DIRECT EVIDENCE OF MG-ZN-P ALLOY FORMATION IN MG/Zn_3P_2 SOLAR CELLS

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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. The record solar energy conversion efficiency for Zn_3P_2 cells of 6% (M. Bhushan et al., *Appl. Phys. Lett.*, 1980) used a Mg/Zn_3P_2 device geometry that required annealing to reach peak performance. Here we report photovoltaic device results and junction composition profiles as a function of annealing treatment for ITO/Mg/Zn_3P_2 devices. Mild annealing at 100 °C in air dramatically increases V_{oc} values from ~150 mV to 550 mV, exceeding those of the record cell ($V_{oc,record}$ = 490 mV). In devices with thinner Mg films we achieved J_{sc} values reaching 26 mA cm^{-2}, significantly greater than those of the record cell ($J_{sc,record}$ = 14.9 mA cm^{-2}). Junction profiling by secondary ion mass spectrometry (SIMS) and x-ray photoelectron spectroscopy (XPS) both show evidence of MgO and Mg-Zn-P alloy formation at the active photovoltaic junction in annealed ITO/Mg/Zn_3P_2 devices. These results indicate that high efficiency should be realizable by optimization of Mg treatment in Mg/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] Evidence from early work with Mg/Zn_3P_2 Schottky diode devices suggested that annealing led to formation of Mg-doped *p-n* homojunctions,[7-8] but Mg impurities have yet to demonstrate n-type conductivity in bulk or thin film Zn_3P_2. Determining the effect of annealing on the Mg/Zn_3P_2 interface would enable optimization of Zn_3P_2 devices for greater V_{oc} values and higher efficiencies. We report data from ITO/Mg/Zn_3P_2 devices showing a strong increase in V_{oc} upon annealing and evidence that the improved performance coincides with the appearance of interfacial Mg-Zn-P alloys.

EXPERIMENTAL

The Zn_3P_2 samples used in this study were grown by a physical vapor transport process. 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 1000-2000 Ω cm. After RF sputter deposition of 10-100 nm of Ag on the rough wafer, annealing with white phosphorus in sealed ampoules at 400 °C for 20 hours was effective at reducing the wafer resistivity to ~0.2-2.0 Ω cm or 10^{17} holes cm^{-3}.[10] Ag-doped samples were polished with diamond abrasive films to produce Zn_3P_2 wafers. Samples with 1 cm diameter and 400 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.

Ag-doped Zn_3P_2 samples were incorporated into solar cells using an ITO/Mg/Zn_3P_2 device configuration. Using optical photolithography a series of devices with 1 mm^2 active area were patterned and 10-40 nm Mg followed by 70 nm ITO were deposited by RF magnetron sputtering on freshly-etched Zn_3P_2 wafers. Ag back contacts of 200 nm thickness were then deposited by vacuum evaporation. Photovoltaic performance of the devices was studied under 1.0 sun AM1.5G illumination at room temperature. Spectral response measurements were conducted at short-circuit using ~10 nm band pass pulsed illumination from a xenon lamp source under 1 sun light bias.

Junction profiling of the metal-semiconductor junction was performed using secondary ion mass spectrometry (SIMS) and x-ray photoelectron spectroscopy (XPS). The ITO/Mg/Zn_3P_2 devices used for composition profiling were fabricated using 30 nm of Mg followed by 70 nm of ITO, annealed for 72 hours at 100 °C in air, and exhibited V_{oc} values from 450-550 mV. Sputtering rates were assumed to be constant for both SIMS and XPS profiling and were approximated using the crater depth as measured by profilometry. SIMS analysis was conducted using an O^- primary ion beam at 10 kV and 20 nA that was rastered over a 100x100 µm analysis area. Atomic concentrations of Zn and P were estimated using the stabilized Zn and P counts in the substrate, and atomic concentrations of Mg were estimated using an ion-implantation standard with 10^{14} cm^{-2} Mg ions.

