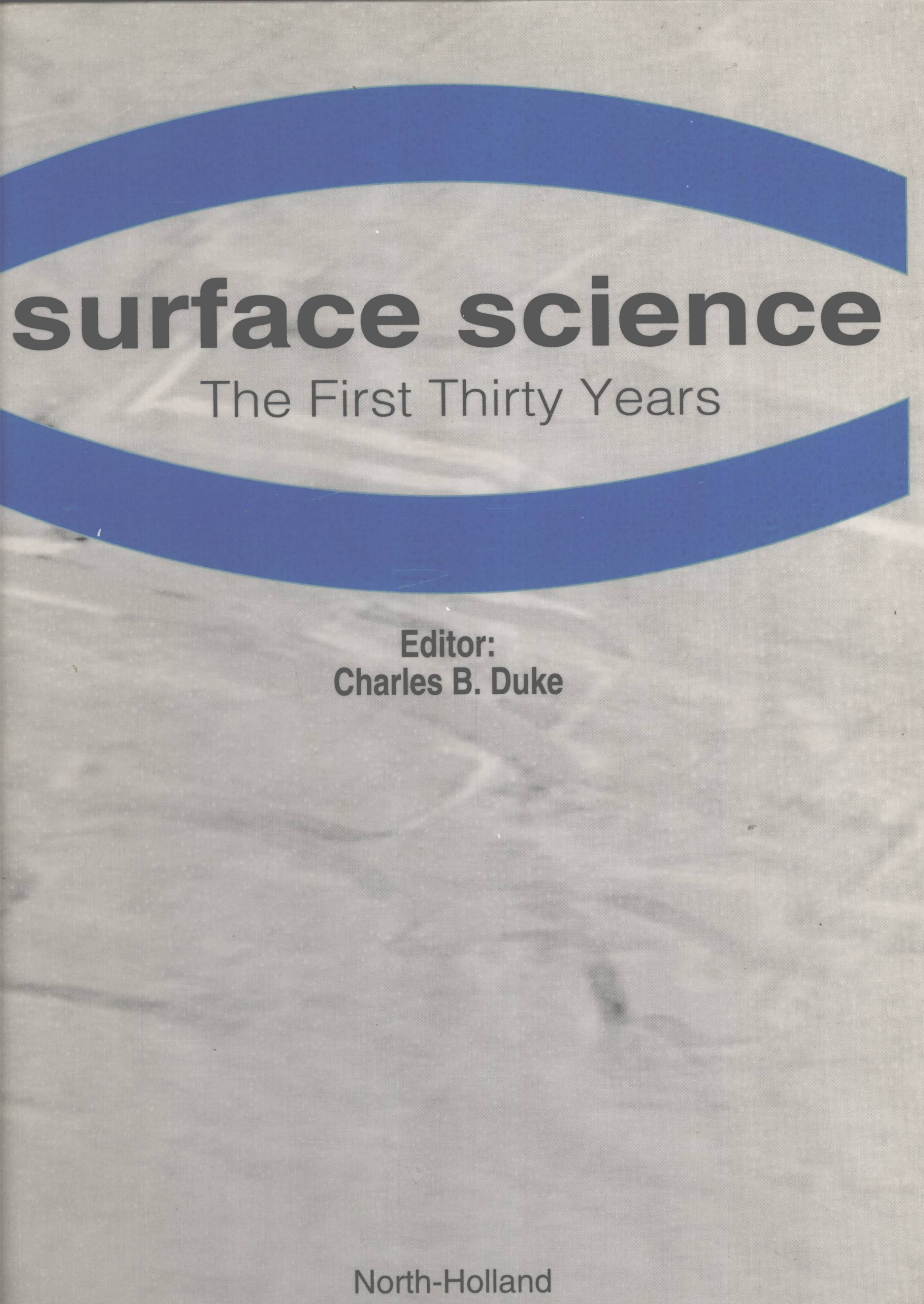

surface science

The First Thirty Years

Editor:
Charles B. Duke

North-Holland

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Editor:
Charles B. Duke
Webster, NY

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Editor's Foreword

Surface Science: The First Thirty Years

This volume is a collection of short articles describing the historical development of selected topics in surface science during the formative years of this field, i.e., 1963–92. It was assembled under the guidance of the Advisory Editorial Board of *Surface Science* for four purposes: to provide a personalized historical record of the first thirty years of surface science as seen by active researchers who founded and developed the field; to serve as an indication of the realized and prospective value of the field for the betterment of the human condition; to commemorate the thirtieth anniversary of the founding of the journal *Surface Science*; and to honor Harry Gatos for his founding and nurturing of this journal during its first twenty eight years of existence.

