In-situ Gas Injection-Heating Atomic Resolution TEM for Nanomaterials

X.F. Zhang[*]

[*]Hitachi High Technologies America, Inc., 5100 Franklin Drive, Pleasanton, CA 94588, USA,
xiao.zhang@hitachi-hta.com

ABSTRACT

In-situ gas environmental transmission electron microscopy (E-TEM) capability was developed based on a Hitachi 300 kV high-resolution transmission electron microscope (H-9500) combined with a Hitachi gas injection-heating sample holder. This simple but high performance system allows for in-situ TEM dynamic observation and chemical analysis of nanomaterials at elevated temperatures with gas environment, and most importantly on an atomic resolution. Various nanomaterials were studied to reveal their structural responses at high temperatures under gaseous conditions. The development of this atomic resolution, in-situ gas-heating TEM system offers an affordable platform for a broad range of user facilities in academic and industry fields to perform gas-solid interaction studies.

Keywords: E-TEM, in-situ gas-heating, atomic resolution

1 E-TEM INTRODUCTION

In-situ E-TEM has been well recognized for its irreplaceable role in performing dynamic observation and analysis of gas-solid interactions [1, 2]. The purpose of the E-TEM is to introduce gas or liquid atmospheres into the sample chamber of a transmission electron microscope to study the interactions between sample and gas or solvent. Since TEM works at high vacuum, introducing gas or solvent in the sample area are realized in two typical ways in E-TEM systems today.

The first method is to seal a sample in an environmental cell (E-cell) confined by electron transparent windows. The window materials need to be nonporous and sufficiently strong to accommodate liquid or gas pressure, and should not be degraded in the environment and by electron beam. Weak electron diffraction from the window materials is also required so to avoid interference with the electron diffraction from sample. Currently the windows are typically made from amorphous carbon or amorphous silica a couple of tens nanometers thick. The advantages of this window type E-cells include simple design and low cost because only regular TEM system is required. It is also good for working with both gas and liquid environments, and the gas pressure can be as high as 300 torr (half atmosphere). Large-angle electron diffraction is obtainable. However, the total thickness of sample, windows, and gas path deteriorates the image resolution, therefore atomic resolution becomes very difficult to achieve if not impossible. Sample tilting makes the situation even worse. Heating sample in a microscope is another big concern because window materials may be damaged and broken at elevated temperatures.

The second method is mainly for providing a gas environment without a confined cell. Specially designed differential pumping system is added to a microscope. In this modified TEM system, two (or more) pairs of restricting apertures above and below the sample area replace the nonporous windows in the window type E-cells to divide up the pressure drop between the pressured sample area and the other high-vacuum regions into individually pumped compartments. This type of differential pumping E-cells ensures no severe change in TEM column vacuum when gas is admitted in the sample area. Perhaps the biggest advantage is that the TEM sample is now directly exposed to electron beam, therefore high resolution imaging, sample tilting, and in-situ heating, which are concerns for the window type E-cells, are not problems anymore. Easy operation is another advantage. The constant efflux of gas from the restricting apertures also helps to prevent contamination of the TEM sample. However, adding restricting apertures in the optical path and the associated extra pumping system turn the microscope into a dedicated E-TEM system. Design, manufacture, and installation will need much longer time, the price and maintenance cost can be doubled compared with the regular TEM systems. The restricting apertures below the sample also narrow down the collectable diffraction angle therefore recoding high-angle electron diffractions become impossible, and in turn the routine characterization capability of such type of microscopes is limited.

2 INNOVATIVE DESIGN OF AN AFFORDABLE AND FLEXIBLE GAS-HEATING TEM SYSTEM

Because the existing commercial E-TEM instruments are either too expensive or limited by spatial resolution, we set out to develop a 300 kV high-resolution transmission electron microscope, Hitachi H-9500, with a partial differential pumping system above the sample area. This is a regular high resolution TEM for daily structural characterization, but the built-in differential pumping system and the associated Hitachi gas injection-heating sample holder allow gas injection into the sample area, and atomic resolution imaging can be performed with gas inlet and at elevated temperatures.

