

# Preparation and Photoelectrochemical Characterization of ZnSiAs<sub>2</sub> Crystals<sup>†</sup>

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ZnSiAs<sub>2</sub> (chalcopyrite structure) single crystals were grown by chemical vapor transport (CVT). Hall effect and photoelectrochemical techniques were used to characterize the properties of the p-type materials. Doping level, mobility, and resistivity were determined and compared with literature values for crystals obtained from other growth techniques. Photocurrent spectroscopy was used to measure the bandgap and transition types in the crystals. The interfacial energetics were measured with capacitance techniques (Mott–Schottky). The effect of various wet chemical etchants on the photocurrent voltage curves and quantum yields for carrier collection was also investigated.

## Introduction

The successful use of III-V semiconductors and their alloys for high efficiency solar cells<sup>1–3</sup> has stimulated the study of isoelectronic ternary semiconductors.<sup>4–6</sup> II-IV-V<sub>2</sub> materials are isoelectronic with III-V semiconductors, but contain more abundant elements (Zn, Cd, Si, Ge, Sn) than In or Ga, whose relative scarcity and high cost may preclude their use in large scale photovoltaic applications. ZnSiAs<sub>2</sub>, a II-IV-V<sub>2</sub> chalcopyrite structure semiconductor, isoelectronic with GaAlAs<sub>2</sub>, has been prepared<sup>7</sup> and investigated as a candidate solar cell material.<sup>8–10</sup> Recent investigations of the epitaxial growth of ZnSiAs<sub>2</sub> on GaAs (lattice mismatch 0.84%) by MOVPE<sup>5</sup> further confirms the possibility of this application. The lowest direct gap of 2.1–2.2 eV<sup>11,12</sup> and other strongly polarization dependent transitions in ZnSiAs<sub>2</sub> may also be useful in nonlinear optical applications. Pseudodirect transitions can occur in II-IV-V<sub>2</sub> materials due to the doubled periodicity in the *c* direction of the chalcopyrite unit cell, placing the conduction band states with minimum energy at the  $\Gamma$  point in the Brillouin zone. Since three equivalent X points in zincblende map into two inequivalent points  $\Gamma$  and *T*, it is sometimes not obvious whether the conduction band at  $\Gamma$  or at *T* will lie at lower energy. In ZnSiAs<sub>2</sub> Zunger has reported both lowest direct and pseudodirect bandgaps to be very close in energy.<sup>13</sup> Direct or pseudodirect transitions result in steeply rising absorption coefficients above the bandgap energy,<sup>11</sup> which is necessary for the construction of thin film photovoltaic devices. So it is important to ascertain the energy and type of transition in ZnSiAs<sub>2</sub>.

The use of photoelectrochemical techniques for the determination of the solid state properties of semiconductor materials has many advantages. They are relatively simple, can be nondestructive, and provide easy access to the Schottky-like junction, so many different experiments can be done to probe the interfacial junction chemistry on one sample since no front contacts need to be deposited on the crystal. In addition the energetics of the junction can be varied quite easily by appropriate choices of redox species, and the effects of surface modification, such as various etchants, can be quickly ascertained.

In previous studies we have used photoelectrochemical techniques to study other II-IV-V<sub>2</sub> materials.<sup>14–16</sup> A summary

of the solid state properties obtained for these materials using photoelectrochemical techniques is given in Table 1. Herein we report the characterization of the basic electronic properties and, for the first time, the photoelectrochemical behavior of ZnSiAs<sub>2</sub> single crystals. Techniques including Hall effect, Mott–Schottky measurements, photocurrent spectroscopy, and photocurrent–voltage analysis are used. The effect of different wet chemical etchants on the junction properties is also reported.

## Experimental Section

**Crystal Growth.** Single crystals of ZnSiAs<sub>2</sub> were synthesized by chemical vapor transport. Stoichiometric quantities of Zn, Si, and As (Johnson Matthey, 99.999%) as powdered elements and the transport agent TeCl<sub>4</sub> (0.63 wt %) were introduced into a quartz ampule, which was then evacuated to about 10<sup>–6</sup> Torr and sealed. The ampule was placed in a two-zone furnace and preheated at 750 °C for 24 h with the growth zone maintained 950 °C to prevent transport and promote reaction. The furnace was then programmed to give the temperature necessary for single-crystal growth with the hot-zone at 965 °C and growth-zone at 940 °C. The transport took 20 days with a temperature gradient of 1–1.5 °C/cm. The crystals usually occurred as bars or small flat plates of a few millimeters on a side. X-ray powder diffraction was used to verify that crystals had the expected lattice parameters and EDAX was used to verify the elemental composition. The unintentionally doped materials were p-type.

