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# Controlled Atmosphere Transmission Electron Microscopy

## Principles and Practice

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# Controlled Atmosphere Transmission Electron Microscopy

# Preface

Electron microscopy has long been the de facto standard for materials scientists to obtain structural information that now approaches the atomic scale. Scanning electron microscopy and transmission electron microscopy, along with the many peripherals now available, provide information about three-dimensional structure, particle size and morphology, layer thickness, as well as elemental, chemical, and magnetic information, to name just a few characteristics. Traditionally, electron microscopy has been performed in high vacuum or even ultrahigh vacuum, in order to prevent sample contamination, preserve the performance of the electron source, and maintain coherence of the electron wave. However, for several applications, observing samples under vacuum conditions is far from a realistic scenario when one considers the actual working environment of the material under study.

To remedy this situation, the controlled atmosphere microscope was conceived. Using various adaptations either to the sample holder or to the microscope, a certain volume of gas can be maintained around the sample without compromising the microscope itself. Such adaptations were suggested previously by Ernst Ruska, the inventor of the transmission electron microscope in the 1940s. Since then, several experimentalists have modified electron microscopes to allow for gas entry.

Over the last three decades, the technique has become much more mainstream and instruments are now commercially available. Inspired by the developments of Boyes and Gai, the concept of differentially pumped electron microscopes now allows samples to be exposed to a gaseous atmosphere of the order of 1000 Pa. The concept has now made its way to the newer microscopy platforms and high-end microscopes.

There are many scientific challenges that can be addressed by electron microscopy. Among these are the structure and stability of two-dimensional materials such as graphene, which has been suggested as a future candidate to replace silicon for semiconductor devices when properly structured, the active state of catalytically active materials, or the structure of semiconducting devices with electrical bias applied in a gaseous environment. In order to move forward in the understanding of

the working state of these materials, a multitude of complementary characterization techniques should be applied.

This text is aimed at graduate students, but the experienced microscopist should also find it to be a valuable reference book. The book describes the development and construction of the environmental transmission electron microscope, or ETEM for short, as well as the peripherals such as cameras and detectors that allow for the thorough and exhaustive characterization of a sample. It is supplemented by several example chapters highlighting the use of the technique for different scientific cases.

We are grateful to a large number of people for fruitful discussions and providing material for the book.

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# Chapter 1
# A Brief History of Controlled Atmosphere Transmission Electron Microscopy

**Ai Leen Koh, Sang Chul Lee, and Robert Sinclair**

**Abstract** In this chapter, the development of controlled atmosphere conditions to study gas-solid reactions inside the transmission electron microscope (TEM) will be presented. The two successful approaches to achieve this, namely the use of electron transparent windows and the incorporation of small-bore apertures inside the TEM combined with differential pumping, will be discussed. Finally, we will also describe the state-of-the-art instrumentation available today to study the behavior of nanomaterials in reactive gas environments, which have been largely brought about by the development of aberration correctors, monochromators, specialized TEM holders, as well as faster and more sensitive spectrometers. Examples that highlight the diverse applications in this field will be provided.

## 1.1 Introduction

It was clear to the original pioneers in the 1930s or so that an electron microscope requires a background high vacuum. Indeed, once the transmission electron microscope (TEM) was being applied to examine the microstructure of metals and alloys, specimen contamination, generally from breakdown of residual hydrocarbons in the TEM atmosphere, became a real issue. This was further exacerbated by the introduction of small probe work in the 1970s for microanalysis of chemical composition. The historical trend therefore required increasingly good vacuum conditions especially in the specimen and electron gun chambers.

This evolution clearly contrasts with the desire to study materials in their natural environment, such as atmospheric gaseous conditions or even in liquids. Accordingly, methods needed to be devised whereby the overall microscope vacuum environment could be maintained while viewing the sample in a controlled

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environment. In this chapter, we will outline the historical progression of these developments alongside the advances in TEM itself.

The main purpose of such experiments is to derive as much information as possible about material interactions with the environment, whether under ambient conditions such as in corrosion or in vivo biological processes, or extreme conditions as might be required for catalytic reactions or non-equilibrium liquid phase processes. This clearly represents a significant broadening to the scope of in situ TEM observations whereby one examines the changes to a material system under a controlled external stimulus such as heating, cooling, electrical bias, and mechanical stress. The behavior of the specimen under high-vacuum conditions already has its own merit as many manufacturing processes are carried out in vacuum, especially for the semiconductor industry. However, the added value of the controlled environment has extensive implications. Indeed, a recent analysis of in situ TEM publications (Sinclair 2013) showed a noticeable increase in recent years attributable mainly to environmental TEM (ETEM) studies, as illustrated in Fig. 1.1, a trend which continues as noted later.