XPS profiling measured the atomic concentration and oxidation state of elements across the junction by

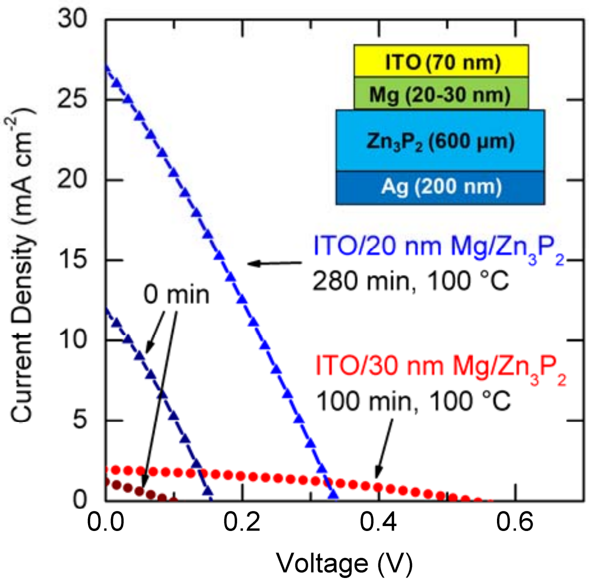

Figure 1. Photovoltaic performance under simulated AM1.5 illumination observed in ITO/Mg/Zn_3P_2 solar cells. Red traces show annealed devices with 30 nm Mg layer, where dark red corresponds to the as-fabricated device; and blue traces show annealed devices with 20 nm Mg layer, where dark blue corresponds to the as-fabricated device.

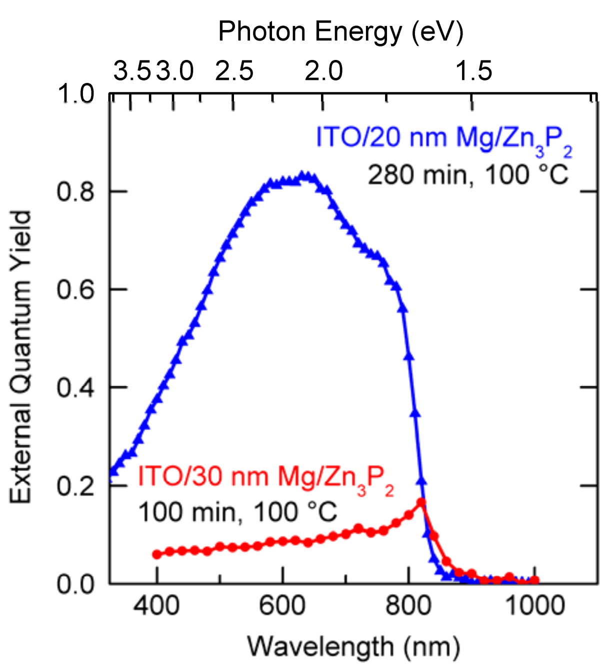

Figure 2. External quantum yield observed in ITO/Mg/Zn_3P_2 solar cells with different Mg layer thicknesses after annealing at 100 °C in air. Devices with thinner 20 nm Mg layers (blue) show high external quantum yield, but devices with thicker 30 nm Mg layers (red) show reduced external quantum yield.

monitoring the photoelectrons from In $3d^{5/2}$, O 1s, Mg KLL, Zn $2p^{3/2}$ and P 2s core levels. Monochromated x-rays of 1468.7 eV from an Al kα source were used to eject photoelectrons from the sample which were collected with the detector 0° from the surface normal. Ar-ion sputtering steps at 2 kV were alternated with XPS analysis to profile the junction. For each step, the photoelectron spectra from the In $3d^{5/2}$, O 1s, Zn $2p^{3/2}$ and P 2s core levels were fit using a Tougaard baseline[15] and a single Gaussian Lorentzian product lineshape to compute the area. The Mg KLL Auger region was fit well by three lineshapes that have been assigned to MgO at binding energy 305.5 eV (kinetic energy of 1181.2 eV), elemental Mg at 301.0 eV (1185.7 eV) and Mg-Zn-P at 303.0 eV (1183.7 eV). The relative sensitivity factor (RSF) for In $3d^{5/2}$, O 1s, Zn $2p^{3/2}$ and P 2s core levels were taken from tabulated values, and the RSF for Mg KLL was estimated using the observed Zn LMM to Zn $2p^{3/2}$ photoelectron count ratio and the tabulated Zn LMM to Mg KLL photoelectron count ratio.[16]

