Nanostructured Semiconductors

Amorphization and Thermal Properties

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Nanostructured Semiconductors: Amorphization and Thermal Properties

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Dedicated to my parents

Anastasia and Christos

and in memory of Georgios Kanellis

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PART II

FABRICATION AND MEASUREMENT TECHNIQUES

Preface

This book is the result of a collective work of 42 authors through 19 chapters on nanostructures and nanostructured materials containing both amorphous and crystalline phases with a particular focus on their thermal properties. There are two distinct parts: The first combines theory and simulations methods with specific examples, and the second part discusses methods to fabricate nanomaterials with crystalline and amorphous phases and experimental techniques to measure the thermal conductivity of such materials.

Chapter 1 details the structural properties of the crystalline and the amorphous phases, highlighting their differences in the density, radial, and angular distribution functions, and analyzing the different amorphous models used in the literature. This chapter introduces and explains a lot of the terms used herein. In Chapter 2, a general theory for the lattice thermal conductivity is developed, for both crystals and disorder systems. This analysis is used for ab initio simulations of the thermal conductivity of bulk materials. The taxonomy of vibration modes in amorphous materials is fully detailed. In Chapter 3, the differences in thermal properties between bulk materials and nanostructures are discussed. The transition from ballistic to diffusive regimes and the underlying scattering processes occurring at the nanoscale are explained. Furthermore, in this chapter, there are sections dedicated to the phonon coherence effects, the phonon rectification, and the amorphous limit of the thermal conductivity. In Chapter 4, the importance of heat transport at the micro/nanoscale for several applications is treated for a wide range of domains such as electronics, bio-engineering, and energy harvesting. In Chapter 5, the Monte Carlo methodology to solve the Boltzmann transport equation is given, with case studies such as nanowires and nanomaterials. The latter methodology is the most adequate simulation method for micro/nanostructures with length scales greater than some tenths of nanometers.

For the prediction of the thermal properties in the ballistic regime, atomistic approaches are preferred. Chapters 6, 7, and 8 present three different molecular dynamics (MD) methodologies: equilibrium MD (EMD) in Chapter 6, non-equilibrium MD (NEMD) in Chapter 7, and the approach to equilibrium MD (AEMD) in Chapter 8. In Chapter 6, an introduction to MD is given and the EMD methodology based on the Green–Kubo formula is derived to estimate the thermal conductivity, thermal conductance, and resistance with an example: the thermal conductance of the argon/heavy argon interface. In Chapter 7, the NEMD methodology is described to calculate the thermal conductivity of nanomaterials and applied in two examples: superlattices and nanowires which incorporate both crystalline and amorphous phases. Striking results show that an amorphous fraction of only 20% in certain geometries of nanostructures is enough to obtain sub-amorphous thermal conductivity. In Chapter 8, the AEMD method is analyzed, which is the only method among the three MD methods appropriate to describe transient regimes. The thermal conductivities of amorphous silica and α-quartz thin films are calculated with this latter method. In Chapter 9, numerical methods to treat the vibrational properties of isolated crystalline and amorphous nanoparticles and nanoinclusions are analyzed: resonant modes analysis, vibrational density of states, and dynamical structural factors. The last chapter of the first part of the book is dedicated to the III-nitrides group and their structural properties and defects as extended defects, polar and non-polar interfaces, diffusion of defects, and surface reconstruction.

The second part of the book starts with Chapter 11, in which a deep analysis of the role of the heavy ion irradiation for the amorphization of porous silicon nanostructures is proposed. It explains why the heavy ion irradiation influences only porous materials while remains unaffected on the bulk ones. The quantification of the amorphous fraction as a function of the ion fluence is also given. The infrared absorbance and the Raman spectra are used to appraise the influence of different irradiation rates on porous silica. In Chapter 12, another crystalline/amorphous porous material is treated for germanium compounds, with a porosity induced by electrochemical etching. A review of the possible geometries of the pores is given. It is also explained how these geometries can be realized in the case of Ge by changing two key parameters during the electrochemical etching: the anodic current density and the hydrogen passivation degree. In Chapter 13, an experimental protocol to achieve amorphous/crystalline composites is described—more precisely, the methodology to obtain crystalline nanoinclusions embedded into an amorphous matrix. Starting from amorphous materials, the strategy is to interrupt the crystallization process before the crystallization peak is completed. Chapter 14 deals with the ball milling technique, which is used to amorphize and to nanocrystallize materials with or without chemical transformation. Pedagogic case studies are given for each category with explanations of each key parameter and their influence on the mechanical properties of the elaborated nanostructures. In Chapter 15, the tin-induced crystallization of amorphous silicon manufactured by physical vapor deposition and the possibility of the crystallization control during laser annealing are analyzed. These methods can advance the wide-scale commercialization of nanocrystalline silicon for the third and next generations of solar cells and other optoelectronic devices. Chapter 16 contains both the experimental methodology and simulation evidence for the crystallization of silicon nanoparticles utilizing magnetron sputtering. Two methods are proposed: first, the use of inert gas temperature control during magnetron sputtering, in which the inert gas pressure and composition are the key parameters to control the size distribution of the nanocrystals, and second, the use of silver atoms for the heterogeneous crystallization of silicon nanoparticles.

