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Michiko Yoshitake

Work Function and Band Alignment of Electrode Materials

The Art of Interface Potential for Electronic Devices, Solar Cells, and Batteries

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Preface

Work function is one of the important physical quantities of materials that is related to various phenomena. However, systematic discussion on the work function is limited possibly because of the following two reasons. One is that the work function is not a quantity that is specific to a bulk material such as dielectric constant, elastic modulus, density, and magnetic susceptibility. Even one single crystalline material has different work function values, depending on the crystal plane. This means that work function values are influenced not only by bulk materials but also by surface conditions. The other is that the measurement of work function values of an intended surface of materials is not easy. The difficulty comes from the fact that work function values are surface sensitive as mentioned above. Surface is very reactive in general, and it is rather difficult to prepare and maintain a surface as intended states.

Basic experimental researches on the work function had progressed upon the development of commercially available vacuum instruments in the 1960s–1970s, which provided tools to maintain surface conditions and observe surface compositions and structures. Most of fundamental issues were established during this time. Then, theoretical calculations of the work function have complimented experimental researches thanks to the development of first-principles calculations in the 1990s. Emergence of electronic devices had required the control of band alignment via work function control at the interface, and the origins of the deviation from ideal Schottky relation were rigorously discussed in the 1980s and later.

This book presents issues on the work function from fundamental physics to examples of band alignment via work function control in device applications. The author hopes the book helpful for all who engage in research and development of materials whose function has related to the work function.

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Michiko Yoshitake

The original version of the book was revised: The copyright of all the chapters has been corrected. The correction to the book is available at https://doi.org/10.1007/978-4-431-56898-8_8

Contents

Chapter 1
Introduction: Functions and Performances Governed by the Work Function

1.1 Why is the Work Function Important?

The work function is an important property for phenomena where electron transfer between two different materials in contact or from a material into vacuum is involved. Electron transfer into vacuum or a gas phase is usually called electron emission (Fig. 1.1a). Electron emission is one of the well-known phenomena governed by the work function. In fact, electron emission has been used to measure values of the work function. Electron emitters with a low work function have been developed for a long time. Electron transfer between two materials (Fig. 1.1b) is another major application field related to electron emission. In the field of semiconductor device physics, it is well known that the ideal Schottky barrier height (SBH) at a metal–semiconductor interface is determined by the work function of the metal and the electron affinity of the semiconductor (Fig. 1.2). There are major application fields that utilize the concept of a Schottky contact, which will be discussed later in the book. Furthermore, several types of chemical reaction on a surface have been reported to be related to the work function. For example, the potential of oxidation in fuel cells has been shown to be related to the work function of the electrode materials [1]. The dissociation of molecules on catalytic metals has also been reported to be affected by the work function of metals [2, 3].

Because the work function is a factor determining electron emission, it affects most phenomena involving electrons and is important in many application fields. In Fig. 1.3, some of the application fields that utilize electron emission phenomena are shown. A scanning electron microscope (SEM) and a transmission electron microscope (TEM), which are familiar in scientific R&D fields, use an electron source whose performance is determined by the work functions of the electron source materials. Here, emitted electrons are made into a beam. Other examples of electron beam applications are electron lithography, accelerators for synchrotron radiation photon sources, and colliders for nuclear physics research. Examples of the practical use of electron emission in daily life are fluorescent lamps, neon lighting in neon

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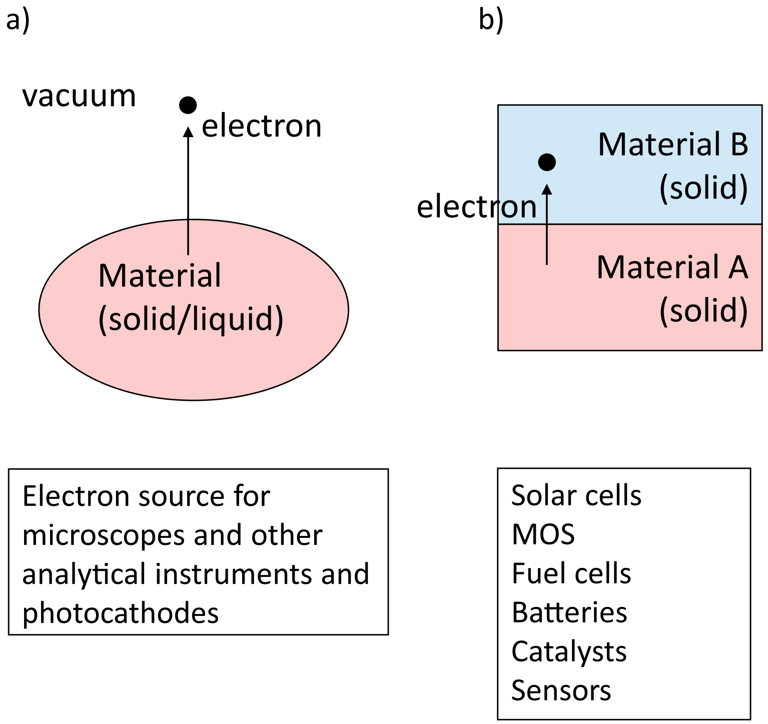

