AN ABSTRACT OF THE DISSERTATION OF

Peter A. Hersh for the degree of Doctor of Philosophy in Chemistry presented on the 4th of October 2007
Title: Wide Band Gap Semiconductors and Insulators: Synthesis, Processing and Characterization

Abstract approved: _____________________________________________________

Douglas A. Keszler

The work presented here is focused on applying basic principles of solid-state chemistry to the study and development of new wide band-gap semiconductors and insulators for photovoltaic and electronic-device applications. Analysis of crystal structure, band structure, optical band gap, morphology and transport properties provides fundamental insight into materials performance as well as determining potential applications. Efforts on the study and development of wide band-gap semiconductors with emphasis on absorber layers and window layers for multijunction solar cells are presented in chapters 2-6. A new process for solution-deposited and composition control of insulating oxide films is presented in chapters 7 and 8.
Doctor of Philosophy dissertation of Peter A. Hersh
presented on October 4, 2007

APPROVED:

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Major Professor, representing Chemistry

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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My Signature below authorizes release of my dissertation to any reader upon request.

_____________________________________________________________________
Peter A. Hersh, Author
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<tr>
<td></td>
<td>(M = Hf or Zr) pellets used in Seebeck measurements to determine carrier type</td>
</tr>
</tbody>
</table>
INSULATORS AND WIDE BAND GAP SEMICONDUCTORS: SYNTHESIS, PROCESSING AND CHARACTERIZATION

CHAPTER 1

INTRODUCTION
The work presented here is focused on applying basic principles of solid-state chemistry to improve current technologies in photovoltaic and semiconductor applications. Analyzing different properties of a material such as crystal structure, band structure, optical band gap, morphology, and transport properties can determine potential applications. Materials for use in thin-film photovoltaic applications such as absorber layers and window layers for multijunction cells are presented in chapters 2-6. Materials for use in semiconductor applications such as thin-film and printed transistors (TFTs) are presented in chapters 7 and 8.

PHOTOVOLATIC CELLS

Photovoltaic (PV) cells absorb light (photons) from the sun and convert it to electricity. All photovoltaic cells consist of a $p$-type layer, i.e., majority hole carriers, and an $n$-type layer, i.e., majority electron carriers. Some cells contain an intrinsic layer having a very low carrier concentration. These layers form a diode in the form of a $p-n$ or $p-i-n$ junction that enables current to flow when electron-hole pairs (carriers) are created. Carriers are created when light is absorbed causing electrons from the valence band to be excited to the conduction band. A schematic energy level diagram for a generic $p-i-n$ PV cell is illustrated in Figure 1.1. The N-layer represents a top $n$-type transparent conductor; the I layer represents a photon absorber film, and the P-layer represents a $p$-type window film (or back contact in a single junction cell). The $p$ and $n$ layers create an electric-field gradient in the I layer. The presence of this gradient is crucial to creating electron flow.
Figure 1.1. Energy-level diagram for a generic p-i-n thin-film photovoltaic cell
Upon exposure to light (hv) electrons in the valence band (VB) of the absorber are excited to the conduction band (CB). Because the presence of the electric field across the I layer, excited electrons flow toward the n-type layer, and holes migrate toward the p-type layer creating the current generated in the PV cell.

The figure of merit for a PV cell is efficiency (\(\eta\)) (Eq. 1.1),

\[
\eta = \frac{P_{\text{max}}}{E_{\text{tot}} A} \times 100 \quad \text{(Eq 1.1)}
\]

where \(P_{\text{max}}\) = peak power, \(E_{\text{tot}}\) = the total energy of irradiance, and \(A\) = the cell area [1,2]. The efficiency measurements are made under conditions established and maintained via ASTM standards [3]. For example, a PV cell having an area of 1 m\(^2\) with \(\eta = 13\%\) will produce 130 W of energy when illuminated by ASTM standard 1000 W/m\(^2\) light.

\(P_{\text{max}}\) and thus the efficiency in a PV cell is limited by two opposing factors. These factors are the short circuit current density (\(J_{\text{SC}}\)) and the open circuit voltage (\(V_{\text{OC}}\)). The short circuit current density is directly related to the number of electron-hole pairs created from light absorption of the material. Materials that absorb large portions of the solar spectrum allow for larger short circuit currents. The open circuit voltage is directly related to the optical band gap of the material. Larger band gap materials allow for larger open circuit voltages. Increasing the band gap of a material increases the maximum obtainable open circuit voltage, but decreases the portion of the solar spectrum absorbed, which limits the maximum obtainable short circuit current. These two factors limit the obtainable \(P_{\text{max}}\) for a material at a certain band gap (Eq 1.2).
To measure $P_{\text{max}}$ a voltage sweep is performed on an illuminated cell. The short circuit current is measured at 0V. The open circuit voltage is the voltage where the current stops completely. The $V_{\text{OC}}$ obtained multiplied by the $J_{\text{SC}}$ gives the maximum available power for the cell. The cell does not reach the maximum available power due to the non-square nature of the I-V curve. This non-square factor is called the fill factor (FF). The fill factor is the percentage of the maximum available power that is actually obtained.

An important aspect of PV cells is their bipolar nature, meaning both minority and majority carriers play a role in current generation (figure 1.1). If minority carriers are to contribute to the current density, they must not recombine with the majority carriers. Recombination is reduced by long minority carrier lifetimes and large carrier mobilities, i.e., maximizing the minority carrier lifetime and minority carrier mobility improves short circuit current density and overall cell efficiency. Photoconductivity experiments can be conducted to examine the effect of minority carrier lifetime and mobility on current density, which are modeled by Equation 1.3 [4,5].

\[ J_{\text{PC}} = q \ast (\mu_n + \mu_p) G_e \ast \tau \ast \xi \]  
(Eq. 1.3)

Here, $J_{\text{PC}}$ = the current density, $q$ = charge of electron, $\mu_n$ = mobility of electrons, $\mu_p$ = mobility of holes, $G_e$ = carrier generation rate, $\xi$ = applied electric field, and $\tau$ = the minority carrier lifetime for a material under illumination. Minority carrier lifetime can be increased by reducing the defect concentration in the absorber layer [5,6]. To increase minority carrier mobility most absorber layers are $p$-type in nature. This makes the electrons the minority carrier, which is advantageous since electrons
typically have a larger mobility than holes. The larger electron mobility is associated with a highly disperse conduction band. According to Equation 1.4, this correlates to a low effective mass \((m^*)\) a long mean scattering time \(<\tau>\), or both [7].

\[
\mu = \frac{q <\tau>}{m^*} \quad \text{(Eq. 1.4)}
\]

Certain characteristics can be studied to determine if a material is a suitable candidate for use in PV applications. The absorber layer must efficiently absorb the light from the sun to produce a significant number of electron-hole pairs produced per photon QE \((\lambda)\) [1].

\[
QE(\lambda) = \frac{qS(\lambda)}{\lambda hc} \quad \text{(Eq. 1.5)}
\]

\(S(\lambda) = \text{spectral responsivity, } h = \text{Plank’s constant, } c = \text{speed of light, } q = \text{charge of electron, and } \lambda = \text{wavelength.} \)

Materials with larger absorption coefficients absorb light at a higher rate and thus have the ability to produce more carriers per photon. Having a high absorption allows the use of thin layers in absorbing a given number of photons. A thinner absorber layer is also advantageous for decreasing the distance that free carriers must travel before exiting the absorber and contributing to the current flow. This shortened distance also contributes to a reduction in recombination probability, again leading to higher current flow [8].

Much of the research on PV cells has been focused on crystalline silicon technology. These cells consist of a \(p-n\) junction of doped silicon, which are similar to the first PV cell [9]. The large amount of research and time dedicated to silicon based photovoltaic cells has raised efficiency to near the theoretical limit of \(~28\%) [1].
little room for improvement in the crystalline silicon PV cells, considerable research has been focused on next generation thin-film PV cells. Thin-film PV cells use less material and have a higher efficiency ceiling (30.8\% for single junction) than the traditional crystalline silicon cell. Maximum cell efficiency is increased relative to the Si cell primarily by optimizing the optical band gap of the absorber layer.

Thin film PV offers many advantages, but also provides many challenges. One of the major challenges in thin film PV is forming a \textit{p-n} or \textit{p-i-n} junction. In traditional devices, silicon can be symmetrically doped \textit{p} and \textit{n} type to form a homojunction. Most materials do not exhibit this bipolar behavior (Chapter 6 provides an example of a novel bipolar material), which means the use of a heterojunction is required to form the diode-like cell. Such a junction can lead to problems such as interface carrier recombination as well unwanted interlayer diffusion and device degradation. A single-junction thin film PV cell is schematically shown in Figure 1.2.
Figure 1.2. Diagram of a thin film PV cell.
The \( n \)-type transparent conductive oxide (TCO) provides electrical contact to the front side of the PV stack without absorbing light. In most cases this layer is Al-doped ZnO or Sb-doped SnO\(_2\). The TCO layer is highly doped to make a conductive layer. To prevent the diffusion of the dopant into the rest of the thin film PV stack an intrinsic transparent oxide layer is used. To prevent the oxidation of the absorber layer a diffusion barrier layer is used. This is a non-oxide material and, it is commonly CdS. Light is absorbed and electron-hole pairs are formed in the absorber layer. The electron reflector is one of the most difficult layers to optimize. This layer must provide good contact to the absorber and prevent electrons from diffusing in the wrong direction. To form high quality ohmic contact, this layer must be heavily doped \( p \)-type. To form an effective electron reflector the band gap must be large enough to create a barrier between the absorber and the back contact, \( cf., \) Figure 1.1. One example of an electron reflector used in thin film PV is MoSe\(_2\).

The complex layer structure makes cell-performance optimization a challenging undertaking, yet it provides many opportunities for introducing new materials into the film stack. In general, changing the absorber layer requires re-engineering the entire thin-film stack. Most thin-film PV research has been focused on three types of cells: amorphous silicon (alloyed with hydrogen) (a-SiH), CdTe, and Cu(In\(_{1-x}\)Ga\(_x\))Se\(_2\) (CIGS) [10-12]. Each of these three types of thin-film photovoltaic cells has advantages and disadvantages.

The amorphous cell does not share the same stacked structure shown in Figure 1.2. Amorphous silicon is bipolar in nature, which allows for a less complex, more
traditional, homojunction device structure. Silicon is a very abundant element and thus the cost of the material in $a$-SiH PV cells is relatively low. The amorphous nature also provides the ability to make flexible photovoltaic cells which have many unique applications. Flexible cells allow for integration into solar windows and roofing tiles. However, $a$-SiH has a low theoretical efficiency because of the non-ideal character of $a$-SiH as an absorber. The bands are not well defined because of the amorphous nature, and the estimated gap $1.7\text{eV}$ is larger than ideal for a single junction [13]. The $a$-SiH also exhibits a light induced degradation known as the Staebler-Wronski effect [14].

CdTe exhibits attractive physical properties for thin-film PV, as its band gap of $1.5\text{eV}$ is nearly ideal for a single-junction device, and it is easily deposited in thin-film form via thermal evaporation. These properties have led to efforts to commercialize CdTe PV cells [15]. Efficiencies have reached over $16\%$, although they trail the theoretical limit [16]. Making high-quality ohmic contacts to $p$-type CdTe is the major hurdle that must be overcome to improve efficiency. There are also concerns about the cadmium because of its toxicity and a known carcinogenicity.

Cu(In$_{1-x}$Ga$_x$)Se$_2$ (CIGS) is currently the most efficient thin-film PV cell known. CIGS offers considerable flexibility by varying the amounts of indium to gallium the band gap can be tuned from $1.1\text{eV}$ to $1.7\text{eV}$. The two major issues associated with CIGS are scalability and raw-materials costs. Currently, the most efficient CIGS cells are produced via four-target evaporation [17]. This method of deposition is very difficult to scale while maintaining high efficiencies. The lack of any known indium-rich deposits coupled with the growing number of applications for
the metal has led to exceptionally high costs, causing concern about CIGS-based thin-film technologies for production significant power on national and global scales.

While some work has been done with other absorbers, a very considerable effort is required to develop and to engineer a full PV stack to demonstrate efficiency improvements. Nevertheless, the desire for efficient energy from the sun provides sufficient impetus to develop and examine new absorbers. In this work, I present results on new absorbers in Chapters 2, 4, and 6. In Chapter 5, production of a potential electron reflector is described.

Another advantage of thin films is the ability to stack absorbers into multiple-junction configurations, which can vastly improve the theoretical efficiency beyond a single junction cell. In multijunction photovoltaic cells, absorbers with different band gaps are incorporated to absorb different parts of the solar spectrum. In this configuration, a smaller portion of the absorbed light is converted to heat. This leads to a more efficient absorption and use of the light by the photovoltaic cell. A schematic of a triple-junction cell is shown in Figure 1.3; optimum band gaps for efficient solar absorption have been derived by Coutts [18].

Thin-film PV research has largely focused on single junction cells primarily because of the lack of suitable transparent $p$-type window materials for CdTe and CIGS cells. A $p$-type window material must have a large band gap, exhibit $p$-type behavior, and form an ohmic contact to the absorber layer. The large band gap is required to allow stacking of the absorber junctions without significant loss of useable light. The window layers must be $p$-type to complete the $p$-$i$-$n$ junction, which is required to produce electron flow in the system (Figure 1.1). To prevent carrier
recombination at the interface, the formation of an ohmic contact is also necessary. Forming such ohmic contacts requires the window layer to be a degenerate semiconductor, which occurs only at high carrier concentrations. These strict requirements coupled with process-integration issues in device fabrication have made the development of such a window a very challenging task [18].
Figure 1.3. Diagram of a triple junction photovoltaic cell
There are many known \( n \)-type wide band-gap semiconductors that can be doped to high carrier concentrations; examples include \( \text{In}_2\text{O}_3: \text{Sn} \) (ITO), \( \text{ZnO}:\text{Al} \), and \( \text{SnO}_2: \text{Sb} \). Conversely, there are very few wide band gap \( p \)-type semiconductors, and none of them are as conductive as their \( n \)-type counterparts. The difficulty in making large band-gap \( p \)-type semiconductors is well documented [19]. One of the major challenges in obtaining such a material is associated with the valence-band orbital composition. Most wide-gap materials tend to have very flat valence bands. For example most oxides have a valence band primarily composed of \( \text{O} \, 2p \) orbitals; such a band is quite flat, inducing localized behavior and very small hole mobilities.

To make the valence band more disperse, cations can be introduced that provide an energetic match and significant overlap with the anion centered levels. In oxides, these features can be achieved through incorporation of \( \text{Cu} \), where the 3\( d \) orbitals can effectively interact with the \( \text{O} \, 2p \) orbitals to produce hole conduction [20]. \( \text{Cu}_2\text{O} \) for example is a well-known \( p \)-type semiconductor exhibiting a single crystal hole mobility of \( 1.8*10^5 \, \text{cm}^2/\text{Vs} \) [21-22]. By diluting \( \text{Cu} \) in ternary oxides such as the delafossites, \( \text{CuAlO}_2 \) and \( \text{CuSeO}_2 \), transparency can be increased with retention of the \( p \)-type behavior [23,24]. But, in this structure type, there are no direct \( \text{Cu–O–Cu} \) interactions, preventing the development of a disperse valence band. As a result there is a trade-off between transparency and conductivity, increasing the optical transparency lowers the conductivity and vice-versa.

