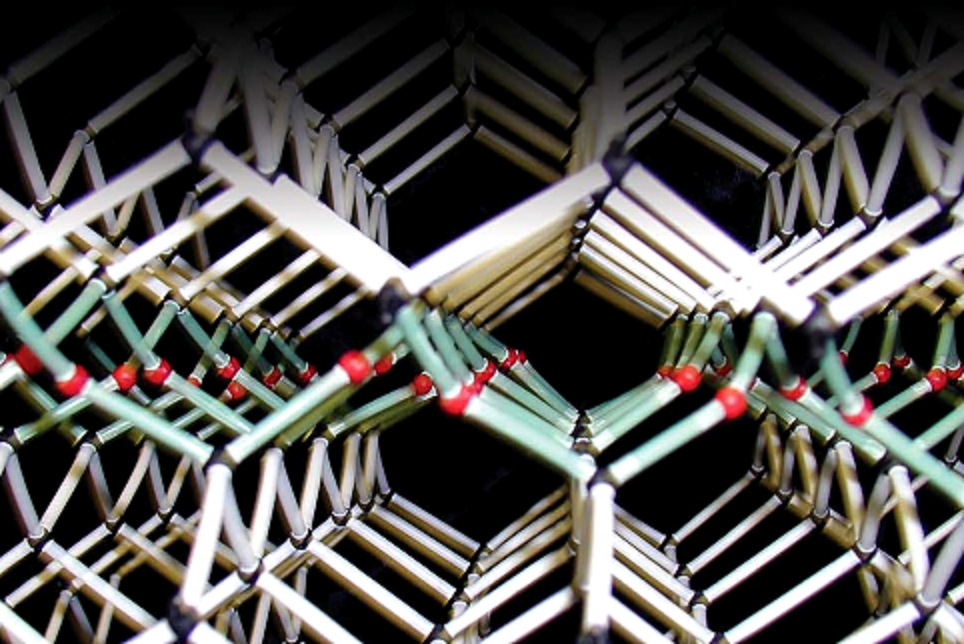




Superlattice to Nanoelectronics

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Preface

More than 30 years ago Leo Esaki and I realized that although there were many semiconductor and solid state materials, only a few achieved wide usage. For example, silicon is overwhelmingly used in electronics, III–V compounds are used in injection lasers and light emitting diodes (LEDs) and niobates are used in nonlinear optoelectronics. We introduced man-made superlattices using periodic heterostructures to mimic solids. The first few years were tough. The first superlattice constructed from GaAs/GaPAs seemed structurally sound, but it did not have the predicted negative differential conductance (NDC). These superlattices were merely metallurgical, without sufficient mean free path to exhibit quantum effects. Among the various quantum effects we identified, a few were clearly due to quantum phase coherence: mini-energy bands, tailor-made optical transitions, and in particular, Bloch oscillation of the electrons driven by the applied electric field reaching the mini-Brillouin zone boundary. Whenever $\omega_B \tau > 1$, with ω_B being the Bloch frequency, current decreases with increase in voltage and NDC appears. During this initial stage, IBM management gave us token backing, but the US Army Research Office soon furnished us with partial support.

After the first experimental verification of NDC in a GaAs/GaAlAs superlattice, Gunn pointed out that the observed NDC may be due to domain oscillation, a nonquantum mechanical effect. To eliminate this possibility, 2 years later we introduced the resonant tunneling diode (RTD), a “superlattice” consisting of a single quantum well. Ten years after that, terahertz RTDs were realized and the age of man-made quantum structures had arrived. In 1996, Robert Lontz, who directed the Physics-Electronic Division of the US Army Research Office during the initial 5 years of the superlattice development, was asked by Mikael Ciften, Head of the Physics Division at ARO during 1996/1997, to put together a document, “The Superlattice Story”. This document was distributed to many agencies, including the White House, to promote awareness and to stimulate the direction of research in electronics in the general areas known as nanoscience. With this as a backdrop, this book has been written not only as a guide to how ideas are perceived and developed, but also to provide some details of the concepts, theories, experiments and physical models of this rather complex subject.

