MG DOPING AND ALLOYING IN ZN_3P_2 HETEROJUNCTION SOLAR CELLS

Gregory M. Kimball, Nathan S. Lewis, Harry A. Atwater
California Institute of Technology, Pasadena, California, United States

ABSTRACT

Zinc phosphide (Zn_3P_2) is a promising and earth-abundant alternative to traditional materials (e.g. CdTe, CIGS, a-Si) for thin film photovoltaics. We report the fabrication of Mg/Zn_3P_2 Schottky diodes with V_{OC} values reaching 550 mV, J_{SC} values up to 21.8 mA/cm^2, and photovoltaic efficiency reaching 4.5%. Previous authors have suggested that Mg impurities behave as n-type dopants in Zn_3P_2, but combined Hall effect measurements and Secondary Ion Mass Spectrometry (SIMS) show that 10^{17} to 10^{19} cm^{-3} Mg impurities compensate p-type doping to form highly resistive Zn_3P_2. Further device work with modified ITO/Mg/Zn_3P_2 heterojunctions suggests that the ITO capping layer improves a passivation reaction between Mg and Zn_3P_2 to yield high voltages > 500 mV without degradation in the blue response of the solar cell. These results indicate that at least 8-10% efficiency cell is realizable by the optimization of Mg treatment in Zn_3P_2 solar cells.

INTRODUCTION

Zinc phosphide (Zn_3P_2) has significant potential as an absorber in thin film photovoltaics, with a reported direct 1.5 eV band gap, high (>10^4-10^5 cm^{-1}) light absorbance in the visible region [1], and long (5-10 µm) minority-carrier diffusion lengths [2]. To date, Zn_3P_2 has been produced almost exclusively with p-type doping [3], preventing the fabrication of *p-n* homojunctions. Solar cells using Zn_3P_2 have therefore been constructed from Schottky contacts, *p-n* semiconductor heterojunctions [4], or liquid contacts [5], with Mg/Zn_3P_2 Schottky diodes having exhibited >6% solar energy-conversion efficiency [6]. Preliminary evidence from early work with Mg/Zn_3P_2 Schottky diode devices suggests that annealing leads to formation of a *p-n* homojunction [7-8] with Mg interstitials behaving as n-type dopants.

In this manuscript, the electronic and material properties of Mg impurities in Zn_3P_2 are studied by the Hall effect and Secondary Ion Mass Spectrometry (SIMS). Investigation of Ag and P dopants is also included in the Hall effect experiments. The interfacial reaction between Mg and Zn_3P_2 is studied by SIMS and implicated in improved junction quality in solar cells with a Mg/Zn_3P_2 interface. The fabrication and photovoltaic properties of both Mg/Zn_3P_2 Schottky diodes and modified ITO/Mg/Zn_3P_2 heterojunction solar cells are presented.

EXPERIMENTAL

The Zn_3P_2 samples used in this study were grown by a physical vapor transport process (Fig. 1). Red phosphorus chips and zinc shot (99.9999%, Alfa Aesar) were combined at 850 °C to form Zn_3P_2 powders. Using procedures described previously [9-14] the powders were then grown into polycrystalline boules 1 cm in diameter and 4 cm in length, with grain sizes of ~1-5 mm^2. The resulting crystals were diced with a diamond saw and had as-grown resistivity between 100-2000 Ω cm. Annealing with white phosphorus in sealed ampoules at 400 °C for 20 hours was effective at reducing the wafer resistivity to ~20 Ω cm due to doping by phosphorus interstitials [10]. Both undoped and P-doped samples were polished with diamond paste to produce Zn_3P_2 wafers. Samples with 1 cm diameter and 500-600 µm thickness were etched for 30 s in 2-3% (v:v) Br_2 in CH_3OH, rinsed in CH_3OH, dried under a stream of N_2, and used promptly thereafter.

Mg/Zn_3P_2 Schottky diodes were fabricated from both undoped and P-doped Zn_3P_2 samples using procedures similar to those previously reported [15]. Mg films of thickness ~200 nm were deposited by RF magnetron sputtering on freshly etched Zn_3P_2 wafers without any sputter etching of the sample. Back contacts of Ag with ~200 nm thickness were then deposited by vacuum evaporation. Using optical photolithography a series of devices with 0.25 mm^2 active area and arrays of 2 µm bus bars were patterned by etching through the Mg top contact with an aqueous solution of 75 mM disodium EDTA and 3% (v:v) H_2O_2 adjusted to pH 10.

