SCANNING TUNNELING MICROSCOPY STUDIES OF DIAMOND FILMS AND OPTOELECTRONIC MATERIALS

Progress Report

Jose M. Perez

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University of North Texas
Physics Department
Denton, Texas 76203

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1. Summary of Progress

In this report, we report on progress achieved from 12/1/92 to 10/1/93 under the grant entitled "Scanning Tunneling Microscopy Studies of Diamond Films and Optoelectronic Materials". We have set-up a chemical vapor deposition (CVD) diamond film growth system and a Raman spectroscopy system to study the nucleation and growth of diamond films with atomic resolution using scanning tunneling microscopy (STM). A unique feature of the diamond film growth system is that diamond films can be transferred directly to the ultrahigh vacuum (UHV) chamber of a scanning tunneling microscope without contaminating the films by exposure to air. The University of North Texas (UNT) provided $20,000 this year as matching funds for the NASA grant to purchase the diamond growth system. In addition, UNT provided a Coherent Innova 90-5 Argon ion laser, a Spex 1404 double spectrometer, and a Newport optical table costing $90,000 to set-up the Raman spectroscopy system. The CVD diamond growth system and Raman spectroscopy system will be used to grow and characterize diamond films with atomic resolution using STM as described in our proposal.

One full-time graduate student and one full-time undergraduate student are supported under this grant. In addition, several graduate and undergraduate students were supported during the summer to assist in setting-up the diamond growth and Raman spectroscopy systems.

We have obtained research results concerning STM of the structural and electronic properties of CVD grown diamond films, and STM and scanning tunneling spectroscopy of carbon nanotubes. In collaboration with the transmission electron microscopy (TEM) group at UNT, we have also obtained results concerning the optoelectronic material siloxene. These results were published in refereed scientific journals, submitted for publication, and presented as invited and contributed talks at scientific conferences.

Research accomplished during the report period. Our most important accomplishment has been designing and setting-up a hot-tungsten filament CVD diamond film growth system attached to the UHV chamber of a scanning tunneling microscope. The diamond film growth system was manufactured by Ulvick Industries, Inc. in Houston, Texas. The system, which cost $20,000, was purchased from matching funds for the NASA grant provided by UNT. A schematic of the system is shown in Fig. 1. The growth chamber consists of a water cooled 5-way cross with 4 5/8" conflat flanges. The system includes two electronic flow meters, two pressure gauges, a filament power supply, a sample heater, and a sample temperature controller. Growth is controlled by adjusting gas flow rates, gas pressure, sample temperature, filament temperature, and filament-sample distance. Detailed schematics of the gas handling system and growth flange are shown in Figs. 2(a) and 2(b), respectively. A picture of the diamond growth system attached to the UHV chamber of the scanning tunnelling microscope in our laboratory is shown in Fig. 3. A detailed picture of the diamond growth chamber is shown in Fig. 4.

We have recently started growing diamond films using the system described above. Fig. 5 shows a scanning electron microscopy (SEM) image of a diamond film grown using this system. The film was grown on a Si (100) substrate using a hydrogen gas flow of 350 sccm, methane gas flow of 1.75 sccm, growth chamber pressure of 35 Torr, sample temperature of 800 C, filament temperature of 2000 C, and growth time of 2 hours. Diamond crystallites measuring

approximately 0.5 μ in width are observed in Fig. 5, in excellent agreement with published SEM images of diamond films. Fig. 6 shows a three-dimensional STM image of the same film obtained using a tip-sample voltage of 3.5 V and tunneling current of 1 nA. The size of crystallites observed in the STM image is in good agreement with that observed in the SEM image of Fig. 5. Fig. 7 shows a Raman spectrum of the same film showing a peak at 1332 Rcm^{-1} which is the characteristic Raman peak for diamond. A Raman peak at 1578 Rcm^{-1} corresponding to graphite was not observed indicating that the diamond film is of high quality.

A unique feature of the diamond growth system described above is that diamond films can be transferred after growth to the UHV chamber of the scanning tunneling microscope without contaminating the films by exposing them to air. This is accomplished by using a vertical linear translator which is attached to the growth flange, and a horizontal linear translator, as shown in Fig. 1. The sample transfer allows atomic resolution studies of the nucleation and growth of diamond films using STM in UHV to be performed, as described below.

We also set-up a state-of-the-art Raman spectroscopy system to characterize the grown diamond films and determine their diamond and graphite content. UNT provided a Coherent Innova 90-5 Argon ion laser, Spex 1404 double spectrometer, and Newport optical table costing $90,000 to set-up the Raman spectroscopy system. In addition, UNT provided $1,000 to exchange the 75 grooves/mm gratings of the double spectrometer for more efficient 1800 grooves/mm gratings. A photon counting system consisting of a Hamamatsu R943-02 GaAs photomultiplier tube, Hamamatsu C3866 photon counting unit, Products for Research, Inc. TE104RF thermoelectric photomultiplier tube cooler, and Keithley CTM-05 counter board and IEEE 488 interface board, costing a total of approximately $7,000, was purchased as permanent equipment from this grant. Students supported under this grant wrote a computer program to automate data acquisition, installed the new gratings, calibrated the double spectrometer, and aligned the optics. A picture of the Raman spectroscopy system in our laboratory is shown in Fig. 8. Figs. 9(a)-(c) show Raman spectra for Si, natural diamond, and highly-oriented-pyrolitic graphite (HOPG) measured using this system. The Raman peak positions for Si, diamond, and HOPG are in excellent agreement with the accepted values of 520 ± 2 Rcm^{-1}, 1332 ± 2 Rcm^{-1}, and 1580 ± 2 Rcm^{-1}, respectively.

