CHAPTER 2

EXPERIMENTAL SYSTEMS AND EQUIPMENT

2.1 The Chemical Vapor Deposition System

The CVD reactor or growth chamber in Figures 2.1 and 2.2 was constructed entirely of UHV-compatible components. This was necessary in order to minimize contamination of the vapor during CVD diamond growth. The main source of contamination or unintentional doping would be from small vacuum leaks that can occur with o-ring type seals. Nitrogen doping from the external atmosphere will lower the CVD diamond film’s conductivity as much as one order of magnitude with nitrogen concentrations as low as 100 parts per million (ppm) [1]. With the use of UHV compatible components, the problem of unintentional doping by nitrogen is minimized. To avoid overheating and outgassing, the CVD growth chamber is water cooled via an external waterjacket.

The CVD growth system also was used as a load lock for sample transfer to the UHV STM. It is equipped with three pressure gauges: a Baratron gauge, a thermocouple gauge and an ion gauge, for almost a continuous measurement of pressure from atmosphere to UHV. A 60 liter per second turbomolecular pump mounted at the back of the growth chamber was used to pump the CVD system below $10^{-7}$ Torr, measured by the ion gauge, before transferring the sample to the STM. After opening the UHV all-metal valve separating the CVD and STM chambers, the sample transfer was accomplished by a linear rotary translator and a tilt bellows. The quartz sample holder, shown
Figure 2.1 The top view CAD drawing of the UHV CVD and UHV STM experimental systems.
Figure 2.2 The side view CAD drawing of the UHV CVD and UHV STM systems. The entire system can be vibration isolated after disconnecting the rotary roughing pump.
in Figure 2.3, is based on the design of the Burleigh Instruments UHV STM sample holder with the addition of two through holes on its side. These holes provide a means of securing the sample holder to the end of the CVD linear rotary translator.

A rotary roughing pump was used during CVD to pump off the used gasses of the diamond synthesis. To avoid rotary pump oil from back diffusing into the CVD system, a molecular sieve and a liquid nitrogen cryogenic-trap were placed between the rotary pump and the CVD system.

There are four main parameters for diamond growth in a hot filament CVD reactor: gas mixture, gas pressure, substrate temperature and filament temperature. In order to produce high quality diamond via CVD the vapor quality must be controlled. It is imperative that the ratio of the main constituent gasses hydrogen, the catalyst, and methane, the carbon source be closely monitored in order to produce a consistent crystal morphology. By varying the ratio, one can choose the dominant growth of low index

![Figure 2.3 The modified Burleigh Instruments quartz sample holder.](image)
planes such as diamond (100), (111) and (110) \cite{2}. Typically, this is done by a combination of gas flow meters and metering valves. The system described in Figure 2.1 that was used to produce all of the CVD diamond films described in this dissertation, uses digital gas flow meters manufactured by Sierra Instruments, Inc. The flow meters that monitor the hydrogen and methane gasses have an accuracy of 1.0 standard cubic centimeter per minute (sccm) and 0.01 sccm, respectively. The gas flow is controlled by needle meter valves manufactured by Nupro, Inc. The typical ratio of methane to hydrogen is between 0 percent for etching and 1 percent for epitaxial diamond film growth. The gas pressure in the CVD growth chamber is monitored by a Baratron diaphragm pressure gauge and maintained at 30.0 Torr.

Figure 2.4 View from the 4 5/8 inch viewport of the CVD system as a homoepitaxial diamond film is grown.
Polished high-pressure high temperature (HPHT) grown diamond (100) substrates from Harris Corporation were used for the epitaxial CVD grown diamond (100) films. During CVD growth, each substrate was resistively heated by a 0.002 inch thick tantalum foil mounted on a quartz sample holder, as shown in Figure 2.4. The sample heater current, as much as 40 amperes AC, was delivered by two water-cooled copper UHV compatible feedthroughs. The substrate temperature, between 800 and 900 °C, was determined by a disappearing filament pyrometer. Also shown in Figure 2.4 are the two copper UHV compatible feedthroughs for the tungsten filament current. Because the filament current was typically small, between 2 and 3 amperes AC, it was unnecessary for these to be water cooled feedthroughs. The filament temperature was also monitored by the disappearing filament pyrometer.

