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Metal–Semiconductor Contacts and Devices

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Preface

The problem of metal–semiconductor contacts has a rather long history that dates back to the very first experiments on semiconductor materials conducted by Ferdinand Braun over a century ago. Ever since then this field has constituted an important part of the intensive research and development efforts in solid-state electronics. A substantial amount of work on theory, fabrication, and characterization of practical metal–semiconductor contacts and related devices has been performed, leading to a good understanding of this system. The knowledge that has been acquired made it possible to address important issues in today's advanced VLSI technologies such as performance, reliability, and scaling requirements. Much of the recently available information, however, is scattered in the literature. In view of many new developments in microelectronics, a comprehensive review of this important field seems to be timely. This book is devoted to the physics, technology, and applications of metal–semiconductor barriers in digital integrated circuits. The emphasis is placed on the interplay among the theory, processing, and characterization techniques in the development of practical metal–semiconductor contacts and devices.

The physics of metal–semiconductor interfaces has been the subject of many reviews and several monographs. In the present work we have tried to stress some recent developments in this field as well as to describe the basic phenomena. In contrast to the detailed theoretical analysis, only limited attention has been paid in the past to the important question of contact fabrication procedures. Some of these techniques have been developed within the past decade and have not been discussed in any detail in standard texts. We thus feel that a comprehensive treatment of this subject will fill an important gap in the existing literature and be beneficial to workers in the field.

The theoretical and processing aspects of the contact system constitute two important issues to be considered. Another aspect of the problem is that of the interface characterization techniques. In particular, with regard to ohmic contacts, these have not been comprehensively reviewed at the monograph level. We therefore pay special attention to the experimental techniques that have been developed over the years for the evaluation of ohmic contact properties.

With the advent of integrated circuit technology, solid-state devices are pushed ever closer to their technological and physical limits. As a result a detailed understanding of the factors affecting device performance and reliability is required from semiconductor engineers involved in all aspects of advanced solid-state technology. The various aspects of the metal–semiconductor problem clearly indicate the multidisciplinary nature of this field. We hope that the selection of the material presented in this work will make it useful for process engineers, device physicists, and circuit designers, as well as for students of these disciplines.

The writing of this book would not have been possible without the help of many of our colleagues. In particular we are indebted to our friends and managements at the General Electric Company and the Digital Equipment Corporation for the assistance and encouragement we have received. Special thanks are extended to M. Garfinkel and N. Einspruch for the critical reading of the manuscript, to J. F. Norton for many of the SEM micrographs that are reproduced in Chapters 5 and 6, and to B. F. Griffing and D. W. Skelly for several micrographs also included in these chapters. We are also indebted to J. M. Gibson for providing us with his TEM micrographs that are included in Chapter 6. We also wish to acknowledge illuminating discussions with M. Ghezzo and D. Antoniadis regarding the material on diffusion profiles presented in Chapter 5 and thank D. E. Nelsen for reading Chapter 8 and for valuable comments. Finally, one of us (S. S. C.) wishes to thank the General Electric Company for a generous grant that enabled him to continue his work on this volume while he was away from the company.

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GENNADY SH. GILDENBLAT

Contents

Chapter 1

Introduction

The vast and ever growing number of practical applications that resulted from the extensive investigations in semiconductor physics is clear evidence of the modern-day industrial revolution, which has taken place since World War II and has been centered in the field of electronics. Scientific progress in semiconductor physics has lead to new technological innovations, which in turn have resulted in a better understanding of the basic concepts. The physics of basic semiconductor phenomena is well established and understood by now. Technological progress, however, is still at the very heart of new applications. Although the basic physical processes have been well described, emerging classes of devices require a more thorough investigation of both the physical and material aspects. In particular, new limits on the physical dimensions of the devices involved require that more adequate theoretical models be invoked and that better tools for material characterization be used. These are necessary in order to enable a full understanding of the mechanisms involved in the operation of these devices and to establish new techniques for their fabrication. This is the case not only for the actual microelectronic devices but also for the test structures that are needed for evaluating their properties.