Some recent work on transparent \( p \)-type materials has focused on non-oxide and mixed-anion materials such as \( \text{BaCu}_2\text{S}_2 \), \( \text{BaCuQF} \) (\( Q = \text{S, Se or Te} \)) and \( \text{LaCuOQ} \) (\( Q = \text{S, Se or Te} \)) [25-31]. Degenerate \( p \)-type behavior is observed when the
LaCuOQ materials are doped with Mg and in undoped BaCuTeF [32-35]. Efforts to integrate BaCuTeF into a thin-film PV cell as a $p$-type window have been made because it exhibits a wide band-gap and high conductivity [36]. The work presented in Chapters 3 and 4 is focused on new alternative $p$-type window materials.

THIN FILM TRANSISTORS (TFTs)

A common type of thin-film transistor is a metal-insulator-semiconductor field effect transistor or MISFET structure that consists of a source, drain, channel, dielectric, and gate layers (Figure 1.4). The source and drain are metal contacts to inject and remove carriers from the channel layer. The channel layer is a semiconductor layer, which has low carrier concentration. The dielectric is an insulating layer that prevents current flow from the gate to the channel layers. The most common dielectric is SiO$_2$, but considerable efforts have been dedicated to developing new high performance dielectrics [37]. The gate is a conductive layer that can withstand heating to some degree. In most cases, the gate is highly doped polycrystalline Si, but other metals and silicides can be used as well.
Figure 1.4 Thin film transistor in bottom gate configuration.
The work presented here will focus on improving the gate dielectric layer in TFTs. The need to replace SiO₂ as a dielectric has become apparent. As device dimensions shrink the need to maintain high capacitance (Equation 1.6) with low leakage currents is required.

\[ C = \frac{\varepsilon A}{d} \]  
(Eq. 1.6)

Here \( C \) is capacitance, \( \varepsilon \) is relative permittivity at vacuum, \( A \) is area, and \( d \) is thickness. To obtain the high capacitance needed in small-area conventional Si CMOS devices, the SiO₂ dielectric must be scaled below 2 nm. At this thickness, SiO₂ is no longer an effective because of the large amount of tunneling current. The same level of capacitance can be reached with a physically thicker layer that has a higher permittivity. The permittivity is directly related to the dielectric constant \( \kappa \) of the material. Other factors besides dielectric constant must be taken into account, such as band gap, film morphology, interface quality, and thermodynamic stability [37].

After consideration of the various factors required for a replacement dielectric in CMOS, a few candidates have been singled out, including Al₂O₃, Y₂O₃, La₂O₃, Ta₂O₅, TiO₂, ZrO₂ and HfO₂, which all have \( \kappa \) higher than SiO₂ as well as other desirable properties [5,37-42]. In the work presented in Chapter 7, I have chosen to focus on a unique solution-based route for the production of ZrO₂ and HfO₂.
REFERENCES


CHAPTER 2

MCu$_2$SnX$_4$ (M = Ba, Sr and X = S, Se) AND PHOTOVOLTAIC APPLICATIONS

Peter A. Hersh, Robert Kykyneshi, Janet Tate, Douglas A. Keszler
ABSTRACT

The compounds MCu$_2$SnCh$_4$ (M = Ba or Sr and Ch = S and Se) were prepared via solid state reaction. Crystal structure, optical and transport properties were examined to identify possible candidates for absorber layers in thin film photovoltaic cells. The Ba analogs maintain the $P3_21$ crystal structure throughout the chalcogen substitution BaCu$_2$Sn$_{4-x}$Se$_x$ ($0 \leq x \leq 4$). For the Sr materials, SrCu$_2$Sn$_{4-x}$Se$_x$ ($0 \leq x \leq 4$) the crystal structure changes from $P3_21$ in the pure sulfide to an orthorhombic $Ama2$ form upon inclusion of selenium. BaCu$_2$SnSe$_4$, which has a band gap of 1.58 eV and a Seebeck coefficient of +66 $\mu$V/K, was chosen as the best candidate for additional studies.
INTRODUCTION

The strong spectral response observed in Cu$_2$Ch (Ch = S, Se) coupled with notable semiconductor attributes led to considerable research and development of thin-films for use in photovoltaic devices [1]. Later, inclusion of In and Ga into Cu$_2$Ch systems contributed to a large increase in conversion efficiency [2-6]. In 1999 Contreras demonstrated a 18.8% efficient Cu(In$_{1-x}$Ga$_x$)Se$_2$ (CIGS) cell [7]. Over the past eight years however, CIGS efficiencies have remained stable, while the availability of In has decreased dramatically, driving costs considerably higher. These developments have prompted our search for new composition of copper chalcogenides that do not contain high-cost indium and gallium. Solar cell efficiency is dependent on two factors the open circuit voltage and the short circuit current, which are described at length in Chapter 1. These two factors limit theoretical conversion efficiency and reduce the number of economically viable materials.

In choosing an absorber layer material for a solar cell, band gap, transport, and other properties must be considered. Solar cells are bipolar devices, which rely on the transport characteristics of both minority and majority carriers. The function of bipolar devices is heavily dependent on minority carrier mobility. To avoid recombination and achieve high performance, $p$-type absorber layers are preferable in PV devices, because the minority carriers are electrons and electrons typically have a higher mobility than holes.
In this study, I focus on a series of copper chalcogenides, MCu$_2$SnX$_4$ (M= Ba or Sr and X = S and Se) with examination of properties relevant to their use in thin film photovoltaic cells. SrCu$_2$SnS$_4$, BaCu$_2$SnS$_4$ and BaCu$_2$SnSe$_4$ are known materials, while SrCu$_2$SnSe$_4$ is studied for the first time [8-11]. A previous study has suggested that BaCu$_2$SnSe$_4$ crystallizes in space group $Ama_2$ this is a disparity from our results which find the space group to be $P3_21$ [12]. This paper examines band gap modulation with chalcogen substitution, crystal structure and carrier type. The results will determine which materials will be good candidates for future development in thin film photovoltaics.

**EXPERIMENTAL**

Powder samples were prepared via solid state reaction by the mixing of stoichiometric amounts of BaS (Cerac 99.9% pure), BaSe (Cerac 99.5% pure), SrS (Cerac 99.9% pure), SrSe (Cerac 99.5% pure), Cu$_2$S (Cerac 99.5% pure), Cu$_2$Se (Cerac 99.5% pure), Sn (Cerac 99.8% pure), S (Cerac 99.999% pure), and Se (Cerac 99.6% pure). Samples were thoroughly mixed and then sealed in evacuated silica ampoules and heated from 650-750°C for 12hrs as previously discussed in earlier experiments [8-11]. Single phase powders were pressed at room temperature with 1.5 tons to produce pellets having a diameter of 1.25cm; these pellets were subsequently sintered at 650°C under flowing Ar. Phase identification was performed through analysis of x-ray diffraction patterns acquired with a Siemens D-5000 diffractometer.
Crystals of BaCu₂SnSe₄ and SrCu₂SnSe₄ suitable for single crystal structure determinations were grown in sealed silica tubes heated to 850°C for 2h and slowly cooled at a rate of 6°C/h. X-ray data were collected on a Bruker SMART APEX CCD diffractometer with MoKα radiation (λ=0.71070 Å) at room temperature (BaCu₂SnSe₄) and 153°C (SrCu₂SnSe₄). Absorption corrections are made by using the program SADABS[13]. The structures were solved by using direct methods and refined with full-matrix least-squares methods based on F². All calculations were performed by using the SHELXTL (v. 6.10) package refinement results are displayed in Table 2.1 [14]. The atomic coordinates for the two crystals are summarized in Tables 2.2 and 2.3.

Optical band gaps of the MCu₂SnCh₄ samples were determined using diffuse reflectance measurements at room temperature. The measurements were performed by using BaSO₄ as a standard, an Oriel 300 Xe arc lamp, a Cary model-15 prism monochromator for excitation, and a Hamamatsu R1767 photomultiplier tube for detection. The diffuse reflectance spectrum was translated into an absorption spectrum using the Kubelka-Munk method [15,16]. Seebeck measurements were performed on sintered pellets by using a system that has been locally designed and constructed [17].
TABLE 2.1 Single crystal summary of $\text{MCu}_2\text{SnSe}_4$ ($M = \text{Ba or Sr}$)

<table>
<thead>
<tr>
<th>Property</th>
<th>BaCu$_2$SnSe$_4$</th>
<th>SrCu$_2$SnSe$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>BaCu$_2$SnSe$_4$</td>
<td>SrCu$_2$SnSe$_4$</td>
</tr>
<tr>
<td>Formula weight (g/mol)</td>
<td>698.95</td>
<td>649.23</td>
</tr>
<tr>
<td>Temperature ($^\circ$K)</td>
<td>293(2)</td>
<td>153(2)</td>
</tr>
<tr>
<td>Space group</td>
<td>P3$_2$1</td>
<td>Ama2</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>6.5886(3)</td>
<td>10.9676(13)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>6.5886(3)</td>
<td>10.7540(13)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>16.4205(14)</td>
<td>6.6950(8)</td>
</tr>
<tr>
<td>Volume Å$^3$</td>
<td>617.31(7)</td>
<td>789.65(16)</td>
</tr>
<tr>
<td>$Z$</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>$\mu$ (mm$^{-1}$)</td>
<td>30.403</td>
<td>60.235</td>
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<tr>
<td>Density (g/cm$^3$)</td>
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<td>5.461</td>
</tr>
<tr>
<td>$R^1$</td>
<td>0.0326</td>
<td>0.0205</td>
</tr>
<tr>
<td>$wR^2$</td>
<td>0.1072</td>
<td>0.0513</td>
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TABLE 2.2 Atomic coordinates and equivalent isotropic displacement parameters for BaCu₂SnSe₄.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Uₑₑ/Å²*10³</th>
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<tr>
<td>Ba</td>
<td>0.4442(2)</td>
<td>0.4442(2)</td>
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<td>15(1)</td>
</tr>
<tr>
<td>Sn</td>
<td>0.7118(2)</td>
<td>0</td>
<td>1/6</td>
<td>11(1)</td>
</tr>
<tr>
<td>Cu</td>
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<td>0.6508(3)</td>
<td>0.0895(1)</td>
<td>27(1)</td>
</tr>
<tr>
<td>Se (1)</td>
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<td>0.0473(1)</td>
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</tr>
<tr>
<td>Se (2)</td>
<td>-0.2301(3)</td>
<td>0.6520(3)</td>
<td>0.1677(1)</td>
<td>21(1)</td>
</tr>
</tbody>
</table>

TABLE 2.3 Atomic coordinates and equivalent isotropic displacement parameters for SrCu₂SnSe₄.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Uₑₑ/Å²*10³</th>
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</thead>
<tbody>
<tr>
<td>Sr</td>
<td>1/2</td>
<td>0</td>
<td>-0.2513(1)</td>
<td>8(1)</td>
</tr>
<tr>
<td>Sn</td>
<td>3/4</td>
<td>0.1507(1)</td>
<td>0.3411(1)</td>
<td>6(1)</td>
</tr>
<tr>
<td>Cu</td>
<td>0.6304(1)</td>
<td>0.2819(1)</td>
<td>-0.1521(1)</td>
<td>11(1)</td>
</tr>
<tr>
<td>Se (1)</td>
<td>3/4</td>
<td>0.0961(1)</td>
<td>-0.0251(1)</td>
<td>7(1)</td>
</tr>
<tr>
<td>Se (2)</td>
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<td>0.5201(1)</td>
<td>7(1)</td>
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<tr>
<td>Se (3)</td>
<td>0.5702(1)</td>
<td>0.2595(1)</td>
<td>0.5013(1)</td>
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RESULTS AND DISCUSSION

The structures of BaCu$_2$SnSe$_4$ (Figure 2.1) and SrCu$_2$SnSe$_4$ (Figure 2.2) are isostructural to the previously refined materials SrCu$_2$SnS$_4$ and SrCu$_2$GeSe$_4$ respectively [9,18,19]. Each of the structures contains MSe$_8$ (M = Ba, Sr) distorted square antiprisms and CuSe$_4$ and SnSe$_4$ distorted tetrahedra. The MSe$_8$ prisms condense to form three-dimensional frameworks via vertex sharing in the Ba derivative and vertex and edge sharing in the Sr derivative (figure 2.3 and 2.4). These frameworks are interpenetrated by condensations of the CuSe$_4$ and SnSe$_4$ distorted tetrahedra. In the Ba compound, these tetrahedral share vertexes (figure 2.5) to form a substructure that is reminiscent of structures such as wurtzite and chalcopyrite. They are further connected to the Ba-centered prisms by sharing vertexes. In the Sr compound, pairs of CuSe$_4$ tetrahedra share a common edge, Se$_1$-Se$_2$, to form Cu$_2$Se$_6$ groups (figure 2.6), which share vertices with like groups and the SnSe$_4$ tetrahedra.
FIGURE 2.1 BaCu$_2$SnSe$_4$ ($P3_21$) structure
FIGURE 2.2 SrCu$_2$SnSe$_4$ (Ama2) structure
Figure 2.3 Vertex sharing BaSe₈ prisms in BaCu₂SnSe₄
Figure 2.4 Vertex and edge sharing SrSe$_8$ prisms in SrCu$_2$SnSe$_4$
FIGURE 2.5 Cu and Sn environments and bond lengths in BaCu$_2$SnSe$_4$
FIGURE 2.6 \( \text{Cu}_2\text{Se}_6 \) and \( \text{SnSe}_4 \) units in \( \text{SrCu}_2\text{SnSe}_4 \)
These units are further fused to the SrSe₆ prisms by sharing both edges and vertexes. Selected interatomic distances and angles for the BaCu₂SnSe₄ are summarized in Table 2.4, and those for the SrCu₂SnSe₄ are listed in Table 2.5. Ba-Se distances range from 3.3249(15) to 3.4279(15)Å, and the average 3.35(8)Å, compares well to the sum of the Shannon-Prewitt crystal radii, 3.40Å [20]. Sr-Se distances range from 3.1849(7) to 3.3356(7)Å and the average distance, 3.25(5)Å, also compares well to the sum of the crystal radii, 3.24Å [20]. Average Sn-Se distances, 2.50(5) and 2.53(1)Å, in the Ba and Sr compounds respectively are comparable to the value, 2.53Å, derived from the crystal radii [20].

