17. ENVIRONMENTAL TRANSMISSION ELECTRON MICROSCOPY IN NANOTECHNOLOGY

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1. INTRODUCTION

Nanotechnology depends on the unique properties and behaviors of nanophase systems and the nanoparticles making up such systems often have properties that are significantly different from bulk materials. The behavior of the system may be strongly influenced by particle size, shape and the interactions between particles. In general, the configuration and evolution of the system will also be influenced by temperature, ambient atmosphere and associated gas-solid reactions. Moreover, in applications, nanoparticles are often subjected to high temperatures and pressures and as a result their structure and chemistry can dramatically change. For these reasons it is important to study nanoparticle systems under a wide range of different ambient atmospheres and temperatures. Since the invention of the transmission electron microscope (TEM), there have been continuous efforts to modify the instrument to observe biological samples in their native form (wet) and in-situ gas-solid reactions, e.g. corrosion, oxidation, reduction etc. These modified microscopes have been called 'controlled atmosphere transmission electron microscopes' or more recently 'environmental transmission electron microscopes' (ETEM). An ETEM can permit researchers to follow structural and chemical changes in nanophase materials, at high spatial resolution, during gas-solid or liquidsolid reactions over a wide range of different pressures. This information can be used to deduce atomic level structural mechanisms of reaction processes. With careful experimental planning, thermodynamic and kinetic data can also be obtained. An ETEM can thus be described as a nanolaboratory for the synthesis and the characterization of nanomaterials.

In order to follow the gas-solid or liquid-solid interactions at the nanometer level, we need to modify the TEM to confine gas or liquid to the area around the sample. In a transmission electron microscope (TEM), high-energy electrons (generally 100-1500 KV) are used to form an image. In order to avoid scattering from gas molecules and to increase the life of the electron source, both the column and the gun chamber are kept under high vacuum conditions (better than 10^{-6} Torr). When a field emission gun (FEG) is used as the electron source, the gun chamber should be better than 10⁻⁹ Torr for optimum performance and long life. However, in order to observe gas-solid reactions, or image hydrated materials (including biological samples), the environment around the sample should be typically 10^{-3} to 150 Torr. In an ETEM-our goal is to confine the reactive gas/liquid to the sample region without significantly compromising the vacuum of the rest of the microscope column. Figure 1 shows the general functioning principle of an ETEM. The ETEM allows the atmosphere around the sample to be controlled while still providing all of the high spatial resolution information (electron diffraction, bright-field images, dark-field images etc . . .) available in a regular TEM.

In this chapter we will give a brief overview of the history and development of the ETEM. This will be followed with a description of time-resolved recording techniques which are particularly important in ETEM experiments because we are interested in following the evolution of the nano-system during gas-solid reactions. Practical aspects of designing and performing controlled atmosphere experiments are discussed in section 4. In our final section on applications, we show that ETEM is useful for obtaining detailed information on nanoparticle synthesis, phase transformations pathways and nanoparticle kinetics.

2. HISTORY OF ETEM

2.1. Early Developments

The concept of controlling the sample environment during observation is almost as old as the idea of using TEM to image thin biological sections. The aim of an early ETEM design [1] was to examine biological samples in the hydrated state and to study the effect of gases on sample contamination. There was a steady development of the technique during the seventies and several review articles on the subject were published during that time [2–4]. A comprehensive review on environmental TEM and other *in-situ* techniques for TEM can be found in the book by Butler and Hale [5].

Environmental cell (E-cell) designs were based on modifying the sample area to restrict or control the gaseous flow from the sample region to the column of the microscope (Figure 1). This was achieved in two ways:

a) Window Method—gas or liquid is confined around the sample region by using thin electron transparent windows of low electron scattering power, e.g. thin amorphous carbon or SiN films.



Figure 1. Schematic diagram of ETEM showing operation principle and available high resolution information. Pressures in the cell are typically 1–50 Torr.

b) Differential Pumping—a pressure difference is maintained by installing small apertures above and below the sample area and using additional pumping.

In the window method, the windows are usually placed in a TEM sample holder. The windowed design has the advantage of being able to handle high gas pressures (depending upon the strength and thickness of the window). They can also handle wet samples and are often called 'wet cell' sample holders. The main disadvantage of the window method is that high-resolution imaging is difficult due to the additional scattering from the amorphous structure of the window films. Moreover, the windows often ruptured, the increased thickness of the sample holder did not leave much room for tilting and the samples could not be heated [5].

Large objective lens pole-piece gaps were required to successfully maneuver the gas confinement system and still leave enough space for tilting and translation of the sample. Therefore, most of the early environmental cells were designed to fit into the column of a high-voltage electron microscope (HVEM; 1000–1500 KV) [2–5]. Moreover, Swan and Tighe [6] studied the loss of intensity with increasing cell pressure for different voltages. They concluded that using high voltage TEM could reduce the loss of intensity due to high gas pressures in the sample area. The use and further development of microscopes with E-cells diminished considerably in the eighties due to several problems associated with the high-voltage microscopes and controlled-atmosphere chambers. First, many materials are damaged by the high-energy electron beam and could not be studied with high-voltage microscopy. The resolution limit, after installation of the E-cell, was not suitable for atomic-level imaging and finally the high-voltage microscopes were expensive to purchase and maintain.

2.2. Later Developments and Current Status

In the early eighties, improvements in the objective lens pole-piece design led to the development of atomic-resolution medium-voltage (200–400 keV) transmission electron microscopes. This stimulated renewed interest in E-cell designs in the nineties because the pole-piece gaps (7–9 mm) were large enough to accommodate the cell while still permitting atomic resolution imaging (0.2 to 0.25 nm). The smaller polepiece gap, 7–9 mm compared to 13–17 mm for high voltage TEM, has an added advantage of reducing the gas path through the cell and thereby reducing the amount of electron scattering from the gas or liquid. Using an intermediate voltage microscope and thin carbon windows, Parkinson was able to demonstrate atomic resolution imaging (0.31 nm) in ceria in an atmosphere of 20 Torr of N₂ [7]. Atomic resolution imaging with the differentially pumped system was demonstrated two years later [8].

In the past decade, attention has concentrated on the design of differentially pumped E-cells (Table 1, 9–18). The modern differential pumping systems are designed after the basic principles outlined by Swann and Tighe [19] and consist of two pairs of apertures with an aperture from each pair being placed above and below the sample. The first pair of apertures is placed closest to the sample and most of the gas leaking through these apertures is pumped out of the system using a turbo molecular pump. The second pair of apertures is larger than the first pair (because they see much lower gas pressure) and is used to further restrict the leakage of gases into the microscope column.

There are several factors to consider when selecting the size of the differential pumping apertures:

Year	Research Group	Microscope	Reported lattice resolution/ p\pressure/Temperature	Reference
1991	Doole, Parkinson, Hutchinson	JEOL 4000	0.31 nm/4.2 Torr H ₂ /670°C	9
1991	Lee, Robertson, Birnbaum	JEOL 4000	Not reported/70 Torr* H ₂	10
1991	Yao, Spindler/ Gatan Inc.	Phillips CM 30	0.34 nm/20 Torr*/No reported	11
1994	Sharma et al.	Phillips 400T	0.42 nm/3 Torr NH ₃	12
1997	Boyes & Gai	Phillips CM 30	0.23 nm/500°C/0.3 Torr N2	13,14
1998	Sharma et al.	Phillips 430	0.31 nm/RT/4 Torr H ₂	15
2001, 1st commercial	Hansen/Haldor Topsoe	Phillips CM 200 FEG	0.23 nm/550°C/4 Torr H ₂ /N ₂	16,17
2003	Sharma <i>et al.</i>	Tecnai F 20 TEM/STEM	0.13/RT/4 Torr N ₂	18

Table 1. Development History of ETEM Since 1991.