The period 1963–92 was the scene of astonishing advances in the ability to characterize surfaces and study surface phenomena: truly the "birth" of surface science as a field of endeavor [1,2]. At the beginning of this period one could not determine any important characteristics of a surface, e.g., the chemical identity of surface species, their atomic geometries, the dynamics of their motions, or the nature and consequences of the surface electronic charge distributions. By 1992 all of these quantities were being determined routinely in surface science experiments. Moreover, dynamic measurements of atomic positions were being used routinely to study surface diffusion, film growth, and surface chemical reactions. In addition, the scientific results obtained from such studies were being utilized for the engineering of new materials and processes, as described, for example, in the articles herein in the section on Applications of Surface Science. Thus, the fruits of surface science research are impacting commercially important industrial problems, for example, the fabrication of microelectronics and the design of catalysts. Not only has a scientific revolution in the sense of Thomas Kuhn [3] occurred, but a technological revolution as well, which is inducing profound effects on such economically vital industries as computers and communications. This volume is the story of the key ingredients in these revolutions as told by the players who "made them happen".

The articles in this volume are written for a technically literate but non-specialist audience. Considerable effort has been invested in rendering them interesting and comprehendable to those familiar with science in general but not surface science in particular, e.g., historians and students. If you, gentle reader, have trouble with one, skip it and try another. Some of these articles are really gems. Others, well, each author was presented with the opportunity to capture your interest and attention. You are the judge of how well or poorly each succeeded. This is designed to be a fun book to browse just to glean an impression of what surface science is all about and to observe the foibles as well as accomplishments of its practitioners. Read accounts from their own hands. Read them at bedtime, on an airplane, at the beach, at your leisure,... enjoy.

The table of contents and authors were selected by concensus of the Advisory Editorial Board during the first few months of 1992; invitations were issued in April; and the volume was closed in May 1993. It is designed to encompass the full scope of the field of surface science: its foundations, major teachings, applications and current frontiers. Articles are grouped within these broad categories in such a fashion that the intellectual structure of the field should be self-evident from the table of contents.

Authors were invited to contribute to this volume based on the Advisory Editorial Board's assessment of their contributions to surface science over the years, their demonstrated ability to write interesting and lucid papers, and their personal involvements with the development of the topical areas to be covered in the volume. An amazing 80% of those invited actually contributed an article which appears in this volume. Therefore the volume represents a comprehensive collection of personalized technical histories by individuals whom the Advisory Editorial Board deemed to be leaders in developing the topical areas about which they write.

The styles of the individual articles vary widely, from personal reminiscences to compact technical reviews of the major events which define the scope and impact of the topic covered. The editor was tolerant of a wide variety of styles, provided the perspective of the writer was clearly specified in the introductory material of the article. Considerably less tolerance was exhibited for inadequate presentation and excessive length. All of the articles were reviewed by one or more members of the Advisory Editorial Board, most were revised in response to these reviews, and a few were recast completely in order to accommodate the style and/or length restrictions of this special volume. Authors were, however, encouraged to tell their stories from an entirely personal perspective without regard to whether or not the reviewers agreed that these stories reflected objective reality with regard to the topic covered. Thus, the reader will occasionally find side by side two accounts of a topic which are mutually exclusive in that neither article even mentions the work and events described in the other. Such is the nature of all human endeavor: each of us constructs his or her own personal interpretation of events within the context of which we make sense out of the happenings around us. The editor's goal in assembling the historical reviews in this volume was to render these personal value systems explicit, not to suppress them under the guise of objectivity.

Harry Gatos, the founder of the journal and one of the founders of the field, is the author of the first article. In it he describes his personal world view of the origins of the field and his group's contributions to it. I cannot envisage a more fitting testimonial to his contributions in a volume dedicated to commemorating the thirtieth anniversary of his founding of *Surface Science* and his twenty eight years as editor thereof. The Advisory Editorial Board and I are thrilled that Harry was willing to prepare this contribution to the anniversary volume. We acknowledge our debt to Harry, both personally and professionally, for his stewardship of the journal during its first twenty eight years. We wish him the very best on this happy occassion, and would like to express to him our collective "thank you" on behalf of the thousands of regular readers, contributors, and referees of *Surface Science*.

And so, on to *Surface Science: The First Thirty Years*: the story of a scientific and technological revolution which is changing the world as we know it, transforming a planet into a global village.

