

Chapter 1

Introduction

When an object is described, its size often is the starting point of the description. This is not surprising, since the importance of physical scale is cross-disciplinary. Viruses are the smallest living organisms and are able to live inside other cells undetected. Diffusion rate of a molecule or a subatomic particle is related to its size and in turn may control the pressure or electrical conductivity. Size is intimately related to function. Dramatically changing the size of an object almost always alters its function by causing new physical and chemical properties to emerge. Accessing a new scale, therefore, often means obtaining new functions. While the worlds of biochemistry and organic chemistry revolve around the nanoscale, inorganic solid-state materials have only relatively recently been able to tap into these dimensions. While tremendous progress in the synthesis and research of nanomaterials has been made, relatively few truly useful properties have been discovered and even fewer successfully applied. This is, in part, because nanoscience is largely cross-disciplinary, and major challenges occur at the interfaces of various fields, such as material science and surface chemistry.

This thesis is a reflection of the merging of different fields to obtain and harness useful properties afforded by the nanostructured materials, in particular silicon. High aspect ratio silicon nanowires (SiNWs) comprise a central theme of this work, and each chapter tackles a particular property characteristic to these materials. In chapter two, I introduce a new fabrication technique, called silicon nanowire pattern transfer (SNAP), for making silicon nanowire arrays of ultrahigh density. This method is characterized by

its tremendous versatility and robustness. It affords unprecedented control over most of the important physical and electronic parameters of a one-dimensional semiconductor nanomaterial, such as diameter, length and doping concentration. SNAP is a perfect platform on which to build systematic studies not only of silicon nanowires, but nanowires of a broad range of materials.

Chapter three addresses the use of SiNWs for the sensing of biological molecules in an electrolyte solution. High surface-to-volume ratio of SiNWs causes the surface charges to exert a significant effect on the electrical conductivity of the nanowires. The NWs can essentially act as solution field-effect transistors (FETs) whose current is modulated by the surface binding of charged biological species. Since the binding event may be directly electrically detected without secondary signal amplification, which is often required for optical detection, label-free real-time sensing is possible. Few sensing techniques are real-time and label-free; therefore, the superior sensitivity and extreme scalability of SiNWs makes these sensors unique for many applications, such as the detection of secreted proteins from single cells, for example. The doping level and surface chemistry are two of several important issues addressed in this chapter for proper engineering of SiNWs to detect oligonucleotides and proteins. While femtomolar sensitivity of DNA can be achieved in high ionic strength (physiological) solution, the detection of proteins is limited by the size of antibodies, which are by far the most widely used high-affinity protein capture agents. The Debye screening by the ions, therefore, prevents the sensing of proteins in the physiologically relevant solution. Alternatives to antibodies, such as aptamers, small molecules or peptides may eventually circumvent this limitation. Finally, I address the method of quantitating the response of SiNW sensors.

A model is developed which may be used to extract kinetic parameters as well as an absolute analyte concentration. This feature, unique to a label-free and real-time method of detection, significantly elevates the possible usefulness of SiNW-based sensors.

Chapter four discusses a novel, spatially selective method of functionalizing silicon micro- and nanostructures based on electrochemical programming. A monolayer of hydroquinone molecules is grown on a hydrogen-terminated silicon surface via a UV-catalyzed hydrosilylation method. An electrochemical oxidation of hydroquinone to benzoquinone allows selective attachments of secondary molecules to the benzoquinone via Diels-Alder or Michael addition. Spatial encoding can be carried out at a resolution far beyond the optical diffraction limit, since this method is only limited by the ability to electrically address individual silicon nanostructures. The motivation is that, in principle, individual SiNWs produced via SNAP method and separated by as few as 35 nm may be individually encoded. This would allow a construction of hundreds of electrical sensors in a $100 \mu\text{m}^2$ area for the purpose of parallel multiparameter analysis. However, the method is by no means limited to this application, and, in fact, could be easily extended to other Si-based micro- and nanodevices or even to other electrode materials. I address in some detail the ways to minimize electrochemical oxidation of silicon, either through controlling the molecular packing density or utilizing the electrodes with different crystal orientations. Finally, an alternative approach is presented, based on electrochemical reduction, which circumvents the electrochemical oxidation of silicon electrodes altogether.

In chapter five, I diverge from the applications of SiNWs to biosensing, and concentrate on the fundamentals of their thermoelectric properties. The motivation

behind this work is to create a highly efficient thermoelectric device out of nanostructured materials. SiNWs are chosen because of our extensive expertise in their fabrication, and because of all the advantages afforded by SNAP which are described in chapter one. Also, heavily doped semiconductor materials are the usual choice for thermoelectric applications because of their relatively high electrical conductivities and Seebeck coefficients and phonon-dominated thermal conductivities. Systematic analysis of the effects of size and doping on the figure of merit (ZT) of SiNWs is presented. Phonon transport can be markedly altered by one-dimensional confinement, leading to a precipitous drop in thermal conductivity of SiNWs compared to bulk silicon and a corresponding increase in the lifetimes of long-wavelength phonons. In addition, the electrical conductivity of NWs can be maintained at a relatively high level, with the bulk-like thermopower. These factors lead to a figure of merit which approaches 1.0 at room temperature and can be tuned across different temperatures. In addition, phonon drag is observed in heavily, but not degenerately, doped 20 nm wide NWs, leading to a significant increase in thermopower of these materials at temperature in the range of 150 K to 250 K. The highest ZT reported here, 1.2, was measured in 20 nm wide SiNWs at 200 K. This study, therefore, clearly demonstrates that the field of thermoelectrics is no longer limited by the discovery of new highly efficient and exotic materials. Instead, modified phonon transport properties which emerge from nanostructuring silicon, or, in principle, many other materials as well, lead to a dramatic enhancement of the thermoelectric figure of merit. ZT values above 3 may be possible in nanowires, which would make thermoelectrics competitive with conventional compressor-based refrigeration.