more defined peaks, suggesting increased crystallinity of the NiO, as shown in figure 2. Although this could also be attributed to improved film coverage (figure 3), a similar improvement in crystallinity was seen when annealing a low O₂ film in air at 500 °C. Whilst the pattern appears noisy, due to the level of crystallinity and relatively low thickness, it is noted that similar traces have been reported in the literature for NiO films, which have given good cell performance [1].

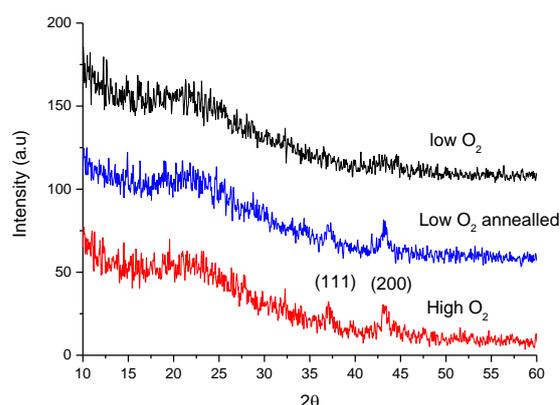


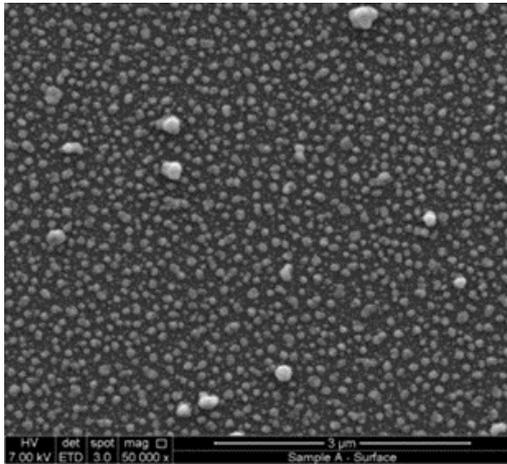
Figure 2: X-Ray diffraction pattern of deposited films processed with different levels of O₂ in the process gas.

SEM Images of the surface (figure 3) suggested a largely particulate film, with the level of oxygen addition influencing the size distribution. Increased O₂ addition gave a more uniformly distributed structure with larger particles. Using the 'ImageJ' software gave a mean particle area of 3.3 x 10⁻³ μm² for the 0.1 l.min⁻¹ O₂ and 5.4 x 10⁻³ μm² for the 0.6 l.min⁻¹ O₂. In each case, the standard deviation was large due to the inclusion of small particles or peaks from underlying layers. This had a greater impact in the case of the 0.6 l.min⁻¹ O₂ film due to the larger particles giving a greater contrast with the underlying peaks, with values of 5.5 x 10⁻³ μm² and 11.1 x 10⁻³ μm² respectively.

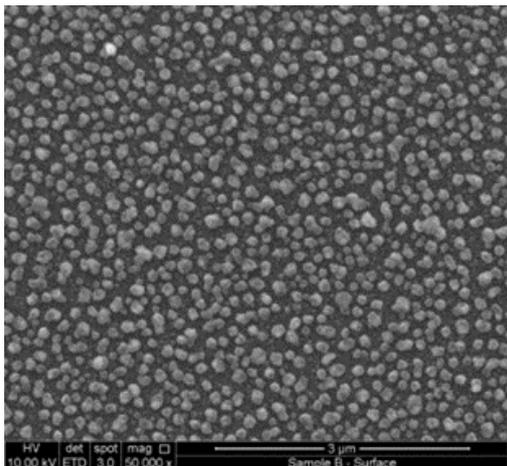
Cross sectional images showed film coverage increasing in uniformity with oxygen addition, achieving thicknesses in the order of ~90 nm with apparent coverage of the glass (figure 3 d). EDX measurements confirmed the presence of Ni both on and between the larger particles across the surface. This suggests that there is more than one layer of

particles, providing complete coverage, if not a fully continuous film.