In the Ba derivative, the Sn atom adopts a distorted tetrahedral geometry having C₂h site symmetry. The extent of the distortion is reflected by the Se-Sn-Se angles of 104.18(8)° and 116.53(5)°. In the Sr derivative the Sn atom adopts a similarly distorted tetrahedral geometry but with the lower site symmetry Cₛ. Representative Se-Sn-Se angles are 102.02(2)° and 121.298(19)°. In both compounds, the Cu site symmetry is C₁. The average distances 2.44(7) and 2.47(1)Å, in the Ba and Sr derivatives, respectively, compares to the value, 2.58Å derived from the crystal radii [20]. Distortions from a tetrahedral geometry are reflected by the angles 95.79(8)° and 132.63(10)° in the Ba compound, and 96.89(3)° and 131.68(4)° in the Sr compound. The Cu-Cu distance within the Cu₂Se₆ unit of the Sr structure is a relatively short 2.6225(14)Å.
TABLE 2.4 Selected Interatomic Distances (Å) and angles (°) for BaCu$_2$SnSe$_4$

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<tr>
<th></th>
<th>2X</th>
<th>3.3249(15)</th>
<th>Se(1)-Sn-Se(1)</th>
<th>1X</th>
<th>104.18(8)</th>
</tr>
</thead>
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<td>2X</td>
<td>3.3357(16)</td>
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<td>2X</td>
<td>116.53(5)</td>
</tr>
<tr>
<td>Ba-Se1</td>
<td>2X</td>
<td>3.4279(15)</td>
<td>Se(1)-Sn-Se(2)</td>
<td>2X</td>
<td>104.18(8)</td>
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<td>Se(1)-Cu(1)-Se(2)</td>
<td>1X</td>
<td>132.63(10)</td>
</tr>
<tr>
<td>Sn-Se2</td>
<td>2X</td>
<td>2.5065(17)</td>
<td>Se(1)-Cu(1)-Se(2)</td>
<td>1X</td>
<td>109.70(9)</td>
</tr>
<tr>
<td>Cu-Se1</td>
<td>1X</td>
<td>2.399(2)</td>
<td>Se(2)-Cu(1)-Se(2)</td>
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<td>99.39(7)</td>
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<td>95.79(8)</td>
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<td>2.509(3)</td>
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<td>100.12(9)</td>
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TABLE 2.5 Selected Interatomic Distances (Å) and angles (°) for SrCu$_2$SnSe$_4$

<table>
<thead>
<tr>
<th></th>
<th>2X</th>
<th>3.1844(7)</th>
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<th>2X</th>
<th>121.298(19)</th>
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</thead>
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<td>104.66(3)</td>
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<tr>
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<td>3.3356(7)</td>
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<td>2X</td>
<td>102.02(2)</td>
</tr>
<tr>
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<td>1X</td>
<td>2.5216(9)</td>
<td>Se(3)-Cu-Se(2)</td>
<td>1X</td>
<td>131.68(4)</td>
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<td>2.5313(6)</td>
<td>Se(3)-Cu-Se(3)</td>
<td>1X</td>
<td>97.88(3)</td>
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<tr>
<td>Sn-Se2</td>
<td>1X</td>
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<td>114.08(3)</td>
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<td>2.4253(10)</td>
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<td>112.52(3)</td>
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<td>1X</td>
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<td>Se(2)-Cu-Se(1)</td>
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<td>96.89(3)</td>
</tr>
<tr>
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<td>Se(3)-Cu-Se(1)</td>
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<td>100.33(3)</td>
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<td>2.5370(9)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-Cu</td>
<td>1X</td>
<td>2.6225(14)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
As seen in Figure 2.7, the lattice parameters and cell volume smoothly increase on substitution of S for Se across the entire series BaCu$_2$Sn$_{4-x}$Se$_x$ ($0 \leq x \leq 4$), indicating a complete solid solution with retention of the trigonal cell. For the SrCu$_2$Sn$_{4-x}$Se$_x$ ($0 \leq x \leq 4$), a similar solid solution is observed, but a change from trigonal to orthorhombic symmetry occurs at $x \sim 1$. Optical band gaps across these solid solutions have been extracted from diffuse reflection measurements by using the Kubleka-Munk method [15,16]. Representative data for the BaCu$_2$SnSe$_4$ composition is shown in Figure 2.8. As seen in Figure 2.9, the band gaps for both the Ba and Sr derivatives decrease with increasing Se content, a result that scales with the ionicity of the Ba(Sr)-S(Se) interactions. On substitution of Se for S in the Sr derivative, the gap changes abruptly from direct to indirect; this also corresponds to the change from trigonal to orthorhombic symmetry. Between $x = 2$ and 3 in the series BaCu$_2$Sn$_{4-x}$Se$_x$ the gap changes from direct to indirect. Here, there is no change in symmetry or crystal structure, and it is likely that the addition of Se leads to greater dispersion in the valence band beyond the $\Gamma$ point, leading to an indirect gap. This supposition could easily be tested via a band-structure calculation.
FIGURE 2.7 Lattice parameters for BaCu$_2$Sn$_{4-x}$Se$_x$, calculated from powder diffraction data.
Figure 2.8 Diffuse reflectance spectroscopy data for indirect band gap approximation of BaCu$_2$SnSe$_4$. 
FIGURE 2.9 Band gaps for compounds $\text{BaCu}_2\text{SnS}_{4-x}\text{Se}_x$ determined by using powder diffuse reflectance. Filled shapes = Ba and open shapes = Sr. Circle = indirect gap, square = direct gap.
Seebeck measurements have been used to determine the carrier type for both solid-solution series. As seen in Table 2.6 all samples exhibit a positive Seebeck coefficients indicating all of the compounds are p-type semiconductors. The Ba materials exhibit a clear trend of decreasing coefficients with the addition of Se. The data for the Sr compounds are more scattered, which may be associated with the change in crystal structure.

<table>
<thead>
<tr>
<th>x</th>
<th>Density</th>
<th>Seebeck $\mu$V/K</th>
<th>x</th>
<th>Density</th>
<th>Seebeck $\mu$V/K</th>
</tr>
</thead>
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<td>0</td>
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<td>339.8</td>
<td>0</td>
<td>75%</td>
<td>431.4</td>
</tr>
<tr>
<td>1</td>
<td>86%</td>
<td>314.5</td>
<td>1</td>
<td>77%</td>
<td>169.8</td>
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<tr>
<td>2</td>
<td>65%</td>
<td>125.3</td>
<td>2</td>
<td>81%</td>
<td>220.1</td>
</tr>
<tr>
<td>3</td>
<td>80%</td>
<td>85.9</td>
<td>3</td>
<td>78%</td>
<td>303.1</td>
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<tr>
<td>4</td>
<td>87%</td>
<td>66</td>
<td>4</td>
<td>88%</td>
<td>101.9</td>
</tr>
</tbody>
</table>

TABLE 2.6 Pellet densities and Seebeck coefficients of $MCu_2SnS_{4-x}Se_x$
CONCLUSION

These quaternary chalcogenides containing Ba or Sr with varying amounts of S and Se provide a rich route to controlling physical properties of interest in developing new absorber layers for photovoltaic devices. As noted in the introduction to this dissertation all of the materials have the desirable trait of being $p$-type semiconductors. In terms of optical properties, the materials SrCu$_2$SnS$_4$ and BaCu$_2$SnS$_{4-x}$Se$_x$ ($0 \leq x \leq 2$) provide direct band gaps. The mixed sulfide, selenides of Ba would appear to provide the best opportunities for continued study. They provide a range of band gaps from 1.6-2.0eV, which is of interest for absorbers and possibly transparent windows. The Seebeck coefficients for these materials are relatively large, also indicating potential viability as absorbers, although doping the Sn site with In could lead to higher carrier concentrations and enhanced conductivity satisfying the requirements for a good window material.
REFERENCES


[14] SHELXTL-6.10 "Program for Structure Solution, Refinement and Presentation" Bruker AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA


CHAPTER 3

PREPARATION AND CHARACTERIZATION OF THE P-TYPE WIDE BAND GAP SEMICONDUCTORS Cu$_3$TaCh$_4$ (Ch = S, Se)

P. A. Hersh, P. F. Newhouse, J. Tate, and D. A. Keszler
ABSTRACT

Physical, optical, electrical and photoluminescence properties of the Cu₃TaCh₄ (Ch = S or Se) series are investigated to determine the potential as a transparent semiconductor. The series crystallizes in a P-43m sulvanite structure. The sulfide has a lattice parameter of $a = 5.5036(4)$ Å and the selenide has a lattice parameter of $a = 5.6535(7)$ Å. The optical band gaps are 2.75 eV for Cu₃TaS₄ and 2.36 eV for Cu₃TaSe₄. Band structure calculations indicate that the valence band maximum and the conduction band minimum are offset in $k$-space leading to an indirect band gap. Seebeck coefficient measurements of $+27 \mu$V/K for Cu₃TaS₄ and $+24 \mu$V/K for Cu₃TaSe₄ confirm that both materials are $p$-type. Sub-band gap green luminescence is observed in undoped Cu₃TaS₄, and red luminescence appears when W substitutes at the Ta site.
INTRODUCTION

Copper chalcogenides have been comprehensively studied partly because their p-type semiconducting behavior makes them useful in photovoltaic cell applications. Cu$_2$Ch (Ch = S, Se or Te) have a strong spectral response, but also exhibit a large and unstable carrier concentration [1,2]. Inclusion of a third element into the copper chalcogenides has led to better control of many optoelectronic properties such as carrier concentration and band gap [3-11]. Adding Ta to Cu$_2$Ch to form Cu$_3$TaCh$_4$ (Ch = S or Se) compounds has yet to be extensively studied despite interesting properties that make these copper chalcogenides unique. The most intriguing attribute of the Cu$_3$TaCh$_4$ system is the isotropic cubic sulvanite crystal structure [6,7]. An unusual characteristic of the structure is the pentavalent Ta found in a distorted $T_d$ environment. Ta is not usually found in a four-coordinate environment and is more commonly tetravalent in sulfide and selenide compounds such as TaS$_2$ and TaSe$_2$. Another interesting property is the appearance of the bulk material. Previous studies do not report full optical characterization, but describe Cu$_3$TaS$_4$ powder as yellow, indicating a large optical band gap [6,8]. Similar copper sulfides, such as Cu$_3$PS$_4$ (2.38eV), Cu$_3$SbS$_4$ (0.47eV) and Cu$_3$AsS$_4$ (1.19eV) have smaller band gaps [9-11]. The large band gap of Cu$_3$TaS$_4$ is unexpected and may be related to the high symmetry found in the cubic crystal structure. The valence band of Cu$_3$TaCh$_4$ is likely to be similar to Cu$_2$Ch, which is comprised of Cu 3$d$ and Ch $p$ orbitals [12]. The valence band make-up should provide a good hole transport path. Moreover, the material is cubic, and its isotropic structure is an important advantage from a processing point of
view. In addition, we have found that Cu$_3$TaS$_4$ exhibits sub-band gap photoluminescence. This paper explores the physical, optical, electrical and photoluminescence properties of Cu$_3$TaCh$_4$ as possible transparent p-type semiconductors.

There has been recent interest in active transparent electronic devices [13], and to date transparent transistors have been based on wide-band-gap n-type semiconductors. The supply of suitable p-type transparent semiconductors is more limited, and there are no reports of similar p-type based transistors. One of the challenges that must be overcome to realize p-type transparent electronics is the character of the valence band maximum (VBM) which, in most oxides, is composed of highly localized O 2p orbitals. The incorporation of Cu (I) leads to hybridization of the O 2p orbitals with the Cu 3d orbitals forming a VBM more conducive to hole transport [14]. This is seen in Cu$_2$O where the Cu 3d orbitals contributing to the VBM in Cu$_2$O lead to good transport properties, but also cause a decrease in the optical band gap of the material (2.0 eV) [15]. One of the major challenges in wide-band-gap p-type semiconductors is to retain optical transparency while improving transport properties.

There has been some progress in overcoming the challenges associated with p-type transparent semiconductors. P-type transparent oxides such as the delafossites CuMO$_2$ (M = Al, Sc, Cr, In or Ga), and the layered structures LaCuOCh (Ch = S, Se or Te) have all shown promising optoelectronic properties [16-26]. Despite this promise, many of the current p-type transparent materials have not yet been integrated into transparent devices. The CuMO$_2$ materials have a large enough band gap ranging
from 3.1eV to 3.9 eV [16-20] but poor electrical conductivity. When samples are doped to improve conductivity, the result is a large sacrifice in optical transparency [16-21]. The LaCuOCh system allows highly conductive materials to remain optically transparent through quantum confinement of the Cu chalcogenide sublattice. The unique alternating layers of La$_2$O$_2$$^{2+}$ and Cu$_2$Ch$_2$$^{2-}$ in LaCuOCh increase the band gap to as much as 3.2 eV [22] and allows good hole transport in two dimensions through the Cu$_2$Ch$_2$$^{2-}$ layer. Band structure calculations of the LaCuOCh show that the valence band is composed of Cu 3$d$ and Ch $p$ orbitals [23] and that hole effective mass is smaller in the $\Gamma$-X direction then in the $\Gamma$-Z direction [22]. This means films must be $c$-axis oriented to achieve the optimum electronic characteristics. High temperature epitaxial growth on single crystal substrates is required to grow $c$-axis oriented LaCuOCh films [24-26]. The processing required to make $c$-axis oriented films makes device integration very difficult and expensive. The isotropic nature of the Cu$_3$TaCh$_4$ structure makes this material less difficult to manufacture and more advantageous in device integration.

Some work has been done exploring non-oxide based $p$-type transparent semiconductors. Compounds that contain Cu (I), such as Cu$_2$Ch (Ch = S, Se) are highly conductive $p$-type materials, but face the same problem as the oxides, namely a lack of optical transparency. Increased band gaps have been found in ternary and quaternary Cu chalcogenides such as BaCu$_2$S$_2$ and BaCuSF. BaCu$_2$S$_2$ has very good electrical properties, but a band gap of only 2.3eV [27]. BaCuSF has the same layered structure as LaCuOCh, and has a large band gap of 3.2 eV [28]. The quantum
confinement of Cu calcogenide sublattice leads to the same issues found in the LaCuOCh.

Cu$_3$TaCh$_4$ is a new example of a cubic system where the VBM contains the Cu 3$d$ orbitals that enable hole transport while maintaining a large optical band gap. Achieving this combination without the anisotropy inherent in the layered systems described above is a significant advantage.

Finally, the sub-band gap photoluminescence found in Cu$_3$TaS$_4$ adds an additional dimension to the material's potential utility. We show here that the mid-band-gap defect is a Cu vacancy, which is found in most Cu (I) compounds.

**EXPERIMENTAL**

Powder samples of Cu$_3$Ta$_{1-x}$M$_x$Ch$_4$ (M = W, Zr; Ch = S or Se), were prepared by heating stoichiometric quantities of the metallic elements with S or Se; reagents were Cu (Cerac, 99.9%), Ta (Cerac 99.9%), W (Cerac 99.5%), Zr (Teledyne 99.5%), S (Cerac 99.999%), and Se (Cerac 99.6%). Mixtures were heated in evacuated silica ampoules to 600°C for 5 h then reground and heated to 750°C for 24 h. Products were characterized via X-ray diffraction on a Siemens D5000 diffractometer using Cu Kα radiation.

Cu$_3$TaS$_4$ crystals were grown using a vapor-assisted method described by Nitsche [29] with Cu, Ta, S, and I$_2$ flux in a sealed silica ampoule. The ampoule was heated to 780°C for 24 h in a tube furnace with a temperature gradient then cooled to room temperature. The temperature gradient was reversed and the tube was heated to
700°C for 72 h and cooled at 10 °C/h to room temperature. Crystals formed on the cold end of the tube indicative of an exothermic vapor transport. After cooling the crystals were washed with deionized water to remove the excess halides. Single crystals of Cu₃TaSe₄ were prepared via reaction of elemental [30] Cu, Ta, and Se in stoichiometric proportion. The elemental mixture was sealed in a silica ampoule and heated to 950 °C for 24 h then cooled at a rate of 10°C/h to room temperature.