Figure 1 schematically illustrates the column design of the H-9500, the turbo molecular pump for the sample chamber, combined with a gas restricting aperture above the sample chamber and a safety valve below electron gun minimize the influence of the gas pressure in the sample chamber on up column. When gas is injected into the sample chamber, the sample is directly exposed to the gas and gas-solid interactions take place at various temperatures. The high speed turbo molecular pump is set to pump out most of the un-reacted gas. Some gas amounts may still leak into the restricting aperture installed among the condenser lens, but the small diameter of the aperture hole reduces the gas pressure therefore the gas leak is taken away by the pump. The safety valve below the electron gun can sense the gas pressure, if too high a pressure is sensed, it will shut off so to prevent the gas leaking into the gun area.

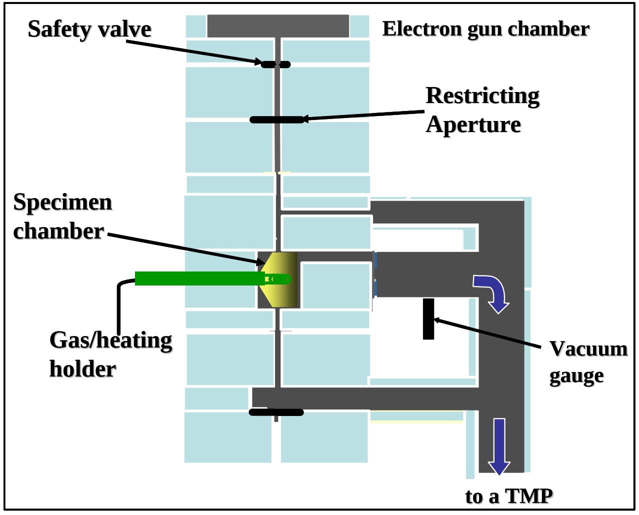

Figure 1: Illustration of TEM/E-TEM vacuum system in a Hitachi 300 kV high-resolution H-9500 transmission electron microscope. TMP denotes turbo molecular pump.

The design of the gas-heating holder is shown in Figure 2. A heating filament and a gas nozzle are put together, particularly good for in-situ TEM study of nanomaterials. The samples are heated while a stream of gas is injected onto the sample directly. Because the sample is directly exposed to gas, atomic resolution is not limited by any sealing windows like in a self-containing E-cell. The atomic resolution imaging with gas and elevated temperature is also guaranteed by a unique mechanical stability design of the sample holder. The holder is inserted into a module inside the H-9500 microscope till the sapphire ball at the tip of the holder touches the bottom of the module. This way, the holder is highly stabilized against environmental vibrations. Sample drifting is usually a big headache in in-situ heating TEM experiments because it will be difficult to keep the sample focused, but the spiral heating filament and the direct contact of the sample to the heating filament minimize the drifting and lost of focus. With all these innovative designs for the holder and the H-9500 microscope, atomic resolution imaging is routinely achievable at elevated temperatures with gas input. The maximum gas pressure that can be injected into the sample area is 0.1 Pa, which is sufficient to introduce changes in structure while the reaction rate is slowed down by the relatively low gas pressure, leaving enough time to record the microstructural changes by TV camera or CCD camera. In our case, a fast Gatan CCD camera is used for dynamic observation and digital movie recording. An electron energy loss spectrometer can be bottom-mounted on the microscope for chemical analysis during dynamic materials study.

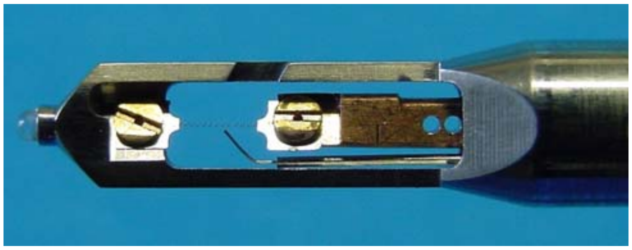

Figure 2: Tip area of a Hitachi-patented gas injection-heating sample holder. A heating filament and a gas injection nozzle are built together.

