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This report describes the accomplishments on this program in obtaining an understanding of the deposition of Group IV thin films by the remote plasma chemical deposition process (RPCVD). We characterized the deposition process by emission spectroscopy and excited state absorption of resonance radiation by metastable states. We deposited and characterized amorphous Si, C, SiC, and heterostructures of Si and SiC. We related the properties of the deposited films to the process parameters. UHV surface chemistry techniques were developed and applied to the study of fundamental deposition processes. A UHV cryogenic cathodoluminescence facility was developed and used to study crystalline diamond and RPCVD-deposited materials.

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RESEARCH ON SILICON, CARBON, AND SILICON CARBIDE HETEROSTRUCTURES

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M. Wallace, and R. M. Young

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1. PROGRAM OVERVIEW

The objective of the program is to gain an understanding of Group IV thin films and heterostructures produced by the remote plasma chemical vapor deposition process (RPCVD). The materials studied were amorphous silicon, carbon, silicon carbide mixtures of various stoichiometries, and heterostructures of silicon and silicon carbide. This program drew from widely interdisciplinary skills and capabilities, which we coordinated and focussed on our objective. We completed the following tasks:

- a. Defining the processes for deposition of the materials of interest by the RPCVD technique, optimizing the process, and realizing films with a wide range of properties;
- b. Characterization of the RPCVD deposition process by diagnostics and modeling to understand the key process issues and how they influence the deposited films;
- c. Characterization of the deposited films to relate their properties to the deposition parameters;
- d. Developing ultra-high-vacuum (UHV) surface chemistry techniques appropriate for studying the fundamental processes occurring at the deposition surface;
- e. Applying the UHV surface chemical techniques to gain an understanding of important fundamental deposition processes;
- f. Building and testing an UHV cryogenic cathodoluminescence apparatus;
- g. Using an UHV cathodoluminescence technique to characterize materials produced by the RPCVD technique, and to study diamond as a basis for comparison to these materials.

The program was completed on time and on budget, despite a considerable number of unanticipated technical surprises and challenges consistent with the lack of predictability of basic research of this nature. In the following sections of the report we will present brief summaries of the research findings, and discuss their significance in perspective to their diverse fields of research. The details of all aspects of the program have been published in the literature, or are presently in the process of publication. We refer the reader who requires more technical depth to these references.

2. DEPOSITION GROUP IV MATERIALS BY THE RPCVD TECHNIQUE

Conventionally, the deposition of materials using chemical activation by plasmas has entailed the immersion of the deposition surface in a plasma which contains significant densities of electrons and positive ions and usually a potpourri of dissociated chemical moieties that can participate in the deposition process.¹⁻³ The primary significance of the technique is that it can be used to deposit "high-temperature" refractory materials such as Si, C, SiC, SiO₂, and Si₃N₄ at temperatures as low as 300K, as compared to the 1300K typical for thermally activated CVD. In addition to materials with some crystallinity, the plasma-deposited films can have amorphous character and be remarkably smooth⁴ and pinhole-free.⁵ These films perform respectably well as insulators or semiconductors^{2,6} and have been a boon to semiconductor fabrication technology, where low-temperature layers of these materials are crucial.

The RPCVD process is an extension of the conventional technique, where the plasma which activates the process is separated from the deposition region,⁷ as shown in Figure 1. The deposition chemistry is carried out in the flowing afterglow of the plasma. At least two advantages can be obtained by this approach. It is possible to greatly reduce or prevent charged species from contacting, and thus damaging the substrate and growing films.⁸ Also, since many reactive species created in the plasma do not survive the afterglow to reach the reaction and deposition zones, the deposition chemistry can be selected and controlled more precisely. The former advantage has been used to deposit high-quality passivation layers on easily damaged surfaces such as GaAs, and the latter advantage has been used to obtain films with greatly reduced concentrations of bonded hydrogen than is usually found in plasma-deposited films.⁹⁻¹¹ The price paid for these advantages is generally a reduction in deposition rates.

In our deposition facility shown in Figure 2, we deposited group IV films by two variations of the RPCVD process on this program. The