Structures of the sulfide and selenide single crystals X-ray of Cu₃TaCh₄ were examined by X-ray diffraction on a Bruker Smart Apex diffractometer with MoKα radiation (λ=0.71070 Å). Absorption corrections were done by SADABS [31]. The structure was solved by using direct methods and refined with full-matrix least-squares methods based on F². In both cases crystals used for data collections were racemic twins; the Flack parameters are 0.19(3) and 0.37(5), respectively for Cu₃TaS₄ and Cu₃TaSe₄. All calculations were performed with the SHELXTL package[32]. The crystallographic data and some details of X-ray diffraction studies and refinement of the crystal structures are given in the Table 3.1.

Optical band gaps of the Cu₃TaCh₄ samples were determined using diffuse reflectance techniques. The measurements were made at room temperature with an Oriel 300 W Xe arc lamp, a Cary model-15 prism monochromator and a Hamamatsu R636-10 photomultiplier tube with BaSO₄ as a standard. The optical band gaps were extracted using the Kubelka-Munk method [33,34]. Photoluminescence of the Cu₃TaS₄ was measured in the same system with the addition of an Oriel 77250 emission monochromator.
Pellets of selected samples were cold pressed at 1.5 tons/in² and sintered at 850°C under flowing Ar(g). For contact, colloidal graphite contacts was deposited on the sintered pellets and annealed at 150°C for 2 to 3 minutes. Room-temperature resistivities of 1.25-cm diameter, 0.15-cm thick sintered pellets were measured in four-contact van der Pauw geometry. Carrier type was determined via the room-temperature Seebeck coefficient, which was measured in a system of in-house design.

Table 3.1 Single crystal summary of Cu₃TaCh₄

<table>
<thead>
<tr>
<th>Property</th>
<th>Cu₃TaS₄</th>
<th>Cu₃TaSe₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>Cu₃TaS₄</td>
<td>Cu₃TaSe₄</td>
</tr>
<tr>
<td>Formula weight</td>
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<td>687.41</td>
</tr>
<tr>
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<td>153(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
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<td>0.71073 Å</td>
</tr>
<tr>
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<td>Cubic</td>
<td>Cubic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-43m</td>
<td>P-43m</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 5.5036(4) Å</td>
<td>a = 5.6535(7) Å</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>166.70(2)</td>
<td>180.70(4)</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Density (calculated)</td>
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<td>6.317 g/cm³</td>
</tr>
<tr>
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<td>26.915 mm⁻¹</td>
<td>43.819 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>224</td>
<td>296</td>
</tr>
<tr>
<td>Crystal size (mm³)</td>
<td>0.08 x 0.06 x 0.04</td>
<td>0.05 x 0.04 x 0.02</td>
</tr>
<tr>
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</tr>
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</tr>
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<td></td>
<td>-7≤k≤4</td>
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<td>881</td>
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</tr>
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<td>100.00%</td>
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<td>R₁ = 0.0117</td>
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<td>wR₂ = 0.0335</td>
<td>wR₂ = 0.0291</td>
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<td>0.37(5)</td>
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<tr>
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<td>0.0073(11)</td>
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<td>Largest diff. peak and hole</td>
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</tbody>
</table>
FLAPW (full-potential linearized augmented plane wave) energy band calculations for \( \text{Cu}_3\text{TaCh}_4 \) (Ch = S or Se) were performed using the software package Wien 2k [35] with the PBE generalized gradient approximation. Structural parameters are those derived from the X-ray analysis, *vide infra*. The details of the calculations are as follows. Muffin tin radii of 2.38 au for Cu and Ta, and 2.11 au for S were used in the \( \text{Cu}_3\text{TaS}_4 \) calculation. The corresponding values in the \( \text{Cu}_3\text{TaSe}_4 \) calculation were 2.44 au for Cu and Ta, and 2.16 au for Se. The potentials and charge densities in the interstitial region were expanded using 2506 (\( \text{Cu}_3\text{TaS}_4 \)) and 2689 (\( \text{Cu}_3\text{TaSe}_4 \)) plane waves. The number of unique \( k \)-points used in the calculations was 204. Inside the spheres these quantities were expanded up to \( l = 10 \). The APW functions were expanded up to \( l = 4 \). The maximum APW wave vector was 2.4 au for \( \text{Cu}_3\text{TaS}_4 \) and 3.2 au for \( \text{Cu}_3\text{TaSe}_4 \), which resulted in about 1200 basis functions per cell, or about 150 basis functions per atom. With these parameters, total energies converged to better than 0.1 mRy, and charge to better than \( 10^{-3} \) e. Numerical errors in the band structure are too small to see in the plots.

**RESULTS AND DISCUSSION**

Single crystal diffraction studies confirm that \( \text{Cu}_3\text{TaCh}_4 \) (Ch = S, Se) crystallizes in a \( \text{P}-4\text{m} \) sulvanite structure with edge-sharing \( \text{TaCh}_4 \) and \( \text{CuCh}_4 \) tetrahedra and corner sharing \( \text{CuCh}_4 \) tetrahedra (Figure 3.1). The \( \text{TaCh}_4 \) and \( \text{CuCh}_4 \) tetrahedra are distorted in both the sulfide and the selenide. Crystallographic data and
refinement details are given in Table 3.1. The atomic positions, bond lengths and bond angles are displayed in Tables 3.2, 3.3, 3.4 and 3.5. The Cu-S and Cu-Se bond distances are 2.359Å and 2.364Å respectively in Cu₃TaCh₄ which are only slightly larger than the 2.25Å in Cu₂S and the 2.325Å in Cu₂Se [36,37]. The symmetry of the crystal structure is isotropic, which means that randomly-oriented thin films may have good transport properties. Randomly-oriented films are easier and cheaper to grow and this could be advantageous for integration of Cu₃TaCh₄ into devices.

Table 3.2 Atomic coordinates and equivalent isotropic displacement parameters (Å²) for Cu₃TaS₄. U(eq) is defined as one third of the trace of the orthogonalized Uᵢⱼ tensor.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
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<td>0</td>
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</tr>
<tr>
<td>Cu</td>
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<td>0</td>
<td>0</td>
<td>0.012(1)</td>
</tr>
<tr>
<td>S</td>
<td>0.2421(3)</td>
<td>0.2421(3)</td>
<td>0.2421(3)</td>
<td>0.010(1)</td>
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</tbody>
</table>

Table 3.3 Atomic coordinates and equivalent isotropic displacement parameters (Å²) for Cu₃TaSe₄. U(eq) is defined as one third of the trace of the orthogonalized Uᵢⱼ tensor.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta</td>
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<td>0</td>
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<tr>
<td>Cu</td>
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<td>0.2495(1)</td>
<td>0.2495(1)</td>
<td>0.009(1)</td>
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</tbody>
</table>
Figure 3.1 Crystal structure for Cu$_3$TaS$_4$ Ta = white, Cu = gray and S = black
Table 3.4 Bond lengths and angles for Cu$_3$TaS$_4$.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance [Å]</th>
<th>Bond</th>
<th>Angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
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<td>S-Cu-S</td>
<td>106.02(13)</td>
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<tr>
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<td>S-Cu-S</td>
<td>111.22(7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu-S-Cu</td>
<td>111.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ta-S-Cu</td>
<td>72.25</td>
</tr>
</tbody>
</table>

Table 3.5 Bond lengths and angles for Cu$_3$TaSe$_4$.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance [Å]</th>
<th>Bond</th>
<th>Angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta-Se</td>
<td>2.36434(10)</td>
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</tr>
<tr>
<td>Cu-Se</td>
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</tr>
<tr>
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<td>109.57(2)</td>
</tr>
<tr>
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<tr>
<td></td>
<td></td>
<td>Ta-Se-Cu</td>
<td>70.63(2)</td>
</tr>
</tbody>
</table>

The band structure calculation of Cu$_3$TaS$_4$ is shown in Figure 3.2. The valence band is primarily composed of hybrid of Cu 3$d$ orbitals and S 3$p$ orbitals. The composition of the valence band is conducive to hole transport. Compounds with similar valence band make up such as LaCuOCh and BaCuChF (Ch = S, Se) have shown excellent p-type mobility [17,18,22-26,38]. The major contribution to the conduction band is from the Cu 4$s$ orbitals. The valence band maximum is found at the R point and the conduction band minimum is found at the X point indicating an indirect band gap. The overall band structure of the selenide is similar to the sulfide, including the indirect nature of the minimum gap energy. The stronger covalency of the Cu-Se bond relative to the Cu-S bond renders the bands broader and the band gaps smaller.
Figure 3.2 Band structure calculation of Cu$_3$TaS$_4$ using the program Wien 2k [35].
The Cu$_3$TaS$_4$ and Cu$_3$TaSe$_4$ powders are yellow and light brown respectively, as also noted in previous reports [6,8]. Optical band gaps are determined using diffuse reflectance measurements. The optical absorption data is analyzed assuming that Cu$_3$TaCh$_4$ has an indirect optical band gap, values of 2.75 eV (Ch=S) and 2.36 eV (Ch=Se), are obtained. The band gap of the sulfide is large enough to consider its use in transparent electronics. The relative magnitudes of the band gaps are in good agreement with the calculation, the absolute value of which however suffers from the widely-quoted underestimation that occurs in DFT calculations.

Both Cu$_3$TaS$_4$ and Cu$_3$TaSe$_4$ exhibit $p$-type behavior as evidenced from the positive Seebeck coefficients $+27\mu$V/K and $+24\mu$V/K respectively. Doping tetravalent Zr on the pentavalent Ta site creates more carriers leading to a reduction in resistivity. Doping with hexavalent W reduces the number of carriers leading to an increase in resistivity. All doped samples also exhibit $p$-type Seebeck coefficients. This ability to control carrier concentration is important for integration of new materials into devices.

When Cu$_3$TaS$_4$ is irradiated with light shorter than 440 nm, it exhibits green photoemission (Figure 3.3). Green emission from undoped ($x = 0$) material has CIE coordinates of $x = 0.352$ and $y = 0.611$. The onset of photoemission is found at the energy equal to the band gap (Figure 3.4). The emission peak maximum is found at 548 nm. This sub-band-gap emission indicates a mid-band-gap charge trap. The trap state is likely to be a Cu vacancy near the valence band maximum that acts as an acceptor. To confirm the nature of the trap state, photoemission of Cu deficient Cu$_3$TaS$_4$ is monitored. The emission intensity is increased when the concentration of
Cu vacancies is increased (Figure 3.5). Samples doped with W (VI) show a decrease in green photoemission while creating red photoemission (Figure 3.3). Thus W (VI) must induce another mid-band-gap trap state that acts as a donor near the conduction band. The emission mechanism for the doped and undoped samples is shown in figure 3.6.
Figure 3.3 Photoluminescence from Cu$_3$Ta$_{1-x}$W$_x$S$_4$ powder using a 420nm excitation source.
Figure 3.4 Excitation spectrum of Cu₃TaS₄ photoemission.
Figure 3.5 Intensity of the photoemission increases with $x$ in $\text{Cu}_{3-x}\text{TaS}_4$. 
Figure 3.6 Emission mechanisms for CuTa_{1-x}WS_{4} showing the direct adsorption from valence band (VB) to conduction band (CB) the emitting back to a copper vacancy.
CONCLUSION

Cu$_3$TaS$_4$ and Cu$_3$TaSe$_4$ are cubic p-type semiconductors with optical and electrical properties that may be useful in photovoltaics and transparent electronics. Their three-dimensional conduction pathways do not require any specific orientation to improve conduction, so that polycrystalline, rather than epitaxial, films should suffice for applications. The VBM is composed of a hybridization of Cu 3$d$ and chalcogen $p$ orbitals, which provide an excellent hole transport pathway. Increased conductivity is seen when Zr is doped on the Ta site. Decreased conductivity is seen when W is doped on the Ta site. The large band gap of the sulfide (2.75eV) makes the material transparent to most visible light.

ACKNOWLEDGMENTS

We thank Lev N. Zakharov of Oregon State University for the single crystal refinements. This material is based upon work supported by the National Science Foundation under DMR0245386.
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CHAPTER 4

BAND GAP MODULATION AND TRANSPORT PROPERTIES OF
Cu$_3$MQ$_4$ (M = Ta or Nb Q = S or Se)
ABSTRACT

Optical and electrical properties of Cu$_3$MQ$_4$ (M = Ta or Nb Q = S or Se) bulk samples are analyzed. Cu$_3$MQ$_4$ compounds crystallize in the cubic P-43m sulvanite structure. The indirect band gaps are extracted from diffuse reflectance spectroscopy and range from 2.13eV for the Cu$_3$NbSe$_4$ to 2.75eV for the Cu$_3$TaS$_4$ (2.18-2.85eV for direct band gap). All of the materials show positive Seebeck coefficients indicating p-type behavior. Conductivity measurements of pressed pellets gave a range of conductivity from 0.0017 S/cm$^2$ to 0.25 S/cm$^2$. 
INTRODUCTION

Ternary and quaternary copper chalcogenides have generated a lot of interest in the field of thin film photovoltaics and transparent semiconductors [1]. Most of these materials exhibit p-type behavior with fairly high mobility. The research presented here is focused on the Cu₃MQ₄ (M = Ta or Nb, Q = S or Se) series of ternary copper chalcogenides.

Cu₃MQ₄ (M = Ta or Nb Q = S or Se) crystallize in the cubic $P\bar{4}m$ sulvanite structure (figure 4.1) [2-4]. This isotropic structure consists of corner sharing CuQ₄ tetrahedra chains (figure 4.2) that share edges with isolated MQ₄ tetrahedra (figure 4.3). The tetrahedral configuration around the M ion is unusual. Usually Ta and Nb are found in higher coordination environment such as, an octahedral environment. The Ta and Nb are pentavalent in these compounds which are not the typical valency for Ta and Nb in sulfide and selenide compounds. Most Ta and Nb sulfides and selenides are found in a tetravalent environment such as MQ₂.