Modified ITO/Mg/Zn_3P_2 heterojunction solar cells were also fabricated from P-doped Zn_3P_2 samples. Freshly etched wafers were patterned with an array of 1 mm^2 active area devices by optical photolithography. Mg films of thickness ~30 nm followed by ITO films of thickness ~100 nm were deposited by RF magnetron sputtering on the patterned Zn_3P_2 wafers without any sputter etching of the sample. Back contacts of Ag with ~100 nm thickness were also deposited by RF magnetron sputtering. The modified heterojunction cells were subjected to mild air annealing at 100 °C. Photovoltaic performance of both types of devices was studied without additional antireflective coatings under 1.0 sun AM1.5G illumination at room temperature.

Explicit Ag- and Mg-doping of Zn_3P_2 samples was performed by solid state diffusion. Etched Zn_3P_2 wafers were metalized with Ag or Mg of thickness ≤ 80 nm and subjected to heat treatment at temperatures in the range

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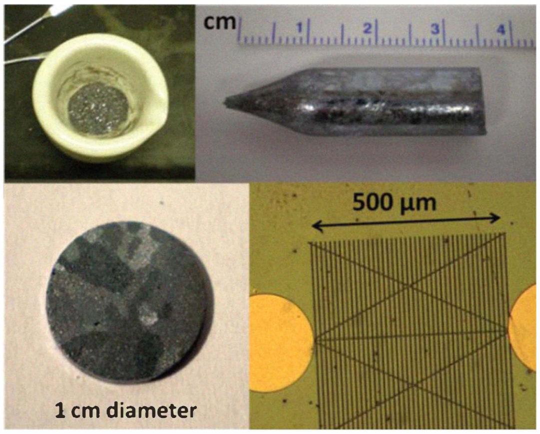

Figure 1 Photographs of Zn_3P_2 as the solar cell fabrication process proceeds: (clockwise from top left) high purity powder, a large crystal, a diced wafer, and a p-Zn_3P_2/Mg Schottky diode solar cell.

of 100-400 °C for up to 24 hours, followed by chemical removal of the remaining metal dopant source. Samples were typically annealed under passive vacuum of ~10^{-5} torr with ~15 mg of added red phosphorus, and in some cases an additional ~40 mg of Mg was added. Samples intended to be uniformly doped for Hall measurements were annealed at 400 °C for 24 hrs, etched with 2% Br_2 in CH_3OH, and contacted at the corners with indium. Samples intended to be Mg-doped for SIMS analysis were annealed at 100-300 °C under active vacuum of ~10^{-6} torr for 20-100 min and stripped of excess Mg with aqueous H_2O_2/EDTA. After the doping treatment, the Zn, P, and Mg concentration profiles were analyzed by SIMS. To calibrate the count rate for Mg in Zn_3P_2, a standard was fabricated by ion-implantation with 10^{14} cm^{-2} Mg ions. An O^- primary ion beam at 10 kV and 20 nA was selected to achieve both a high count rate for Mg^+ ions and good depth resolution.

RESULTS

Both undoped and P-doped Zn_3P_2 wafers show significant photovoltaic response in Mg-Schottky diodes as illustrated in Fig. 2. Cells made from undoped Zn_3P_2 wafers typically exhibited efficiencies of 1.0-1.5%, with V_{OC} reaching 550 mV; a large series resistance prevented good current collection and high fill factors. The large bulk resistivity of the 500-600 μm thick, undoped wafer is the primary contributor to the ~1-10 kΩ series resistance. Cells made from P-doped Zn_3P_2 typically have efficiency between 4.0-4.5%, with somewhat reduced V_{OC} values of 400 mV, and better overall performance due to improved current collection and fill factors. The solar cell parameters of representative devices are given in Table 1.

