Passivation of Zn$_3$P$_2$ substrates by aqueous chemical etching and air oxidation

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Surface recombination velocities measured by time-resolved photoluminescence and compositions of Zn$_3$P$_2$ surfaces measured by x-ray photoelectron spectroscopy (XPS) have been correlated for a series of wet chemical etches of Zn$_3$P$_2$ substrates. Zn$_3$P$_2$ substrates that were etched with Br$_2$ in methanol exhibited surface recombination velocity values of 2.8x$10^4$ cm s$^{-1}$, whereas substrates that were further treated by aqueous HF–H$_2$O$_2$ exhibited surface recombination velocity values of 1.0x$10^4$ cm s$^{-1}$. Zn$_3$P$_2$ substrates that were etched with Br$_2$ in methanol and exposed to air for 1 week exhibited surface recombination velocity values of 1.8x$10^4$ cm s$^{-1}$, as well as improved ideality in metal/insulator/semiconductor devices. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4765030]

With a direct band gap at 1.5 eV, long (5–10 μm) minority-carrier diffusion lengths, and controllable p-type doping (10$^{13}$–10$^{18}$ cm$^{-3}$), zinc phosphide (Zn$_3$P$_2$) is an interesting candidate for the active semiconductor absorber in solar energy-conversion devices. Due to the difficulty in preparing n-type Zn$_3$P$_2$, device fabrication with Zn$_3$P$_2$ has focused on p-n heterojunctions and Schottky diodes, with p-Zn$_3$P$_2$/Mg devices exhibiting solar energy-conversion efficiencies up to 6%.

However, Zn$_3$P$_2$ p-n heterojunctions have only reached solar energy-conversion efficiencies of ≤2% and are limited by high concentrations of interface states. Zn$_3$P$_2$/ZnO and Zn$_3$P$_2$/Al$_2$O$_3$ interfaces have exhibited interfacial recombination velocity values of >10$^7$ cm s$^{-1}$ and defect distributions of >10$^{11}$ eV$^{-1}$ cm$^{-2}$, respectively. The high concentration of interface states has been related to the wet chemical preparation process, and/or to damage during physical deposition, and/or to deleterious solid-state interface reactions. Etching with Br$_2$ in CH$_3$OH has been used to prepare Zn$_3$P$_2$ surfaces for device fabrication but detailed information on the surface composition is not yet available. In this study, we describe the surface recombination characteristics and surface composition of chemically treated Zn$_3$P$_2$ substrates. Time-resolved photoluminescence (PL) was used to provide quantitative estimates of the surface recombination velocity (SRV) and surface defect density, whereas x-ray photoelectron spectroscopy (XPS) was used to monitor the composition of chemically treated Zn$_3$P$_2$ surfaces. Hg/Al$_2$O$_3$/Zn$_3$P$_2$ metal–insulator–semiconductor (MIS) devices were also fabricated to correlate the surface defect density distributions that were inferred from impedance measurements with the surface recombination rates that were inferred from time-resolved PL measurements.

To prepare the Zn$_3$P$_2$ substrates, red phosphorus chips and zinc shot (99.9999%, Alfa Aesar) were combined at 850°C to form Zn$_3$P$_2$ crystals by a physical vapor transport process. Hall-effect measurements indicated that the samples were p-type and intrinsically doped with an average hole density of ~10$^{18}$ cm$^{-3}$ and a hole mobility of 18 ± 3 cm$^2$ V$^{-1}$ s$^{-1}$. “Br-etched” samples were immersed for 30 s in 3-2% (v:v) Br$_2$ in CH$_3$OH, rinsed in CH$_3$OH, and dried under a stream of N$_2$(g). 2% Br$_2$ in CH$_3$OH yielded a bulk etch rate of ~30 nm s$^{-1}$ and resulted in surfaces with 1.3 nm RMS roughness. “HF-treated” samples were stirred rapidly in 10% HF–0.25% H$_2$O$_2$ (v:v) (aq) for 60 s, rinsed in distilled 10 MΩ cm resistivity water, and dried under a stream of N$_2$(g).

Steady-state PL measurements were performed using the 488 nm line of an Ar-ion laser, with the beam chopped at 10 kHz using an acousto-optic modulator. Time-resolved PL measurements were performed at 10 Hz with 70 ps, 355 nm, 1 μJ pulses that were produced by tripling the frequency of a regeneratively amplified, mode-locked, Nd:YAG laser. The high intensity of the laser pulses used for time-resolved PL was sufficient to reach the flat-band condition, by producing peak excess carrier densities of ~10$^{17}$ cm$^{-3}$. The time-resolved PL data were analyzed by numerically solving the continuity equations under the assumption of high-level injection, assuming a nonradiative lifetime of 23 ± 2 ns and an ambipolar diffusion coefficient of 1 cm$^2$ s$^{-1}$. The only adjustable parameter was the SRV, which was varied from 10$^3$ to 10$^7$ cm s$^{-1}$.

