SYNTHESIS AND SURFACE CHEMISTRY OF ZN3P2

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ABSTRACT

Zinc phosphide (Zn_3P_2) is a promising alternative to traditional materials (e.g. CIGS, CdTe, a-Si) for thin film photovoltaics. Open circuit voltage in Zn_3P_2 cells has been limited by Fermi-level pinning due to surfaces states and heterojunction interdiffusion, motivating the need to prepare interfaces that are electrically passive and chemically inert. We investigated the surface chemistry of Zn_3P_2 via etching with bromine in methanol and passivation with ammonium sulfide in t-butanol. The treatment decreases surface oxidation as determined by x-ray photoelectron spectroscopy and provides a stable, low-defect interface as monitored by steady-state photoluminescence. Magnesium Schottky diodes fabricated with sulfur-passivated interfaces show evidence of enhanced barrier heights in comparison to control devices.

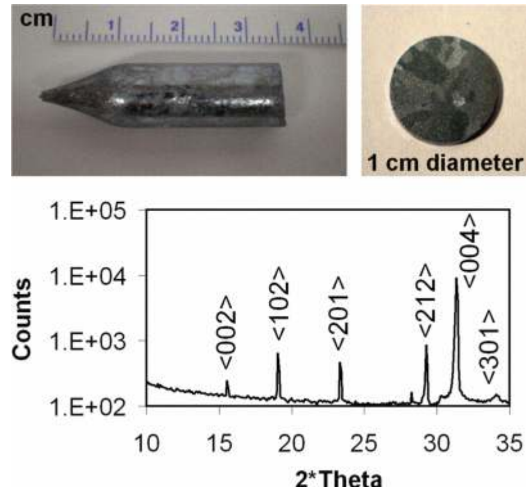

Fig. 1. Photographs of (a) Zn_3P_2 boule, (b) unpolished polycrystalline wafer. (c) XRD pattern of polished wafer.

INTRODUCTION

Zn_3P_2 is an earth-abundant material that has shown promise for solar energy conversion but has not been investigated as thoroughly as other thin film materials. It is one of the very few materials that happens to possess both a direct energy gap near the terrestrial optimum (1.5 eV) [1] and earth abundant constituent elements. Predominantly p-type doping has been observed in Zn_3P_2, requiring photovoltaic devices to use Schottky barriers and semiconductor heterojunctions. The record solar energy conversion efficiency for a device with a Zn_3P_2 absorber was set in 1979, reaching 6.08% with a diffused Mg_3P_2 heterojunction [2]. Despite considerable effort, other device structures using *p-n* heterojunctions have not demonstrated good performance [3].

The lack of a systematic study of Zn_3P_2 surface and interface chemistry has impeded progress in realizing its potential for solar energy conversion. In particular, the nature of the surface prepared using the traditional etchant, bromine in methanol, has not been fully characterized. Kato et al. used X-ray photoelectron spectra (XPS) to show that an additional phosphorus species remains on the surface, but this species has yet to be conclusively identified [14]. Native oxides grew quickly upon exposure to air, limiting the quality of the surface. Sulfur passivation has been used with InP and GaAs materials to decrease surface recombination sites and protect the surface against oxidation in air [16]. Although sulfur passivation has been shown to be effective for a number of materials, this study is the first attempt to extend the treatment to Zn_3P_2 surfaces.

EXPERIMENTAL

Production of Zn_3P_2 Wafers

As Zn_3P_2 wafers cannot be purchased commercially, the samples used in this study were synthesized from elemental red phosphorus and zinc metal by established methods [4]. Red phosphorus lump and zinc shot of 99.9999% purity (Alfa Aesar) were loaded in opposite ends of a quartz tube so that the red phosphorus could be converted to white phosphorus in situ at 500°C. Then the zinc metal was heated to 850°C to allow the vapor phase reaction of white phosphorus and zinc to form raw Zn_3P_2 crystals. These crystals were ground into a powder and purified by sublimation in a fresh quartz tube to remove less volatile impurities.

The purified powder was then grown into large mm-grain size boules by physical vapor transport in carbon-coated Bridgman quartz ampoules (see Fig. 1a). Approximately 10 g of Zn_3P_2 were loaded with 10 mg of Ag shot 99.9999% (ESPI) for in situ doping. Then the ampoule was translated at a rate of 1-2 mm per day for several weeks into the cold zone of the furnace held at

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850°C [5]. As-grown boules with ~1 cm^2 grain size were cylindrical with 1 cm diameter and about 6 cm in length.