*Reported Pressure limit.

- (1) The gas leak rate through the aperture should be comparable to the pumping rate on the high vacuum side of the aperture in order to keep the column vacuum in the 10^{-6} Torr range.
- (2) The angular range in the diffraction pattern should not be severely limited by the aperture.
- (3) A reasonable field of view of the sample should be preserved.

Since the most critical part requiring high vacuum is the gun area, it is desirable to have a lower leak rate from the upper aperture so this aperture may have a smaller diameter than the lower aperture. Typical aperture sizes for the first set are in the range $100-200 \ \mu\text{m}$ giving a good compromise between reducing the gas leak rate to the gun area while at the same time maintain high angle diffraction capabilities and large viewing areas.

Boyes and Gai [13] successfully incorporated a multilevel differential pumping system into their Philips CM 30. Recently, FEI (previously Philips Electron Optics) redesigned the vacuum system of a CM 300-FEG in order to convert it to an ETEM [16, 17]. This modification was also incorporated into the new generation Tecnai microscopes [18] and is now commercially available (Figure 2). The modifications to the objective pole-piece region of the column are shown in Figure 3. In the commercially available instrument, the first and second sets of differential pumping apertures are located at the ends of the upper and the lower objective polepiece bores (Figure 3). The gas leaking through the first pair of apertures (Figure 3, first level pumping) is pumped out through top and bottom objective pole-pieces. The gas flow is further restricted by the second set of apertures (Figure 3, second level pumping). The region above the condenser aperture and the viewing chamber are evacuated by separate pumping systems (Figure 3, third level of pumping).



Figure 2. Tecnai F 20 field emission gun ETEM at Arizona State University operated at 200 KV and equipped with Gatan Imaging Filter.



Figure 3. Block diagram showing the modifications in the objective pole-piece area to accommodate 1st level of differential pumping. The residual gases leaking out from the aperture b and b' are pumped out by 2nd level of pumping and the 3rd level of pumping is performed using separate pumps for the viewing chamber and column-section between condenser aperture and gun chamber.

The gas inlet pressure from a gas reservoir is measured outside the microscope column. A gas manifold with numerous gas inlets from various gas cylinders and one gas outlet to the sample region of the ETEM is used to handle gases. This arrangement not only makes it easy to switch between various gasses but also allows different gases to be mixed in desired ratios before leaking them into the sample area. The microscope column is isolated from the gas inlet, outlet and associated pumps using pneumatic valves. A control system can be designed to automatically open and close the valves in order to switch between high vacuum TEM and ETEM modes [18]. The ability

to rapidly switch between modes is particularly important in a multi-user facility because it permits the microscope to be easily operated in the conventional high-vacuum mode. On our Tecnai F 20, we have demonstrated an information limit of 0.13 nm in 4 Torr of H_2 proving that atomic resolution capability can be easily attained [18].

To eliminate the effect of inelastic gas scattering at high pressures, a Gatan Imaging Filter (GIF) has been fitted to the ETEM. This configuration has the added advantage of permitting chemical information to be obtained through the use of electron energy-loss spectroscopy (EELS) and chemical maps by energy filtered (EFTEM) imaging. The field-emission gun permits high spatial resolution spectroscopy and scanning transmission electron microscopy (STEM) to be performed *in situ*. In the Tecnai F 20 ETEM, the electron beam can be focused down to about 0.2 nm in diameter. Annular dark-field STEM imaging can also be performed although the lower differential pumping aperture restricts the highest angle of scattering to about 50 mrad.

3. DATA COLLECTION

The data collection using an ETEM is usually performed with the same detectors used for TEM. The main difference is that the rate of data collection is directed by the rate of the reaction process of interest and often very high collection speeds are required. ETEM is usually undertaken to study dynamic processes such as phase transformations. In a typical experiment, sample temperature and pressure are varied with time in order to study gas-solid reactions at the nanometer or sub-nanometer level and extract information about reaction mechanisms and kinetics. For rapid transformation processes, it is necessary to continuously acquire and store data with good temporal resolution to ensure that the critical events are recorded. The high data collection rates result in large amounts of data being acquired during an experiment introducing practical data processing problems. In a typical experiment, many hours of data is recorded and stored although later analysis may show that only several minutes of data is scientifically interesting. Here we describe some of the considerations necessary for collecting different data types in an ETEM.

3.1. Real-Time Imaging Systems

The ideal detector for continuous image acquisition would consist of a low-noise digital camera system with a detection quantum efficiency close to unity, a large number of pixels (at least 1024²) and the ability to perform rapid readouts (>50 frames per second). Data would be written continuously to a high-density storage media. Sophisticated image processing software would be capable of performing quantitative batch processing on extensive sequences of images and generate video output for review. Unfortunately no such system is readily available at present and most facilities use a television camera (TV) coupled to a video recording system. In the best systems, a phosphor or single crystal scintillator converts the incident electron signal to a photon signal which is then fed into an image intensifier coupled to a high-performance TV camera. The output from the TV camera is fed to a monitor and digital video recorder.

In a typical video recording set-up, several hours of data can be recorded with a time resolution of $1/30^{\text{th}}$ or even $1/60^{\text{th}}$ of a second (note the actual frame rate in the NTSC system is 29.97 Hz). For ETEM applications, the differential pumping below the sample should be reasonably good to ensure that gas products cannot deposit and react on the scintillator during electron irradiation.

The main advantage of such a video system is that the data can be recorded using reasonably priced commercially available digital cameras/recorders and the storage format can be easily transferred between labs. However this setup also suffers from a number of disadvantages which significantly compromise the data quality. The number of pixels associated with conventional television recording techniques is rather small. For example, in the NTSC system, the conventional television picture has a resolution of 480×640 pixels. In image recording, the highest spatial frequency should be sampled by at least 3 pixels so that if a resolution of d nanometers is desired in the image, the width of the field of view in the vertical direction will be $(480 \times d)/3$. For atomic resolution with 0.2 nm resolution, the width of the field of view in the vertical direction will be only 32 nm. Consequently, the field of view for real-time in situ observations is very much reduced making the probability of observing critical nucleation events rather small. The current development and implementation of high definition television systems (HDTV) should increase the number of pixels by about a factor of 4 and give a corresponding increase in the sampled area. However, this is still a factor of 10 less area than currently possible on conventional photographic micrographs.