The chemical composition of the Zn$_3$P$_2$ surfaces was monitored by XPS using a Kratos surface science instrument with monochromatic 1486.7 eV x-rays and a detection 30 nm s$^{-1}$ and an ambipolar diffusion coefficient of 1 cm$^2$ s$^{-1}$. The only adjustable parameter was the SRV, which was varied from 10$^3$ to 10$^7$ cm s$^{-1}$. The coverages of chemical overlayers were

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calculated by the method of Seah,20 with photoelectron escape depths that were estimated assuming monolayer thicknesses of 0.27 nm for Zn$_3$P$_2$, 0.28 nm for elemental phosphorus, and 0.23 nm for Zn$_x$(PO$_y$)$_z$.

Impedance measurements on Hg/Al$_2$O$_3$/Zn$_3$P$_2$ devices were performed using Hg-drop electrodes and ~60 nm insulating layers of Al$_2$O$_3$ that were deposited by electron-beam evaporation. The devices were swept from accumulation to depletion at 80 mV s$^{-1}$ and the differential capacitance was monitored at 10 kHz with a 10 mV AC potential. The distribution of the surface state density was estimated by use of high-frequency capacitance methods19,21 taking $\varepsilon_{\text{Al}_2\text{O}_3}$ = 4.5, $\varepsilon_{\text{Zn}_3\text{P}_2}$ = 11, and a Zn$_3$P$_2$ dopant density of 10$^{15}$ cm$^{-3}$.

Figure 1 shows time-resolved PL decay traces and steady-state PL spectra for chemically treated Zn$_3$P$_2$ substrates. Under high-level injection, the PL decay dynamics immediately after the laser pulse were dominated by the effects of surface recombination, yielding quantitative estimates of the surface recombination velocity (Table I). Freshly polished samples did not exhibit detectable PL (black line, inset Fig. 1). However, etching with 2% Br$_2$ in CH$_3$OH yielded readily observable PL, and SRV values of (2.8 ± 0.1) × 10$^4$ cm s$^{-1}$. Br-etched samples that were further treated with 10% HF–0.25% H$_2$O$_2$ (aq) for 60 s showed an increase in steady-state PL intensity by a factor of 2.3 ± 0.2 and had SRV values of (1.0 ± 0.1) × 10$^4$ cm s$^{-1}$. Br-etched Zn$_3$P$_2$ samples that were exposed to air for 1 week showed even longer PL decays than samples that were tested immediately after chemical treatment, with SRV values of (1.8 ± 0.1) × 10$^3$ cm s$^{-1}$. Assuming similar cross sections for carrier capture, the formation of native oxides on Br-etched Zn$_3$P$_2$ samples thus passivated >90% of the electrically active surface recombination sites.

Figure 2 shows the high-resolution XPS data of the Zn 2p$^{3/2}$ and P 2p regions of chemically treated Zn$_3$P$_2$ substrates. After etching with 2% Br$_2$ in CH$_3$OH for 30 s, the substrates exhibited bulk stoichiometric Zn and P species, 0.4 ± 0.2 monolayers of oxidized zinc, 0.3 ± 0.1 monolayers of oxidized phosphorus, and 4.1 ± 0.5 monolayers of elemental phosphorus (P$^0$) (Fig. 2(a)). Treatment of the Br-etched substrates with 10% HF–0.25% H$_2$O$_2$ (aq) for 60 s decreased the P$^0$ surface coverage to 1.4 ± 0.2 monolayers without introducing additional surface oxidation of Zn or P species (Fig. 2(b)). Substrates that had been etched with 2% Br$_2$ in CH$_3$OH for 30 s and then exposed to air for 1 week (Fig. 2(c)) showed oxidized phosphorus and oxidized zinc signals that were consistent with the presence of 4 ± 2 monolayers of Zn$_x$(PO$_y$)$_z$ species. Table II shows the binding energies and Gaussian peak widths observed for the surface zinc and phosphorus species of the series of Zn$_3$P$_2$ surfaces.

