New materials for high-efficiency spin-polarized electron source

A. Janotti
Metals and Ceramics Division, Oak Ridge National Laboratory, TN

In Collaboration with S.-H. Wei, National Renewable Energy Laboratory, CO

Work supported by Basic Energy Sciences- DOE
Outline

• Generating spin-polarized electrons from semiconductors using near-band-edge photo-excitation

• GaAs, GaAsP, and SL’s as SPES
• CuPt-ordered semiconductor alloys
• Chalcopryrites I-III-VI₂ and II-IV-V₂

• How to improve the spin polarization

• CuAu-ordered AgGaSe₂ as an high quality spin-polarized electron source
High-quality spin-polarized electron source

- High spin polarization
- High quantum efficiency
- High Reliability

Applications:
- Atomic physics
- Condensed-matter physics
- Nuclear physics
- High-energy particle physics
Seminal Works: GaAs as SPES (1976)

Photoemission of spin-polarized electron from GaAs
Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule, CH 8049, Zürich, Switzerland

Source of Spin-Polarized Electrons from GaAs

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**FIG. 2.** On the left, an $E$-vs-$k$ diagram of the energy bands of GaAs near $k = 0$ shows the energy gap $E_g$ and the spin-orbit splitting $\Delta$ of the valence bands. The degenerate states at $k = 0$ are labeled on the right by their $m_j$ quantum numbers. The allowed transitions for $\sigma^+$ ($\Delta m_j = 1$) and $\sigma^-$ ($\Delta m_j = -1$) circularly polarized light are shown by the solid and dashed lines, respectively. The circles numbers represent the relative transition probabilities.

**FIG. 4.** Schematic diagram of the apparatus: 1, Movable He cryostat with sample gripper; 2, He cryostat; 3, liquid nitrogen; 4, superconducting coil; 5, sample in measuring position; 6, accelerating electrodes; 7, rotatable wheel with samples; 8, parallel beam shifters; 9, plane condenser; 10, cylindrical condenser; 11, aperture; 12, light source; 13, gripper for cleaving; 14, cleaving mechanism; 15, ultrahigh-vacuum valve; 16, rack-and-pinion linear motion; 17, sample preparation chamber; 18, ion-pumped pumps; 19, seven-stage accelerator; 20, gold foil; 21, detectors to measure Mott asymmetry; 22, forward detectors to monitor beam.
GaAs as SPES revolutionized the study of spin-dependent phenomena

**Spin-orbit interaction**
Interaction of the spin of the electron with its own orbital angular momentum
Polarized electron scattering from a W(100) surface

**Exchange interaction**
Consequence of Pauli principle
Surface Magnetization of Ferromagnetic Ni(110)
GaAs as SPES revolutionized the study of spin-dependent phenomena

Spin-orbit interaction
Interaction of the spin of the electron with its own orbital angular momentum
Polarized electron scattering from a W(100) surface

*Phys. Rev. Lett.* 42, 1349 (1979)

Symmetry in Low-Energy-Polarized-Electron Diffraction
G. -C. Wang, B. I. Dunlap, R. J. Celotta, and D. T. Pierce
National Bureau of Standards, Washington, D. C. 20234

**FIG. 2.** The spin dependence of the scattering $S(E, \theta)$ is plotted for specular diffraction from W(100) at an angle of incidence of 15°. The scattered intensities resulting from an incident beam consisting of only spin up ($\uparrow$) or of only spin down ($\downarrow$) electrons are shown as $I_{\uparrow}$ and $I_{\downarrow}$.

**FIG. 3.** Our measurements of $S(E, \theta)$ (solid line) are compared to the measurements $P(E, \theta)$ (crosses) of Ref. 2 of the (00) beam for angles of incidence from 10° to 17°. The scattering plane is in a (010) plane of the crystal. The curves are normalized as described in the text.
GaAs as SPES revolutionized the study of spin-dependent phenomena

**Exchange interaction**
Consequence of Pauli principle


Surface Magnetization of Ferromagnetic Ni(110):
A Polarized Low-Energy Electron Diffraction Experiment
R. J. Celotta, D. T. Pierce, and G. -C. Wang

*National Bureau of Standards, Washington, D. C. 20234*
S. D. Bader and G. P. Felcher

*Argonne National Laboratory, Argonne, Illinois 60439*

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**Fig. 1.** The electron beam at an angle of incidence $\theta_0$ is diffracted from the Ni(110) crystal into the Faraday cup (a). Ta rods (b) support the crystal which closes the magnetic circuit of the miniature electromagnet (c). The incident-electron spin polarization and the crystal magnetization lie in the scattering plane.