3 EXPERIMENTAL

A Hitachi H-9500 300 kV transmission electron microscope was used for high resolution imaging with gas injection and heating inside the microscope. Powder sample was pasted on the heating filament therefore the sample can be heated up to 1500°C. In some experiments, air is injected while heating. The heating filament can be replaced after experiment. All application data shown in this paper were obtained in National Application Center of Hitachi High Technologies in Japan, under a leading by Dr. Takeo Kamino.

4 EXAMPLES OF RESEARCH RESULTS

Figure 3 shows an application example using the Hitachi gas-heating E-TEM technology. The high resolution image was taken at 200°C to show the growth of SnO_2 crystal in an air atmosphere with a pressure of 0.02 Pa (1.5 x 10^{-4} Torr). The dark contrast spots in the image correspond to the projected atomic columns.

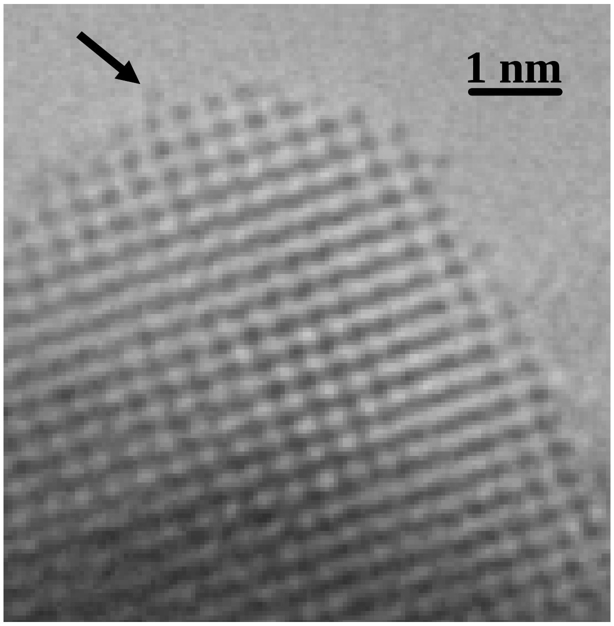

Figure 3: Atomic resolution study of SnO_2 crystal growth at 200°C in a 0.02 Pa air environment. The arrow indicates a single atom on the growth surface.

The same atomic resolution was obtained in another experiment, in which In_2O_3 was heated to 140°C in an air environment of 0.02 Pa. Figure 4 shows the images taken at 0s and 40s after gas injection. In_2O_3 (440) lattice with a 0.18 nm lattice spacing is clearly distinguishable.

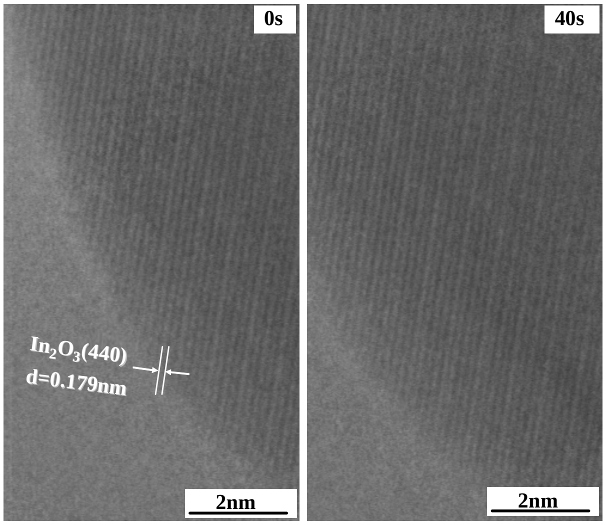

Figure 4: Atomic resolution study of In_2O_3 crystal growth at 140°C in a 0.02 Pa air environment. In_2O_3 (004) lattice is clearly visible.

