

Quaternary semiconductors with positive crystal field splitting: Potential high-efficiency spin-polarized electron sources

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Traditional high efficiency spin-polarized electron sources (SPES) consist mainly of binary or pseudobinary zinc-blende GaAs based materials, whereas their ternary analogs II-IV-V₂ (II=Zn, Cd, IV=Si, Ge, Sn, and V=As) as well as II-VI ternary analogs I-III-VI₂ (I=Cu, Ag, III=Al, Ga, In, and VI=Se) have not drawn wide attention because their crystal field splitting Δ_{CF} near the valence band maximum is either negative or close to zero in their ground state chalcopyrite structure. Using first-principles calculations, we show that some derivative quaternary I-III-II₂-V₄ and II-IV-III₂-V₄ compounds can have coherent ground state stannite or kesterite structures with large and positive Δ_{CF} due to their increased chemical and structural flexibility. We propose that ZnSiAl₂As₄ and CdGeAl₂As₄ in the stannite structure, and ZnSnGa₂As₄ and CuAlCd₂Se₄ in the kesterite structure could be good candidate SPES materials with high polarization and quantum efficiency. © 2009 American Institute of Physics. [DOI: 10.1063/1.3193662]

High-quality spin-polarized electron sources (SPES) have extensive application in the investigation of spin-dependent phenomena, such as the nucleon spin structure, the electroweak interaction, surface and thin-film magnetism and so on.¹ It is well known that the spin-polarization $P = (n_{\uparrow} - n_{\downarrow}) / (n_{\uparrow} + n_{\downarrow})$, where n_{\uparrow} and n_{\downarrow} are number of spin-up and spin-down electrons, is limited to 50% for photoemitted electrons extracted from highly symmetric zinc-blende crystals such as GaAs and ZnSe using near gap optical pumping by circularly polarized light between the band-edge states.² To break this polarization limit, semiconducting materials with large spin-orbit (SO) and positive crystal field (CF) splitting are sought [Fig. 1(a)].³ It has been proposed that applying epitaxial strain on semiconducting thin films grown on lattice-mismatched substrates could remove the degeneracy at the valence band maximum (VBM) and thus obtain 100% spin polarization.^{4,5} However, the misfit dislocations caused by the stress relaxation in the thick layers required for sufficient optical absorption are still obstacles in the further improvement of quantum efficiency and thus, wide application.

Another way to lower the high symmetry of zinc-blende GaAs or ZnSe is through cation mutation, e.g., mutating two Ga atoms into one Zn and one Ge in GaAs to form ZnGeAs₂ (II-IV-V₂), and similarly mutating ZnSe into CuGaSe₂ (I-III-VI₂). Unfortunately, the resulting ternary semiconductors all have the chalcopyrite (CH) ground state structure [Fig. 1(b)], and the CF splitting near the VBM (Δ_{CF}) is either negative or near zero,⁶ therefore, not ideal for SPES application.⁷⁻⁹ Although approaches have been proposed to stabilize AgGaSe₂ in the metastable CuAu phase [Fig. 1(c)], which has a large positive Δ_{CF} , as an ideal SPES with 100% polarization,⁸ the difficulty to grow a metastable phase on a substrate has dampened progress in this direction.

In this letter, using first-principles calculations,^{10,11} we show that although the constituents have no (or negative) CF splitting, some of the lowest energy $x=0.5$ alloys (III-V)_{2x}(II-IV-V₂)_{1-x} and (II-VI)_{2x}(I-III-VI₂)_{1-x}, which can also be considered as ordered quaternary compounds (II-IV-III₂-V₄ and I-III-II₂-VI₄, respectively), can have large and positive CF splitting in their coherent ground state structure when the cations are from different rows of the periodic table, thus are ideal choices for designing high efficiency SPES materials.