Previous studies have described the color of the Cu₃MQ₄ (M = Ta or Nb Q = S or Se), but full band gap determination has not been performed [3,5]. The range of colors from red for the Cu₃NbSe₄ to yellow in the Cu₃TaS₄ indicates a shift in band gaps. The ability to modulate band gaps has been observed in pervious studies of ternary and quaternary Cu based chalocogenides [6,7]. Modulation of band gaps can prove advantageous in thin-film photovoltaic applications allowing for different parts of the spectrum to be transmitted or absorbed [8-10]. Larger band gap materials can be used as window layers to transmit light while; smaller band gap materials can be
used as photon absorbers. Band gaps of photon absorbers for 2 and 3 junction PV cells were optimized by Coutts [11]. The ideal band gaps for 2 junction cells are 1.8eV for the top cell and 1.1eV for the bottom cell. For a 3 junction cell the band gaps are 2.15eV for the top cell 1.55eV for the middle and 1.0eV for the bottom cell. Figure 1.2 shows a diagram of a 3 junction photovoltaic cell with the optimum band gaps for each layer. Window layers must have a large enough band gap to transmit the unabsorbed light to the lower cells.
Figure 4.1 $P-43m$ cubic sulvanite structure of $\text{Cu}_3\text{MQ}_4$ ($\text{M} = \text{Ta} \text{ or } \text{Nb}$ and $\text{Q} = \text{S} \text{ or } \text{Se}$)
Figure 4.2 Configuration of CuQ₄ tetrahedra in the P-43m cubic sulvanite structure of Cu₃MQ₄ (M = Ta or Nb and Q = S or Se)
Figure 4.3 Configuration of MQ₄ tetrahedra in the P-43m cubic sulvanite structure of Cu₃MQ₄ (M = Ta or Nb and Q = S or Se)
EXPERIMENTAL

Powders of $\text{Cu}_3\text{MQ}_4$ were synthesized via solid state reaction of the elements Cu (Cerac 99.9% pure), Ta (Cerac 99.9% pure), Nb (Cerac 99.9% pure), S (Cerac 99.999% pure), Se (99.6% pure). Before synthesis the Cu was reduced by heating to 500°C under flowing 5%$\text{H}_2$·95%$\text{N}_2$ to remove oxide. The elements were thoroughly mixed then sealed in an evacuated silica ampoule at pressures <500mtorr. The ampoules where heated to 750°C at a rate of 2.5°C/min to prevent the buildup of chalcogen vapor pressure. The samples were held at 750°C for 12h then reground, resealed and reheated to 750°C for 24h. The resultant compounds were characterized using a Siemens D5000 diffractometer with Cu Kα radiation.

Powder samples optical band gaps were estimated using diffuse reflectance spectroscopy. The measurements were carried out at room temperature using an Oriel-300 W Xe lamp, a Cary model 15 prism monochromator and a Hamamatsu R636-10 photomultiplier tube. For a reference standard $\text{BaSO}_4$ powder was used.

Pellets of ½” diameter were synthesized using a cold press at 1.5 tons per square inch. Pellets were sintered in an AIP6-30H hot isostatic press at 875-975°C under 2000-4000 PSI of argon. Transport measurements were carried out at room temperature using a Seebeck measurement to determine carrier type and the Van der Pauw method to determine conductivity. To improve the contact quality to the pellets, colloidal graphite was deposited and then cured at 150°C for 2-3 min.
RESULTS AND DISCUSSION

X-ray diffraction of the Cu$_3$NbSe$_4$, Cu$_3$NbS$_4$, Cu$_3$TaSe$_4$ and Cu$_3$TaS$_4$ are displayed in figure 4.4 and 4.5. The Cu$_3$TaSe$_4$ and Cu$_3$NbSe$_4$ have larger lattice parameters than their sulfide counterparts. This shift in lattice parameter can be seen by the peak positions of the XRD spectra and has been observed previously [12,13].

The Kubelka-Munk equation is used to determine optical band gaps from diffuse reflectance spectroscopy [14,15]. The reflectance of the sample is compared to the reflectance of BaSO$_4$ to get a relative reflectance ($R_d$). The $R_d$ value is used to determine an absorption coefficient relative to the scattering coefficient ($k/s$). This is done using the Kubleka-Munk equation:

$$\frac{k}{s} = \frac{(1 - R_d)^2}{2 \times R_d}$$  \hspace{1cm} (Eq 4.1)
Figure 4.4 XRD plot of A = Cu$_3$NbS$_4$ reference pattern, B = Cu$_3$NbS$_4$ and C = Cu$_3$NbSe$_4$ dashed line shows the 2θ position shift from the sulfide to the selenide.
Figure 4.5 XRD plot of A = Cu$_3$TaS$_4$ reference pattern, B = Cu$_3$TaS$_4$ and C = Cu$_3$TaSe$_4$ dashed line shows the 2θ position shift from the sulfide to the selenide.
To best approximate the band gap, it is important to know whether band gap is direct or indirect. For direct band gap determination the following is plotted \((k/s \times E)^2\) vs. \(E\). For indirect band gap determination the plot used to determine the band gap is \((k/s \times E)^{1/2}\) vs. \(E\). In both cases the linear region of the plot is extrapolated to the baseline; the energy value at the intersection is the band gap estimate (figure 4.6). From band structure calculations in a previous study it was found that the Cu₃TaS₄ has an indirect band gap [2]. For comparison the indirect as well as the direct band gap determination were carried out the direct band gaps have a higher value (0.03-0.09eV) then their indirect counterpart.

The band gap modulation in the Cu₃MQ₄ occurs with substitution on the M site and on the Q site. Substituting Nb for Ta in the M site causes a reduction in band gap from 2.75eV to 2.56eV in the sulfide shown in Table 4.1. A reduction in the band gap is also seen when Se is substituted for S on the Q site 2.76-2.36 eV indirect, (2.85-2.45eV direct) for the Ta and 2.48-2.13 eV indirect, (2.56-2.18 direct) for the Nb these results are shown in figure 4.7 and 4.8. The band gap trends observed are consistent with normal periodic trends. The substitution of Nb for Ta or Se for S has the same effect on the compound. In both cases the bonding becomes more covalent in nature. Covalent bonding leads to more disperse bands which in reduces the size of the band gap and thus the trend is observed.

<table>
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<tr>
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<th>0.5</th>
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<tr>
<td>(E_g) (eV)</td>
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<td>2.69</td>
<td>2.65</td>
<td>2.58</td>
<td>2.56</td>
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</table>
Figure 4.6 Cu$_3$TaS$_4$ band gap determined using diffuse reflectance spectroscopy coupled with the Kubelka-Munk equation.
The size and density of the pressed pellets used to determine transport characteristics is shown in table 4.2. The Seebeck coefficients (also shown in table 4.2) for all of the materials measures were positive indicating p-type behavior. This is expected due to the presence of Cu (I) in the Cu$_3$MQ$_4$ materials. Cu (I) containing materials often form $V_{Cu}$ due to the presence of Cu (II) [16,17]. The pellet conductivities are range from $1.67 \times 10^{-3}$ to $2.55 \times 10^{-1}$ S/cm.

<table>
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<tr>
<th>Material</th>
<th>Weight (g)</th>
<th>Diameter (cm)</th>
<th>Thickness (cm)</th>
<th>Theoretical density %</th>
<th>Seebeck (μV/K)</th>
<th>Conductivity (S/cm)</th>
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<td>0.173</td>
<td>74</td>
<td>26</td>
<td>1.67E-03</td>
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</table>
Figure 4.7 Indirect optical band gap summary of Cu$_3$NbS$_4$$_x$Se$_x$ (circles) and Cu$_3$TaS$_4$$_x$Se$_x$ (squares) as the amount of Se increases the band gap decreases.
Figure 4.8 Direct optical band gap summary of Cu$_3$NbS$_4$$_x$Se$_x$ (circles) and Cu$_3$TaS$_4$$_x$Se$_x$ (squares) as the amount of Se increases the band gap decreases.
CONCLUSION

The Cu$_3$MQ$_4$ system (M = Ta or Nb and Q = S or Se) demonstrates the ability to modulate the optical band gap from 2.13-2.76 eV. The band gap modulation occurs without disrupting the cubic P-43m structure. All the materials are p-type in nature this is shown by the positive Seebeck coefficients. The band gap and p-type nature make these materials good candidates for p-type window materials in multi-junction photovoltaic cells.
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CHAPTER 5

SYNTHESES AND PROPERTIES OF BiCuSeO

Peter A Hersh, Paul Newhouse, Douglas A. Keszler, Janet Tate
ABSTRACT

Thin films of BiCuSeO have been deposited and crystallized \textit{in-situ} via pulsed laser deposition. All films are \textit{p}-type in nature. Polycrystalline films exhibiting a hole mobility of 2 cm$^2$/Vs have been deposited on SiO$_2$. Films deposited on SrTiO$_3$ are \textit{c}-axis oriented, exhibiting a hole mobility of 4cm$^2$/Vs. Films doped with Ca display degenerate-semiconductor behavior with conductivities up to 170 S/cm.
INTRODUCTION

The chalcogenide oxide of LnCuXO (Ln = La, Bi; X = S, Se) and MCuXF (M = Ba or Sr) compounds crystallize in a $P4/nmm$ layered structure (Figure 5.1) that gives rise to several interesting and technologically significant properties [1-8]. These properties include $p$-type electrical conductivity and a natural quantum-well crystal structure that consists of wide band-gap $(\text{Ln}_2\text{O}_2)^{2+}$ or $(\text{M}_2\text{F}_2)^{2+}$ and narrow band-gap $(\text{Cu}_2\text{X}_2)^{2-}$ layers stacked alternately along the $c$ axis of the tetragonal unit cell [9]. The $p$-type electrical conductivity found in these compounds is attributed to the edge sharing $\text{CuX}_4$ distorted tetrahedra within the $(\text{Cu}_2\text{X}_2)^{2-}$ layers. Due to the layered nature of the structure, conduction is presumed to occur predominately in the $ab$ plane. Thus, forming $c$ axis oriented films is desirable to improve transport properties. Such, oriented thin films of LaCuXO and MCuXF, however have not been realized in-situ by physical vapor deposition (PVD) techniques, as fabrication of high-quality films requires multiple deposition and annealing steps [1,6]. In this contribution, we address in-situ crystallization of this family of films through pulsed laser deposition of BiCuSeO and the Ca-doped derivative $\text{Bi}_{1-x}\text{Ca}_x\text{CuSeO}$ ($0 \leq x \leq 0.15$). $\text{Bi}_2\text{O}_3$ (mp = 824°C) is a much less refractory component that La$_2$O$_3$ (mp = 2315°C) and BaF$_2$ (mp = 1368°C), providing a higher reactivity conducive to grain growth at low temperatures.
Figure 5.1 Layer of edge sharing Cu-centered \((\text{Cu}_2\text{Se}_2)^2^-\) tetrahedra (grey) interleaved with \((\text{Bi}_2\text{O}_2)^{2+}\) layers (Bi white spheres, O black spheres)
EXPERIMENTAL

Powder samples of Bi\textsubscript{1-x}Ca\textsubscript{x}CuSeO were prepared by solid state reaction of Bi\textsubscript{2}O\textsubscript{3} (Strem, 99.999\%), CaO (Cerac, 99.8\%), Bi (Strem, 99.9\%), Cu (Cerac, 99.5\%), and Se (Cerac, 99.6\%) by heating in evacuated silica tubes at 500°C for 12 h. This is a slight variation in preparation from previous studies of this material [12 - 16]. Samples were characterized by X-ray powder diffraction on a Siemens D5000 diffractometer. 25.4-mm diameter and 2.5 to 4.0-mm thick targets of Bi\textsubscript{1-x}Ca\textsubscript{x}CuSeO (x = 0.00, 0.10, and 0.15) for pulsed laser were initially pressed at 4 tons/in\textsuperscript{2} and sintered at 850°C under 2000 PSI of Ar(g) in an AIP isostatic press.

Thin films of Bi\textsubscript{1-x}Ca\textsubscript{x}CuSeO were deposited via PLD by using a 248-nm KrF laser operating at a power density of 1.0-1.6 J/cm\textsuperscript{2}. Films were deposited on silica, MgO (100), and SrTiO\textsubscript{3} (001) substrates. The power density was selected to limit pitting and bolder ejection from the ceramic target. Crystalline thin-films were deposited in-situ by using P\textsubscript{Ar} = 1.5-1.7 mTorr and a substrate temperature of 450 °C; the films were subsequently annealed in vacuum 545°C for 30-90 min. X-ray θ/2θ and rocking curve-scans of the films were acquired by using R-axis Rigaku and Siemens D5000 diffractometers, respectively. Transport measurements were made by using a Seebeck machine designed in-house and a Lakeshore 7504 Hall effect measurement system.
RESULTS AND DISCUSSION

Powder XRD results for Bi\textsubscript{1-x}Ca\textsubscript{x}CuSeO (0 ≤ x ≤ 0.2) are illustrated in figure 5.2. Compositions with x < 0.2 exhibit only diffraction lines attributable to the desired tetragonal structure. At x = 0.2, additional peaks are evident, indicating the presence of secondary phases. Decreases in lattice parameters are expected on substitution of the smaller Ca (r = 1.26 Å) for the larger Bi (r = 1.31 Å). Refinement of the cell parameters (Table 5.1 and Figure 5.3) reveals that the a axis contracts by 0.64%, the c axis contracts by 0.39% and the volume decreases by 1.7% as the Ca concentration increases to 15 at%. These data indicate that Ca substitutes onto the Bi-site to concentrations near 15 at% Ca.

Thin films of BiCuSeO deposited on MgO (100) and SrTiO\textsubscript{3} (100) single crystal substrates grow preferentially along {001}, while films prepared on a-SiO\textsubscript{2} exhibit unoriented polycrystalline growth. Additionally, X-ray rocking curve analysis of the BiCuSeO films reveals that the c-axis orientation was strongest for films on SrTiO\textsubscript{3} with a full width at half maximum of ~1 degree. This high degree of orientation is a result of a smaller lattice mismatch with SrTiO\textsubscript{3} (0.4%) than with MgO (7.4%).

In past studies, alkaline-earth dopants on the Ln site of LnCuQX compounds have led to an increase in conductivity [5,7,14,15]. At high dopant concentrations films exhibit a metallic-like behavior. Bulk samples of BiCuSeO exhibit the same metallic-like behavior when doped with alkaline-earth metals [16]. Undoped and Ca
doped BiCuSeO thin films were tested to determine if BiCuSeO maintains this characteristic in the thin-film form.

