First-Principles Study of One-dimensional Nano-structures

A Thesis

Submitted For the Degree of

DOCTOR OF PHILOSOPHY

by

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To my parents

DECLARATION

I hereby declare that the matter embodied in the thesis entitled "**First-Principles Study of One-dimensional Nano-structures**" is the result of investigations carried out by me at the Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India under the supervision of Prof. Umesh V. Waghmare and that it has not been submitted elsewhere for the award of any degree or diploma.

In keeping with the general practice in reporting scientific observations, due acknowledgement has been made whenever the work described is based on the findings of other investigators.

Mousumi Upadhyay Kahaly

CERTIFICATE

I hereby certify that the matter embodied in this thesis entitled "**First-Principles Study of One-dimensional Nano-structures**" has been carried out by Ms. Mousumi Upadhyay Kahaly at the Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India under my supervision and that it has not been submitted elsewhere for the award of any degree or diploma.

Prof. Umesh V. Waghmare
(Research Supervisor)

Acknowledgements

At the moment of this thesis submission, I have two reasons to celebrate: firstly, I see my dream of becoming a doctorate coming to fruition very soon, and secondly, I inched one step closer to being what I always wanted to be, a scientist. Its seems apparently paradoxical that at this juncture, instead of remembering all the moments that truly gave me immense satisfaction as a student of science, I feel very emotional, remembering them on whose shoulders I built my ph.D. First among them is undoubtedly, my research supervisor, Prof. Umesh V. Waghmare. He has been an epitome of excellence, patience and kindheartedness. His sheer enthusiasm for science, drive for perfection and elan in pointing out the basics have always amazed me. He taught me how to understand a problem in terms of mathematics and search for concrete solutions. I am and will remain deeply indebted to Umesh sir, whose help, stimulating suggestions and encouragement to be independent helped me during the time of research and which I would carry forward rest of my life. But, for his inputs, teachings and support, this thesis would not have shaped up.

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Synopsis

For the last fifteen years, the field of nanomaterials has been an active area in scientific research due to the enormous promise of nanosystems for prospective applications in areas like nano-electronics, nano-mechanics, and medical instrumentation etc. This doctoral thesis is aimed at gaining a theoretical understanding of the physical and chemical properties of one dimensional nanostructures, and use this understanding for novel applications. Most of this work is performed within the framework of first-principles density functional theory.

In the first project, we study interaction of inorganic metal ions (M) with organic molecules like acetic acid, resulting in the formation of metal diacetates and attempt to understand the diversity in geometry and properties of binding of different metal ions with -COOH group. The estimates of metal-acetate bond energies follow trends found experimentally, and can be used for selective removal of metal ions, i.e. in ion sensor.

The second project determines the size-dependence of atomic and electronic structures, elastic properties and most importantly, optical conductivity of selenium nanowires. Though the interchain bonding between two helical chains in trigonal selenium based nanowires is weak enough to have only a small impact on structure, the features in the optical conductivity obtained from the electronic structure show marked anisotropy and interesting dependence on the diameter of a Se nanowire. Our results raise the possibility that bundles of aligned Se nanowires can be used as nano-polarizers. Further, the origin of stability of the helical structure of selenium is investigated through Wannier functions based study of chemical bonding in Se nanowires and clusters.

In the third project we estimate and understand effects of curvature on structures and vibrations of armchair and zigzag carbon nanotubes. An understanding of the effect of curvature on phonon dispersion of nanotubes is developed through its correlation with the normal modes of an unrolled graphene sheet. Within a quasiharmonic approximation, we estimate thermal expansion coefficient of carbon nanotubes and identify the low energy vibrational modes that dominate their negative thermal expansion at low temperatures. Further, we study size-dependence of thermal properties of carbon nanotubes to find that while the specific heat is found to depend rather weakly on the diameter of nanotubes, their negative thermal expansion behavior exhibits a relatively stronger dependence on the diameter. Study of full phonon dispersion and thermal properties in double wall carbon nanotubes illustrates the effect on inter-tube interaction on their negative thermal expansion at low temperatures.

