Nickel Oxide Thin Films by Radio Frequency Sputter for Inverted Perovskite Solar Cells

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***Abstract* — The Fabrication of efficient hole transport layer (HTL) is one of essential components for high efficiency of inverted perovskite solar cells because the HTL plays an important role for hole transport, electron blocking, and light penetration for light energy conversion. In contrary to conventional solution process, we here fabricate the nickel oxide thin films by radio frequency sputter as HTL and investigate their optical and electrical properties. The conversion efficiency is reached to 12.39% with the control of deposition parameters.**

I. INTRODUCTION

Perovskite solar cells have become great interest for photovoltaic research owing to their striking progress on research only in few years. The light-to-electricity conversion efficiency has already been reached to more than 20% [1] because the perovskite have superior properties as an efficient active layer: a direct band gap of ~1.5 eV, a high absorption coefficient of $>10^4$ cm^{-1} at 550 nm, a low exciton binding energy of 20-30 meV, and long carrier diffusion length of 0.1-1μm, a simple fabrication process [2]. Widely adopted nip structure incorporating TiO_2 electron transport layer for the fabrication of perovskite solar cells have some disadvantages relating to instability in long term operation and severe hysteresis because of unbalanced carrier diffusion lengths. To solve these problems, inverted structure adopting different hole transport materials such as poly (3,4-ethylenedioxythiophene) poly (styrene sulfonate) (PEDOT:PSS) and nickel oxide (NiO) that lead pin structure have been suggested because the structure is favorable to achieve the balanced carrier diffusion length. However, the long term stability of perovskite solar cells with PEDOT:PSS is still questionable owing to its hygroscopic and acidic nature[2-4]. In this aspect, NiO would be better option for efficient and long term stable hole transport layers (HTL) owing to its inorganic nature, wide bandgap (3.6 eV), and favorable band alignment to perovskite layer [2, 5, 6].

For the deposition of the NiO layer, solution process through spin coating are predominant [2, 6]. Yet, the solution process is not favorable to obtain uniform and pinhole-free films. For this reason, physical vapor deposition such as sputtering would be one of solutions because deposition parameters are controllable in exact manner and conformal and compact films are easily formed via this technique. However, since Cui et al. [5] have reported their seminal work for sputtered NiO films for the inverted perovskite solar cells, there have no promising results that have been reported with sputter and no breakthrough has been reported in conversion efficiency over 10%.

Here we demonstrate efficient inverted perovskite solar cells based on radio frequency (RF) sputtered NiO thin films. The conversion efficiency exhibits 12.39% with controlled deposition parameters. Optical and electrical properties are investigated.

II. EXPERIMENTAL DETAILS

NiO thin films were deposited by RF sputter from 80mm diameter NiO target. The base pressure was 5×10^{-4} Pa and the deposition pressure varied from 2 Pa to 6 Pa. The sputtering was carried out under argon atmosphere with 250 W power without any substrate heating on cleaned indium tin oxide (ITO) glasses. Prepared NiO thin films were subjected to annealing at 200 °C for 1h.

Perovskite layers were prepared, following the reference [6]. 2.3g of PbI_2, 0.8g of CH_3NH_3I were dissolved in the solvent that mixed with 1.5 mL of DMSO and 3.5 mL of DMF at 70 °C for 12h. Prepared solution were spread out by spin coating at 1000 rpm for 5s and 5000 rpm for 30s sequentially. During the second spin coating, 130 μl of chlorobenzene was dropped onto the samples. Resulted samples were dried at 100 °C for 30min.

Prepared [6,6]-phenyl C61-butyric acid methyl ester (PCBM) solution (20 mg/mL in chlorobenzene) was subsequently spin-coated onto NiO substrates at 1500 rpm for 30s. Bathocuproine (BCP) layers were deposited by spin coater at 4000 rpm for 40s from the BCP solution (0.5 mg/mL in anhydrous absolute ethanol). Finally, Ag metal contact was deposited by thermal evaporator.

III. RESULTS AND DISCUSSION

Photovoltaic conversion efficiency (PCE) of perovskite solar cells incorporating NiO thin films was evaluated under AM1.5 illumination as shown in Fig. 1 and Table 1.

The solar cells fabricated with NiO HTL prepared under 2 and 4 Pa of deposition pressure exhibit similar performance with small difference in FF. Among the samples, the perovskite solar cells with NiO thin films sputtered under 4 Pa deposition pressure shows remarkable performance. In case of the champion cell, J_{sc} is 14.83 mA/cm^2 and PCE is 10.08%.