Research results concerning STM of the structural and electronic properties of CVD grown diamond films,[1,2] STM and scanning tunneling microscopy of carbon nanotubes,[3,4] and TEM of siloxene[5] were obtained and published in refereed journals and presented at scientific conferences. These results are described in the enclosed copies of preprints, reprints and manuscripts of papers. STM studies of diamond films using gold and tungsten tips were performed to corroborate previous results obtained using platinum tips. Tunneling current versus tip-sample distance measurements were obtained for diamond films. These results were included in Ref. 1 to further support the paper. Our STM studies of carbon nanotubes showed that carbon nanotubes having diameters of approximately 5.5 nm and greater have a metallic density of states,[3,4] in agreement with recent theoretical predictions. Carbon nanotubes have potential applications in optoelectronics and fiber reinforced materials. In collaboration with other research groups at UNT, we performed TEM studies of the optoelectronic material siloxene. These studies showed that siloxene contains Si nanocrystals approximately 3-4 nm in diameter.[5] Quantum confinement in these nanocrystals may be responsible for the visible photoluminescence

of this material whose origin is currently not known.

2. Plans for Next Year

Using the CVD diamond growth system described above, we plan to study with atomic resolution the nucleation and growth of diamond films using STM in UHV. The Raman spectroscopy system will be used to determine the diamond and graphite content of the grown films. As described in our proposal, we will study the nucleation sites on Si and graphite substrates, and the mechanism by which atomic hydrogen produces diamond growth, which are currently not known. We will also study the epitaxial growth of diamond films on natural diamond substrates.

i. **Nucleation and Growth on Si and Graphite.** As described in our proposal, we will determine the nucleation sites on Si and graphite substrates by directly imaging the initial nucleation on the surface using STM in UHV. Polished Si and graphite substrates with varying degrees of exposure to the CVD process will be transferred to the UHV chamber of the scanning tunneling microscope. The samples will then be imaged using STM in UHV. The samples will be transferred back to the growth chamber for additional growth and then re-imaged using STM to observe directly how growth proceeds. Information of interest that can be obtained from these experiments are the size and shape of islands as a function of deposition time, and statistics concerning the size of islands versus number of nucleation sites for different substrates and surface reconstructions. As described in our proposal, similar STM experiments on the nucleation and growth of Si and GaAs have determined the nucleation sites and growth mechanisms at the atomic scale and added a wealth of new information about the growth of these materials. To our knowledge, the experiments described above for diamond films have not yet been reported.

ii. **Mechanism by which Atomic Hydrogen Produces Diamond Growth.** As described in our proposal, we will study diamond films grown at different hydrogen concentrations using STM in UHV to find out more about the CVD growth mechanism for diamond which is currently not known. A diamond film grown on a Si or natural diamond substrate at low hydrogen concentration and containing some graphite will be studied using STM. The film will then be heated and exposed to atomic hydrogen in UHV and studied using STM to observe the changes in atomic structure that occur as a result of exposure to atomic hydrogen. The film will be repeatedly heated and exposed to atomic hydrogen, and the progression of changes in atomic structure of the film studied using STM. We expect to observe new and interesting results concerning the role of atomic hydrogen in growth as a result of these experiments. As described in our proposal, similar UHV STM experiments involving the role of hydrogen in the epitaxial growth of Si and Ge at low temperatures have recently been reported. Both Si and Ge are covalently bonded in the same crystal lattice as diamond. Hydrogen is observed to promote epitaxial Si and Ge growth at low temperatures where amorphous growth normally occurs. Using UHV STM, the mechanism by which hydrogen produces epitaxial Si and Ge at low temperatures was identified. Hydrogen breaks the strained bonds in amorphous Si and Ge thereby allowing clusters of atoms moving on the surface to bond covalently. Our experiments will directly probe if this mechanism applies to CVD growth of diamond. If this mechanism does not apply, our experiments will provide new detailed information on the actual mechanism.

iii. **Epitaxial Growth on Natural Diamond Substrates.** We plan to perform the above experiments on natural diamond substrates where epitaxial diamond growth is known to occur. Epitaxial growth of diamond films is technologically important because it would allow transistors and other electronic devices to be made from this material. In addition, studying epitaxial instead of polycrystalline growth using STM has the advantage that the deposited atoms are in registry with the crystalline substrate and therefore easier to study. Nucleation sites and growth processes for epitaxial growth on a natural diamond substrate will be studied with atomic resolution. Samples with varying degrees of exposure to the CVD process will be studied using STM in UHV to identify the nucleation sites and growth processes.

Concerning feasibility, atomic resolution imaging of epitaxial diamond films on a natural diamond substrate using STM in air was recently reported by T. Tsuno, T. Imai, Y. Nishibayashi, K. Hamada, and N. Fujimori in *Japanese Journal of Applied Physics*, vol. 30, pg. 1063, 1991. Therefore, our planned experiments involving epitaxial growth using the diamond growth system described above and STM system are feasible.

