





Harvesting Heat through Seebeck Spin Tunneling Effect

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Outline

- 1. Spintronics vs. Spin Caloritronics.
- 2. Novel Spin Caloritronics Device.
- 3. Introduction to Seebeck Effect.

4. TiO₂ Nanolayer Growth by Atomic Layer Deposition and Preliminary Results.

5. Thermoelectric and Optical Studies of PEDOT-PSS/Glass substrates.

Spintronics

What is spintronics?

-The ability of using the electron's spin as an information carrier.

How can we do that? One needs a spin injection mechanism (a transfer of spin from one material to another).

1. By sandwiching a nonmagnetic metal between two ferromagnetic materials. This is called giant magnetoresistance system

2. By creating a so called Dilute Magnetic Semiconductors (DMS) also called ferromagnetic semiconductors.



Problems with DMS materials

1. Maintaining ferromagnetism (Tc) at or above 300K?

So far manganese gallium arsenide (MnGaAs) can only reach Tc ~ 173 K [1]. Other suitable candidates need to be explored.

2. Avoiding clustering of the magnetic atoms.

It is very common that manganese atoms would like to cluster together rather then be randomly distributed throughout the entire crystal structure.

Muhammad B. Haider, Costel Constantin, Hamad Al-Brithen, Haiqiang Yang, Eugen Trifan, David C. Ingram, and Arthur R. Smith, C.V. Kelly and Y. Ijiri, "Ga/N flux ratio influence on Mn incorporation, surface morphology, and lattice polarity during radio frequency molecular-beam epitaxy of (Ga,Mn)N," J. Appl. Phys. 93(9), 5274, (2003).



We found that either metal-rich or N-rich conditions are necessary for achieving substitutional Mn incorporation on the Ga sites.



Fig. 4 AFM images as a function of Ga/N flux ratio .

Fig. 3 RHEED patterns during (Ga,Mn!N growth as a function of Ga/N flux ratio .

[1] Magnetism inm (Ga, Mn)As Thin Films with TC Up to 173K", K.Y. Wang et al., AIP Conf. Proc. Vol. 772, 333-334 (2005).

Spin Caloritronics

What is Spin Caloritronics?

-The ability to control the spin transport within materials by applying heat and magnetic field.



 [a] Ni₈₀Fe₂₀/SiO₂-Al₂O₃/p-type Si device that uses the Seebeck Spin Tunneling Effect.
[b] Thermal spin signal as a function of magnetic field.
[c] Thermal spin signal as a function of Joule heating.

 $\Delta V = TSP * \Delta \mu/2$

TSP - tunneling spin polarization for FM/oxide interface Dm - thermally induced spin accumulation.



J-C Le Breton, S. Sharma, H. Saito, S. Yuasa & R. Jansen,

Thermal spin current from a ferromagnet to silicon by Seebeck spin tunneling. Nature, vol. 475, 2011.

Novel Concept Device



> MnGa/TiO₂/GaN device

>But, first we need to study the thermoelectric properties of interfaces that are present in this device.

Interfaces such as N-rich GaN/n-type GaN, Ga-rich GaN/n-type GaN, L10-MnGa/TiO2

Seebeck Effect



Seebeck Effect



Seebeck Effect



[b] After Thermal Excitation 0 Voltage **Substrate**

>Seebeck coefficient, S = DV/ DT.

> Typical values in the order of $mV/(\circ)$.

>It can give an easy carrier type determination for semiconductor substrates.

> Thermoelectric materials are characterized by the Figure of Merit (ZT).

$$ZT = \frac{S^2 \sigma}{\kappa} T$$

Where: S -Seebeck Coefficient σ - Electrical conductivity κ - Thermal Conductivity

TiO₂ Nanolayers Grown by Atomic Layer Deposition



- 1. Pulse precursor P1 into the reactor.
- 2. Remove the extra P1 by purging with N_2 gas.
- 3. Pulse precursor P2 into the reactor.
- 4. Remove the extra P2 by purging with N_2 gas.

At the end of these 4 steps a monolayer of material has been grown.