2.2 The Ultrahigh Vacuum System

Figure 2.5 shows my design of the UHV STM chamber that was custom built by MDC Vacuum products Corporation [3]. The 8 inch viewport provides an unobstructed side view of the STM as shown in Figure 2.6. This makes sample transfer and tip manipulation reasonably simple. Also, a 4-5/8 inch view port provides a top view of the STM. The three angled 2-3/4 inch ports on top are aimed precisely at the center of the quartz STM sample holder when it is parked in the STM heater stage. One of the angled ports was fitted with a residual gas analyzer (RGA) manufactured by Stanford Research Systems. The location of the RGA makes it possible to monitor the gasses that evolve from the STM sample when it is heated for cleaning or annealing. The RGA is also used for routine vacuum analysis and leak checking. Another angled port is fitted with an ion
**Figure 2.5** The custom design of the UHV STM chamber. (a) The perspective view. (b) The top view showing four 8 inch ports, three 2-3/4 inch ports that aim at the STM heater stage, and the top 4-5/8 inch port for viewing.
sputter gun manufactured by Omicron [4]. The ion gun aimed at the sample in the heater stage allows cycles of ion sputter cleaning and annealing. This well-known technique for cleaning materials in UHV is not useful for the cleaning of diamond. Ion sputtering causes the diamond surface to graphitize, and therefore would be detrimental to the STM study of the diamond surface [5]. Nevertheless, the ion sputter gun is a good addition to the system for the study of other materials. The third angled port is used for deposition of materials using evaporation. An inner aperture is placed between the evaporator and the STM sample that narrows the particle cone to only cover the sample and decreases contamination of the UHV STM chamber. A mini 1-1/3 inch port for future use is also aimed at the sample and is located top right of the top 4-5/8 inch view port.
The UHV STM chamber described above is attached to the larger main UHV chamber. The main chamber is equipped with a 400 liter per second Varion ion pump, which after a thorough out-gassing of the system can produce a vacuum below $10^{-10}$ Torr. For added pumping during times of high gas load the attached titanium sublimation pump was used. The main chamber has four 8 inch ports, one of which is used as a view port. The top 6 inch port is fitted with an Omicron Auger system that consists of a cylindrical mirror analyzer (CMA) and coaxial electron gun. Figure 2.7 shows a typical Auger electron scan of an epitaxial diamond (100) CVD film after it has been degassed. The Auger system is used in determining the amount of surface contamination or the degree of surface interaction after a controlled gas exposure. The UHV chamber is also equipped

**Figure 2.7** Auger of homoepitaxial diamond (100) film showing no contamination of the surface.
with several Varian leak valves for accurate gas dosing. As shown in figure 2.1, the UHV chamber is equipped with a similar arrangement of linear translator and tilt bellows as the CVD system. This provides the ability to move the quartz sample holder from the STM chamber to the main chamber for Auger analysis and other functions. The end of the translator is equipped with a pivoting sample clamp of my own design, as shown in Figure 2.8. The clamp is simple in design. In order to retrieve the sample holder from the STM, the clamp must be positioned in a 90 degree configuration. The two clamp pins are then inserted into the sample holder’s two side holes. The assembly is then rotated out of the STM and then straightened by nudging the sample holder against the lower support of

Figure 2.8 The view from the 8 inch UHV chamber viewport while Auger analysis is done on an epitaxial diamond film. The bright spot is from electron stimulated photon emission. Also shown is the pivoting sample clamp.
the STM. The sample holder can then be linearly translated and positioned directly under the CMA, as shown in Figure 2.8.

2.3 The Ultrahigh Vacuum Scanning Tunneling Microscope

The Burleigh Instruments Aris 5000 UHV-compatible STM is the heart of the system and is mounted in the front 8 inch port of the STM chamber. Shown in Figure 2.6, the STM consists of an inchworm motor for coarse approach and a piezoelectric x-, y-, and z- scanner mounted at the end of the motor. The motor scanner assembly is mounted on an Invar plate that is supported by a vibration isolation system that consists of four Inconel springs and four eddy current damping magnet assemblies. Control signals, tunneling current and bias voltage are delivered to the STM by UHV feedthroughs and 0.005 inch copper wires. A magnetic tip holder is attached to the piezoelectric scanner and is used for in situ tip exchange. The STM sample stage is also made of Invar and is mounted directly to the Invar plate. The quartz sample holder is held by the sample stage so that the sample holder electrically isolates the diamond sample that is to be scanned by the tunneling probe.

The basic principle of the STM is quantum tunneling of electrons between the scanning tip and the conducting sample. The direction that the electrons flow, tunneling into unoccupied states or from occupied states, is controlled by the polarity of the tunneling bias. Typical tunneling currents are between 0.1 nA and 1.0 nA with a tip sample separation on the order of a few angstroms and a bias on the order of a volt. As depicted in Figures 2.9(a) and (b), the tip is then moved across the sample by modulating
Figure 2.9 A graphical description of the most common STM scanning modes. (a) Feedback off, constant height mode. (b) Feedback on, constant current or topographic mode. (Adapted from the instruction manual of the Burleigh UHV STM).
the piezoelectric scanner in the $x$- and $y$- direction. Depending on which mode of operation the STM is in, the digital feedback is either, on or off. With the feedback off, the tunneling current between the sample and tip is recorded as the tip is scanned in the $x$- and $y$- direction. With the feedback on, the tunneling current is held constant by maintaining a constant tip and sample separation by also modulating the $z$- piezo as the tip is scanned in the $x$- and $y$- direction. This second mode of operation, called

Figure 2.10 SEM images of STM tips. (a) An ultrasharp tungsten tip. (b) A diagram of the tip etching system. (c) A tip with a tail caused by immediate shut off after the drop section falls. (d) A tungsten tip etched without the aid of the electronic controller.
topographic, is the most common and produces a three dimensional image of the surface of study.