The progress made in both the physics of semiconductor devices and device fabrication techniques has been fully documented in several textbooks [1–3]. These textbooks, however, by their general nature, cannot always provide a thorough discussion for all the important subjects. Hence, several of these must be treated separately. The problem of metal–semiconductor contacts is one such subject. Contacts between metals and semiconductors play a major role in all classes of devices. Contacts are used in controlling certain device functions, as well as providing means for communication between the active devices and the outside world. In view of the major role of these device components, it is surprising to note how few general texts and reviews have been dedicated to the subject [4–9]. Several other reviews concerned with a more limited scope of this subject have also been published [10–12]. The only works that are dedicated to this subject are those by Rhoderick [7], Henisch [8], and the volume editted by Sharma [9]. These books, however, are mainly concerned with the physics of metal–semiconductor contacts and only briefly discuss the electrical properties of some practical systems. Most other reviews are rather old and, at least from the experimental point of view, seem to be outdated.

The problem of metal–semiconductor contacts may be divided into three interdependent parts. First, there exists the theoretical formulation that describes the essential physical processes that govern the carrier transport across the interface. A good presentation of this is found in the review by Padovani [13] and in the book by Rhoderick [7]. Next, there is the question of practical rectifying and ohmic contacts. The former has been discussed in several reviews. Practical ohmic contacts to semiconductors in general, and to silicon in particular, have unfortunately not been discussed to any real extent in any of the previously mentioned publications. Finally, there is the problem of barrier height and contact resistance determinations. Several well-established techniques for barrier height determination exist by now.

Over the years, many test structures have been proposed and utilized in the evaluation of the properties of ohmic contact. However, except for a recent short review [14], no comprehensive discussion of this important issue has appeared in the literature. This situation has become particularly serious with the recent advent of the very large scale integration (VLSI) technology, in which exact and meaningful determination of contact resistance values is of prime importance. In recent years, several refined test structures have been developed that are capable of providing the necessary experimental information that could be compared with available theoretical models. A thorough discussion of these test structures has thus become essential.

The present treatise will fill in some of these gaps and thus provide a thorough and comprehensive treatment of the various aspects of this important subject. We plan to review the theoretical development in detail and emphasize some recent achievements that enable a better understanding of the electrical properties of metal–semiconductor interfaces. All of these theoretical discussions are necessary in order to understand the practical contact studies, along with their relevant fabrication procedures. Although the present volume is meant to treat various aspects of the metal–semiconductor contact system, these are not given equal weights. Thus, ohmic contacts and certain selected rectifying contacts are more emphasized than others.

From the practical point of view, the discussion here will concentrate on silicon and gallium arsenide, although other semiconductor materials are also mentioned. This choice, of course, reflects the role that silicon and gallium arsenide play in modern integrated circuits (ICs). The current level of integration in VLSI technologies has created a genuine need to study both the metallurgical and electrical properties of new metal–silicon contact systems. All of the recently available studies on the subject, together with all relevant previous studies, will be discussed here to provide a comprehensive source for these important systems. As befits the host series of this volume, the discussion is heavily biased in favor of contact systems encountered in VLSI technologies. We thus hope that this treatise will be found useful by those interested in advanced circuit fabrication technologies and those interested in the basic physics of this system, as well as for those working in related, albeit somewhat different, fields.

In the past several excellent historical accounts of the developments that led to the present state of the microelectronics industry have appeared. We mention the early work of Kass [15], the vivid description in "Revolution in Miniature" by Braun and MacDonald [16], and "Silicon Valley Fever" by Rogers and Larson [17]. Many other historical reviews and accounts have also been published, and most are cited in these references.

The first report on the electrical properties of metal–semiconductor contacts dates back to 1874, when Ferdinand Braun observed that point contacts made to certain sulfides resulted in rectification, i.e., the current conduction depended on the current direction [18]. This device would then find use as an electrical detector and would come to be known as the "cat's whisker" device. In this application, a sharpened metal wire (hence the name given to the device) was pressed against a semiconductor surface. Sometimes thermal annealing was employed to create an alloyed junction of small contact area. Due to the relatively small contact area, this diode suffered from high noise characteristics, high series resistance, and low power capability. However, it did find extensive use until further advances were made and the Schottky barrier devices came to being.

The cat's whisker diode was, in fact, a product of early solid-state physics, although, as noted by Braun and MacDonald [16], the name for this important subfield of physics had to wait an entire century before it would be first introduced. Perhaps the first semiconductor material to be investigated was silver sulfide, the electrical properties of which were studied by Michael Faraday in 1833. Faraday discovered that its electrical resistance decreases with increasing temperature, contrary to what was known for metallic substances. This puzzling behavior aroused the curiosity of many physicists, Ferdinand Braun among them, who, as already mentioned, discovered the phenomenon of rectification by metal contacts to such substances. The next development by Braun was to use his cat's whisker device as a detector of radio waves. Braun, who for over 20 years kept the point contact rectifier at the back of his mind, became aware of Marconi's experiments with wireless telegraphy. He realized that the cat's whisker would make a more sensitive detector than the then-available carbon spark gap detector. In view of this, it is intriguing to recall Braun's description of his discovery of rectification, stating that his problem was in fabricating reliable contacts to those sulfides. Obtaining reliable contacts remains a major task for today's scientists and technologists.

