Photovoltaic Response of Natural Kesterite Crystals

Brandon Durant and B. A. Parkinson

Department of Chemistry and School of Energy Resources

University of Wyoming

Laramie, WY 82071

Phone: 307-766-9891

Email: bparkin1@uwyo.edu

Fax: 307-766-2807

Abstract

The photoelectrochemical performance of naturally occurring single and multicrystalline Kesterite or $\text{Cu}_2(\text{Zn,Fe})\text{SnS}_4$ (CZTS) is presented. Elemental analyses of the crystals indicate high sulfur to metal atomic ratios and the presence of 12.3-14.5 atomic percent of iron presumably in the 2+ metal site replacing zinc in the lattice. Raman spectroscopy indicates the possible presence of a Cu_2SnS_3 impurity phase. Photocurrent spectroscopy measurements give a bandgap of 1.61-1.63 eV, higher than most reported values for pure $\text{Cu}_2\text{ZnSnS}_4$ films. Mott-Schottky measurements show that these crystals have a high doping density of about 10^{19} cm^{-3} , that reduces to about 10^{17} cm^{-3} after a brief etch in 10% KCN (aq.) solution. Although still low, the carrier diffusion length is increased by the removal of surface defects. This work demonstrates the ability to simply and easily evaluate the photovoltaic potential for a plethora of naturally occurring semiconducting materials.

Introduction

Thin film solar cells are already making a contribution to solar electricity generation however the two favored commercial technologies, copper indium gallium diselenide ($\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ or CIGS)[1] and cadmium telluride (CdTe)[2] have issues for very large scale implementation of both the abundance (In, Te) and the toxicity (Cd, Te) of some constituent elements. Therefore semiconductors with the appropriate band gap and consisting of earth abundant materials, such as copper zinc tin sulfide or selenide (CZTSSe , $\text{Cu}_2\text{ZnSnSe}_x\text{S}_{4-x}$) or Kesterite have been the subject of increasing research and development [3-5]. Recently laboratory cells have reached up to 12.6% conversion efficiency from just 5.45% in 2005.[6][7] Both CIGS and CdTe are considered defect tolerant of forgiving materials since it is relatively easy to prepare 5-10% efficient solar cells from these materials using a variety of deposition techniques, whereas for other II-VI and related I-III-V₂ as well as earth abundant materials such as pyrite (FeS_2), solar cells of even 5% efficiency are difficult to fabricate at least partly due to native defects. Therefore it is somewhat surprising that CZTSSe appears to be somewhat defect tolerant despite being a quaternary compound with many possible vacancy and antisite defects.

Structural, vibrational, photoluminescence, and some electronic structure studies[8-22] have been reported for single crystal CZTS, CZTSe, and CZTSSe. Photoelectrochemical photocurrent measurements on single crystals have not been reported for Kesterite despite evidence for a direct correlation with completed device short circuit currents (J_{sc}) and overall photoconversion efficiency.[23]

Natural crystals have shown their usefulness in photoelectrochemical studies.[24-27] Well crystallized CZTS occurs in nature as the mineral Kesterite that can be found up to dimensions of 1 cm or larger. Therefore we thought it would be interesting to examine the photovoltaic response of some natural Kesterite crystals and investigate their impurity levels to perhaps gain some insight into the performance of CZTS thin films. Surprisingly, single crystals of some chalcogenide absorber materials such as CdTe [28] and CIS[29] show disappointingly low photocurrents compared to thin film devices due to enhanced minority carrier collection at grain boundaries in polycrystalline films.[30][31] Although this compassion has not been extensively done for CZTSSe, similar phenomena might be expected.

Experimental

A natural Kesterite crystal was obtained from a well-known deposit in the Xue Bing Mountains in the Sichuan Province in China. The large crystal was cut into smaller pieces. Kesterite from this locality are often coated with a blue-green film of the mineral Mushistonite ($(\text{Cu,Zn,Fe})^{2+}(\text{Sn}(\text{OH})_6)$) that was removed by immersing them in concentrated HCl (Fisher Sci. Fair Lawn, NJ). Kesterite pieces were then cut using a slow speed diamond saw (MTI Corp., Richmond, CA) from larger pieces of the natural crystal and faces with a (110) orientation were easily cleaved with a razorblade with 9.5 and 17 mm² active surface areas. Other crystals with similar elemental composition and sizes were also etched in a 10%wt KCN aqueous solution. These 2-4 mm thick crystal slabs were mounted onto copper disks with conductive In/Ga paste for ohmic contact and potted in epoxy (Epoxy Patch) to insulate the metallic substrate from electrolyte solutions. The smaller sample is referred to as the Small Kesterite (SK) and

the larger as the Large Kesterite (LK). The pieces had a DC resistance, measured using a multimeter, on the order of several k Ω s to the back contact.