Charles B. Duke, Editor
Webster, New York, August 27, 1993

[1] C.B. Duke, J. Vac. Sci. Technol. A 2 (1984) 139.
[2] C.B. Duke, J. Vac. Sci. Technol. B 11 (1993) 1336.
[3] Thomas S. Kuhn, The Structure of Scientific Revolutions (University of Chicago Press, Chicago, 1962).

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surface science

Semiconductor electronics and the birth of the modern science of surfaces

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Semiconductor surfaces were the launching platform for the solid state electronic revolution. The brilliant concept of surface states led directly to the discovery of the transistor in 1947. The chemical instability of the Ge surfaces, however, rendered the new devices irreproducible and unstable. This threat to the viability of semiconductor electronics, precipitated an international search, of a magnitude unparalleled in the history of science and technology, directed at the understanding and controlling of semiconductor surfaces. The roots of all of today's powerful experimental tools, techniques, procedures and fundamental concepts at the disposal of surface science and engineering can be traced to that gigantic effort on the study of semiconductor surfaces. Clearly, solid state electronics, born and nurtured on semiconductor surfaces, gave, in turn, birth to the modern science of all surfaces. In this article, I attempt to convey a general impression of the mutually constructive interplay between the evolution of solid state electronics on the one hand and surface science and engineering on the other. I take this opportunity to highlight my own experiences and research involvement with semiconductor surfaces.

1. General introductory remarks

The importance of surfaces in the applications of solids has been recognized ever since man put solids into use. However, as late as in the early years of the transistor, surface technologies and their understanding rested primarily on empiricism and phenomenological models. This situation prevailed even in the light of the fact that surface phenomena bear directly on all facets of technology and all aspects of our daily life. There were immense problems to be overcome before meaningful insight into the fundamentals of the surfaces of crystalline solids could be realized. No motives commensurate with the magnitude of such problems emerged that could amass the necessary driving force to tackle them head on. I will review how solid state electronics generated such motives.

Solid surfaces constitute an abrupt termination of the periodicity of the crystalline lattice; they are essentially giant lattice defects. Consequently, they could not be submitted to the theoretical treatments which assume crystalline periodicity. Appropriate theoretical treatments, taking into consideration such an abrupt termination and the relevant energetics, presented complexities beyond the reaches of intellectual curiosity.

Fundamental experimental approaches simply did not exist in the 40s. Good vacuum systems reached down to 10^{-6} mm Hg and under special circumstances 10^{-8} mm Hg became possible. In the late 40s, I was very proud of my vacuum system which would consistently achieve pressures below 10^{-6} mm Hg. Thus, "clean" surfaces by today's standards could not be realized. All surface studies were just carried out on contaminated surfaces. Beyond the uncertainties in chemical composition, the actual structure of solid surfaces could not be probed with the available approaches and techniques.

These remarks should not, of course, be taken as a general condemnation of all surface studies carried out on "real" surfaces. Numerous such

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studies of the pre- as well as of the post-transistor eras have been very informative and have yielded very useful results. Actually, real surfaces can lead to meaningful studies and useful results, provided some key criteria are met: real surfaces need to be reproducibly prepared and sensitive to changes of the parameters pertinent to the phenomena under study.

2. The very beginning

In the middle 40s the Bell Telephone Laboratories engaged a group of scientists, under the leadership of Bill Shockley, to carry out research on semiconductors [1] with the ultimate goal the development of a solid state amplifier. Walter Brattain, a member of the group, set out to optimize the rectification characteristics of semiconductor–metal diodes (maximize the potential barrier in the semiconductor side of the contact) using Ge. According to the well accepted theory of Schottky, the magnitude of this potential barrier is equal to the difference in work function between the metal and the semiconductor. Walter Brattain, however, came to an impasse: no matter what metal he brought in contact with Ge, the potential barrier did not vary. John Bardeen, a theoretical physicist in the group, was confronted with this inconsistency. He came up with a brilliant idea, a stroke of genius, to account for the inconsistency: he reasoned that, on the surface of Ge, there are energy levels (surface states) within the forbidden energy gap. These states trap majority carriers and lead to the creation of a potential barrier (space charge region) which can extend some microns into the semiconductor (Fig. 1) [2]. This barrier is unrelated to the contacting metal and, thus, it is not affected by it. With that concept in mind, within a very short period of time, perhaps the greatest invention in the history of science was made: the invention of a solid state amplifier i.e., the transistor [3]. The original transistor was based on the appropriate bias of the newly conceived potential surface barrier by two, very closely spaced, metal point contacts (point contact or type-A transistor).

