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Successful application of Low Voltage Electron Microscopy to practical materials problems

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ABSTRACT

Low-voltage High-Resolution Electron Microscopy (LVHREM) has several advantages, including increased cross-sections for inelastic and elastic scattering, increased contrast per electron, decreased delocalization effects and reduced knock-on damage. Imaging at differing voltages has shown advantages for imaging materials that are knock-on damage sensitive. We show experimentally that different materials systems benefit from low voltage high-resolution microscopy. There are advantages for imaging single layer materials such as graphene at below the knock-on threshold; we present an example of imaging a graphene sheet at 40 kV. We have also examined mesoporous silica decorated with Pd nanoparticles and carbon black functionalized with Pd/Pt nanoparticles. In these cases we show that the lower voltage imaging maintains the structure of the surrounding matrix during imaging, whereas aberration correction provides the higher resolution for imaging the nanoparticle lattice. Perhaps surprisingly we show that zeolites damage preferentially by ionization effects (radiolysis). The current literature suggests that below incident energies of 40 kV the damage is mainly radiolitic, whereas at incident energies above 200 kV the knock-on damage and material sputtering will be the dominant effect. Our experimental observations support this conclusion and the effects we have observed at 40 kV are not indicative of knock-on damage.

Other nanoscale materials such as thin silicon nanowires also benefit from lower voltage imaging. LVHREM imaging provides an excellent option to avoid beam damage to nanowires; our results suggest that LVHREM is suitable for nanowire-biological composites. Our experimental observations serve as a clear demonstration that even at 40 keV accelerating voltage, LVHREM can be used without inducing beam damage to locate dislocations and other crystalline defects, which may have adverse effects on nanowire device performance. Low voltage operation will likely become the new mode of imaging for many electron microscopes, with the instrument being, in essence, tuned to extract all the information possible from each electron that transits the sample.

1. Introduction

Imaging with electron microscopy directly relates to the physics of the interactions between the electron beam and sample. Energetic electrons are described as “ionizing radiation,” the general term used to describe radiation that is able to ionize or remove the tightly bound inner shell electrons from a material. One of the advantages of electron microscopy is that it produces a wide range of signals including secondary electrons and X-rays; though it also has a disadvantage from the perspective that the sample is “ionized” by the electron beam and possibly structurally damaged, which depending on the accelerating voltage occurs in a number of different ways. The advantages of using a lower accelerating voltage for the electron beam are that the energy, and thus the momentum, that can be transferred to sample from the electron is reduced. This, however, has the unwanted effect of reducing the signal-to-noise ratio in images. However, with recent improvements in detectors and the use of aberration correctors, the signal to noise and the resolution of the final image can not only be maintained but can actually be improved.

2. A historical perspective

The early steps in the development of the electron microscope in the 1930s and 1940s by different research groups led ultimately

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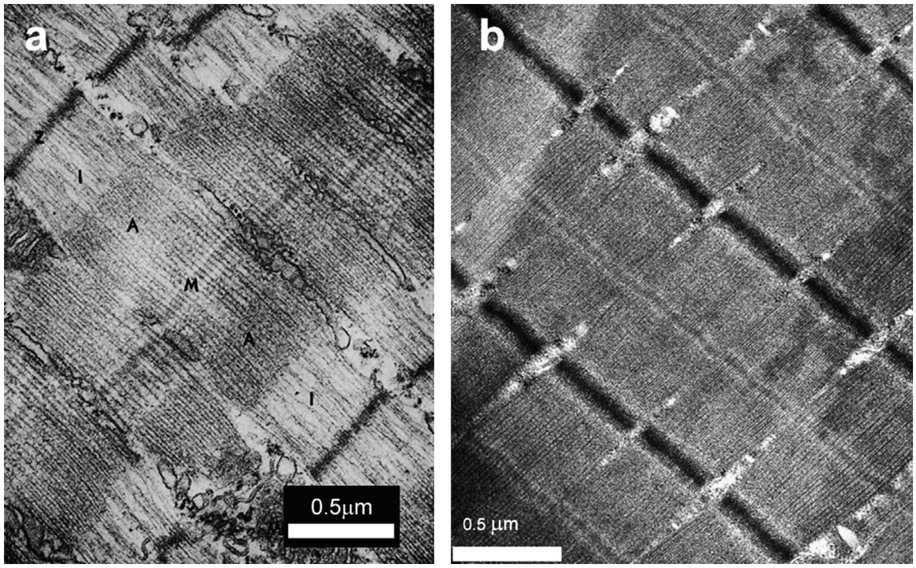

