P-type InP thin films prepared by a non-vacuum process for photoelectrochemical water splitting

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Abstract. Photoelectrochemical (PEC) water splitting has been considered as a promising way to produce hydrogen production. Herein, we present an inexpensive and simple method for preparing high active p-type InP thin films photocathode with Zn doped at 500 °C. The amount of dopant was optimized to obtain the high PEC activity films. Electrical measurements indicated that the optimized film had the hole mobility of \(350 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}\) and carrier density of \(7.5 \times 10^{17} \text{ cm}^{-3}\). Optical measurements demonstrated the high absorption of 90% in 450–750 nm, and the bandgaps of the samples ranged from 2.08 eV to 2.3 eV. PEC test showed that the onset potential of the optimized InP thin film was about 0.35 V vs. RHE and the saturation photocurrent of 8 mA/cm\(^2\) occurred at -0.3 V vs. RHE. These results indicated that our p type InP thin films were a potential material in PEC devices.

1. Introduction

Due to the increasingly attention of environmental protection and seeking sustainable and renewable chemical fuels, hydrogen has emerged as an excellent candidate. Photoelectrochemical (PEC) water splitting for hydrogen production has been considered as a clean and environmentally friendly method without CO\(_2\) emission[1-3]. In order to find a suitable photocathode, several key criteria should be satisfied: favorable band gap energy, band edge positions, chemical stability, raw material, and fabrication cost[3]. Among various photocathode catalysts, InP, with the zincblende (ZnS) structure, has a huge potential due to the direct small band gap, the appropriate band-edge potential, high electron mobility and low unpassivated surface recombination velocity[4-7]. Thus, InP based photocathode has been considered as one of the promising candidates.

However, as an alternative to vacuum processes (e.g., metal organic chemical vapor deposition (MOCVD) or metal organic vapor phase epitaxy (MOVPE))[8-11], various solution based process approaches (e.g., vapor–liquid–solid (VLS) and chemical liquid phase synthesis)[12-14] have been reported for the fabrication of InP thin film with the aiming of low-cost and large scale industrial production. However, the higher PEC activity has still not been achieved due to the poor crystal quality in solution fabrication processes (i.e., undesirable binary compounds), leading to a short lifetime of charge carrier in InP films[15].

In this study, we developed a way to fabricate p type InP polycrystalline films with a great amount nanospheres structure in the surface, which greatly increased the specific surface area and was favorable
to the photoabsorption and PEC. To obtain the highest efficient p type InP thin film, we optimized the amount of Zn dopant. To understand its PEC property, the p type InP thin film was examined for water splitting under simulated sunlight irradiation. Significantly, the p type InP films prepared by this method showed excellent PEC performance. To shed light on the origins of the advantage of p type InP films, the thin films were investigated by X-ray powder diffraction, Hall effect measurements, and optical absorption. A detailed description and discussion will be given in the following sections.

2. Materials and methods

All chemicals are commercially available and used as received. InP film was prepared on the FTO glass substrate by spin-coating method. 1.12 g In(NO$_3$)$_3$ and 1g polyvinyl acetate were dissolved in 17 mL methanol, Zn(NO$_3$)$_3$ acted as the dopant was added into the solution by different amount (1%, 2%, 3%, 4%, mol %). The ink was spin-coated on the FTO glass with 2000r for 40 s and annealed at 300 °C for 30 min. The spin-coating and annealing process was repeated two times to obtain 1 μm thickness film. This film was then phosphating in the tube furnace at 500 °C for 2 hours under the H$_2$ (7%)/Ar gas flow with the rate of 300 mL/min, and the sodium hypophosphite precursor was kept at 300 °C, followed by natural cool-down.

XRD patterns of the InP thin films were obtained by a PANalytical X-pert diffractometer (PANalytical, Netherlands). The Hall system in a Vander Pauw configuration was used to measure the mobilities and carrier concentrations of the InP thin films at room temperature. The transmittance spectra of the samples were measured with a HITACHI U-4100UV–vis spectrophotometer. Scanning electron microscope (SEM, Hitachi SU8000) was used to obtain the morphology of the samples. Linear sweep voltammetry (LSV; 2 mV·s$^{-1}$) was conducted to perform the photoelectrochemical properties of the InP photocathodes in a three-electrode cell in 0.5 M of H$_2$SO$_4$ electrolyte (pH 0.56). In the three electrodes measurements, InP photocathodes, the carbon sheet and saturated calomel electrodes were used as the working electrodes, the counter electrode and the reference electrode, respectively. During the test, the contact area between all samples and the solution was 0.07 cm$^2$. The photocurrent measurement was conducted in a solar simulator (Newport 94021A) equipped with a 150 W Xe lamp and an AM 1.5 filter.

3. Results and discussion

In order to demonstrate the structures of the as-prepared InP thin film with Zn doped, the X-ray powder diffraction (XRD) patterns were obtained. As shown in Figure 1, the diffraction peaks of all samples at 26.4°, 43.8°, 51.8° can be well assigned to the (111), (220) and (311) planes of a zinc blende InP phase according to the XRD PDF card No. 11111, which matches the precious report.[16] For the samples doped from 1% to 4%, the intensity of InP (111) increases and (220) and (311) of InP appear at the sample of 3% and 4%. In addition, with the amount of dopant increases, there are no peaks of doping Zn appearing, indicating that Zn is doped into the InP lattice.

