Doped Semiconductor Nanoparticles:
Ferromagnetism and Photoluminescence above Room Temperature

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• Interest in wide bandgap semiconductor nanoclusters: TM-doped ZnO
• Experimental setup and synthesis of nanoclusters
• Magnetism: analysis and discussion
• Photoluminescence: analysis and discussion
• Summary

References

Interest in doped ZnO nanoclusters

Spintronics: spin transport electronics

Information storage & processing on same spintronic chip
ZnO is a wide bandgap semiconductor that has attracted tremendous interest as blue light emitting materials, gas sensors and transparent conductors in solar cells.

1. **“Green Technology”**. Unlike other semiconductor compounds that contain cadmium, arsenic, or other environmental toxins, zinc and oxygen are “environment friendly” elements. In fact, ZnO is used as a dietary supplement in animal feed.

2. **Energy efficiency**. The stability of excitons in ZnO results in a very high quantum efficiency at temperatures of 300 K and higher. It is an ideal material for room-temperature magneto-optic applications.

3. **Transparency**. At RT the bandgap of ZnO is 3.4 eV, which is the UV region of the spectrum, making it an optically transparent semiconductor. Transparent ferromagnetic memory devices could be integrated with transparent transistors, providing “invisible” computing systems.
Advantages of nano-semiconductors over bulk materials

1. **Electronic and optical properties can be tuned by varying nanocluster size.**

2. **Nanoclusters are embedded in a matrix to make nanocomposites or films.**

3. **By reducing dimensions to the nanoscale, high storage densities may be achieved by addressing the spin states of single quantum dots.**

From a fundamental point of view, the study of nanoclusters provides insight into the mesoscopic regime between single molecules and bulk crystals. Nanoclusters exhibit strong quantum confinement and surface effects. Using nanoclusters as “building blocks” for novel materials offers the opportunity to understand how atomic structure can lead to physical and chemical properties of macroscopic materials. Moreover, it is possible to produce nanoclusters with atomic arrangements that do not normally exist in nature, leading to novel optical and magnetic properties.
Theoretical work has predicted ferromagnetism above RT for Mn-doped ZnO (given a large hole concentration). Spurred by that prediction, research into ZnO crystals for spintronic applications is an active area of experimental research.

1. No systematic study of size and dopant-concentration dependence on magnetic and optical properties of nanoclusters has been undertaken experimentally.
2. The fundamental magnetic and optical properties of TM-doped ZnO nanoclusters remain essentially unexplored.
3. Most recent reports have focused on the synthesis, structural properties, UV-visible optical, and magnetic properties of ZnO-based on thin films and bulk materials.
4. Dr. Gamelin’s group at the University of Washington has studied ZnO and TiO$_2$ DMS nanoparticles synthesized using a colloidal method.

There is a significant lack of knowledge about the fundamental properties of doped semiconductor nanoclusters.
Interest in TM-doped ZnO Nanoclusters

- Ferromagnetic semiconductor: applications in spintronics and nonvolatile memory storage.
- Manipulation of spins: memory storage efficiency increases.
- Ferromagnetic behavior in DMS: optical devices

- Room-temperature ferromagnetic and optical spintronic materials: practical applications.
- Very few studies have been done on the ferromagnetic and UV-PL properties of TM-doped ZnO nanoclusters.
Nanocluster Sources

(a) Supersonic nozzle source
(b) Gas-aggregation source
(c) Laser evaporation source
(d) Pulse arc cluster ion source
Sputtering-Gas-Aggregation Source

- Deposition rate > 5 Å/s, ~ 10 mg/hour
- Ionization rate > 60%, (35% positive charged ion, 30% negative charged ion for Cu clusters),
- Controlled monodispersive size range 1 to 100 nm
History of SGA Cluster Source

1st generation, University of Freiburg, 1995, ~0.1 mg/h

2nd generation, University of Nebraska-Lincoln, 2000, < 1 mg/h

3rd generation, University of Idaho, 2003, ~10 mg/h

4th generation, University of Idaho, 2005, testing, ~2 g/h

Nth generation, 20??, up to kg/h.
• Cluster size: D = 1 to 100 nm
• Materials: Co, Fe, Ni, Ag, Al, Cu, Mg, Mo, ZnO, Si, Ti, TM-ZnO, TiO₂, CoPt, FePt, TiN, TiAlN, Al₂O₃
Cluster Deposition System
Nanocluster-Assembled Materials


2: PRB 66, 064404 (2002)


Porous nanofilm of soft landing Fe nanoclusters

FePt nanoclusters embedded in C matrix
TiN cluster films:

- a) 0.03 eV/atom
- b) 0.5 eV/atom
- c) 1.0 eV/atom
- d) 10 eV/atom
Experimental Set-up

Cluster Beam

Neutral beam

+0-40 kV

- ~40% negatively charged,
- 35% positive charged,
- ~25% neutral

In the cluster beam measured by a microbalance.