The atomic resolution is also achievable at higher temperatures. Figure 5a shows a high resolution TEM image of Si projected on the [110] direction. A 3 nm thick amorphous oxidation layer is observed on the surface. This naturally formed oxidation layer was burned off by heating the sample to 700°C in the vacuum of the microscope as shown in Figure 5b. The sample was then remained at the same temperature but exposed to the injected air, and the dynamic procedure of formation of oxidation layer again on the surface was observed at an atomic resolution as shown in Figure 5c.

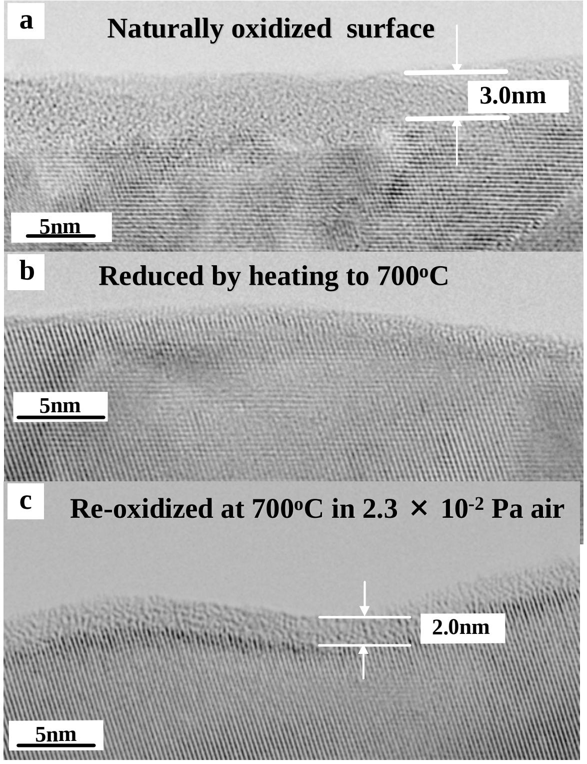

Figure 5: (a) Atomic resolution image of a Si single crystal with a 3 nm thick amorphous Si-O layer on the surface. (b) The Si sample was heated to 700°C for 25 min to burn off the surface layer. (c) 2.3 x 10^{-2} Pa air was injected to the sample area at 700°C and the formation of the surface oxidation layer is observed.

The atomic resolution in-situ gas-heating E-TEM is very valuable in research of nanocatalysts. The dynamic changes in shape, structure, and phase transition during the gas-solid interactions can be observed and recorded. Figure 6 shows an image cropped out from a recorded movie of Pt nanocatalysts. The movie shows the coalescence of Pt particles at 800°C in air pressure.

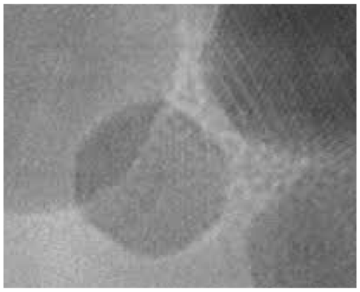

Figure 6: Pt nanoparticles at 800°C in an air environment of 2 x 10^{-3} Pa.

CONCLUSION

A gas-heating E-TEM system has been developed containing a specimen holder and a regular Hitachi 300 kV H-9500 high resolution transmission electron microscope equipped with a partial differential pumping system. The application of such a microscope is flexible, it can be regarded as a regular high resolution tool for routine structural characterization works. Once E-TEM is needed, this system also allows injecting gas directly into the sample chamber while heating sample to elevated temperatures (up to 1500°C). Images can be recorded at atomic resolution with gas injection and heating activated. Research results can have a great impact on nanoscience and nanotechnology associated with catalysts, fuel cells, environmental safety, gas sensors, geochemistry, and toxicity.

REFERENCES

[1] L. Marton, Nature 133, 911, 1934.

[2] T. Kamino and H. Saka, Microsc. Microanal. Microstruct. 4, 127, 1993.

[3] T. Kamino, T. Yaguchi, M. Konno, A. Watabe, T. Marukawa, T. Mima, K. Kuroda, H. Saka, S. Arai, H. Makino, Y. Suzuki and K. Kishita, J. of Electron Microscopy 54, 497, 2005.