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Progress in Nanoscale Characterization and Manipulation

纳米表征与调控研究进展

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序　　言

物理学是研究物质、能量以及它们之间相互作用的科学。她不仅是化学、生命、材料、信息、能源和环境等相关学科的基础，同时还是许多新兴学科和交叉学科的前沿。在科技发展日新月异和国际竞争日趋激烈的今天，物理学不仅囿于基础科学和技术应用研究的范畴，而且在社会发展与人类进步的历史进程中发挥着越来越关键的作用。

我们欣喜地看到，改革开放三十多年来，随着中国政治、经济、教育、文化等领域各项事业的持续稳定发展，我国物理学取得了跨越式的进步，做出了很多为世界瞩目的研究成果。今日的中国物理正在经历一个历史上少有的黄金时代。

在我国物理学科快速发展的背景下，近年来物理学相关书籍也呈现百花齐放的良好态势，在知识传承、学术交流、人才培养等方面发挥着无可替代的作用。从另一方面看，尽管国内各出版社相继推出了一些质量很高的物理教材和图书，但系统总结物理学各门类知识和发展，深入浅出地介绍其与现代科学技术之间的渊源，并针对不同层次的读者提供有价值的教材和研究参考，仍是我国科学传播与出版界面临的一个极富挑战性的课题。

为有力推动我国物理学研究、加快相关学科的建设与发展，特别是展现近年来中国物理学者的研究水平和成果，北京大学出版社在国家出版基金的支持下推出了"中外物理学精品书系"，试图对以上难题进行大胆的尝试和探索。该书系编委会集结了数十位来自内地和香港顶尖高校及科研院所的知名专家学者。他们都是目前该领域十分活跃的专家，确保了整套丛书的权威性和前瞻性。

这套书系内容丰富，涵盖面广，可读性强，其中既有对我国传统物理学发展的梳理和总结，也有对正在蓬勃发展的物理学前沿的全面展示；既引进和介绍了世界物理学研究的发展动态，也面向国际主流领域传播中国物理的优秀专著。可以说，"中外物理学精品书系"力图完整呈现近现代世界和中国物理科学发展的全貌，是一部目前国内为数不多的兼具学术价值和阅读乐趣的经典物理丛书。

“中外物理学精品书系”另一个突出特点是,在把西方物理的精华要义“请进来”的同时,也将我国近现代物理的优秀成果“送出去”。物理学科在世界范围内的重要性不言而喻,引进和翻译世界物理的经典著作和前沿动态,可以满足当前国内物理教学和科研工作的迫切需求。另一方面,改革开放几十年来,我国的物理学研究取得了长足发展,一大批具有较高学术价值的著作相继问世。这套丛书首次将一些中国物理学者的优秀论著以英文版的形式直接推向国际相关研究的主流领域,使世界对中国物理学的过去和现状有更多的深入了解,不仅充分展示出中国物理学研究和积累的“硬实力”,也向世界主动传播我国科技文化领域不断创新的“软实力”,对全面提升中国科学、教育和文化领域的国际形象起到重要的促进作用。

值得一提的是,“中外物理学精品书系”还对中国近现代物理学科的经典著作进行了全面收录。20世纪以来,中国物理界诞生了很多经典作品,但当时大都分散出版,如今很多代表性的作品已经淹没在浩瀚的图书海洋中,读者们对这些论著也都是“只闻其声,未见其真”。该书系的编者们在这方面下了很大工夫,对中国物理学科不同时期、不同分支的经典著作进行了系统的整理和收录。这项工作具有非常重要的学术意义和社会价值,不仅可以很好地保护和传承我国物理学的经典文献,充分发挥其应有的传世育人的作用,更能使广大物理学人和青年学子切身体会我国物理学研究的发展脉络和优良传统,真正领悟到老一辈科学家严谨求实、追求卓越、博大精深的治学之美。

温家宝总理在2006年中国科学技术大会上指出,“加强基础研究是提升国家创新能力、积累智力资本的重要途径,是我国跻身世界科技强国的必要条件”。中国的发展在于创新,而基础研究正是一切创新的根本和源泉。我相信,这套“中外物理学精品书系”的出版,不仅可以使所有热爱和研究物理学的人们从中获取思维的启迪、智力的挑战和阅读的乐趣,也将进一步推动其他相关基础科学更好更快地发展,为我国今后的科技创新和社会进步做出应有的贡献。

“中外物理学精品书系”编委会 主任

中国科学院院士,北京大学教授

王恩哥

2010年5月于燕园

Preface

Nanoscale characterization has enabled the discovery of many novel functional materials which started from understanding important relationships between material properties and morphologies. Therefore, nanoscale characterization has become an important research topic in nanoscience. It fosters the foundation for the design of functional nanodevices and applications of these nanomaterials.