About half of the topics covered in this book have been taken from publications in which I was involved. The reasons why certain assumptions were made and certain approaches were taken has been left out of many published works but are fully discussed in this book. Among the topics covered here, I have devoted considerable space to the semiconductor–atomic superlattice, which consists of a monolayer of atoms sandwiched between two semiconductors forming a superlattice. This is an extreme extension of the strained-layer superlattice like the Si/SiGe heterojunction structures. Moving into the area

of quantum dots (QDs), resonant tunneling via 3 nm particles of crystalline silicon embedded in SiO₂ captivated Nicollian and myself for more than 3 years. The positive side is that the observation of stepwise conductance always seems to involve multiples of $G_0 = e^2/h$, being $\sim 40 \mu\text{S}$, typically 40, 120, 240 μS . The negative side is the occurrence of hysteresis and oscillations, sometimes with frequencies of $\sim 0.1 \text{ Hz}$ to $> 10 \text{ MHz}$. I am convinced that the source of this instability is trapping, magnified by the very large coupling between the QD states and trapping sites. The interesting thing is that the defects do not even need to be inside the QD. A disappointing discovery is that QDs have much lower dielectric constants, resulting in a much higher binding energy of dopants. Simply put, QDs cannot be doped and therefore they are mostly intrinsic. Instability of RTDs, attributed to space charge effects, and G_0 attributed to contacts are basically clarified in this book. Instability is due to coupling of the quantum well states with an unintended quantum well produced in the buffer spacer of the RTDs, and G_0 comes from the wave impedance of electrons.

The brighter side of work with QDs is the fact that some of these CdSe-, PbS-, QDs are truly unique in the sense that they are relatively stable and somewhat self-passivated. Incorporating these nanodots into a matrix such as porous silicon and solgel may lead to widespread usage. However, no one has the vaguest idea of the electrical input/output (I/O) for QDs. This book does not cover some bench-top results, such as the single electron and molecular transistors that utilize QDs. In fact it does not even cover some of the latest RTDs and the latest uses of superlattices like the quantum cascade laser (QCL). Early in my career, I did not think magnetic properties played a major role in electronic devices. Therefore, quantum devices with magnetic properties, including Aharonov–Bohm effects, quantum hall effects and magnetic superlattices have been excluded. However this book does prepare the reader for a proper mindset, i.e. how to pursue an idea and develop it. Today there is an obvious problem with funding for the pursuance of new ideas. The simple fact is that the development of an idea takes huge resources.

Lastly, I want to give some indication of what sort of technical background is required of the reader. Naturally, one needs some working knowledge of basic mathematics such as complex variables, partial differential equations and some skill in computer programming, the kind taught in any graduate program for physical scientists and engineers. Intermediate to advanced courses in electromagnetics, quantum mechanics, solid state and semiconductor physics are necessary to understand and appreciate many concepts presented in this book. However, the reader does not need to read this book from the first page to the last. For example, when I first started my career, my all time savior was Morse and Feshbach's two volumes. However, this book requires the reader to have a generally rigorous mindset rather than being overly concerned with detail. In short, almost anyone with graduate school training can work through any part of this book. Obviously one may ask whether this book can be used for a graduate level course. Well, I used parts of this book in my course on advanced semiconductors.

Before I close I want to give couple of observations and experiences about this period of my career. I was fairly sure about the man-made superlattice at the very beginning because I had just read Pippard's 1965 book. In fact, he discussed the possibility of Bloch oscillation being totally unobservable in real solids! Being now over 70 years old, I can say to younger people that one should not rely too much on books because what is most intriguing is most likely not in any book. And do not be intimidated by highly complex theories because in most cases, there are simpler ways to arrive at a version that is sufficient to understand a complex system. I would like to take this opportunity to give my views about how sad the world is now for we technologists. When I started my career at Bell Telephone Laboratories (BTL), now a part of Lucent Technologies, 950 PhDs were attributed that year. Young men of many disciplines worked together. The cross-disciplinary interchange of ideas really breaks down the boundaries between people trained in different areas. Because we were young, we were capable of learning "new tricks" thoroughly and efficiently. One may say that the same thing exists in universities today. I have been long enough in the university environment to tell you that universities are not as open as one imagines. The typical syndromes: I am engineer who makes things work; I am physicist who makes point understandable; I am biologist to tell you who we are, and so on, are very much a part of the tradition except perhaps in some of the "great" universities. The reader of this book will soon recognize that the subject crosses into a number of disciplines, although mostly within the physical, mathematical, engineering fields, as well as chemistry and material science. To my mind crystallography and group theory are very difficult subjects. Fortunately, most of us do not involve ourselves with highly complex structures, neither do we get involved with the group representations of these structures. The bottom line is to learn enough to get the job done.