Extensive Hall measurements were conducted on Zn_3P_2 samples doped with Ag, P and Mg and in all cases p-type conductivity was observed (Table 2). The electronic

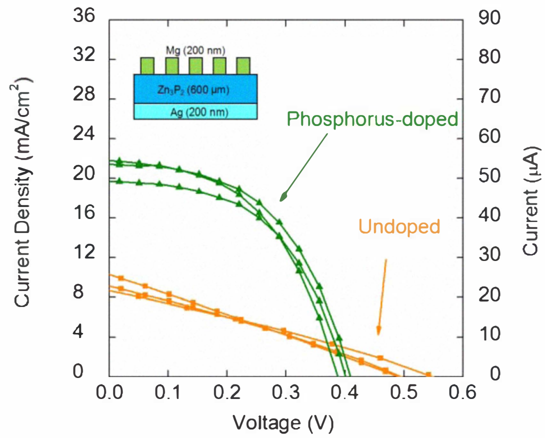

Figure 2 J-V characteristics of several Mg/Zn_3P_2 Schottky diode devices under simulated AM1.5 illumination fabricated from as-grown (undoped) and white phosphorus annealed (Phosphorus-doped) Zn_3P_2 wafers.

	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	η (%)
Undoped	8.5	0.55	0.29	1.4
Undoped	10.3	0.49	0.26	1.3
Undoped	9.1	0.50	0.29	1.3
P-doped	21.8	0.39	0.50	4.2
P-doped	21.4	0.41	0.51	4.5
P-doped	19.7	0.40	0.52	4.1

Table 1 Photovoltaic parameters of Mg-Zn_3P_2 Schottky diode devices fabricated from as-grown (undoped) and white phosphorus annealed (P-doped) Zn_3P_2 wafers.

properties of Ag-doped Zn_3P_2 samples annealed in white phosphorus are broadly consistent with previous reports and p-type doping in the high 10^{17} cm^{-3} with hole mobility of 17 ± 1 cm^2 V^{-1} s^{-1} can be readily achieved. Additional Ag diffusion source does not appear to increase the acceptor concentration above the threshold of ~8 x 10^{17} cm^{-3}. The measurements of P-doped Zn_3P_2 samples are consistent with previous reports, corresponding to acceptor concentrations in the mid 10^{16} cm^{-3} and hole mobility in the range of 11-13 cm^2 V^{-1} s^{-1}. Substrates doped with Mg at 400 °C show p-type conductivity with very low acceptor concentrations in the range of 10^{12} to 10^{14} cm^{-3} despite Mg concentrations estimated in the range of 10^{17} to 10^{19} cm^{-3}.

SIMS profiling of the Mg content in Zn_3P_2 samples doped by solid source diffusion revealed a narrow region of reaction at the Mg/Zn_3P_2 interface as well as penetration of Mg into the substrate at high concentration (Fig. 3a). For diffusions carried out at 100 °C for 100 minutes, the first 10-50 nm of the sample shows greatly increased Mg and P counts along with extensive Zn depletion. Crystal orientation dependence was observed for the Mg profile at depths greater than 100 nm with peak concentrations in the range of 10^{18} to 10^{20} cm^{-3} (Fig. 3a (i), (ii)) that varied between crystal domains. At a depth ≤ 500 nm, samples treated at 100 °C show a return to background levels in Mg concentration, < 10^{15} cm^{-3}. On the other hand, samples treated at 300 °C for 100 minutes show an extensive reaction at the Mg/Zn_3P_2 interface in addition to high levels of Mg incorporation in the Zn_3P_2 substrate. The first 500 nm of the sample shows strongly elevated P and Mg counts as well as greatly reduced Zn counts consistent with a $Mg_xZn_{3-x}P_2$ alloy rather than a pure Zn_3P_2 matrix. At depths approaching 800 nm to 1 µm the data is consistent with a Zn_3P_2 matrix doped 10^{19} to 10^{20} cm^{-3} with Mg. In samples processed at 300 °C the depth at which Mg concentration reached baseline was not reached but appears to be greater than 2 µm.

Dopant deposition	Anneal Ambient	p (cm^{-3})	μ_p (cm^2/Vs)
Ag (80 nm)	P_4	7.5 ± 0.4 x 10^{17}	17 ± 1
Ag (12 nm)	P_4	7.6 ± 0.8 x 10^{17}	17 ± 2
Ag (1.3 nm)	P_4	3.0 ± 0.1 x 10^{17}	14 ± 1
none	P_4	3.7 ± 0.4 x 10^{16}	12 ± 1
Mg (80 nm)	P_4	3.8 ± 0.8 x 10^{13}	19 ± 3
Mg (80 nm)	P_4 + Mg	5.4 ± 0.8 x 10^{13}	41 ± 18
Mg (80 nm)	vacuum	6.0 ± 3.2 x 10^{12}	48 ± 25
Mg (80 nm)	Mg	1.5 ± 0.4 x 10^{14}	9 ± 2

Table 2 Carrier concentration and mobility results from Hall measurements of doped Zn_3P_2 samples. Ag and Mg dopants were introduced by solid source diffusion at 400 °C for 24 hours in vacuum ampoules containing small quantities of P_4 and/or Mg. The samples tested exclusively exhibit p-type doping.