The book "Progress in Nanoscale Characterization and Manipulation" is focused on charged-particle optics and microscopy as well as their applications in materials sciences. Prof. Rongming Wang acts as editor-in-chief of this volume. This book involves many cutting-edge theoretical and methodological advances in electron microscopy and microanalysis, testifying their crucial roles in modern materials research. It will be of primary importance to all researcher who work on ultramicroscopy and/or materials research.

While nanomaterials find wider and more significant applications in almost every aspect of modern science and technology, researchers have been trying to gain detailed knowledge of novel materials with atomic (even sub-Å) scale resolution that are responsible for their unique properties, including chemical composition, atomic organization, coordinates, valence states, etc. This has been driving the development of ultramicroscopy. This book addresses the growing opportunities in this field and introduces the state-of-the-art charged-particle microscopy techniques. It showcases the recent progress in scanning electron microscopy, transmission electron microscopy and helium ion microscopy including the advanced spectroscopy, spherical-corrected microscopy, focused-ion imaging and in-situ microscopy. To appreciate the synergies of the above-mentioned charged-particle methods, the common features of their optical systems are summarized in the first chapter.

Our authors are active international researchers working at the forefront of the field, while we have received direction and assistance from several senior Chinese scientists (Prof. Hengqiang Ye, Prof. Fanghua Li, Prof. Ze Zhang, Prof. Junen

Yao and Prof. Xiaofeng Duan, etc.). Based on their extensive expertise in ultramicroscopy, our authors have provided many their cutting-edge research outputs and demonstrated the indispensable roles of charged-beam microscopy in the development of modern materials research. This defines the unique style of the book: an excellent integration of fundamental theories and practical applications. Therefore, it can meet the needs of a range of readers who are either working on those microscopy techniques or applying them to the investigation of advanced materials. While the development of Cs-corrected microscopy, in-situ microscopy and high-resolution spectroscopy is stepping into a golden age, it is clearly imperative to gain a big picture of the development. The book covers many timely topics and it can serve as a good reference for researchers or students working in many fields such as materials sciences, physics, chemistry, electronics, the semiconductor industry and biology.

We have received numerous constructive suggestions and comments from many colleagues. On behalf of all the editors, I would like to offer our sincere gratitude to those who have contributed to the book.

On behalf of the editors, I would like to thank all our authors. They have been working diligently. I would like to thank my fellow editors for their hard work. I hope this book can facilitate the development of microscopy techniques, inspire young researchers, and make due contributions to the field.

Prof. Rongming Wang

April, 2017

Contents

1

Electron/Ion Optics

Jing Tao, Rongming Wang and Hongzhou Zhang

Transmission electron microscopes (TEM) have very delicate optical systems in order to fulfill their research purpose, i.e., the characterization of material's structures in a versatile manner in modern science. High-energy electrons are generated, forming an electron probe with variable sizes to bombard the sample materials. The scattered electrons, which carry details of material's structures, are reflected to produce a set of data including diffraction patterns, images and spectra. The processes of the electron generation, interaction with the materials and data acquisition are all accomplished in high-level vacuum inside the microscopes. Unlike optical microscopes, most of the lenses in the TEM use electric currents in a particular geometry to generate magnetic fields, which are used to bend the path of the electron beam. Therefore, the experimental operation of TEM and interpretation of the TEM results require background in electromagnetism, vacuum physics, scattering theory and specimen-related solid state physics, among which understanding the optical structure of the microscopes should be considered as the first step of the TEM-based study to but not limited to those who plan and perform experiments using TEM.