3. Students Supported under this Grant and Contribution of the Research in the Area of Education

One full-time graduate student, Albert Aviles (Black of Hispanic origin), and one full time undergraduate student, Luis Villareal (Hispanic), who are U.S. citizens, are supported under this grant. In addition, the following students were supported during the summer to assist in setting-up the diamond growth system and Raman spectroscopy system:

1. Ikerionwu Akwani (Black), graduate student.
2. Wayner Rivera (Hispanic), graduate student.
3. Veronica Criado (Hispanic), undergraduate student.
4. Justin Jose (Pacific Islander), undergraduate student.
5. Nataglia Murrillo (Hispanic), undergraduate student.
6. Richard Stallcup (White), undergraduate student.
7. Jeremy Steinshnider (White), undergraduate student.

UNT is supportive of this research project and the contribution of the research to education. In addition to matching funds and equipment, UNT has provided a Faculty Research Grant this year for $3,500 to perform preliminary studies of diamond coating of titanium for medical implant applications. The grant will be used to partly support a student and purchase additional supplies.

4. Full Bibliographic References to Publications (Preprints, reprints, and manuscripts are enclosed).

1. J.M. Perez, C. Lin, W. Rivera, R.C. Hyer, M. Green, S.C. Sharma, D.R. Chopra, and A.R. Chourasia, "Scanning Tunneling Microscopy of the Electronic Structure of Chemical Vapor Deposited Diamond Films", *Appl. Phys. Lett* **62**, 1889 (1993).

2. J.M. Perez, W. Rivera, C. Lin, R.C. Hyer, M. Green, S.C. Sharma, D.R. Chopra, and A.R. Chourasia, "Scanning Tunneling Microscopy of the Structural and Electronic Properties of Chemical Vapor Deposited Diamond Films", to appear in *Proceedings of the Atomic Force/Scanning Tunneling Microscopy Symposium* (Plenum Press, New York, 1993).

3. W. Rivera, J.M. Perez, R.S. Ruoff, D.C. Lorents, R. Malhotra, S. Lim, Y.G. Rho, E.G. Jacobs, and R.S. Pinizzotto, "Scanning Tunneling Microscopy and Spectroscopy of Carbon Nanotubes", to appear in *Proceedings of the Atomic Force/Scanning Tunneling Microscopy Symposium* (Plenum Press, New York, 1993).

4. R.F. Pinizzotto, H. Yang, J.M. Perez, and J.L. Coffer, "The Observation of Silicon Nanocrystals in Siloxene", accepted for publication *J. Appl. Phys.*

5. W. Rivera, J.M. Perez, R.S. Ruoff, D.C. Lorents, R. Malhotra, S. Lim, Y.G. Rho, E.G. Jacobs, and R.S. Pinizzotto, "Scanning Tunneling Microscopy and Spectroscopy of Carbon Nanotubes", submitted to *Appl. Phys. Lett.*

5. Presentations at Scientific Conferences

1. J.M. Perez, W. Rivera, C. Lin, R.C. Hyer, M. Green, S.C. Sharma, D.R. Chopra, and A.R. Chourasia, "Scanning Tunneling Microscopy of the Structural and Electronic Properties of Chemical Vapor Deposited Diamond Films", Atomic Force/Scanning Tunneling Microscopy Symposium, U.S. Army Natick Research, Development and Engineering Center, Natick, MA, June 8-10, 1993.

2. W. Rivera, J.M. Perez, R.S. Ruoff, D.C. Lorents, R. Malhotra, S. Lim, Y.G. Rho, E.G. Jacobs, and R.S. Pinizzotto, "Scanning Tunneling Microscopy and Spectroscopy of Carbon Nanotubes", Atomic Force/Scanning Tunneling Microscopy Symposium, U.S. Army Natick Research, Development and Engineering Center, Natick, MA, June 8-10, 1993.

3. J.M. Perez, W. Rivera, R.S. Ruoff, D.C. Lorents, R. Malhotra, S. Lim, Y.G. Rho, E.G. Jacobs, and R.S. Pinizzotto, "Scanning Tunneling Microscopy of Carbon Nanotubes", invited talk, Materials Research Society Meeting, Symposium on Fullerenes and Related Materials, San Francisco, April 12-16, 1993.

4. J.M. Perez, W. Rivera, C. Lin, R.C. Hyer, S.C. Sharma, D.R. Chopra, and A.R. Chourasia, "Scanning Tunneling Microscopy of the Surface Electronic Structure of Chemical Vapor Deposited Diamond Films", March 1993 Meeting of the American Physical Society, Seattle, WA, March 22-26, 1993.

5. J.M. Perez, J. Villalobos, P. McNeill, J. Prasad, R. Cheek, J. Kelber, Y. Hong, R.F. Pinizzotto, J.P. Estrera, P.D. Stevens, and R. Glosser, "Evidence for Amorphous and Nanocrystalline Silicon in Porous Silicon", March 1993 Meeting of the American Physical Society, Seattle, WA, March 22-26, 1993.

Invited Seminars:

1. J.M. Perez, "Scanning Tunneling Microscopy Studies of Diamond Films", joint Physics-Chemistry Seminar, Department of Chemistry, Oklahoma State University, Stillwater, OK, November 4, 1993.

2. J.M. Perez, "Scanning Tunneling Microscopy Characterization of Diamond Films", Colloquium, Physics Department, Sam Houston State University, Huntsville, TX, October 14, 1993.

3. J.M. Perez, "Scanning Tunneling Microscopy of Carbon Nanotubes", Colloquium, SRI, International, Menlo Park, CA, April 14, 1993.