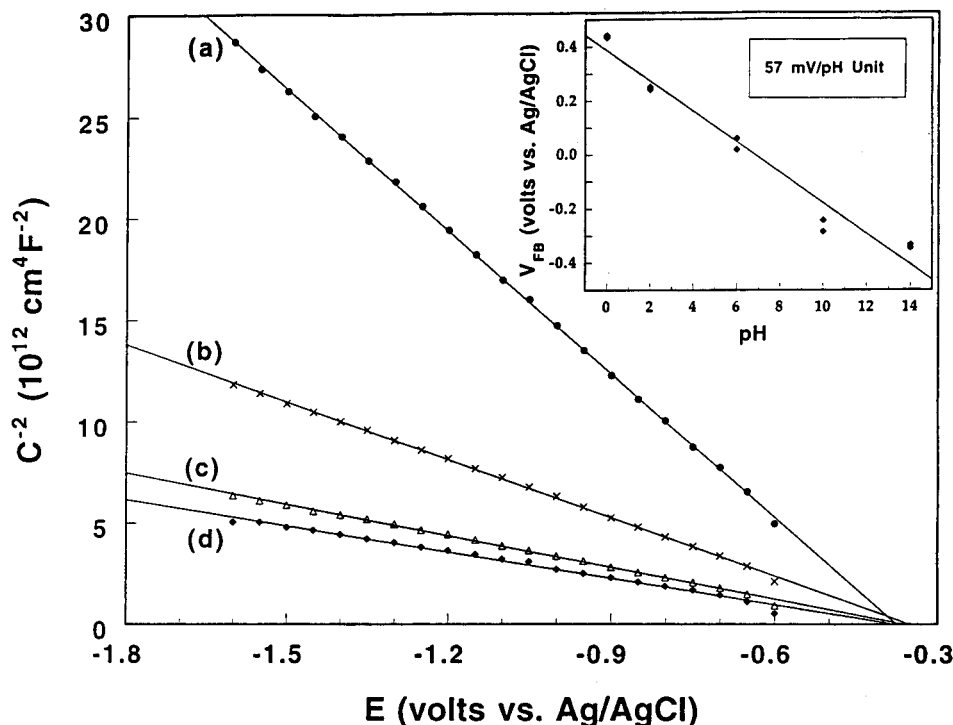
**Ohmic Contact/Hall Measurements.** For the investigations of the electrical properties, ohmic contacts were made by etching the single-crystal samples in 24% HF and then 7 N HNO<sub>3</sub> for several seconds and then rinsing, followed by attaching copper wires with gold epoxy directly on the samples. Poor electrical contacts sometimes were improved by arcing with a gold wire. The voltage and time of the arcing was between 10 and 17.5 V and 0.1 and 1.0 s. Electrodes were prepared by first making low-resistance contacts to crystals with gold epoxy, followed by arcing with the gold wire and then securing them to a small copper plate. The copper plate was then connected to a wire and mounted at the end of a glass tube. Epoxi-Patch epoxy was used to insulate the copper and all but the desired crystal face. The electrical resistivity and Hall-effect measurements were carried out between 80 and 300 K with van der Pauw geometry using a computer-controlled data acquisition system (Models K-20 and H-50, MMR Technologies, Inc.).

**Photoelectrochemical Characterization.** Mott–Schottky (*C*<sup>–2</sup>–*V*) plots were obtained using a computer-controlled

<sup>†</sup> This paper is dedicated to the memory of Professor Heinz Gerischer, whose leadership, integrity, and intellect started and kept the field of photoelectrochemistry on a fruitful path for many years.

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**Figure 1.** Mott-Schottky plots of p-ZnSiAs<sub>2</sub> in 1 M NaOH. Modulation frequencies were the following: (a) 10 kHz, (b) 5000 Hz, (c) 2000 Hz, (d) 1000 Hz. Modulation amplitude: 20 mVpp. Inset: Flat-band potential as a function of pH for p-ZnSiAs<sub>2</sub>. Buffers used: pH = 2, HOOCCH<sub>2</sub>COOK + H<sub>3</sub>PO<sub>3</sub>; pH = 6, Na<sub>3</sub>PO<sub>4</sub> + K<sub>3</sub>PO<sub>4</sub>; pH = 10, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> + Na<sub>2</sub>CO<sub>3</sub>.