The lifetime of the point contact rectifier was short, precisely due to the reliability problem. The cat's whisker device went into a state of dormancy. It would continue to find some use in laboratories, mainly for measuring UHF power, and with radio ham operators. We note in passing that the advent of quantum mechanics in the 1920s and the 1930s has led to extensive experimental studies that resulted in, among many other new ideas, the development of new solid-state devices such as the photocells used in commercial applications. These devices, known in fact since the turn of the century, were basically made of large-area metal–semiconductor contacts. To explain the characteristics of their operation, the interface barrier had to be invoked. The stage was thus set for the latter introduction of the Schottky barrier devices.

Attempts to fabricate a solid-state amplifier eventually led to the invention of the point-contact transistor in 1947. This, however, proved to be difficult for mass production and its reliability could not be assured. In addition, it was a rather noisy device that did not perform well at high frequencies. By 1952, the junction transistor, first conceived by William Schockley, was in production. The new device, made of three semiconductor layers, in which the center layer had a different type of dopant, was made possible by new crystal growing techniques.

The contacts to the three different regions in the semiconductor (germanium) were made manually under a microscope. This device was much less noisy and was capable of handling more power. However, it had a serious disadvantage in that it was restricted to even lower frequencies. A major improvement in the operation of the junction transistor was provided by a new contact metallization technique. In 1952, Robert Hall developed a method of alloying indium to opposite sides of a thin germanium slice [19]. The alloyed junctions that were thus obtained could operate at much higher frequencies and currents than possible with the junction device. The thickness of the slice, however, had to be made thinner than 10 μm. Electrolytic etching techniques were soon developed that enable a controlled fabrication of such thin germanium slices.

In 1954, the first silicon transistor was fabricated. Owing to the wider band gap in silicon, this device could operate at much higher temperatures than possible for germanium. Silicon is abundant in the earth crust, while germanium is relatively rare. For this and other reasons, it became clear that silicon was about to assume a major role in this technology. What was needed for the final replacement between the two materials was a new fabrication technology. This was, indeed, developed and came to be known as the planar technology. It opened the way to the modern era of integrated circuitry.

The development of the planar process required a better understanding of interfaces. The knowledge that was thus acquired, led to enhanced activities in the field of metal–semiconductor contacts. This was aimed at satisfying two needs: contacts to the active components of the field-effect transistor (FET), which was the main reason for the development of the planar process, and metal–semiconductor rectifiers. By the mid-1960s, several important developments in the field of metal contacts to semiconductors were made. Deposition and definition techniques were established, and material phenomena, such as silicidation, that allowed the formation of intimate silicon contacts to an intermetallic alloy, were studied.

Initially, gold was accepted as the preferred contact metallization. It was quickly realized, however, that gold could not be in direct contact with silicon due to the low eutectic temperature of this pair. Barrier metals, notably molybdenum, were suggested to solve the reliability problem that direct gold contacts posed. Gold is also an expensive metal. So, before long, it was replaced in most applications by aluminum. This material is a good electrical and heat conductor and adheres well to both silicon and its oxide. Aluminum was not found suitable for fabrication of Schottky barrier devices, but is uniquely suitable as an ohmic contact agent to heavily doped regions in silicon.

Even though aluminum enjoyed wide success as a contact metallization candidate in IC fabrication, work on other possible contact metallization systems has been performed over the years. Reasons for this and the sequence of events are described in Chapter 6. Here, we only note that the advent of VLSI has put stringent requirements on contact metallization. Although aluminum is still widely used today, we expect that it will eventually be replaced by more stable metals or alloys as direct contact metallization to silicon for both applications of ohmic and rectifying contacts. This would most probably come from the wide group of refractory materials. Indeed, as detailed in Chapter 6, several such studies and even first applications have been reported.

Although silicon continues to be the major semiconductor material used, certain specific applications have required that other semiconductors be used. Among these, gallium arsenide enjoys a leading position owing to its many excellent electrical and metallurgical properties. Metal contacts to gallium arsenide are different in certain respects than those made to silicon. Thus, in many cases the contact alloy also serves as the doping source. In Chapter 7 these interesting contact systems are discussed.