In our previous study about quaternary chalcogenides,^{10,11} we have shown that the lowest energy

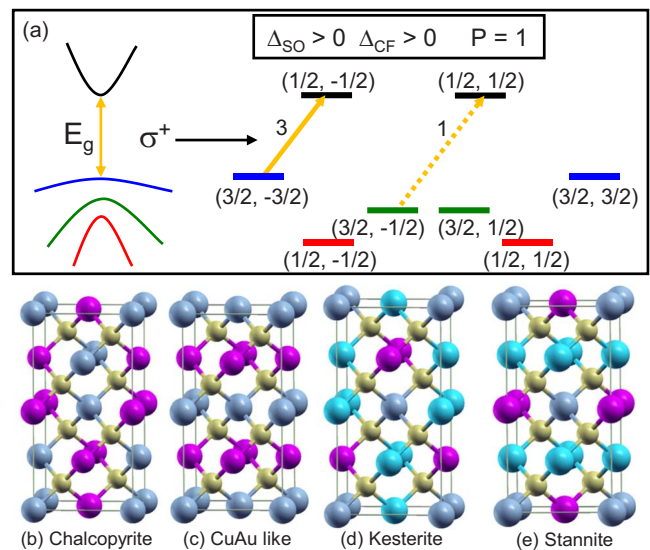


FIG. 1. (Color online) The near-gap energy level diagram and transition probabilities at the Γ point, and the crystal structure of (b) chalcopyrite and (c) CuAu-like CuGaSe₂, (d) kesterite, and (e) stannite CuGaCd₂Se₄ (sky-blue stands for Cu, purple for Ga, cyan for Cd and yellow for Se). Only the transitions for right circularly polarized σ^+ light and near-gap excitation are shown. When $\Delta_{CF} > 0$ and $\Delta_{SO} > 0$, $P = 1$, i.e., 100% spin-polarization is achieved. See Ref. 8 for details.

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TABLE I. Calculated lattice constant a , tetragonal distortion parameter $\eta=c/2a$, crystal field splitting Δ_{CF} , spin-orbit splitting Δ_{SO} , and valence band splitting Δ_{12} for the quaternary compounds in their ground state structure, and their total energy difference per atom $\Delta E_{\text{ST-KS}}$ between ST and KS structures.

Compound	Structure	a (Å)	η	Δ_{CF} (meV)	Δ_{SO} (meV)	Δ_{12} (meV)	$\Delta E_{\text{ST-KS}}$ (meV)
CuAlCd ₂ Se ₄	KS	5.917	0.988	93.8	133.9	40.2	9.99
CuGaCd ₂ Se ₄	KS	5.949	0.987	55.4	166.6	29.1	10.29
CuInCd ₂ Se ₄	KS	6.042	0.998	20.3	163.5	13.4	3.66
AgInZn ₂ Se ₄	KS	5.933	0.996	37.0	260.4	18.9	2.19
ZnSiAl ₂ As ₄	ST	5.700	0.986	66.5	289.3	45.9	-10.81
ZnSiIn ₂ As ₄	KS	5.909	0.990	40.7	305.1	25.1	11.56
ZnGeAl ₂ As ₄	ST	5.737	0.991	8.7	295.7	8.3	-7.68
ZnGeIn ₂ As ₄	KS	5.964	0.993	39.9	317.3	26.7	9.73
ZnSnAl ₂ As ₄	KS	5.833	0.999	48.9	296.5	31.2	0.66
ZnSnGa ₂ As ₄	KS	5.847	0.998	65.2	317.7	41.3	1.34
ZnSnIn ₂ As ₄	KS	6.059	0.999	58.7	323.8	37.5	3.19
CdGeAl ₂ As ₄	ST	5.864	0.977	116.1	301.1	70.7	-20.66
CdSnAl ₂ As ₄	KS	5.940	0.996	20.9	293.0	12.0	1.85
CdSnGa ₂ As ₄	KS	5.964	0.994	56.3	302.5	16.6	3.63

coherent structures of I-III-II₂-VI₄ are either stannite (ST) [space group $I\bar{4}2m$, Fig. 1(e)] or kesterite (KS) [space group $I\bar{4}$, Fig. 1(d)]. Both ST and KS structures have tetragonal unit cells, as the CH structure, but relative to CH which has only three structural parameters, a , $\eta=c/2a$ and one anion displacement parameter, quaternary ST and KS have more structural freedom, i.e., they have three anion displacement parameters. Their electronic band structure are similar to that of CH and the valence band splitting can be described by the quas cubic model, the same as for CH.^{7,9}