Historically, the interest for environmental chambers inside the electron microscope came about as a means to allow wet specimens to be examined in vivo (Marton 1934) while at the same time, minimizing any possible damage and artifacts associated with conventional biological specimen preparation. The presence of an environmental chamber was also thought to be advantageous in reducing specimen contamination produced by the electron beam and residual hydrocarbon gases present in the microscope. In the 1970s, the reason to pursue this expanded to include the study of chemical reactions at elevated temperatures, as described later.

In 1935, Marton (1935) suggested two methods in which gas pressure and composition could be controlled inside the electron microscope. The first involved modifying the specimen holder by placing a pair of electron transparent "windows" above and below the specimen to seal it, and the gas atmosphere, from the column. The second involved modifying the objective pole pieces of the electron microscope, by placing a pair of small apertures above and below the specimen (see also later papers by Ruska 1942, and Abrams and McBain in 1944). Gas leakage into the column is then limited to that which escapes via the apertures. These two approaches have evolved separately, and successfully, alongside the TEM and are referred to as the closed cell ("window") and "apertures," respectively, in this chapter.

In the 1970s, the term "controlled atmosphere electron microscopy" (CAEM) was coined by several groups including Feates et al. (1970) and Baker (Baker and Harris 1972; Baker 1979). Despite the sub-nanometer imaging resolution of the TEM (about 0.25 nm or so in the 1970s), its value was found to be limited because materials can only be viewed in a vacuum environment, and the tactic had been to examine a specimen before and after reaction. Of significant interest is the actual appearance of the specimen during reaction. Thus, CAEM is used to describe the technique in TEM in which reactions between gases and solids are studied at very high magnifications, while they are taking place, under realistic conditions of temperature, pressure, and reaction time (Baker 1979). The key design feature of