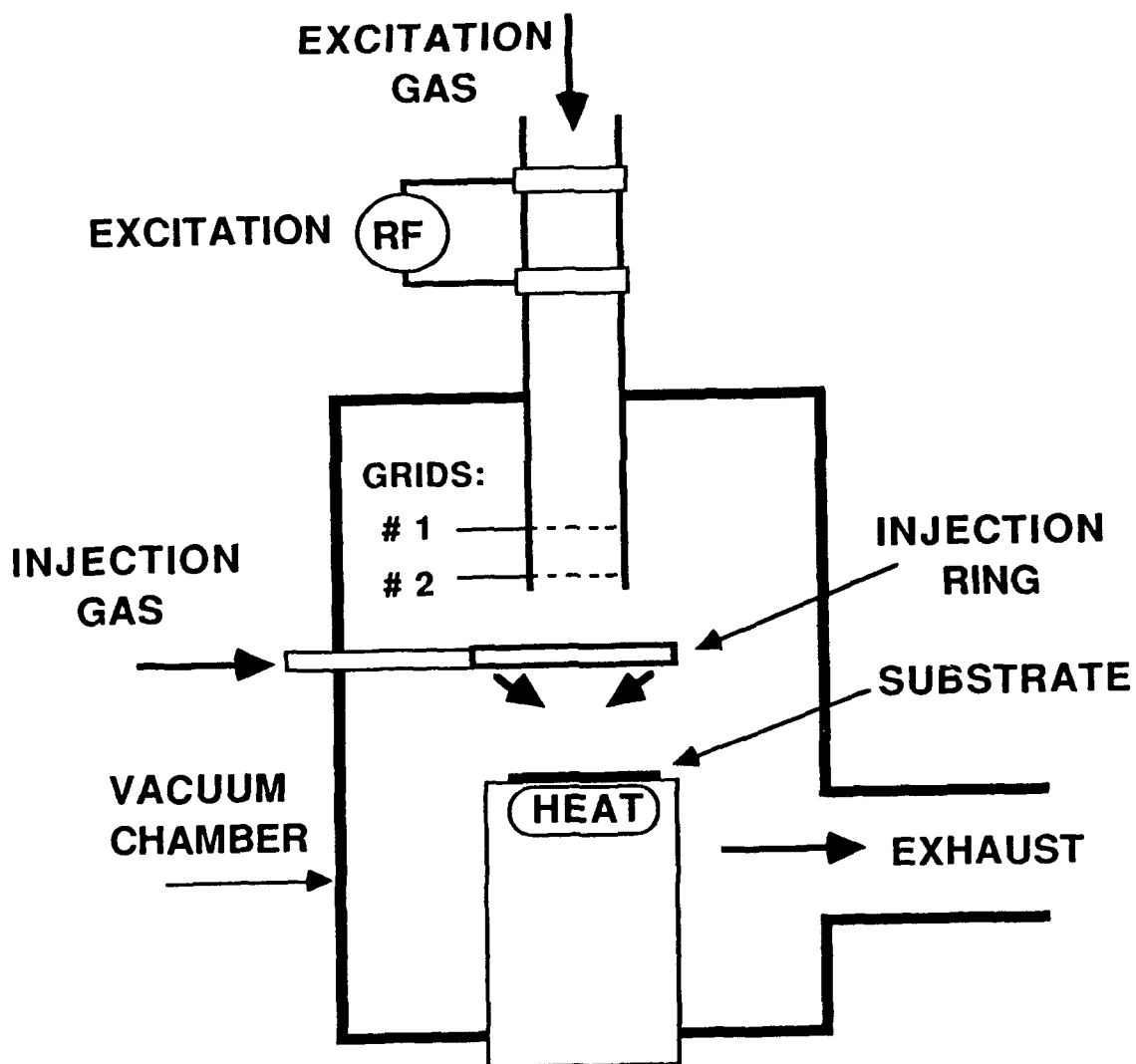


Figure 1. Schematic diagram of the RPCVD process configured for capacitively coupled RF excitation.