The plan of this volume is as follows. In Chapter 2, basic concepts in the physics of the metal-semiconductor interface are presented. Chapter 3 then takes a close look at barrier properties and emphasizes practical methods of barrier height determination. In recent years, a new theoretical understanding of the barrier properties has been gained. The relevant developments are discussed here. Chapter 4 is devoted to discussions of the various test structures that have been developed over the years for the determination of ohmic contact resistance values. Along with describing the theoretical models behind these test structures, an emphasis is made on discussing their practical aspects. In particular, test elements that have been recently introduced are fully evaluated. Their merits and limitations in VLSI applications are stressed. Metal contacts to a semiconductor substrate are, of course, only one part of the overall fabrication procedure of the integrated circuit. These contacts can be greatly affected by details of the processing technology. For this reason, we discuss in Chapter 5 all the relevant steps in the contact preparation procedure, along with a basic description of some current advanced technologies. In Chapter 6, a thorough discussion of practical ohmic contacts to silicon is given. Ohmic contacts in other systems are discussed in Chapter 7, and in Chapter 8 we describe certain devices based on the properties of the metal-semiconductor contact.

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Chapter 2

Electrical Characteristics of the Metal-Semiconductor Interface

2.1. INTRODUCTION

The metal-semiconductor contact system has been the subject of many investigations that date back to 1874, when Braun [1] observed that the resistance between mercury and several sulfides was dependent on the polarity of the applied voltage. In 1904 a patent was granted to Bose [2] for a practical application of the point-contact rectifier. Major developments awaited until the transport theory of semiconductors was later formulated and applied to the metal-semiconductor system. Schottky *et al.* [3] were the first to relate the formation of the potential barrier with the rectifying properties of the metal-semiconductor contacts. In subsequent investigations, Schottky [4] and Mott [5] determined the shape of the potential barrier and proposed models for the current transport known presently as the diffusion theory. Bethe [6] developed the thermionic transport theory, that may be applied to Schottky diodes fabricated on high-mobility semiconductors, which are being used at the present time. The practical use of Schottky diodes before the 1960s was limited primarily to frequency conversion and microwave detection [7].

Since the early 1960s, metal-semiconductor contact systems have been studied intensively. These contacts can be either rectifying or of low resistance, depending on several material properties that will be discussed in this and the following chapters. Both types of these contacts are of prime importance in the performance of semiconductor devices. With the advent of VLSI technology, new requirements have been posted on the metal–semiconductor system. These have created a spur in the activity in this field in recent years. Particular emphasis has been made on metallurgical and reliability aspects, but a better understanding of the underlving physics has also been achieved. Of special importance is the progress made in recent years in defining and understanding adequate methods for the measurement of the various parameters that pertain to the metal–semiconductor interface system. Several different test structures have been devised in order to enable the determination of the specific contact resistance. Methods for determining important basic quantities, such as the energy barrier at the interface, have also been refined. They will be discussed in the next chapter, while here we consider the relevant aspects of the Schottky barrier physics.

2.2. THE INTERFACE BARRIER AND SPACE CHARGE REGION

A perfect metal–semiconductor contact may be defined as one that allows charge carriers to flow in either direction without presenting any resistance at the interface. In reality, however, a potential barrier always develops at the interface. In the absence of interface states this barrier is mainly due to the difference in the work functions of the metal and the semiconductor. When the work function of the metal is larger than that of the semiconductor, electrons will be transferred from the semiconductor into the metal. The process continues until the Fermi levels in the two materials reach the same position. In such a case, a space charge region forms in the semiconductor in the immediate vicinity of the interface. The space charge region is also known as the depletion region. A schematic illustration of this situation is given in Fig. 2.1 for an *n*-type semiconductor. In this case, the energy bands are seen to be bent upward in the depletion region. (For the sake of brevity, we limit the discussions throughout this chapter to *n*-type material, keeping in mind that similar arguments apply for the *p*-type case). The potential barrier presents an impediment to the current flow and determines the electrical characteristics of the contact.

In the first theory of barrier formation developed by Schottky [4] and Mott [5] the barrier height Φ_{Bn} is given by

$$\Phi_{Bn} = \Phi_m - X_s, \tag{2.1}$$

where Φ_m denotes the metal work function and X_s is the electron affinity of the semiconductor. The parameter Φ_{Bn} describes the barrier for the flow of electrons from the metal to the semiconductor. For the reverse process, i.e.,