Outline

October 18
• Basics of an IR probe of electronic processes in solids
• Electrostatic doping of new materials: challenges, opportunities and first accomplishments
• Intrinsic electronic transport in organic molecular crystals

October 25
• High $T_c$ superconductivity: new materials or new state of matter?
• The search for a pairing glue in high-$T_c$ superconductors

November 1
• High $T_c$ superconductivity by kinetic energy saving?
• Infrared spectroscopy of correlated electron matter at the nano-scale

November 8
• Magnetic phenomena in semiconductors
• $Ga_{1-x}Mn_xAs$: first correlated electron semiconductor?
Electron: particle with negative electric charge $q = -e$ and spin $1/2$ (magnetic moment $m = \mu_B$)

**Why bother with spintronics?**
- new fundamental physical questions
- new phenomena
- new devices and applications

**Potential advantages:**
- non-volatility of memory
- increased data processing speed
- increased integration densities
- decreased electric power consumption

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**Magnetism timeline. 1988: Spin Electronics (Spintronics)**

Peter Grunberg

Albert Fert

Electron addition:

\[ \text{Electron} + \text{Electron} = \text{Electron} \]

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Giant Magneto-Resistance of (001) Fe/(001) Cr Magnetic Superlattices

J. Broto, A. Fert, F. Nguyen Van Dau, and F. Petroff

des Solides, Université Paris-Sud, F-91405 Orsay, France

G. Creuzet, A. Friederic, and J. Chazelas
All-metals spintronics: giant magneto-resistance /GMR/

\[ MR = \frac{R_{AF} - R_F}{R_{AF} + R_F} \]

F configuration

AF configuration
All-metals spintronics: spin tunneling device

Low $\rho_{dc}$  

High $\rho_{dc}$  

Band structure

Schematics

Half-metallic FM

Fe*

Majority

Minority

Energy (ev)

CrO$_2$

GaMnAs?
All-metals spintronics: spin tunneling device

low $\rho_{dc}$

high $\rho_{dc}$
Spin field effect transistor

Spin field effect transistor

Requirements: effective spin injection, slow spin relaxation, reliable spin detection.

Ferromagnetic semiconductors!

Electro-optical modulator

Electronic analog of the electro-optic modulator

Supriyo Datta and Biswajit Das
School of Electrical Engineering, Purdue University, West Lafayette, Indiana

Requirements: effective spin injection, slow spin relaxation, reliable spin detection.

Ferromagnetic semiconductors!
Charge FETs and spin FETs

Control of barrier for charge transport
Min barrier height requirement: 25 meV

Control of the spin state
No switching barriers!
Requirements:
effective spin injection,
(relatively) slow spin relaxation,
reliable spin detection.

Ferromagnetic semiconductors!
Magnetism timeline. 1996: Ferromagnetic III-V semiconductors

(Ga,Mn)As: A new diluted magnetic semiconductor based on GaAs

H. Ohno
Laboratory for Electronic Intelligent Systems, Research Institute of Electrical Communication, Tohoku University, Sendai 980-77, Japan, and Research Development Corporation of Japan (JRDC)

A. Shen and F. Matsukura
Laboratory for Electronic Intelligent Systems, Research Institute of Electrical Communication, Tohoku University, Sendai 980-77, Japan

A. Oiwa, A. Endo, S. Katsumoto, and Y. Iye
Institute for Solid State Physics, University of Tokyo, Tokyo 106, Japan

(Received 2 February 1996; accepted for publication 10 May 1996)

A.M. Nazmul et al. PRL95, 17201 (2005)

T_c up to 250 K

Diluted Magnetic III-V Semiconductors

IBM T. J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598
(Received 8 August 1989)

A new diluted magnetic III-V semiconductor of In_{1-x}Mn_xAs (x \leq 0.18) has been produced by molecular-beam epitaxy. Films grown at 300°C are predominantly ferromagnetic and their properties suggest the presence of MnAs clusters. Films grown at 200°C, however, are predominantly paramagnetic, and the lattice constant decreases with increasing Mn composition; both are indicative of the formation of a homogeneous alloy. These films have n-type conductivity and reduced band gaps.
Basics of III-V semiconductors

Undoped (intrinsic):

<table>
<thead>
<tr>
<th>Material</th>
<th>Eg, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>InAs</td>
<td>0.2</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.42</td>
</tr>
<tr>
<td>GaN</td>
<td>3.5</td>
</tr>
<tr>
<td>GaP</td>
<td>2.2</td>
</tr>
</tbody>
</table>


conduction band

valence band

GaAs

gap
Basics of III-V semiconductors

**Doping:** Introduce charged impurities

**Example:** replace Ga by Si in GaAs

Si has one valence electron *more* → introduces extra electron: **donor**

\[ \text{Si}^{4+} \text{ weakly binds the electron: hydrogenic (shallow) donor state} \]