Figure 5.2 Powder XRD scans for Bi$_{1-x}$Ca$_x$CuSeO
Figure 5.3 Cell volume and unit-cell parameters for Bi$_{1-x}$Ca$_x$CuSeO ($x = 0, 0.05, 0.10, 0.15, 0.20$)
Table 5.1 lattice parameters and volume of Bi$_{1-x}$Ca$_x$CuSeO

<table>
<thead>
<tr>
<th>$x$</th>
<th>$a$</th>
<th>$c$</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.93(17)</td>
<td>8.93(46)</td>
<td>138.(11)</td>
</tr>
<tr>
<td>0.05</td>
<td>3.92(96)</td>
<td>8.93(03)</td>
<td>137.(90)</td>
</tr>
<tr>
<td>0.1</td>
<td>3.91(53)</td>
<td>8.90(43)</td>
<td>136.(50)</td>
</tr>
<tr>
<td>0.15</td>
<td>3.90(65)</td>
<td>8.89(99)</td>
<td>135.(82)</td>
</tr>
<tr>
<td>0.20</td>
<td>3.90(48)</td>
<td>8.89(68)</td>
<td>135.(65)</td>
</tr>
</tbody>
</table>

XRD scans of BiCuSeO films deposited on SiO$_2$ and SrTiO$_3$ are shown in Figure 5.4. The film on SiO$_2$ compares well to the powder data, indicating a polycrystalline film with no preferred orientation has been deposited. The patterns for the films on MgO and SrTiO$_3$ are dominated by 00$l$ reflections indicating a strong $c$-axis orientation. X-ray rocking-curve data for the $c$-axis oriented films on MgO and SrTiO$_3$ (001) are diagrammed in Figure 5.5. The FWHM on MgO is 3.5º and that on SrTiO3 is 1.0º. Because the $a$ lattice parameter, 3.931Å, in BiCuSeO is a better match to SrTiO$_3$ (3.905Å) than to MgO (4.195Å), less strain is encountered with SrTiO$_3$ as a substrate, providing a much sharper diffraction line.
Figure 5.4 BiCuSeO X-ray diffraction patterns A. powder, B. film on fused SiO$_2$, C. film on MgO (* = substrate peak), D. film on SrTiO$_3$
Figure 5.5 Rocking curves for the (005) peaks of BiCuSeO
Polycrystalline films of BiCuSeO on SiO\textsubscript{2} have mobilities of 2.0 cm\textsuperscript{2}/Vs, while oriented films exhibit slightly increased mobilities of 2.4 cm\textsuperscript{2}/Vs on MgO and 4.0 cm\textsuperscript{2}/Vs on SrTiO\textsubscript{3}. The enhanced mobilities observed in the oriented films arise from the 2D conduction pathway found in the BiCuSeO quantum-well structure. The less strained films on SrTiO\textsubscript{3} also exhibit a significant increase in mobility relative to the films on MgO. Doping Ca onto the Bi site increases the carrier concentration as well as the overall conductivity (Figure 5.6). This result is consistent with that observed in the bulk [12]. In the films, carrier concentration increases from $p = 5\times10^{18}$ cm\textsuperscript{-3} for BiCuSeO to $p = 7\times10^{20}$ cm\textsuperscript{-3} for the Bi$_{0.85}$Ca$_{0.15}$CuSeO, leading to a jump in conductivity from 8 to 170 S/cm. The increased number of defects in the doped samples, however, leads to significant carrier scattering and a drop in mobility from 4.0 cm\textsuperscript{2}/Vs for the undoped sample to 1.6 cm\textsuperscript{2}/Vs for the 15 at% Ca material (Figure 5.6).
Figure 5.6 Conductivity (●), mobility (▲), and carrier concentration (■) as a function of Ca concentration
CONCLUSION

Thin films of BiCuSeO were prepared *in-situ* via pulsed laser deposition, providing a straightforward path to the realization of polycrystalline and oriented thin-films. Films prepared on SrTiO$_3$ and MgO grow in a $c$-axis oriented fashion, leading to higher carrier mobilities relative to that observed in unoriented films. Undoped films on SrTiO$_3$ exhibit a mobility of 4 cm$^2$/Vs and carrier concentration of $p = 5 \times 10^{18}$ cm$^{-3}$ resulting in a conductivity of 8 S/cm. As a result of heightened carrier concentrations, films doped with Ca exhibit an increase in conductivity with values up to 170 S/cm.
REFERENCES


CHAPTER 6

PROPERTIES OF SnXS₃ (X = Hf or Zr): POTENTIAL BIPOLAR ABSORBERS FOR PHOTOVOLTAIC CELLS
ABSTRACT

The compounds SnMS₃ (M = Hf or Zr) were synthesized in bulk form by heating the elements in fused silica tubes at 750°C. Samples doped with 5at % Y on the M site exhibit p-type behavior with Seebeck coefficients of +427 μV/K and +1180 μV/K for the Zr and Hf derivatives, respectively. Samples doped with 5at % Nb on the M site exhibit n-type behavior with Seebeck coefficients of -94μV/K and -392 μV/K, for the Zr and Hf compounds, respectively.
INTRODUCTION

The ability to symmetrically dope materials $n$- and $p$-type is very advantageous for a variety of applications, including light emitting diodes [1], photovoltaics [2], and bipolar junction transistors [3]. In many cases, however, large band-gap semiconductors are difficult to dope symmetrically [4]. Identifying large band gap materials (> 1.2eV) that exhibit bipolar behavior is important to advancing technology, especially in the field of photovoltaics. Photovoltaic cells require the formation of a $p$-$n$ junction that exhibits a strong photoresponse, which occurs for materials with band-gaps in the range of 1.2 to 1.7 eV. The challenge of producing new bipolar materials for use in photovoltaic cells inspired the research presented here.

To identify materials compositions for realizing bipolar semiconductor behavior, we consider three criteria:

- Materials must contain a combination of cations that are known to produce bands appropriate for inducing $p$- or $n$-type character
- Cations must form submatrix structures that lead to band development, i.e., the cations cannot be diluted and isolated in a structure
- Doping pathways must be available to realize stable $p$- and $n$-type behavior.

The propensity of an extended metal (cation) substructure to exhibit $p$- or $n$-type behavior is usually linked to the oxidation state of the cation. An example is Sn, which is found in oxidation states II or IV. Compounds that contain Sn (II) tend to be $p$-type because of the presence of Sn vacancies $V_{\text{Sn}}$ [5], which effectively produce Sn
(IV) and holes in the valence band. In contrast compounds that contain Sn (IV) tend to be n-type because the presence of anion vacancies, [6], which effectively produce Sn (II) and electrons in the conduction band. To exhibit bipolar behavior there must be conduction pathways for both electrons and holes. Complex materials that are compositionally dominated by a cation, generally lead to structural isolation of minority cations affording no opportunity for them to contribute to the dispersion of the conduction or valence bands. The feasibility of potential n and p-type dopants must be considered for inducing the desired carrier type, while maintaining material chemical stability.

On the basis of these considerations for identifying bipolar materials, we settled for this study on the materials SnHfS$_3$ and SnZrS$_3$. Both of these compounds contain a cation that leans p-type, i.e., Sn (II) and one that leans n-type, i.e., Hf (IV) or Zr (IV). Both crystallize in the NH$_4$CdCl$_3$ structure type which contains submatrices corresponding to SnS and MS$_2$ (Figure 6.1) [7-9]. With a 5s$^2$ electron configuration for the Sn (II) and 4d$^0$ and 5d$^0$ configuration for Zr (IV) and Hf (IV), respectively, means are potentially available for doping the Sn(II) submatrix to realize p-type behavior, while the Zr(IV) and Hf(IV) submatrix can be doped to realize n-type behavior. The SnS polyhedra form edge sharing strings, providing a pathway for hole conduction. The MS$_2$ polyhedra form edge sharing M-centered octahedral, providing the conduction pathway for electrons. These linked submatrices should contribute to the valence and conduction bands, respectively. The presence of Zr or Hf provides many different possibilities for doping, e.g., p-type dopants Y$_{Zr}$ and La$_{Zr}$ and n-type
dopants Ta$_{Zr}$, Nb$_{Zr}$, Bi$_{Sn}$, and Sb$_{Sn}$. These Zr and Hf sulfides satisfy all of the criteria for a bipolar material and were thus selected for further study.

Figure 6.1 *Pnma* crystal structure of SnMS$_3$ showing matrices of SnS and MS$_2$ (M = Hf or Zr)
EXPERIMENTAL

The sulfides SnM$_{1-x}$(Y,Nb)$_x$S$_3$ (M = Hf, Zr and x = 0, 0.05) were synthesized from the appropriate combination of the elements Sn (99.8 %, Cerac), Zr (99.7%, Cerac), Hf (99.8%, Cerac), S (99.999%, Cerac), Y (99.9%, Cerac), and Nb (99.8%, Alfa Aesar). The elements were thoroughly mixed and sealed in an evacuated silica ampoule. Ampoules were heated to 750°C for 24 h and then cooled. The contents were ground, sealed in a fresh tube, and heated to 750°C for 48 h. The resultant powder was characterized by using a Siemens D5000 X-ray diffractometer with Cu Kα radiation. The powders where cold pressed in a 1/2" or 3/8" die at 1 ton/in$^2$ for 10 min and then were sintered in an AIP6-30H hot isostatic pressure furnace at 925-975°C for 2-5 hours at $P_{Ar} = 1000-2000$ PSI. The resulting pellets were 0.9-1.3 cm in diameter and 0.14-0.23 cm thick with theoretical densities of 68-79%. The pellets were used to determine carrier type and Seebeck coefficients at room temperature by using the system of in-house design described by Kykyneshi [10].

Optical measurements to determine band gaps were made at room temperature by using an Oriel 300-W Xe arc lamp and a Cary model-15 prism monochromator with MgO as a standard. The standard was used to determine the relative reflectance $R_d$. The optical band gaps were extracted from the relative reflectance by using the Kubelka-Munk method in which $k/s*E^2$ is plotted against $E$ ($k/s = (1-R_d)^2/(2 * R_d))$, where the linear portion of the graph is extrapolated to the baseline to estimate the band gap [11,12].
RESULTS

Powder samples of the sulfides were confirmed to be single phase by XRD analysis (Figures 6.2 and 6.3). These powders were used to estimate band gaps from diffuse reflectance with results corresponding to $E_g = 1.5 \text{ eV}$ for SnZrS$_3$ and $E_g = 1.6 \text{ eV}$ for SnHfS$_3$.

The powders were pressed into pellets and densified via hot-isostatic processing for Seebeck measurements. The sizes and densities of the pellets are summarized in Table 6.1. The undoped pellets were too resistive to measure a Seebeck coefficient. The pellets doped with Y exhibit positive Seebeck coefficients ($+427 \mu \text{V/K}$ for Zr and $+1180 \mu \text{V/K}$ for Hf), indicating that the samples are $p$-type (Figures 6.4 and 6.5). In contrast, the pellets doped with Nb exhibit negative Seebeck coefficients ($-94 \mu \text{V/K}$ for Zr and $-392 \mu \text{V/K}$ for Hf), indicating $n$-type nature (Figures 6.6 and 6.7). Hence, the Seebeck results confirm the ability to symmetrically dope the SnMS$_3$ system both $p$- and $n$-type.

Table 6.1 Size, weight and density of SnMS$_3$ (M = Hf or Zr) pellets used in Seebeck measurements to determine carrier type

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dopant</th>
<th>mass (g)</th>
<th>diameter (cm)</th>
<th>thickness (cm)</th>
<th>theoretical density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnZrS$_3$</td>
<td>undoped</td>
<td>0.2969</td>
<td>0.922</td>
<td>0.147</td>
<td>70.4</td>
</tr>
<tr>
<td></td>
<td>5% Y</td>
<td>0.6976</td>
<td>1.225</td>
<td>0.188</td>
<td>75.9</td>
</tr>
<tr>
<td></td>
<td>5% Nb</td>
<td>0.8931</td>
<td>1.226</td>
<td>0.225</td>
<td>78.1</td>
</tr>
<tr>
<td>SnHfS$_3$</td>
<td>undoped</td>
<td>0.9421</td>
<td>1.275</td>
<td>0.197</td>
<td>75.1</td>
</tr>
<tr>
<td></td>
<td>5% Y</td>
<td>1.0368</td>
<td>1.277</td>
<td>0.216</td>
<td>68.1</td>
</tr>
<tr>
<td></td>
<td>5% Nb</td>
<td>0.9505</td>
<td>1.278</td>
<td>0.218</td>
<td>75.1</td>
</tr>
</tbody>
</table>
Figure 6.2 XRD scans of SnZrS$_3$ doped with 5 at\% Y and 5 at\% Nb on the Zr site
Figure 6.3 XRD scans of SnHfS$_3$ powders doped with 5 at% Y and 5 at% Nb on the Hf site.
Figure 6.4 Seebeck data for SnZr$_{0.95}$Y$_{0.05}$S$_3$. (slope = + 427 $\mu$V/K)
Figure 6.5 Seebeck plot of SnHf$_{0.95}$Y$_{0.05}$S$_3$. (slope = +1177 μV/K)
Figure 6.6 Seebeck data for $\text{SnZr}_{0.95}\text{Nb}_{0.05}\text{S}_3$. (slope = -94 $\mu$V/K)
Figure 6.7 Seebeck plot of SHf_{0.95}Nb_{0.05}S_3. (slope = -392 \text{ \( \mu \)V/K})
DISCUSSION

These sulfides SnMS₃ exhibit band gaps of 1.5 eV and 1.6 eV for the M = Zr and Hf derivatives, respectively. Both values mean the materials should be considered for study as absorber layers in homojunction photovoltaic cells. SnS is a known $p$-type semiconductor, [13], and MS₂ (M = Hf, Zr) compounds are known to be $n$-type semiconductors [14]. Bipolar behavior is observed upon combining submatrices of SnS and MS₂ in SnMS₃. Doping Nb and Y onto the M-site accomplishes $n$- and $p$-type behavior, respectively. Doping on the Sn site has yet to be studied; potential $n$-type dopants include Bi and Sb, while $p$-type doping may problematic, although a +1 cation should produce holes.

The use of homojunctions in photovoltaic applications is very advantageous due to the reduction of interfaces. Interfaces tend to accumulate defects, which act as recombination centers, reducing the concentration of photogenerated carriers. Bipolar materials such as SnMS₃ potentially provide a means to limit killer defects and improve performance in PV cells.
REFERENCES


CHAPTER 7

SOLUTION PROCESSED HfO$_2$ AND ZrO$_2$ THIN FILMS

Peter A. Hersh, Jeremy T. Anderson, Benjamin Schmid, David C. Johnson, and Douglas A. Keszler
ABSTRACT

High quality, ultra-thin, smooth, pinhole-free, and dense films of HfO$_2$ and ZrO$_2$ were prepared by solution-based processing via spin coating. Pinhole-free crystalline thin-films having thickness ~2nm and rms roughness ~1Å were characterized via high-resolution transmission electron microscopy (HRTEM) and X-ray reflectivity (XRR). As modeled from the XRR measurements, the HfO$_2$ films have a density that is 72% of the theoretical value.
INTRODUCTION

Solution-based processing of thin films offers many potential advantages over vapor deposition processing. Solution deposition is performed in a non-vacuum environment, which lowers cost and reduces deposition time leading to highly scalable techniques. Solution-based thin-film deposition provides an attractive route to the realization of high-throughput, high-performance electronics. Much of the solution-based processing to date has focused on organic and polymeric materials. These materials exhibit modest performance in devices, which are approaching the modest fundamental limitations of organic materials [1-3]. Solution-processed inorganic materials provide a much higher performance ceiling and have already yielded better characteristics [4-6].

