Semiconductors in presence of gases: The relationship between charge transfer and charge transport

Dr. Juan J. Velasco-Vélez
Berlin 01-12-2017
Outline

- Motivation

- Classic semiconductor theory
  - Ideal „Bulk“

- Semiconductor theory at the bulk edge
  - Semiconductor surface-gas interactions

- One example of device operation
  - Electro-adsorptive effect
  - Thin film transistor
  - Drift of vacancies (dopants)

- Remarks
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Change in the electron transport in semiconductors in presence of gases (Thin films)

- Resistance is a macro effect, however it is affected by atomic scale interactions
- The interaction at the solid-gas interface influences the bulk properties. Is the other way around also true?
Catalysis on semiconductors

Why are important the semiconductors in catalysis?
- In most case, metals are enclosed in a semiconductor coat.
- Reactions take place at the surface, on the semiconductor.

The electron Theory of Catalysis on Semiconductors*.
- Heterogeneous catalytic process are based on electronic mechanisms.
- Elucidate the relationship between catalytic process and electronic properties of semiconductors.

Theory limits
- Fully applicable to dielectrics.
- Cannot be applied directly to metals.
  *Based on the “many-electron” approach.

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Semiconductors

- Is a material with an electrical conductivity between metal and insulator
  - Conductivity can be modified by different parameters:
    - Temperature
    - Electric field
  - Two types of carriers: electrons and holes
Physics of solids

- Weakly bound valence electrons interact with positively charged atomic cores
  - Schrödinger equations rules the motion of electrons in solids
    - Charge doesn't change with time
      \[ E \psi(r) = (-\frac{\hbar^2}{2m}) \nabla^2 \psi(r) + U(r)\psi(r) \]
    - Equipotential \( U(r) = 0 \)
  - \[ E\psi(x) + \frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = 0 \]
    solution \( \psi(0) = \psi(L) = 0 \)
    \[ \psi_n(x) = A \sin \left( \frac{\pi n}{L} x \right) \]

Then we obtain as Eigenvalue:

\[ E_n = \frac{\hbar^2}{2m} \left( \frac{\pi n}{L} \right)^2 \]
Fermi distribution ($U(r)=0$)

- For $N$ valence electrons, highest occupied level energy
  \[ E_F = \frac{\hbar^2}{2m} \left( \frac{\pi N}{2L} \right)^2 \]

- KE of electrons increases with temperature: distribution function

\[ f(E) = \frac{1}{e^{(E-\mu)/k_B T} + 1} \]

$E$...Energy
$k_B$...Boltzmann constant
$T$...Temperature
$\mu$...(Electro-)Chemical potential

Diagram showing probability of occupation at different temperatures.

No electrons can be above the valence band at 0K, since none have energy above the Fermi level and there are no available energy states in the band gap.

At high temperatures, some electrons can reach the conduction band and contribute to electric current.
Types of semiconductors

- Intrinsic
- Extrinsic
  - Type n
  - Type p
- Degenerate:
  - $|E_C - E_D| < 3K_BT$
  - $|E_V - E_A| < 3K_BT$
Conductivity in semiconductors

- **Intrinsic carriers**
  
  \[ n_i = \int_{E_c} f(E)g(E)dE \]
  
  \[ n_i = N_C e^{-(E_C-E_{F})/k_BT} \]
  
  \[ n_i = N_V e^{-(E_F-E_V)/k_BT} \]

- **Extrinsic carriers**
  
  - Electrons
  
  \[ n = \frac{N_D}{e^{(E-C-E_D)/k_BT} + 1} \approx N_D e^{-(E_C-E_D)/k_BT} \]
  
  - Electron holes
  
  \[ p = \frac{N_A}{e^{(E_A-E_V)/k_BT} + 1} \approx N_A e^{-(E_A-E_V)/k_BT} \]

- **Resistance:**
  
  \[ R = \frac{\rho L}{A} \]
  
  **Thermo-ionic description!!**

- **Resistivity**
  
  \[ \rho = \frac{1}{\sigma} \]

- **Conductivity**
  
  \[ \sigma = q(\mu_p p - \mu_n n) \]

  \[ \mu_n k_B T = qD_n \]

- **Current density**
  
  \[ J = qn\mu E + qD \frac{dn}{dx} \]

Berlin 01-12-2017

Dr. J. J. Velasco-Vélez
Band bending (MOS)
Summary

- Semiconductor technology is everywhere
  - Scaling-down Close to the quantum limit
    - $L_D/2$: quantum confinement:
      - 5n node (end of Moore law)
  - Defects grain domains
  - Surface???