Although this chapter attempts to provide a comprehensive overview of the optical system of the TEM and cover the main components inside the electron microscopes, we note that this is a developing research area, in which new designs of the electron paths and new generations of lenses/detectors are emerging very quickly in academic institutes and industries all over the world. Some of the forefront technology in high-end TEM, such as aberration correctors both for the probe forming and imaging, will be elaborated in detail in following Chapters.

1.1 General ray diagram of TEM

The optical system of a conventional TEM consists of three main components: illumination system, imaging system and projection system. As shown in Fig. 1.1.1, those three systems, each with their own apertures, lenses and other necessary pieces, are arranged following the sequence of the electron beam path. In particular, 1) high-energy electrons are released from an electron gun and such an elec-

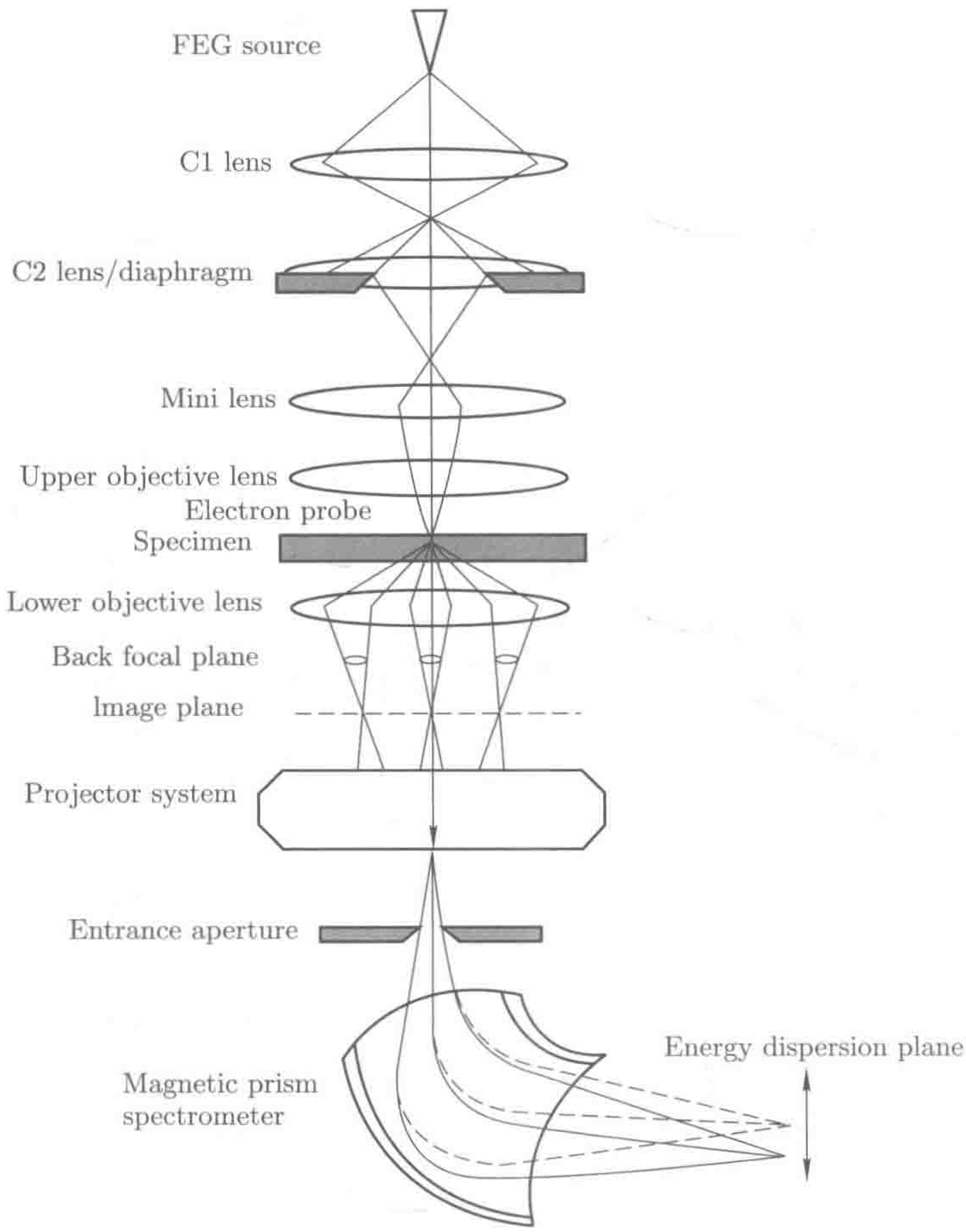

Fig. 1.1.1 A general ray diagram of conventional transmission electron microscopes.