The use of solution-processed inorganic materials in thin film transistors (TFTs) as gate dielectrics [7,8] and channel materials [9,10] has recently been described. Device integration requires high quality thin films. TFT channel materials must exhibit a high mobility with a low defect concentration. Milliron and co-workers have demonstrated suitable channel materials from inorganic solution-based processing [9]. Gate dielectrics for TFTs must be smooth, dense, and pinhole-free while exhibiting low leakage current and high breakdown strength. High quality solution-processed dielectrics have been integrated into thin-film transistors with retention of excellent dielectric behavior [7-8]. These results have prompted this work directed to the development of high-quality, high-κ dielectric thin films from solution-based processing.
Shrinking device dimensions have led to the need to replace SiO₂ as a dielectric in standard Si CMOS technologies. The requirements have been summarized in the International Technology Roadmap for Semiconductors [11]. The replacement dielectrics must exhibit a high permittivity (dielectric constant) to allow thicker layers that exhibit capacitance equivalent to SiO₂, while maintaining smaller leakage currents. HfO₂ and ZrO₂ have attracted considerable attention as replacement gate dielectrics because of their desirable dielectric (κ ~ 25 for both) and thermal properties [12-13]. One of the challenges for implementing HfO₂ and ZrO₂ dielectrics is making smooth, dense, and pinhole-free ultra thin-films (≤13nm). These stringent requirements rule out many PVD processes such as sputtering and pulsed laser deposition due to irregular coverage and uniformity of ultra thin-films. To accomplish uniform coverage with such films, much of the development has focused on atomic layer deposition (ALD). The ALD deposition of MO₂ (M = Hf or Zr) is typically performed by using a hydroxylated substrate in the presence of a sufficient vapor pressure of MQ₄ (Q = Cl [14-16], I [17], NO₃ [18], alkylamides [19,20] or cyclopentadienyl [21]) precursor. Ligand exchange is performed by using a source of oxygen usually H₂O or O₃. There are often high amounts of contaminants left after the ligand exchange, which degrades film quality [21]. Contaminants have been limited through appropriate processing; resultant films have exhibited large dielectric constants (κ = 10-23) [13,18], while maintaining low leakage current densities (~10⁻⁶ A/cm² at 1.5 V) [13]. Despite such promising results from ALD, the processing requires vacuum and thus leads to high cost and low throughput. This has driven
some work on the solution-based deposition of HfO$_2$ and ZrO$_2$. To date these films have not reached the same uniformity and density of the ALD films [22-24].

We have developed a method to produce ultra-thin films (~2nm) of MO$_2$ (M = Hf or Zr) from solution-based processing that rival the morphological quality observed via ALD. Films are initially deposited at room temperature in a sulfated form by using spin coating and prompt inorganic condensation. The sulfate is then removed by a treatment in a basic bath. The as-deposited films are smooth, dense, and pinhole free and remain so at temperatures up to 850°C.

EXPERIMENTAL

Precursor solutions were prepared from HfOCl$_2$·8H$_2$O (Alfa Aesar, 98% pure), ZrOCl$_2$·8H$_2$O (Wah chang spectrographic grade), H$_2$O$_2$ (30% Solution, Mallinckrodt Chemicals) and H$_2$SO$_4$ (aq) (EM Science Gr ACS, 95-98%) by following previously described methods [7]. Precursor solutions for thin-film deposition contain a metal ion concentration of 0.05 M to 0.4 M with 70% H$_2$O$_2$(aq) and 50% sulfate relative to the metal. The difference in metal ion concentrations allows a thickness per coat variation from 3 nm up to 25 nm.

Thin films were deposited on Si substrates with a 170-nm thermally grown SiO$_2$ buffer layer. Substrates were cleaned in an ultrasonic bath with Contrad-70 cleaning solution at 45°C for 60 min followed by a final rinse with deionized water. Films were deposited by using a spin coater with a spin rate of 3000 rpm for 30 s, followed by hotplate polymerization at 125°C for 1-2 min. Spin-coating and polymerization steps were repeated until the desired thickness was reached. After the
desired thickness has been reached, some films were heated to crystallization temperatures. Other films were first treated in a 0.1 M to 0.5 M NaOH(aq) bath for 1-2 min and then rinsed in a deionized water bath for 1-2 min before the thermal treatment.

X-ray diffraction (XRD) analysis on the thin films was performed on a Rigaku R-axis Rapid with Cu Kα radiation. Atomic force microscopy (AFM) measurements were made by using a Digital Instruments Nanoscope III Multimode AFM operated in contact mode with a Veeco NP-20 SiN probe and a scan frequency of 1.15 Hz. X-ray reflectivity (XRR) data were acquired by using a Bruker Discover D8. Compositional analyses were determined on a Cameca SX-50 electron microprobe equipped with 4 tunable wavelength dispersive spectrometers. Accelerating voltages of 12, 16, and 22 kV were used; data were collected at five points while monitoring O, Cl, Na, S, and Si Kα intensities and Zr and Hf Lα intensities. Standards used for the analysis were MgO, Hf, Zr, FeS₂ (pyrite), Ca₅(PO₄)₃Cl (apatite), Si, and NaSi₃AlO₈ (albite). Corrections to the raw intensity were made using the Probe for Windows automation and analysis package [25]. The StrataGEM compositional analysis software package was used for thin-film geometry corrections by comparing experimental K-ratios to simulated values.

RESULTS AND DISCUSSION

Amorphous, atomically flat, dense and pinhole free thin films of hydrous hafnium oxide sulfate (HafSOx) are deposited via spin coating, cf., Figure 7.1. These films remain smooth and amorphous after heat treatments up to 650°C for Zr and
700°C for Hf. At higher temperatures, however, the films crystallize and roughen, forming volcano-like features at the surface, cf., Figure 7.2. These features are most likely caused by the loss of SO\textsubscript{3} (g). This is supported by thermal gravimetric analyses of Hf sulfate powders, which reveal that mass loss associated with decomposition of sulfate and release of SO\textsubscript{3}(g) \[\text{SO}_3 (g) \rightarrow \text{SO}_2 (g) \text{ and } \frac{1}{2} \text{O}_2 (g)\] occurs at temperatures above 700°C [7].
Figure 7.1 5 x 5-μm AFM scan of as-deposited sulfated hafnia exhibiting rms roughness ~0.1 nm
Figure 7.2. 5 x 5-μm AFM scan of untreated HafSOx film heated to 850°C for 10 min (rms roughness ~5nm)
To counteract this effect, films were treated in a 0.1 to 0.5 M NaOH(aq) bath for 1-2 min to remove sulfate and chloride from the HafSOx and ZircSOx films prior to heating. NaOH(aq) has been shown to effectively exchange hydroxo anions for other anions in zirconium salts [26-28]. The NaOH treatment results in a thickness reduction of 40-45%, giving final layer thicknesses of 2-15 nm from initial layers 3-40nm. The treatment, however, has little impact on the smoothness (~1Å) or amorphous nature of the films heated below 500 and 550ºC for the zirconia and hafnia films, respectively. A representative AFM scan for a 53nm thick film is illustrated in Figure 7.3. The smooth nature of the films is also retained up to temperatures as high as 850ºC (Figure 7.4). The drop in crystallization temperature can be seen in the X-ray diffraction plots (Figures 7.5-7.8). The untreated HafSOx film crystallizes as a mixture of tetragonal and monoclinic phases at 700ºC (figure 7.5). From the XRD data, only the monoclinic phase is observed following heat treatment at 550ºC (Figure 7.6). The untreated ZircSOx films crystallize in a mixed monoclinic and tetragonal phase at 650ºC (Figure 7.7). The treated zirconia films crystallize in the tetragonal phase at 500ºC. Upon further heating films develop both monoclinic and tetragonal phases (figure 7.8). The tetragonal phase of HfO₂ and ZrO₂ have been observed in previous thin film studies [16,19,24,29,30]. The lower crystallization temperature and loss of thickness following NaOH treatment are consistent with anion-exchange and replacement of SO₄²⁻ with OH⁻ in the films.
Figure 7.3. 5 x 5-μm AFM scan of HafSOx film treated with 0.1 M NaOH and heated at 450°C for 10 min. (rms roughness ~0.1 nm)
Figure 7.4. 5 x 5-μm AFM scan of HafSOx treated with 0.1-M NaOH(aq) and heated to 850ºC for 10 min (rms roughness ~0.2nm)
Figure 7.5. XRD plots of untreated HafSOx films. HfO$_2$ plot is a reference plot for the monoclinic phase. The (*) represents the $2\theta$ position of two major tetragonal phase peaks [31-32].
Figure 7.6. XRD plots of 0.13M NaOH treated HafSOx film. (↓ indicated position of substrate peak). The HfO₂ plot is a reference plot for the monoclinic phase. The (*) represent the 2θ position of two major HfO₂ tetragonal peaks.
Figure 7.7. XRD plots of untreated ZircSOx films. The ZrO$_2$ plot is a reference plot for the monoclinic phase. The (*) indicates the 2θ positions of two major tetragonal phase peaks [33,34].
Figure 7.8. XRD plots of 0.13 M NaOH treated ZirSOx films. The ZrO$_2$ plot is a reference plot for the monoclinic phase. The (*) represent the 2θ position of two major tetragonal phase peaks.
Electron probe microanalysis (EPMA) of a film deposited from the 0.4 M Hf solution and heated to 350ºC for 5 mins gives a film with composition HfO$_{1.32}$(SO$_4$)$_{0.61}$Cl$_{0.15}$. The chlorine in the film is a result of kinetic trapping, a consequence of the rapid thermal dehydration. Films that are treated in the NaOH bath do not have measurable levels of sulfur (less than 0.01 atomic percent) and less than 0.3 atomic percent chlorine. This confirms that the sulfur and chlorine are both removed from the films following treatment in the NaOH bath. EPMA also verifies that the amount of residual Na left in the film after the treatment is less than 0.3 atomic percent.

The qualities of the films are confirmed by the TEM images of Figures 7.9 and 7.10, which indicate thicknesses near 2 nm are readily achieved via the anion exchange reaction. From XRR data, the HfO$_2$ films produced by treating HafSOx with 0.1 M NaOH and subsequently heating to 850ºC have a density of 6.93 g/cm$^3$ (72% dense), while films produced from directly annealed HafSOx have a density of 6.02 g/cm$^3$ (62% dense). The removal of the sulfate and chlorine groups prior to annealing allows the films to crystallize more densely.

Clearly, the as-deposited semi-solid films allow for anion exchange without degradation of film morphology. This provides opportunities to use these films for other applications such as ion-exchange chromatography and filtration [35,36].
Figure 7.9 TEM image of spin coated amorphous HfO$_2$ (dark layer) on SiO$_2$ with a Pt coating on top.
Figure 7.10. TEM image of HfO$_2$ (dark layer) thin film produced via anion exchange and heating at 850°C.
CONCLUSION

High-quality dense and pinhole free thin films of HafSO$_x$ and ZircSO$_x$ are deposited from solution-based processing via prompt inorganic condensation. Films are treated in a 0.1 M-0.5 M NaOH(aq) bath which removes the sulfate and chlorine and leaves behind hydroxylated Hf and Zr films. Following thermal treatment, smooth, dense, and pinhole-free HfO$_2$ and ZrO$_2$ films are produced. Film quality rivals that of ALD in a bench top non vacuum deposition allowing for thickness down to 2 nm. This method of deposition offers a potentially low cost, efficient route for the production high-quality, ultra-thin high-κ gate dielectrics.
REFERENCES


CHAPTER 8

ANION EXCHANGE IN HYDROUS HAFNIUM OXIDE FILMS
ABSTRACT

Semi-solid films of HfO_x(SO_4)_xCl_yH_2O were deposited via solution-based processing and spin coating. A NaOH(aq) bath is used to exchange hydroxide for sulfate and chloride, leaving a hydroxylated hydrate HfO_x(OH)_{4-2x}·yH_2O. The exchange proceeds without disruption of film morphology. Selected anions, such as phosphate and sulfate, can then be reincorporated in the hydrous film via anion exchange in an acidic solution.
INTRODUCTION

Hydrous zirconia has been shown to exhibit ion exchange behavior, which is thought to stem from surface hydroxyl groups [1-3]. The hydrous zirconia exhibits amphoteric behavior, i.e., anions are exchanged for hydroxyl groups at low pH, while cations are exchanged for protons at high pH. Ion exchange materials such as hydrous zirconia are widely used in chromatography [4] and filtration [5]. In contrast to the considerable work on the exchange properties of hydrous zirconia, very little work has been reported on hydrous hafnia [1,3,6-8].

This paper will focus on solution-based thin film deposition of hydrous hafnia and the ion exchange capabilities of these films. Solution-based processing of thin films has been studied at with a recent focus on hafnium materials [9]. High quality solution-based hydrous hafnia films have been made from a sulfated precursor solution followed by an ion-exchange process [10]. The ion exchange is possible because of the highly hydrated nature of the as-deposited films. These semi-solid films allow ion exchange without disruption of the morphology.

EXPERIMENTAL

Precursor solutions were prepared from HfOCl₂·8H₂O (Alfa Aesar, 98%), H₂O₂ (30% Solution, Mallinckrodt Chemicals) with H₂SO₄ (aq) (EM Science, ACS, 95-98%) [9,10]. A metal ion concentration of 0.4 M with 0.28 M H₂O₂(aq) and 0.2 M
H$_2$SO$_4$(aq) was used. Films were deposited by applying the solution to an SiO$_2$/Si substrate on a spin coater operating at 3000 rpm for 30 s. The spinning is followed by a hot plate polymerization at 125°C for 1 to 2 min. The polymerization step allows the film to become solid enough to build thickness. The spin coating and hot plate polymerization steps were repeated until the desired thickness of the films was reached.

Films were then treated with 0.1 M NaOH(aq), which removes the sulfate replacing it with hydroxide groups [10]. The resulting films were then treated in H$_2$SO$_4$(aq) or H$_3$PO$_4$(aq) at varying concentrations (0.01-0.5M) and times (1-30 min).

Compositional analyses of products were determined with a Cameca SX-50 electron microprobe equipped with 4 tunable wavelength dispersive spectrometers. Accelerating voltages of 12, 16, and 22 kV were used and averaged over 5 points to monitor P, O, Cl, Na, S, and Si K$_\alpha$ intensities and Zr and Hf L$_\alpha$ intensities. Standards used for analysis were MgO, Hf, Zr, FeS$_2$ (pyrite), Ca$_5$(PO$_4$)$_3$Cl (apatite), Si, and Si$_3$AlNaO$_8$ (albite). Corrections to the raw intensity were made by using Probe for Windows automation and analysis package [11]. The StrataGEM compositional analysis software package was used for thin-film geometry corrections by comparing experimental K-ratios to simulated values.
RESULTS AND DISCUSSION

Thin semi-solid films of HfO$_{2-x-y-z}$(SO$_4$)$_x$(OH)$_{2y}$(Cl)$_{2z}$·aH$_2$O were deposited from solution-based processing via spin coating. The composition of the as-deposited thin film is HfO$_{1.32-y}$(SO$_4$)$_{0.61}$(OH)$_{2y}$Cl$_{0.15}$·aH$_2$O. The chloride is incorporated in the film as a result of kinetic trapping in the rapid polymerization process [9]. To remove sulfate and chloride from the films, a treatment in NaOH(aq) is administered. This treatment promotes ion exchange, resulting in the removal of the sulfate and chloride and replacing both with hydroxide. To confirm the loss of sulfate and chloride, compositional analyses were performed by using EPMA. The films after the NaOH treatment have only small amounts of contaminants remaining: S (< 0.01 atomic percent), Na (< 0.3 atomic percent), and Cl (< 0.3 atomic percent).

After removal of the sulfate and chloride, the resultant films are hydrous hafnia. The XRD plot of film reveals its amorphous nature (Figure 8.1). The amorphous nature is due to the randomness of the structure caused by the rapid polymerization [12].
Figure 8.1. XRD plot of amorphous hydrous hafnia
Following formation of the hydrous hafnia films, they were treated in acid to promote anion exchange. Varying the reaction time was found to have very little effect on the amount of anion exchange. This is supported by the lack of thickness change observed and confirmed by EPMA. Varying the acid concentration did not affect the anion exchange, but at high concentrations of acid (> 0.2M) the films were completely etched away. The composition of the film treated in H₂SO₄(aq) and then heated to 350°C to remove excess water is HfO₁.₇₃(SO₄)₀.₂₇. The composition of films treated in H₃PO₄(aq) and then heated to 350°C is HfO₁.₈₇(PO₄)₀.₀₉. These results indicate that a significant anion exchange occurs when hydrated hafnia films are treated in acid.

