Surface Engineering of ZnO Photoelectrode for Perovskite Solar Cells

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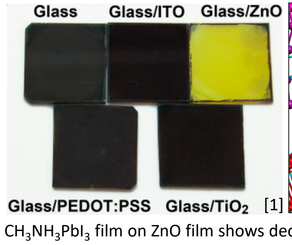
Abstract

Although ZnO nanorods (NRs) have suitable electrical properties as a photoelectrode for perovskites solar cells, including: high electron mobility, appropriate band gap and conduction band edge, it suffers from poor stability. These drawbacks can be minimized by: 1) improving stability of the perovskite layer on the ZnO surface and 2) enhancing the adhesion at the interface between the ZnO surface and the perovskite layer ($CH_3NH_3PbI_3$). In this work, the effect of annealing on the ZnO NRs photoelectrode as the substrate for $CH_3NH_3PbI_3$ layer has been investigated by analyzing the stability of the $CH_3NH_3PbI_3$ layer on the ZnO NRs before and after annealing. We have used hydrothermal method for synthesis of ZnO NRs and spin-coating and solution method for $CH_3NH_3PbI_3$. Materials properties of synthesized ZnO NRs before and after annealing process and the perovskite film are characterized by scanning electron microscopy, X-ray diffraction, and UV-Vis-NIR spectrophotometer.

Motivation

❑ $CH_3NH_3PbI_3$ layer on ZnO film



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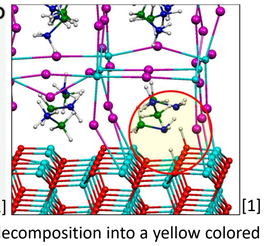

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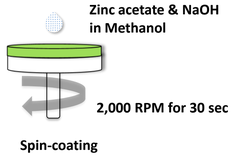
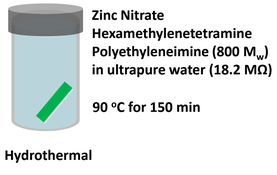
$CH_3NH_3PbI_3$ film on ZnO film shows decomposition into a yellow colored byproduct among various substrates. This is evidence of the instability of $CH_3NH_3PbI_3$ film on the ZnO film, which causes the deprotonation of two surface $CH_3NH_3^+$ molecules to produce CH_3NH_2. The released protons are adsorbed on vicinal surface oxygen atoms. A higher number of deprotonated CH_3NH_2 was discovered on $CH_3NH_3PbI_3$ film on ZnO film, demanding further research on the prevention of deprotonation.

Experiment

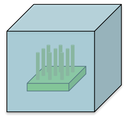
1. ZnO seed layer formation



2. ZnO NRs growth

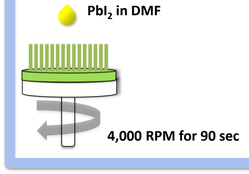


3. Thermal annealing

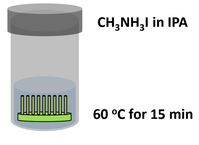


600 °C for 10 hr in air

4. Perovskite precursor deposition

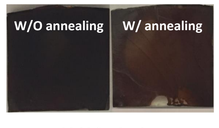


5. Perovskite synthesis



6. Thermal annealing

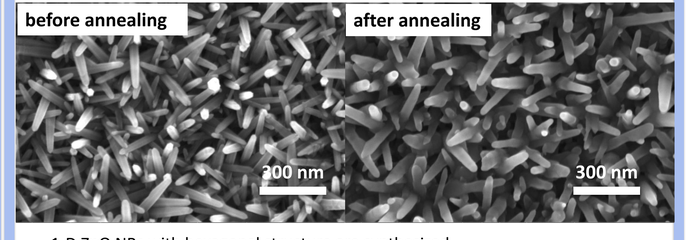
Perovskite ($CH_3NH_3PbI_3$) film



90 °C for 2 min

Results & Discussion

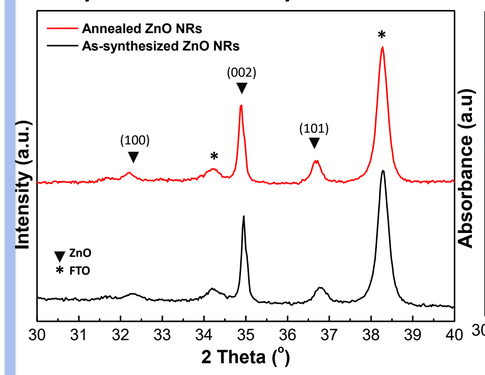
❑ Morphology of ZnO NRs before and after annealing



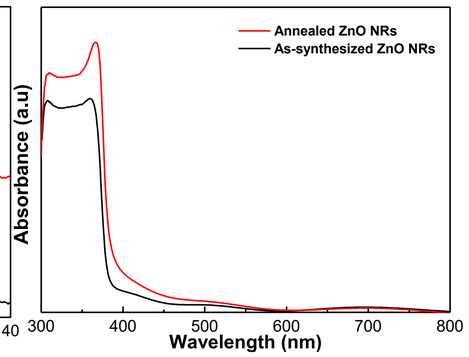
- 1-D ZnO NRs with hexagonal structure are synthesized.
- Average diameter is 39 nm.
- After annealing the ZnO NRs lost their hexagonal structure and become quasi-conical in shape.
- There is no significant change in the density and aspect ratio after the annealing process.