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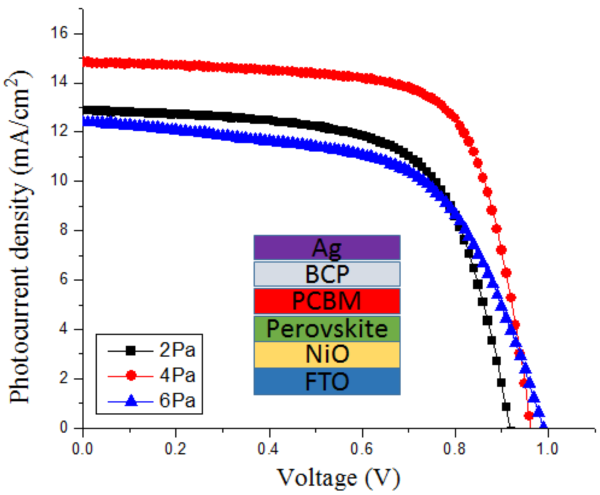

Fig. 1. J-V characteristics of inverted perovskite solar cells incorporating NiO thin films deposited under varied deposition pressure. The inset is the structure of the solar cells

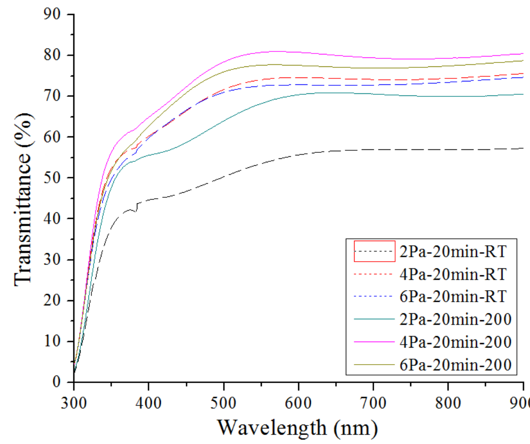

Fig. 2. Transmittance spectra of NiO thin films on ITO glasses sputtered with different deposition pressures. RT and 200 indicate the samples without and with annealing at 200 °C.

Deposition pressure (Pa)	Deposition time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
2	20	10.72	0.927	0.655	6.51
2	20	12.87	0.919	0.654	7.74*
4	20	13.12	0.948	0.656	8.15
4	20	14.83	0.964	0.706	10.08*
6	20	11.89	0.959	0.540	6.17
6	20	12.38	0.990	0.597	7.33*

Table 1. J-V characteristic parameters of the inverted perovskite solar cells. Asterisk(*) indicates the performance from the champion cell.

This outstanding performance of 4 Pa NiO sample is possibly resulted from the excellent optical transparency of the NiO thin films as shown in Fig. 2. 4 Pa NiO samples shows superior transparency through entire wavelength measured in comparison with other samples, even with and without annealing. This can contribute to improved photocurrent and PCE owing to larger availability of incident photon flux for efficient light absorption by perovskite.

Fig. 3 shows the work functions of NiO films measured by Kelvin probe. The work functions of the NiO samples are increased from 4.51 to 4.87 eV as the deposition pressure increased from 2 to 6 Pa for as-deposited samples. After annealing at 200 ºC for 1h, all work functions of the NiO films are increased, indicating the enhancement of carrier concentration. Yet, considering the work function of ITO (4.6 eV), 2 Pa NiO films are more favorable in efficient collection of carriers at Ag/NiO interface because lower energy barrier is formed because of smaller difference in work functions.

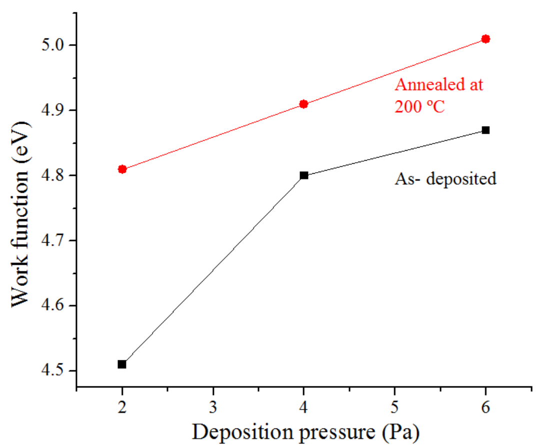

Fig. 3. Work function of NiO thin films by kelvin probe.