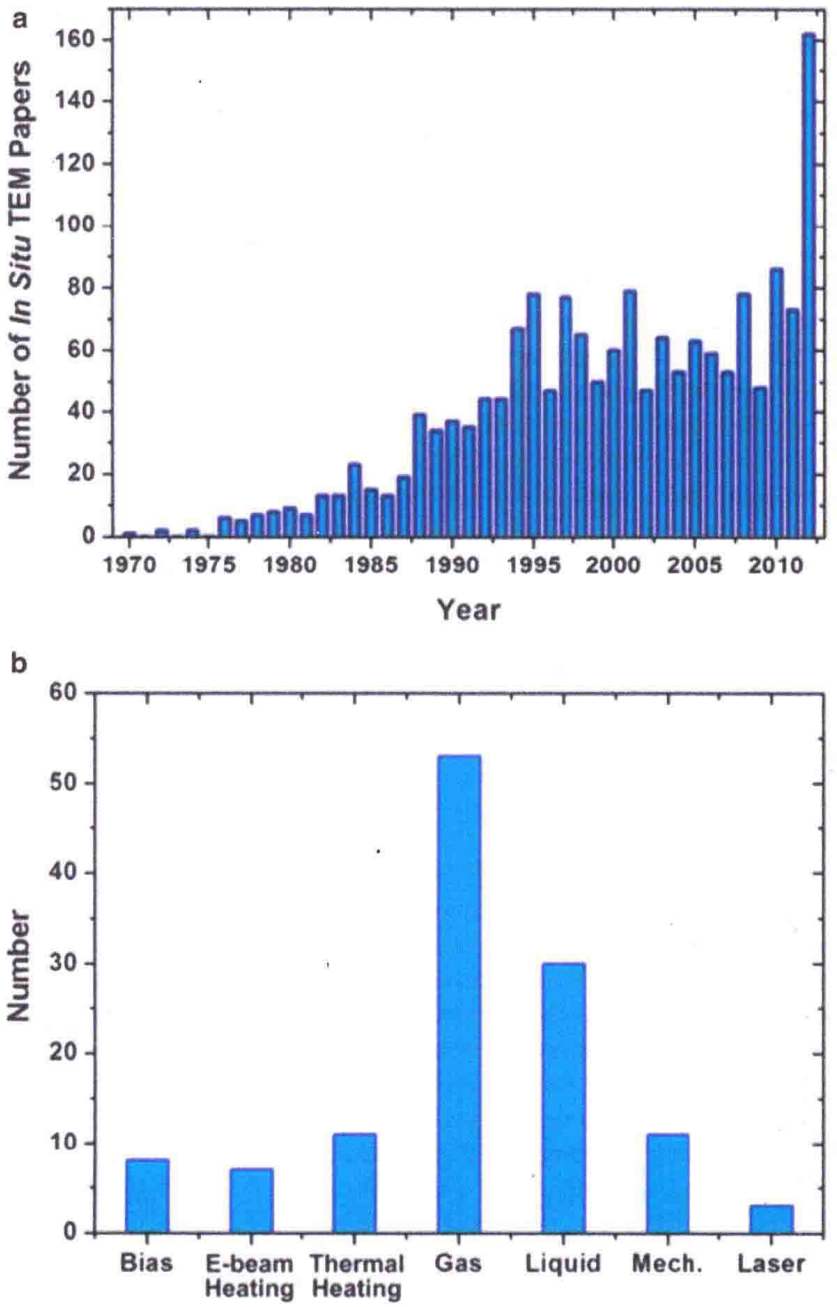


**Fig. 1.1** (**a**) Number of publications identified using the keywords "in situ", "transmission electron microscopy" and "TEM", showing a steady increase over the last 20 years and a marked increase in 2012; (**b**) Breakdown by various subcategories of in situ papers presented at the 2012 Microscopy and Microanalysis Conference (USA) and the 2012 European Microscopy Conference (UK). These subcategories are in situ electrical biasing, electron beam heating, thermal heating, gaseous environment, liquid environment, mechanical loading, and laser stimulation. Reprinted with permission from Sinclair (2013)

CAEM is the ability to operate at high pressure in the specimen region ($3 \times 10^4$ Pa, or 225 Torr), while maintaining very low pressure ($10^{-3}$ Pa, or $10^{-5}$ Torr) in the rest of the microscope.

Since the 1970s, there have been a number of comprehensive reviews highlighting the developments in the field of CAEM, or environmental transmission electron microscopy (ETEM) as it is more commonly known today, as well as its diverse applications. Readers can refer to the articles and book chapters by Flower (1973), Allinson (1975), Butler and Hale (1981a), Sharma (2001, 2005), Sharma and Crozier (2005), Gai et al. (2007, 2008), Jinschek and Helveg (2012), publications from the Technical University of Denmark (Hansen and Wagner 2012; Wagner et al. 2012), Jinschek (2014), the Takeda group from Osaka University (Takeda et al. 2015) as well as their references therein. We have elected to present the historical developments in this field in a chronological sequence, with an emphasis toward gas-solid reactions in the TEM. For comprehensive reviews and applications for liquid-solid reactions and interactions, articles and book chapters by Parsons (1974), Parsons et al. (1974), Butler and Hale (1981b) and de Jonge and Ross (2011), and their references therein, are good starting points. A later chapter of this book also discusses liquid phase electron microscopy techniques and applications. We conclude with a number of examples spanning from the 1970s that highlight the diverse applications in this field, and where we think the future in this area lies.

### *1.1.1 Window Approach*

The first approach to attain environmental conditions inside the transmission electron microscope is by use of a specialized specimen holder combined with a windowed cell. A pair of electron transparent "windows" is placed above and below the specimen to seal it, and the gas atmosphere, from the column. In this method, containment is total—the windows completely seal off the specimen and its surrounding gas environment so that the high vacuum of the microscope remains unchanged. The windowed design has the advantage of working with higher gas pressures (depending on the strength and thickness of the windows). Wet samples can also be imaged with this setup. The reader can refer to a later chapter in this book which describes the developments in the field of liquid cell electron microscopy.

There are several advantages using a specialized holder combined with windowed cells. First of all, the holder can be used in different TEMs without modifications to the microscope column. To date, this approach is the only one that is capable of achieving ambient pressure conditions. However, the specimen geometry and the field of view are usually significantly smaller than in a conventional TEM, and the sample can only be moved or tilted together with the windows since it is sandwiched between them. Additional scattering information from the (usually amorphous) window material is superimposed on the image and

diffraction pattern of the sample, leading to compromises in image resolution. The interaction also hinders the acquisition of energy-dispersive X-ray spectroscopy (EDS) signals. The thin films used as windows should have low gas or vapor permeability, and must be able to withstand the pressure difference between the microscope vacuum and the design pressure of the holder device when mounted. There is the possibility of windows rupturing inside the microscope during an experiment, leading to the degradation of the electron column and source vacuum.

The earliest documentation of a closed cell for electron microscopy was by Marton in 1935, who attempted to use two 0.5-μm aluminum foils as windows. In 1944, Abrams and McBain constructed a closed chamber out of two perforated platinum disks covered with plastic film windows less than 100 nm thick, and sealed to vacuum-tightness using wax. It could withstand an atmospheric pressure difference between the inside of the cell and the remainder of the electron microscope. Using this setup, the authors were able to observe the movement of liquid and bubbles inside the electron microscope. However, they found water of one micron thickness to be "practically opaque to electrons." The lack of fast, continuous recording capability also precluded the possibility of the observations of Brownian movement in colloidal particles. Moreover, the cell was completely sealed and hence capable of operating at only a single (fixed) pressure.