**TABLE 1: Summary of Photoelectrochemical Data for ZnSnP<sub>2</sub> and CdSnP<sub>2</sub>**

II-IV-V <sub>2</sub> crystals	bandgap (eV)	doping density (cm <sup>-3</sup> )	flat-band potential (V)	quantum yield (max %)
ZnSnP <sub>2</sub>	1.64 (chalcopyrite)	$3 \times 10^{16}$ to $4 \times 10^{18}$ (p)	-0.05	~20 (700 nm)
(ref 16)	1.24 (sphalerite)			
CdSnP <sub>2</sub>	1.17	$\sim 8 \times 10^{17}$ (n)	-1.17	~50 (800 nm)
(ref 15)				

capacitance measurement system. The frequency and the amplitude of the ac signal were set at 5 kHz and 10 mV, respectively. Phase shifts due to the instrumentation were compensated using an external dummy cell. Photocurrent spectra were measured with an automated system that controls the monochromator, collects photocurrent data, and corrects for the lamp spectrum from a 50 W tungsten lamp. Photocurrent-voltage data were measured every 20 mV using chopped monochromatic light, a lock-in amplifier, and a computer-controlled data collection system. VCl<sub>3</sub>-VCl<sub>2</sub>-HCl, Na<sub>2</sub>S-Na<sub>2</sub>S<sub>2</sub>-NaOH, and the other redox electrolytes were prepared from reagent-grade chemicals which were used as received with water purified through a Millipore ion exchange system with an organic absorption column. The photoelectrochemical measurements were carried out using a three-electrode system with a platinum counter electrode and a Ag/AgCl reference electrode. The semiconductor electrode was routinely treated in 1 M HCl prior to every measurement. The effect of a variety of etchants (24% HF, 6 M HCl, 5 M KOH, 7 N HNO<sub>3</sub>, and aqua regia) on quantum yield was also investigated.

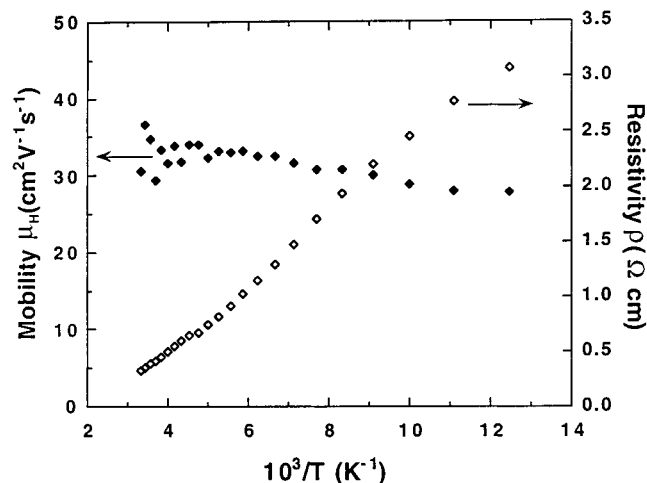
## Results and Discussion

Figure 1 shows Mott-Schottky plots obtained for a p-ZnSiAs<sub>2</sub> electrode in 1 M NaOH solution. These plots show close to linear behavior with little frequency dispersion in the 1–2 kHz range. However, larger dispersion is apparent above 5 kHz. The flatband values, obtained from the intersection of

the linear fit of the potentials in the depletion region with the x axis, varied between -0.38 and -0.35 V (vs Ag/AgCl).