When the cations originate from a common row of the periodic table, e.g., CuGaZn₂Se₄, calculations show that the ST structure has always lower energy than the KS structure and the Δ_{CF} is always negative, while when the cations are from different rows (cross row), both ST and KS may become ground states.¹¹ Our exhaustive calculations for all compounds with I=Cu, Ag, II=Zn, Cd, III=Al, Ga, In, VI=Se (Table I) show that CuAlCd₂Se₄, CuGaCd₂Se₄, CuInCd₂Se₄, and AgInZn₂Se₄ have positive Δ_{CF} in their ground state KS structure, and the value is as large as 93.8 meV for CuAlCd₂Se₄ in which Al and Cd have the largest size difference. The calculated results also show that the trends in Δ_{CF} and the ground state structure are similar for sulfides, selenides, and tellurides, but the value of Δ_{CF} decreases when the anion size increases. We list in Table I only the results for selenides because their Δ_{SO} are larger than sulfides and Δ_{CF} are larger than the tellurides, so they give the optimal valence band splitting Δ_{12} , which is less than $\frac{2}{3}\min(\Delta_{\text{CF}}, \Delta_{\text{SO}})$. As we know, in binary selenides the spin-orbit splitting Δ_{SO} is determined mostly by the Se p component and has value around 0.4 eV.¹² In the ternary and quaternary compounds, Δ_{SO} is significantly smaller, especially for Cu-based selenides with values only about 0.15 eV (Table I). This can be explained by the stronger p - d coupling between Se and Cu at VBM and the fact that d component has negative contribution to Δ_{SO} .¹²

Similarly, we can derive quaternary II-IV-III₂-V₄ semiconductors from II-IV-V₂ and III-V systems. Here, IV=Si, Ge, Sn, and V=As. Relative to I-III-II₂-VI₄, II-IV-III₂-V₄ relates more closely to the currently used GaAs or InGaAs/GaAs-based SPES, thus may be more readily synthesized

and tested with experiment. Our calculations show that the trends observed in I-III-II₂-VI₄ also hold for II-IV-III₂-V₄, i.e., for common-row-cation compounds the ground state is the ST structure with negative Δ_{CF} and for cross-row-cation compounds both ST and KS can be ground state structures, depending on the relative size of the cations. Encouragingly, in this system we find ten compounds that have positive Δ_{CF} in their ground state structures (Table I), in which ST-CdGeAl₂As₄ has the largest Δ_{CF} =116.1 meV and Δ_{SO} =301.1 meV. It is interesting to see that in this system, the Δ_{SO} for the quaternary system is similar to those of their binary analogs because the group II, III, and IV cations all have high d binding energies, thus much less contribution to the VBM.

According to the results in Table I, four compounds including CuAlCd₂Se₄, ZnSiAl₂As₄, ZnSnGa₂As₄, and CdGeAl₂As₄ have the largest crystal field splitting Δ_{CF} and valence band splitting Δ_{12} , thus are good candidate SPES materials. To help the future experimental investigations, we estimate their band gap according to the generalized gradient approximation (GGA) calculated values and the GGA band gap error of their binary and ternary constituents, as described in Ref. 11. The GGA-corrected band gaps are 1.92 eV for CuAlCd₂Se₄, 2.27 eV for ZnSiAl₂As₄, 1.06 eV for ZnSnGa₂As₄, and 1.63 eV for CdGeAl₂As₄. It should be noted that this correction is simple and the error is around ± 0.3 eV for alloys with large cation differences.