I thank Jennifer and Jamie Stewart for helping me in the preparation of this manuscript. Leo Esaki has always been my friend and my teacher. He believed in me. When he took me on he told me that he had checked with a few people at Bell Laboratories about me and what prompted him to hire me was a comment that was made, "Ray likes to do theory, but he also likes experiments. But do not get him involved with too complicated experiments". He confided in me that he himself did not like very complicated experiments. I am especially grateful to my wife, Danusia, who truly suffered from my remarks "Don't talk to me because every time you do, you set my thoughts back ten minutes". Thanks to her support, this remark has turned into the family joke and made writing this book a pleasant experience. *With these remarks, I dedicate this book to my wife Danusia and to Leo Esaki.*

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Introduction

This book follows the development of superlattices and quantum wells from their inception in 1969. My role paused after 1977, and I re-entered the field in 1984 after 7 years devoted to laser annealing and amorphous silicon. During the initial period, I was involved with most phases beginning with the creation of man-made superlattices with Esaki, later joined by Chang and followed by efforts to characterize the materials, structures and properties, branching into resonant tunneling, optical response, Raman scattering and type II superlattices. The theoretical results that helped to launch the endeavor came from a few things we learned from a published book by Pippard.

The reason we became involved in Raman scattering was because we used it to characterize alloy compositions and structures. Besides I always have had a fascination with Raman scattering, partially because it was a personal challenge to master a subject which I considered to be very complex, which needed a working knowledge of group theory. It was not apparent when we were tackling the theory of resonant tunneling that we needed to introduce a new method of tunneling calculation. This is mainly because methods of calculating tunneling, such as the Bardeen's transfer Hamiltonian and the Wentzel-Kramers-Brillouin (WKB) approximation, subjects covered in detail by Duke, simply could not work. In retrospect, it was the use of a computer that provided us with a handle on resonant tunneling through a double barrier structure.

In 1984, I went to Brazil for an extended stay. Ioriatti and I started calculating the dielectric constant and doping of a superlattice. During this period, I reopened some old data and computations using a complex k -vector which were replaced by a formulation with Green's function with a finite self energy function, usually denoted by Σ , with $\Sigma \neq 0$. The usual way of summing the diagrams is nothing more than a perturbation calculation, only that perturbation may be carried to infinite order. My view was, let us tackle the "holy cow" instead, by assuming the Hamiltonian of an open system to be non-Hermitian, allowing a simple way of accounting for losses and their effects on the resonant state. Basically, we gave up pretending that there is an eigenstate. The $\text{Im } G$ gives us the local spectral density and that is all we need. In fact Sir Mott took a fairly receptive view towards my contention, after I pointed out to him that some parameters are directly measurable, such as the mobility or the scattering time. This simple theory does not single out the details of scattering such as from impurities, phonons, deformations, and so on. Nevertheless they are not parameters that fit; rather, they represent a quantity such as the mobility of electrons in the quantum well.

After I joined the University of North Carolina at Charlotte in 1988, Zypman became my first postdoctoral fellow. We calculated the surface states of GaP on GaAs without fitting parameters, and the results we obtained are applicable to the Si-O superlattice.