DATA AND RESULTS

Fig. 1 displays the light J-V results from ITO/Mg/Zn_3P_2 solar cells as-fabricated and after annealing at 100 °C in air. The performance of devices with 30 and 20 nm thick Mg layers are shown in blue and red, respectively. For solar cells with a 30 nm Mg layer, as-fabricated devices exhibited poor V_{oc} values ≤100 mV, but annealing at 100 °C for 100 min in air greatly improved the junction properties and yielded V_{oc} values reaching 550 mV. The low observed J_{sc} values were consistent with expected reflection losses from the optically-thick 30 nm Mg layer. For solar cells with a 20 nm Mg layer, annealing at 100 °C in air also increased V_{oc} values, but only to 350 mV. The lower V_{oc} values were likely due to increased shunting because thinner ≤15 nm Mg layers (data not shown) resulted in cells that were completely shorted. J_{sc} values reaching 26.0 mA cm^{-2} and solar energy conversion efficiencies of 2.7% were observed in the cells with 20 nm Mg layers due to reduced reflection losses from the Mg metal. The spectrally-resolved external quantum yield data also showed the strong relationship between Mg layer thickness and photocurrent in ITO/Mg/Zn_3P_2 solar cells (Fig. 2). Although devices with a 30 nm Mg layer showed less than 20% external quantum yield, devices with thinner 20 nm Mg layers were observed to have external quantum yields approaching 80%. Minority carrier diffusion lengths of ≥3 µm were estimated from the external quantum yield data in the 650-850 nm spectral range using previously reported absorption data and assuming a depletion width of 300 nm in the Zn_3P_2.[17-18] As demonstrated in the device results, the annealing treatment of Mg/Zn_3P_2 diodes was critical for improved device performance.

SIMS profiling was performed to probe the composition of the interface after annealing ITO/Mg/Zn_3P_2 solar cells (Fig. 3). Quantitative SIMS analysis was used in regions with >99% Zn_3P_2 composition to directly measure Mg impurity concentrations. However, in mixed regions the SIMS data was only qualitatively reliable due to the unknown matrix. After reading baseline counts in the ITO layer, the next layer was observed to contain counts from Mg, Zn and P