3. Surface states

With the discovery of the transistor, the surface states were catapulted to real prominence. Now, William Shockley's turn came to display his brilliant mind. He devised the field effect experiment, an approach with which not only the presence of surface states can be demonstrated but also their energy position in the energy gap and their density on the semiconductor surface can be quantitatively determined [4]. By monitoring the surface conductance of a thin Ge slab, as a function of applied field in a parallel plate capacitor configuration, it became possible to determine the number of carriers trapped in the space charge region and, thus, the density of surface states. It should be noted here that the field effect experiment, the p–n junction [5] and the concept of the field effect transistor [6] were some of the early major contributions made by William Shockley.

The origin of surface states was phenomenologically attributed to the unsaturated bonds (unpaired electrons) of the surface atoms resulting from the termination of the lattice at the surface. Actually, such an origin was corroborated by the experimentally determined surface state densities on Ge surfaces. These values (on real surfaces) were within 2 to 3 orders of magnitude from the densities of surface atoms [7]. Each surface atom

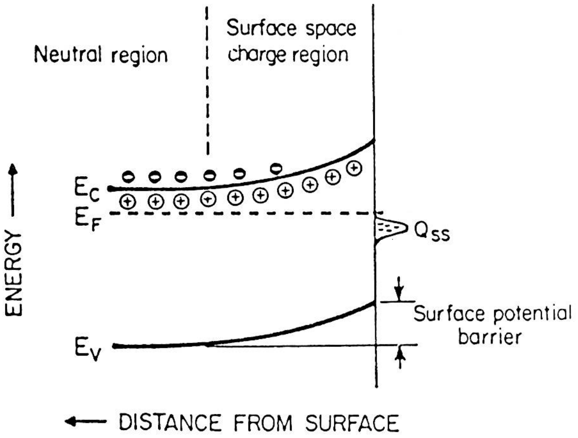

Fig. 1. Surface potential barrier resulting from the capture of electrons by the surface state (Q_{ss}). E_c and E_v is the electron energy at the bottom of the conduction band and the top of the valence band, respectively; E_F is the Fermi energy.

with an unpaired electron is a potential electron trap or a surface state. Thus, the concepts of dangling electrons and dangling bonds were formulated and, as I discuss later, they proved to be extremely useful in pursuing the study of semiconductor surfaces and semiconductor defects in general.

Intellectually at first, surface states raised numerous key questions and certainly challenges. Here are some: how are surface states affected by physical adsorption, chemisorption or oxide formation? Do adsorbed, chemisorbed species or oxide films introduce surface or interface states of their own? What is the configuration of the space charge resulting from the surface states? What are the effects of dopant impurities? What are the effects of surface stresses and/or surface deformation?

Extensive researches were undertaken to address these types of questions. By and large, however, they led to irreproducible and conflicting results. All kinds of surface states were found which exhibited various rates of charging and discharging and had various positions within the forbidden energy gap.

Three fundamental reasons were responsible for this confusing situation. First, the growth of Ge single crystals was in its embryonic stages. Thus, the defect densities were very high. For example, millions and often billions of dislocations intercepted every square centimeter of the surfaces (today's Si and Ge crystals are dislocation-free). Secondly, the crystals contained relatively large amounts of background impurities (several orders of magnitude larger than today's crystals do). Thirdly, the surfaces used in experimentation could not be characterized and assessed on an atomic scale, a process which turned out to be an essential prerequisite in some of these types of studies.

Perhaps the most critical problem was the fact that neither defect densities nor chemical composition (purity) could be reproduced from crystal to crystal within the same laboratory, not to mention the discrepancies found from one laboratory to another. To these problems we must add the uncertainties associated with the reproducibility of the surfaces under study. It is no wonder then that, in some instances, in the early years, each major laboratory had its own family of surface states and expounded its own phenomenological theories. One can say that, in general, new results on semiconductors represented the characteristics of the individual crystal employed rather than fundamental truths. Unfortunately, this type of a situation is reencountered with the introduction of every new compound semiconductor. The reliable growth of single crystals of compound semiconductors presents immensely more complex chemical and structural problems than that of elemental semiconductors [8].

4. The transformation from the vacuum tube to solid state electronics

Before proceeding with developments in the science and engineering of surfaces, I consider it useful to comment on the nature of the vacuum tube to solid state electronics transformation, on some of its characteristics and the novel interplay among the classical and engineering disciplines precipitated by this transformation.