FIGURE CAPTIONS

Fig. 1 (a) Side-view of the chemical vapor deposition (CVD) diamond growth system. The diamond growth system is attached to the ultrahigh vacuum (UHV) chamber of the scanning tunneling microscope. Samples are transferred from the growth chamber to the UHV chamber using linear translators. (b) Top-view of the CVD diamond growth system.

Fig. 2 (a) Schematic of the gas handling system of the CVD diamond growth system. The gas handling system includes two electronic flow meters, a thermocouple gauge, and a capacitance pressure gauge. (b) Schematic of the growth flange of the CVD diamond growth system. Samples are heated using water-cooled heater electrodes. Sample temperature is measured using a thermocouple. The growth flange is attached to a vertical linear translator, as shown in Fig. 1.

Fig. 3 Picture of the diamond growth system in our laboratory.

Fig. 4 Detailed picture of the diamond growth chamber.

Fig. 5 Scanning electron microscopy image of a diamond film grown using our system. Crystallites measuring approximately 0.5 μ in width are observed.

Fig. 6 Three-dimensional scanning tunneling microscopy image of the diamond film shown in Fig. 5. Crystallites measuring approximately 0.5 μ are observed, in agreement with Fig. 5.

Fig. 7 Raman spectrum of the diamond film shown in Fig. 5.

Fig. 8 Picture of the Raman spectroscopy system in our laboratory.

Fig. 9 (a)-(c) Raman spectra of Si, natural diamond crystal, and highly-oriented-pyrolitic graphite measured using our system.

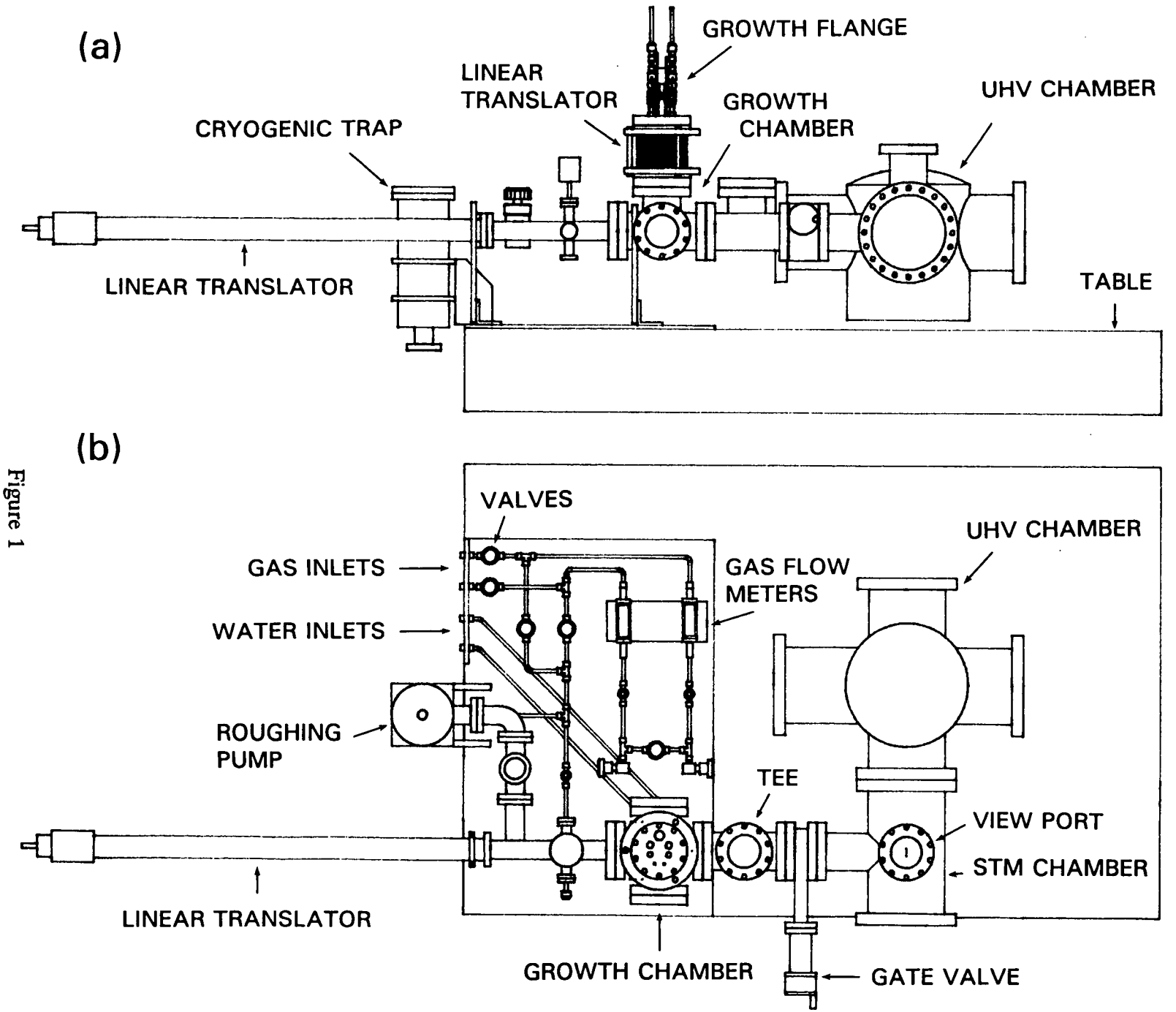
(a)
GROWTH FLANGE
LINEAR TRANSLATOR
GROWTH CHAMBER
UHV CHAMBER
CRYOGENIC TRAP
LINEAR TRANSLATOR
TABLE
(b)
VALVES
UHV CHAMBER
GAS INLETS
GAS FLOW METERS
WATER INLETS
ROUGHING PUMP
TEE
VIEW PORT
STM CHAMBER
LINEAR TRANSLATOR
GROWTH CHAMBER
GATE VALVE