Figure 2.10(a) is a scanning electron microscope (SEM) of an ultrasharp STM tip. The tip was made by electrochemically etching a 0.020 inch diameter tungsten wire in a 1 molar solution of NaOH. Figure 2.10(b) shows the schematic for electrochemically etching ultrasharp tungsten tips. The drop technique shown in Figure 2.10(b) is employed because it gives the best tip geometry [6]. Also, the drop section of the tungsten wire provides an event that can be electronically detected and used to signal that the etch process has completed [7]. The electronic control box that I and D. Maxson designed provides the bias voltage and the circuitry to detect the drop and terminate the etching process by opening the electrical circuit. It is important that the voltage be controlled electronically because a manually operated switch cannot be opened quickly enough in order to obtain an ultra sharp tip. It is also possible to shut off the bias voltage too soon. If that occurs then the tip will have a stretched and curved tail, as shown in figure 2.10(c). The curvature is probably due to recoil of the tip as the drop section falls and no longer supplies tension to the sub-micron tip. A small delay after the drop section has fallen, on the order of a few microseconds, is necessary to etch away the tail portion. If the shut off delay is too long, the tip sharpness rapidly decreases. Figure 2.10(d) shows the sharpest tip that I have been able to obtain using a manual cutoff. If the tip is not sharp enough, it is possible, as the STM scans over a sharp protrusion on the sample, to get an image of the tip instead of an image of the sample, as shown in Figure 2.11. If the sample and tip
are equally rough, one would not know if the image was of the tip or the sample or a combination of the two.

2.4 The Raman System

Raman scattering spectroscopy has proven to be a valuable tool in characterizing CVD diamond films. The \( sp^2 \) graphitic carbon bond and the \( sp^3 \) diamond bond are very Raman active. Therefore, one can determine the quality of a CVD diamond film by comparing the \( sp^2 \) vs \( sp^3 \) carbon ratio [8]. As shown in Figure 2.12, the main two Raman carbon peaks are the \( sp^2 \) bond of highly ordered pyrolytic graphite (HOPG) at 1579 cm\(^{-1}\) and the \( sp^3 \) bond of carbon corresponding to diamond at 1332 cm\(^{-1}\). Carbon also has several other peaks located at 1150 cm\(^{-1}\), 1350 cm\(^{-1}\), and 1527 cm\(^{-1}\) corresponding to disordered or nanocrystalline diamond, disordered or nanocrystalline graphite, and \( sp^3 \)-\( sp^2 \) carbon networks, respectively [8,9].

Figure 2.11 Indicated by the arrows are images of the tip caused by sharp protrusions on the surface or a dull tip. (a) A higher resolution image of the area in Figure (b).
Raman spectroscopy can also give information about crystalline domain size, which is manifest in the peak width in a Raman spectrograph. The crystalline domain size must be on the order of nanometers in order to have an appreciable effect. The domains of a homoepitaxial film are large and a quality homoepitaxial film contains virtually no graphitic or $sp^2$ carbon. Therefore, Raman spectroscopy is most powerful as a tool for the study of polycrystalline diamond films rather than single crystal homoepitaxial diamond films. As shown in Figure 2.12(d), there is no measurable graphitic carbon in the Raman spectra of a single crystal HPHT diamond substrate after homoepitaxial CVD diamond growth. However, Raman spectroscopy can be useful as a means of measuring the temperature of a diamond film of any type by monitoring the shift in the 1332 cm$^{-1}$ line.

Figure 2.12 Raman spectra. (a)-(c) CVD polycrystalline diamond films on Si with different CH$_4$ to hydrogen ratios. d) CVD homoepitaxial diamond (100) film on a type 2b diamond substrate. (e) Highly-oriented-pyrolitic graphite (HOPG).
Raman spectroscopy was used to accurately measure the temperature of the epitaxial diamond films that are described in Chapter 5. A block diagram of the Raman system developed to characterize the CVD diamond films produced for this dissertation is shown in Figure 2.13. The system consists of a Coherent Inova 90 argon-ion-laser, a Spex 1404 double monochromator, a cooled Hamamatsu GaAs photomultiplier tube and a PC compatible computer for controlling the spectrometer and collecting data. The optics and calibration of the spectrometer were done by myself and the computer programming was done by J. Steinshnider.

Figure 2.13 A block diagram of the Raman system.
REFERENCES


3. MDC Vacuum Products Corporation, 23842 Cabot Boulevard, Hayward, CA 94545-1651.

4. Omicron Associates, 1226 Stoltz Road, Bethel Park, PA 15102.