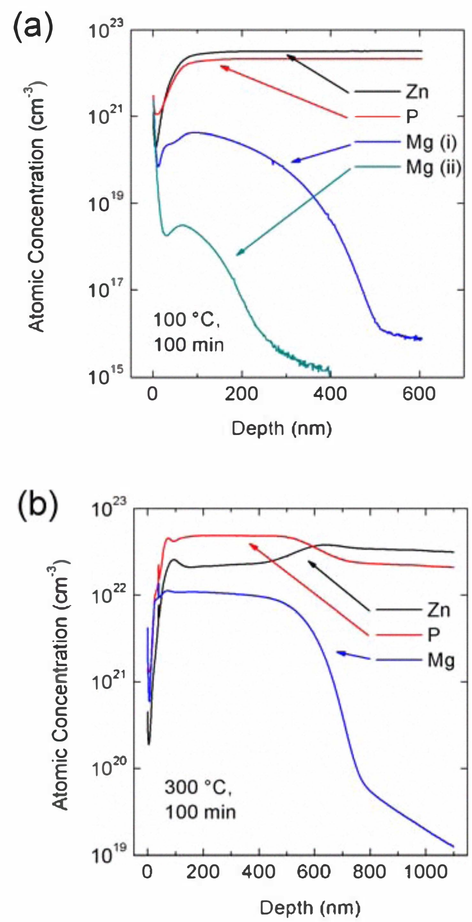

Figure 3 SIMS profiles of Zn, P and Mg atomic concentrations as a function of depth in Mg-diffused Zn_3P_2 samples. The profiles were collected from samples annealed for (a) 100 °C and (b) 300 °C under active vacuum of ~10^{-6} torr for 100 min. Traces (i) Mg and (ii) Mg correspond to the profiles of two different regions of the sample.

P-doped Zn_3P_2 wafers were also used to fabricate solar cells based on a modified ITO/Mg/Zn_3P_2 heterojunction device geometry. Although as-fabricated cells exhibit poor performance and V_{OC} ≤ 100 mV, mild air annealing at 100 °C for 100 min greatly improves the junction properties with V_{OC} reaching 540 mV (Fig. 4a). The overall low external quantum efficiency throughout the visible is consistent with expected reflection losses from the optically thick ~30 nm Mg layer (Fig. 4b). Heat treatments of longer than 16 hrs were found to affect a significant increase in the collection efficiency. Annealed samples also exhibited greatly increased series resistance, typical of the Mg-doped samples used for Hall measurements.

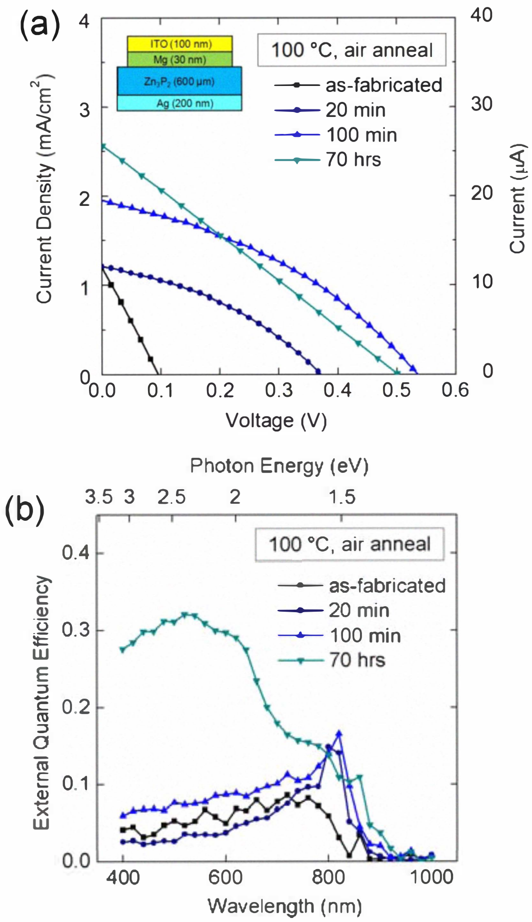

Figure 4 Photovoltaic performance observed in modified ITO/Mg/Zn_3P_2 heterojunction solar cells as a function of air annealing times including (a) light J-V traces under simulated AM1.5 illumination and (b) EQE characteristics.