The pH dependence of  $V_{FB}$  was investigated by measuring the Mott-Schottky behavior in a variety of buffer solutions and redox electrolytes. The results of the pH study are plotted in the inset in Figure 1 for a typical p-ZnSiAs<sub>2</sub> electrode. The slope of the pH dependence of  $V_{FB}$  was 57 mV/pH unit, close to the value of 59 mV/pH unit expected for an oxide semiconductor surface in ionic equilibrium with protons. The flatband potential obtained from the intercept of the Mott-Schottky plot at 5 kHz in sulfide/polysulfide (pH  $\approx$  14.3) solution was -0.37 V (vs Ag/AgCl), in agreement with the value measured in NaOH solution. The doping density obtained from the slope of the plot was  $3.8 \times 10^{17}$  cm<sup>-3</sup>, which agrees with the values obtained with the Hall technique ( $(3-5) \times 10^{17}$  cm<sup>-3</sup>), albeit on a different crystal from the same growth run. The resistivity and mobility values for temperatures between 80 and 300 K obtained from the Hall measurement are plotted in Figure 2. The small resistivities, 0.3–3.1  $\Omega$ -cm, are in agreement with literature values for crystals with similar doping densities.<sup>17</sup> The mobility of the majority of carriers ( $28-37$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) is 4–5 times smaller than measured by the van der Pauw method on crystals prepared either by horizontal vapor phase transport or by the Bridgman method.<sup>18,19</sup> These measurements are summarized and compared with literature values in Table 2.

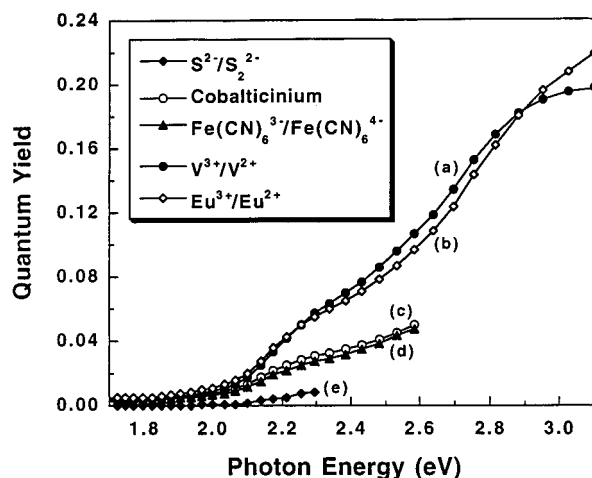
The photocurrent spectra (Figure 3) for a p-type ZnSiAs<sub>2</sub> sample in various electrolytes (S<sup>2-</sup>/S<sub>2</sub><sup>2-</sup>, Fe(CN)<sub>6</sub><sup>3-</sup>/Fe(CN)<sub>6</sub><sup>4-</sup>, cobalticinium, Eu<sup>3+</sup>/Eu<sup>2+</sup>, and V<sup>3+</sup>/V<sup>2+</sup>) show a gradual photocurrent onset at about 1.7 eV, followed by a more abrupt increase in the photoresponse above 2.0 eV. The quantum yields are close to 20% for wavelengths around 400 nm in Eu<sup>3+</sup>/Eu<sup>2+</sup> and V<sup>3+</sup>/V<sup>2+</sup> electrolytes. The larger quantum yields may be explained by a better overlap of the electrons in the conduction band of p-type ZnSiAs<sub>2</sub> electrodes with the empty states of the redox couples with more negative redox potentials and the relative transparency of these redox solutions in this wavelength region. Fitting the photocurrent spectra to power laws and



**Figure 2.** Electrical resistivity and Hall mobility vs reciprocal temperature for a typical p-ZnSiAs<sub>2</sub> crystal.

**TABLE 2: Comparison of Photoelectrochemical Result of p-ZnSiAs<sub>2</sub> with Values from Other Sources**

parameter	PEC value (this work)	ref 18	ref 19
doping density	$3.8 \times 10^{17}$ ( $3-5$ ) $\times 10^{17}$	$3.6 \times 10^{17}$	$1.83 \times 10^{15}$ (cm <sup>-3</sup> )
hole mobility	28–37 (Hall)	136	121 (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
resistivity	0.57 (Hall)	0.13	28 (Ω cm)