Raman spectra were collected by an IM-52 spectrometer (Snowy Range Instruments) with a 532nm laser excitation source. Elemental analysis was performed by energy dispersive X-Ray spectroscopy using a scanning electron microscope (FEI Quanta 450 FEG) with pure metal standards. Photoelectrochemical measurements were performed with in-house fabricated electrochemical cells with 10mM cobalticinium hexafluorophosphate (Strem Chemicals, Newburyport, MA) and 100mM tetrabutylammonium hexafluorophosphate ($E^0 = -0.755$ V vs Ag wire) (Sigma Aldrich, St. Louis, MO) as redox couple and electrolyte respectively in acetonitrile (Fisher Sci.). Acetonitrile was chosen over water to provide a broader potential window for electrochemical measurements and for a reduced likelihood of corrosion. Platinum and silver wires were used as counter and pseudo-reference electrodes, respectively. Transient photocurrent and Mott-Schottky measurements were performed with an Ivium CompactStat potentiostat with photocurrent interrupted by hand chopping a 40 mW (as measured by power meter through cell with electrolyte) 532nm laser.

Incident Photon to Current Efficiency (IPCE) spectra were collected at 2nm intervals with 100W Oriel tungsten lamp, computer controlled monochromator, Stanford Research Systems model SR830 DSP lock-in amplifier, 450 nm cutoff filter and in-house software utilizing a thermopile and ThorLab C-series photodiode detector to measure the photon flux. The applied potential for IPCE and chronoamperometric measurements was -0.5 V vs Ag wire.

Results and Discussion

Figure 1 shows an optical microscopic image of the Large Kesterite (LK-21.8 mm² exposed area) and Figures 2a and 2b show scanning electron microscopy (SEM) images for the Large Kesterite and Small Kesterite (SK-6.3 mm²) pieces obtained from cutting the larger mineral crystal with a diamond saw. Using a razor blade to score the crystals, both pieces exposed smooth cleavage faces from the larger crystal. The larger sample was polycrystalline with smooth faces and smaller crystal grains while the small sample showed 2 smooth exposed faces. Five areas of the LK and 3 areas for the SK samples were investigated using EDX to obtain the elemental composition. Elemental analysis shown in Table 1 reveals that the crystal is rather sulfur rich, with a S/metal atm% ratio greater than one for all areas except the third area on the SK. Both crystals showed a 12.3-14.5% Fe that is probably occupying a 2+ metal site replacing Zn as is expected for the natural mineral from this locale.[32] The SK sample shows a lower Fe/Zn ratio. After exposing a crystal to an aqueous 10%wt KCN solution for 90 seconds, the stoichiometry was similar to the LK and SK samples indicating there wasn't a change in the bulk composition which is expected from a short etching procedure.

Raman spectra (Figure 3) confirmed presence of the Kesterite phase with peaks at 338-341 and 288-291 cm⁻¹ matching those of synthetic CZTS single crystals. Peaks at 355 cm⁻¹ were present in both the Large and Small Kesterite pieces that have been associated with the monoclinic Cu₂SnS₃ (CTS) phase, an unwanted impurity in CZTS thin films since it lowers the power conversion efficiencies of finished devices. The CTS phase also has a vibrational mode at 290 cm⁻¹ that is coincident with a CZTS peak. No

distinct Raman peaks from ZnS were evident, but this phase not distinguishable in Raman spectra with 532nm excitation. Recent reports discuss the difficulty of quantitative analysis of these common secondary phases, but any detection indicates a relatively high presence.[33]

Figure 4 show chopped light voltammetry measured by illuminating 5 different areas of the LK and one area after etching with a 10%wt KCN (aq.) solution for 90 seconds. The SK sample showed similar photocurrents as the LK sample. Both samples showed p-type behavior with high anodic dark currents in the positive potential range (forward bias) and some cathodic photocurrents at more negative potentials (reverse bias). The photocurrent onset was approximately +0.1 V vs a Ag wire and the photocurrent increased with more negative applied potentials associated with increased band bending and thicker space charge layer at semiconductor/electrolyte junction allowing for more efficient extraction of minority carriers (electrons in the case of p-type materials). Residual dark currents are possibly due to the reduction of dissolved O₂ in the acetonitrile or some corrosion of the Kesterite.

