Effect of Metals (Au, Ag, and Ni) as Cathode Electrode on Perovskite Solar Cells

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Abstract. Gold, silver and nickel used as electrodes in the fabrication of perovskite solar cell by using thermal evaporation deposition method with direct structure FTO/ TiO₂/ MAPbI₃/ spiro-MeOTAD/ metal electrode. The cell efficiency was compared between the electrodes material as a function of time to explaining the effect of these metals electrode on cell performance, X-ray diffraction pattern showed that the samples that contain gold and nickel do not contain a compound indicating the interaction of the metal with the components of the cell or the formation of a new compound, while in the cell containing silver it was found that silver iodide is formed after the passage of time. Under standard AM1.5 illumination, the device shows a power conversion efficiency of 4.42%, 3.50%, and 1.61% for Au, Ni and Ag electrodes respectively. Devices with Au and Ni give same behaviours where reduce efficiency after 7day to 20% but for Ag reduce efficiency to 80%. The results revealed that, Nickel can become the best choice as an electrode for the perovskite solar cell in terms of price and efficiency approach to gold.

Keywords: perovskite; solar cell; metal electrode; nickel; gold; silver;

1. Introduction

In perovskite solar cells (PSCs) the cathode type is very important to transition the generated charge without effect on the cell’s operation. The behaviour of metals is different through interaction and diffusion in layers, some metals tend to diffusion inside the hole transport layer (HTL) and reached to perovskite layer and in sometimes interaction with a component of the perovskite layer. The impurity incorporation in MAPbI₃ could lead to significant device degradation. Many transition and noble metals (e.g. Au, Ni, Ag, Cr, Cu, Mo) have been used as electrodes in MAPbI₃ solar cells [1-3], which are potential sources of impurity contamination for the MAPbI₃ light absorption layer. The large dielectric constant in MAPbI₃ should promote the formation and diffusion of not only native defects but also impurities. Thus, the metal atoms in the electrode may diffuse into the MAPbI₃ layer as impurities and potentially cause degradation of the solar cell. Such degradation mechanism should be a serious concern for the solar cells in which the metal electrode is directly in contact with the MAPbI₃ layer without a hole transport layer (HTL) in between. The HTL-free MAPbI₃ solar cells [4,5] have gained significant interest because the commonly used hole transport material, [2,2′,7,7′-tetrakis(N, N-di-pmethoxyphenyl-amine) 9,9′-spirobifluorene] (spiro-MeOTAD), suffers from long-term stability issues and costly processing[3,6]. the metal atoms may still diffuse through the HTL causing contamination of the MAPbI₃ layer, Even if there is an HTL separating the MAPbI₃ layer and the
metal electrode [2]. Among the metals studied here, Au and Ag are the most widely used electrodes in MAPbI₃ solar cells while the Ni electrode has also been reported [1,3,7]. The Fermi level of the metal electrode should be above the valence band maximum (VBM) and below the conduction band minimum (CBM) of MAPbI₃, which were measured to be −5.5 and −3.9 eV, respectively Fig. 1, to efficiently extract photogenerated carriers from MAPbI₃ [1,3]. The MAPbI₃ solar cells with Au and Ag electrodes both exhibit good power conversion efficiency although their work functions are very different (Au: 5.1 eV; Ag: 4.26 eV) [3]. There are also other mechanisms that the metal electrode can influence the performance of solar cells. For example, the iodine ions in MAPbI₃ can diffuse to the electrode surface forming iodides and causing electrode corrosion, especially when the moisture level in the environment is significant [8-10]. In this work some of metals electrode Au, Ag, and Ni were choose to study their effects on the performance of the perovskite solar cell through measuring the efficiency with electrodes and take the cost with consideration.