tron beam is confined by a multiple-aperture-lens system before the electron beam reaches the specimen. Sometimes a mini lens or a combination of lenses is added to the microscope, together with the upper objective lens, for further confinement of the beam size and shape. Controllable parallel illumination is thus formed on the specimen by the lenses and apertures described above. 2) The objective lens and objective apertures constitute the imaging system. After the interaction between the electron beam and the specimen, scattered electrons interfere at the back focal plane of the objective lens to form electron diffraction patterns and at the imaging plane of the objective lens to form images of the specimen. Usually objective apertures are placed at or very close to the back focal plane so that the direct beam or a particular diffracted beam can be selected to form bright-field (BF) or dark-field (DF) images, respectively. 3) However, both the diffraction patterns and the images formed by the imaging system might still be too small to view, and thus a projection system, which is composed of several lenses, is required to significantly magnify the patterns and images for data detection and acquisition.

In addition, electrons that undergo inelastic scattering with the specimen are analyzed by a magnetic prism spectrometer to reveal their energy distribution in the electron energy-loss spectra formed at the energy dispersion plane of the spectrometer system. Most of the spectrometer systems are attached at the end of the electron paths, however some commercial TEMs have the spectrometer system incorporated in the design of the column.

In the following sections of this chapter, details of the illumination system, imaging system and projection system will be introduced in this sequence. Due to the importance and the uniqueness of the electron sources to the microscopes their description including classification and characterization of the electron sources are discussed in the next section. Moreover, the quality of the TEM data is critically dependent on the detectors. Thus the detectors with recent updates and applications will be described after the optics section. Different types of detectors and their functions in a TEM will be discussed in Section 1.4. For example, energy-dispersive X-ray (EDX; the X-ray is generated from specimen by the electron beam) spectroscopy, which is not shown in Fig. 1.1.1, plays a key role in charactering the heavy metal elements in materials with catalytic applications. Finally, a different but similar microscope using ion beams, as well as the details of their unique optic system, will be discussed in this Chapter.

1.2 Electron sources

The type and quality of electron sources are essential to the performance of a microscope and to the final results coming out from the TEM. Before using a TEM, a researcher should know the type of the electron source and the basic characteristics of the electron beam, such as how bright it is and the energy spread of the beam, in order to achieve their particular research purposes. Usually users of a TEM do not need to measure by themselves the characteristics of the electron source, which could be provided by the manufacturer or the instrument maintainer. For the above reasons, this section will focus on the types of the electron sources and the characterizations of the electron beam that is emitted from the gun assembly. The optics of a TEM is specifically designed for certain types of the electron sources. Therefore, the type of the electron source in one TEM is not interchangeable between thermionic and field emission kinds.

1.2.1 Types of electron sources

The types of the electron sources are determined by the physical mechanisms of electron emission from the gun tip materials. There are basically three kinds of electron emission in most of the TEM guns: thermionic emission, field emission and Schottky emission, where Schottky emission can be considered as a mixture of thermionic and field emission (Williams and Carter, 2009; Richardson, 2003; Murphy and Good, 1956).

Thermionic emission: Thermionic sources have often been called filaments and sometimes cathodes. If the material of the source is heated and electrons gain sufficient thermal energy to overcome the potential barrier at the material's surface, i.e., the material's work function ϕ, the electrons can be emitted from the surface of the source. The electron flow is described by current density J and has the following relationship with the heating temperature T in the Richardson equation

(Richardson, 2003):

$$J = AT^2 e^{-\frac{\phi}{kT}}$$

where k is the Boltzmann constant. The proportional coefficient, A, is called Richardson's constant, determined by the source material. The work functions of most metal materials are about a few eV. In order to have a large current of electron emission and a long lifetime of the electron source, a low material work function is required and the source should not melt or evaporate at the operating temperature. Williams and Carter's book shows a good comparison of the work function, operating temperature and lifetime etc., between different source materials. Tungsten and lanthanum hexaboride (LaB_6) crystals are the most common materials selected for thermionic TEM sources, mainly for their low work functions and high melting temperatures. On the other hand, thermionic guns are measured to have a saturate emission current and the operating temperature/heating current is set at the optimum value below the saturation condition in order to maximize the emission current and the source lifetime (Williams and Carter, 2009).

