Development of an environmental high voltage electron microscope and its application to nano and bio-materials

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Abstract. Environmental transmission electron microscopy has recently emerged as topics of great interest as well as ultra-high resolution electron microscopy using aberration correctors. Current research in this area has been focusing on dynamic observation with atomic resolution under gaseous atmospheres and in liquids. Nagoya University has been developing a new 1-MV high voltage (scanning) transmission electron microscope, which can be used to observe nano-materials under conditions that include the presence of gases, liquids and illuminating lights, and it can be also used to perform mechanical operations to nm-sized areas as well as electron tomography and elemental analysis by electron energy loss spectroscopy.

1. Introduction
Energy and environmental problems are the important concerns in our future society. Attention must be paid to these concerns from the first step of the development of new materials and devices. To properly assess the development, the test samples need to be analysed under actual usage/reaction conditions. The necessity of environmental and in-situ observation/analysis is increased for structural and elemental estimations[1]. Transmission electron microscopy (TEM) is one of the useful methods for the analysis of nano-materials and nano-devices with atomic dimensions. There are, however, several limitations in TEM such as (1) the requirement of small sample thickness, (2) observation in vacuum, and (3) projected images. As a resolution of the problems, we have been developing a new high-voltage(HV) scanning transmission electron microscope equipped with an open-type environmental cell, large tilting holders, high-sensitivity TV cameras and an imaging filter for electron energy loss spectroscopy(EELS)[2]. It was named HVEM for reaction science(RSHVEM). In this paper, we describe the development and some applications.

2. Instrumental development
Figure 1 shows a front-view of the RSHVEM (JEM-1000K RS). The height of the high-voltage tank is 6.7 m, and the length of the microscope column is 3.6 m. The electron gun uses a LaB$_6$ thermionic cathode, whose chamber is evacuated independently by two ion pumps to improve the vacuum and increase the life time of the cathode. The three-stage condenser lens system focuses an electron beam to a diameter of less than 1 nm, which enables bright-field and dark-field STEM and elemental-mapping STEM using EELS.
The most important specification of the RSHVEM is high-resolution observation at 1 MV under gas pressures, for example, 13,300 Pa (=100 Torr). The other specifications are a point-to-point resolution in TEM of less than 0.15 nm, in STEM, less than 1 nm, an energy resolution in EELS less than 1.5 eV, and the use of dedicated sample holders for 3D tomography without the missing edge problems. In the RSHVEM, we adopted the open-type environmental cell in the pole-piece gap with help of differential pumping system. For this purpose, we developed a new side-entry sample holder without a stopper, and enabled the environmental cell to be inserted from the side of the stopper. When the cell is extracted, the instrument can be used as an ordinary HVEM under vacuum conditions. The image recording system for the RSHVEM consists of three CCD cameras for recording low magnification images and electron diffraction patterns (Hamamatsu; 2k x 2k), for high-resolution images (ORIUS; 2k x 2k), for EEL spectra and energy-filtered images (Gatan; imaging filter (GIF); 2k x 2k). Figure 2 shows a high-resolution TEM image of a [110]-oriented cubic silicon carbide (SiC) crystal recorded at 1 MV, where the dumbbell structure composed of silicon (Si) atomic columns and carbon (C) columns is clearly resolved. The separation of the dumbbell is 0.109 nm. For EELS at 1 MV, the zero-loss peak of a width of 0.87 eV was recorded, which proved a good performance of the GIF for spectrometry and a high stability of the total electric system of the RSHVEM. The instrument showed that 200 and 220 lattice fringes of gold are imaged at 11,000 Pa of nitrogen gas[2].

3. Examples showing unique features of the RSHVEM

(1) Copper particles in oxygen and hydrogen

Copper (Cu) particles were prepared by the vacuum deposition of Cu onto commercial silica (SiO$_2$) powders inside the RSHVEM. A specially designed sample holder with two filaments, one for sample support and heating, and the other for metal deposition, was used[3]. First, in-situ oxidation was performed at 700 C through the introduction of oxygen gas at 1 Pa. Identification of formation of copper mono-oxide was made from lattice images and EELS spectra. Reduction process was also observed dynamically. During the oxidation and reduction processes, the particle shape was similar[2]. Similar observation for gas reaction was made on porous gold catalysts in various gases including CO gas[4].