2. Experimental part:
Three types of metals as a cathode electrode were chosen in PSC with MAPbI₃ active layer to explain the effect of cathode material on PSC performance were chosen. The steps of work were as following, firstly prepared PSCs in the structure C.TiO₂\m.TiO₂ \ 1step psk\Spiro-MeOTAD\ metal cathode. Secondly measure the efficiency at the time and after of fix periods of time. The general structure of Perovskite solar cell in present work is n-i-p (regular or forward) structure ((AE/ETL/PSK/HTL/CE)/ETL/PSK/HTL/CE)) as shown in fig.1 where AE: is the Anode electrode (FTO Glass), ETL is the Electron transport layer (TiO₂), PSK is the Perovskite layer (MAPbI₃), HTL is the hole transport layer (Spiro) and CE is the cathode electrode (Au, Ag and Ni) were used each time test one of them.

2.1. Preparation of solar cell’s layers
The method of preparing cell parts is explained in more detail in our previous [11]. The FTO/glass substrates patterned by laser etching and washed with detergent, deionized water, isopropanol and acetone sequentially before drying in oven at 60 °C overnight or by nitrogen gas. For the electron transport layer, compact TiO₂ (c.TiO₂) and mesoporous TiO₂ (m. TiO₂) were used, Fig. 2 shows the steps consider to deposit ETL on FTO-glass. The c.TiO₂ layer prepared by using titanium tetraisopropoxide (TTIP) and deposited using spin technique (3000 rpm, 20 s, 8 R-time) with sintered at 500°C. Also, using TiO₂ past (from Sharif solar company) to prepare m. TiO₂ layer and deposit by spin coating (3000 rpm, 20 s, 8 R-time) sintered and annealing at 500°C for 1h.

Figure 1. (a) energy levels [3], (b) the general structure of PSC layers.
The MAPbI₃ Perovskite (PSK) was prepared by 1step method according to [11,12] which done by mixing PbI₂, MAI, DMSO and DMF in certain quantity at room temperature then used to deposited PSK layer by spin coating technology in three speeds (2000 rpm, 4000 rpm, 2000 rpm) of 10 s for each step. Chlorobenzene (CB) was used with the last step as anti-solvent. The hole transport prepared by using spiro-ometad and deposited by spin coating at 4000 rpm for 20s as in Fig.3.

Cathode electrode were prepared by using thermal evaporate deposition method to deposit Au, Ag and Ni layer with the thickness between 70 - 100 nm using the mask in fig. 4. For Ni electrode need special method of thermally evaporated deposition because has very high boiling point 2730 °C and thermal evaporating nickel is a very difficult. Like titanium, it has a strong tendency to alloy with refractory metals. Attempting to thermal evaporate nickel out of a tungsten boat has proven futile. As the boat heats up and the nickel melts, it alloys with the boat, causing it to become brittle and crack shortly after exposure to the liquid nickel. Therefore, deposition is very limited.
Alumina coated evaporation tungsten source shown in Fig. 5 has been developed to replace the tungsten source for some specific applications. The advantages of this type of evaporation source are good heat transfer and the inertness of alumina with most metals. Also, the evaporator does not wet the alumina resulting in no resistant change of the boat when the evaporator melts. Due to the non-wetting characteristics of alumina, the evaporator forms a sphere when melted resulting in a point source. This type of evaporation source will give a long life compared to the non-protected sources.

Figure 5. Alumina coated evaporation tungsten source used to deposit Ni electrode.

3. Result and discussion
To verify the presence of interaction between the metal electrode and the cell layers XRD were examined for samples. The XRD test for Au and Ni in Fig. 6 and 7 don’t show new structures have composite contain Ni or Au. The XRD in Fig. 8 for the cell with Ag electrode show AgI structure in a sample that refer Au and Ni don’t have change or interaction with under layer while Ag got interaction with iodine in perovskite layer tend to damage both Ag electrode and perovskite layer.

Figure 6. XRD pattern for cell with Au electrode after one month.

1 https://www.lesker.com/newweb/evaporation_sources/alumina-coated-evaporation-sources.cfm
Figure 7. XRD pattern for cell with Ni electrode after one month.