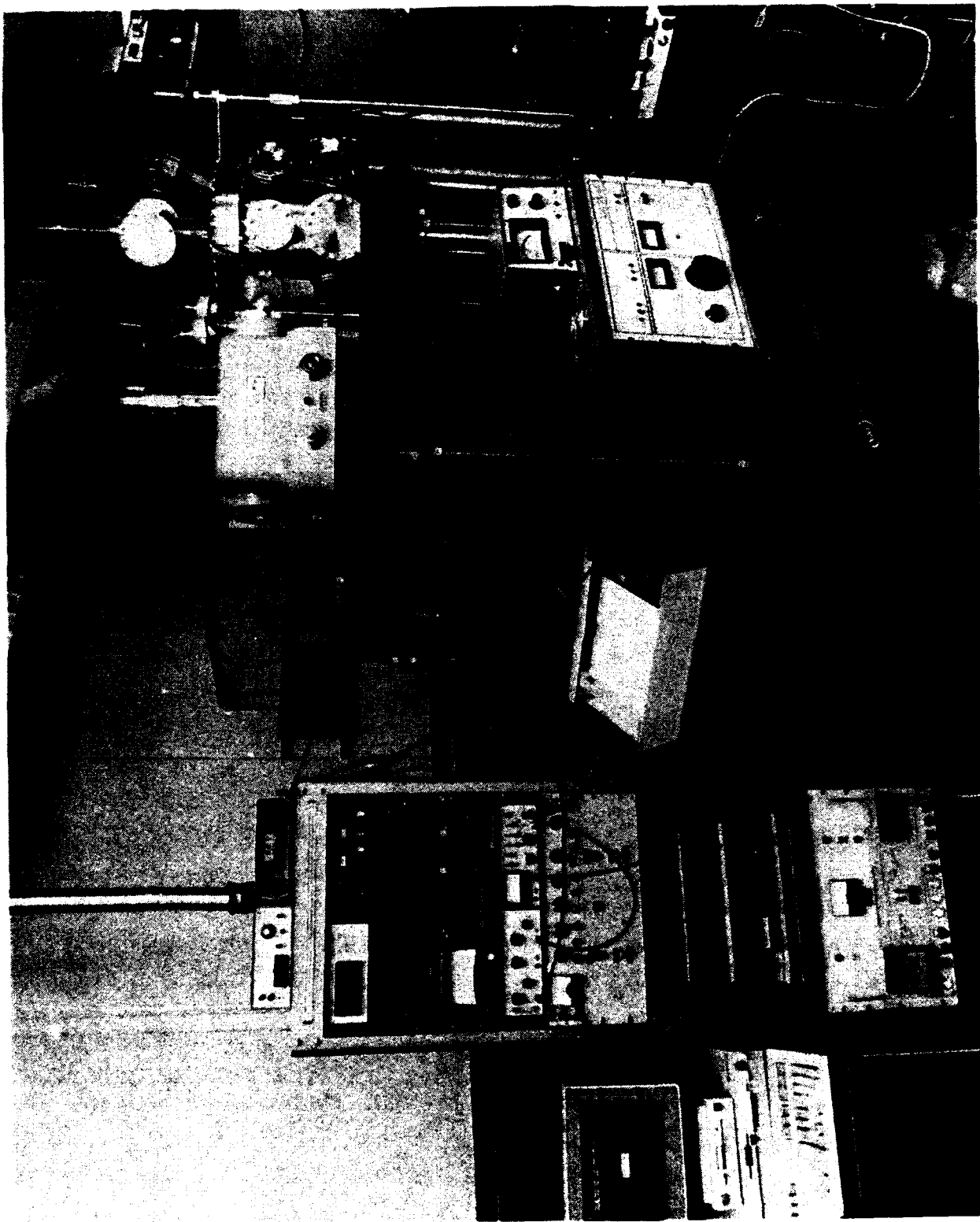


Figure 2. Photograph of the RPCVD deposition facility. The 12-inch steel reactor chamber is seen in the upper right, along with the associated excitation, control, and diagnostic equipment.

first studies were carried out on a microwave-excited afterglow of Ar, used to activate the deposition of amorphous carbon films. The characterization studies of this process led us to the conclusion that microwave excitation results in the production of such large quantities of charged species that the process is difficult to control. The diagnostic and modeling of these afterglows confirmed this conclusion,¹² which is mainly a result of the fact that the 2.45 GHz microwave excitation frequency is fast compared to the collision frequency of electrons in our experimental conditions. The density of the important species that we determined in the microwave-excited Ar afterglow is shown in Figure 3. Reducing the excitation to 13.45 MHz greatly reduced the problems associated with charged species. By controlling the afterglow with downstream grids and selecting the excitation power, feed gas composition, and substrate temperature, we were able to produce and characterize a wide range of carefully controlled films in the Si-C composition series,¹³ as well as heterostructures of Si and SiC both with discrete interfaces and with rugate-wise, continuous composition variation of the Si/C ratio. Several examples of results of this study are shown. In Figure 4, the dependence of the refractive index of Si-C mixtures versus temperature for several ratios of C to Si in the feed gases shows the interdependence of film composition on temperature and gas composition. The Tauc plot in Figure 5 shows how the bandgap varies the Si-C composition. Figure 6 presents cross-section TEM micrographs of two heterostructures, which have discrete and continuous composition variations and demonstrate the suitability of the RPCVD process for producing these structures.

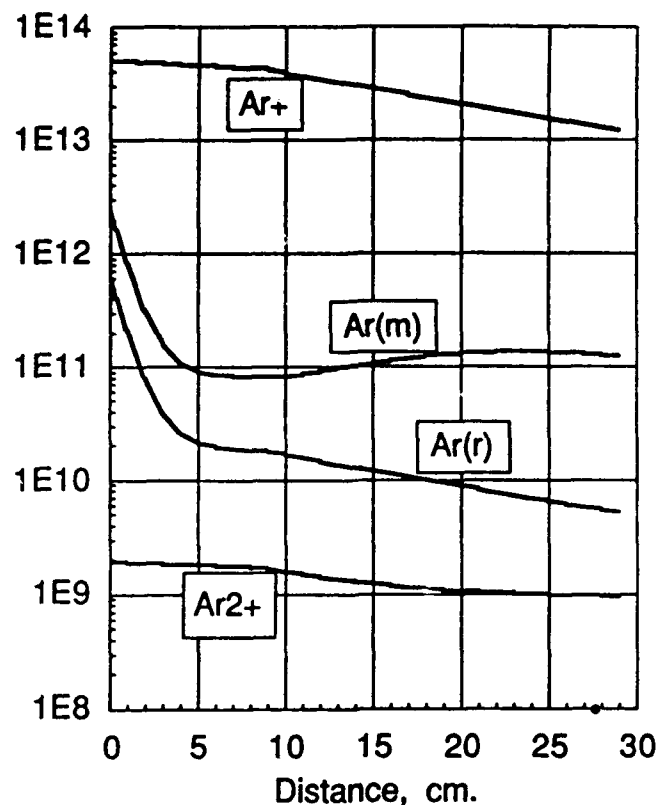


Figure 3. Calculated densities of important species in the afterglow of a microwave-excited argon plasma, providing realistic predictions of our measured values of the metastable densities $[Ar(m)]$, along with excited neutral densities $[Ar(r)]$, argon ions $[Ar^+]$, and argon dimer ions $[Ar_2^+]$.

