

# 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<sup>2</sup>, 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<sup>-3</sup> 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<sup>-1</sup>) light absorbance in the visible region [1], and long (5-10  $\mu$ m) 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.

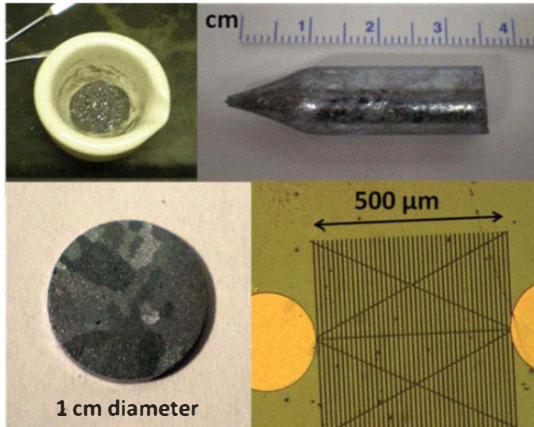
## EXPERIMENTAL

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<sup>2</sup>. The resulting crystals were diced with a diamond saw and had as-grown resistivity between 100-2000  $\Omega$  cm. Annealing with white phosphorus in sealed ampoules at 400 °C for 20 hours was effective at reducing the wafer resistivity to ~20  $\Omega$  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  $\mu$ m thickness were etched for 30 s in 2-3% (v:v) Br<sub>2</sub> in CH<sub>3</sub>OH, rinsed in CH<sub>3</sub>OH, dried under a stream of N<sub>2</sub>, 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<sup>2</sup> active area and arrays of 2  $\mu$ m 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<sub>2</sub>O<sub>2</sub> 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<sup>2</sup> 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  $\leq$  80 nm and subjected to heat treatment at temperatures in the range



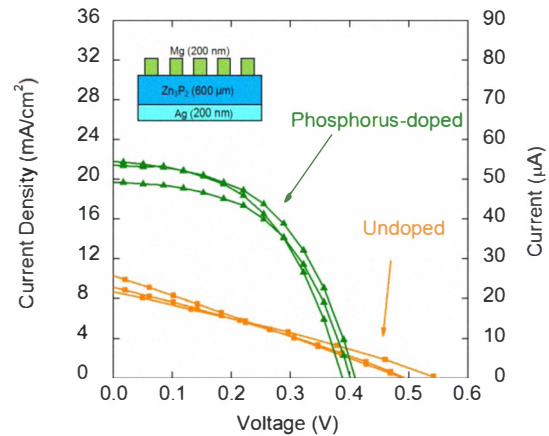
**Figure 1** Photographs of  $Zn_3P_2$  as the solar cell fabrication process proceeds: (clockwise from top left) high purity powder, a large crystal, a diced wafer, and a p- $Zn_3P_2$ /Mg Schottky diode solar cell.

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  $\sim 10^{-5}$  torr with  $\sim 15$  mg of added red phosphorus, and in some cases an additional  $\sim 40$  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  $\sim 10^{-6}$  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  $10^{14} \text{ cm}^{-2}$  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  $\mu\text{m}$  thick, undoped wafer is the primary contributor to the  $\sim 1$ -10 k $\Omega$  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.

	$J_{SC}$ ( $\text{mA cm}^{-2}$ )	$V_{OC}$ (V)	FF	$\eta$ (%)
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

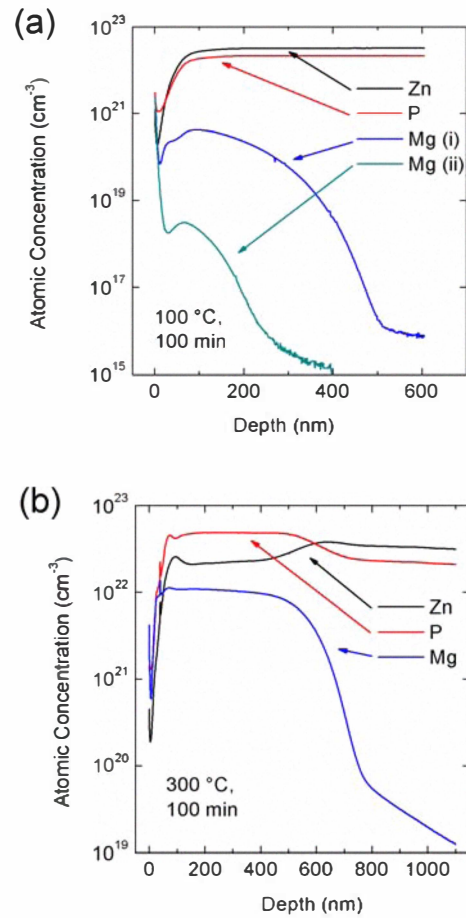
**Table 1** Photovoltaic parameters of Mg- $Zn_3P_2$  Schottky diode devices fabricated from as-grown (undoped) and white phosphorus annealed (P-doped)  $Zn_3P_2$  wafers.

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

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  $\leq 500$  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  $\mu m$  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  $\mu m$ .