Advanced cine-photography techniques could be used to record more data with improved temporal resolution (see Butler and Hale [5] for discussion of some early cine-photography setups). Improving the temporal resolution τ would be advantageous but may also be limited to low-resolution applications because of radiation damage considerations associated with atomic resolution imaging. It is common to record atomic resolution HREM images with doses of $\sim 5 \times 10^3$ e/Å² to obtain reasonable signal-to-noise ratios. To maintain this signal-to-noise level in each frame, the dose D that is necessary to record a sequence of length *t* with a temporal resolution τ is given by:

 $D(t) = 5 \times 10^3 t / \tau$

With 30 frames/second ($\tau = 0.0333$ s) the dose rate will be 1.5×10^5 e/s/Å² which may result in significant damage in many materials. This simple expression shows that the dose rate has an inverse dependence on the temporal resolution; doubling the frame speed will require the electron dose to be doubled to maintain the same signal-to-noise per frame. In ETEM, it is usually desirable to run experiments with the lowest possible electron dose to minimize the impact of electron irradiation on the processes under study. It is possible to acquire high-resolution images using low-dose techniques. For example, atomic resolution images can be recorded from zeolites with 0.2 nm resolution and doses of around 100 e/Å² on a slow-scan CCD camera [20, 21]. However, with this dose, the information in the image is ultimately limited by counting statistics and is useful only for extracting average periodic information at the 0.2 nm level. By utilizing frame-averaging techniques, temporal resolution can be sacrificed in order to obtain improved signal-to-noise if necessary. In an ideal system, we would combine higher frame rates and low readout noise with suitable frame averaging to maximize the flexibility.

Data storage and quantitative image processing continue to be a challenge. It is necessary to convert digital video sequences into series of still frames which must be processed and re-assembled back into video format for playback. Since the data we are dealing with in ETEM has relatively high noise content, it is undesirable to utilize image compression techniques before quantitative analysis is performed. Consequently, very large volumes of digital data are generated which may consume enormous storage space. At present, some compression is often necessary to generate manageable files for presentation purposes.

For some ETEM experiments, it is not necessary to record data with high temporal resolution. For example, in metal particle sintering studies, many of the processes take place over a period of hours and data can be recorded with either a slow-scan CCD camera or using conventional photographic plates. In both cases, the image quality is better than that obtained from the TV system.

3.2. Spectroscopy and Chemical Analysis

Energy-dispersive x-ray spectroscopy (EDX) is a powerful technique for extracting elemental information in TEM. However, the EDX spectrometer is normally located in the pole-piece gap which effectively puts it in the middle of the E-cell for ETEM application. This can significantly complicate the design and implementation of the cell and spurious scattering from the windows or differential pumping apertures dramatically increases the background in the EDX spectrum. For these reasons, most of the current ETEMs rely on EELS to obtain chemical information. Detailed information about the technique can be found elsewhere [22]. In EELS, the fast electron is inelastically scattered as it passes through the thin sample resulting in significant energy transfers to the atomic electrons in the sample. The spectrum of energy losses carries detailed information about the elemental composition and electronic structure of the sample. Implementation of EELS on the ETEM is essentially identical to that on conventional microscopes because the detector is located a significant distance away from the environmental cell and, provided the differential pumping in the lower part of the column is effective, there is no negative impact on the energy-loss performance. The technique is best suited to light and medium atomic number materials in very thin samples (ideally <50 nm). The spatial resolution of the EELS analysis is limited by the probe size and instruments equipped with field emission guns can record fast spectral series from sub-nanometer areas.

It is common to install energy filters to permit energy filtering of images and electron diffraction patterns. The effect of inelastic scattering from the gases and thick samples can also be removed with zero-loss imaging. In many of the commercially available spectral processing routines, there are powerful features for batch processing of time resolved spectral data. This makes it relatively easy to study changes in composition and bonding during gas-solid reactions.

4. EXPERIMENTAL DESIGN STRATEGIES

To perform successful *in-situ* observations using an ETEM, experiments must be designed with extreme care. There are a number of parameters that must be considered mainly dependent on the following:

- 1. Type of data to be collected, i.e. high-resolution images, electron diffraction, electron energy-loss spectroscopy etc.
- 2. Type of gas and gas pressures to be used.
- 3. Reaction temperature.

Both the data type and the reaction rates determine the choice of recording media for data collection. While chemical processes with high reaction rates can only be observed by high-resolution imaging or electron diffraction data recorded on digital video tapes, processes with low reaction rates can be recorded using CCD cameras or photographic films. Moreover, time-resolved spectroscopic information can also be collected for high reaction rate processes provided that the very intense low-loss part of the spectrum can be utilized.

Gas contaminants may deposit in the gas delivery tubes and/or the microscope column. Therefore it is extremely important to use ultra-pure gases and keep the gas lines and samples clean for *in-situ* experiments. Contaminants can alter the reaction path and/or influence the reaction rates, for example, the presence of carbon contamination has been found to increase the reduction rate of iron oxide [23]. Similarly, if the microscope is used with different gases, cross contamination of gases could affect the reaction path. For example, we found the presence of water vapor in the system retarded the reduction rate for CeO₂ [24]. Water vapor also poisoned Ziegler-Natta catalyst used for polymerization of propylene [25]. Therefore, it is necessary to purge both the gas lines and microscope column with ultra-pure nitrogen before and after performing *in-situ* reactions. It is also advisable to purge the system with the gas that will be used for the reaction (if possible) before starting the experiment. The microscope column and gas lines should be baked (if possible) and pumped over night after purging.

Many of the experiments performed in the ETEM are conducted at elevated temperatures. Guidelines on calibration and use of heating stages are covered on the chapter on *in-situ* microscopy. However there are a number of practical situations that must be taken into account when performing heating experiments in the ETEM because of the possible reactive nature of the gases. Most of the commercially available heating holders are made from tantalum because of its high melting point and structural stability after many thermal cycles. Tantalum holders are well suited for working in vacuum and under reducing conditions; however the power required to reach a given temperature is higher under the typical gas pressures used in the ETEM compared to vacuum operation. The increased power is necessary because gases are usually admitted at room temperature and are a source considerable heat loss due to conduction. The amount of additional heating power required depends on the thermal conductivity and pressure of the gas in the cell. Table 2 gives the thermal conductivities of gases that are

Gas Type	Thermal Conductivity (W m ⁻¹ K ⁻¹)
H ₂	1684
H_2O	158
He	1415
N_2	243
O ₂	151
CO	232
Ar	162
5% H ₂ /Ar	237
$5\% \; H_2/N_2$	314

Table 2. Thermal Conductivity of Various Gases.

often used in ETEM experiments. This table shows that the thermal conductivity for H_2 is extremely high so that high-temperature work will require significantly higher heating currents. It is common to mix H_2 with Ar or N_2 to generate a lower thermal conductivity reducing gas. If possible it is advisable to obtain the required reaction pressures before heating the samples because introducing high gas pressures during heating will drastically cool the sample due to thermal losses to the gas.

Ta holders are not suitable for oxidizing environments because of the corrosive effects of the gas environment at elevated temperatures. Inconel alloy or Pt holders have been successfully developed (Gatan Incorporated) to provide more robust solutions when oxygen is present permitting heating up to $\sim 1000^{\circ}$ C. Kamino *et al.* have designed heating holders that are capable of heating powder samples to very high temperatures (1500°C) [26]. The temperatures attainable in the microscope are usually restricted by the design of the heating holder but for the ETEM it is also restricted by the material and placement of the differential pumping apertures. For example, the viton seals used to keep the apertures in place can be destroyed at high temperature due to heat transfer from the sample to the seals via the gas.