The transformation from the vacuum tube to solid state electronics cannot be referred to as an improvement or a change. Going from the vacuum tube to the silicon chip, which can contain many millions of vacuum-tube-equivalent devices, cannot be called an improvement. The first advanced vacuum tube computer the ENIAC, built in the 40s in Philadelphia, had 18000 vacuum tubes, 70000 resistors, 10000 capacitors, 6000 switches and a maze of connecting wires [9]. It was one hundred feet long, ten feet high and three feet deep. It weighed thirty tons. The temperature in the room soared to 120 F. Tube replacing teams searched the machine for burned out tubes. It is alleged that the lights of the city of Philadelphia dimmed when ENIAC was turned on. What ENIAC did then, a hand-held computer does much better today! A hand-held computer cannot be referred to as an improvement of ENIAC.

The transformation to solid state electronics constituted a birth of a new and different era for science and technology. The birth took place in

1947, the first infant steps were taken in the early 50s. From there on, there has been an explosive growth carrying with it motives with unprecedented powers for tackling head-on problems considered, only a few years earlier, beyond the scope and/or the capabilities of science and technology.

Let us look first at the heart of the transformation. Vacuum tube electronics is based on the generation and control of electrons in vacuum. In transistor electronics the current carriers (electrons or holes) originate in the atoms within the solid and their characteristics depend on the atomic scale structure and composition of the solid.

It is instructive to go back to about 1950. The understanding of the conduction of carriers in semiconductors and their manipulation to achieve device functions were at a respectably high level even by today's standards. In fact, the book by William Shockley, "Electrons and Holes in Semiconductors", a classic in that field, was published in 1950 [10].

What about the state of suitable materials to fabricate working semiconductor devices at that time? For all practical purposes such materials did not exist. Germanium single crystals with reproducible characteristics were necessary (Ge was then the key semiconductor). Technology for single crystal growth from the melt was hardly in existence. Starting materials were needed with background impurities less than a few parts per billion; that meant many orders of magnitude beyond the prevailing limits. No crystalline defects, planar, line or point, should be present. At that time, these requirements were just fantasies; and so was the realization of devices which were being conceived and even patented. Some of these theoretically conceived devices were fabricated many years later (as suitable materials and processes were developed) and were proven to be valid and valuable.

I quote from the book "The New Alchemist" by Dirk Hanson, a journalist, reporting on this period of the early 50s [9]. He states: "At first the financial arguments of sticking with the vacuum tube were persuasive and tube engineers could readily temper the enthusiasm of the solid state people with the weight of experience. Maybe the transistor was not going to be such a big thing after all. The early fuss died down. For one thing, the manufacturing methods were completely ad hoc and seat-of-the-pants. Controlling electricity by rearranging the atoms was nice practice in theory but not quite so awe-inspiring when it came to the production line, where almost anything could go wrong and frequently did. It was like trying to do surgery on the head of a pin. It was wondrous that transistors worked at all, and quite often they did not. Those that did varied widely in performance, and it was some times easier to test them after production and, on that basis, find out what kind of electronic component they had turned out to be. If they failed it could have been due to any number of undesirable impurities that had sneaked into the doping process. It was as if the Ford Motor Company was running a production line so uncontrollable that it had to test the finished product to find out if it was a truck, a convertible or a sedan".

5. Surfaces on the front line

Actually, the situation was worse than that described in the above quotation. The electronic characteristics of the devices that tested well after fabrication, did not remain constant with time. A fraction of them, presumed to live forever, died within months. For a while, in the early 50s, it appeared that semiconductor electronics was heading for an early crash. The embryo of our transformation, rather than grow, was being consumed.

The cause of the instability of the p–n junction devices was found to be chemical changes of the Ge surfaces leading to changes in surface conductivity. These changes caused conduction between the p- and n-type surfaces which degraded the n–p junctions and eventually caused shorting and failure. Thus, in addition to the acute problems of the semiconductor bulk, even more acute problems emerged associated with surfaces [11].

Fortunately, it was realized by a handful of industrial organizations that solid state technology had no learned disciples and that no single existing technical discipline could accommodate it. They decided to go forward from ground zero, building on intimate interactions among the classical disciplines.

Bell Telephone Laboratories (BTL) was the world's most advanced center. The point contact, the p–n junction and the field effect transistors were discovered there. There, also, single crystals had begun to be grown from the melt [12] and purification breakthroughs (such as zone refining) were taking place [13]. In parallel, extensive studies were initiated on the preparation of clean and reproducible surfaces and on their electrical characteristics, chemical properties and structure. Following the lead of BTL, traditional disciplines were merging and joining forces in other semiconductor research centers in this country (in the 50s). Among such centers were the industrial research laboratories of General Electric, IBM, Raytheon, RCA, Texas Instruments and Westinghouse. In Europe the research laboratory of Philips followed.