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Shockley, Bardeen, Brattain 1948

Thin Solid Films Volume 531, 15 March 2013, Pages 172-178
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Remarks
Surface physics

- Thin film Co$_3$O$_4$
  - Charge transfer information
  - Macro-scale


- Cobalt thin film 240°C
  - Chemical information
  - Atomic scale
Charge Transfer Model:
Needs Electron Transfer
Band Bending
Thermodynamics

Wolkenstein Model:
Fully Quantum Mechanical
Easy Access to $E_F$, 
Semiconductor Device Modeling

LCAO:
Quantum Chemistry
d, p and s orbitals
Overlap
Stereochemistry
Some Access to EF
Linear combination of atomic orbitals

- It can not describe macro effects:
  - Different particle size
  - Or tortuosity

\[ E \psi(r) = (-\hbar^2/2m) \nabla^2 \psi(r) + U(r)\psi(r) \]

Z. Fan and Jia G. Lu IEEE Trans Nanotech. 5(4), 393, 2006

Zhang, Nano Letters 4(10):1919-1924 2004
**Types of adsorptions**

- Heterogeneous catalysis begins with the act of adsorption.
  - Physisorption
    - Treated as dipol-dipol interaction (van der Waals interaction).
    - "Long distance interactions“, from $3 \times 10^{-10}$ m to $5 \times 10^{-10}$ m.
    - Novel-gas adsorbed on a metal.
  - Chemisorption:
    - Weak or neutral.
    - Strong or charged.
  - Ionsorption

\[
V = \frac{e^-}{4\pi\varepsilon_02z}
\]
Chemisorption

- Chemisorbed particle simultaneously both affinity:
  - Acceptor
  - Donor

- Weak chemisorption (CL)
  - Particle remains electrically neutral.
  - Lattice electrons or holes do not participate in the bond.

- Strong chemisorption
  - Particle adsorbs free electrons or holes
    - $n$-bond (acceptor bond), CeL.
    - $p$-bond (donor bond), CpL.
If the electron at the conduction band and adatom has parallel spin, then a repulsive potential is produced. Therefore due to Van der Waals forces, particles are localized at a minimum potential resulting in a physisorbed state. Alternatively, if they have antiparallel spin, the wave functions are overlapped, which leads to chemisorption. Because of this, Wolkenstein postulated a subdivision into two states: Neutral or "weak chemisorbed" and charged or "strong chemisorbed". They are represented as discrete states, meaning that.

Only strong chemisorbed molecules produce change in the conductivity

Fermi statistics

- When still valid the Fermi statistics?
  - Non-degenerated semiconductor,
    \[ E_V + 3kT < E_F < E_C - 3kT. \]

- Fermi level
  - Controls the catalytic properties at the surface.
  - Once electronic equilibrium is established:
    - Surface and bulk have the same Fermi level.

  \[
  f^0 = \frac{1}{1 + \frac{1}{2} \exp \left( \frac{E_F + e\Delta V_S - E_a^- + E_a^0}{kT} \right)}; \quad f^- = \frac{1}{1 + 2 \exp \left( \frac{E_a^- - E_a^0 - E_F - e\Delta V_S}{kT} \right)}
  \]

- Many factors control the Fermi level position.
The Fermi level determines the probably of weak and strong occupancy

\[ \frac{N^-}{N} = f^- = \frac{1}{1 + 2 \cdot \exp\left(\frac{E_l - E_g - e\Delta V_S}{kT}\right)}, \]

\[ \frac{N^0}{N} = f^0 = 1 - f^- = \frac{1}{1 + \frac{1}{2}\exp\left(\frac{E_F + e\Delta V_S - E_l}{kT}\right)} \]

The number of chemisorbed particles and adsorption sites are related to the coverage:

\[ \theta = \frac{N}{N^*} = \frac{N^0 + N^-}{N^*} = f^0\theta + f^-\theta = \theta^0 + \theta^- \]

The Langmuir isotherm is defined as

\[ b = \frac{\alpha}{v_0} \exp\left(\frac{q^0}{kT}\right) \]

The Wolkenstein isotherm is expressed as

\[ \beta = b\left[f^0\left[1 + 2 \cdot \frac{v^- f^-}{v_0 f^0} \exp\left(\frac{E_l - E_c}{kT}\right)\right]\right]^{-1} \]

\[ \theta(p) = \frac{\beta p}{1 + \beta p} \]
They don’t reach with each other

Certain interaction

- Adsorbates compete for the free adsorption centres

\[ \theta_j^{-} = \frac{\beta_j \cdot p_j}{1 + \sum_{i=0}^{n} \beta_i \cdot p_i} \cdot f^{-} \]

\[ N^{-} = \sum_{i=0}^{n} N_{\text{Surf}} \cdot \theta_i^{-} \]

Problem to extend this model to catalysis

- Same problem with Langmuir isotherm
Charge transfer

- Band bending
  - Surface potential.
  - Work function change
  - Depleted zone (SCR).
  - Electrical neutrality
    \[ Q_{SCR} = Q_{SS} \]