The last three chapters of the book—Chapter 17 (scanning thermal microscopy, SThM), Chapter 18 (thermal wave methods), and Chapter 19 (X-rays and neutron spectroscopy)—are focused on experimental methods for the measurement of thermal properties appropriate for structures that contains both crystalline and amorphous phases. In Chapter 17, a review of SThM in the active mode is given, which enables nanometer-scale heat flow measurements and materials' thermal characterization. Then, the approaches to modeling and calibrating SThM probes are explained and finally the method is used to measure the thermal conductivity of nanoporous silicon with amorphous shells around the pores. In Chapter 18, a review of experimental thermal wave methods is presented. With the ac-current ($2\omega/3\omega$) method, the thermal conductivity components of thin films (in-plane/cross-plane) can be estimated, using thin metallic layers acting as a heater and/or a thermometer. The photothermal gas-microphone technique uses light to generate a heat source while the measured pressure variations can be directly related to the thermal properties. The method is applied on a partially amorphous porous silicon. The last chapter also focuses on experimental techniques: inelastic neutron scattering and X-ray scattering to measure phonon velocities and lifetimes. The authors explain the measurement principles and the experimental limitations while in the second part of Chapter 19, the atomic dynamics differences of an amorphous and a crystalline system are detailed.

Foreword

Nanostructured Semiconductors: Amorphization and Thermal Properties aims to expose the reader to the state of the art in several areas of modern science of materials. The most prominent focus of this book is on theory and simulations of thermal conduction in all major types of materials microstructures, including bulk crystals, nanocrystalline and nanoporous materials, and fully amorphous materials. Chapters 2 to 9 provide a comprehensive description of all major theoretical and simulation methods used to understand, model, and predict thermal conduction characteristics of materials and their interfaces. What is of particular value in this book is the presentation of a number of topics from multiple perspectives. For example, the rigorous theoretical foundations of thermal conductivity formulas derived from the equilibrium-based, fluctuation-dissipation theory presented in Chapter 2 are complemented by structure/problem-specific perspectives presented in Chapter 3, the application of the theory to molecular dynamics simulations presented Chapter 6, and to the phonon-level description of thermal conduction based on the Boltzmann transport equation in Chapter 5. For molecular-level simulation practitioners, Chapters 7 and 8 provide an introduction to major non-equilibrium methods, i.e., methods employing macroscopic heat flux and temperature gradients and relying directly on Fourier's law of diffusive heat conduction. Chapter 9 completes the presentation of atomic-level modeling and calculation tools with a focus on direct phonon lifetime determination and vibrational analysis of complex, non-periodic systems. For those practicing or contemplating research in modeling and simulations of phonon-based thermal transport in complex structure materials, the first part of the book provides a one-stop store for all major state-of-the-art tools and concepts they need.

The second part of the book focuses on experimental synthesis, the processing and characterization of complex nanostructure, and porous and amorphous material and their composites. Amorphization via ion irradiation is the subject of Chapter 11, while electrochemical etching–based synthesis of similar materials is described in Chapter 12. The following three chapters focus on different processing methods such as annealing-based recrystallization, mechanical-based ball milling–induced nanostructuring and amorphization, and laser processing. Finally, Chapters 17 and 18 introduce modern techniques for thermal transport characterization, allowing for the completion of a concept of structure—thermal property relationship determination with the synergistic approach based on theory, modeling, simulations, and experiments as described comprehensively throughout this book.

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