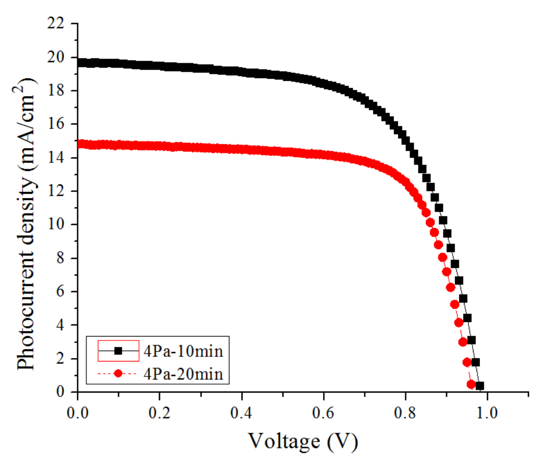

Fig. 4. Performance of inverted perovskite solar cells depending on deposition time of NiO.

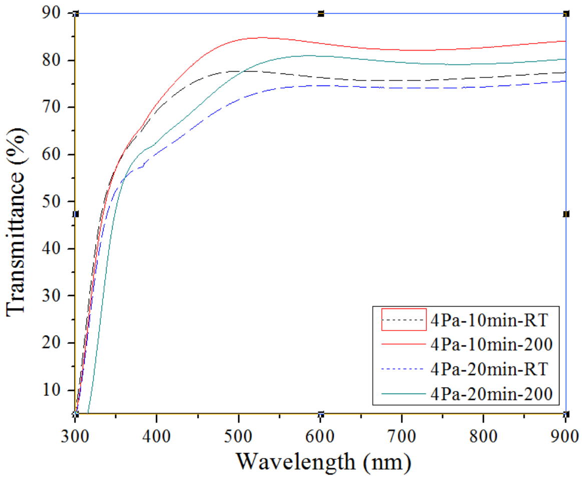

Fig. 5. Transmittance spectra for deposition-time varied NiO thin films.

Therefore, it is speculated that this offset between transmittance and work function is the main reason for similar performance in 2 Pa and 6 Pa samples. In other words, 4 Pa possesses advantageous transmittance and work function for high efficiency.

In order to enhance the performance of solar cells further, the shorter time deposition (10 min) was implemented and inverted perovskite solar cells were fabricated with the NiO samples. All photovoltaic parameters are improved with NiO deposited for 10 min (4Pa-10min) in Fig. 4. The champion cell exhibits 19.69 mA/cm^2 and its PCE reached to 12.39 %. In the same manner, the improvement of performance can be explained by enhanced transmittance in 4Pa-10min-200 as shown in Fig. 5. In addition, decreased work function (4.91 eV → 4.87 eV) is also helpful in achieving higher performance of the solar cells with efficient carrier collection.

IV. Conclusions

Inverted perovskite solar cells incorporating RF sputtered NiO thin films as HTL are demonstrated. The performance of the solar cells were largely affected by transmittance of sputtered NiO thin films and work function of the NiO films was also influential factor for high efficiency of solar cells. With further control of deposition parameters, 19.69 mA/cm^2 of J_{sc} and 12.39% of PCE were achieved.

References

[1] W. S. Yang *et al.*, "High-performance photovoltaic perovskite layers fabricated through intramolecular exchange," *Science,* vol. 348, no. 6240, pp. 1234-1237, 2015.

[2] S. Seo *et al.*, "An ultra-thin, un-doped NiO hole transporting layer of highly efficient (16.4%) organic–inorganic hybrid perovskite solar cells," *Nanoscale,* vol. 8, no. 22, pp. 11403-11412, 2016.

[3] A. Garcia, G. C. Welch, E. L. Ratcliff, D. S. Ginley, G. C. Bazan, and D. C. Olson, "Improvement of Interfacial Contacts for New Small‐Molecule Bulk‐Heterojunction Organic Photovoltaics," *Advanced Materials,* vol. 24, no. 39, pp. 5368-5373, 2012.

[4] A. M. Nardes, M. Kemerink, M. De Kok, E. Vinken, K. Maturova, and R. Janssen, "Conductivity, work function, and environmental stability of PEDOT: PSS thin films treated with sorbitol," *Organic electronics,* vol. 9, no. 5, pp. 727-734, 2008.

[5] J. Cui *et al.*, "CH3NH3PbI3-based planar solar cells with magnetron-sputtered nickel oxide," *ACS applied materials & interfaces,* vol. 6, no. 24, pp. 22862-22870, 2014.

[6] X. Yin *et al.*, "Highly efficient flexible perovskite solar cells using solution-derived NiO x hole contacts," *ACS nano,* vol. 10, no. 3, pp. 3630-3636, 2016.