- Electric properties
  - Changes in the bulk conductivity
Charge transfer

- **Charge neutrality** \( Q_{SCR} = Q_{SS} \)

- **Charge surface** \( Q_{SS} = e^- \cdot \int_{-\infty}^{+\infty} D_{SS}(E) f_{SS}(E) dE \)

- **Distribution function** \( f_{SS}(E, E_F) \to f_{SS}(E, E_{F,\text{bulk}} + e\Delta V_S(\theta^-)) \)

- **Poisson equation** \( \frac{d^2V}{dz} = -\frac{\rho}{\varepsilon_0\varepsilon_r} \)

- **Surface potential** \( V_S = \frac{eN_D^2_{\text{SCR}}}{2\varepsilon_0\varepsilon_r}, \quad V_S = \frac{e(N^-)^2}{2\varepsilon_0\varepsilon_r N_D} \)

- **Mobility thermally activated** \( \mu = \mu_0 \cdot \exp(-eV_S/kT) \)
Weisz limit

\[(N^- / N) = f^{-}\left( E_{a}^{0/-}, E_F, e\Delta V_S \right) \]

\[ f^{-} = \frac{1}{1 + 2 \cdot \exp \left( \frac{E_{a}^{0/-} - E_F - e\Delta V_S}{kT} \right)} \]

\[ V_S = \frac{e(N^-)^2}{2\varepsilon_0\varepsilon_r N_D} \]

Self Limitation of Strong (=charged) Chemisorption

This is the Weisz Effect

Electrochemistry knows the same Effect: Mott-Schottky

Grain size

- Flat band limit
  - Crystallites $d_{\text{Grain}} \sim d_{\text{Space Charge}}$
  - Fermi statistics:
  - Thermoionics vs tunneling

$$L_D = \sqrt{\frac{\varepsilon_0 \cdot \varepsilon_r \cdot kT}{(e^-)^2 \cdot N_D}}$$

$$E \psi(\mathbf{r}) = (-\frac{\hbar^2}{2m}) \nabla^2 \psi(\mathbf{r}) + U(\mathbf{r})\psi(\mathbf{r})$$
Summary

- **Charge transport and transfer description**
  - Flat band conditions (Fermi-Dirac statistic): Thermo-ionic
  - Wolkenstein isotherm
  - Charge transfer

- **Complex description**
  - Schrödinger equation
  - Shockley-Read statictics: Tunneling
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■ Remarks
The challenge

Operation temperature approx: 300°C → CMOS!
Control adsorption/desorption

- Temperature
- Doping change
- Fermi level
- Surface functionalization
- External electric field

Nano Lett. 2011, 11, 751–756
Electroadsorptive Effect

EAE:

“Surface states electrical modulation on the metal-oxide surface by means of an external electric field”
Field-Effect devices

- JSE. Lilienfeld, "Method and apparatus for controlling electric currents", US Patent 1, 745, 175, 1930.
  - It didn't work
  - Why...

- O. Heil control of the layer conductivity by the surface states, 1935.

  - 10% were mobile.
  - Surface states acts like electrical tramps.

Short history: EAE

Adsorption of Methanol in Ge: Keier and Mikheeva 1964
O₂ in ZnO: Hoenig and Lane, Surf. Sci 11, 1968

ZnO Film, $E = 34 \text{ kV/cm}$

Oxygen
**With micro always high electric field**

SnO\textsubscript{2} Gate Transistor: Popova and Stoyanov 1994  
Consistency to the theory: Geistlinger 1994  
SnO\textsubscript{2} thin film: Hellmich and Müller 1996  
SnO\textsubscript{2} multi-electrode Sensor:  

Hausner and Binder 1997  
Thin film transistor gas sensor:  

Jaegle and Wöllenstein 1998
Thickness:

- Must be in the Debye Length range.
- Energy levels are modulated
- Reaction on the surface

Estimated strong occupancy probability vs. gate voltage:
Example at UHV: Fast transfer, EAE

**Development**

- **Suspended Gate**
  - Effective control on the surface states
  - Very difficult to realize this geometry with standard CMOS processes.

- **Thin-Film-Transistor Gas Sensor**
  - Debye-Length:
    \[ L_D = \sqrt{\frac{\varepsilon_0 \varepsilon_r kT}{(e^-)^2 N_D}} \]
  - Effective control of the Fermi-Level
  - Technology: CMOS-Standard processes

- **Multi-Gates**
  - Homogeneous surface reaction
Multigate concept
Technology

- SEM image „Multi-Gates“ Structure*
  - Source-Drain TFT
  - Semiconductor SnO₂ and insulator Si₃N₄
  - Contact Pt

- Compact poly-crystalline**
  - Non predominant orientation
  - Grain size from 5 to 25 nm (Flat-band condition)