Field emission: A TEM with a field emission gun (FEG) costs much more than a TEM with a thermionic source. The mechanism of field emission is shown in Fig. 1.2.1. Electron emission of this kind is induced by an electrostatic field applied at the source (Fowler and Nordheim, 1928). There is a potential gradient such that

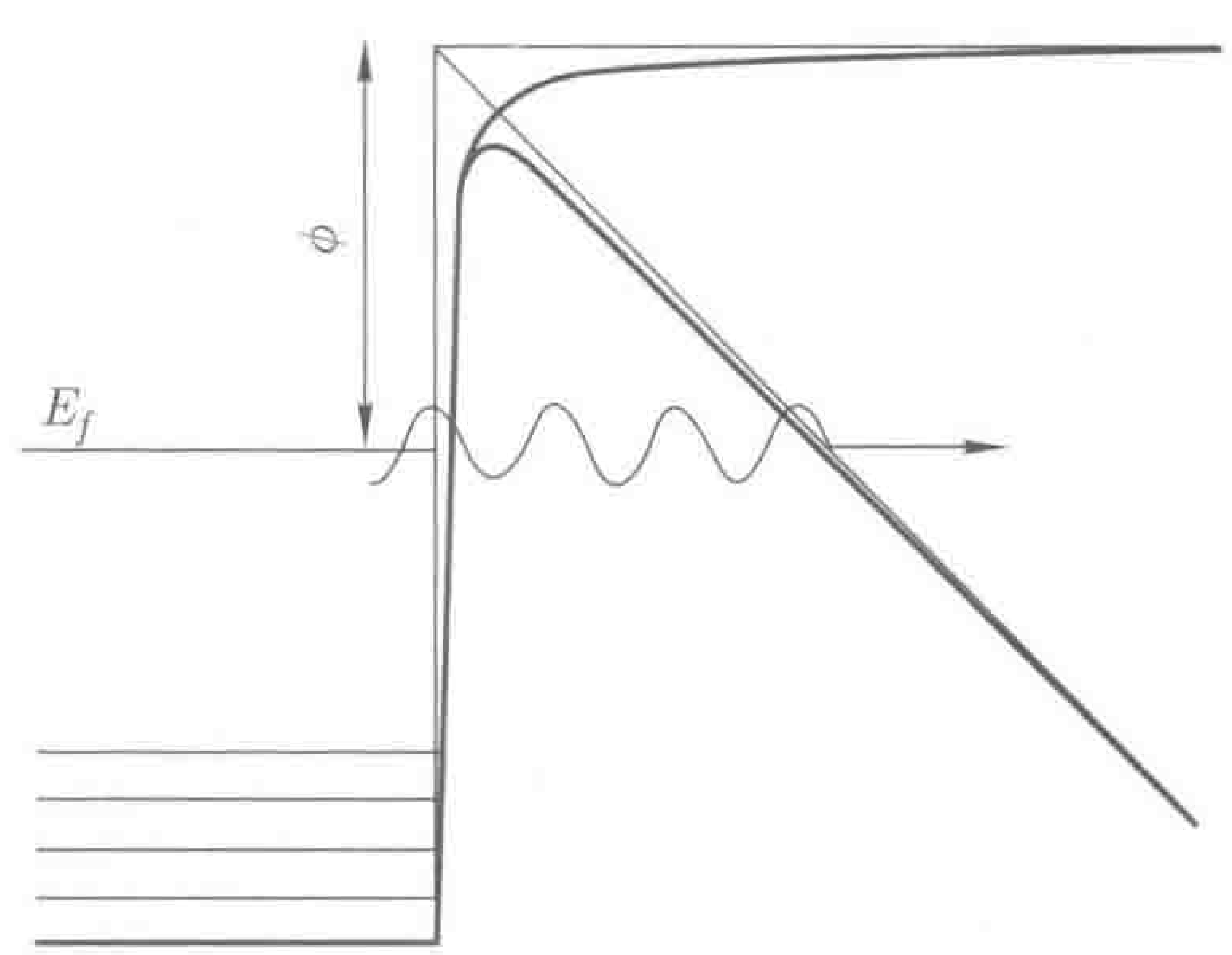

Fig.1.2.1 Principle of field electron emission by quantum tunneling of electrons from surface into vacuum induced by an electrostatic field.

the energy level at vacuum is tremendously lowered. Thus the energy barrier at the surface is narrow enough so that the electrons inside the source material have a certain probability to tunnel out and generate emission current.