Figure 1
8

GAS HANDLING SYSTEM

(connection between doser shut-off valves and main sample flange not shown)

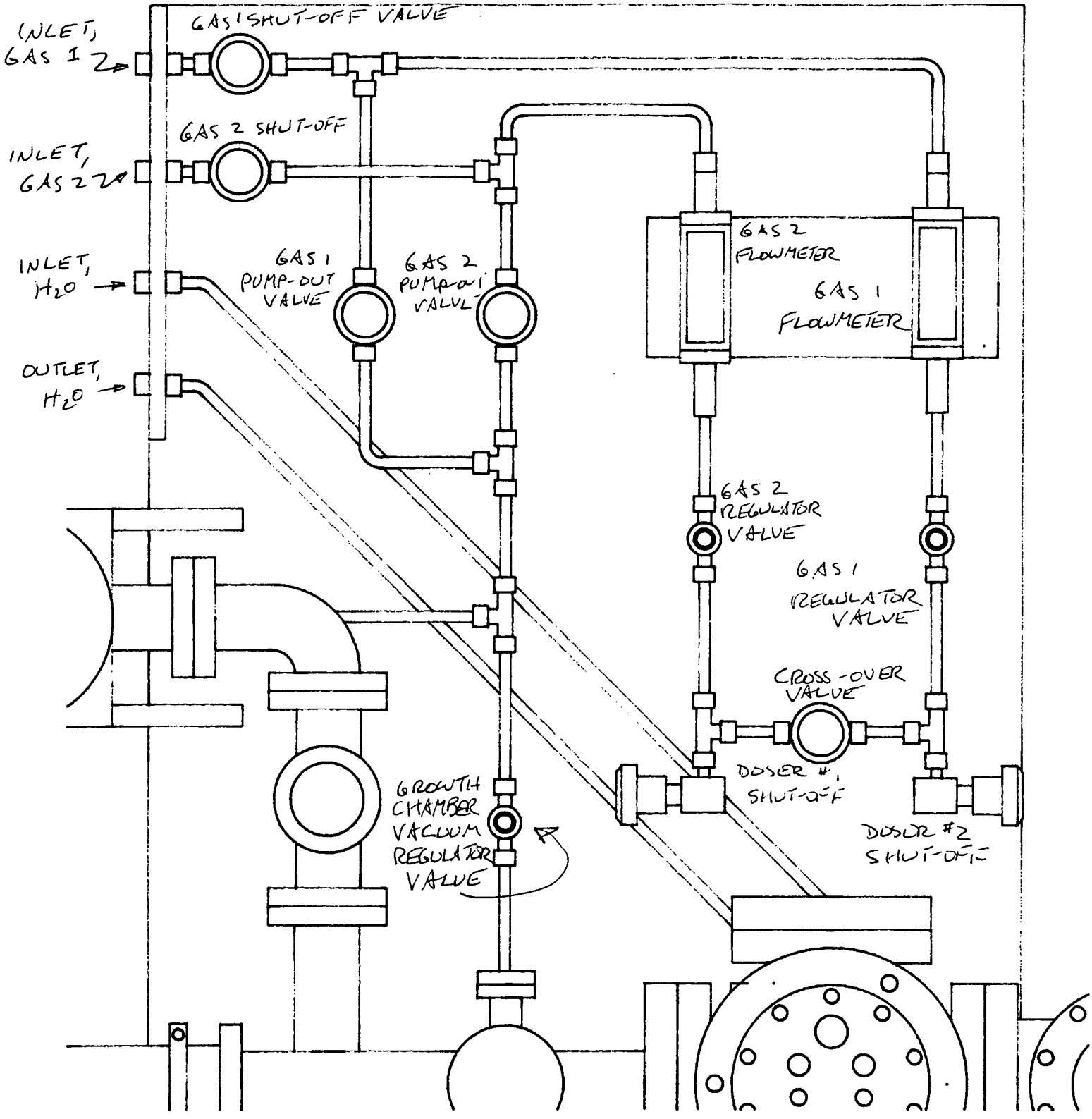

Figure 2 (a)