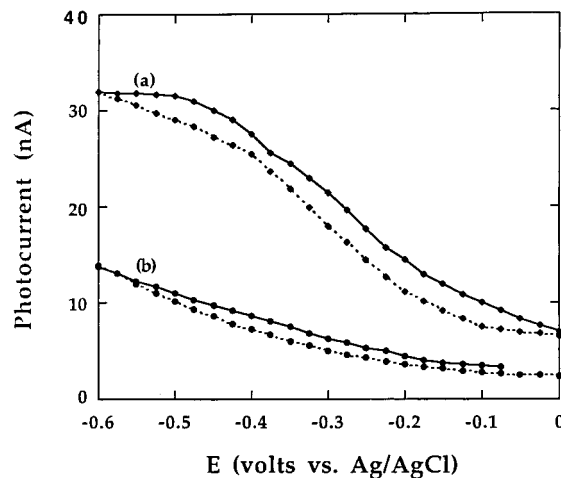


**Figure 3.** Photocurrent spectra of p-ZnSiAs<sub>2</sub> in (a) V<sup>3+</sup>/V<sup>2+</sup>, (b) Eu<sup>3+</sup>/Eu<sup>2+</sup>, (c) cobalticinium, (d) Fe(CN)<sub>6</sub><sup>3-</sup>/Fe(CN)<sub>6</sub><sup>4-</sup>, and (e) S<sup>2-</sup>/S<sub>2</sub><sup>2-</sup> electrolytes.

**TABLE 3: Summary of Measured and Literature Bandgaps**

	bandgap	
	indirect (eV)	direct (eV)
this work		
in S <sup>2-</sup> /S <sub>2</sub> <sup>2-</sup>	1.74	2.02
in Fe(CN) <sub>6</sub> <sup>3-</sup> /Fe(CN) <sub>6</sub> <sup>4-</sup>	1.72	2.00, 2.23
ref 7	1.74	
ref 11		2.12, 2.22, 2.44
ref 12		2.16, 2.25, 2.49

extrapolating to the corresponding photon energy resulted in direct energy gaps at about 2.01 and 2.23 eV. An indirect bandgap was also found at about 1.74 eV using the square root of the photoresponse in this energy region. Table 3 shows a summary of the bandgaps obtained from photoelectrochemical techniques in comparison to literature data obtained by electroreflectance (ER) measurements. The transitions above 2.0 eV were interpreted as pseudodirect energy gaps corresponding to the  $E_0$  and  $E_0 + \Delta_0$  direct energy gaps in zinc blende.

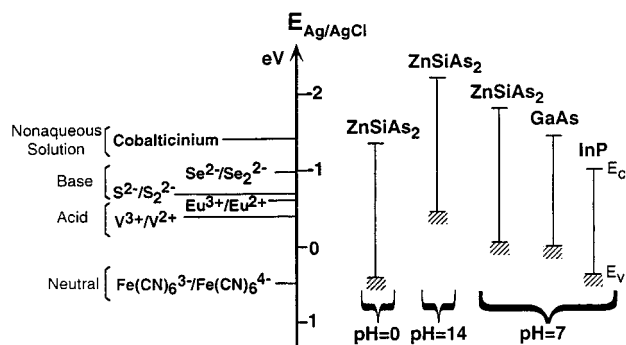


**Figure 4.** Photocurrent–voltage behavior of p-ZnSiAs<sub>2</sub> in (a) V<sup>3+</sup>/V<sup>2+</sup> and (b) S<sub>2</sub><sup>2-</sup>/S<sup>2-</sup> solution illuminated with 13 W of 550 nm light.

Additional structures due to pseudodirect transitions (direct in chalcopyrite derived from indirect in zinc blende) were also observed above 3.0 eV by ER.<sup>11,12</sup> It is clear from this study that the lowest transition in ZnSiAs<sub>2</sub> is indirect, as is the case for the isoelectronic GaAlAs<sub>2</sub> alloy. The indirect transition makes optoelectronic applications involving the emission of light, such as LEDs or lasers, unlikely for this material. For solar cells, the direct transitions only 0.3 eV higher energy than the indirect transition will result in strong absorption of light of energies 0.3 eV above the bandgap, and losses due to short diffusion lengths of photogenerated carriers may be limited to the 1.7–2.0 eV region of the solar spectrum. The maximum open circuit voltage will still be limited by the 1.7 eV indirect transition however. The main use of the material in a photovoltaic device would most probably be in a top or window material of a heterojunction cell.