**Fig. 2.** A hysteresis curve, $S(H)$, at $E = 125$ eV and $\theta_0 = 12^\circ$. The raw data points, which are connected by straight lines, were obtained between the $S(T)$ measurements (× and +) of Fig. 3.
Although GaAs is an efficient photoemitter, the maximum spin polarization of the emitted electrons is limited to 50%.

FIG. 6. Spectrum of spin polarization from GaAs + CsOCS at $T < 10$ K [the same sample and conditions as curve (a) of Fig. 5]. Note the high value of $P = 40\%$ at threshold ($\hbar \omega \sim 1.5$ eV) and positive and negative peaks at $\hbar \omega = 3.0$ and 3.2 eV.
Nowadays, most of the sources are still based on GaAs and related materials

Polarized Gas Targets and Polarized Beams, 7th International Workshop, Urbana, IL 1997

Many important research institutes have a significant amount of the approved scientific projects based on polarized electron beams, and many of these experiments require high polarization (~80%).

SLAC in Stanford, CA - USA
Jefferson Lab. in Newport News, VA - USA
NIKHEF in Amsterdam, Netherlands
MIT-Bates in Middleton, MA – USA
MAMI in Mainz, Germany
• Generating spin-polarized electrons from semiconductors using near-band-edge photo-excitation
\[ \Delta_{SO} = 0 \quad \Delta_{CF} = 0 \quad P = 0 \]

\[ \Delta_{SO} > 0 \quad \Delta_{CF} = 0 \quad P = 1/2 \]

\[ \Delta_{SO} > 0 \quad \Delta_{CF} > 0 \quad P = 1 \]

\[ P = \begin{vmatrix} I \downarrow -I \uparrow \\ I \downarrow +I \uparrow \end{vmatrix} \]

\[ I = \left| \langle \Psi_f | H_{int} | \Psi_i \rangle \right|^2 \]

\[ H_{int} = X + iY \quad \text{for } \sigma^+ \text{ light} \]

Ideal material for SPES application
- Direct band gap
- Large spin-orbit splitting
- Large and positive crystal field splitting
Collecting the spin-polarized electrons

“The art of activating GaAs photocatodes”

Negative electron affinity condition
Ideal material for SPES application

• Direct band gap

• Large spin-orbit splitting

• Large and positive crystal field splitting
Substantial effort have been made to break GaAs 50% polarization limit

Strained materials

- GaAsP grown on GaAs
- GaAs grown on InGaAs
- GaAsP/GaAs superlattice
- CuPt-ordered GaAsP and InGaAs alloys

Chalcopyrites

- I-III-VI$_2$  CuInSe$_2$, CuGaSe$_2$, AgGaSe$_2$, AgGaS$_2$
- II-IV-V$_2$ ZnGeP$_2$, ZnGeAs$_2$, CdGeP$_2$, CdGeAs$_2$
Spin-polarized electron from strained SL


- Large crystal field splitting requires large strain
- Reduced critical layer thickness lead to low quantum efficiency
Spin-polarized electron from strained SL

- Large crystal field splitting requires large strain
- Reduced critical layer thickness lead to low quantum efficiency
Spin-polarized electron from ordered alloy

CuPt ordered semiconductor alloy is unstable in the bulk, the degree of ordering and $\Delta E_{12}$ are small.

Spin-polarized electron from ternary compounds


All the chalcopyrites have negative or zero crystal field splitting

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$a$ (Å)</th>
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Schematic diagram of near-gap optical transition for circularly polarized light

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P = \begin{vmatrix} I \downarrow -I \uparrow \\ I \downarrow +I \uparrow \end{vmatrix}
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I = \left| \langle \Psi_f | H_{\text{int}} | \Psi_i \rangle \right|^2
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All the chalcopyrites have negative or zero crystal field splitting.
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- GaAs grown on InGaAs

Reduced critical layer thickness
Poor material quality
Low quantum efficiency

Chalcopyrites

- I-III-VI$_2$
- II-IV-V$_2$

Negative or zero crystal field splitting
Low quantum efficiency
The total energy, including exchange and correlations, of an electron gas (even in the presence of a static external potential), is a unique functional of the electron density. The minimum value of the total energy functional is the ground-state energy of the system, and the density that yields this minimum value is the exact single-particle ground state density.

