Virtual Synthesis of 3D Nanomaterials With Pre-Designed Electronic Properties

INTRODUCTION

In the beginning of the third millennium, nanotechnology has proven to be a dominant force facilitating further advances in computing, communication and information storage technologies in the coming decades. The Semiconductor Industry Association (SIA) has developed a roadmap for continuing improvements in miniaturization, speed and power reduction in information processing devices, such as sensors for signal acquisition, logic devices for processing, storage devices for memory, displays for visualization and transmission devices for communication. This roadmap projects the future to approximately the year 2010 and to 0.1-micron (100 nm) structures that are on the brink of fully nanostructured devices. The SIA roadmap stops here, because the principles, fabrication methods and device system integration concepts for nanostructures are largely unknown at present. Among other achievements, priority fields of research have to facilitate breakthroughs (1) in nanostructured microprocessor devices to improve the efficacy of computers by a factor of millions and in (2) integrated nanoprocessor systems capable of collecting, processing and communicating massive amount of data with minimum size, weight and power consumption restrictions. Formidable challenges remain, however, in fundamental understanding of nanoscale system properties before the potential of nanotechnology can be realized. In this project we address development of approaches to prediction of electronic transport properties of 3D nanosystems of 1 to 10 nm in linear dimensions.

Recent advances in fundamental and materials sciences have made possible fabrication of nanoscale electronic devices composed of alternating layers of several (doped or "pure") *n*- and *p*-type semiconductors of several hundred angstroms in width (superlattices and nanoheterostructures, or SLs and NHSs). Development of experimental nanotechniques, such as scanning near field optical microscopy (SNOM or NSOM) and improved epitaxial growth procedures (MBE and Stranski-Krastanow methods, and improved chemical processing) has lead to fabrication of (i) single quantum dots (QDs) and "artificial atoms" of GaAs, InAs, InP, CuCl, Si, Ge, etc. where from several thousand to a few electrons are confined to spatial regions from 100 to 10 nm in linear dimensions, respectively; (ii) 2D and 3D ordered arrays of QDs, and 2 types of QD systems: those where electron – hole pairs (excitons) reside in a dot (type I) and those where holes of the pairs reside in the dot while the corresponding electrons are in the matrix in which the dots are distributed, or at the interface. It has been proven experimentally that the extent of the line broadening for the optical absorption and luminescence peaks can be limited by variation in the QD size, the conductance through a quantum dot is characterized by quantum coherence, and that the photoluminescence efficiency of such systems can be extremely high. These studies also helped in identification and resolution of exited states of excitons, biexcitons, higher excited states, charged excitons and their interactions, that had been first introduced theoretically. Smaller structures, or the "artificial atoms" , such as very clean metallic nanoparticles, C_{60} deposited on gold surfaces, carbon nanotubes, arrays of nanowires with the individual wire size of about 30 angstroms, and other atomic/molecular assemblies have also been fabricated and studied. The advantage of the artificial nanoscale systems is that their properties can be controlled by changes in the processing and systems parameters, including the system dimensions. The latest experimental developments concern fabrication of nanostructures composed of semiconductor element atoms confined in atomic dimension, well-characterized nanopores of nanoporous solids (such as silicates fabricated

via templated synthesis). Such nanosystems have a potential to become building units for future ultrafast and ultradense integrated circuits. Therefore, understanding of electronic transport properties of such nanosystems (in particular, their conductance) is extremely important.

Modern theoretical physics and computational methods have played a unique role in prediction of extraordinary properties of nanoscale systems of about 100 nm in linear dimensions and have led to the latest experimental and technological achievements. In particular, *equilibrium* electronic structure theory of the solid state of matter (both fundamental and phenomenological approaches) and its computational methods have been intensively employed to "invent" structures that exhibit new physical phenomena and conditions at which such phenomena can be exploited. The theory evaluated and predicted band gaps and other electronic properties of compositional, doped and mixed superlattices (SLs) where the electronic potential is modulated by composition variations, electric fields generated by the charged dopants, or both. It explained quantum confinement effects leading to observations of negative differential resistance in SLs, suggested some prescriptions of the conduction-band edge adjustment by choosing the alloy composition (for example, in $In_{1-x}Ga_xAs/GaSb_{1-y}As_y$ alloys), predicted the zero-band gap of the HgTe semiconductor and HgTe/CdTe systems, showed that lattice-constant mismatch-induced strain caused new behavior in strained-layer SLs via deformation-potential effects, predicted large electric fields of alternating polarity in two constituent materials making up the SLs, etc. The major conclusion of these developments is that because of different band-edge line-ups, strain conditions and growth orientations, various SL systems can show qualitatively different physical behavior. The electronic structure of SLs and generally, nanoheterostructures (NHSs) depends on the properties of the constituent materials and the layer thickness, that can be precisely controlled. The nanodimensions and the flexibility of the electronic properties that is introduced by such a design make NHSs suitable for applications in modern electronics (optoelectronics, infrared sensors) or development of entirely new fields of electronics (spintronics, quantum chips, etc.).