For powder samples, the choice of grid material is very important. The grid material should not react with the sample or gases used for experiments. Only Au or Pt grids should be used in oxidizing atmospheres as most other metals will be corroded in oxygen. The grid melting point should be significantly higher than the experimental temperatures. In general, atoms from the grid will become mobile when the experimental temperature exceeds the Tamman temperature (half metal melting point in degrees Kelvin). If the experimental temperatures exceed the Tamman temperature, metal atoms from the grid may diffuse over the sample and change the gas-solid reactions. For example, Cu melts at ~900°C, hence Cu grids should not be used for reaction temperatures above 300°C. In practice it is advisable to observe the behavior of grid material at the experimental temperatures and pressures using well-known samples. Carbon thin films often break due to thermal expansion and/or oxidation at elevated temperatures. Dusting bare grids with powder samples and observing the regions near grid bars give the best results. These regions also have good thermal contact with the heating furnace. The support material for cross-sectional samples should be given the same considerations as described above.

Preliminary experiments are usually performed to determine the reaction conditions, mainly temperature and pressure. The electron beam can alter the reaction rate/mechanism, therefore it is very important to monitor sample regions not exposed to the electron beam and/or confirm the results using *ex-situ* methods.

5. APPLICATIONS TO NANOMATERIALS

ETEM has been successfully used to understand many different gas-solid reactions [e.g. 27–36]. In general, one of the main advantages of performing *in-situ* measurements compared to *ex-situ* measurements is that the structural and chemical information is obtained under reaction conditions. *In situ* methods provide us with information on the reaction process, thus all the intermediate phases/steps (if any) are easily identified. Moreover, nanoparticle synthesis and characterizations can be performed and studied simultaneously. Some of the specific applications to nanotechnology are described in this section.

5.1. Transformation Mechanisms in Nanostructures Due to Gas-Solid Reactions

The majority of previous work on applying ETEM to elucidate transformation mechanisms during gas-solid reactions comes from the field of catalysis. Most heterogeneous catalysis involves gas-solid or gas-liquid reactions occurring directly on the surface of the catalyst. For this reason it is necessary to utilize nanoparticles simply to maximize the surface area. Indeed, heterogeneous catalysts may be one of the earliest technologically important areas to exploit the unique properties of nanophase materials. We now also realize that the properties of nanoparticles can be fundamentally different from their bulk counterparts and that these changes can yield unique catalytic activity. The catalytic activity may be related to structural or electronic transformations taking place as a result of the small particle size, the interaction between the particle and the support or as direct result of the interaction with the gaseous reactants. ETEM is particularly powerful for studying catalysts because it permits us to make atomic level observations of the response of the nanoparticles to gaseous environments. For catalytic research, the ETEM essentially acts as a small micro-reactor allowing us to observe the changes in nanostructure and nanochemistry under near reactor conditions.

Baker and co-workers were the first to extensively use ETEM to study heterogeneous catalysts. His first work focused on the growth of carbon filaments using Ni based catalysts [27]. Catalytic gasification of carbon and filamentous growth remained common themes for many of Baker's publications in the 80 and 90 s [28–30, 37–39]. He has also worked on a wide range of metal catalysts studying the influence of gaseous environments on particle shape and metal-support interactions [40–45]. Gai and Boyes have also developed ETEM and applied it extensively to a wide number of different heterogeneous catalysts [e.g. 31–34]. Our group and the group at Haldor Topsoe have also been studying various catalytic processes at atomic level under reaction conditions [e.g. 17, 24, 46].

5.1.1. Oxidation and Reduction Reactions

Oxidation and reduction plays a central role in many catalytic processes related to pollution control and chemical synthesis. ETEM can provide detailed information on the structural, compositional and electronic transformations associated with reduction-oxidation (redox) processes. Palladium based catalysts are of considerable importance in automotive technology for the elimination of NO_x in the exhaust gases of gaso-line engines and for combustion of methane [47–48]. For both applications, oxygen is involved in the combustion and there is considerable evidence to show that the formation of palladium oxide may play a critical role in both catalytic processes. It has also been suggested that particle morphology and the Pd oxidation state are important in defining the active sites in Pd catalysts. For palladium supported on silica, it is known that under certain conditions, reduction of PdO can lead to the formation of small Pd metal particles formed after *in-situ* reduction of PdO at 200°C in 1 Torr of H₂. These metal nanoshells form under a variety of different reducing atmospheres and at different reducing rates.

The mechanism for the void formation process was determined by following the evolution of individual nanoparticles during *in-situ* reduction [51]. A typical atomicresolution image recorded from a particle at an intermediate state of reduction is shown in Figure 4B. Fourier analysis of this image shows that it is composed of two sets of atomic lattice planes corresponding to Pd metal and PdO confirming that the particles is indeed at an intermediate state of reduction. The coarse Moiré fringe pattern at the center of the particle arises due to overlap between the Pd and PdO fringes. By further processing this image, it is possible to reconstruct two digital dark-field images; one corresponds to the Pd metal spacing and the other to the oxide spacing. In Figure 4C these two images are overlaid using false color in order to see the distribution of Pd metal and PdO during the transformation process. The image shows that the initial reduction occurs uniformly over the surface of the particle and leads to the formation of a continuous metal shell around the oxide particle. Subsequent reduction of the particle occurs via oxygen diffusion through the metal shell. Reduction of PdO to Pd is accompanied by a 40% reduction in the overall volume of the particle. The metal shell associated with the initial reduction is rather rigid and fixes the final particle size. Consequently, part of the change in particle volume that occurs during the reduction must be accommodated by the formation of a void in the center of the metal particle. Continued heating of the sample resulted in a gradual reduction of the oxide and a steady increase in the thickness of the metal shell. Eventually the oxide disappears from the particle and a small void remains at the particle center. The voids collapse at temperatures above 500°C suggesting that voids will not form during high temperature reduction.

In the previous example, we determined the mechanism for oxide nanoparticles transforming completely to metal accompanied by a drastic change in particle morphology. In many cases, the redox processes of interest may involve transformations between different oxides states. Cerium based oxides are a technologically important



Figure 4. A) Pd metal particles formed after in situ reduction from PdO. Metal particles show evidence for void formation. B) Atomic resolution micrograph recorded from particle at an intermediate stage of transformation. C) Digital dark-field analysis of the image clearly shows that PdO (blue) gets initially reduced to Pd metal (red) on the outside of the particle. (See color plate 16.)

catalytic material for pollution control where transformations can occur between many different oxide forms depending on the reducing conditions. To follow the transformation pathways requires the combined use of imaging, spectroscopy and electron diffraction.

Three-way catalysts (TWC) are used to reduce the common pollutants CO, NO_x, and unburned hydrocarbons escaping from the exhaust system of automobiles [52]. The TWC functions by providing additional oxygen to complete combustion during fuel rich conditions. During fuel lean conditions, the catalyst can restore the oxygen reservoir by absorbing oxygen from the ambient atmosphere and reducing NO_x in the process. The effectiveness of the catalyst is directly related to the oxygen storage capacity (OSC) capacity of the material. This in turn depends on the degree and ease with which the catalysts can run through oxidation and reduction cycles. CeO₂ based catalysts are commonly used in catalytic converters because Ce can exist in both +3 and +4 oxidation states and the oxides possess high oxygen mobility at low temperature ($\approx 300^{\circ}$ C) resulting in an easy redox cycles [53–54]. The ceria/zirconia mixed oxide systems (Ce_{1-x}Zr_xO₂) have been found to have higher OSC than the pure oxides and consequently are the material of choice for many TWC applications [55].