- Sensitiven layer 55 nm

*M. Lehmann, H. Frerichs **J. Wöllenstein
Technology

- Gate electrode
  - Multi-Gate-Structure, top view (Right)
  - Gate electrode, Crosssection (Left)
Material SnO2

- Octahedron and rutile (a=b=0.47nm, c=0.32nm, O-Sn-O=77°20´)
- Inert to the acid-base reaction
- Heat of formation $\Delta H=1.9E13\text{(J/mol)}$
- Density at 300 K is 6.95 (g/cm$^3$)
- Melting point at 1630°C
- Direct band gap 3.5 eV
- Small electron effective mass $m^*=0.275\ m_0$, good conductivity
- Neutral oxygen vacancies ($V_0$, they play role as donators) form energy states at 0.035 eV and 0.140 eV
- It is a n-type semiconductor due the existence of native donators levels
Technology

- SEM view of a multi-gate structure
  - Source and drain area of a multiple TFT (left)
  - SnO$_2$ and Si$_3$N$_4$, on right
Electric model

- **Sensor-Modell:**
  - Poisson + continuity equation: Signal behaviour
    \[ \Delta \cdot \psi = -\frac{\rho}{\varepsilon_0 \cdot \varepsilon_r} \]
    \[ \nabla J_{th} + e^- \cdot \frac{\partial}{\partial t} (p - n) = 0 \]
    \[ Q_{SS} = Q_{SCR} \]
  - Wolkenstein-Modell: Surface reaction
    \[ \theta(p) = \frac{\beta \cdot p}{1 + \beta \cdot p} \]
    \[ \beta = b \left\{ f^0 \left[ 1 + \frac{v^- f^-}{\nu^0 f^0} \exp \left( \frac{E_i^f - E_c}{kT} \right) \right] \right\}^{-1} \]
- **Drain-current:** Controled by \( V_{DS} \)
- **Sensor works like MOSFET with reaction to gases**
Gas measurements

- Ideal current signal
  - Proportional to the gate potential
  - Not time depending (stable)

- Measurements with GasFET

- Solution: Pulse at the gate

- Parameter:
  - Synthetic air 80% N\textsubscript{2} and 20% O\textsubscript{2}, RH 40%, Work temperature 200°C, V\textsubscript{DS}=1 V
AP 2 Gasabhängige Charakterisierung der Schichten

Lichteinfluss auf gassensitive Nanoschichten

Messaufbau:

Gassensoren  Messkammer  LEDs bei verschiedenen Wellenlängen (blau und UV)
Signal drift

- MIS-condensator
  - Low: $C = 2.2$ pf

- Charge carriers Generation
  - Illumination (LED 340 nm)
    - $t_{ON}$: 40-60 s
    - $t_{OFF}$: 80-120 s

- Surface kinetic reaction*
  - Simulation parameters: $10^{10}$ times smaller than real parameters

- Chemical reaction
  - Vacuum measurements, same signal behaviour

*V. Brynzari et al. Sensors and Actuators B,61,143-153, 1999
High vacuum

H.L. Tuller, Massachusetts Institute of Technology*

„We're all in the same boat“
Oxygen vacancies diffusion

- Doping diffusion by electric field
  - Fick diffusion
    \[ \frac{\partial N}{\partial t} = D_{\text{vac}} \Delta \cdot N \]
  - Fokker-Planck-Equation
    \[ \frac{\partial N}{\partial t} = \frac{e}{m_{\text{vac}}} \nabla \cdot (E \cdot N) + D_{\text{vac}} \Delta \cdot N \]
  - Drift-Diffusions-Equation
    \[ \frac{\partial n}{\partial t} = -\mu_n \nabla \cdot (E \cdot n) + D_e \Delta \cdot n \]
  - Coupling of FP+DD by Poisson-equation
    \[ \Delta \cdot \psi = -\frac{e}{\varepsilon_0 \cdot \varepsilon_r} (n - N) \]
Normalized vacancies distribution.

Internal electric field distribution.
Memristor

Summary

EAE Adsorption  Co-Adsorption  Gas-adsorption

Doping
Continuity equation
Poisson-equation

Electric Potential

Standard Halbleiter-Theorie

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Conclusions

■ Charge transport in semiconductors can be accurately described
  ➢ Semiconductor theory

■ IMPORTANT: Not only the material properties are important in the charge transport also geometry!

■ Gas-solid interaction influences the transport of charge in solid due to a charge transfer process.
  ➢ Atomistic interaction at the surface modifies the conductivity of solid
  ➢ It can be accurately described by an extended semiconductor theory
    ✴ Wolkenstein theory
    ✴ Charge transfer (band bending)
  ➢ IMPORTANT! Check if this model is applicable directly to your system
    ✴ Grain size effects (Debye length)

■ Note: In catalytic processes the surface change continuously:
  ➢ Dynamic phase transitions
Greatings

Thank you!