Babic and I started a series of calculations on capacitance, doping and exciton of a quantum dot. My interest clearly moved into quantum dots, a subject very much in fashion today. The main finding was rather surprising. It is obvious that the dielectric screening should go down because as the electron becomes more and more confined, it cannot even move so how can it screen? During this initial phase of the theory, I called Ioriatti on the phone and asked him point blank whether the Kramers–Kronig’s (the “holy cow”) relation should be taken as gospel. He told me that K–K relation applies when $\varepsilon(r, r'; t, t') = \varepsilon(r - r'; t - t')$; quantum dots do not satisfy this assumption. I invited him to spend 3 months with me because I needed someone who was not bound by tradition. My original paper on the size-dependent dielectric constant was delayed for 3 years before it finally appeared in print. This story has a happy ending because today size-dependent dielectric function, perhaps more appropriately called size-dependent response function, is well accepted.

The reader should refer to Chapter 8 which contains additional discussions regarding capacitance and doping. The traditional dielectric function is global; however, the size-dependent dielectric function, like any response function is local. However, I would like to say a few words about the classical calculation of the capacitance. We learn in elementary electricity and magnetism (E&M) that the capacitance of a sphere may be simply calculated with two lines using the Gauss law. This is so if we assume electronic charges may be infinitesimally divisible. A purely electrostatic calculation with discrete electronic charges is quite involved. In fact it takes more computation time than a quantum mechanical calculation, because in the latter calculation one does not need to specify the position of the electrons, simply calculating the energy difference between a He-like atom and hydrogen atom, or a Li-like atom and the He-like atom, etc. With classical calculation, one is required to find the minimum energy for n electron positions in a three-dimensional way inside a sphere, involving the age-old Platonic geometry. I have two graduate students doing this calculation at this moment. The results are very interesting. Who ever thought that a 100-year-old problem would resurface to research status? It is this type of discussion throughout this book that hopefully readers may find worthwhile. Also throughout this book, detailed accounts are devoted in each subject to how the ideas were first conceived and in what circumstances, and the means to develop those ideas. I must say that often nothing new came into our minds whenever we were feeling rather inventive. On the contrary, new ideas in which I was involved invariably came about because something or someone provided a trigger.

I want to mention something about the work done on silicon quantum dots with Nicollian and our postdoctoral fellow Q-Y. Ye who came to us from F. Koch in Germany. It was because of her willingness “secretly” to disagree with us that progress was made at the beginning. When we first obtained results in 1990 on conductance steps, they were numerous and had variable steps instead of equally spaced jumps in conductance. We were having a hard time having the work published. Today, I can state with some certainty, that

most of our (or my) work that had problems being accepted then for publication turned out to be well cited later. I have been praised by the reviewer on several occasions upon acceptance, but the work turned out to be poorly cited by others. So again, I take this opportunity to urge you not to despair when your manuscript is brutally rejected.

I was one of the first to get involved when visible light emission in porous silicon was reported. I was able to get started quickly while working mainly with J. Harvey at the US Army Research Laboratory (called ETDL in 1990), because there were plenty of human and material resources. We have determined experimentally that quantum confinement at least contributed to pushing up the emission, and the refractive index reduction is greater than could be explained by porosity alone. In this book, I have clearly accepted the dual role of quantum confinement and surface complexes. It is a good example why well qualified groups disagree and usually both are right.

Quantum conductance, explained in terms of an input conductance to a quantum system such as a quantum wire with a wave conductance, in my view, has a more general role than contact conductance. The discussion centered on the difference between an open and closed system has deeper conceptual meaning. It may become quite important if phase coherent electronic devices become more widely used in the future.

Forty years ago I was able to read a book quickly and retain a good part of what I read. Unfortunately I cannot quite do the same now. I do urge younger researchers to take every advantage of being young, energetic and having an inquisitive mind. The old song, *Anything you can do I can do better*, should be a motto for us all. Lastly, every book has some good passages, but we must realize that we cannot find all the answers in one book. The thing to do is to read one and then another, until you find one that has some of the details you are looking for. Then, spend all the time necessary to absorb it all. Even though I have taken care to eliminate any mistakes in this book, I apologize for any that do remain. Below is a partial list of the books that I found useful in preparing this book.

Good luck and best wishes.

Raphael Tsu, Charlotte NC 2004

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