Results & Discussion

❑ Crystal structure analysis of ZnO NRs

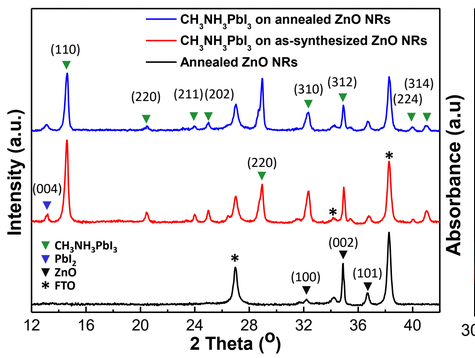


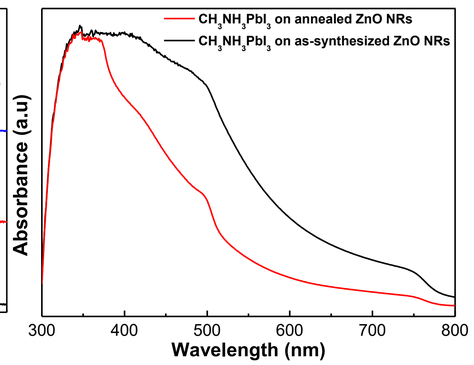
❑ Optical properties of ZnO NRs



- X-ray diffraction (XRD) results show that as-synthesized ZnO has a wurtzite crystal structure grown along c-axis.
- Full width at half maximum of annealed ZnO at (100) direction has 0.2371° lower than as-synthesized ZnO NRs (0.3620°).
- Annealing process influences crystal direction of ZnO NRs which correspond to SEM result.

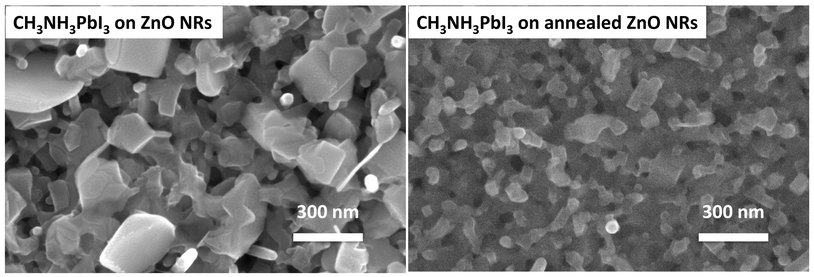
❑ Crystal structure and optical property of $CH_3NH_3PbI_3$ film on the ZnO NRs





- The XRD patterns shows $CH_3NH_3PbI_3$ films formed on the ZnO NRs irrespective of the annealing process.
- Unreacted PbI_2 (004) peak at 13.03° is found on both type of samples.
- Even though the $CH_3NH_3PbI_3$ film on the annealed ZnO NRs has lower absorbance in the visible range, a fabricated solar cell with this photoelectrode may show higher efficiency due to its higher ZnO film coverage, which could increase the fill factor of the solar cell device.

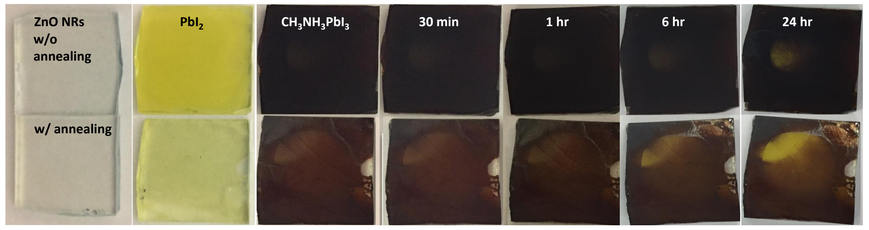
❑ Morphology of $CH_3NH_3PbI_3$ film on ZnO NRs



- $CH_3NH_3PbI_3$ on annealed ZnO NRs shows higher surface coverage and density than as-synthesized ZnO NRs.
- $CH_3NH_3PbI_3$ ZnO NRs after annealing process has a higher filling factor (coverage) on the ZnO film.
- Cube-like $CH_3NH_3PbI_3$ crystals on the top of ZnO NRs crystalize due to unreacted PbI_2 as shown in the reaction formula:

$$PbI_2 + 2I^- \rightarrow PbI_4^{2-} \quad (1) \qquad PbI_4^{2-} + CH_3NH_3^+ \rightarrow CH_3NH_3PbI_3 + I^- \quad (2)$$

❑ Stability of $CH_3NH_3PbI_3$ on ZnO NRs



- Surface of PbI_2 and $CH_3NH_3PbI_3$ film on the annealed ZnO NRs is glassy due to its low density of voids.
- Color change is monitored as a stability test of $CH_3NH_3PbI_3$ film at RT in air condition.
- The appearance of a yellow color representing the decomposition of $CH_3NH_3PbI_3$ crystal is observed after 6 hr for both samples.
- The annealing process for the ZnO NRs does not influence significantly the stability of the $CH_3NH_3PbI_3$ film.

Conclusion

In summary, we have studied the effect of the annealing process on as-synthesized ZnO NRs for their utilization as a photoelectrode for perovskite solar cells. ZnO NRs after annealing process have higher crystallinity in the (100) plane than as-synthesized ZnO NRs. The as-synthesized ZnO NRs sample shows uneven surface coverage and voids, as well as cube-like $CH_3NH_3PbI_3$ crystal on the top. However, the annealed ZnO NRs have a higher pore filling factor of $CH_3NH_3PbI_3$ and improved surface coverage. The crystallinity of $CH_3NH_3PbI_3$ film is similar regardless of annealing process. Therefore, the annealed ZnO NRs used for photoelectrode in the perovskite solar cells should obtain a higher fill factor due to the increased surface coverage. Stability of $CH_3NH_3PbI_3$ film is not significantly affected by the annealing process. In order to verify the enhanced performance of fabricated devices with annealed ZnO NRs, we will study the power conversion efficiency and stability over time.

Reference

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