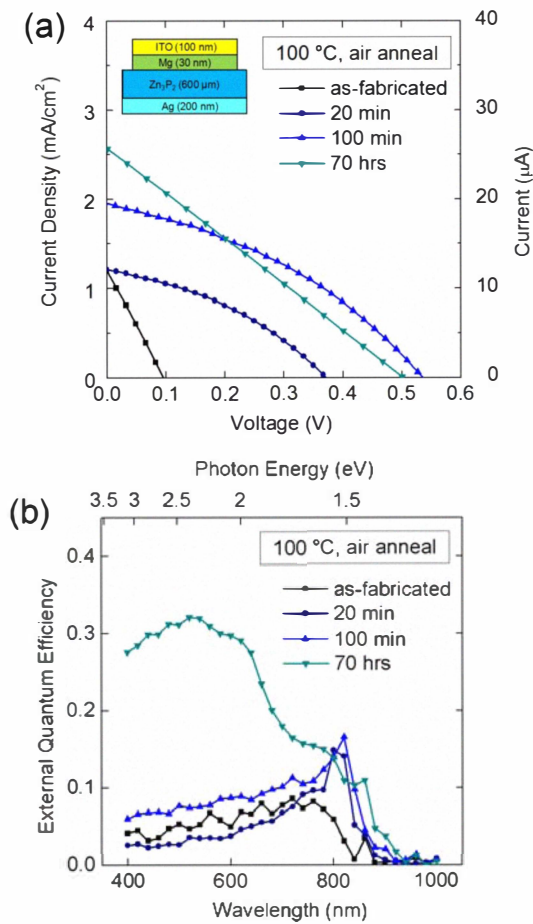
Dopant deposition	Anneal Ambient	$p$ ( $cm^{-3}$ )	$\mu_p$ ( $cm^2/Vs$ )
Ag (80 nm)	$P_4$	$7.5 \pm 0.4 \times 10^{17}$	$17 \pm 1$
Ag (12 nm)	$P_4$	$7.6 \pm 0.8 \times 10^{17}$	$17 \pm 2$
Ag (1.3 nm)	$P_4$	$3.0 \pm 0.1 \times 10^{17}$	$14 \pm 1$
none	$P_4$	$3.7 \pm 0.4 \times 10^{16}$	$12 \pm 1$
Mg (80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

**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  $\sim 10^{-6}$  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  $V_{OC} \leq 100$  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  $\sim 30$  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<sub>3</sub>P<sub>2</sub> 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<sub>3</sub>P<sub>2</sub> Schottky devices reported here show some improvements over record cells of similar design [6]. In undoped Zn<sub>3</sub>P<sub>2</sub> 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<sub>3</sub>P<sub>2</sub> 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  $\geq 7 \mu\text{m}$  of the Zn<sub>3</sub>P<sub>2</sub> substrates used for the fabrication [16]. Continuing work to combine the high voltage of the cells based on undoped Zn<sub>3</sub>P<sub>2</sub> with the high current of the cells based on P-doped Zn<sub>3</sub>P<sub>2</sub> is expected to yield solar cells with solar energy conversion efficiency > 8%.

In previous literature, Mg/Zn<sub>3</sub>P<sub>2</sub> 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<sub>3</sub>P<sub>2</sub> was suspected to create the Zn<sub>3</sub>P<sub>2</sub> *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  $\mu\text{m}$  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<sub>3</sub>P<sub>2</sub> is consistent with the formation of Mg<sub>x</sub>Zn<sub>3-x</sub>P<sub>2</sub> at the interface, distinct from the Mg<sub>3</sub>P<sub>2</sub> 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<sub>3</sub>P<sub>2</sub> interface (Figure 4a) by acting as a passivation or hole-blocking layer. At the same time, Hall measurements on Mg-doped Zn<sub>3</sub>P<sub>2</sub> suggest that Mg impurities in bulk Zn<sub>3</sub>P<sub>2</sub> degrade device performance. As a result the optimal annealing conditions for Mg/Zn<sub>3</sub>P<sub>2</sub> solar cells minimize Mg diffusion while still allowing Mg<sub>x</sub>Zn<sub>3-x</sub>P<sub>2</sub> formation.

The modified ITO/Mg/Zn<sub>3</sub>P<sub>2</sub> heterojunction devices reported here demonstrate the improvements in photovoltaic performance that result from the interfacial reaction between Mg and Zn<sub>3</sub>P<sub>2</sub>. 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<sub>x</sub>Zn<sub>3-x</sub>P<sub>2</sub>. 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<sub>3</sub>P<sub>2</sub>. 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<sub>3</sub>P<sub>2</sub>, 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<sub>3</sub>P<sub>2</sub> Schottky diodes. In undoped Zn<sub>3</sub>P<sub>2</sub> devices we observe  $V_{OC}$  values up to 550 mV, and in P-doped Zn<sub>3</sub>P<sub>2</sub> 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<sub>3</sub>P<sub>2</sub> 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<sub>3</sub>P<sub>2</sub> 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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