**Example:** replace Ga by Zn in GaAs

Zn has one valence electron *less* → introduces extra hole: **acceptor**

\[ \text{Zn}^{2+} \text{ weakly binds the hole: hydrogenic (shallow) acceptor state} \]

For *heavy* doping the impurity band overlaps with the VB or CB
$\text{Ga}_{1-x}\text{Mn}_x\text{As}$

Ferromagnetic: $x=2-10\%$

Ga$_{1-x}$Mn$_x$As/GaAs

MBE Lab @ UCSB

LT - MBE
Mn doping:

- magnetic moments
- holes
- localization
- defects
  As anti-sites
  Mn interstitials
Ferromagnetic Ga$_{1-x}$Mn$_x$As

H. Ohno
JMMM 200, 110 (1999)

“metallic”

“insulating”

Jungwirth et al. PRB72, 165204 (05)

Penn State, UCSB, Nottingham
Tunable ferromagnetism in III-V series


For $V_g > 0$, there is a decrease in $T_C$.

For $V_g = 0$, $T_C$ remains unchanged.

For $V_g < 0$, there is an increase in $T_C$. 
Spin polarization and optics

Y. Ohno et al.
Exchange interaction in magnetic semiconductor

Exchange interaction: Coulomb repulsion + Pauli exclusion

Spin Hamiltonian: \( H_{\text{int}} = -J \vec{S}_1 \cdot \vec{S}_2 \) \quad J = E_s - E_t

Heisenberg model:

\[ H_{\text{int}} = -\sum J_{mn} \vec{S}_m \vec{S}_n \]

Direct exchange: wave function overlap \textbf{FM}

Super-exchange: \textbf{AF} (typically)
Exchange interaction in magnetic semiconductors

Exchange interaction: Coulomb repulsion + Pauli exclusion

Spin Hamiltonian: \( H_{\text{int}} = -J \vec{S}_1 \cdot \vec{S}_2 \)

Heisenberg model:

\[
H_{\text{int}} = - \sum J_{mn} \vec{S}_m \vec{S}_n
\]

Direct exchange: wave function overlap \( \text{FM} \)

Super-exchange: \( \text{AF} \) (typically)

Double exchange: \( \text{FM} \)

La\(_{1-x}\)Sr\(_x\)MnO\(_3\): La\(^{3+}\), Sr\(^{2+}\) O\(^{2-}\) Mn – mixed valence

\[
\sigma \propto x \frac{T_c}{T}
\]
Exchange interaction in magnetic semiconductors

Exchange interaction: Coulomb repulsion + Pauli exclusion
Spin Hamiltonian: \( H_{\text{int}} = -J \mathbf{S}_1 \cdot \mathbf{S}_2 \)
\( J = E_s - E_t \)

Heisenberg model:
\( H_{\text{int}} = -\sum J_{mn} \mathbf{S}_m \cdot \mathbf{S}_n \)

Direct exchange: wave function overlap \textbf{FM}
Super-exchange: \textbf{AF} (typically)
Double exchange: \textbf{FM}

Kinetic exchange: \textbf{FM}; spin polarized Fermi sea

\[ H = -J_{pd} \sum \mathbf{S}_i \cdot \mathbf{S}_l \delta \left( \mathbf{r}_i - \mathbf{R}_l \right) \]

- hole spin 1/2
- impurity spin 5/2

- hole position
- impurity position
Ferromagnetism in III-Mn-V semiconductors

Double-exchange?

Kinetic exchange?

Band energy change in impurity d-band

Hole mediated ferromagnetism

Band energy change in valence band
From dilute Mn impurities to ferromagnetic $\text{Ga}_{1-x}\text{Mn}_x\text{As}$

$\text{GaAs: Mn}$

$\text{Ga}_{1-x}\text{Mn}_x\text{As}$ $x=1-5\%$
doped semiconductor
$T_C < 70$ K
FM mediated by:
localized holes
in the impurity band
Akai 1998; Alvarez et al. 2002
Savinto et al. 01; Berciu and Bhatt 01
Kaminski and Das Sarma 02
Durst 2002; Fiete 2003
Litvinov 2003; Zunger 04;
Tang and Flatte 2004

$\text{Ga}_{1-x}\text{Mn}_x\text{As}$ $x=5-10\%$
Metal
$T_C < 180$ K
FM mediated by:
delocalized holes
in the valence band
Dietl et al. 2001
Jungwirth, Yang, Sinova, Timm, Masek, Kucera, MacDonald 2001-06
Priour, Hwang, and Das Sarma 04