(2) Fracture process of Cu/Si interfaces in hydrogen

The mechanical strength of such interfaces is sensitive to foreign gas atoms which are diffusively supplied from an external environment. In particular, the effect of hydrogen on the interfacial...
strength is an important issue to study because hydrogen behaves as a typical embrittle element. Using the RSHVEM, we can realize in-situ observation of the fracture process of a semiconductor/metal interface in a LSI device in hydrogen gas.

The experimental TEM sample including a micro-cantilever was a sputter-deposited multilayer prepared via the focused ion beam(FIB) instrument, as shown in Fig. 3. The sample was mounted on a gold wire and attached to a piezo-driven nano-indenter holder (Nanofactory). The hardest SiN layer was pressed with a diamond indenter tip (upper-right) to avoid plastic deformation at the loading point. The atmospheric gas was a mixture of N$_2$/H$_2$ gases(95:5), and the pressure was 300 Pa. The in-situ observation revealed that the fracture initiated at the upper edge of the Cu/Si interface as shown in Fig. 3. Simultaneously, we measured the applied load; the measured fracture load of the Cu/Si interface was 75.3 μN. Such quantitative data is compared with calculation using the finite element method (FEM)[5].

(3) Elemental and chemical mapping using a post-column energy filter

We have studied semiconductor interfaces and oxide multilayers using EELS with help of multivariate curve resolution (MCR) method[6]. HVEM is advantageous for small beam broadening in samples, which is related to deterioration of the image resolution of energy filtered TEM images. The data demonstrate that energy-filtered (EF) images with better spatial resolution can be obtained with a shorter recording time using core-loss edges of a lower-energy region compared with those obtained by medium-voltage instruments. Higher voltages increase the mean free path (MFP) for the inelastically scattered electrons, and facilitate the low-loss region to utilize for EF imaging.

(4) Three-dimensional reconstruction in RSHVEM

Other characteristic feature of the RSHVEM is a tomographic imaging without so-called missing edge(or cone) problems. By using a dedicated sample holder with 360 degree rotation, we observed carbon micro-coils(CMC) made from heat-decomposition from acetylene gas with iron or nickel catalysts[7], and studied the growth process from three-dimensional data of the coil. The 3D electron tomography of biological samples is also advantageous in HVEM because of its higher transmittance of electrons. We have observed cells and chromosomes of rat and yeast of a few μm size without slicing[8].

The RSHVEM incorporates scanning-image functions for STEM. Fig. 4 shows a bright-field (BF) STEM images of a yeast cell. We used the budding yeast (Saccharomyces cerevisiae) cell to observe the structure of a whole cell. The sample was embedded in epoxy resin with 1 μm thickness after being chemically fixed. Using these images, the 3D reconstruction was successfully realized[9]. HV-STEM tomography has shown the
potential to visualize a whole cell structure clearly. This is because STEM avoids the deterioration of images caused by inelastic scattering in membrane films, embedding resins and gas atmospheres.

4. Trail of 'in-place observation' for reducing the effects of irradiation

One of the most important problems to be considered in environmental electron microscopy is the effect of irradiation by ions of atmospheric gases produced by electron irradiation inside the cell. This effect increases with increasing gas pressures. Here we propose 'in-place observation' or 'in-vestigio' observation as one of the solutions to this problem, where electron beam is timely switched off during the chemical reaction between samples and gases by beam blanking. The RSHVEM is equipped with a reliable blanking system. The blanking is performed with electrostatic deflectors above the third condenser lens. We have succeeded in performing the 'in place observation' of (200) lattice fringes of a gold film on the TV screen of the present instrument at 1 MV without a large amount of sample drift[2].

5. Conclusion

In the present paper, the characteristic features of a new HVEM for reaction science were described as well as its experimental data, particularly focusing on mechanical operation in hydrogen atmosphere, 3D tomography by using STEM mode at 1 MV. Finally, we emphasize the importance of 'in-place observation', where the electron beam was smartly blanked during chemical reactions on various kinds of advanced materials to minimize the effects of irradiation of electrons and ions caused by incident electrons.

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