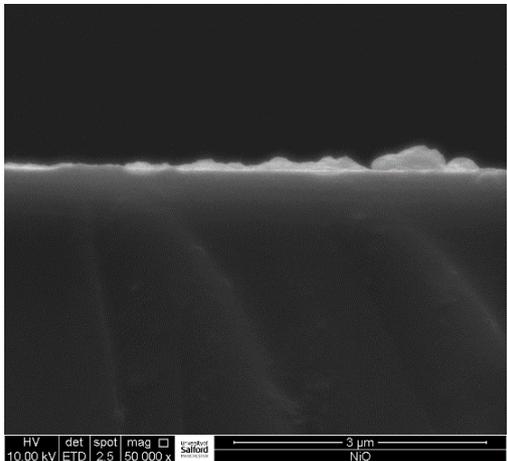
This type of surface structure (Volmer-Weber growth mode) has been previously seen in FACVD [6] where growth leads to the nucleation of isolated islands, which gradually extend and finally coalesce to form grain boundaries.



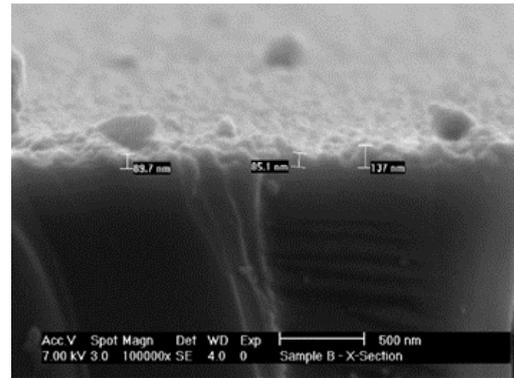
a)



b)



c)



d)

Figure 3: SEM image of the NiO surface a) $0.1 \text{ l.min}^{-1} \text{ O}_2$ b) $0.6 \text{ l.min}^{-1} \text{ O}_2$ and cross section c) $0.1 \text{ l.min}^{-1} \text{ O}_2$ d) $0.6 \text{ l.min}^{-1} \text{ O}_2$.

The changing nature of the film is reflected in the visible region with the average (400 – 800 nm) transmission measurements (Figure 4) initially increasing to a maximum for $0.3 \text{ l.min}^{-1} \text{ O}_2$ additions perhaps due to an increasing proportion of stoichiometric oxide. Further addition of O_2 resulted in reduced and variable transmission possibly resulting from the increasing particle size and reduction in voids within the semi-particulate films. The reflection values show a similar trend to that of the transmission.

There was an approximate correlation of surface roughness with optical haze. For example, the sample with the lowest addition of O_2 gave the highest haze value of 2% (at a wavelength of 450 nm) and the greatest roughness with an RMS value of 15 nm. This is in comparison to samples produced under higher levels of O_2 with, for example, the $0.3 \text{ l.min}^{-1} \text{ O}_2$ samples having the lowest RMS of 8 nm and haze of 1%, partially explaining the observed variation in specular reflection. This is in agreement with the observed haze values and the SEM images.

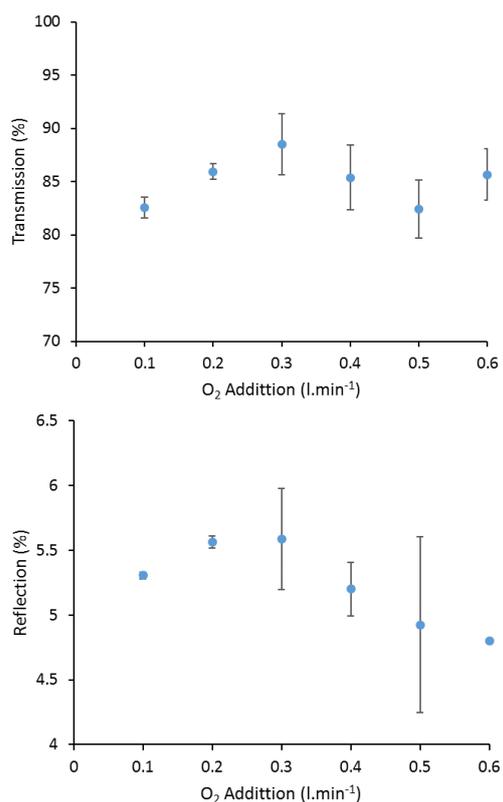


Figure 4: The influence of O₂ addition on visible region transmission and reflection (400-800 nm).

The results show that the level of oxygen in the combustion mix is a key variable in the optimisation of film properties.

It is considered that further improvements in film density may be achieved by variation in process parameters such as flame height above the glass or by variation in flame temperature via dilution of a given propane / air mixture.

Conclusion

We have demonstrated the production of nickel oxide films via a relatively low cost and highly scalable FACVD process. Future work aims to improve film density and evaluate performance in planar perovskite cell structures.

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