Theoretical approach: Theoretical approach: 
Density Functional Theory

Rev. Mod. Phys., Vol. 71, No. 5, October 1999

Nobel Lecture: Electronic structure of matter—wave functions and density functionals*

W. Kohn

Department of Physics, University of California, Santa Barbara, California 93106


“The total energy, including exchange and correlations, of an electron gas (even in the presence of a static external potential), is a unique functional of the electron density. The minimum value of the total energy functional is the ground-state energy of the system, and the density that yields this minimum value is the exact single-particle ground state density.”

many-electron problem ⇔ set of self-consistent one electron equations
Theoretical approach: Density Functional Theory

$$E[\{\psi_i\}] = 2 \sum_i \int \psi_i \left[ -\frac{\hbar^2}{2m} \nabla^2 \psi_i + \int V_{\text{ion}}(r)n(r)d^3r + \frac{e^2}{2} \int \frac{n(r)n(r')}{|r-r'|} d^3r d^3r' + E_{\text{XC}}[n(r)] + E_{\text{ion}}(\{ R_i \}) \right]$$

$$n(r) = 2 \sum_i |\psi_i(r)|^2 \quad \rightarrow \quad \left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{ion}}(r) + V_H(r) + V_{\text{XC}}(r) \right] \psi_i(r) = \varepsilon_i \psi_i(r)$$

$$V_H(r) = e^2 \int \frac{n(r')}{|r-r'|} d^3r' \quad V_{\text{XC}}(r) = \frac{\delta E_{\text{XC}}[n(r)]}{\delta n(r)}$$

Local Density Approximation:

$$E_{\text{XC}}[n(r)] = \int \varepsilon_{\text{XC}}(r)n(r)d^3r$$

$$\frac{\delta E_{\text{XC}}[n(r)]}{\delta n(r)} = \frac{\partial [n(r)\varepsilon_{\text{XC}}(r)]}{\partial n(r)} \quad \varepsilon_{\text{XC}}(r) = \varepsilon_{\text{XC}}^{\text{hom}}[n(r)]$$

M. C. Payne et al.: *Ab initio* iterative minimization techniques *Rev. Mod. Phys.*, Vol. 64, No. 4, October 1992
Theoretical approach: Density Functional Theory

Periodic supercells

Bloch's theorem $\psi_i(r) = \exp[i \cdot r] f_i(r)$

\[ f_i(r) = \sum_G c_{i,G} \exp[i \cdot G \cdot r] \]

\[ \psi_i(r) = \sum_G c_{i,k+G} \exp[i \cdot (k+G) \cdot r] \]

k-point sampling

Plane-wave basis sets

\[ \sum_{G'} \left[ \frac{\hbar^2}{2m} |k+G|^2 \delta_{GG'} + V_{\text{ion}}(G-G') + V_H(G-G') + V_{XC}(G-G') \right] c_{i,k+G'} = \varepsilon_i c_{i,k+G} \]

M. C. Payne et al.: Ab initio iterative minimization techniques
Rev. Mod. Phys., Vol. 64, No. 4, October 1992
Self-consistent loop for the calculation of the total energy of a solid

Construct $V_{\text{ion}}$ given atomic numbers and positions of ions

Pick a cutoff for the plane-wave basis set \( \{ e^{i(k+G\cdot r)} \} \)

Pick a trial density \( n(r) \)

Calculate \( V_H(n) \) and \( V_{XC}(n) \)

Solve \( H\psi = \left( -\frac{\hbar^2 \nabla^2}{2m} + V_{\text{ion}} + V_H + V_{XC} \right) \psi = \varepsilon \psi \) by diagonalization of \( H_{k+G, k+G'} \)

Calculate new \( n(r) \)

IS SOLUTION SELF-CONSISTENT?