Fully oxidized CeO₂ has a fluorite structure similar to most of the rare earth oxides, e.g. PrO_2 and TbO_2 . These oxides can also exist in both +3 and +4 oxidation states and possess high oxygen mobility. For PrO_2 and TbO_2 , the oxygen vacancies introduced during reduction cause the formation of ordered superstructure phases, and a number of discrete intermediate phases with a general formula, R_nO_{2n-2m} have been identified [54]. Similar intermediate phases have been predicted to form for CeO_2 during reduction. However this system has been more difficult to study in reduced form because of its high oxygen affinity.

Recently ETEM has been used to follow the formation of superstructures under reducing environments at high temperatures [24]. Figure 5A shows the HREM image and the digital diffractogram of a single crystal oriented along $<111>_F$ (F = fluorite) zone axes at 800°C in 2 Torr of dry hydrogen. The reduction process for single crystals was observed to be very slow as expected due to their low surface area. After about 5 minutes of observation, a strained structure was observed to start forming (Figure 5B), probably due to oxygen vacancy formation. After 14 minutes, semiordered fringes were observed (Figure 5C) and after 40 minutes of isothermal heating at 800°C, a domain of ordered superstructure was observed to grow to \sim 30 nm in size (Figure 5D). Simultaneously, extra superlattice reflections could also be observed in the digital diffractogram (Figure 5D) indicating that the oxygen vacancies formed during reduction were ordering. Since the superstructure reflections observed here do not have a simple relationship with the fluorite lattice, it is not possible to determine the exact nature of the phase formed. In other words, the fluorite orientation is not a superstructure zone perpendicular to the plane in which the ordered vacancies are being formed. CeO₂ nanopartcles reduced quite easily and vacancy ordering was observed together with sintering processes. The measured reduction temperature and rates for samples with different surface areas confirmed that the fastest reductions were obtained for high surface-area nanoparticles.



Figure 5. High resolution electron microscopy images recorded from a single crystal CeO₂ sample oriented with $<110>_F$ zone axis parallel to the electron beam, recorded at A) room temperature (RT) and B–D) at 800° C in \approx 2 Torr dry H₂ showing development of defected area and (C, D) ordered superstructure after 40 minutes. A comparison of digital diffractogram inset in (A) and (D) confirms the formation of superstructure.

Electron energy-loss spectroscopy provides a convenient method to follow the average oxidation state of the Ce when exposed to different reducing conditions. Figure 6A shows a series of Ce M_{45} edges recorded from high surface-area nanoparticles of CeO₂ during *in situ* reduction in dry H₂. The large peaks at the beginning of the edge are called white lines and correspond to electron transitions from the $3d^{5/2}$ (M_5 –884 eV) and the $3d^{3/2}$ (M_4 –902 eV)) to unoccupied states in the 4f band. It has been shown that the relative intensity of the M_5 and M_4 peaks depends on the occupancy in the 4f band, which in turn depends on the oxidation state of Ce [56]. The occupancy of the 4f band changes from approximately 0 to 1 as the Ce transforms from an oxidation state of +4 to +3. Inspection of the Ce spectra in Figure 6A shows a reversal in the relative



Figure 6. A) Background subtracted Ce M_{45} peaks from pure CeO₂ sample showing relative change in the white-line intensity with temperature. A small shoulder (marked by arrow) also disappeared with reduction. B) Ce oxidation state for CeZrO₂ samples showing reduction and oxidation of Ce with heating (diamonds) and cooling (squares) in dry H_2 .

intensities of the M_5 and M_4 white lines as ceria is heated from room temperature to $700^\circ \text{C}.$

There are several different methods of extracting the variation of the white-line intensity in order to determine the occupancy of the 4f band [57]. Some of these methods require significant spectral processing and impose restrictive conditions on the data acquisition. However, in the Ce system, the change in the white-line intensity is pronounced and thus we can use a simplified procedure to quantify changes

in the Ce oxidation state. Here we remove the background beneath the M_{45} edge, integrate the M_5 and M_4 intensities and determine the M_5/M_4 intensity ratio. It is not easy to calibrate the white-line ratios simply by directly measuring the O/Ce concentration because of difficulties associated with adsorbates and non-stochiometry. Instead, we obtain a calibration simply by examining the spread of white-line ratios obtained over the entire temperature range and assume that the low value obtained at room temperature corresponds to Ce⁺⁴ and the value obtained under severe reducing conditions (800°C in 2 Torr of H₂) corresponds to Ce⁺³. We further assume a linear relationship between the white-line ratio and the Ce oxidation state. These assumptions seem reasonable and based on the statistical spread in data points give oxidation states that are accurate to within 5% [24].

The Ce oxidation state determined from the white-lines of a $Ce_xZr_{1-x}O_2$ mixed oxide sample is plotted as a function of temperature in Figure 6b. The mixed oxide samples consisted of grains with an average size of about 5 nm. The initial average oxidation state of this material is about 3.85 and the onset of reduction occurs between 400 and 450°C and by 550°C the average oxidation state drops to around 3.3. This reduction temperature is about 150°C lower than the equivalent reduction temperature in pure CeO₂. The cooling cycle is also shown in Figure 6B. Even though the sample was cooled in an H₂ atmosphere the ceria still re-oxidized back to the original 3.85 state by 400°C. The oxygen to re-oxidize the sample is presumable obtained from the residual background gases. HREM did reveal some very small nanometer sized superstructure domains in samples subjected to severe reduction at 800°C. However the vast majority of the material did not show evidence for ordering of oxygen vacancies. The combination of *in-situ* HREM and EELS strongly suggest that the Zr strongly retards the ordering of vacancies resulting in an increase in the mobility of oxygen vacancies leading to a significant lowering of the temperature for the onset of reduction.

Strong gas-solid interactions often rely on suitable sites on the surface which can catalyze a particular reaction. These active sites are usually associated with dangling bonds at special surface sites such as Brönstead or Lewis acid centers. In some cases, the sites may only be created when the material is "activated" by exposure to a suitable gaseous environment. The location of active sites on the surface of materials and the activation process are not well understood but in many instances the active centers may be associated with crystallographic defects. Strong interaction between such materials and their environment depends not only on the high surface area but also on extended defects with nanometer separation within the crystals. Gai et al. has pioneered the use of ETEM to study oxide catalyst and the relationship between crystal defects and catalytic activity. One example of this approach is the behavior of vanadyl pyrophosphate (VPO) catalyst under reducing atmospheres and its impact on selective oxidation of alkanes [58]. They conducted a series of ex-situ and in-situ experiments to elucidate the relationship between the catalytic activity and the crystal defect structure. Figure 7 shows the microstructure of VPO after reduction in butane. The low-magnification TEM image and electron diffraction pattern show that extended defects have been introduced into the material as oxygen is removed from the lattice to oxidize the butane. High densities of extended defects appear throughout the crystal running in



Figure 7. VPO after reducing in butane. Two sets of extended defects (arrowed) parallel to [201] and symmetry-related [201] directions in (010) orientation in diffraction contrast (\sim 400°C several hours). The diffraction pattern reveals two sets of diffuse streaks along these directions. (Gai and Kourtakis, Science, 1995, reproduced with permission)

either the [201] direction or the symmetry related [201] direction. Under reducing conditions many oxygen vacancies are generated at the surfaces which diffuse into the crystal. In this case, the lattice minimizes strain by gliding along the [201] directions with a pure shear mechanism to reduce the misfit between the reduced surface and the adjacent matrix. The anion vacancies generated where the extended defect intersects the crystal surface are associated with the strong Lewis acid sites responsible for the high catalytic activity.