Merging of the classical disciplines was not particularly smooth nor effective from the start. Communication was not at a very high level because of "technical language problems", basic training and discipline tradition. It was not uncommon to encounter physicists developing advanced measurement techniques, only to apply them on chemically very poorly prepared and assessed samples. Conversely, chemists did engage in carrying out primitive physical measurements on chemically, state of art samples.

The pressure was immense, however, to develop materials, processes and structures to bring to life phenomena and devices already theoretically conceived and even patented. Key electronic characteristics (of the bulk and of the surfaces) needed to be related quantitatively to structural and/or compositional parameters. Thus, it is easy to see that aspects of physics, chemistry, metallurgy, chemical engineering, electrical engineering and possibly other disciplines were needed to enter this undertaking and to function in an interactive mode. From such new polygamous relationships among all these disciplines, inevitably a new offspring began to take shape: materials science and engineering. One can certainly state that surface science and engineering is a very close relative to that offspring, if not its twin.

6. The early days: an overview

In view of the critical role of the surfaces in device fabrication and device performance, the pressure was ever rising to understand and control their chemical as well as their electrical behavior. It was very clear indeed that for successful solutions the pay off was enormous. Accordingly, in the 50s and particularly in the first part of the decade, the major emphasis in nearly all semiconductor research centers was on semiconductor surfaces.

In parallel to the intensive fundamental studies, the engineering aspects of surfaces were being studied, including cutting, polishing, etching, oxidation and crystallographic orientation effects. These types of investigations were essential for the ongoing development and fabrication of devices.

Along fundamental lines and for the longer range, it was universally realized that an indispensable prerequisite for meaningfully pursuing the basic understanding of the structural, chemical and electrical properties of surfaces was the availability of atomically "clean" surfaces to begin with. The direction was clear: development of ultrahigh vacuum environments (with pressures 2 to 3 orders of magnitude lower than those then attainable) and in situ surface fabrication technology. These environments should permit removing any oxide or thin films present on the surfaces, cleaving single crystals to expose "virgin" surfaces, carrying out electrical and structural measurements and the introduction of controlled atmospheres. Only a few years earlier, such goals would have been dismissed outright (as apparently they had been) as figments of the imagination.

The above goals were essentially achieved in the middle 50s by Harry Farnsworth and his group at Brown University [14] and by the BTL group [15]. The "cleanliness" of the surfaces was assessed by low energy electron diffraction (LEED). No diffraction of the surface structure could be obained even if a fraction of a monolayer of a contaminent was present. This technique was also used to monitor, for the first time, the truly initial stages of oxidation and other chemical reactions on Ge and Si clean surfaces by monitoring the status of the diffraction pattern. In addition, electrical measurements were carried out for the determination of the work function (as a function of orientation), the density of surface states and other physical parameters. It is very important to point out that the density of surface states on clean Ge surfaces was found to be of the same order of magnitude as the density of atoms. Thus, these results gave credence to the hypothesis that surface states were introduced by the unpaired (dangling) electrons on the surface atoms. Indeed, surface chemical reactions could be studied by monitoring the changes in the density of states. A number of very useful studies were carried out on that basis [16].

Once ultrahigh vacuum systems and relevant experimentation were demonstrated, many surface research groups were instrumented and functioning in a very short period of time (as has been invariably the case in the history of science and engineering). The development of very versatile metal vacuum systems followed which permitted the convenient introduction of a number of powerful new optoelectronic spectroscopies (now common place) to the study of surfaces. For example, Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS), introduced in the 60s, made possible the chemical characterization of surfaces (composition and bonding) on a submonolayer scale [15]. The fundamental science of surfaces, was advancing at a high rate.