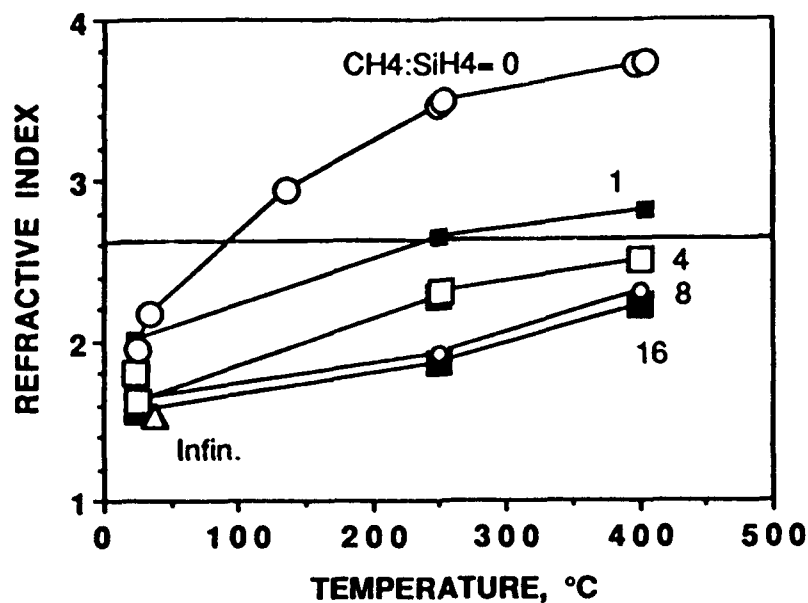


Figure 4. Dependence of the refractive index of RPCVD-deposited silicon-carbon alloys on substrate temperature for several different ratios of silane to methane in the feed gas.

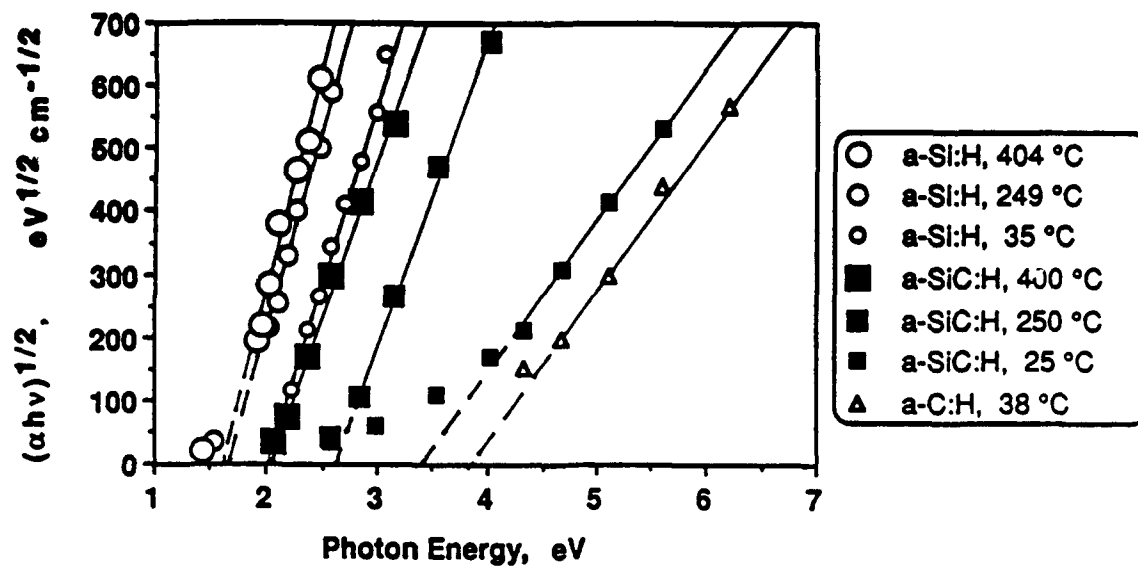


Figure 5. Tauc plots of a-Si, a-SiC, and a-C films deposited by RPCVD. The three a-SiC films were deposited with $\text{CH}_4:\text{SiH}_4$ flow ratio of 8:1.