5.1.2. Evolution of Nanoparticle Systems and Sintering Mechanisms

The ambient atmosphere can strongly affect the evolution of nanoparticles giving rise to behaviors that can be much more complex than those observed under UHV conditions. Even when gross chemical transformations of the particles do not take place, gas induced surface effects can result in dramatic changes in particle shape

and sintering behavior [46, 59-61]. Hansen et al. [46] have shown that the shape change of Cu nanoparticles on a ZnO support, formed by in-situ reduction of CuO, depends upon the gaseous composition of the reducing atmosphere. Model catalysts were prepared by impregnating ZnO support with copper acetate. The formation of Cu nanocrystals during reduction in an H₂ atmosphere was recorded by highresolution imaging (Figure 8). The atomic resolution images, recorded at 280°C in 4 Torr of H₂, confirm the metallic nature of the Cu particles formed (Figure 8A). These particles are faceted and bound by (100), (110) and (111) lattice planes (Figure 8B). On the other hand round Cu particles were formed when the catalyst sample was exposed to slightly oxidizing environment generated by adding H2O vapor to the hydrogen gas (Figure 8C). The shape of the Cu particle was observed to change in a more reducing environment, obtained by adding CO to hydrogen gas (Figure 8E). The Wulff's construction for the corresponding shapes (Figure 8B, 8D and 8F) was used to determine surface free energies. The observed dynamic restructuring of the catalyst shows that relevant active sites are generated during catalytic processes. Such information is crucial to determine the amount of H_2 adsorption on various surfaces and hence reduction rates.

Sintering and ripening processes are expected to be strongly influenced by ambient atmosphere. For example, it is well known in the catalysis literature that the presence of oxidizing agents like water can significantly alter sintering processes. Here we illustrate sintering processes for catalyst regeneration where complex interactions between the nanoparticles, the support and the ambient atmosphere result in significant noble metal sintering during low-temperatures catalyst regeneration.

Pd/alumina catalysts are widely used for hydrogenation of alkynes [62]. During the hydrogenation process, the catalysts are gradually deactivated by hydrocarbon build-up and eventually need to be regenerated. The regenerated catalysts usually exhibit less activity and different selectivity compared with the fresh catalysts. This phenomenon is often attributed to the decrease in the active metal surface area caused by sintering during the regeneration process [63]. In traditional metal particle sintering processes, significant metal atom mobility on the substrate is not achieved until the temperature reaches about half the melting point in Kelvin (the Tamman temperature). However, the temperature during catalyst regeneration is usually much lower than the Tamman temperature of Pd (~ 650° C) and Pd is not expected to sinter easily. The catalyst regeneration process was observed in the ETEM in order to determine the mechanism for sintering at these low temperatures.

 Pd/α -alumina catalysts were run in an industrial reactor for the hydrogenation of acetylene. The catalysts were kept on-stream for 124 hours and the temperature was varied from 110 to 145°F to keep a constant acetylene conversion level. Electron diffraction and electron energy-loss spectroscopy analysis revealed that in the used catalysts, most of the Pd particles were lifted from the alumina surface and embedded in the amorphous hydrocarbon material. The regeneration process was performed *in situ* by heating the system in either steam or air to remove the hydrocarbon via either sublimation or combustion respectively. Figure 9 shows a series of images recorded from the catalyst while heating in 500 mTorr of air at 350°C. The hydrocarbon develops pores







Figure 9. Time series of used Pd/Al_2O_3 catalyst heating in 500 mTorr air at 350°C for A) 0 hour; B) 1 hour C) 4 hours and D) 7 hours. Pd particles are marked and HC indicates hydrocarbon.

due in part to catalytic combustion of the hydrocarbon by the Pd particles. Calculations suggest that the local temperature rises to about 500° C. This is still significantly below the Tamman temperature (~ 650° C for Pd) and we would not normally expect atomic diffusion of Pd to give rise to sintering. ETEM reveals several reasons for Pd sintering in this case. First, on fresh catalyst, we have shown that major structural rearrangements can occur within the Pd particles at temperatures as low as 500° C [64]. This agrees with shape transformation measurements described earlier in this chapter in which Pd nanoshells were shown to undergo significant atomic rearrangement at 500° C. Although the atoms are mobile within the clusters, we do not see any evidence for significant diffusion of Pd atoms away from the clusters i.e. the atoms remain bonded to the metal cluster. However, during the regeneration process, particles are passively brought into physical contact via oxidation of the underlying hydrocarbon support. When physical contact between particles occurs, the high atom mobility within each Pd particle causes the two-particle cluster to rapidly reconfigure into a single crystal

Substrate	Growth Rate (atoms/cm ² /sec.)	Electron Beam Enhanced	Growth Rate
Temperature		Growth rate (atoms/cm ² /sec.)	Enhancement
125°C 150°C 200°C	$8.5 \times 10^{10} 5 \times 10^{11} 1.2 \times 10^{13}$	$\begin{array}{c} 1.2 \times 10^{13} \\ 1.7 \times 10^{13} \\ 5.8 \times 10^{13} \end{array}$	160 140 5

Table 3. Rate of Au Particle Growth with and Without Electron Beam

cluster. This mechanism is completely different from the traditional Ostwald ripening process and is the primary sintering mechanism during the regeneration of the Pd based catalysts.

5.2. Controlled Synthesis of Nanostructures

The E-TEM can also be used as a cold-wall chemical vapor deposition (CVD) cell. The chemical vapor deposition involves precursor adsorption and dissociation on a substrate. The materials deposited after dissociation may nucleate and grow to form nanoparticles or continuous films. The ETEM can be used for direct observation of the deposition process, and the nucleation and growth process. The dissociation of a precursor (vapor) can proceed by any of the following three main mechanisms:

- a) Thermal dissociation.
- b) Catalytic dissociation
- c) Electron beam induced dissociation.

An advantage of performing such experiments in an electron microscope is that we can use imaging, diffraction and spectroscopy to simultaneously characterize the resulting material *in situ* allowing synthesis conditions to be varied and optimized.

Drucker *et al.* [65, 66] have used ETEM to study the CVD process of Al and Au on SiO₂ and Si surfaces respectively. They reported that the electron beam enhanced the growth rates but the effect is lower at higher temperatures (Table 3). The observed dendritic growth of Al was believed to be responsible for the frosty and non-reflective appearance of Al films reported by Beach *et al.* [67]. Surface treatment by TiCl₄ produced high quality conformal Al films with growth rates dependent on pressure and temperatures. The growth rates of Au films on clean Si were observed to be dependent on temperature with a higher rate at higher temperature (Table 3). These model studies have established the validity of this technique to study CVD *in situ* at near atomic level using the ETEM. Similar *in-situ* CVD studies can also be performed using specially modified ultra high vacuum (UHV) TEM [68]. For example, the *in situ* observation of the nucleation and growth mechanism of Ge islands on clean Si surfaces under low Ge₂H₆ pressures were found to follow Ostwald ripening process [69].