~20 nm negatively charged Fe nanoclusters impact on the surface of Si to form a dense iron thin film.
Soft landing Fe nanoclusters on Si

MD simulation (1 eV/atom)

15 keV, Fe nanoclusters on Si

100 nm
a, b, and c are the ellipsoidal axes of the deposited clusters with a>b>c.
**Summary of Magnetic Measurements**

<table>
<thead>
<tr>
<th>Potential (kV)</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_c$ (Oe)</td>
<td>$H_{ex}$ (Oe)</td>
<td>$H_c$ (Oe)</td>
</tr>
<tr>
<td>0</td>
<td>78</td>
<td>0</td>
<td>78</td>
</tr>
<tr>
<td>5</td>
<td>0.50</td>
<td>0.63</td>
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<tr>
<td>15</td>
<td>0.65</td>
<td>0.22</td>
<td>2.46</td>
</tr>
</tbody>
</table>

1. As small shifting of the hysteresis curve ($H_{ex}$) was observed for each sample. This is due to the formation of a thin oxide layer over the film of pure Fe cluster films.

2. Magnetic moments: a) 102 emu/g for 0 kV, and b) 201 emu/g for 15 kV.
Synthesis of TM-doped ZnO Nanoclusters

Cluster formation: *Target (Zn-TM), control percentage of TM-dopant* » *Cluster growth process (He, Ar, O₂)* » *Cluster deposition.*
Average crystallite size of ZnO nanocluster film ~ 7nm.

As no dopant elements are observed with XRD analysis, XPS was done on the samples

ZnO bulk

Identical to bulk ZnO wurtzite structure

Average crystallite size of 5% Co-doped ZnO ~ 7.5nm.

Co is incorporated into the zinc oxide wurtzite structure.
XPS spectra of 2% and 5% Co doped ZnO nanocluster films, the composition in atomic percent:

1) 2% sample: Co=1.82, O=48.64 and Zn=49.64;
2) 5% sample: Co=5.12, O=48.31 and Zn=46.57.
Magnetic Properties

- Magnetic field: 7 T
- Temperature: 1.5 – 400 K
- Sensitivity: $1 \times 10^{-8}$ emu

MPMS XL 7 System, Quantum Design Inc.

University of Idaho
Tradition, Change, Excellence.
Magnetic properties of TM-doped ZnO nanoclusters

Hysteresis loop is observed for 5% TM-doped ZnO nanoclusters at 400K.
Saturation magnetization and coercivity decreased with increase in temperature.
Coercivity varied with the dopant elements: mechanism?
Saturation magnetizations for 4 different dopants at 5K and 300K. Isovalent Ti and Co exhibit smaller magnetization compared to the dopants that exhibit mixed valancy.
Depth Profile

- Ti-ZnO
- V-ZnO

Depth (nm)

Concentration (%)

+4

+5

surf 2.5 5
Nanoclusters deposited on Si wafer before and after Ar⁺ sputtering

Ti and Co are isovalent before and after Ar⁺ sputtering
V and Ni showed mixed valancy, i.e. the oxidation state altered before and after Ar\(^+\) sputtering.
Double-exchange interaction via carriers can be the reason for enhanced ferromagnetism in Ni (V)-doped ZnO nanoclusters.

Ferromagnetism is expected in systems where TM atoms with incomplete d-shells do not form the nearest neighbors so that indirect ferromagnetism dominates over the direct antiferromagnetic coupling in the presence of carriers.

This indirect ferromagnetism by Zener is used to explain the magnetism observed in Ti (Co)-doped ZnO nanoclusters.
Schematic electronic configurations of the dopants in ZnO nanoclusters in the tetrahedral substitution sites
Double-Exchange

The electronic configurations of V$^{5+}$, V$^{4+}$, Ni$^{3+}$ and Ni$^{2+}$ are 3d$^0$, 3d$^1$, 3d$^7$ and 3d$^8$, which results in unoccupied or partially occupied spin-up or spin-down levels, allowing the electrons to hop to the 3d level of its neighbor with parallel spin through interactions with p-orbital and thus reducing the kinetic energy through the charge state coupling. Double-exchange interactions due to the mixed valance states [Blundell 2001] via holes can be a reason why Ni (V)-doped ZnO clusters exhibits a higher magnetic moment than the Ti (Co)-doped clusters [Dietl 2000].