ALD precursors used for TiO₂ growth



P2-Water



ALD chemical reaction during growth:

 $Ti(OCH(CH_3)_2)_{4(1)} + 2H_2O \rightarrow TiO_{2(s)} + 4(CH_3)_2CHOH_{(g)}$

Optimization of TiO_2 growth by ALD

-Varying parameters such as sample temperature, precursor temperature, and precursor time.

-Preliminary results Ti_{Ox} films grown on top of aluminium foil. The substrate temperature was $T_s = 250 \degree C$, and the precursor pulse times were $t_{Ti\text{-}isopropoxide} = t_{H2O} = 2 \text{ s}$, and $t_{N2} = 5 \text{ s}$.

-The thickness was measured to be 84 nm for 650 ALD cycles, therefore we obtained a thickness per number of cycles ratio of 0.13 nm/cycle.

-An optimized TiO_x layer would mean to achieve the highest value of thickness per number of cycles.





Preliminary Seebeck Coefficient measurements



Thermoelectric Properties of PEDOT-PSS/Semiconductor substrates

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- Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT-PSS)
- Conjugated polymers: alternating single and double bonded carbon backbone (p-orbitals)
 - Single bond: only localized σ -bond (strong)
 - Double bond: less strongly localized π -bond (weak)
- HOMO: highest occupied molecular orbital (top of valence band)
- LUMO: lowest unoccupied molecular orbital (bottom of conduction band)
- Delocalization of π -bonds along polymer chain decreases band gap
- Transport properties usually determined by defects or charge "hopping"



Ellipsometry Measurements of PEDOT-PSS/Glass

- Complex Refractive Index : $\tilde{n} = n + ik$
- Alternatively, the optical properties can be represented complex dielectric function: $\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2$ such that $\tilde{\varepsilon} = \tilde{n}^2$
- index (*n*) describes the phase velocity of light as it travels in a material compared to the speed of light in vacuum, *c*: v = c/n
- Extinction coefficient (k) describes loss of wave energy to the material and is related to the absorption coefficient, α : $\alpha = 4\pi k / \lambda$
- Light loses intensity in an absorbing material according to Beer's Law:



Results



Conclusions

-Optimize Titanium Oxide growth by Atomic Layer Deposition.

-Structural, thermoelectric, and magnetic characterization of $MnGa/TiO_2$ and TiO_2/GaN interfaces.

-Structural, thermoelectric, and magnetic characterization of PEDOT-PSS/Semiconductor

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-My collaborators: Arthur R. Smith (OU), Kai Sun (UM).





ALD reactor at JMU?





[b]

AtomicLayerDepositionV2.vi Front Panel		
<u>File Edit View Project</u>	<u>Operate</u> <u>T</u> ools	<u>W</u> indow <u>H</u> elp
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Number of Cycles	Valves	Ytterbium (Integer sec)
40	Yterbium	0
Current Cycle	Water	Water (integer sec)
STOP	Nitrogen	Nitrogen Wait (Integer sec)

Why MnGa/TiO₂/GaN

 $MnGa/TiO_2/GaN$ (Our device)

-GaN: 3.44 eV (D), 3×10⁶ V/cm. -TiO₂: 3.2 eV, k = 114 $Ni_{80}Fe_{20}/SiO_2-Al_2O_3/p$ -type Si (Le Breton *et al.*)

-Si: 1.12 eV (I), 3×10^5 V/cm. - SiO₂: 9 eV, k = 3.9 - Al₂O₃: 8.8 eV, k = 9.5



MnGa alloy grown on GaN, Sapphire, and MgO substrates. Red arrow shows the magnetic easy axis (energetically favorable direction of spontaneous magnetization).

How can we construct our device?

Strategy

-Build 2 sets of devices: N-rich, and Ga-rich. -Carefully study the interface TiO_2/GaN and MnGa/TiO₂

-Nanolayers thickness optimization as a function of Seebeck coefficient with or without magnetic field.

-At OU, we will deposit the MnGa nanolayers by MBE. -At JMU, we will use the state-of-art Atomic Layer Deposition reactor to deposit the TiO_{2} .