In an ETEM equipped with a field emission gun, nanolithography can be performed to synthesize nanostructures. The characterization techniques available in the TEM can be employed to immediately characterize the resulting structures and understand the



Figure 10. A) Z-contrast image of two-dimensional periodic array of GaN dots. Insert shows line profiles through the Z-contrast images showing FWHM of 4 nm. B) Surface plot of array of dots showing the height of dots derived from the ADF image intensity. Average dot height 5 nm.

deposition processes. Nanolithography proceeds by admitting a gaseous precursor into the sample area of the microscope and using the fast electron beam to locally decompose the precursor. Electron nanolithography in a modern TEM has been demonstrated for creating nanostructures from carbonaceous contamination and tungsten metal [70–72]. However, if more exotic gaseous precursors can be designed then a much wider range of materials synthesis can be performed including binary compounds.

Figure 10 shows a periodic array of uniform GaN dots generated using nanolithography in the ETEM [73]. The array was generated by exposing the SiO_x substrate to a unique inorganic and highly reactive hydride D_2GaN_3 , that dissociates exothermally under electron irradiation resulting in formation of stoichiometric GaN and volatile and robust D_2 and N_2 byproducts as shown by the equation

 $\mathrm{D}_2\mathrm{GaN}_3 \rightarrow \mathrm{D}_2 + \mathrm{N}_2 + \mathrm{GaN}.$

This compound was previously used in GaN film growth by gas source molecular beam epitaxy to form standard heterostructures and luminescent nanostructures at extremely low temperatures, between 150°C and 450°C [74]. The dot array is generated by rastering a 0.5 nm electron probe over the substrate in well define steps. The dots are highly uniform and display an average full-width half maximum of about 4 nm, a base width of about 9 nm and a height of about 5 nm. Such arrays are small enough to manifest true quantum size effects and are likely to possess unique electronic and optical properties which may be beneficial to optoelectronic applications and information processing [75–77].

The spatial extent of the dot (5-10 nm) is considerably larger than the size of the primary electron probe (~0.5 nm). Similar results have recently been obtained on in situ TEM deposition of carbon nanowires and dots of tungsten metal [70, 71]. In both cases, features with dimensions in the range 2-5 nm were reported. Most processes for nanolithography rely on ionization of the valence electrons of the precursor species. The cross sections for these ionization processes are much higher for lowenergy electrons and consequently the secondary electrons emitted from the surface of the substrate are more efficient at dissociation. For this reason in electron lithography, precursor decomposition is associated with the spatial distribution of emitted secondary electrons. For high-energy sub-nanometer electron probes, the spatial distribution of secondary electrons emitted from the surface of a thin film is controlled primarily by the secondary electron mean free path. Careful measurements for 100 keV electrons show that the majority of secondary electrons are emitted with energy between 2-10 eV [78, 79]. The mean free paths of secondary electrons can be estimated from universal curves to lie in the range 1-5 nm [80]. Our dot dimensions are certainly consistent with this model and provide evidence for the strong role that secondary electrons play in the electron beam assisted nanolithography.

5.3. Kinetics

The kinetics of gas-solid interactions at the nanometer level can be obtained by *insitu* measurements of reaction rates using an ETEM. Most of the time it is possible to obtain the reaction rates from the time resolved data (mostly from video images). Sometimes it is possible to collect both time and temperature resolved data allowing us to estimate activation energies of the reaction process. Baker *et al.* [81, 82] were the first to use ETEM to make quantitative measurements of reaction kinetics. They used time resolved images to measure the growth rate of carbon nanofibers at different temperatures for different metal particles [82]. Activation energies of carbon nanofiber formation for different catalysts were obtained from Arrhenius plots (see below). This information was used to model the growth mechanisms of carbon nanofibers by comparing the activation energies obtained with carbon dissolution energies for various metal catalysts.

The reaction rate k is given by the well-known Maxwell-Boltzman equation:

 $k = A e^{-E} a^{/RT}$

where A is a constant called the frequency factor, E_a is the activation energy, R is the gas constant and T is the absolute temperature. In most reactions, the rate of the reaction increases with increasing temperature. The reaction rates can be obtained by measuring (a) the growth rates and/or (b) conversion rates. Taking logarithms and re-arranging the Maxwell-Boltzman equation gives the Arrhenius equation:

 $\ln k = \ln A - E_a / RT$

This equation shows that plotting the reaction rate against inverse temperature (Arrhenius plot) gives a straight line and the activation energy can be determined directly from the gradient.

5.3.1. Nucleation and Growth of Cu Nanoparticles

TiN is commonly used as a barrier layer in the semiconductor industry to retard Si diffusion into the interconnect layer (Au, Al or Cu etc.). One of the ways to incorporate a TiN or CrN layer in very small integrated circuits is by depositing a thin layer of Ti or Cr on Si or SiO₂ and subjecting this layer to rapid thermal annealing in NH₃ to form the respective nitride. Au, Al or Cu is then deposited to form the interconnect layer. This two-step process could be reduced to a single step by depositing a thin layer of Cu/Ti or Cu/Cr alloy on Si or SiO₂ and performing rapid thermal annealing in NH₃ at suitable temperatures. As Ti or Cr will convert to respective nitrides, Cu will be depleted from the matrix to form nanoparticles giving the desired metal contact and nitride barrier layer. In order to understand the effect of temperature and pressure on the nitridation reaction, the process was followed by heating Cu/Ti and Cu/Cr thin films, of different compositions, in \approx 3–4 Torr of high purity NH₃ up to 650°C using a modified Phillips 400-T E-TEM operated at 120 KV [35]. The nitridation temperature of Ti and Cr metals was determined by time and temperature resolved SAED patterns [35, 36]. The growth rates of Cu particles depleted during the nitridation of Cu/Ti and Cu/Cr thin films were measured using time and temperature resolved video imaging [36]. A typical sequence used for such measurements is shown in Figure 11. The images are digital still frames extracted from a video sequence recorded during growth of Cu particles at 630°C in 4 Torr of NH₃. It was also observed that the Cu grains do not grow isotropically, rather, certain facets have a preferential growth rate.

The area of two (of several measurements) Cu grains was plotted as a function of annealing time during heat treatment of the CuCr film at 630°C (Figure 12). Two growth regimes are observed for both grains. Growth is rapid initially (solid symbols, region A), whereas at longer anneal times, growth is slower and the grain area varies linearly with time (open symbols, region B). This behavior indicates that for longer annealing times, the growth is controlled by diffusion of Cu in the nitride matrix. The calculated average value of the slopes of those curves, $K = 3.0 \pm 0.4 \times 10^{-11}$ cm²/sec, is proportional to the diffusion constant of Cu through the CrN matrix. It should be noted that for very long annealing times (t > 10 min), the curve becomes completely flat as the Cu grain growth process was completed. This phenomenon



Figure 11. A time sequence of *in situ* still video frames showing the growth of a Cu particle during the nitridation process of the Cu_{1-x}Cr_x (x = 0.40) thin film at 630°C. The corresponding video times in seconds are also shown in the top left of each picture.