Fig. 1.1 Some examples of applications related to **a** electron emission (electron transfer into vacuum or gas phase) and **b** electron transfer between two materials (see text for details)

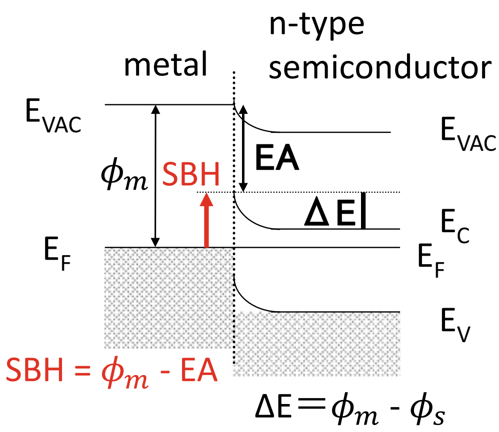

Fig. 1.2 Band alignment for ideal Schottky contact between metal and n-type semiconductor (see text for explanation)

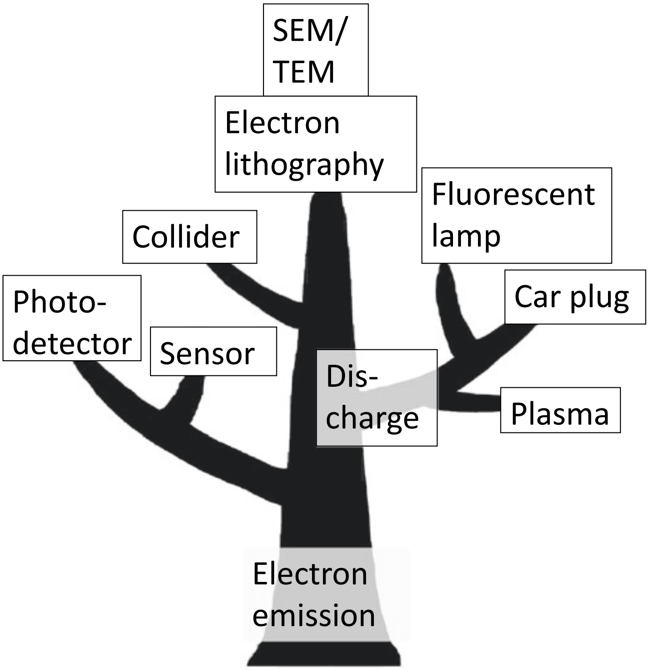

Fig. 1.3 Applications related to electron emission phenomena. See text for explanation

signs, and car plugs. For these applications, electron emission is mostly utilized to initiate electric discharge. Electric discharge initiated by electron emission is used for plasma formation, and plasma is utilized for many industrial applications such as film deposition. Another important application is based on photoelectron emission. When light irradiates a metal, electrons are emitted if the energy of the light exceeds the work function. This phenomenon is utilized for photodetectors and gas sensors (which detect light emission from gas). Detectors or sensors for a specific photon energy or gas species can be fabricated by tuning the work function of materials.

Electron emission not to vacuum or a gas phase but to another solid (electron transfer) has an even wider range of applications. The performances of almost all devices that involve an electric circuit are related to the work function. Figure 1.4 illustrates some of the application fields that utilize electron transfer phenomena. Electron transfer is controlled via the electric voltage in electric devices such as transistors and CMOS. The work function is a key factor determining the operation voltage. Light-emitting devices including organic devices convert electric energy to light, where the work function is an important factor determining the conversion efficiency. The performance of devices involving energy conversion in the opposite direction, i.e., solar cells, is also influenced by the work function. For other energy conversion devices with various types of energy, such as fuel cells and batteries