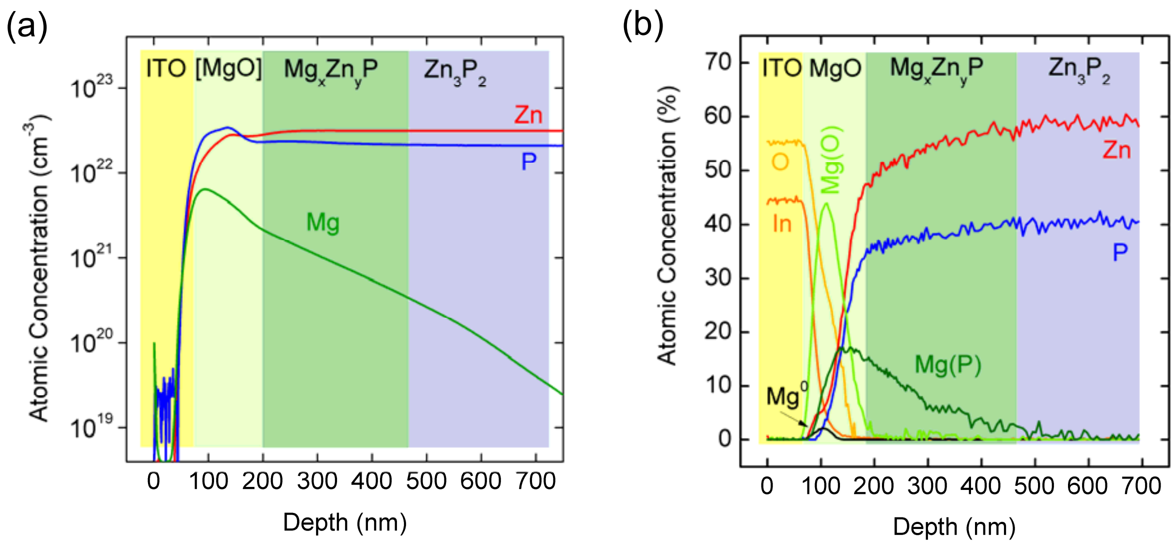

Figure 3. Composition profiling of ITO/Mg/Zn_3P_2 solar cells by (a) secondary ion mass spectrometry (SIMS) and (b) x-ray photoelectron spectroscopy (XPS) after annealing at 100 °C for 72 hours in air. The data show layers corresponding to ITO (yellow), MgO (light green), Mg_xZn_yP (dark green) and Mg-doped Zn_3P_2 (light blue). Mg metal reacts to form both MgO and Mg_xZn_yP at the junction of ITO/Mg/Zn_3P_2 solar cells.

but varied too quickly to estimate the composition. The region is denoted in brackets as [MgO] because it cannot be assigned from only the SIMS data. At greater depths, a 1-10% Mg-rich Zn_3P_2 alloyed region was observed followed by Mg-doped Zn_3P_2 with Mg impurity concentrations in the range of 10^{19}-10^{20} cm^{-3}. Because rapidly-changing compositions can be difficult to quantify by SIMS, profiling by XPS was selected to characterize the ITO/Mg interface.

By XPS profiling, the concentration and bonding environment of In, O, Mg, Zn and P were tracked across the junction interface of annealed ITO/Mg/Zn_3P_2 solar cells. The behavior of In, O, Zn and P showed little intermixing and the profile clearly transitioned past ITO after 100 nanometers and into bulk Zn_3P_2 after several hundred nanometers into the profile. The Mg KLL photoelectron spectra showed complex behavior during the transition from ITO to Zn_3P_2 and was fit by line shapes corresponding to MgO, Mg metal and Mg-Zn-P. After the ITO layer, the MgO signal centered at binding energy 305.5 eV was found to increase rapidly along with a small Mg metal signal centered at 301.0 eV. As the Zn and P concentrations began to increase, the Mg-Zn-P signal at binding energy 303.0 eV grew in to become the dominant signal in the Mg KLL region. After several hundred nanometers into the profile, the Mg-Zn-P signal decreased to yield the bulk Zn_3P_2 composition of the substrate.

DISCUSSION

Reactive metal Schottky barrier devices such as Mg/Zn_3P_2 appear to show the best performance for Zn_3P_2 absorbers likely due to their ability to form metal phosphide alloys at the interface.[19] High concentrations of surface states have been measured in metal-insulator-semiconductor structures incorporating Zn_3P_2 substrates, and have been implicated in the <300 mV V_{oc} values observed for ITO/Zn_3P_2 and ZnO/Zn_3P_2 solar cells.[20] Although as-deposited Mg does not appear to form thick Mg-Zn-P alloys, the profiling data show that mild annealing is sufficient to drive the formation of 100-200 nm of Mg-Zn-P alloys at the interface of Mg/Zn_3P_2 diodes. The improvements in barrier height occur with even brief (less than 20 min) annealing times, demonstrating that even thin reacted layers are effective at reducing surface recombination and Fermi-level pinning. The data suggest that Mg_xZn_yP-Zn_3P_2 *p-n* heterojunctions form upon annealing Mg/Zn_3P_2 diodes and that their formation may contribute to the improved V_{oc} of annealed devices.

SUMMARY

We report improvements over previous results in photovoltaic performance for solar cells based on Mg/Zn_3P_2 diodes and provide evidence for the formation of Mg-Zn-P alloys upon annealing Mg/Zn_3P_2 diodes. In ITO/Mg/Zn_3P_2 devices with 30 nm Mg layers we observe V_{oc} values up to 550 mV, and in ITO/Mg/Zn_3P_2 devices with 20 nm Mg layers we observe J_{sc} values up to 26.0 mA cm^{-2}. Both values constitute improvements over the record Zn_3P_2 cell, but so far the high voltage and high current performance have not been realized in the same device. We have also identified the presence of Mg-Zn-P in annealed ITO/Mg/Zn_3P_2 devices by combined SIMS and XPS profiling measurements. These results indicate that high efficiency cells are realizable by optimization of Mg treatment in Zn_3P_2 solar cells.

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