Fig. 1. (a) 80 keV TEM image of frog muscle section, imaged with JEOL JEM-7 1964 (Image courtesy of JEOL Japan LTD.) and (b) contemporary 80 keV Cs-TEM image of rat muscle section imaged with an aberration corrected Zeiss Libra TEM.

to the development of two distinct groups of instruments: the scanning electron microscope (SEM) and the transmission (or scanning transmission) electron microscope (TEM and STEM). The early microscope designs by Knoll and Ruska [1] showed transmission electron images of solid surfaces at 10–16 × magnification. In 1936 through his contract with the company Siemens, Manfred von Ardenne started the development of a STEM, mainly to avoid detrimental effects of chromatic aberration during observation of thick specimens in TEM. The work by von Ardenne, though interrupted by the events of World War II, nonetheless established a theoretical and design background for future SEM and STEM development, particularly regarding our understanding of beam/specimen interactions, the effect of accelerating voltage on resolution, as well as detector design and positioning within the microscope [2–4].

From 1938 to 1942, Zworykin at the Radio Corporation of America (RCA) headlined parallel SEM and TEM development projects that resulted in a SEM with accelerating voltage of 800 V [5]. However, poor vacuum in the system significantly impacted the resulting micrographs, and the quality of the recorded images was disappointing as they yielded mostly topographic contrast and no meaningful compositional information. The work on SEM instrumentation development continued in Cambridge University in the early 1950s [6,7]. Thornley successfully developed the first low voltage SEM [8] in Oatley's lab at Cambridge University in the early 1960s.

Over the years, significant improvements in electronics, vacuum and electron column design, as well as detector technology have improved instrument performance to the level where the resolution at 1 kV is on the order of 1–2 nm for high-end field emission (FE) systems [9]. The recent addition of monochromators to aberration corrected TEM and STEM instruments have further improved their performance for both high and low accelerating voltage applications [10–12].

From a historical perspective, electron microscopy imaging at low voltage was typically geared toward biological samples prone to specimen damage at higher accelerating voltages, keeping in mind that the limiting factor in resolution of traditionally prepared samples (via fixation, embedding, staining, and microtoming) is the sample thickness itself and not the microscope optics. There is little practical difference in imaging a microtomed biological thin section prepared in a traditional way at 80 keV in 1964 as compared to today, as shown by Fig. 1. The figure shows a comparison image of a thin section of muscle tissue recorded at 80 kV in 1964 without correction and the modern corrected image. There are, of course, many subtle differences between the two images and, as expected, the aberration corrected image appears sharper and reveals more details. Interestingly, from a biological and diagnostic viewpoint, the non-corrected image is equally useful. In reality, of course, biologists have been using low voltage imaging for decades and aberration corrected microscopes are not much of an advantage for basic thin section imaging where the resolution is limited by the thickness and staining of the sample, as shown by our example. This is not to say that biological sciences have not benefited in recent years from higher resolution instruments, especially for protein and virus imaging with resolutions of 0.3 nm or better [13,14]. Traditionally, the development of higher voltage microscopes has been dictated by materials scientists looking for atomic and sub-atomic resolution. Solid crystalline samples can be prepared to produce very thin electron-transparent specimens, thus facilitating the quest for atomic structure phase-contrast imaging. High voltage TEM's have made way for aberration corrected TEM's with even better resolution than could have been foreseen in the 1960s. This article will review the benefits of current state-of-the-art low voltage microscopy for materials science applications. Higher power in terms of resolution has been the typical benchmark by which to measure the development of the electron microscope both for the SEM and the TEM; however, with new instrumental advances it now becomes possible for an instrument operating at a greatly reduced voltage to not only provide the same resolution but also improve contrast at the same time. The purpose of this article is not to cover every single subject under the umbrella of “low voltage microscopy” but rather to target practical aspects of this emerging field as it pertains to the imaging techniques in widely used commercial instruments such as TEMs.

3. Low Voltage Electron Microscopy for materials analysis

3.1. Graphene

Graphene is a crystalline form of carbon defined as a hexagonal arrangement of carbon atoms forming a one-atom thick planar

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