Zn_3P_2 boules were sliced and polished to produce wafers with a mirror finish. An ISOMET low speed diamond saw sliced wafers of approximately 600 μm in thickness (see Fig. 1b). These wafers were then polished with a MINIMET polishing instrument using 15, 6, 3, 1, and finally 0.25 μm diamond paste. A Philips X'Pert Pro X-ray diffractometer using copper K-α x-rays was used to collect diffraction patterns that show the wafers to be highly crystalline phase-pure Zn_3P_2 (see Fig. 1c) [6].

As-grown wafers have a resistivity of 10^4 to 10^6 Ω-cm that can be reduced to ~10^3 Ω-cm by annealing in white phosphorus at 400°C for 24 hours [7]. Resistivity measurements allowed for an estimate of carrier concentration by the following relation [8]:

$$\rho = \frac{1}{q(n\mu_n + p\mu_p)} \quad (1)$$

where n is the electron concentration, μ_n is the electron mobility, p is the hole concentration, and μ_p is the hole mobility. Minority carrier conduction was neglected and the reported hole mobility of 20 cm^2/Vs for Zn_3P_2 [4] was used. Wafers used in this study are near intrinsic with an estimated acceptor concentration of 10^{13} to 10^{14} cm^{-3}.

Surface Chemistry and Passivation

Native oxides were removed by etching samples with a 1-3% by volume Br_2 in methanol for one minute and then thoroughly rinsing with methanol [2]. The sulfur passivation solution consisted of a saturated solution of $(NH_4)_2S$ in t-butanol [9]. Sulfur treatments were for one minute followed by a methanol dip for one minute to remove excess sulfur solution.

Chemical surface species were analyzed by x-ray photoelectron spectroscopy (XPS) immediately after treatment and after prescribed periods of air aging. XPS data were collected using an M-probe spectrometer (VG Instruments) using monochromatic Al K-α X-rays (1486.6 eV) that were incident at 35° from the sample surface. Surface overlayers of element phosphorus, phosphorus sulfides, and native oxides were fit to a standard overlayer-substrate model [10,11]:

$$d = \lambda_{ov} \sin(\theta) \ln\left(1 + \frac{I_s^\infty}{I_{ov}^\infty} * \frac{I_{ov}}{I_s}\right) \quad (2)$$

where λ_{ov} is the electron escape depth through the overlayer in nm, θ is the angle of incident x-rays, $I_s°/I_{ov}°$ is the ratio of signal intensities of pure samples, I_s is the intensity of the signal from the substrate, and I_{ov} is the intensity of the signal from the overlayer. Electron escape depths were calculated for electrons of 128.3 eV using the following relations [11]:

$$\lambda_{ov} = 538E^{-2} + 0.41(aE)^{\frac{1}{2}} \quad (3)$$

$$a = \left(\frac{A}{1000\rho N}\right)^{\frac{1}{3}} \quad (4)$$

where λ_{ov} is the electron escape depth through the overlayer in nm, E is the electron kinetic energy signal of the substrate, a is atomic size in nm, A is the mean of the atomic masses in kg/mol, ρ is density in g/cm^3, and N is Avagadro's number. Escape depths of 128.3 eV electrons from elemental phosphorus, phosphorus sulfides, and zinc phosphate were calculated to be 2.5 nm, 2.6 nm, and 2.3 nm respectively.

The surface quality was monitored using steady-state photoluminescence (PL) intensity. PL spectra were collected with a Princeton Instruments SPEC-10 visible/infrared CCD using excitation from the 488 nm line of an Argon laser. Spectra were collected before surface treatment and every two minutes thereafter.

Barrier Height Calculations

Optically thick magnesium films probed the junction properties of Mg-Zn_3P_2 Schottky diodes [2]. Zn_3P_2 wafers were etched and then half were subjected to the sulfur treatment previously described. Then they were loaded into a RF plasma sputtering system for the deposition of a 200 nm Mg rectifying front contact. As soon as the sputtering was complete, the wafers were immediately loaded into an evaporator for deposition of a 250 nm Ag ohmic back contact.

Current-voltage data were collected with a Solarton model 1286 electrochemical analyzer using a scan rate of 20 mV/sec. Values for the diode ideality factor η and the reverse bias saturation current J_0 were derived from fits to the ideal diode equation [8]:

$$J(V) = J_0 * \left(\exp\left(\frac{qV}{kT\eta}\right) - 1\right) \quad (5)$$

$$\phi_{Bp} = \frac{kT}{q} * \ln\left(\frac{A^{**}T^2}{J_0}\right) \quad (6)$$

where k is the Boltzmann constant, T is temperature in Kelvin, q is the charge of the electron, Φ_{Bp} is the barrier height for holes, and A^{**} is the Richardson's constant (value for Si used [8]).