Chronoamperometry with 40mW 532nm laser illumination at -0.5 V vs a Ag wire showed photocurrents of 40 and 50 nA for the LK and SK samples respectively, indicating that the quantum efficiencies are quite low. High photocurrent yields are not expected due to the presence of Fe in the material as well as the Cu₂SnS₃ impurity phase where both have been shown to degrade efficiencies.[34][35] The slow rise and fall of the cathodic photocurrent current is probably related to the high series resistance and resulting large RC time constant. The higher photocurrents in the SK sample could be attributed to the lower Fe content than the LK sample.

The KCN solution is a commonly used etching procedure and shows greatly enhanced photocurrents from the 10's nA to over 1 μ A. It has been known that KCN etching removes Cu_xS/Se secondary phases [36-39] of CIGSSe and CZTSSe thin films by preferentially removing Cu, chalcogens, and also to a lesser extent Sn [40][41]. Because the short etching time only affects the surface composition of the absorber layers and not the bulk composition, most have concluded that it beneficially lowers the surface defect density of the CZTSSe/CdS interface. In our study, we are able to photoelectrochemically investigate the Kesterite/electrolyte interface without the need for CdS deposition to fabricate a solid state device. Therefore the photocurrent enhancement is likely due to improvement in near surface carrier collection efficiency and lowering of surface defect density and trap states that would lower the surface recombination rate.

The spectral response of the SK sample and post KCN sample were measured in the same electrolyte and electrochemical cell with the monochromatic light illuminating the entire exposed crystal surface. As seen in Figure 5, a clear rise in the incident photon current efficiency (IPCE) was observed around 775 nm (1.6 eV). Nonzero photocurrents at longer wavelengths were also measured. This sub-bandgap response or band tailing is usually attributed to lattice disorder or impurities with states in the band gap.[42] There is evidence that the crystal also showed multiple band gaps by the increase in IPCE at wavelengths below 600nm. Figure 6 shows the direct band gap estimated by plotting $[IPCE/(1-IPCE)*hv]^2$. [43] The linear region x-axis intercept was 1.61 eV for the SK piece (A) and 1.63 eV for the post KCN piece (B), a value higher than most reported CZTS films perhaps due to the incorporation of Fe into the Kesterite structure. Pure stoichiometric CZTS has been reported to have a band gap around 1.5

eV.[44] Etching in KCN solution produces a less noisy IPCE spectrum with higher quantum yields and slightly increased the bandgap to 1.63 eV.

Mott-Schottky analysis (Figure 7) of a pre etched crystal showed a negative slope that was characteristic of p-type material indicating carrier concentrations of $7.6\text{--}7.8 \times 10^{18} \text{ cm}^{-3}$. The carrier concentration for the LK and SK samples were 1.6×10^{19} and $8.5 \times 10^{19} \text{ cm}^{-3}$ respectively (not shown). The AC series resistance was 5-7 k Ω , in agreement with the DC measurements of the mounted crystals. The high doping density results in very shallow (<8nm) calculated space charge layer thickness. Even a high absorption coefficient at 532nm ($3.0 \times 10^5 \text{ cm}^{-1}$) [45] results in an absorption depth of 33nm partially explaining the low collection of minority carriers at most visible wavelengths. Carrier diffusion lengths are also expected to be low due to defects and impurities.

Etching with a KCN solution also influenced the Mott-Schottky results for the natural Kesterite mineral. Prior to etching, the slope of the Mott-Schottky plot was shallow (higher doping density) and the x-axis intercept (associated with the flat band potential) was highly positive. After etching, the slope was steeper associated with a lower effective doping density ($\sim 10^{17} \text{ cm}^{-3}$). The lower doping density results in a thicker space charge layer thickness, and collection of more carriers by the electron scavenger in solution. Additionally the intercept was a more physically reasonable +0.5 V vs Ag wire, much closer to the photocurrent onset potential noticeable around +0.35 V.

Conclusion

Although two single crystal Kesterite samples both showed low photocurrent yields they allowed the measurement of their spectral response indicating a bandgap of 1.61 eV, slightly larger than the 1.5 eV reported for pure $\text{Cu}_2\text{ZnSnS}_4$. [44] The large amount of Fe impurities (12.3-14.5% presumably in the 2+ cationic site) as well as possible Cu_2SnS_3 phases results in very low photocurrent yields. However, etching the surface in 10%wt KCN (aq.) improves the photocurrent yields, presumably by removing many surface defects and producing a thicker space charge layer. The large number of semiconducting natural minerals provides an opportunity to take advantage of the naturally provided crystals to assess the photovoltaic potential of these many compounds.