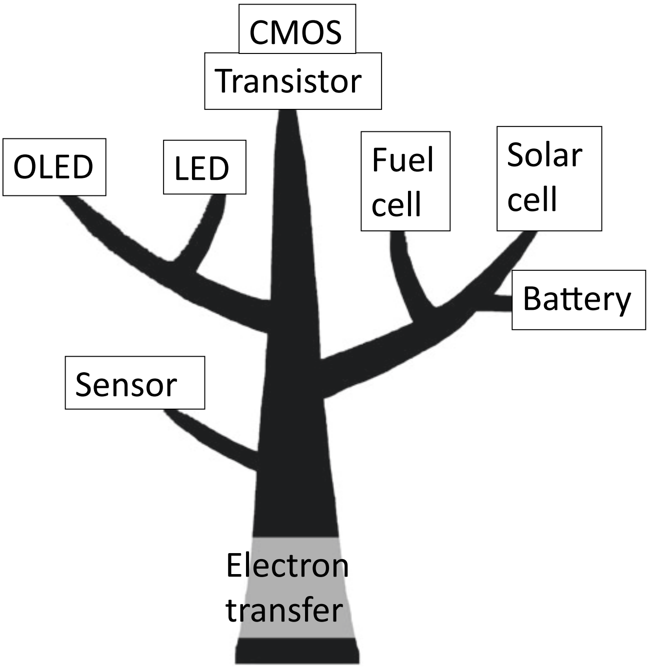

Fig. 1.4 Applications related to electron transfer phenomena. See text for explanation

(chemical energy), the work function is a key to extracting electricity from the energy. Another field related to energy conversion is sensors, where the amount of energy to be converted is small. Again, the energy conversion efficiency is related to the work function, where the efficiency determines the sensitivity.

1.2 Contents of the Following Chapters

As briefly overviewed in the above section, the work function plays an important role in a very wide range of scientific, technological, and industrial fields. In the following chapters, we discuss the physical origin of the work function, how the work function can be controlled on the basis of physics, and how to design interfaces. In this section, a guide to the following chapters is given.

In Chap. 2, the definition and the origin of the work function are given, and factors that determine the value of the work function are explained. The most important point is that the work function is defined for the surface of a material as well as for bulk materials. In Chap. 3, strategies for tuning the work function are demonstrated on the basis of the discussion in Chap. 2. Examples of work function modifications using these strategies are also given for concrete material systems. In Chap. 4, various methods of measuring work function are given with both their physical principles and technical issues.

From Chaps. 5–7, band alignment at the interface is discussed on the basis of the relationship with the work function. In Chap. 5, band alignment is handled as an ideal case, where the modification of the work function directly controls the band alignment. The relationship between the band alignment and the work function in general, and concrete examples of band alignment modification via tuning of the work function are given. In Chap. 6, cases where the relationship between the band alignment and the work function is not ideal are discussed. Here, although the relationship is not ideal, a linear relationship with the work function is obtained in many cases. A correlation factor for the linear relationship is introduced, which is determined by the dielectric property of the material in contact. Chapter 7 discusses band alignment with interface-specific cases. By extending the idea that the work function is surface-sensitive, either an appropriate interface terminating species or the insertion of a very thin layer that can be regarded as having only a surface and no bulk is adopted to modify the band alignment. Some concrete examples are also given. Practically, the former technique is extensively adopted in the field of compound semiconductors and the latter technique is used in organic semiconductor fields. The relationship between the chapters of this book is summarized in Fig. 1.5.

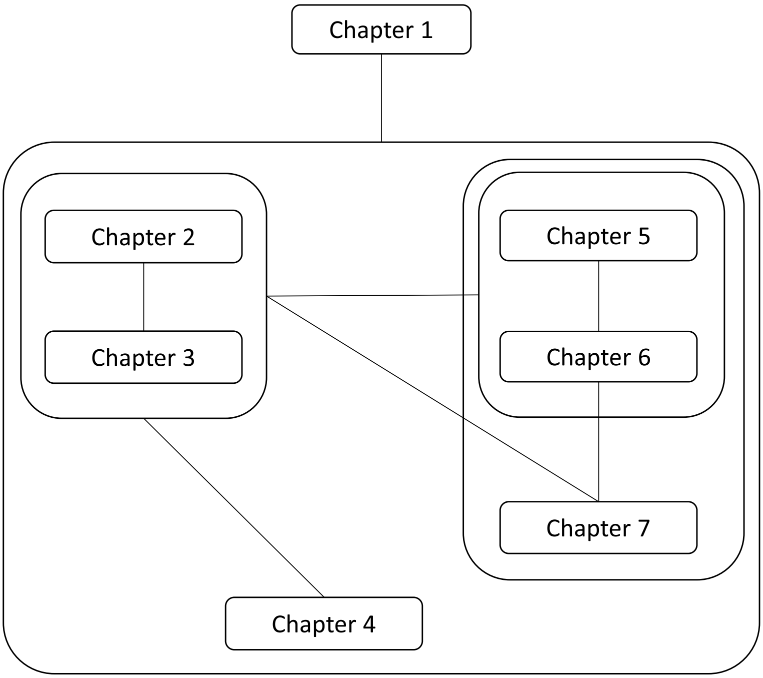

Fig. 1.5 Relationship between the chapters of the book

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