Capacitance-voltage data was collected using a Schlumberger BI 1260 Impedance/Gain Phase Analyzer across a range of frequencies from 10 Hz to 100 kHz. Frequency dependent traces were collected using a 10

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mV alternating bias imposed upon a –0.1 to –2.0 V constant bias. Barrier heights and carrier concentrations were calculated from the Mott-Schottky equation [8]:

$$C^{-2}(V) = -A^2\left(\frac{2}{q\varepsilon_s\varepsilon_0 N_A}\right)\left(V_{bi} + V - \frac{kT}{q}\right) \qquad (7)$$

$$\phi_{Bp} = -V_{bi} + \frac{kT}{q}\left(\ln\left(\frac{N_V}{N_A}\right) + 1\right) \qquad (8)$$

where C is junction capacitance, A is device area, $\varepsilon_s\varepsilon_0$ is the dielectric constant of the semiconductor (value for InP used [8]), N_A is the acceptor density, V_{bi} is the built-in voltage, and N_V is the density of states in the valence band (value for InP used [12]).

DATA AND RESULTS

X-Ray Photoelectron Spectra

XPS spectra of the P2p and $Zn2p^{3/2}$ peaks of the as-polished surface showed a stoichiometric surface (3:2 Zn:P) with substantial phosphorus and zinc oxides. We assign 133.2 eV to P2p phosphorus oxide, 128.3 eV to P2p phosphide, and 1022.8 to $Zn2p^{3/2}$ zinc oxide (see Fig. 2a,b) [13]. The underlying Zn_3P_2 was exposed by argon ion sputtering for several minutes, showing clean P2p and $Zn2p^{3/2}$ peaks (see Fig. 2c,d).

Upon treatment of the as-polished surface with 1% v/v Br_2 in methanol for 30 sec, the resulting surface no longer showed sign of oxidation. There was no bromine detectable on the surface within the limits of XPS, but another phosphorus 2p doublet at 130.0 eV was observed distinct from the P2p phosphide peak (see Fig. 3a). Although previous authors have attributed this peak to phosphorus sub-oxides [14], we assign it to elemental phosphorus [15]. The overlayer model (2) predicts that about 2 monolayers of elemental phosphorus remain on the surface. As the etched surface aged, both zinc and phosphorus oxides grew in within the first few hours.

Next, we passivated the Zn_3P_2 surface using an ammonium sulfide treatment that has been shown to be effective for stabilizing the surface of III-V semiconductors [16]. Immediately after treatment, the P2p spectrum showed a new species attributable to P-S bonding at 132.1 eV (see Fig. 3c). A nearly 1:1 phosphorus sulfide film was estimated to be about 4 monolayers in thickness. Studies with sulfur passivation of indium phosphide surfaces have assigned S2p signals at 162.1 eV to polysulfide [17], which corresponds well with the signal at 162.3 eV seen in these samples. As the sulfur treated samples aged in air, phosphorus oxides grew in, but the zinc peak did not show strong evidence of oxidation. A shift in the $Zn2p^{3/2}$ peak to 1022.4 eV could be attributed to Zn-S bonding, but not conclusively. Additionally, the sulfur S2p signal appears unaffected by the air aging.

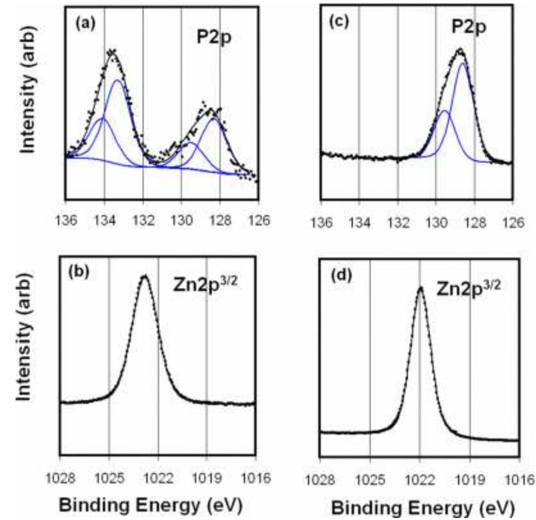

Fig. 2. XPS spectra of (a) P2p and (b) $Zn2p^{3/2}$ for the as polished surface showing native oxide. Spectra of (c) P2p and (d) $Zn2p^{3/2}$ for argon ion etched surface showing clean Zn_3P_2.