Figure 8. XRD pattern for cell with Ag electrode after one month.

The colour of Ag electrode and perovskite layer begins to change to yellow after three days as prepared in Fig. 9, so the efficiency in the cells with Au and Ni because the degradation in perovskite layer but for a cell with Ag electrode not only because degradation in perovskite but also because of interaction of Ag electrode.

The XRD patterns of samples analysis by XRD (Shimadzu 6000) using Cu-Kα target and radiation of wave length 1.5406 Å. The gold miller indices (hkl) according to the angle from Fig. 6 are (111)38.27°, (200) 44.48°, (202) 64.73°, (311) 77.76°, (222) 81.937°, (400) 98.4°, (313) 111.17°, (202) 115.65° corresponding with cubic structure Space group Fm-3m, a=4.069 Å. In Fig. 7 the Nickel miller indices (hkl) according to angle are (111) 43.65°, (200) 50.81°, (202) 74.66°, (311) 91.47°, (222) 95.4°, (400) 117.98° corresponding with tetragonal structure Space group Fm-3m, a= 3.5810 Å. The miller indices (hkl) according to angle from Fig. 8 are (111) 23.8°, (020) 39.4°, (311) 46.6°, (202) 48.9°, (040) 56.8°, (313) 62.1°, (402) 64.48°, (242) 71.5°, (511) 76.6°, (404) 84.5° refer to Silver iodide corresponding with tetragonal structure Space group Pm-3m, a= 4.3100 Å. The phase analysis for XRD data draw by using Match! Software from Crystal Impact - Software for Chemists and
Material Scientists is. It compares the diffraction pattern of samples to a database containing reference patterns to identify the phases which are present.

The relation between the current density (J) and the bias voltage (V) is very important to understand the behavior of solar cells like efficiency and filling factor (FF). Figure 9 shown J-V characterization for perovskite solar cell with three metals as the electrode material. The efficiency of cells with Gold, Nickel and silver electrodes are 4.42%, 3.50% and 1.61%, respectively. The same parameters were measured after 7 days to show the effect of time on solar cell performance. The results show that the efficiency decreased by 20% for each of gold and nickel, while for silver reduce by 80%. The curve of J. V in Fig.10 shows that Au and Ni electrode have the same behaviour and cell's perform for both they have the same effect with time where there have same reduce rate of efficiency. For a cell with Ag electrode has high reduction rate for efficiency with time. Also, noted I_{sc} for Ni electrode is 11.98 mA higher than that of Au electrode 11.64 mA but FF value for Ni is 0.41 lower than that of Au with 0.55, where Nickel is an earth-abundant and non-precious metal with a high work function close to gold. The Qinglong Jiang et al. reported on a sputter-deposited Ni electrode for glass/FTO/TiO2 nanowire/ MAPbI3/Spiro-OMeTAD/Ni devices. Up to 7.7% PCE was obtained compared to 10.4% PCE for Ni-based devices with 150- and 300-nm-thick electrodes, respectively [13]. The material cost makes it attractive factor for PSC electrodes while conductivity needs to be addressed.

Figure 9. perovskite solar cell with Ag electrode after 7 days.

Figure 10. J. V characterization for PCS with Au, Ag and Ni electrodes at two times.
V_{oc}, I_{sc}, V_{max}, I_{max} were measured and comparable in Table 1. The calculated FF and η% revealed that lower FF values for Ni-based devices were attributed to the low series resistance of Ni, which could be remedied using thicker Ni films.

Table 1 summarized the parameters of perovskite solar cells using three types of electrodes metal. The parameters measured at time of fabrication and after 7 days.