Among all classes of materials, semiconductors were by far the best suited to bring about the birth of materials science and surface science. Their covalent, highly directional tetrahedral bonding is a major advantage both from the theoretical and the experimental point of view. It simplifies theoretical approaches as compared to metallic bond. It limits the solubility of other components. Thus, attaining high purity becomes much easier. (Today, single crystals of Ge and Si can readily be obtained with total impurities not exceeding one part in 10^{12} [17].) Furthermore, prevention of defect formation is relatively simple. (Si single crystals, eight inches in diameter and a few feet long, are routinely grown dislocation-free.) As a result of their covalent bonding, semiconductors exhibit cleavage at a well defined crystallographic orientation. It was by cleavage of Ge in high vacuum that the first "virgin" surfaces were obtained and studied. In addition, tetrahedral bonding lends itself to atomistic approaches both of the bulk and of the surfaces [18]. Such approaches, in contrast to the more rigorous statistical ones, lend themselves to making predictions leading to the development of materials and structures with needed properties. For example, the discovery of the III–V semiconductor compounds was based on the simple "octet rule". The behavior of the surfaces of these compounds was, at first, accounted for on the basis of a simple atomistic model which I discuss later. Finally, it is due to their covalent bonding that their electrical properties can be readily modulated by many orders of magnitude. For example, one part per million of an impurity from either Group III or V of the periodic table increases the electrical conductivity of intrinsic Si by five orders of magnitude.

I now proceed with a discussion of my personal experiences and involvement with semiconductor surfaces. Here again, I will attempt to convey impressions rather than detailed and rigorous accounts.

7. "Real" semiconductor surfaces

7.1. Elemental semiconductors

When I joined MIT's Lincoln Laboratory in 1955 the research emphasis was still on Ge surfaces just as it was in all solid state research centers. It was generally expected or at least hoped that the problems stemming from the chemical instabilities of these surfaces would be overcome and that Ge-based solid state electronics would go forward.

Having done my doctorate research on the passivity of metal surfaces, I embarked immediately on the search for means to passivate and, thus, stabilize Ge surfaces. We found that strong oxidizing agents (such as concentrated nitric acid) which passivate metal surfaces (such as Fe and Cr) passivate also Ge surfaces and render their electrode potential more noble which is a confirmation of the state of passivity [19].

Before practical passivating processes could be developed, however, much needed to be learned about the chemical characteristics of real Ge surfaces. In view of the sp^3 tetrahedral bonding of Ge, we speculated, along with others, that the "dangling" bonds of the surface atoms must control chemical surface reactions. Since relatively pure single crystals of Ge could be readily grown by now, and, thus, samples could be prepared with surfaces of the desired orientation, we undertook to pursue some basic chemical reactions in water solutions. Our first basic finding was that Ge surfaces do not react with oxygen-free water, although the reaction is thermodynamically feasible. Furthermore, the germanium oxide, commonly encountered on real Ge surfaces, is soluble in water. Thus, in oxygen-free water we could obtain clean and reproducible Ge surfaces which we employed in our studies with liquid media. Some highlights of the results are indicated below [20].

We found that, for the three principal crystallographic faces, the order of the dissolution rates in oxygen-saturated water, in the temperature range of 30 to 40°C, is

$$\{100\} > \{110\} > \{111\}.$$

This order is the same as the order of the densities of dangling bonds on these faces (Table 1). Clearly, the unpaired surface electrons control the reduction of oxygen to form water-soluble germanium oxide. In the light of these results it became possible to control the reactivity of Ge surfaces by the proper choice of species which upon contacting the surface atoms can share, accept or donate electrons. These findings helped put chemical etching, which was essentially an empirical process, on a rational if not on a scientific basis. Thus, chemical etchants with the desired action (polishing, defect definition and others) could be developed much more directly than before [21]. Actually, high resolution chemical etching, combined with phase contrast and interference microscopy, was for many years the only powerful tool for the identification and study of chemical and structural inhomogeneities in semiconductors on a microscale (with a resolution of about 2000 ångström units) [22].

Table 1
Density of free bonds on germanium surfaces and dissolution rates in oxygen-saturated water

Orientation	Free bonds (cm^{-2})	Relative free bond density	Relative dissolution rate
{100}	1.25×10^{15}	1.00	1.00
{110}	8.83×10^{14}	0.71	0.89
{111}	7.22×10^{14}	0.58	0.62

By the late 50s it became clear that, inspite of the remarkable progress that had been made on the technology and science of Ge surfaces, their reliable and permanent stabilization, indispensable in solid state electronics, remained a moving target. Naturally, the emphasis shifted from Ge to Si. The very thin surface oxide on Si was found to be chemically refractory and, thus, assured surface chemical stability. Later on, this oxide film proved to be a godsent for achieving device isolation in integrated circuits on Si chips. I should point out, however, that it took many years of intensive efforts to overcome the electronic difficulties presented by the $Si-SiO_x$ interfaces. My group took a small part in those efforts. Methods were needed to be developed for assessing the electronic characteristics of the interfaces. Specifically, the density of interface states (within the forbidden energy gap), originally estimated to be of the order of $10^{13}/cm^2$, needed to be reduced by five orders of magnitude. The efforts were successful and extremely rewarding. Metal–oxide–semiconductor (MOS) structures became functional and today they are key structures in integrated circuitry. Here we have a truly exciting phase in the development of the science and engineering of solid interfaces [17,23].

