Defects and dopants in carbon related materials

Submitted by Hugo Manuel Pinto to the University of Exeter as a thesis for the degree of Doctor of Philosophy in Physics.

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Abstract

This thesis presents theoretical studies of the optical and electronic properties of defects in diamond and of the mechanisms of doping graphene.

The birefringence of the four petalled defect commonly observed in CVD diamond is explained by four linear arrays of dislocations along $\langle 110 \rangle$ directions with $\langle \bar{1}10 \rangle$ Burgers vectors. Such an arrangement of dislocations reproduces the extension and the features of the birefringence patterns observed experimentally.

Density functional theory via the AIMPRO code was used to study the electronic and optical properties of different nitrogen-related point defects in diamond. It was found that the zero-phonon luminescence line of the NV^- defects can split in the presence of a surface or other NV^- defects.

Since VNH and VN_2 are expected to have similar optical properties, the optical transitions for VN_2 were used to correct the transitions for VNH calculated by local density approximation. The absorption band at 2.38 eV (520 nm) observed in CVD diamond is then attributed to an internal transition of VNH. The weak zero-phonon line and broad vibronic sidebands for VN^- and VN_2^- and its absence for VNH^- is explained by the large structural change when the defect is excited.

Finally, different mechanisms for doping graphene were considered. The calculations predict the electropositive metals, such as Ti and Cr, act as donors, while molecules with strong electron affinity, such as F4-TCNQ, act as acceptors in graphene. An unexpected mechanism of doping graphene was shown by Au which dopes bilayer graphene but not single layer. In the presence of water, electrochemical reactions on the graphene can also lead to p or n-type doping.

To my family,

Teresa, Francisco and João

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Contents