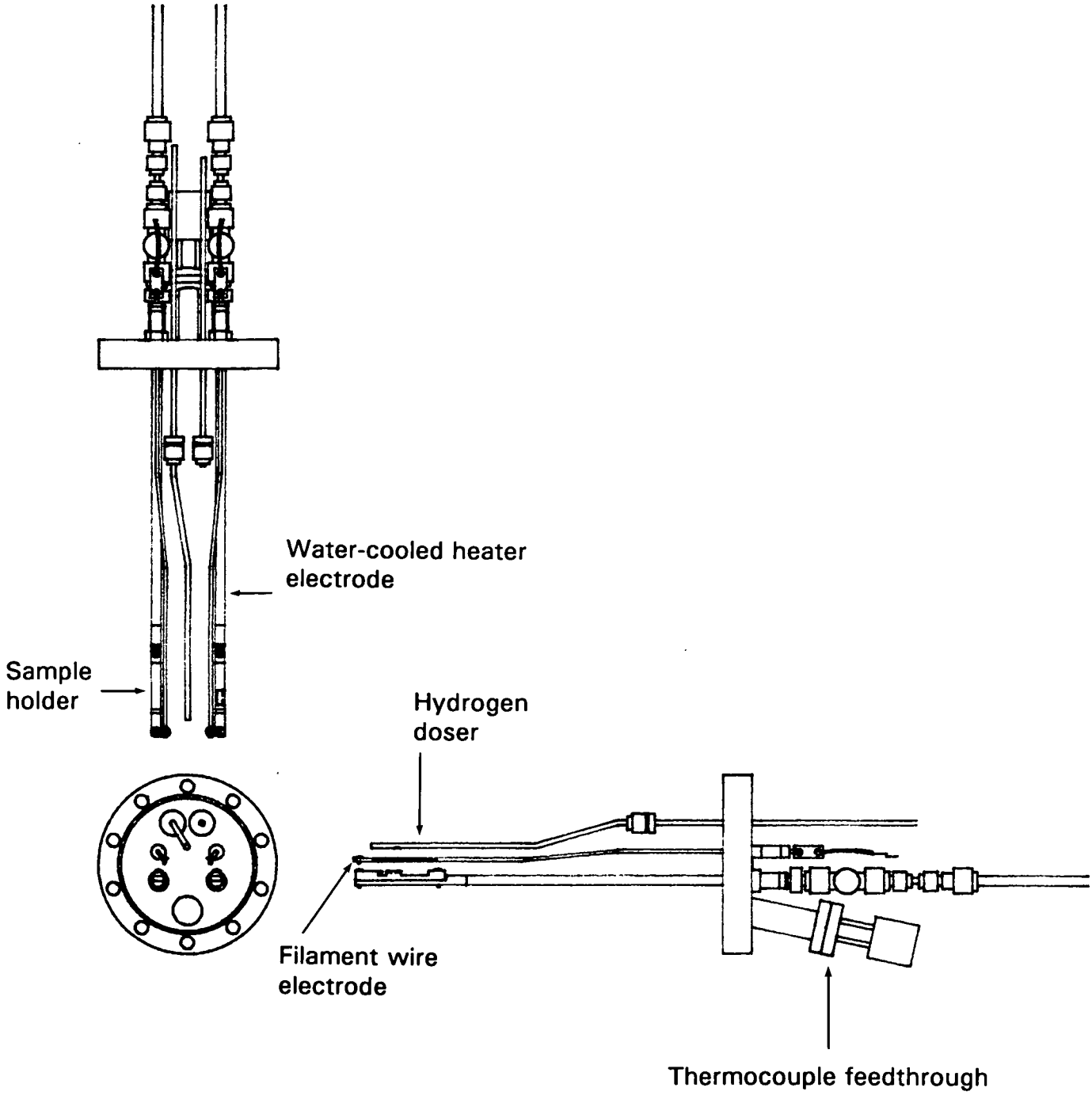
Water-cooled heater electrode
Sample holder
Hydrogen doser
Filament wire electrode
Thermocouple feedthrough

Figure 2 (b)

