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Tetrahedrally coordinated disordered Cu_2SnS_3–Cu_2ZnSnS_4–ZnS alloys with tunable optical and electronic properties

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ABSTRACT

A key requirement for large-scale deployment of photovoltaic technologies is the development of highly functional materials with controllable opto-electronic properties. In this work, we report on the room-temperature synthesis of disordered alloys of the Earth-abundant, tetrahedrally coordinated semiconductors Cu_2SnS_3, Cu_2ZnSnS_4 (CZTS), and ZnS as $(Cu_2SnS_3)_{1-x}(ZnS)_x$. The resulting disordered semiconductors are found to have continuously and independently tunable optical and electronic properties. Quasi-isovalent alloying on the cation sublattice allows the optical band gap to be varied continuously from 1.1 eV to 2.8 eV. Aliovalent alloying leads to independent control of carrier concentration over at least three orders of magnitude. A conceptual framework describing these disordered materials is presented, in which the structural disorder, constrained by local tetrahedral coordination of both anions and cations, leads to the observed high degree of tunability of the opto-electronic properties. These materials are not only independently interesting, but the developed framework also applies to the opto-electronic properties of kesterite CZTS materials as well as provides a basis for the development of new semiconductors.

1. Introduction

The Earth-abundance and availability of raw materials used in the manufacture of photovoltaic (PV) modules are a critical issue that must be addressed to achieve terawatt-level PV power generation. Decades of research on silicon-based materials and devices has led to a robust Si-based PV industry with high efficiencies. Intrinsic point-defect concentrations in crystalline silicon can be reduced to very low levels, so that extrinsic dopants such as As, P, and B allow precise control over carrier concentrations without degrading the materials properties significantly. On the other hand, single junction Si PV cells face fundamental performance limitations based on the lower-than-optimal 1.1 eV indirect band gap of Si. In $Cu(In,Ga)Se_2$ materials, optical band gap control is accomplished through In–Ga alloying, while the carrier concentration is controlled via native point defects dictated by the Cu:(In+Ga) ratio [1,2]. Unfortunately, the supply of In is likely to limit the scalability of CIGS solar cells to a best case scenario of 70 GWp/yr by the year 2020, and similar material constraints apply to CdTe-based PV technologies [3]. Here we discuss the development of an Earth-abundant room-temperature deposited semiconductor—disordered alloys of $(Cu_{2-\Delta}Sn_{1+\Delta}S_3)_{1-x}(ZnS)_x$—with independent, intrinsic control over both the optical band gap [by the Zn:(Cu+Zn+Sn) fraction] and the electronic properties (via the parameter Δ, which controls the Cu:Sn ratio).

Amorphous chalcogenide materials have been investigated for a wide variety of technological applications. However, difficulty in controlling the doping type and carrier concentration has limited their usefulness [4–8]. For example, it was initially believed that prototypical amorphous chalcogenide materials such as $Ge_2Sb_2Te_5$ had very low defect densities of states (DOS) within the band gap, as evidenced by very low sub-band gap photoabsorption and no evidence of hopping conduction (carriers exhibiting long-range transport as a result of tunneling between localized defect states) [9,10]. However, these properties were juxtaposed with strong sub-band gap photoluminescence signals suggesting a large defect DOS in the band gap, and evidence for strong DC screening of carriers. These seemingly disparate properties were reconciled in the model proposed by Anderson [11] in which trap states prefer to either have two charge carriers or none. In most systems,

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electron–electron repulsion prohibits two carriers from occupying the same site. However, the lattice energy lost by permitting two electrons on the same defect overcomes the electron–electron repulsion, leading to negative *effective* electron correlation energies U_{eff} [6]. These states tend to reside very near to mid-gap and at high DOS, on the order of 10^{18}–10^{19} cm^{-3} eV^{-1} [9]. Thus, in spite of the aforementioned evidence suggesting low defect DOS within the gap, on the contrary it came to be understood that there is a large defect DOS that pins the Fermi level at mid-gap. In addition, most amorphous chalcogenides are characterized by 2- and 3-fold atomic coordination, which leads to relatively flexible atomic networks in these materials [11]. A consequence of this lack of rigidity is that atomic species that are potential dopants generally can be accommodated in the network in their preferred bonding configurations, and therefore do not contribute charge carriers. Chalcogenide glasses in the AgInSbTe class and $Ge_2Sb_2Te_5$ are used in phase-change memory applications such as rewriteable compact disks and DVDs, where control over the carrier concentration is unnecessary. Instead, the large differences in conductivity and reflectivity between the amorphous and crystalline states drive these applications.

Some progress was made towards "firming up" the amorphous network by adding metals such as Cu or Ag to the amorphous chalcogenides [12]. This eliminated the photodarkening effects that were associated with the low coordination numbers of the chalcogen. The explanation for this effect, consistent with experimental observations, is that anions tend to become fourfold coordinated when a sufficient quantity of metal atoms is incorporated into the network. Interestingly, the most technologically prevalent amorphous semiconductor, amorphous Si, is also tetrahedrally coordinated, and can be doped both *n*- and *p*- type after hydrogenation [13]. Some preliminary works were undertaken on amorphous $CuInSe_2$ and CdTe thin films as well [14–16]. The studies produced some noteworthy results, such as differences in the activation energy of conductivity suggesting a variable Fermi energy; however the results were not pursued further. It is also worthwhile to note that all of the crystalline semiconductors that have been successfully developed for use as photovoltaic absorbers are tetrahedrally coordinated, including Si, CdTe, III–V alloys, and $CuInSe_2$ and related alloys [17]. Kesterite Cu_2ZnSnS_4 (CZTS) is a promising absorber material at an earlier stage of development that is also based on tetrahedral coordination [18–20].