While the *theory of equilibrium* properties of nanosystems is relatively well developed and suggests a number of rigorous and half-heuristic approaches and computational methods, *non-equilibrium theory* of nanosystems of 1 to 10 nm in linear dimensions is in its infancy stage. Such important properties of nanosystems as quantization of the conductance, quantum dephasing of electrons, the structure of excited electron energy levels, relaxation times, high-frequency susceptibilities and dielectric response, response to time-dependent electrical and magnetic fields, time-dependent composition, temperature and pressure gradients, effects of all those on quantum confinement properties, etc. are studied intensively primarily for larger systems, such as QDs, and are not well undestood for 10nm-size nanosystems. The major theoretical developments (addressed below in section C3: Present State of Theoretical Knowledge) constitute several approaches each of which features a number of assumptions and describes some particular type of nanosystems, nanosystem evolution or nanosystem property. While some of these approaches are based in the basic principles and are rigorous in nature, none of them provides means for a systematic description of all electronic transport properties of small nanosystem. The absence of a "unified" and tractable theoretical approach to electronic transport properties of small nanosystems limits possibilities of the corresponding technological developments. At present, manipulation of small nanostructures' electronic properties at the stage of experimental fabrication of such nanostructures is an extremely challenging task, because the correlations between the structure and electronic properties of the fabricated nanoheterosystem, on one hand, and (i) the carrier lattice properties (the structure, composition, topology, and chemistry of the host lattice framing nanopores that contain guest atom structures), (ii) properties of "guest lattices" formed by guest atoms inside of such pores, and (iii) parameters (composition, temperature and pressure gradients, field frequency, etc) of the processes

used for deposition of the guest atoms into the nanopores are known only from laboratory experience for a very restricted number of particular nanosystem samles (that are primarily 2D quantum dots of about 100 nm in linear dimensions, or carbon nanotubes, similar in size).

C2. AIMS, OBJECTIVES AND SIGNIFICANCE.

In the course of this project we plan to apply a fundamental field-theoretical technique based on a generalization of the Mori-Zwantzig projection operator method [so-called functional perturbation theory, or FPT, previously developed by a co-PI of this project, Liudmila A. Pozhar (LAP), in collaboration with K.E. Gubbins] to establish a rigorous, and at the same time, tractable, non-equilibrium quantum theory of electronic transport in nanosystems of sub-10 nm scale. An important feature of the FPT-based concept of transport is that the transport coefficients are expressed in terms of *equilibrium* correlation functions (CFs) specific to a considered system. This supplies an opportunity to use the FTP-based transport theory in conjunction with various sources of data on the equilibrium CFs, such as those obtain by theoretical means (in the framework of equilibrium statistical mechanics), computational data (calculated using the Hartree-Fock and density functional theory-based methods), data obtained from molecular simulations, and from experimental studies. The CFs obtained on the basis of computations and molecular simulations feature many details relevant to a considered particular system that are difficult to obtain by purely theoretical means (solving integral equations of equilibrium statistical mechanics). The use of such accurate CFs as input data in theoretical expressions for the transport coefficients enhances the accuracy of the transport property predictions. A classical version of FPT has been successfully used to derive a transport theory of classical nanosystems of several atomic diameters in linear dimensions (see for details section C4: Previous Work). The predicted transport coefficients of such classical nanosystems agree quantitatively well with the corresponding values obtained by means of molecular simulations methods and reflect all experimentally available information on the transport properties.

The principal aims of the project are:

- (i) to develop a rigorous and tractable theoretical concept of quantum transport in 3D nanosystems based on the FPT approach;
- (ii) to use Hartree-Fock-based computations to calculate equilibrium correlation functions of a model nanostructure composed of a guest lattice built of Ga and As atoms and confined in a nanopore of framed by a silicon carrier lattice (further called GaAs/Si-NS) ;
- (iii) to apply the developed FPT-based concept and the obtained equilibrium correlation functions to predict conductance of the GaAs/Si-NS;
- (iv) to simplify the developed quantum theory of charge transport in nanostructures to a suitable quasiclassical description of the transport;
- (v) to compare the obtained theoretical predictions with available experimental data on similar nanosystems.

The primary objectives are:

- (i) to estimate fundamental constraints as applied to collective mode description of charge transport in nanosystems of several atomic diameter in linear dimensions;
- (ii) to use the FPT to develop quantum kinetic and transport theories of charge transport in the nanosystems; to derive explicit expressions for the charge transport coefficients and effective conductance in terms of equilibrium correlation functions of the nanosystems;

- (iii) to evaluate accuracy of the Hartree-Fock and density functional theory-based calculations of the quantum CFs specific to a model GaAs/Si-NS;
- (iv) to use the developed transport theory to reveal effects of the host and guest lattice structure and composition on (1) the electron scattering from the host-guest lattice boundaries that defines electron phase coherence phenomena, (2) structure of the excitation spectrum of the model nanosystem, (3) the tunneling and co-tunneling conductance, (4) Coulomb blockade effects;
- (v) to investigate possibilities of simplified quasi-classical description of conductance of nanostructures and to derive the corresponding quasi-classical theory of charge transport in such nanosystems.

Significance of the proposed research is manifold. Fundamental and, at the same time tractable, the FPT-based quantum theory of charge transport in nanosystems can be used as a source of simplified quasi-classical descriptions of charge transport in nanosystems of significant interest for nanoelectronics. Its classical version (already developed and tested) supplies a reliable decription of transport phenomena in classical nanosystems. Used in conjunction with the corresponding FTP-based classical transport theory, the FTP-based quantum theory of charge transport in nanosystems has a capacity to become a foundation of a “unified” fundamental approach that is designed to supply a link between the electronic transport properties of fabricated nanosystems, on the one hand, and conditions and parameters of their fabrication, on the other hand. From application point of view, development of such a unified approach is an important step toward virtual fabrication of electronic materials by design.