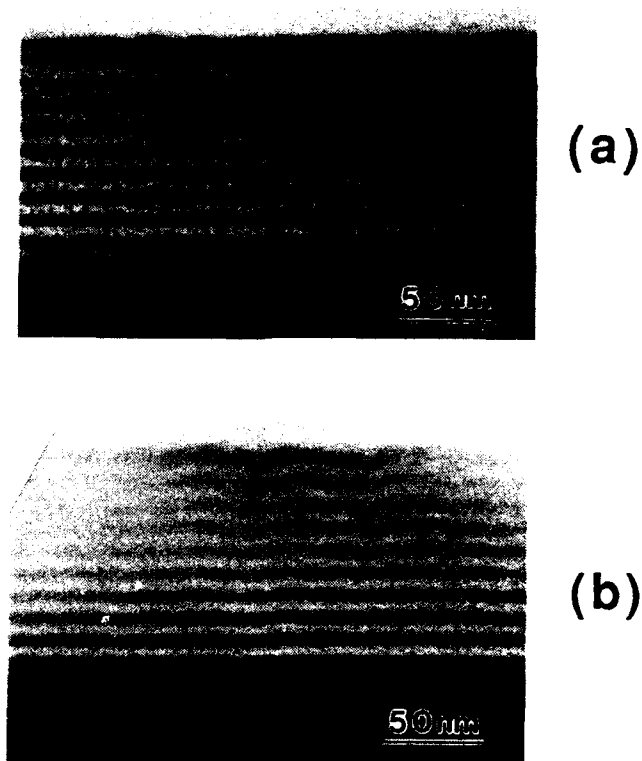
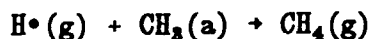


Figure 6. TEM views of a ten-layer pair of a-Si/a-SiC heterostructures deposited by the RPCVD process, with (a) discrete interfaces and (b) regate-wise continuation of the C:Si ratio.

3. SURFACE CHEMISTRY OF DEPOSITION PROCESSES

The UHV equipment for the surface chemistry experiments was upgraded to permit the measurement of absolute coverages of chemisorbed species on Si surfaces, building on the capability we developed on AFOSR Contract F49260-84-C-0063¹⁴ for using surface chemistry techniques to understand the fundamental interactions of hydrocarbons on Si surfaces.¹⁵⁻¹⁷ A top view of the apparatus in Figure 7 shows the different components of the equipment. The new capability was applied to the study of C₂H₂ and C₂H₄ chemisorption on Si(100) surfaces.¹⁸ By carefully calibrating the pumping speed of the chemisorbing surface and the flux of a molecular doser, the kinetics of the process were tracked quantitatively. The surface coverages that were determined in this way were related to models for the C₂H₂ and C₂H₄ absorption complexes on the Si₂ dimer sites.

Following these studies, the surface techniques were directed toward the study of active species that are known to participate in deposition processes. The methyl radical, CH₃, produced by dissociative chemisorption of CH₃I on Si(100), was found to be very stable, having no significant C-H bond scission at temperatures below 800 K. In addition, H-atom bombardment of chemisorbed CH₃ with atomic hydrogen does not lead to the desorption of CH₄, indicating that elementary processes such as:



are kinetically unfavorable on Si(100). These results may have significance in the understanding of the deposition of diamond by CVD. If the situation is similar on the growing diamond surface, these results provide clues as to why the quality of diamond films decreases dramatically below 800K, and suggests that CH₃ radical is a prime candidate as a deposition precursor because of its stability.

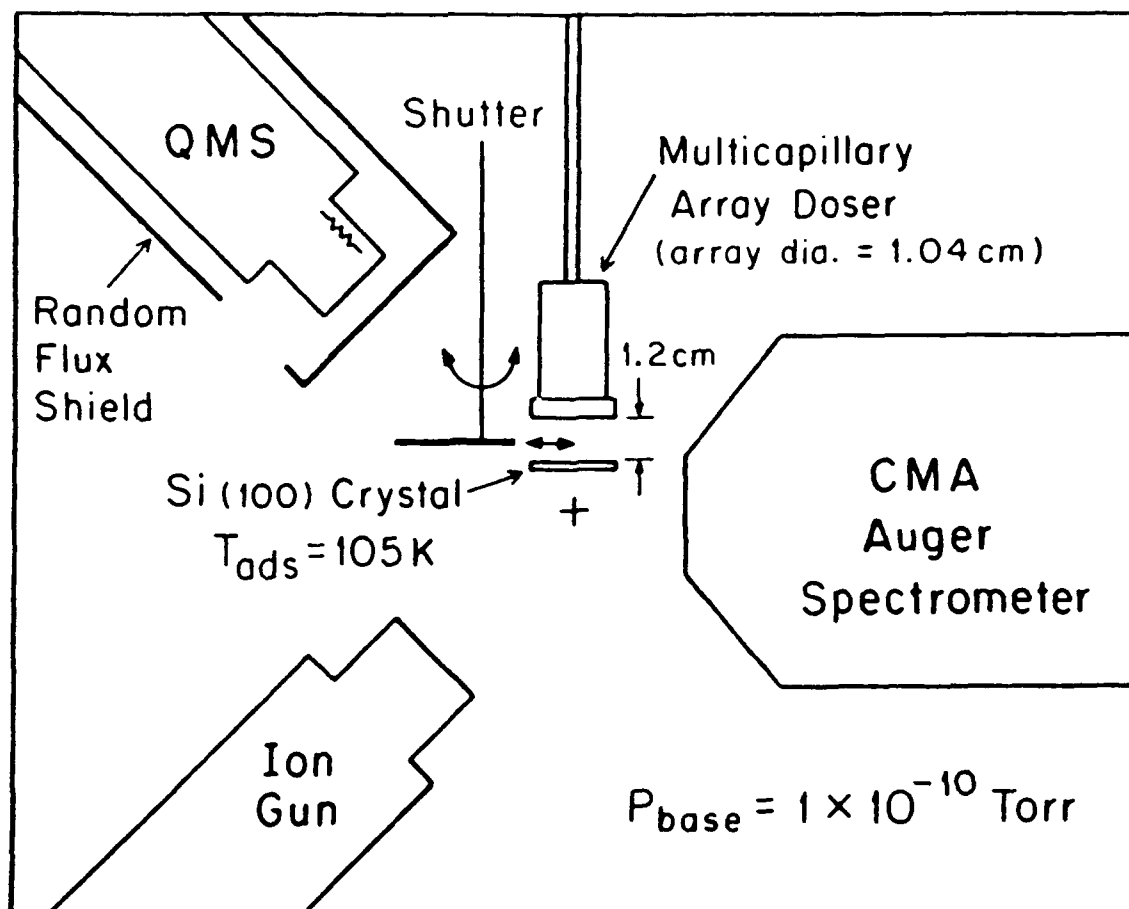
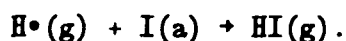