Figure 3

ORIGINAL PAGE
COLOR PHOTOGRAPH

Figure 4

Figure 5

3900 Å
y: 6800 Å
fdggfdgfd
File
Setpoint
Bias
x: 6800 Å
zoom1022
.70 nA
3000 mV

Figure 6

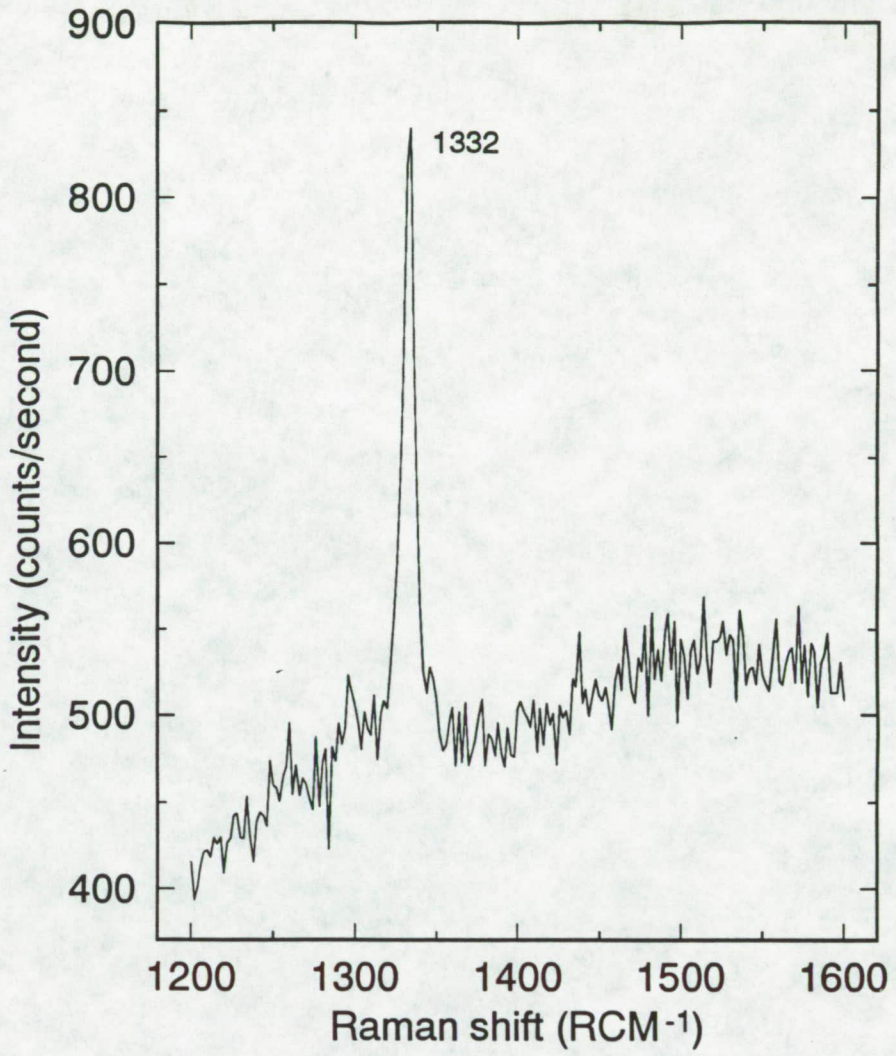

Fig. 7 Raman spectrum of a chemical vapor deposition grown diamond film grown using our system showing a peak at 1332 Rcm^{-1} which is the characteristic Raman line for diamond. A peak at 1478 Rcm^{-1} corresponding to graphite is not observed indicating that the diamond film is of high quality.

Figure 8
16

ORIGINAL PAGE
COLOR PHOTOGRAPH

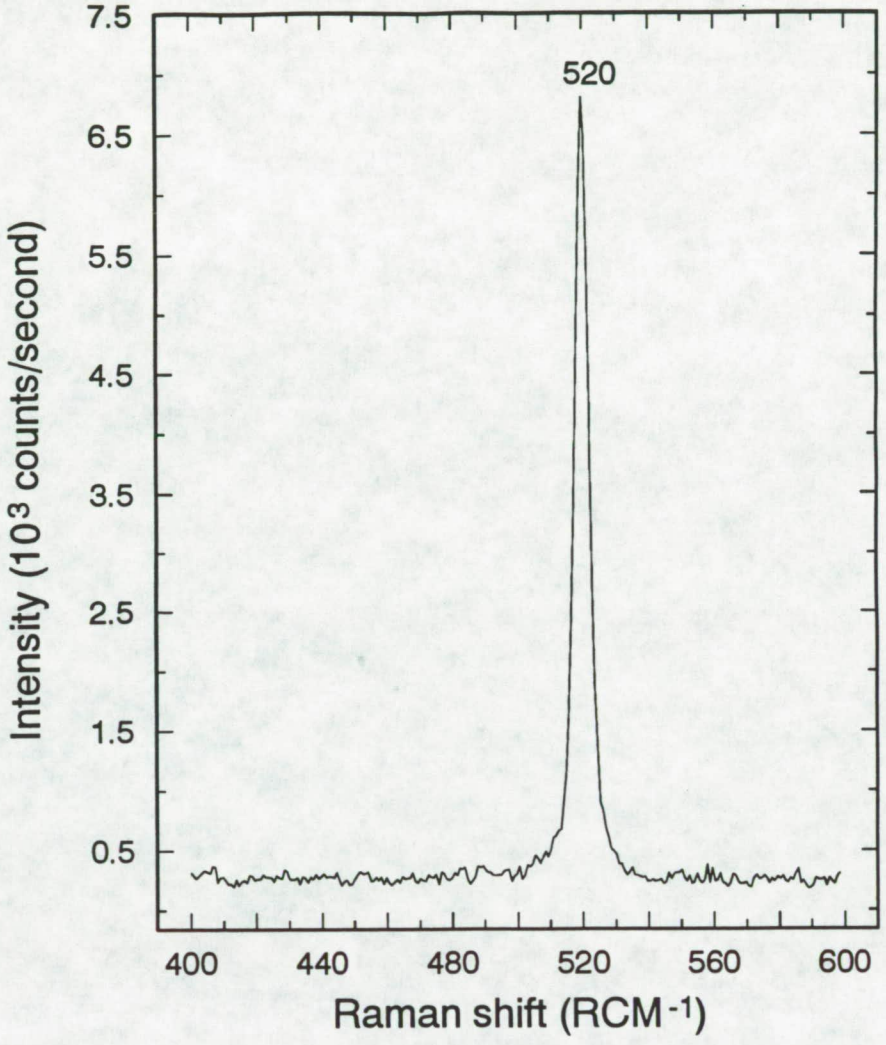

Fig. 9 (a) Raman spectrum of Si(100) showing a peak at 520 Rcm^{-1} in agreement with the accepted value.

