Drastic onset potential shift of Ta_3N_5 photoanode with Mg:GaN modification

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Abstract: Ta_3N_5 is a promising material for photoelectrochemical (PEC) water splitting application thanks to its low bandgap energy and suitable band positions. An optimum current density and a long stability up to 12 h has been demonstrated. However, Ta_3N_5 suffers from high onset potential. Here we report a remarkable improvement of Ta_3N_5 onset potential with Mg:GaN modification on the surface followed by post annealing in N_2 or NH_3. PEC performances and characterization have revealed the mechanism of Mg activation/Ta_3N_5 damage recovery by N_2/ NH_3 post annealing. Despite the current density loss, this finding unlocks the prospect of unassisted PEC water splitting.

Keywords: Ta_3N_5, photoanode, water splitting.

1. Introduction

Photoelectrochemical (PEC) water splitting offers an attractive solution to convert solar energy to hydrogen in the most eloquent ways in term of chemical robustness, high durability, and technological design for large scale application. The challenge lies on finding a suitable material for semiconductor electrodes which has to fulfill stringent requirements at once. Numerous materials have been explored as a suitable photoanode candidate and among them, Ta_3N_5 has emerged as one of the most attractive material due to its low bandgap energy (2.1 eV) and suitable band positions. [1-3] However, Ta_3N_5 suffers from poor stability and high onset potential.[1-3] Given that the flatband potential of Ta_3N_5 is more negative than water reduction potential (ca. 0 vs NHE), the reported onset potential is excessively positive.[1-3]

In this work we report improvement of the onset potential of Ta_3N_5 photoanode by Mg:GaN modification followed by post annealing treatment. The sample exhibited a significant negative onset potential towards 0 V vs RHE, one of the best ever reported on Ta_3N_5 photoanode. The samples were fabricated by Mg:GaN deposition utilizing plasma-enhanced chemical vapor deposition (PCVD) on sputtered-Ta_3N_5.

2. Experimental

Ta_3N_5 thin films were prepared by reactive RF magnetron sputtering of TaO_δ followed by nitridation process. Mg:GaN was deposited on the surface of Ta_3N_5 by applying a plasma-enhanced chemical vapor deposition (PCVD) apparatus. Trimethylgallium as the Ga source and Bis(cyclopentadienyl)magnesium(II) as the Mg source were carried into the deposition chamber with N_2 flow (5 mL·min^{-1}). Radio frequency plasma was conducted at 1000 W with the additional N_2 flow (20 mL·min^{-1}). The Mg:GaN/Ta_3N_5 sample was then subjected to N_2 or NH_3 post annealing treatment. N_2 post annealing was conducted in different temperature from 600 – 800 °C for 30 min in the presence of 200 mL.min^{-1} N_2 flow while NH_3 post annealing was done from 800 – 1000 °C for 1 h in the presence of 200 mL.min^{-1} NH_3 flow.

The photoanode was fabricated by simply connecting the backside Ta substrate of the sample to a copper wire with indium solder and covered the unnecessary part with epoxy resin. The deposition of CoPi on Ta_3N_5 and Mg:GaN/Ta_3N_5 photoanodes was performed in a 0.1 M potassium phosphate (KPi) solution containing 0.5 mM $Co(NO_3)_3$ at pH 7 by chronoamperometry.

3. Results and discussion

The PEC performance of CoPi/Mg:GaN/Ta_3N_5 with N_2 or NH_3 post annealing was investigated. The linear sweep voltammetry (LSV) scans in Figure 1 show that upon Mg:GaN deposition followed by N_2 post annealing, the onset potential shifted toward 0 vs RHE. However, the current density decreased more than 20 folds. There was no negative onset potential shift upon NH_3 post annealing. However, the current density increased, reaching the original current density of Ta_3N_5.

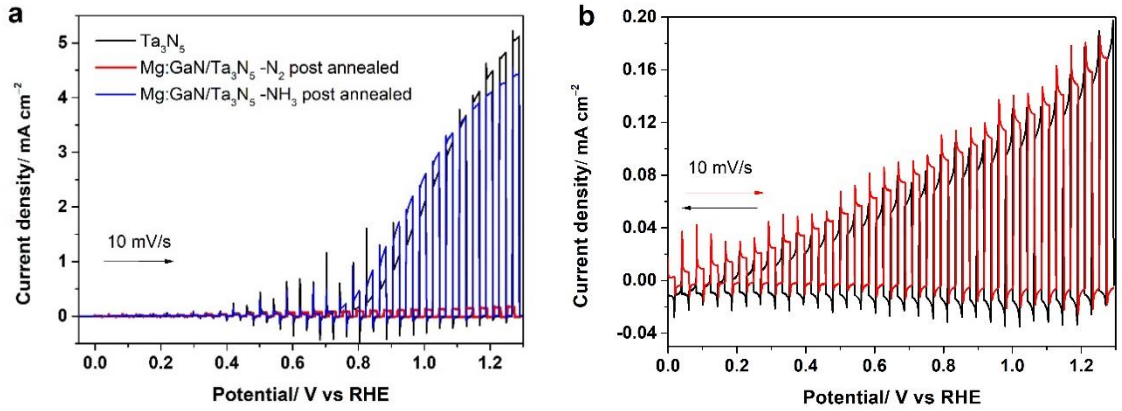

Figure 1. a) LSV of Ta_3N_5 and Mg:GaN/Ta_3N_5 after N_2 and NH_3 post annealing, b) Magnification of N_2 post annealed Mg:GaN/Ta_3N_5 LSV in Fig. a

Among all the characterization of Mg:GaN before and after N_2 post annealing, only XPS and Mott-Schottky detected some differences. It is apparent that Mg 1s peak is slightly shifted to more reduced state whereas the E_{fb} shifted to more negative value after N_2 post annealing. These findings are favorable conditions for the negative onset potential shift of Mg:GaN/Ta_3N_5. Mg:GaN/Ta_3N_5 possesses E_{VB} higher by 0.25 V than that of Ta_3N_5. This favors faster hole transfer from Ta_3N_5 to Mg:GaN. As for electrons, E_{fb} of Mg:GaN, higher by 0.1 V than E_{fb} of Ta_3N_5, facilitates effective electron transfer from Mg:GaN to Ta_3N_5. NH_3 post annealing was demonstrated to increase the current density of the sample without onset potential shift, which is probably due to accumulated effects evidenced from its characterization results. The surface damage of Ta_3N_5 was healed and the new pinholes appeared on the surface of Mg:GaN. Thus the PEC performance is solely coming from Ta_3N_5. The shift of E_{VB} to a more positive value seems to be an effect of the loss of Mg concentration, resembling undoped GaN.

4. Conclusions

In summary, a negative shift of onset potential has been realized on Mg:GaN modified-Ta_3N_5. Detailed studies revealed the correlation of the PEC performance with the results of structural and chemical characterization. N_2 post annealing treatment is a crucial step for further improvement of the onset potential reaching 0 vs RHE by Mg activation mechanism. The trade-off between low onset potential and current density decrease is due to the thermally induced damage on Ta_3N_5 near the surface during the process. Improvement and recovery of Ta_3N_5 photocurrent was realized by NH_3 post annealing however without negative shift of the onset potential.

References

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