Photocurrent–voltage curves of p-ZnSiAs<sub>2</sub> electrodes in different aqueous redox solutions (S<sup>2-</sup>/S<sub>2</sub><sup>2-</sup>, V<sup>3+</sup>/V<sup>2+</sup>) illuminated with monochromatic light ( $E_{\text{photon}} \approx 2.25$  eV, 550 nm) are shown in Figure 4. The figure shows that the photocathodic current in the vanadium electrolyte is higher than that in the polysulfide electrolyte for this crystal. The formation of a blocking layer of ZnS on the electrode surface is a possibility for the smaller yield in sulfide solution; however, the small change in flat-band potential in strongly basic solutions with or without sulfide ion being present argues against formation of such a layer. Future studies using X-ray photoelectron spectroscopy will shed some light on this problem. The energy positions of the bands in acid and basic electrolytes and the position of the redox levels of the redox electrolytes are schematically shown in Figure 5. As can be seen from the figure, the conduction band of ZnSiAs<sub>2</sub> is at quite negative potentials ((–1.4)–(–2.2) V) depending on the pH of the solution. The conduction band energies of similar III–V materials are about –1.0 and –1.4 V vs Ag/AgCl for InP and GaAs, respectively.<sup>20</sup> The more nearly isoelectronic GaAlAs<sub>2</sub> alloys' conduction band is at –1.7 V.<sup>21</sup>

We investigated the effect of various surface etchants on the quantum yield for photocurrent production measured in V<sup>3+</sup>/V<sup>2+</sup> electrolytes under illumination with the 488 nm line of an Ar ion laser. The potential of the ZnSiAs<sub>2</sub> electrode was kept at –0.6 V vs Ag/AgCl, and the measured quantum efficiencies of as-grown crystals were in the range of 0.6–7.2% for electrodes made from different crystals. Each individual electrode was then used for each experiment with acid etching. One of the electrodes showed the quantum yield improved by a factor of about 2 after etching in 7 N HNO<sub>3</sub> for 30 s. Another



**Figure 5.** Energy positions of the bands of  $\text{ZnSiAs}_2$  (at pH = 0, 7, and 14) and similar III-V semiconductors, and the position of the redox potentials relative to the Ag/AgCl electrode. The pH values for various electrolytes:  $\text{S}^{2-}/\text{S}_2^{2-}$  (14.3);  $\text{Eu}^{3+}/\text{Eu}^{2+}$  (−0.78);  $\text{V}^{3+}/\text{V}^{2+}$  (−0.81);  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  (−7.0).

electrode showed a larger improvement in quantum yield of about 6 times to 3.96% by 8 repeated sequential etches in 7 N  $\text{HNO}_3$  and 24% HF for 15 s each. This improvement may be explained by the acids' ability to oxidize the metal layers or remove the silicon oxide from the surface of the crystals. Short-time etching with aqua regia (10 s) and 6 N HCl (30 s) also showed an improvement of the quantum yields by a factor of 1.4 and 1.1, respectively. It is clear that a more complete systematic study of etching and the related surface condition would be desirable; however, the cumulative effects of etching and the differences from crystal to crystal make such a study difficult.

The sensitivity of the interfacial electron transfer rate and the competing surface recombination rate to the surface condition associated with the different etchants emphasizes that the surface chemistry of a material is very important for the stability and efficiency of the illuminated photoelectrochemical cell. The surface of p-InP was shown to be stabilized by the formation of a thin layer of  $\text{In}_2\text{O}_3$  on the surface.<sup>22–25</sup> Stable and efficient photovoltaic cells using the  $\text{V}^{2+}/\text{V}^{3+}$  redox couple could be made from this material. In addition, by plating Pt islands onto the surface of p-InP, hydrogen evolution could be efficiently accomplished.<sup>26</sup> p- $\text{ZnSiAs}_2$  has very negative conduction band energy, making it potentially useful for hydrogen evolution or other reduction reactions useful for energy storage such as  $\text{CO}_2$  reduction. The potential for a surface stabilized and passivated by  $\text{SiO}_2$ , such as that formed on the surface of Si itself, makes further study of the surface chemistry of Si-containing II-IV- $\text{V}_2$  materials of interest to both photoelectrochemical and photovoltaic energy conversion as well as other optoelectronic applications. Such studies are under way in our laboratory and will be reported in future publications.

## Conclusion

Photoelectrochemical techniques have been used to characterize the solid state and interfacial properties of the potential solar cell material  $\text{ZnSiAs}_2$ . The bandgap, doping level, and carrier type of crystals grown with chemical vapor transport were determined using solid–liquid junctions. In addition Hall effect

and resistivity measurements were performed as a comparison with some of the photoelectrochemically determined parameters. The results indicate that  $\text{ZnSiAs}_2$  could be used as a material for solar energy conversion provided better carrier mobilities could be obtained with more refined crystal growth techniques or methods of thin film growth of high-quality polycrystalline material could be developed.

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