Figure 3 compares the normalized capacitance data collected from Hg/Al$_2$O$_3$/Zn$_3$P$_2$ devices to the expected ideal performance in the absence of surface trap states. Ideal MIS devices with p-type semiconductors show decreasing capacitance with increasing positive gate bias as the semiconductor is swept into depletion. However, freshly Br-etched Zn$_3$P$_2$ substrates showed only a small modulation of capacitance with gate bias, consistent with a high density of surface defects (>10$^{13}$ eV$^{-1}$ cm$^{-2}$). The capacitance data from Br-etched Zn$_3$P$_2$ substrates that had been exposed to air for 1 week instead showed a significant depletion of the semiconductor at positive gate bias, and allowed for an estimate of the surface trap density distribution, $D_s$, of ~10$^{12}$ eV$^{-1}$ cm$^{-2}$ (Figure 3 inset). The surface trap density distributions derived from capacitance measurements of MIS devices were consistent with the surface trap density values that were derived from time-resolved PL measurements.

The estimated surface trap density values in Table II support the hypothesis that the electronic quality of the surface prepared by etching with 2% Br$_2$ in CH$_3$OH limits the performance of the resulting Zn$_3$P$_2$ devices, rather than damage during physical deposition or deleterious solid-state interface reactions. The presence of residual P$^0$ correlated with poor electronic quality in that the coverage of P$^0$ and the surface recombination rates both decreased after treatment of Br-etched Zn$_3$P$_2$ substrates with 10% HF–0.25% H$_2$O$_2$ (aq). A low residual P$^0$ coverage on Zn$_3$P$_2$ thus appeared to reduce the surface trap density and offers a promising approach to unpin the Fermi level in p-n

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**TABLE I. Photoluminescence-based characterization of chemically treated Zn$_3$P$_2$ devices.** Relative PL intensity was recorded at 890 nm, and time-resolved PL decays were used to determine surface recombination velocity ($v_{th}$). The surface trap density ($N_t$) was derived using the relationship, $S = N_t v_{th}$, assuming a carrier capture cross section $\sigma = 10^{-16}$ cm$^2$ and a thermal velocity $v_{th} = 10^5$ cm s$^{-1}$.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Relative PL signal (arb. units)</th>
<th>$v_{th}$ (cm s$^{-1}$)</th>
<th>$N_t$ (cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polished</td>
<td>&lt;0.02</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>(i) 2% (v/v) Br$_2$ in CH$_3$OH for 30 s</td>
<td>1.0 ± 0.2</td>
<td>(2.8 ± 0.1) × 10$^4$</td>
<td>3 × 10$^{13}$</td>
</tr>
<tr>
<td>(ii) 2% (v/v) Br$_2$ in CH$_3$OH for 60 s</td>
<td>2.3 ± 0.2</td>
<td>(1.0 ± 0.1) × 10$^3$</td>
<td>1 × 10$^{13}$</td>
</tr>
<tr>
<td>(i) 1 week air</td>
<td>1.7 ± 0.2</td>
<td>(1.8 ± 0.1) × 10$^3$</td>
<td>2 × 10$^{13}$</td>
</tr>
<tr>
<td>(ii) followed by 10% HF–0.25% H$_2$O$_2$ (aq) for 60 s</td>
<td>0.2 (2.8 ± 0.1) × 10$^4$</td>
<td>3 × 10$^{13}$</td>
<td></td>
</tr>
</tbody>
</table>

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**FIG. 1.** Time-resolved PL decay data collected under Ar(g) at 295 K for Zn$_3$P$_2$ substrates that were (a) etched in 2% Br$_2$ in CH$_3$OH for 30 s, (b) etched in 2% Br$_2$ in CH$_3$OH for 30 s and then treated with 10% HF–0.25% H$_2$O$_2$ (aq) for 60 s, and (c) etched in 2% Br$_2$ in CH$_3$OH for 30 s and then exposed to air for 1 week. The inset shows the steady-state PL spectra that were collected in ambient conditions for Zn$_3$P$_2$ substrates with surface treatments (a), (b), and (c).
heterojunction devices. The surface recombination velocity values of $<2 \times 10^3$ cm s$^{-1}$, and the improved MIS performance of oxidized Zn$_3$P$_2$ surfaces, highlight the potential of the method for surface passivation and device integration. The data suggest that the native oxides of Zn$_3$P$_2$ are similar to those of InP, which have been incorporated in high efficiency MIS solar cells, motivating further effort to apply physical and/or chemical oxidation techniques to Zn$_3$P$_2$ prior to device integration.

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16See supplementary material at http://dx.doi.org/10.1063/1.4765030 for substrate orientation maps collected by electron backscattered diffraction; MATLAB code used for numerical simulation of time-resolved photoluminescence data.