In the fourth project, we determine atomic and electronic structures of arm-chair and zigzag boron nitride nanotubes of different diameters, and understand the effect of doping in such nanotubes. We find that carbon substitution either at B-site, or at N-site in a pristine boron nitride nanotube yields magnetically polarized semiconducting state, whereas carbon substitution at neighbouring B and N sites yields a non-magnetic insulating structure. In contrast to the above spontaneous magnetization, B or N doping in carbon nanotubes gives a simple shift in the Fermi energy and maintains a non-magnetic state. Thus, C-doped boron nitride nanotubes opens up the possibility of getting metal-free magnetic semiconducting nanotubes which can be used as memory device or nano-manipulator.

Finally, in our fifth project, we propose novel types of nano-tubes, such as carbon nanotubes with fractional indices of helicity These carbon based nano-structures of considerable stabilities open up possibilities of design of novel nano-composites, nano-electronic interconnects etc. For example, the class of carbon nano-tubes based on stacking faults in graphene sheet exhibit unusual electronic structure with carrier states confined truly within one dimensional space.

In summary, this thesis is a first-principles theoretical investigation of

different one dimensional nano-structures and related systems, with emphasis on both their fundamental and applied aspects.

Nomenclature

0D : zero-dimensional

1D : one-dimensional

2D : two-dimensional

3D : three-dimensional

e : charge of an electron

BE : binding energy

BFGS : Broyden, Fletcher, Goldfarb, Shannon

BO : Born and Oppenheimer

DFT : density funtional theory

DFPT : density functional perturbation theory

DOF : degrees of freedom

DOS : density of states

HK : Hohenberg and Kohn

GGA : feneralized gradient approximation

LDA : local density approximation

PBE : Perdew, Burke and Ernzerhof exchange-correlation functional

PW91 : Perdew and Wang exchange-correlation functional

m_e : mass of an electron

M_I : mass of nuclei

Se-h : a single Se helix

Se-w1 : Se wire with one shell

Se-w2 : Se wire with two shells

α, β : Cartesian indices

a : lattice spacing

A : area

d_b : bond length

E : total energy of a system

E_{cut} : Plane wave energy cut-off

E_{e-e} : electron-electron interaction energy

$E_n(\mathbf{R})$: BO potential energy surface

$E_{tot}[n]$: Total energy functional

E_{Ewald} : nuclear-nuclear interaction for a particular ionic configuration

E_{HK} : HK functional

$E_{\mathrm{XC}}[n]$: exchange-correlation energy

$E_{\mathrm{XC}}^{\mathrm{LDA}}$: exchange-correlation energy within the LDA

$E_{\mathrm{XC}}^{\mathrm{GGA}}$: exchange-correlation energy within the GGA

h : Planck's constant

$\hbar$: $h/2\pi$

$\hat{H}$: Hamiltonian

$\mathbf{k}$: wave vector

k_B : Boltzmann constant

μ_B : Bohr magneton

∇ : spatial derivative

$n(\mathbf{r})$: electronic charge density

$n_0(\mathbf{r})$: ground state electronic charge density

N : number of electrons

ω : frequency

Ω : volume of the unit cell

r_c : cut-off radius

$\mathbf{r}_i$: position of i^{th} electron

$\mathbf{R}_I$: position of I^{th} ion

R : radius of nanowire

σ : conductivity tensor

θ : bond angle

T : temperature

$T[n]$: kinetic energy functional

$T_0[n]$: ground state kinetic energy functional

v_{XC} : functional derivative of the exchange-correlation energy

$v_{\text{XC}}^{\text{LDA}}$: exchange-correlation potential within LDA

$v_{\text{XC}}^{\text{GGA}}$: exchange-correlation energy within the GGA

$V_{\text{ext}}(\mathbf{r})$: external potential

V : volume

V_0 : volume of nanowires

Y : Young's modulus

Z_I: charge of nuclei

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CNT: carbon nanotubes

SWCNT: single walled carbon nanotubes

α: thermal expansion coefficient

C_p: specific heat

GP: Gruneisen parameter

NTE: negative thermal expansion

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