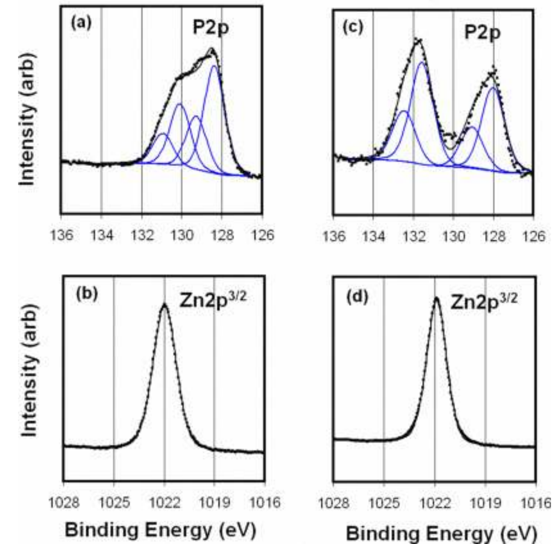

Fig. 3. XPS spectra of (a) P2p and (b) $Zn2p^{3/2}$ for the bromine etched surface showing residual elemental phosphorus. Spectra of (c) P2p and (d) $Zn2p^{3/2}$ for sulfur treated surface showing phosphorus sulfides.

Steady-State Photoluminescence

Polished wafers showed a weak signal around 830 nm near the band edge of Zn_3P_2. Upon etching with bromine in methanol, steady-state photoluminescence was greatly enhanced but as the sample oxidized in air this signal lost intensity. After several hours the signal returned to intensities comparable to untreated samples.

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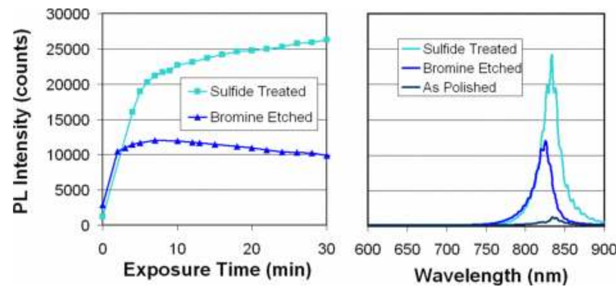


Fig. 4. Steady-state photoluminescence intensity during air exposure at room temperature for samples as polished, freshly etched with 3% v/v Br in MeOH for 1 min, and freshly etched and soaked in sat $(NH_4)_2S$ in t-ButOH for 1 min.

Sulfide passivated wafers show larger emission intensity compared to etched wafers (see Fig. 4). Even more striking, they exhibited a rise in photoluminescence intensity over time. The increasing steady-state room temperature photoluminescence intensity continues for the first few hours, but gradually fell to the intensity of the as-polished wafers over a period of 24 hours.

Dark Current-Voltage Characteristics

Dark current-voltage measurements revealed strongly rectifying behavior in the magnesium Schottky diodes (see Fig. 5). Samples displayed a small leakage current that grew exponentially with reverse bias. In forward bias, the devices adhere to the ideal diode equation well for several hundred millivolts before large series resistance dominates the behavior. The bulk resistivity of the wafers currently limits the performance of the diodes for photovoltaic applications. Fits to the ideal diode equation (5,6) using the first few hundred millivolts of forward bias show striking differences between devices fabricated with and without sulfur passivation (see Table 1). Diode ideality factors of 1.55 +/- 0.08 were found for samples treated with sulfur, while ideality factors of 2.40 +/- 0.15 were found for samples prepared without sulfur passivation. Barrier heights estimated from J_0 showed an improvement for samples treated with sulfur, increasing from 844 +/- 12 mV to 867 +/- 6 mV. These results compare favorably with literature reported barrier heights of 800 mV [2].

Capacitance-Voltage Characteristics

Frequency-dependent impedance measurements showed evidence for even greater barrier heights. The sulfur-passivated devices following the Mott-Schottky equation (7,8) gave barrier heights as high as 983 mV (see Fig. 6). Although some devices performed ideally across a range of frequencies, many of the devices tested had significant frequency dispersion in the derived barrier heights. Carrier concentrations calculated from the slopes of $1/C^2$-V traces corresponded well to estimates from four-point resistivity measurements (see Table 2). Preliminary results suggested that sulfur passivation enhanced barrier

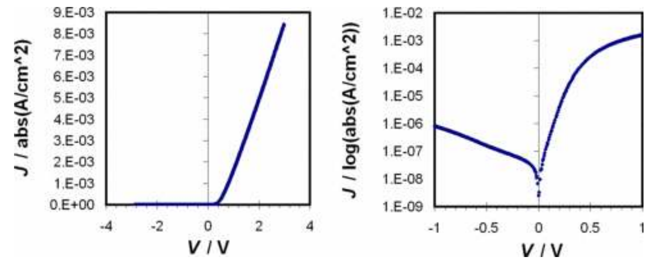


Fig. 5. Dark J-V traces of Zn_3P_2-Mg Schottky diodes.