In the present study, we report on tunability of the optical and electronic properties of tetrahedrally coordinated disordered alloys in the Cu–Zn–Sn–S system (hereafter, d-CZTS) along the Cu_2SnS_3–ZnS tie line in the pseudo-ternary phase diagram as illustrated in Fig. 1(a). The crystalline counterparts to these alloys include kesterite CZTS, sphalerite ZnS [21], and Cu_2SnS_3 [22] (CTS), all of which are tetrahedrally coordinated semiconductors. In these materials, each sulfur anion is coordinated with four cations, and each cation is coordinated with four sulfur atoms. Here we present results demonstrating that d-CZTS thin films deposited via elemental co-evaporation at room temperature maintain tetrahedral coordination, even though long-range order is sharply reduced, with evidence for a high degree of disorder especially on the cation sublattice. As described below, this disordered structure based on tetrahedral coordination enables independent tunability of both the band gap and electronic properties of d-CZTS materials. Recently, other studies have explored the properties of off-stoichiometric CZTS [23] and nanocrystals comprised of alloys of $Cu_2Sn(S,Se)_3$–Zn(S,Se) [24,25]. The studies report similarities in the ability to tune the band gap of the materials from near 1.0 eV to >3.0 eV by increasing the Zn fraction. However, the atomistic mechanism for alloying in these nanocrystals is unclear and the use of oleyamine capping agents precludes the electrical characterization of the nanocrystals. We also note the previous work of Schorr et al. [26] and Wagner et al. [27] on crystalline alloys of 2 (ZnX)–$CuInX_2$ (X=S,Se,Te). These investigations observed similar trends in optical band gap vs. composition in spite of a very small single-phase disordered cation composition window before the two-phase region. Here we present a model for the effects of alloying in the d-CZTS system, as well as optical and electrical characterizations of the thin films. Potential technological applications of d-CZTS materials such as photovoltaic solar cells are also discussed.

2. Materials and methods

Films of d-CZTS were grown via co-evaporation to thicknesses ranging between 0.1 μm and 1.5 μm. Effusion cells supplied elemental Cu and Sn (Alfa Aesar, 99.999% pure). Zn was supplied from an effusion cell loaded with ZnS (Alfa Aesar, 99.995% pure) and an overpressure of elemental sulfur (Alfa, 99.9995%) was supplied with a valved cracking source that yielded a sulfur flux primarily in the form of S_2 molecules. The substrate was not intentionally heated; however some radiative heating would have occurred from the metal deposition sources. Films were deposited on a Mo-coated soda-lime glass (SLG), microscope slide glass, and quartz substrates, depending on the requirements of subsequent measurements. The deposition-chamber base pressure was $\sim 7\times10^{-6}$ Torr (primarily consisting of background sulfur vapor). The pressure during deposition typically rose to $\sim 2\times10^{-4}$ Torr. For all depositions, the net metal flux was set at 3 Å/s regardless of film composition. Specific samples were grown to investigate the effects of aliovalent alloying close to the Cu:Sn=2 tie line connecting the single-phase regions of ZnS, CZTS, and CTS. In these samples, the ZnS content was fixed but the Cu:Sn ratio was combinatorially graded from one corner of the rectangular substrate to the opposite corner. That is, one corner was Cu-rich and Sn-poor while the other was Cu-poor and Sn-rich. After deposition, film composition and thickness were determined with X-ray fluorescence (XRF) using a RoentgenAnalytik Maxxi5pin. XRF under atmospheric pressure is unable to measure S content; however the lack of clear secondary phases suggests that the composition is near equilibrium for cations and anions. A Rigaku DMax in the Bragg–Brentano geometry was used to determine the degree of crystallinity within the films.

Extended X-ray absorption fine structure (EXAFS) measurements of the metal cations were performed at Beamline 20-BM of the Advanced Photon Source (APS) in Argonne, IL, with an X-ray spot size of 0.5×0.5 mm^2. In EXAFS measurements, photoexcited electrons generated by the incident X-rays absorbed by one (type of) atom scatter off neighboring atoms. The resulting interference in the K-edge absorption of the element is then analyzed to find information about the local structure in the material [28]. EXAFS spectra were processed using standard procedures to obtain the Fourier transforms of the spectra [29]. All spectra were *k*-weighted by 2, with a transform range of 2.0–10.4 $Å^{-1}$.

Optical absorption (transmission/reflection, *T*/*R*) experiments were performed using a custom built system at NREL that measures both the optical transmission and reflection of a thin-film semiconductor sample from 300 nm to 1700 nm. In some cases, multiple films with similar compositions but differing thicknesses were deposited on microscope slide glass to extend the range of optical absorption data. The *T*/*R* measurement system has a spot size of ~1 mm diameter and was used to map a grid over the 15 mm × 20 mm substrates. The optical absorption coefficient was determined as

$$\alpha = \frac{1}{d}\ln\left(\frac{(1-R)^2}{T}\right) \quad (1)$$