If the magnetic moments of the neighboring transition metals are in the same direction, the d band of the transition metal is widened by the hybridization between the spin states introducing carriers in the d band that can lower the band energy in ferromagnetic configuration and hopping is possible.
\[ H_{H-DE} = -J_H \sum_{i,u,\alpha,\beta} S_i \cdot a^+_{iu\alpha} \bar{\sigma}^{\alpha\beta} a_{iu\beta} - \sum_{\langle ij \rangle,u,v,\alpha} t_{ij}^{uvw} a^+_{iu\alpha} a_{jv\alpha} \]

where 1’st term with \( J_H \) is the Hunds coupling term between e\(_g\) and t\(_{2g}\) electron and 2’nd term is due to e\(_g\) electron hopping.

The double-exchange appears only when the spins of the d shells of both Ni\(^{2+}\) (V\(^{4+}\)) and Ni\(^{3+}\) (V\(^{5+}\)) sites are parallel or one of the hopping site is empty so that there is no impedance for the electron transfer.

In the case of Ni (V) doped ZnO, the system is inherently degenerate due to the presence of Ni (V) ions of two charges as explained by Zener 1951.

The origin of ferromagnetism in Ti (Co)-doped ZnO nanoclusters is due to the domination of indirect ferromagnetic coupling via carriers over direct antiferromagnetic coupling.
Optical Properties

Ultraviolet Photoluminescence and Raman Lab
(Dr. L. Bergman, Physics Department, UI)
The PL spectra of bulk ZnO vs ZnO nanoclusters.

No visible luminescence

PL energy peak of bulk ZnO=3.30 eV

PL energy peak of 2% Co-doped ZnO=3.331 eV, at RT

Blue shift in PL energy is observed for pure ZnO nanoclusters and 2% Co-doped ZnO nanoclusters.
Quantum Confinement Effect at RT

ZnO Nanoparticles

ZnO Nanoclusters (7 nm in diameter)

Wong and Searson, APL, 74, 2939 (1999)

ZnO was fabricated by a colloidal process.

No visible PL

~ 125 meV blueshift in VU

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Wong and Searson, APL, 74, 2939 (1999)

ZnO was fabricated by a colloidal process.
\[ E_{ex} = E_g - \frac{13.6 \mu}{m_e \varepsilon_r^2} + \frac{2\pi^2 \hbar^2}{(m_e^* + m_h^*)D^2} \]

Bandgap energy (3.36 eV), Confinement effect

Binding energy (60 meV),

Reduced masses: \( m_e^* = 0.32m_e \), and \( m_h^* = 0.27m_e \). \( \varepsilon_r = 5.8 \), \( D \) is the quantum dot diameter, \( E_{ex} \) is the PL excitonic emission as measured via PL.

Calculated result showed a particle size of ~ 7 nm, a prediction which is consistent with the XRD and the TEM studies.
UV-PL spectra of bulk ZnO, ZnO nanoclusters and 3% Co-doped ZnO nanoclusters at RT. There is no PL for larger than 5% Co-doped ZnO nanoclusters at RT.
Doped ZnO nanoclusters deposited on indium tin oxide (ITO) coated glass substrate and the sample is assembled with a carbon nanotube (CNT) electron emission in a diode mode with 600 microns gap between them. The cathode cross section is \( \sim 1 \text{ cm}^2 \). A bias is applied between anode and cathode: a) 10 mA (1.7 kV) current, and b) 20 mA (1.8 kV).
Cathodoluminescence spectra of ZnO nanoclusters measured using different electron emission currents. The blue curve is from 10 mA CNT electron emission current and the red curve is from the 20 mA.
Summary and Future Plan

- A cluster deposition system has been developed to make cluster-assembled materials.
- TEM, XRD, AFM and XPS have used for studying the nanoclusters.
- Magnetic and optical properties of the nanomaterials made out of clusters as building blocks have been investigated.
- Systematic study regarding the origin of ferromagnetic and UV-PL properties of Co-doped ZnO clusters and also detail study on the effect of oxygen concentration on these properties.
- 2%, 3% and 5% Co-doped ZnO nanocluster films are ferromagnetic. Only 2% - 3% Co-doped ZnO has ferromagnetic and UV optical emission at RT.
• 5% Co, V, Ni and Ti-doped ZnO nanocluster films are synthesized at room temperature.
• Anomalous double-exchange enhanced ferromagnetism in transition metal-doped ZnO nanoclusters above RT for the dopants that exhibit mixed valance.
• Core-shell nanostructured Zn/ZnO clusters are synthesized and characterized.
• In future we will investigate size effect and dopant concentration dependence of clusters on magnetic and optic behavior.
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