CONCLUSION

Semi-solid films of a hafnia sulfate chloride are deposited via spin coating by using prompt inorganic condensation. Sulfate and chloride were removed from the films following treatment in NaOH(aq). These films are highly hydrated and allow for anion exchange without disrupting film morphology. The final concentration of films treated with sulfuric acid is HfO₁.₇₃(SO₄)₀.₂₇ and films treated in phosphoric acid result in HfO₁.₈₇(PO₄)₀.₀₉. These reactions provide a unique means for selectively incorporation species into oxide films, providing a unique synthesis approach to realizing new compositions and properties.
REFERENCES


CHAPTER 9

CONCLUSIONS

Quaternary Cu and Sn chalcogenides containing Ba or Sr provide a rich route to controlling physical properties of interest in developing new absorber layers for photovoltaic devices.

The Cu$_3$MQ$_4$ materials (M = Ta or Nb and Q = S or Se) are cubic $p$-type semiconductors with optical and electrical properties that may be useful in photovoltaic cells and transparent electronics. These materials have optical band gaps in the range 2.13-2.76 eV. Band-gap modulation occurs without disruption of the cubic P-43m structure.

BiCuOSe films prepared in-situ on SrTiO$_3$ and MgO grow in a c-axis oriented fashion leading to high quality $p$-type conducting films. Films doped with Ca exhibit a conductivity of 170 S/cm.

The materials SnMS$_3$ (M = Hf or Zr) have been symmetrically doped $n$- and $p$-type with Nb and Y, respectively. The samples exhibit band gaps of 1.5 eV and 1.6 eV, for the Zr and Hf materials, respectively. Both fall in the range of interest for study as absorber layers in thin-film PV cells.

Smooth, dense, and pinhole-free HfO$_2$ and ZrO$_2$ films were produced via solution-based processing. Semi-solid films of HafSO$_x$ and ZircSO$_x$ were deposited via spin coating. The anions in the films were subsequently removed anion exchange
through treatment in a NaOH(aq) bath, yielding unique hydroxylated films. The quality of the films is retained through the exchange process and at annealing temperatures as high as 850°C. The resulting film qualities rival those of films produced by ALD; here, bench-top deposition and processing in air allow the realization of films as thin as 2 nm. The hydroxylated films also provide a new opportunity to selectively reintroduce desired anions such as sulfate and phosphate via the anion-exchange process.
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APPENDIX

AIP6-30H OPERATION AND MAINTENANCE
EQUIPMENT AND SETUP

The AIP6-30H hot isostatic press is located in the basement of Gilbert room 36. The AIP6-30H consists of a cylindrical blue chamber (from AIP), a large square blue chamber (from AIP), an air compressor (purchased from bi-mart), and a 4 tank manifold (purchased from air gas). The blue cylindrical chamber contains the high pressure furnace. The large square blue chamber contains all the electrical connections as well as the mechanical vacuum pump, the compressor and release valves. For any questions or concerns about these two chambers you may contact AIP (In May 2006 our contact was Paul Geuy e-mail pgeuy@aiphip.com).

The equipment and plumbing was set up by Ted Hinke and me. All of the high pressure gas lines are stainless steel swagelock ½” gauge and pressure rated to 3000 PSI. The vent line which, runs along the ceiling to a fan hooked to the exterior is a larger steel pipe that allows for less noise during the venting process.
RUNNING THE HIP

1. Turning on the HIP
   a. Turn on large throw switch on side of large blue cabinet
   b. Press green button on front of large blue cabinet
   c. Watch the monitor on the CPU wait for the control power light to turn green and say control power energized (if this does not happen in about 1 minute go to system alarms and silence alarms)

2. Venting chamber
   a. At the CPU under operating modes click the button that says Semi Auto Mode
   b. Click on Operator window (from here you should be able to see pressure and temperature in the chamber, which should be around 100PSI and room temperature)
   c. Make sure the pressure and temperature look OK (ie not to hot or to much pressure) if it looks good skip to step d.
      i. If the pressure is too high then you must heat the chamber before venting to prevent the formation of ice on the out side of the chamber
      ii. To raise the temperature manually go to furnace control out of the main menu
        1. Energize contactor
2. Raise power (to no higher than 10%) with the sliding bars and hit accept button

3. Watch temperature rise when it reaches desired temp (this will change depending on pressure in chamber, but usually around 100°C for every 6000PSI) lower sliding bars and hit accept make sure to deenergize contactor when finished

4. Click back to operator window
   iii. If temperature is too high you must wait for it to cool before venting
d. Shut sliding door to bomb shelter then hit open vent valve depending on the amount of pressure this can be very loud
e. Watch the temperature while venting if it drops below ~15°C you should stop the vent and reheat the chamber see above
f. When the pressure drops below 19PSI close the vent valve

3. Opening the chamber
   a. If connected disconnect the H₂O lines to the large metal lid of the cylindrical chamber
   b. Use gloves and a lab coat when opening chamber there is a lot of grease
c. Use the two metal bars with foam handles located on the stool to unscrew the lid counter clockwise
i. If turning the lid is too difficult you might have too much pressure built up in the chamber still

ii. Attempt to vent further and reopen

d. When the lid is completely unscrewed lift it on to stool (careful lid is heavy if not comfortable lifting by yourself get assistance)

e. Looking down into the chamber there should be a metal ring with a rubber o-ring on top and then a loose metal plate below the ring with a screw hole in the middle of the plate

f. Take the red colored dent puller located on the bench outside of the bomb shelter and screw it into the plate and use the dent puller to remove the ring

g. Looking into the chamber now you should see the top of the heat shield which has two screw holes

h. Using the two screws connected by a bar located next to the dent puller remove the heat shield

4. Determining furnace type

a. There are two furnaces a Hoskins and a Graphite furnace that are easily distinguishable from each other

b. The Hoskins furnace using typical heating coil type elements this furnace is used for oxides and has a maximum temperature of 1000°C

c. The Graphite furnace uses high temperature MoSi\textsubscript{2} heating elements this furnace has a maximum temperature of 1700°C in vacuum and up to 2200°C at pressures above 500PSI this is used for all elements.
d. The furnace type can also be determined by looking at the operators window of the program each furnace uses different thermal couples and this will distinguish which furnace is in the chamber

e. The spare furnace will be sitting on the bench next to the dent puller if you have any questions

5. Changing furnaces

a. If you don’t need to change furnaces go to step 6

b. To remove the furnace take the heat shield and screw screws into the bottom of the shield in to the three screw holes make sure the screws will not fall out but don’t screw them in all the way

c. Look into the chamber at the bottom of the furnace there are three holes that you have to get the screws to fit in then use a clock wise turn to lock the furnace to the heat shield and lift.

d. Move the screws and the handle bar from the furnace you just pulled out to the new furnace. Make sure to not swap heat shields the heat shield is specific to the furnace and swapping shields can cause major damage.

e. Lower the new furnace into the chamber use the metal pin at the bottom of the chamber as a guide it should line up with the hole in the bottom of the furnace.

f. Once the furnace is in place you will see the thermal couples start to give readings on the CPU in the operator window
g. Turn the heat shield counterclockwise to remove it from the furnace be careful when lifting the shield as sometimes the furnace has not detached

h. Once the heat shield is removed take the screws out of the bottom

6. Loading sample

a. Samples should be in an alumina boat with a cap to reduce the amount of contamination.

b. Lower sample on to block in furnace make sure it is stable and will not tilt during the heating

c. Put heat shield over furnace

d. Put metal plate on top of furnace

e. Check o-rings on metal ring upper o-ring needs to be replaced every 3-5 runs

   i. If your o-ring is OK skip to step f. If your o-ring has gone bad you will not be able to pull a vacuum or build up pressure

   ii. Replacement o-rings are found in a plastic bag underneath the counter

   iii. New o-rings are a little small and need to be stretched out to fit into the groove of the metal ring

f. Load metal ring with o-ring in the groove make sure metal ring is flat on the lip of the chamber
g. Put metal lid back onto chamber (again careful it is very heavy) screw down tight the water inlet and outlet should be pointed the same place as when you found it (toward the bomb shelter door in August 2007)

h. Connect H₂O lines to the metal lid it does not matter which line goes to which inlet.

i. Open both H₂O in and out valves on the wall behind the chamber

7. Setting up run

a. Once sample is loaded go to computer and switch operating modes from semi-auto mode to full auto mode

b. Go to Cycle recipes and write your program

   i. Program writing

      1. Segment (order of steps does not need to be changed)

      2. Temperature to change this you must use furnace for heating and cooling

      3. Pressure is changed by Vac, Vent, Gas, or Comp this also changes while heating keep in mind when trying to get to high pressures * Comp should not be run at pressures below 1000PSI

      4. Vacuum is increased by Vac and decrease by Gas

      5. Segment time indicates how long you want to ramp or hold at certain temperatures and pressures

      6. Segment transition can be set to time or setpoint I have found that using the Setpoint more than once does not
seem to work very well (this could be just operator error) so I set the vacuum level with setpoint then do every other step with time

7. PID group just leave at 0

8. Pressure Makeup this is to allow you to keep a constant pressure with the vent or the compressor (to use this feature make sure pressure makeup is turned on in the operator window) i.e. if you want to keep the pressure at 10,000 psi while you ramp temperature up or down this will allow you to keep pressure constant with out it your pressure will change. I usually activate this during my dwell to make sure not too much pressure is lost

9. Events make sure everything you want running is highlighted should only be one thing at a time i.e. run the compressor then the furnace

10. Next segment all should say yes until you are finished then after you last line of programs switch to END

ii. Make sure you hit enter after changing any value or it will not change

iii. First segment should default to no events

iv. Always run the vacuum first to remove any oxygen that got into if you do not run the vacuum this can cause unnecessary wear to
the heating elements and heat shield especially in the graphite furnace

v. Make sure to put END in the next segment instead of yes in the next segment category or the program will keep running

vi. It is easiest to modify an existing program then to create on completely new

c. Replace Argon tank label #1 with new tank from chemstores (for high pressure runs >20,000 PSI sometimes replacing 2 cylinders is necessary)

i. Close all Argon tanks

ii. Close the valve on the manifold for the tank you are replacing (this is to limit the amount of oxygen that gets into the lines)

iii. Connect new argon tank without opening manifold

iv. Open gas tank (not manifold) then vent by loosing connection to gas tank (don’t remove completely) then retighten the connection to the gas tank

v. Repeat the venting of the gas line 3-4 times (this is to remove as much oxygen as possible from the line)

vi. Make sure connection to tank is secure then close argon tank and open manifold valve from that tank (NEVER CLOSE THE VALVE FROM THE MANIFOLD TO THE CHAMBER)
1. Move the labels so that the newest tank is tank 4 i.e. tank 2 is now tank 1 and so on

d. Before running program make sure that the oldest argon tank with the label 1 is open and all other tanks are closed (open and closed tanks not the valve on the manifold)

e. When your program is complete go to initialize program

   i. Under programmer information next to the initialize program button you should see a read out that says program download complete in green (if this is not up yet the program is still downloading and it should only take a few minutes)

   ii. Click the initialize program button and it will check your program for errors

   iii. Once that is complete you should see a green note next to the initialize button that says program ready to run.

   iv. Click Run Program

   v. The confirm program run request screen will pop-up make sure the starting segment says 1 and hit run program

f. Vacuum should start immediately if it does not the pressure in the chamber maybe too high to run the vacuum (if it is above 17 PSI it usually won’t start).

   i. To fix this problem go back to operator window and click Semi Auto mode

   ii. Go to operator window
iii. Click vent valve open (wait until pressure is below 17 PSI if pressure never gets that low pressure release valve inside the large blue chamber must be adjusted this can only be done while the machine is off consult the manual from AIP or contact AIP if this needs to be done)

iv. Go back to main menu switch to full auto mode then re initialize program and run

8. Running program

   a. While pressure is ramping up you need to change over tanks to reach new higher pressures to monitor this you should go to operator window

      i. Make sure you close old tank before opening new tank i.e. close tank 1 then open tank 2 (ALWAYS OPEN AND CLOSE TANKS AT CYLINDER NOT AT THE MANIFOLD)

      ii. Be sure that you reach at least 1000 PSI before the compressor turns on this will usually only happen in tanks 3 or 4

   b. Make sure compressor is running before you leave the furnace the compressor should make a fairly loud sound of a piston moving up and down and the pressure should be increasing

      i. If the compressor is not running stop run immediately

      ii. Contact AIP and ask for assistance

   c. Log your run

9. Removing sample
a. Make sure furnace has cooled down to room temperature before you begin sample removal process
b. Chamber should be at elevated pressure
c. Switch from full auto mode to semi auto mode
d. Make sure to run furnace before venting to prevent the formation of ice on the furnace (Consult above for any questions)
e. In operator window open vent valve and watch temperature to make sure it does not go below ~15°C.
f. Once pressure is below 19 PSI you can disconnect H₂O lines and remove large lid, metal plate, metal ring and heat shield (for questions see above)
g. Remove sample from chamber
h. Place heat shield metal plate, metal ring with o-ring in groove and lid back onto chamber (don’t connect H₂O lines

10. Shutting down HIP

a. Once lid is sealed on the HIP make sure to switch open argon tank to tank number 1
b. Go to operator window make sure to close vent valve then open gas pre-fill
c. Watch pressure increase to about 100 PSI and turn off gas pre-fill
d. Close H₂O valves
e. Turn off throw switch on side of large blue cabinet
f. Leave computer on
MAINTENANCE

1. Every 2-5 runs
   a. Replace upper closure o-ring description above
   b. Apply more Cu base lubricant to threads on lid
      i. Lubricant is kept on bench next to dent puller
      ii. Apply thin coat with brush make sure there is not clumping

2. Every 3-6 months
   a. Replace coolant fluid with the hydrolubric 2-A coolant (Houghton international our contact in May 2006 was Tom Groce his e-mail is tgroce@houghtonint.com)
      i. If the oil looks black it is time to replace the coolant
      ii. Also should be changed at least once every 6 months no mater how much use
      iii. To drain coolant fluid hook up hose piece kept on the bench top to the water spigot located directly below the coolant fluid reservoir.
      iv. Get a bucket to drain fluid into
      v. Open spigot and start flow total reservoir volume should be 3 gallons
      vi. Once completely drained close spigot completely
      vii. Make sure to dispose of fluid properly call EH and S for pickup (i.e. not down the drain)
viii. Mix 1 and ½ to 2 quarts of hydrolubric 2A with 3 and ½ gallons of Deionized water to make new cooling solution

ix. Make note of when the coolant was replace on the HIP logbook

b. Replace water jacket o-rings (When these go bad you will see a lot of water leakage after each run)

3. Every year

a. Replace rupture disk (OSECO U-4963-01)

b. Replace vacuum pump oil (Oil type N 62 Leybold part number 177-01 for 1 liter)

4. For less frequent maintenance check AIP manual