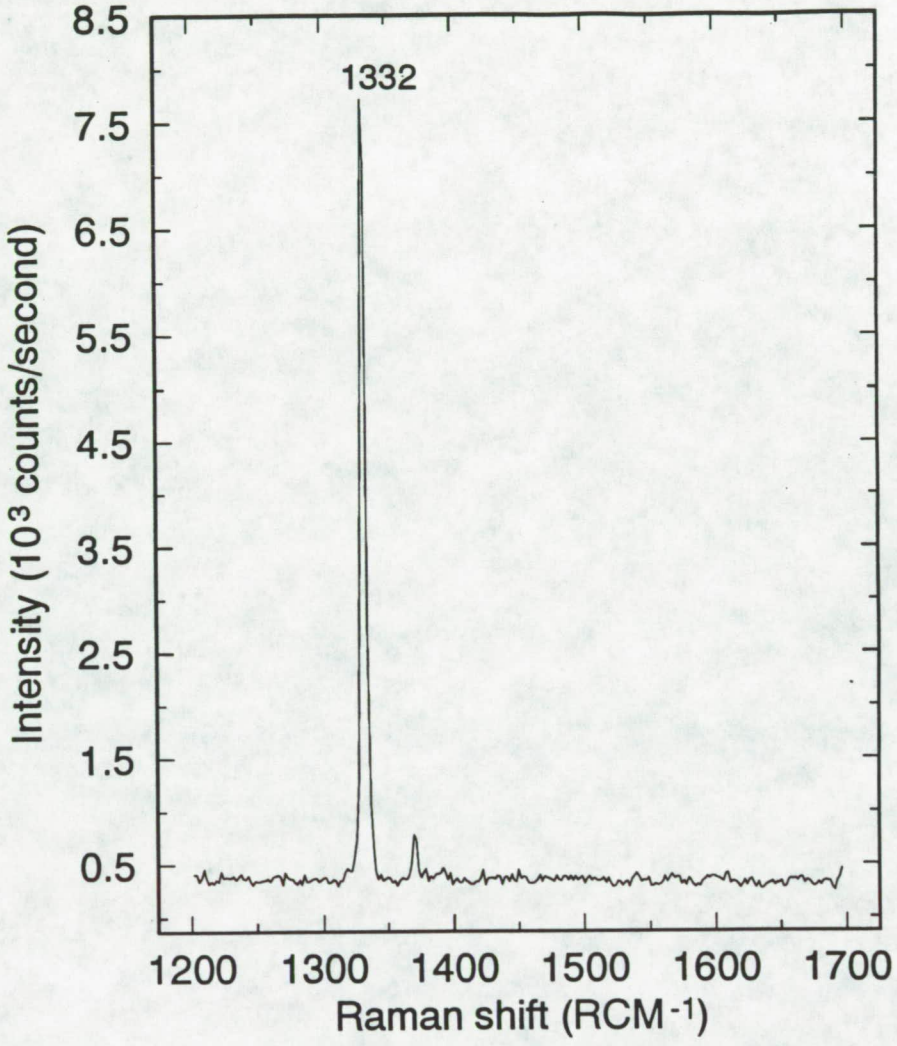

Fig. 9 (b) Raman spectrum of a natural diamond crystal showing a peak at 1332 Rcm^{-1} in agreement with the accepted value.

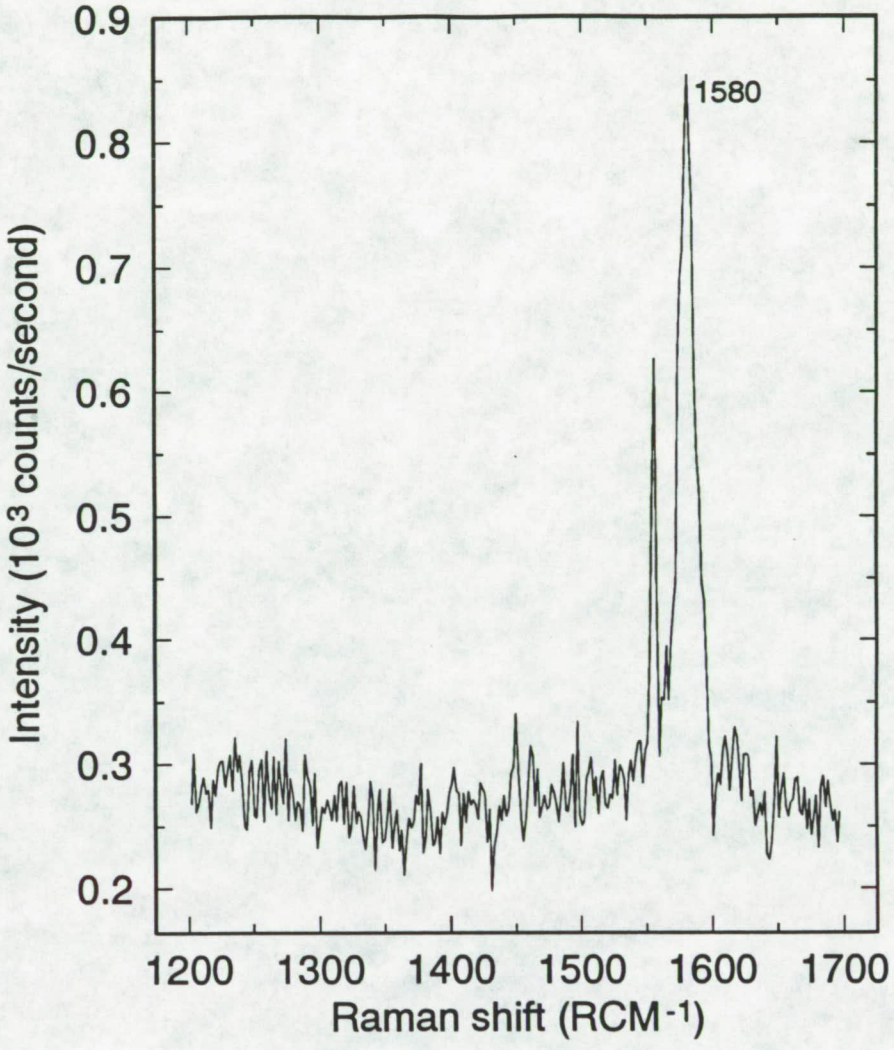

Fig. 9 (c) Raman spectrum of highly-oriented-pyrolitic graphite showing a peak at 1580 Rcm^{-1} in agreement with the accepted value.