Field emission takes place only when the electrostatic field is very high at the source. To produce high electrostatic fields, the source material is manufactured to be a needle tip because the sharper the tip is the higher the electrostatic field will be. Without help from thermal heating the emission is called cold field emission. Usually the cold field-emission source is made of single-crystal tungsten that is a sharp needle tip. If the electrons are heated and an electrostatic field is still applied at the tip, thermal energy can assist the electron escape over the reduced barrier and the emission current is significantly enhanced. This is known as Schottky emission or field-enhanced thermionic emission. Schottky emitters are the predominant source in modern TEMs. They are made of tungsten tips coated with a layer of zirconium oxide (ZrO_2) to improve the emission stability. The emission current from a Schottky emitter can be determined by Richardson equation with modification of the work function term.

The vacuum in the surrounding space of the cold field-emission gun should reach ultra-high vacuum (UHV; $< 10^{-9}$ Pa) level to maintain the gun tip in pristine condition without contamination or oxidation. However, as time goes by, contamination of the residual gas occurs at the tip surface of a cold FEG. In order to remove the contaminants accumulated at the tip, we need to flash the tip once or twice a day in practice by heating the tip in a very short time to evaporate the contaminants. No flashing is needed for Schottky FEG and thermionic sources.

Without regard to the cost, each of the three types of the electron sources has its pros and cons in terms of brightness, coherency and stability, which will be introduced in Section 1.2.2. The development of TEM technology includes finding new materials and establishing new types of the electron source, always pursuing better performance of the electron source with versatile functions. A new generation of ultra-bright electron sources has been studied and developed recently based on advanced materials. For example, carbon nanotubes have shown excellent field-emission properties to be good candidates for this purpose (de Jonge and van Druten, 2003). Furthermore, polarized electron source (PES) has been developed for many years, especially for low-energy (< 40 keV) electron microscopy. Recently such a technique was established in TEM with operating voltage ~20 kV at Nagoya University in Japan (Kuwahara et al., 2011). By modifying the setup of the illumination system of a conventional TEM, the instrument with PES has achieved a high level of electron spin polarization, quantum efficiency and large electron dose on the specimen. With PES, it is possible that the materials' magnetic structures that remain undetectable by conventional TEM will be unveiled by the spin-polarized TEM in the future.

1.2.2 Characteristics of electron beams

The electron sources introduced above have clear definitions that are specifically referred to the electron emitter. However, electron beams are more complicated than simply the electron flow out from the emitter. Indeed, a TEM needs a gun assembly to have the electrons accelerated and focused at a crossover. Once an electron beam is formed, we are able to characterize the beam in terms of its brightness, coherency and stability. The outcome results, including high resolution TEM images, electron diffraction, electron energy-loss spectroscopy, etc., by using a TEM critically depend on these characteristics of the electron beam.

Gun assembly: Fig. 1.2.2 shows a schematic diagram of a gun assembly of a thermionic source. Modern TEM instruments with thermionic sources use LaB_6 crystal as the filament. The high tension is applied between the filament and the anode to accelerate the electrons with the anode at the earth potential. Wehnelt cylinder acts as the first lens in a TEM along the electron path. Unlike the magnetic lens, it is indeed an electrostatic lens. The role of the Wehnelt cylinder is to focus the emitted electrons at a crossover before the anode by applying an optimum bias at the Wehnelt cylinder. The purpose of the Wehnelt bias is to maximize the beam brightness. The beam's diameter at the crossover is d_0. The emission beam that goes through the anode has a divergent semi-angle α_0 and the current i_e. The beam from this point can be considered as the object of the first lens in the illumination system of TEM optics.

On the other hand, the gun assembly of an FEG has two sets of anodes. The first anode has a positive potential of a few kV with respect to the tip, which enhances