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Electronic Supplementary Information

DFT Insights into the Electronic Properties and Adsorption of NO_2 on Metal-Doped Carbon Nanotubes for Gas Sensing Applications

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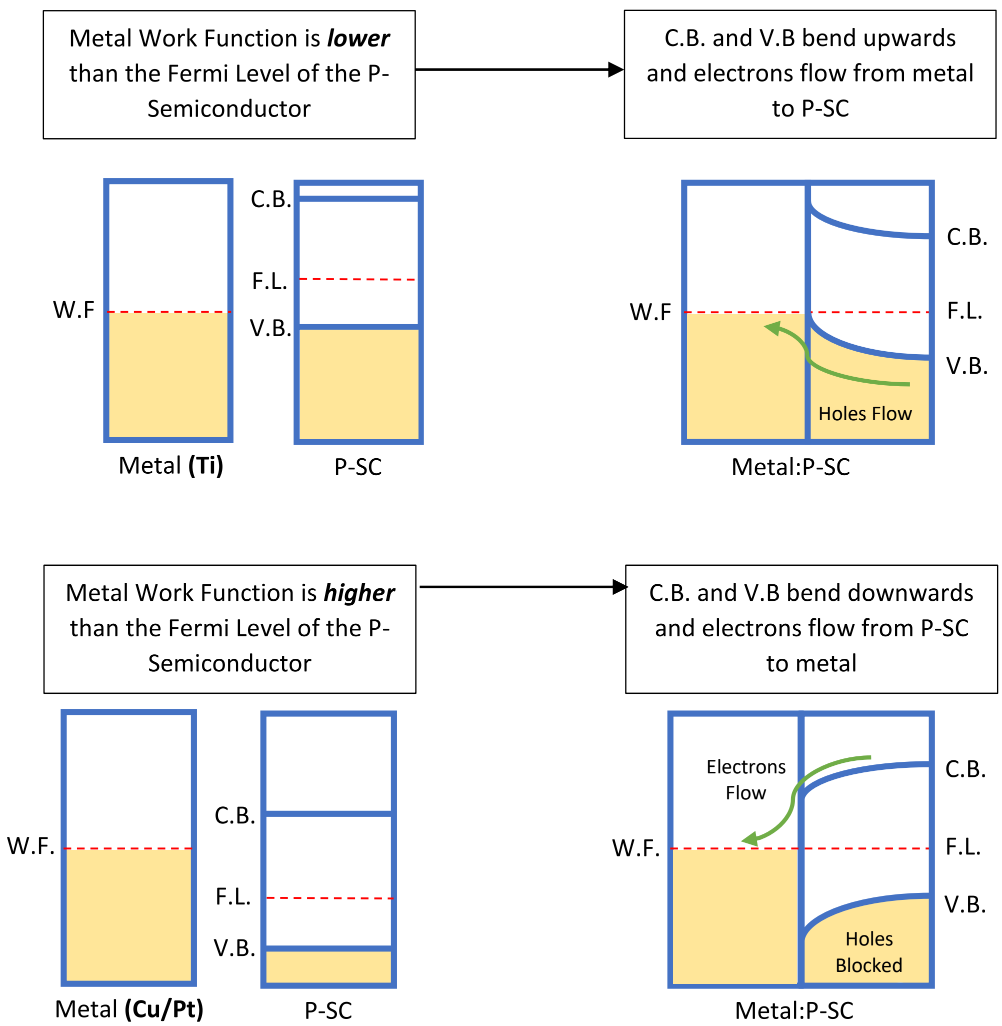
The work function of the metal dopant plays a crucial role in the charge transfer between the metal and the carbon nanotube upon doping. The p-type single walled carbon nanotube has semiconducting properties and a Fermi level of ca. 4.8 eV.[1] Figure S1 depicts the tendencies of charge transfer between a p-type semiconductor (P-SC) as it comes in contact with a metal of high and low work function. The Fermi levels of the metal and CNT align on contact and for this to happen there must be a transfer of charge between them. When the metal work function is smaller than the Fermi level of the P-SC, the Fermi level of the semiconductor shifts to the lower value to align with the metal Fermi level causing the conduction and valance bands to bend upwards thereby allowing the electrons to flow easily from the metal to the P-SC and the holes in the reverse direction. This leads to a decrease in the bandgap which increases the conductivity of the M-CNT complex.



When the work function of the metal is larger than the Fermi level of the semiconductor, as in the case for Cu and Pt, the Fermi level of the CNT will shift upwards to align itself with the metal's Fermi level resulting in the bending of the conduction and valence band downwards. When the bands bend downwards a large potential barrier is created for the holes, which prevents them from flowing towards the metal, thereby constricting the current flow in that direction. However, the electrons in the conduction band of the p-type semiconductor will flow from the higher energy level to the lower energy level in the equilibration process thereby also resulting in a charge transfer but in the opposite direction to that of the Ti-doping case stated above. This is reflected in the opposite charge transfer values derived in table 3. This charge transfer also results in a narrowing of the band gap as shown in table 4 but not to the extent of the large narrowing observed for TI-CNT because the major hole transfer pathway is restricted compared to that of Ti-CNT.

The process described above focuses on the effects due to metal doping, a similar process is observed upon exposure to the target NO_2 gas. NO_2 gas exposure further narrows the band gap due to the transfer of charge from the M-CNT complex to the gas where in the special case of Ti-Doped CNT the band gap disappears and shows a metallic overlap.

References

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