Today, Si is used in about 95% of all electronic applications. They touch nearly all facets of our lives and culture. We can safely say that we are well into the Silicon Age. The reason for this outcome is not Si's semiconducting superiority but rather the superiority of the properties of its surface oxide.

7.2. Compound semiconductors

By the late 50s the solid state centers were switching from Ge to Si. At MIT's Lincoln Laboratory we decided to bypass Si and go directly to semiconductor compounds. It was for this reason that I started my long association with semiconductor compounds, although later on I too became involved with Si surfaces and Si–SiO_x interfaces.

I should mention, parenthetically, that a few groups, particularly in the eastern European countries, kept on working for many years on Ge surfaces [24]. They concentrated on the formation of the tetragonal GeO_x which, we, and others, found to be chemically refractory. However, the reproducible formation of this oxide on Ge surfaces turned out to be unattainable.

The first tantalizing problem we encountered working with Group III Group V compounds (usually referred as III–V compounds, e.g. GaAs) was associated with their parallel (111) and $(\bar{1}\bar{1}\bar{1})$ surfaces. Thus, the (parallel) surfaces of an $\langle 111 \rangle$ oriented wafer exhibited totally different chemical characteristics, as seen in Fig. 2, where the two parallel (111) surfaces of a chemically etched GaAs wafer are shown. We observed such striking differences between the parallel {111} surfaces in all III–V as well as in II–VI semiconductor compounds.

7.2.1. The bonding model

We developed an atomistic bonding model [25] which not only accounted for the above differences in behavior but made it possible to predict a number of new chemical, structural and electronic phenomena (some with important techno-

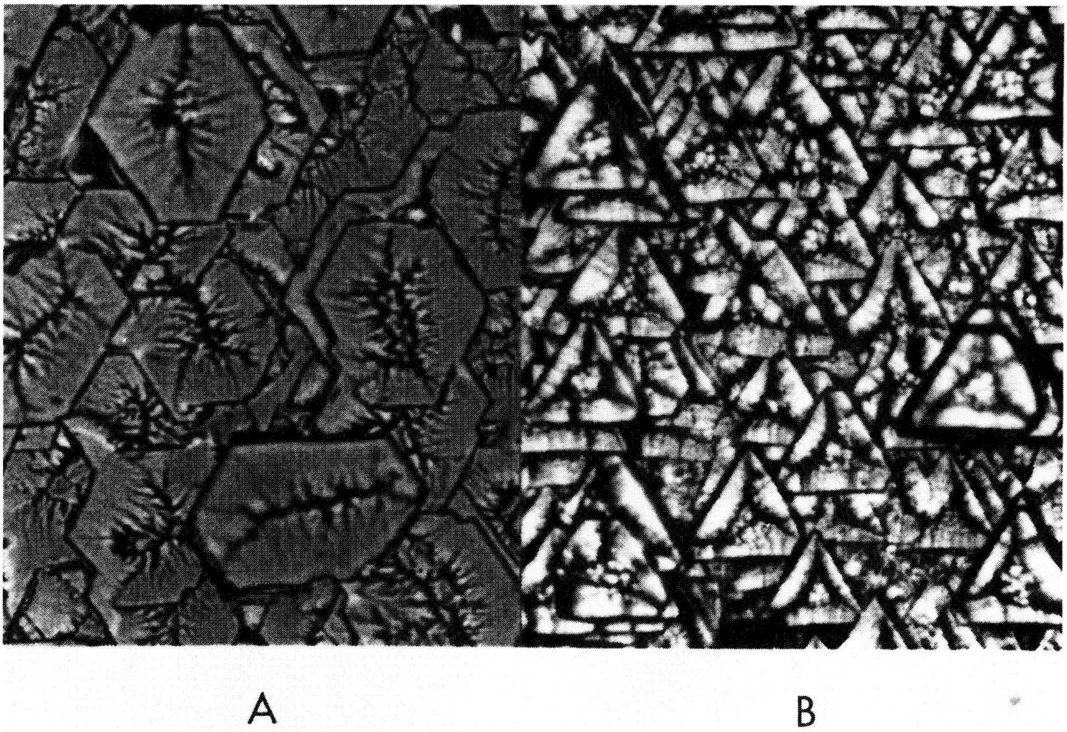

Fig. 2. Etched A and B parallel surfaces of a GaAs(111) wafer, 750 × .