Figure 7. Top view schematic diagram of the ultra-high-vacuum apparatus used for absolute coverage measurements.

Atomic hydrogen does, however, effectively remove adsorbed I at 375K. A likely elementary process which occurs is:



This ability to remove halogen atoms from semiconductor surfaces at low surface temperatures by means of atomic hydrogen is very important, and demonstrates a mechanism for the replacement of semiconductor-halogen bonds with semiconductor-hydrogen bonds in a CVD reaction.

4. CATHODOLUMINESCENCE CHARACTERIZATION TECHNIQUE

The cryogenic cathodoluminescence facility was assembled, put into operation, and used to provide fundamental new data on Group IV materials on this program. A schematic diagram of the facility is shown in Figure 8. Spectra from 200 to 800 nm are taken by an automated system on samples at temperatures as low as 4.2K. A sample turret can accommodate six samples in one run, without warming the cryostat. A great deal of difficulty was encountered obtaining the 4.2K temperature capability in a manner that was cost effective in the use of liquid helium, so most of our data was obtained at 77K. Fortunately, this is adequate for studying wide bandgap materials such as diamond, which was chosen as the subject to be studied first with this technique. We have achieved 4.2K operation at present but we still work at 77K when possible to save money.

Our initial studies on diamond were very productive. Our first work consisted of a comparison of the CL spectra of natural diamond crystals to CVD diamond films deposited under various deposition conditions in a microwave-excited plasma.^{19,20} In Figure 9, the natural diamond CL spectrum is compared to that of CVD diamond, showing the large number of similar features. In the CVD diamond coatings, we identified the intrinsic diamond excitons and most of the important impurity and defect features seen in natural crystals, and correlated their intensities with other measures of "quality" such as Raman spectra and crystal morphology. We also carried out several experimental investigations to identify the nature of the spectral features, a historically difficult undertaking in this material.²¹ By performing high-vacuum annealing studies, comparisons were made of the temperature dependences of centers in CVD materials to the dependences in natural diamond.^{22,23} An example showing the changes in the spectra of a CVD diamond sample after several annealing temperatures is presented in Figure 10. We noticed that the wavelength of the feature at 1.680 eV in