To understand why the cross-row-cation I-III-II₂-VI₄ and II-IV-III₂-V₄ have positive Δ_{CF} in their ground state structure, we performed a three-step calculation for the representative CuAlCd₂Se₄ and CdGeAl₂As₄, following the theoretical work of Rowe and Shay.⁷ They pointed out that there are three contributions to the noncubic crystal field: (a) the ordering of the different metal cations Δ_{ord} , (b) the anion displacement from the ideal zinc-blende site Δ_{dis} , and (c) the tetragonal distortion Δ_{str} . In our study we analyze the three contributions through a three-step calculation as described in Ref. 11. The results are listed in Table II. We find that (i) the cation ordering and anion displacement dominate the large positive value of Δ_{CF} in KS-CuAlCd₂Se₄ and ST-CdGeAl₂As₄, (ii) the sign of tetragonal distortion contri-

TABLE II. With different degrees (a, b, and c) for the structural relaxation, the calculated a , η , and Δ_{CF} of $\text{CuAlCd}_2\text{Se}_4$ and $\text{CdGeAl}_2\text{As}_4$ in ST and KS structures, respectively, and their total energy difference per atom $\Delta E_{\text{ST-KS}}$.

	a (Å)	η	Δ_{CF} (meV)	a (Å)	η	Δ_{CF} (meV)	$\Delta E_{\text{ST-KS}}$ (meV)
	ST- $\text{CuAlCd}_2\text{Se}_4$			KS- $\text{CuAlCd}_2\text{Se}_4$			
a	5.897	1.000	-73.7	5.893	1.000	77.7	-3.30
b	5.897	1.000	-83.0	5.893	1.000	120.8	9.69
c	5.882	1.007	-72.4	5.917	0.988	93.8	9.99
	ST- $\text{CdGeAl}_2\text{As}_4$			KS- $\text{CdGeAl}_2\text{As}_4$			
a	5.818	1.000	44.1	5.823	1.000	48.7	-9.69
b	5.818	1.000	210.0	5.823	1.000	102.8	-19.01
c	5.864	0.977	116.1	5.820	1.001	107.7	-20.66

bution Δ_{str} follows that of $\eta-1$, consistent with the [001] tetragonal deformation potential of the VBM being negative.⁹ Δ_{str} is as large as -94 meV for ST- $\text{CdGeAl}_2\text{As}_4$ which has small η , and (iii) for $\text{CuAlCd}_2\text{Se}_4$ the anion displacement (resulting from the cation size differences) determines the energy priority of KS relative to ST, while for $\text{CdGeAl}_2\text{As}_4$ the cation ordering and anion displacement determine together the lower energy of the ST phase. From the above discussion, we conclude that the increased chemical and structural freedom in these quaternary compounds are responsible for the positive Δ_{CF} , thus opening new possibilities for band structure engineering and spin-polarized electron sources.

Considering that at low temperature almost all lattice-mismatched semiconductor alloys have positive formation enthalpy and phase segregate into constituent compounds, it is not surprising that the quaternary alloy with large CF splitting is unstable with respect to phase separation into ternary and binary constituents. However, as in most alloys, it can be stabilized under coherent condition (i.e., no bond-breaking phase separation).¹³ For example, our calculation shows under coherent condition KS- $\text{CuAlCd}_2\text{Se}_4$ is 17 meV/atom lower in energy than phase-separated CuAlSe_2 and CdSe , meaning that the ordered KS structure is preferred in the coherent growth.

In conclusion, we have investigated the crystal and electronic structure of two classes of quaternary compounds, I-III-II₂-VI₄ and II-IV-III₂-V₄ and found that some of these compounds, such as $\text{CuAlCd}_2\text{Se}_4$, $\text{ZnSiAl}_2\text{As}_4$, $\text{ZnSnGa}_2\text{As}_4$, and $\text{CdGeAl}_2\text{As}_4$, have large positive crystal field splitting and large valence band splitting in their ground state structure, thus can be considered as ideal SPES with 100% spin

polarization. Our analysis on the factors influencing Δ_{CF} indicates that the abnormal band structure for these quaternary compounds with cross-row cations are due to the increased chemical and structural freedom.

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