![Figure 1. XRD patterns of the samples with different doping amount.](image_url)
Figure 2 shows the morphologies of InP thin films with different amount of Zn doped photocathode. The thin films are uniformly covered by nanospheres with the diameter of ~ 150 nm. However, when the dopant reaches 4%, the size of spheres is bigger than those of other thin films with Zn doped. These nanospheres are favourable to the PEC water splitting for hydrogen production according to the precious report [17]: first, nanostructures process a large interface between semiconductor and electrolyte where the charge separation and redox reactions can be occurred; Secondly, compared with planar structures, nanostructures provide shorter diffusion length for minority carriers.

Figure 2. Morphologies of InP thin films with different amount of dopant: (a) 1%; (b) 2%; (c) 3%; (d) 4%.

As is well known, the sample with no dopant shows an n-type behavior. From the Hall measurements, Figure 3a reveals that the hole mobility decreases with the amount of dopant increases from 1% to 4%. It is understandable since the increased amount of dopant from 1% to 4% can enhance lattice scattering, which would reduce mobility of samples [18]. The plot of the carrier concentration with different amount of dopant is also investigated in Figure 3b. The highest carrier concentration (7.5×10^{17}) occurs at 3% dopant.

Figure 3. Variation of (a) mobility (μ), (b) carrier concentration (N) for the samples with different amount of dopant.
Figure 4 shows the optical properties of InP thin films, where Figure 4a is the transmittance spectra and Figure 4b is the band gap calculated based on Figure 4a. As shown in Figure 4a, with an increase of amount of dopant, the optical transmittances gradually decrease from 0 to 4%. Meanwhile, the absorbance of InP thin films with 3% and 4% Zn doped at the wavelength range of 450-750 nm are very strong, meaning that almost 90% visible light can be absorbed. The direct band gaps of all InP thin films can be calculated by the Tauc relation [19] in Figure 4b:

\[ \alpha h\nu = B (h\nu - E_g)^{1/2} \]  

where \( \alpha \) is the absorption coefficient, \( h\nu \) is the photon energy, \( B \) is a constant, and \( E_g \) is the optical direct bandgap. As shown in Figure 4b, the band gaps are 2.08 eV, 2.13 eV, 2.2 eV and 2.3 eV for the sample corresponding to the amount of doping at 1%, 2%, 3% and 4%, respectively. The sample with 1% Zn doped has a larger band gap of 2.2 eV than other doped InP thin films. And with the amount of doping increased, the bandgap of the InP turns to diminish. However, when doping amount reaches 4%, the bandgap of InP increases as same as the 2% doping sample. Moreover, the bandgaps of the doped InP are all smaller than the intrinsic InP, which is consistent with the theory that the proper doping can diminish the intrinsic semiconductor. However, the bandgaps of all samples are larger than the theoretical InP bandgap (1.35 eV), which may be affected by the films’ crystallinity, defects, etc[19]. If the process conditions would be optimized, the parameters would be close to the theoretical data, and even the data of bandgap would be smaller.

**Figure 4.** (a) Optical transparent spectrum of the samples with different doping amount; (b) Curves of the variation of \((\alpha h\nu)^2\) with photon energy \(h\nu\) for all samples.

**Figure 5.** Linear sweep voltammetry of InP thin film electrodes with different amount of dopant in darkness and under illumination.
Furthermore, we characterize the PEC performance of InP photocathode with different amount of Zn dopant in a three-electrode electrochemical cell with 0.5 M H$_2$SO$_4$ solution as the electrolyte. Figure 5 compares the j-V curves of Zn doped InP thin films under dark and light. The improved cathodic photocurrent indicates that as prepared Zn doped InP thin films play a role of p-type semiconductor during the PEC water splitting process. In a comparison of the PEC performance of the InP photocathode with and without light irradiation, the irradiated 1% doped InP photocathode presents an almost 3 times higher photocurrent than that without light irradiation at the bias potential (-0.70 V vs RHE), which means that it has a good photoresponse due to its good absorption in the visible light range. It is clear that the photocurrent increases with the amount of Zn dopant increases. The largest photocurrent density of the sample is 8 mA/cm$^2$ at -0.70 V vs. RHE and the onset overpotential reaches 0.35 V vs. RHE when the dopant amount reaches 3%, which are consistent with the results of optical transmittance spectra. Though the efficiency of photoelectrocatalyst needs to be further optimized and developed, such thin film shows its potential value as a kind of photoelectrode materials.

4. Conclusion
In summary, p type InP thin film was prepared by an cheap and simple sol-gel method. The amount of dopant was optimized to obtain a high PEC activity film. A great number of nanospheres could be found in the thin film surface, which can help to be used as the catalyst. Electrical measurements indicated that the optimized film had the hole mobility of 350 cm$^2$/V·s and carrier density of 7.5×10$^{17}$ cm$^3$. Optical measurements demonstrated the high absorption of 90% in 450–750 nm, and the bandgaps of the samples ranged from 2.08 eV to 2.3 eV. PEC test showed that the onset potential of the optimized InP thin film was about 0.35 V vs. RHE and the saturation photocurrent of 8 mA/cm$^2$ occurred at -0.3 V vs. RHE. These results indicated that our p type InP thin films were a potential material in PEC devices.

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