Sulfur	*n*	$J_0(A/cm^2)$	$\Phi_{BP}^{J-V}(V)$
Yes	1.48	2.66E-08	0.870
Yes	1.64	3.77E-08	0.861
Yes	1.54	2.53E-08	0.872
No	2.52	1.02E-07	0.836
No	2.23	9.45E-08	0.838
No	2.45	4.32E-08	0.858

Table 1. Parameters derived from J-V measurements.

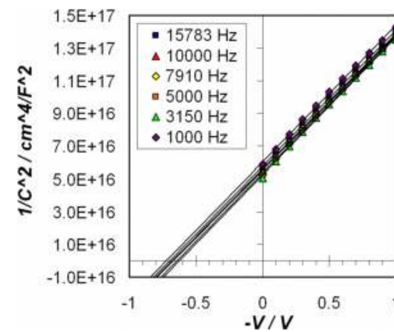


Fig. 6. Capacitance-Voltage traces of Zn_3P_2-Mg Schottky diodes.

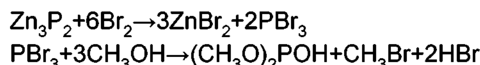
Sulfur	$\Phi_{Bp}^{C-V}(V)$	$N_A^{C-V}(cm^{-3})$	$N_A^{\rho}(cm^{-3})$
Yes	0.641	3.29E+13	5.97E+13
Yes	0.924	8.97E+13	1.72E+13
Yes	0.983	1.35E+14	9.64E+13

Table 2. Parameters derived from capacitance-voltage and resistivity measurements.

heights in Zn_3P_2-Mg Schottky diodes by almost 200 mV as compared to those reported in the literature [2].

DISCUSSION AND FUTURE WORK

Nearly all previous work involving Zn_3P_2 used a 1-3% solution by volume of bromine in methanol, but little characterization has been performed of the resulting surface. The mechanism of the etching process is thought to occur as follows [18]:



$$Zn_3P_2 + 6Br_2 \rightarrow 3ZnBr_2 + 2PBr_3$$
$$PBr_3 + 3CH_3OH \rightarrow (CH_3O)_2POH + CH_3Br + 2HBr$$

Etched samples were consistently phosphorus-rich, suggesting that the etching process was not completely congruent. Even diluted bromine solutions resulted in Zn_3P_2 surfaces with a similar residue of elemental phosphorus several monolayers in thickness. The elemental phosphorus resisted rinsing and sonication, motivating future work to explore etchants for its removal. To date, chemical methods have not established a preparation for clean, stoichiometric Zn_3P_2 surfaces.

Combined AES and XPS sputter profiling has shown the etched Zn_3P_2 surface to be susceptible to reaction with Mg. Ireland et al. demonstrated that a Mg_3P_2 layer about 20-40 nm in thickness formed at the metal-semiconductor interface [19]. We hypothesize that treatment with ammonium sulfide helps prevent Mg diffusion by forming a buffer layer of amorphous magnesium phosphide-sulfide alloy. The resulting interface has fewer recombination sites, allowing for better diode ideality factors. MgS may act as a barrier for hole injection across the Mg-Zn_3P_2 interface, allowing for increased barrier heights. XPS sputter profiling studies will help discern the efficacy of buffer layers at the metal-semiconductor interface.

Low effective carrier concentrations limited the performance of the devices in this report. We have made recent progress in the diffusion doping of Zn_3P_2 wafers with Ag. As-grown wafers of 10^4 to 10^5 Ω-cm resistivity were etched as previously described, and then 100 nm of Ag were evaporated on the front of the wafer. After an annealing treatment of 550°C for 24 hrs to drive in the silver, both sides of the wafer had resistivities of about 1-10 Ω-cm. This corresponds to an increase of nearly four orders of magnitude in carrier concentration, raising the wafers to an estimated 10^{17} to 10^{18} cm^{-3} acceptors. Continuing work will explore the effects of various surface treatments on the performance of high-quality Mg-Zn_3P_2 Schottky diodes.

ACKNOWLEDGEMENTS

This work was supported by the Office of Energy Efficiency and Renewable Energy, US Department of Energy under grant DE-FG36-08GO18006. One of us (GMK) acknowledges support under an NDSEG graduate fellowship. We also acknowledge use of facilities supported by the Center for Science and Engineering of Materials, an NSF MRSEC.

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