Surface Transfer Doping of Diamond by Organic Molecules

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Scope of presentation

- **Overview**
  - Properties of Diamond
  - Surface transfer doping model
- **Surface transfer doping of diamond by F4-TCNQ**
  - C 1s and N 1s PES
  - Valence Band and work function measurements.
  - Energy-level alignment
- **Comparison: CuPc**
  - correlation of doping efficiency and molecular EA.
- **Beyond Diamond: application in other systems**
- **Conclusion**
The unique properties of Diamond

- Extreme hardness & optical transparency
- High thermal conductivity
- High carrier mobilities ($\mu_n=2200$ cm$^2$/V s, $\mu_p=1600$ cm$^2$/V s)
- High breakdown filed ($10^7$ V/cm)
- Negative Electron affinity and surface conductivity (hydrogen-terminated)

Excellent materials for making electronic devices working at high temperature, high frequencies and high power *et.al.*
Obstacles: Doping of Diamond

- High dopant activation energy

Conventional doping: only partially activated at room T (~0.026 eV) due to very high activation energy!

- Processing and patterning difficulty
Beyond conventional doping

Surface conductivity (SC) of diamond

The Fact:

- On hydrogenated diamond surface
- P type
- In the order of $10^{-4}$ to $10^{-5}$ $\Omega^{-1}$
- Areal hole density: $10^{12}$ to $10^{13}$ cm$^{-2}$
- Mobility: 10 to 100 cm$^2$V$^{-1}$S$^{-1}$

The Origin:

Surface Transfer Doping model is proposed to explain

Classical doping Vs Surface Transfer doping

- dopants incorporated in bulk lattice
- by implantation
- 3D, deep junction
- a few selection of dopants

- dopants reside on surface
- by deposition or adsorption
- 2D hole layer, ultrashallow
- large pool of dopants: atmospheric adsorbates, C\textsubscript{60}, C\textsubscript{60}F\textsubscript{48} etc.

*Nano-scale planar doped electronic devices*
Does surface transfer doping really happen on diamond surface?

- Is there a really a charge transfer at the diamond/acceptor interface?
- What is the electronic structures at the interface?
- Correlation of doping efficiency with surface dopant’s electron affinity (EA).

**Experiment Design**

- Molecular acceptor
  - Highest known EA (5.24 eV)
- Negative EA (-1.0 eV)
  - Lowest IP (~4.5 eV) among semiconductors


Using X-ray photoemission spectroscopy (PES) to probe
Surface, Interface and Nanostructure Science (SINS) beamline, Singapore Synchrotron Light Source (SSLS)

We are here!
Surface, Interface and Nanostructure Science (SINS) beamline, Singapore Synchrotron Light Source (SSLS)

- Dragon type grating: 50-1200 eV
- Omicron hemispherical energy analyzer: 0-2000 eV
- Common Surface Analysis instruments.
- Scanning tunneling microscopy
- Details on [Http://ssls.nus.edu.sg](http://ssls.nus.edu.sg)
Results: PES of core levels

Electrons are indeed transferred from diamond to F4-TCNQ

Cyano groups extracting electrons from diamond
Does surface transfer doping really happen on diamond surface?

➤ Is there really a charge transfer at the diamond/acceptor interface?

➤ What is the electronic structures at the interface?

➤ Correlation of doping efficiency with surface dopant’s electron affinity (EA).
Valence Band Structure

Electrons are transferred from diamond valence band to molecular LUMO
Work Function evolution

![Graph showing the evolution of work function](image)

- **Cut-off**: vacuum level
- **Interface dipole**: caused by charge separation
Energy-level alignment diagram

before contact

C(100)2x1:H F4-TCNQ

after contact

C(100)2x1:H F4-TCNQ

Graduate Congress 2007
Does surface transfer doping really happen on diamond surface?

- Is there really a charge transfer at the diamond/acceptor interface?
- What is the electronic structures at the interface?
- Correlation of doping efficiency with surface dopant’s electron affinity (EA).
Comparison: Copper Phthalocyanine (CuPc)

- Organic semiconductor
- Small EA: \( \sim 3 \text{ eV} \)
- No charge transfer across the interface
- Due to large activation energy \( \Delta = 1.5 \text{ eV} \)
Areal hole density

non-degenerate case

\[ p(u) = \lambda_N V_N \cdot \exp\left(\frac{u}{2kT}\right) \]

degenerate case

\[ p(u) = \lambda_N V_N \cdot \sqrt{1 + \frac{u}{kT} + \frac{8}{15\sqrt{\pi}} \left(\frac{u}{kT}\right)^{5/2}} \]

\[ \lambda_N V_N = 2.1 \times 10^{12} \text{ cm}^{-2} \text{ for diamond} \]

\[ u = E_V - E_F \]


Doping efficiency are directly correlated to molecular electron affinity
Beyond Diamond

- Surface transfer doping of organic semiconductors

- Surface transfer doping of graphene

- Surface transfer doping of silicon (silicon-on-insulator SOI system)

*Versatile scheme to dope nano-scale planar electronic devices.*

Conclusions

- Provide the first spectroscopic evidence for surface transfer doping
- Unambiguously demonstrated a controllable surface transfer doping of diamond by the adsorption of F4-TCNQ molecules.
- High areal density of holes in diamond are formed.
- Doping efficiency is correlated to surface dopant’s EA.
- The surface transfer doping scheme could be applied to other semiconductor systems.
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Q&A