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Figure 1

Photograph of Kesterite crystal prior to cutting (a) and optical microscope image of the Large Kesterite crystal piece (b)

a

b

Figure 2

Scanning Electron Microscope images of Large (a) and Small Kesterite (b) pieces.

a

b

HV	det	HFW	WD	pressure	3 mm	HV	det	HFW	WD	pressure	3 mm
20.00 kV	ETD	7.79 mm	12.3 mm	2.92e-5 Torr		20.00 kV	ETD	7.28 mm	10.9 mm	2.57e-6 Torr	

Table 1

Summary of elemental analysis results from Energy Dispersive X-Ray Spectroscopy of Large Kesterite (5 areas), Small Kesterite (3 areas), and Post KCN etched (4 areas) samples. Standard deviation is a result of analyses of multiple points within an area (12 per area).

Crystal/Area	S/metals	Cu/Fe+Zn+Sn	Fe+Zn/Sn	Fe/Zn	Fe/Fe+Zn	Cu/Fe+Zn
Large/1	1.211 ± .013	0.957 ± .011	.956 ± .011	.162 ± .004	.139 ± .003	1.96 ± .03
Large/2	1.101 ± .004	.988 ± .008	1.032 ± .009	.155 ± .004	.135 ± .003	1.95 ± .02
Large/3	1.190 ± .014	.958 ± .012	.974 ± .012	.167 ± .004	.143 ± .004	1.94 ± .03
Large/4	1.135 ± .009	.982 ± .010	1.007 ± .016	.169 ± .005	.145 ± .004	1.96 ± .02
Large/5	1.094 ± .127	.990 ± .044	1.051 ± .114	.166 ± .008	.142 ± .006	1.94 ± .03
Small/1	1.266 ± .006	.939 ± .008	.948 ± .012	.154 ± .004	.133 ± .003	1.93 ± .02
Small/2	1.270 ± .007	.942 ± .008	.943 ± .011	.156 ± .005	.135 ± .004	1.94 ± .02
Small/3	.849 ± .005	1.087 ± .012	1.276 ± .018	.141 ± .003	.123 ± .003	1.94 ± .02
PostKCN/1	1.073±.020	.999±.017	1.044±.031	.152±.010	.132±.008	1.957±.054
PostKCN/2	1.158±.010	.971±.022	.999±.018	.155±.010	.134±.005	1.942±.050
PostKCN/3	1.125±.012	.975±.015	1.007±.022	.153±.008	.133±.006	1.943±.035
PostKCN/4	1.096±.010	.993±.018	1.020±.025	.156±.008	.135±.006	1.968±.053

Figure 3

Raman Spectra of synthetic CZTS single crystal (black), the Large Kesterite (red) and the Small Kesterite (blue) samples using a 532 nm laser excitation. Peaks at $288\text{-}291\text{ cm}^{-1}$ and $338\text{-}341\text{ cm}^{-1}$ match with reported CZTS stretches and single crystal CZTS. Shoulders at 355 cm^{-1} have been associated with the Cu_2SnS_3 (monoclinic) phase.

Figure 4

Chopped photocurrent voltammetry of the large kesterite piece (LK) and post KCN etched piece in contact with 10mM cobaltacinium hexafluorophosphate and 100mM tetrabutylammonium hexafluorophosphate in acetonitrile solution while chopping a 40mW 532nm laser while illuminating different areas of crystals (25 mV/s scan rate).

Figure 5

Incident Photon to Current Efficiency (IPCE) spectrum of the Small Kesterite piece (A) and post KCN piece (B) in contact with 10mM cobaltacinium hexafluorophosphate ($E^0 = -.755\text{V}$ vs Ag wire) and 100mM tetrabutylammonium hexafluorophosphate in acetonitrile solution at -0.5V vs Ag wire bias using a lock-in amplifier with a chopping frequency of 17 Hz.

Figure 6

Determination of the bandgap of small kesterite piece (A) and post KCN piece (B) based on the assumption that it is a direct bandgap material.

Figure 7

Mott-Schottky plots for negative to positive potential sweeps of pre (dark blue) and post (red) as well as positive to negative potential sweeps of pre (open light blue) and post (open pink) KCN etched crystals. The pre etching crystal acceptor densities were calculated to be $7.6\text{--}7.8\text{E}18\text{ cm}^{-3}$, whereas the post etching densities were $6.3\text{--}8.8\text{E}17\text{ cm}^{-3}$. The intercepts also significantly changed from +2.1 V vs Ag wire to +.5 V vs Ag wire.