Variable-pressure controlled dynamic experiments were not possible until cells were designed such that a connection existed between the gas space around the specimen and the outside of the microscope. Heide (1962) constructed a specimen holder for a Siemens Elmiskop I electron microscope using two specimen grids with the flat surfaces facing each other. The separation of the two grids was controlled by pieces of thin metal foil. Both specimen grids were covered with a supporting film of low contrast, which could withstand the gas pressure over the central openings, and one of the grids served at the same time as a supporting film for the specimen. The gas inlet was sealed against the microscope column vacuum when the holder was inserted inside the microscope, and gas was injected through a tube placed in the opening of the column along the specimen holder. Air or gas pressures could be varied up to atmospheric pressure with this design.

There were a number of limitations to these earlier basic designs of the closed cells, as highlighted in the review article by Butler and Hale (1981a):

1. The single gas line does not enable experiments to be performed with gas flowing continuously over the specimen.
2. The relatively poor metal-to-metal seal between the apertures and the cartridge results in some leakage into the column.
3. The specimen cannot be heated unless it is supported independently of the windows.

Improvements in these three areas were realized in later designs. Escaig and Sella (1969) incorporated a heater and twin gas lines in their holder so that the temperature of the specimen could be varied while gas continuously circulated over it. Earlier window cells were made out of plastic which were generally not suitable

for high temperature work because of damage during heating and were thus employed mainly in the biological field to provide a hydrated environment for in vivo studies. Escaig and Sella (1966, 1968, 1969) made improvements to the windowed cells that consist of triple layers of carbon, nitrocellulose, and silica (facing the specimen), maintaining a gap of approximately 1 mm between window and specimen, which was successfully employed for in situ oxidation of copper, tungsten, and titanium (Escaig and Sella 1972).

Another limitation of the windowed cells is that they tend to bulge under pressure, resulting in a longer electron beam path length at higher pressure. In order to reduce the beam path length and stabilize the films, Fukami and Adachi (1965) developed plastic micro grids consisting of holes of 0.1–10 μm in diameter which were used as the supporting frame for a continuous carbon film. The plastic micro grids were also used as substrates in the production of micro metal grids with thicknesses >30 nm which were stronger and more resistant to heat than their plastic counterparts (Fukami et al. 1966, 1972).

In the late 1960s and 1970s, the development of high-voltage (1 MeV) electron microscopes (HVEM) led to enclosed gas reaction cells with thicker, stronger windows being developed. Dupouy (1968) designed a single gas-line room temperature device with windows constructed out of carbon/colloidion of 60 nm thickness. Twin gas-line top entry designs capable of a range of temperatures were also constructed by Fujita et al. (1976) and Doi et al. (1977). Fujita et al. (1976) built a holder for gas and liquid experiments on a 3MV-class electron microscope, which could be used in the temperature range of −100 to 1000 °C and up to a pressure close to two atmospheres. The window cell consisted of three films whose materials could be vapor-deposited aluminum, $SiO_x$ and carbon films, depending on the purpose, and they were supported with metal (Ni) of 300 and 400 mesh in size. The specimen was set directly on the center Ni mesh, or on a vapor-deposited film coated on the Ni mesh. The specimen was directly heated by the application of a current to the Ni mesh. The increased penetration ability of the HVEM led to a significant improvement in contrast at these high operating voltages. Specimen damage was found to depend on the heat conductivity of the supporting film, and decreases when the supporting film has high heat conductivity. The use of crystalline window materials of higher strength also became a consideration for use with HVEM, and single crystal corundum which was ion-beam-thinned to ~180 nm was one possible material option (Allinson 1970). In window-limited holders, the strength and thickness of the window material determines the maximum gas pressure and, in principle, pressures as high as atmospheric pressure can be attained, although the thickness of window material needed to sustain such pressures may not be compatible with instrument performance.

Progress in the development of closed window cell systems was stalled until the 2000s, when holders based on micro-electro-mechanical systems (MEMS) technology for both gas (Creemer et al. 2008; de Jonge et al. 2010; Yokosawa et al. 2012; Yaguchi et al. 2011; Allard et al. 2012; Alsem et al. 2012) and liquid (Williamson et al. 2003; de Jonge et al. 2009; Ring and de Jonge 2010; Klein