DISCUSSION

The Mg/Zn_3P_2 Schottky devices reported here show some improvements over record cells of similar design [6]. In undoped Zn_3P_2 devices we observe V_{OC} values reaching 550 mV, somewhat higher than the typical V_{OC} of ~400 mV reported in devices without heat treatment. In P-doped Zn_3P_2 devices we observe J_{SC} increases of 30% relative to previous record cells, an effect that is attributable to the high minority carrier diffusion lengths ≥ 7 µm of the Zn_3P_2 substrates used for the fabrication [16]. Continuing work to combine the high voltage of the cells based on undoped Zn_3P_2 with the high current of the cells based on P-doped Zn_3P_2 is expected to yield solar cells with solar energy conversion efficiency > 8%.

In previous literature, Mg/Zn_3P_2 Schottky devices subjected to heat treatments were observed to have increased junction depth and higher V_{OC} consistent with the transition from a Schottky diode to a diffused *p-n* homojunction [7-8]. Mg dopants forming n-type Zn_3P_2 was suspected to create the Zn_3P_2 *p-n* homojunction, but the results in Table 2 suggest that Mg impurities behave as traps rather than well-ionized donors and form highly compensated p-type material. For samples annealed at 100 °C for 100 min, the Mg diffusion depth determined by SIMS, 300-500 nm (Fig. 3a), is remarkably shorter than the junction depth of 1.3 µm estimated by Bhushan et al for similarly-treated samples [7], providing further indirect evidence that Mg do not behave as n-type dopants.

SIMS analysis of Mg-diffused Zn_3P_2 is consistent with the formation of $Mg_xZn_{3-x}P_2$ at the interface, distinct from the Mg_3P_2 that as has been observed using sputter AES/XPS by other authors [17]. The reacted layer appears to be important for improving the junction properties of the Mg/Zn_3P_2 interface (Figure 4a) by acting as a passivation or hole-blocking layer. At the same time, Hall measurements on Mg-doped Zn_3P_2 suggest that Mg impurities in bulk Zn_3P_2 degrade device performance. As a result the optimal annealing conditions for Mg/Zn_3P_2 solar cells minimize Mg diffusion while still allowing $Mg_xZn_{3-x}P_2$ formation.

The modified ITO/Mg/Zn_3P_2 heterojunction devices reported here demonstrate the improvements in photovoltaic performance that result from the interfacial reaction between Mg and Zn_3P_2. The very low barrier height of the solar cells as-fabricated is likely due to surface defects and oxidation caused by the photolithographic patterning process. Heating the device in air at 100 °C for 100 min greatly improves the barrier height, and the SIMS profiles indicate that the benefit comes from the formation of $Mg_xZn_{3-x}P_2$. Although the reported cells appear to be absorption-limited due to the Mg film, prolonged heating reduces reflection losses by diffusing excess Mg into the substrate. An additional effect of the heat treatment is a large increase series resistance attributable to the compensating effect of Mg impurities in Zn_3P_2. In contrast to devices with the thin Mg film exposed to air [7], the ITO-capped devices presented here show substantial blue response even after heating for several days. The ITO capping layer is suspected to moderate the reaction between Mg and Zn_3P_2, resulting in an interface with low surface recombination velocity.

CONCLUSIONS

We report improvements over previous results in photovoltaic performance for solar cells based on p-Mg/Zn_3P_2 Schottky diodes. In undoped Zn_3P_2 devices we observe V_{OC} values up to 550 mV, and in P-doped Zn_3P_2 devices we observe J_{SC} increases of 30% relative to previous record cells. We have also begun the first analysis of Mg dopant profiles in Zn_3P_2 substrates by combined Hall measurements and SIMS profiling to determine that Mg dopants do not behave as well-ionized n-type dopants. Further device work with modified ITO/Mg/Zn_3P_2 heterojunctions suggests that the TCO capping layer improves a passivation reaction between Mg and Zn_3P_2 to yield high voltages reaching 540 mV without reducing the current collection of the solar cell. These results indicate that at least 8-10% efficiency cell is realizable by the optimization of Mg treatment in Zn_3P_2 solar cells.

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