YES

Compute Total Energy

NO

Generate New Density \( n(r) \)

M. C. Payne et al.: Ab initio iterative minimization techniques  Rev. Mod. Phys., Vol. 64, No. 4, October 1992
Theoretical approach: Density Functional Theory - Local Density Approximation

Equilibrium lattice constant
Elastic constants
Defects
Surfaces
Alloys
High Pressure phases
Earth’s core composition

FIG. 1. Theoretical determination of an equilibrium lattice constant. Calculations (open circles) at various possible lattice constants are performed and a smooth function is fitted through the points. The predicted lattice constant is determined by the minimum in the curve.
All the chalcopryrites have negative or zero crystal field splitting

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CuAu and Chalcopyrite crystal structure

CH: c and u are in perpendicular directions
CuAu: c and u are in the same direction

\[ \eta_{CH} = \frac{c}{2a} \]
\[ \eta_{CuAu} = \frac{c}{a} \]

\[ \eta_{CuAu} = \frac{2}{3 \eta_{CH} - 1} \]

\[ \Delta a = a_{CH} - a_{CuAu} \approx \frac{5}{6} (1 - \eta_{CH}) a_{CH} \]
CuAu and Chalcopyrite crystal structure

Large $\eta_{\text{CuAu}}$ and large $\Delta a$ can lead to large positive crystal field splitting and epitaxial stabilization energy.
Large $\eta_{\text{CuAu}}$ and large $\Delta a$ can lead to large positive crystal field splitting and epitaxial stabilization energy.
CuAu-like AgGaS$_2$ has the largest $\eta$ and largest epitaxial stabilization energy. However, spin-orbit coupling for the sulphide is very small ($\Delta_{so}=0.02$ eV).

Strain-free CuAu-like AgGaSe$_2$ can be stabilized if it is grown epitaxially on an appropriate substrate (e.g., ZnSe $a_0 = 5.66$ Å).
AgGaSe$_2$ and AgGaS$_2$: Total energy vs. lattice constant $a$

- CuAu-like AgGaS$_2$ has the largest $\eta$ and largest epitaxial stabilization energy. However, spin-orbit coupling for the sulphide is very small ($\Delta_{so}=0.02$ eV)
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### AgGaSe$_2$ : CuAu vs. Chalcopyrite

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<th>Expt.</th>
<th>CuAu</th>
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<tr>
<td>$a$ (Å)</td>
<td>6.054</td>
<td>5.980</td>
<td>5.675</td>
</tr>
<tr>
<td>$\eta$</td>
<td>0.926</td>
<td>0.910</td>
<td>1.124</td>
</tr>
<tr>
<td>$\nu$</td>
<td>0.280</td>
<td>0.278</td>
<td>0.274</td>
</tr>
<tr>
<td>$V$/atom (Å$^3$)</td>
<td>25.68</td>
<td>24.33</td>
<td>25.68</td>
</tr>
<tr>
<td>$\Delta E_g$ (eV)</td>
<td>0.00</td>
<td>⋯</td>
<td>−0.42</td>
</tr>
<tr>
<td>$\Delta_{CF}$ (eV)</td>
<td>−0.24</td>
<td>−0.25</td>
<td>0.76</td>
</tr>
<tr>
<td>$\Delta_{SO}$ (eV)</td>
<td>0.25</td>
<td>0.31</td>
<td>0.21</td>
</tr>
<tr>
<td>$\Delta E^+_f$ (eV/4 atoms)</td>
<td>0.000</td>
<td>⋯</td>
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AgGaSe$_2$ in the CuAu phase has large positive crystal-field and spin-orbit splitting and is epitaxially stable with respect to the chalcopyrite phase.
Small lattice mismatch between AgGaSe$_2$ and ZnSe
Common anion avoids the problem of polarity mismatch at the interface
CuAu- AgGaSe$_2$ is not strained
Summary

• AgGaSe$_2$ in CuAu-like phase is a strong candidate for a high-quality SPES material.
  
  • Direct band gap close to that of GaAs
  • Large spin-orbit splitting
  • Large and positive crystal field splitting

• bulk strain-free films can be obtained if grown under epitaxial conditions with appropriate choice of substrate (ZnSe)