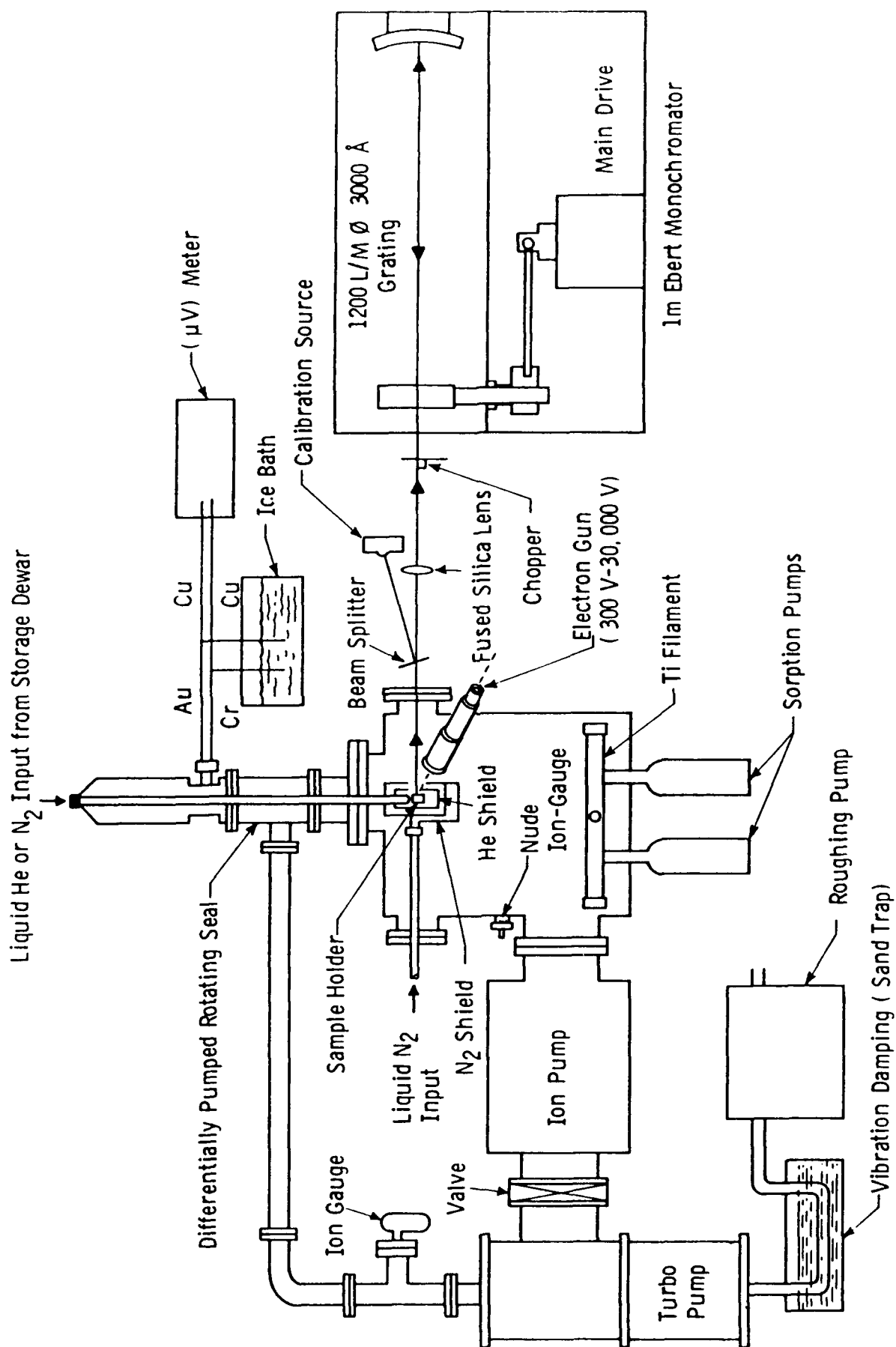


Figure 8. Schematic of the ultra-high-vacuum cryogenic cathodoluminescence facility.