Figure 12. Cu grain area measured from the video sequence shown in Figure 12 as a function of the annealing time at 630°C when a Cu/Cr thin film was heated in \approx 3 Torr of high purity NH₃ gas. The growth rate from two different particles given is obtained from the curves.

might be attributed to the fact that after long annealing times, Cu was fully depleted from the CrN matrix. Although the nitridation temperature for Ti was found to be lower (370°C) compared to Cr (580°C), the growth rate of Cu particles was an order of magnitude lower in Cr/Cu (3.05×10^{-11} cm²/sec.) thin films than in Cu/Ti ($2.2 \times 10^{-12} - 5.0 \times 10^{-12}$ cm²/sec.) thin films.

5.3.2. Carbon Nanotube Growth

Carbon nanotubes (CNTs) were dramatically novel nanoscale materials when they were first discovered in 1991 by Iijima using a carbon arc discharge process [83]. They have since become one of the most sought out materials for nanotechnology due to their remarkable magnetic, electronic and mechanical properties [84]. The structure of a CNT can be described in terms of a single graphite layer (graphene) rolled up to form a single cylinder or concentrically arranged cylinders. The former is referred to as a single wall nanotube (SWNT) and the latter are called multiwall nanotubes (MWNTs). Although, a number of growth mechanisms have been proposed, deduced from high-resolution electron microscopy (HREM) images and theoretical simulations [81, 85–88], there is no direct evidence to support these models.

We have been successful in recording images of the growth of CNTs at video rate. We have used the specimen area of this microscope as a chemical vapor deposition chamber [89–90]. Our preliminary observations were made using Ni/SiO₂ catalyst, and propylene and acetylene as carbon sources (precursor). Although fibrous structures were observed to grow when propylene was used as a precursor, CNTs were observed to form only when acetylene (C_2H_2) was used as the precursor. Multi-wall carbon nanotubes were often observed to form with a catalyst particle at their apex, as has been observed previously in HREM images of carbon nanotubes formed by the CVD processes.

Figures 13A–I show digitized individual frames of a typical growth process for multiwall carbon nanotubes. A small finger shaped hollow structure (Figure 13A) moved out from the substrate, where another tube has been formed (Figure 13B), and created the tip of a multi-wall nanotube. After growing linearly for a short time, it curved and started to grow straight out again (Figure 13C). The process of changing directions continued until the apex anchored back to the substrate forming a loop (Figure 13D–F). CNT were often observed to grow in such a zigzag manner forming waves, spirals or loops. The length of the tube formed at the substrate to the end was used to measure the growth rate. Measured growth rates at 475° C and 20 m Torr of C₂H₂ pressure were 38–40 nm/second (Figure 14). It is clear from the length vs. time plot (Figure 14) that the growth of the tube is not continuous. The total growth period was observed to be in the range of 1-2.5 seconds. Nanotubes were not observed to grow after 1-2 seconds of their nucleation, on the other hand, new CNTs were observed to nucleate and grow during the first 2-5 minutes, after which significant deposition of CNTs was not observed. We observed no difference in the reaction morphology or length of CNTs formed in the area under *in-situ* observation or the area not irradiated by electron beam during conditions. The growth mechanisms for various CNT are currently being investigated.

5.3.3. Activation Energy of Nucleation and Growth of Au Nanoparticles

Drucker *et al.* [65–66] had made the first *in-situ* observations of growth and nucleation mechanism of gold CVD on Si/SiO_x from ethyl (trimethylphosphine) gold (Et Au(PMe₃)) at different temperatures and constant pressure with time using a



Figure 13. Individual frames digitized from a video sequence showing the nucleation and growth of a multiwall carbon nanotube. The apex is marked by arrows (A–F) showing the zigzag growth direction bending 360° (E) and finally attaching back to the substrate forming a loop (F). The bar is 10 nm and the time interval between various frames is given in the top right hand corner.

modified Philips 400T ETEM [11]. Si <111> samples were cleaned by dipping in HF and quickly transferring to the microscope in order to minimize the oxidation of the Si. The samples were heated to the deposition temperature and time-resolved images were recorded using a video recorder. Figure 15A shows that the number of nuclei formed did not increase with time but the Au nanoparticles grew in size. These particles coalesced to form continuous thin films once their growth brought them into direct contact with other particles [66]. The survey of the sample region not exposed to the electron beam indicated that the Au growth rates were lower in the areas not under direct observation (Table 3). In order to obtain growth rates without electron



Figure 14. The discontinuous growth rates for CNT measured from individual frames (1/30 second) of the video sequence shown in Figure 14.

beam effects, the following procedure was adopted. The precursor was introduced in the sample region for 5 minutes at deposition temperature and then the ETEM column was evacuated before making TEM observations. The absence of Au particle growth during the observation confirmed that no residual precursor was present in the sample area and the deposition was not enhanced by the electron beam. The process was repeated to obtain time resolved growth rates for each temperature.

The change in particle size with time at constant temperature and pressure was used to obtain average growth rates for the Au particles. As TEM data only provides us with two-dimensional growth rates, the height of the Au particles was measured after depositions using scanning tunneling microscopy. The measure change in volume thus obtained was used to determine growth rates at three different temperatures (125°C, 150°C and 200°C) for depositions with and without electron beam effects (Table 3).

The logarithm of the growth rates (no of Au atoms/cm²) plotted against 1/T can thus be used to obtain the activation energy (E_a) for nucleation and growth of Au nanoparticles by CVD (Figure 15B). The slope of the curve can directly be used to obtain the activation energy using Arrhenius equation (1):

 $E_a = -(\text{slope}^*\text{R})$ = 22.67 k cal/mole

As Au particles, once formed, were not observed to grow with time in the absence of precursor, it is safe to assume that ripening is not responsible for the growth at these low temperatures and the particles coalesced only when they were in direct contact. Moreover, the reported activation energy for Au surface diffusion on carbon is 39 kcal/mole [91] which is higher than measured here. Therefore the activation energy measured is for the nucleation and growth of Au during CVD.

Measurement of reaction kinetics thus provides us with an insight in to the reaction mechanisms and processes involved.



Arrhenius Plot of Au Deposition



Figure 15. Bright field images showing nucleation and growth of Au particles on Si <111> surface at 125°C after exposure of A) 5 minutes and B) 15 minutes. C) Arrhenius plot showing the temperature dependence of the growth rate obtained.

6. CONCLUSIONS

We have shown that ETEM is a valuable technique for understanding the response of nanoparticle systems to a gaseous environment at near atomic-level. The modern ETEM allows the dynamic behavior of the nanoparticles to be studied in real time with atomic-resolution imaging and electron diffraction in up to 50 Torr of gas pressure. On a machine equipped with a field-emission gun, electron energy-loss spectra can be recorded using a sub-nanometer probe so that elemental and electronic structural changes occurring in individual nanoparticles can be followed *in situ*. This powerful combination of *in-situ* imaging, diffraction and spectroscopy provides detailed information about gas-solid phase transformation mechanisms in individual nanoparticles. Quantitative measurements can be used to derive reaction rates and activation energies from very small areas and should allow full reaction kinetics to be determined as a function of nanoparticles size. The ETEM can also be used to perform *in-situ* synthesis of nanophase materials. The simultaneous characterization can be performed during synthesis allowing synthesis conditions to be varied and optimized rapidly. Sub-nanometer electron probes can also permit nano-lithographic structures to be deposited and studied under a wide variety of different conditions.

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