Mn doped semiconductor

Mn

Mn

Mn
Infrared and optical spectroscopy of magnetic semiconductors

Ga$_{1-x}$Mn$_x$As, $x$=5-10%

Detector: $T(\omega)$
Detector: $R(\omega)$

$\sigma_1(\omega) + i\sigma_2(\omega)$
GaAs: optical conductivity

Re conductivity, \((\Omega \text{cm})^{-1}\)

\(E_G\)

\(E_G\)
Ga$_{1-x}$Mn$_x$As: optical conductivity

Re conductivity, (Ωcm)$^{-1}$

$E$ (meV)

$E$ (eV)

x=1.7%

LT-GaAs

Mn

As

Ga

R.M. Feenstra et al.

PRL 71, 1176 (93)

Singley et al.

PRL 89, 97203 (02)
Ga$_{1-x}$Mn$_x$As: optical conductivity

Mn doping:

gap edge smearing
increase of intragap $\sigma_1(\omega)$
resonance at 2000 cm$^{-1}$
metallic transport

Singley et al. PRL 89, 97203 (02)
Ga$_{1-x}$Mn$_x$As: sum rule analysis of $\sigma_1(\omega)$

\[ \frac{n}{m^*} = \int_0^\Omega \sigma_1(\omega) \, d\omega \]

$T_c$ vs. $x$ (% Mn)

Re conductivity, (Ωcm)$^{-1}$

Wavenumber cm$^{-1}$

Singley et al. PRL 89, 97203 (02)
Understanding the optical conductivity of Ga$_{1-x}$Mn$_x$As

\[ \sigma_1(\omega), \ (\Omega \text{cm})^{-1} \]

$k E (eV)$

$x = 0.052$

$10^{17} \text{ Mn/cm}^3$

$x50$

Wavenumber cm$^{-1}$
Understanding the optical conductivity of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$

$\sigma_1(\omega)$, $(\Omega\text{cm})^{-1}$

J. Sinova et al.

$E(\text{eV})$

$10^{17}$ Mn/cm$^3$

$x=0.052$

$x\times50$

Wavenumber cm$^{-1}$
Intra-gap conductivity

σ(ω), Ω^{-1}cm^{-1}

Ga_{1-x}Mn_xAs 5.2%
T_C=70 K
c.2001

Ga_{1-x}Mn_xAs 5.2%
T_C=80 K
c.2005

Ga_{1-x}Mn_xAs 5.2%
T_C=120 K
annealed

E.J. Singley et al. PRL 89, 97203 (02)

Burch et al. PRL 97, 87208 (2006)
Understanding intra-gap conductivity: doping dependence

$E$, eV

$\sigma(\omega)$, $\Omega^{-1} \text{cm}^{-1}$

Ga$_{1-x}$Mn$_x$As 5.2%

$T_C = 120$ K

annealed

E.J. Singley et al. PRL 89, 97203 (02)

Burch et al. PRL 97, 87208 (2006)
Understanding intra-gap conductivity: doping dependence

J. Sinova et al. PRB 66, 41202 (02)

Burch et al. PRL 97, 87208 (2006)
Impurity band and intra-gap conductivity of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$

$\sigma(\omega), \Omega^{-1}\text{cm}^{-1}$

$E, \text{eV}$

$R.\text{Braunstein (1959)}$

$W.\text{Songprakob et al JAP 91, 171 (2002)}$

$\Lambda \Gamma \Delta X$

$L$ $\Lambda$ $\Gamma$ $\Delta$ $X$

$5 \times 10^{20}$ $1 \times 10^{21}$

$4 \times 10^{20}$ $8 \times 10^{20}$

$p (\text{cm}^{-3})$

$N_{\text{eff}} (\text{cm}^{-3}/m_0)$

$Burch et al. \text{PRL 97, 87208 (2006)}$
Impurity band and intra-gap conductivity of Ga$_{1-x}$Mn$_x$As

Hwang, Milis and Das Sarma PRB65, 233206 (02)

Burch et al. PRL 97, 87208 (2006)
Intra-gap conductivity: Drude response revisited

$\sigma(\omega), \Omega^{-1}\text{cm}^{-1}$

Ga$_{1-x}$Mn$_x$As 5.2%
$T_C=70$ K
c.2001

Ga$_{1-x}$Mn$_x$As 5.2%
$T_C=80$ K
c.2005

Ga$_{1-x}$Mn$_x$As 5.2%
$T_C=120$ K annealed

$1/\tau = \frac{p}{m^*}$

E.J. Singley et al. PRL 89, 97203 (02)