Table 1: Perovskite solar cells parameters measured with different metals electrode and time.

| Metal with time | V_{oc} Volt | I_{sc} mA | V_{max} Volt | I_{max} mA | FF | η% |
|----------------|-------------|-----------|--------------|------------|----|----|
| Au at time     | 0.69        | 11.64     | 0.47         | 9.33       | 0.55 | 4.42|
| Au after 7 days| 0.71        | 11.30     | 0.47         | 7.41       | 0.44 | 3.51|
| Ni at time     | 0.71        | 11.98     | 0.47         | 7.39       | 0.41 | 4.50|
| Ni after 7 days| 0.71        | 11.53     | 0.39         | 7.26       | 0.35 | 2.87|
| Ag at time     | 0.71        | 9.73      | 0.39         | 4.07       | 0.23 | 1.61|
| Ag after 7 days| 0.24        | 0.59      | 0.16         | 0.17       | 0.19 | 0.03|

4. Conclusions

The perovskite solar cell with direct structure FTO\ TiO2\ MAPbI3\ spiro-MeOTAD\ metal electrode were fabricated successfully using three types of metals for electrodes (Au, Ag, Ni). Au electrode consider best choose for getting best efficiency and stability for cell but it may be consider expansive. The silver (Ag) electrode can diffused and interact with the perovskite layer, this will damage and reduce the age of the cell. The nickel electrode can become the best choice as an electrode for the cell in terms of price and efficiency, comparable to gold at a thickness higher than the thickness of gold. Also believe that thermal evaporation is an easy and available method for depositing nickel less complex than a sputter-deposited because nickel is a metal that is affected by magnetism. Finally, the Nickle (Ni) electrode may be conceded the best choice in the future for fabrication perovskite solar cells because have performance closer to the gold but need more thickness where Ni had low series resistance also need to develop thermal evaporate deposition method to get best and easy fabrication.

Reference

[1] Wenmei Ming, Dongwen Yang, Tianshu Li, Lijun Zhang, Mao-Hua Du, 2018 Adv. Sci. 5, 1700662. DOI: 10.1002/advs.201700662
[2] K. Domanski, J.-P. Correa-Baena, N. Mine, M. K. Nazeeruddin, A. Abate et al, 2016 ACS Nano, 10, 6306. https://doi.org/10.1021/acsnano.6b02613
[3] Sining Yun and Anders Hagfeldt 2018 Volume 2, Wiley-VCH.
[4] W. Abu Laban, L. Etgar, 2013Energy Environ. Sci. 6, 3249.
[5] L. Etgar, P. Gao, Z. Xue, Q. Peng, A. K. Chandiran et al 2012 J. Am. Chem. Soc. 134, 17396. https://doi.org/10.1021/ja307789s
[6] J. You, L. Meng, T. B. Song, T. F. Guo, Y. Michael Yang et al 2016 Nat.Nanotechnol,11, 75.
[7] I. Jeong, H. J. Kim, B.-S. Lee, H. J. Son, J. Y. Kim et al 2015 Nano Energy, 17, 131.
[8] 4 Y. Kato, L. K. Ono, M. V. Lee, S. Wang, S. R. Raga, Y. Qi 2015 Adv. Mater. Interfaces, 2, 1500195. https://doi.org/10.1002/admi.201500195
[9] J. Zhao, X. Zheng, Y. Deng, T. Li, Y. Shao, A. Gruverman, J. Shield, J. Huang 2016 Energy Environ. Sci. 9, 3650. https://doi.org/10.1039/C6EE02980A
[10] Aqel Mashot Jafar. Fabrication and Characterization of Perovskite Solar Cells. PhD, University of Baghdad, Baghdad, Iraq, 2017.
[11] Ahmed A. Assi, Wasan R. Saleh, Ezzedin Mohajerani 2020 Investigate of TiO2 and SnO2 as Electron Transport Layer for Perovskite Solar Cells. In: AIP Conference Proceedings.
[12] Amrita Mandal Bera, Dan Ralf Wargulski, Thomas Unold 2018 AIP Conference Proceedings
1942, 140038 https://doi.org/10.1063/1.5029169

[13] Jiang, Q., Sheng, X., Shi, B. et al 2014 J. Phys. Chem. C 118 (45): 25878. https://doi.org/10.1021/jp506991x