Burch et al. PRL 97, 87208 (2006)
**Intra-gap conductivity: Drude response revisited**

**Ga$_{1-x}$Mn$_x$As Transport:**

*Ku et al. APL 82, 2302 (03)*  
*Wang et al. PRB72, 115207 (05)*

\[
p \approx 10^{21} \text{ cm}^{-3}
\]

\[
\mu \approx 1 - 5 \text{ cm}^2 / V_s \\
polymers, a-Si
\]

\[
\mu \approx 80 - 120 \text{ cm}^2 / V_s \\
p-GaAs
\]

\[
\mu = \frac{e \tau}{m^*}
\]

<table>
<thead>
<tr>
<th></th>
<th>5.2 % annealed</th>
<th>7.3% annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$</td>
<td>120 K</td>
<td>140 K</td>
</tr>
<tr>
<td>$m^*$</td>
<td>35-70 $m_e$</td>
<td>15-30 $m_e$</td>
</tr>
</tbody>
</table>

\[
\frac{1}{\tau} = \frac{p}{m^*}
\]

*Gaussian conductivity, $\sigma(\omega)$, $\Omega^{-1}\text{cm}^{-1}$*

*Ga$_{1-x}$Mn$_x$As 5.2%  
$T_c=120$ K annealed*

*Burch et al. PRL 97, 87208 (2006)*

*Intra-gap conductivity, $\mu = \sigma(\omega)$, $\Omega^{-1}\text{cm}^{-1}$*
Spectroscopic evidence for the impurity band in Ga$_{1-x}$Mn$_x$As

**MCD**
B. Beschoten et al. PRL 83, 3073 (99)
Tang & Flatte PRL 92, 47201 (04)

**ARPES**
Fujimori prb 64, 125304 (2001)

**Infrared**
Singley et al. PRL 89, 97203 (02)
Hirakawa et al. PRB 65, 193312 (02)

**Hot electron PL**
Sapega et al. PRL 94, 137401 (05)

**STM**
Yakunin et al. PRL 95, 256402 (05)

**Transport**
\[
\mu = \frac{e\tau}{m^*} = 1 - 5 \text{cm}^2/\text{Vs}
\]
\[
m^* = 15 - 50m_e
\]
Digital ferromagnetic heterostructures

Sub-monolayer MnAs?
Continuous film? Clusters? Overdoped Ga$_{1-x}$Mn$_x$As?

$\sigma_1(\omega)$, Ga$_{1-x}$Mn$_x$As
$x=5.2\%$

$\sigma_1(\omega)$, MnAs$_{(0.5)}$/GaAs$_{(10)}$

300 K

Wavenumber, cm$^{-1}$
Digitally doped Ga$_{1-x}$Mn$_x$As

Metallic FM

Insulating FM

Scanning near field optical microscopy of Ga$_{1-x}$Mn$_x$As?

\[ \frac{n}{m^*} = \int d\omega \sigma_1(\omega) \]

Homogeneous Ga$_{1-x}$Mn$_x$As?

- Hole-rich regions in hole-depleted host? (Hamaya et al., PRL 94, 147203 (2005))
- Mn clusters?
- MnAs clusters?
- Sphere resonance? (S. Seo et al., JAP 95, 8172 (04))
- More?

Optics of inhomogeneous medium

- Problematic absolute values
- New features / artifacts
- Kramers-Kronig breakdown

Far-IR – Mid IR
Scanning near field infrared microscopy of Ga$_{1-x}$Mn$_x$As

$\sigma(\omega)$, $\Omega^{-1}\text{cm}^{-1}$

Burch et al. PRL 97, 87208 (2006)

Far-IR – mid IR

$\omega=960$ cm$^{-1}$

$S_2(x), ru$

Near Field Profile

Topography

$\omega=960$ cm$^{-1}$

$S_2(x), ru$

Near Field Profile

$S_2(x), ru$

Near Field Profile

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$S_2(x), ru$
Scanning near field IR microscopy of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$: implications

- $x=3$-7%: homogeneous
- $x>7%$: oxide clusters on the surface
- $\sigma(\omega)$ analysis is valid!
- heavy effective masses

$\omega=960 \text{ cm}^{-1}$

$x=0.077$

annealed

$S_2(x)$, ru

Near Field Profile

12 nm

0 nm

500 nm
1. Impurity band

- Infrared
- STM
- ARPES
- PL
- MCD
- Transport

- High $T_C$ samples

2. Unconventional metal-Insulator transition

3. Ferromagnetism mediated by mobile and localized holes

4. Disorder

Homogeneous?