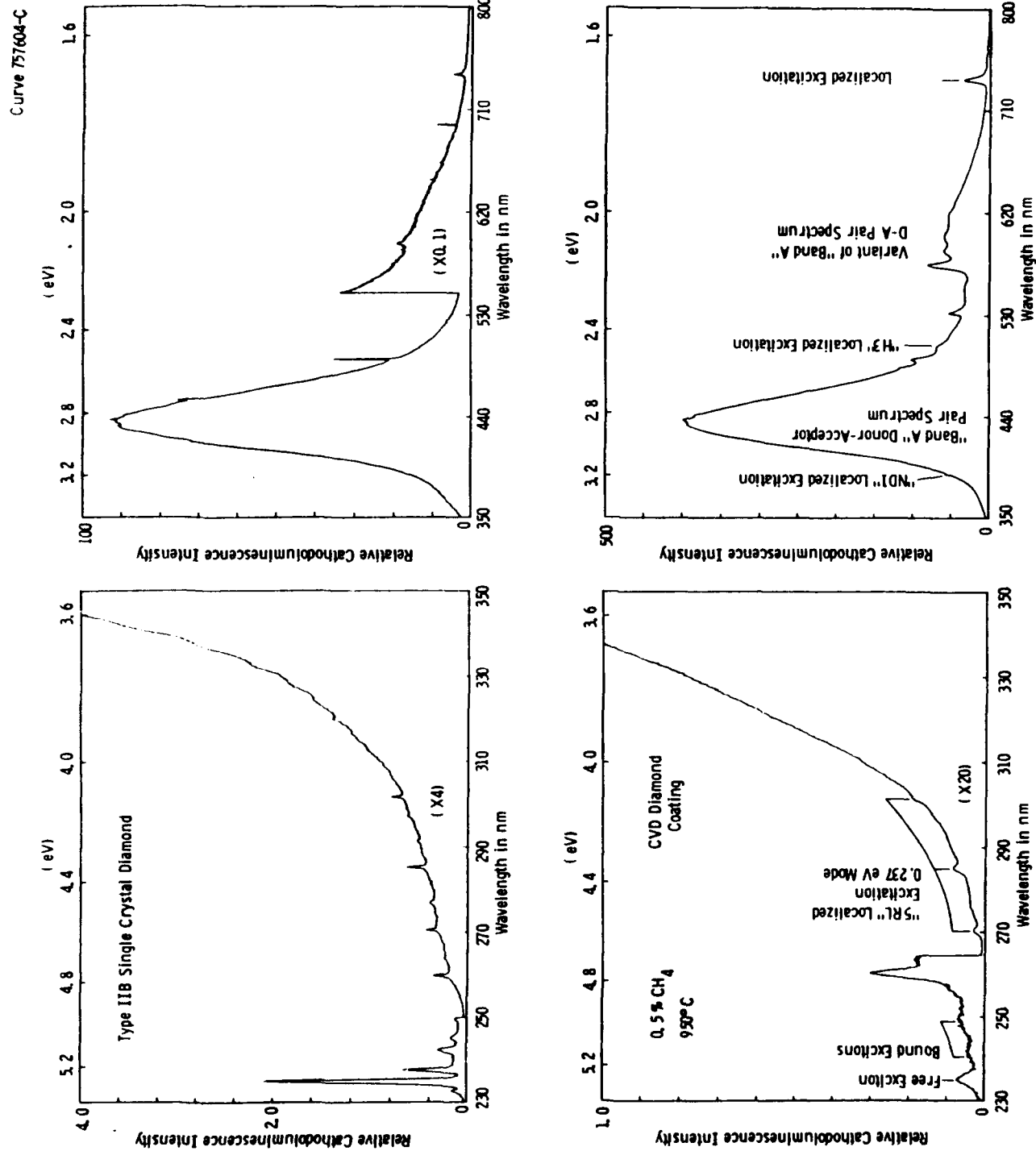


Figure 9. Comparison of the cathodoluminescence (CL) spectrum of a CVD diamond coating to natural IIB single-crystal diamond from 230 to 800 nm.

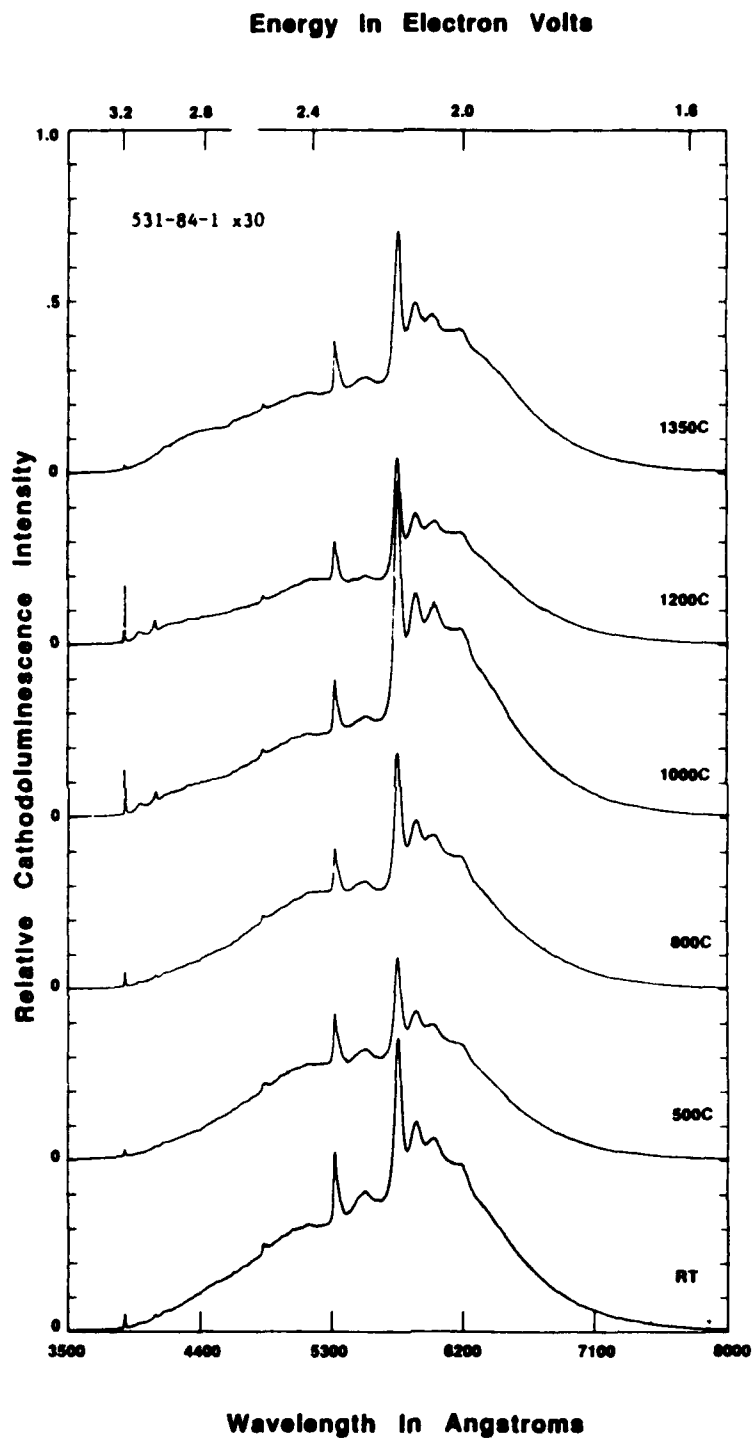


Figure 10. CL spectrum from 350 to 800 nm of a CVD diamond sample as-deposited and after five annealing steps at the temperatures indicated.

the CVD diamond is slightly different from the "GR1" center of natural diamond, located at 1.673 eV. Its annealing behavior is quite different from the center in natural diamond, and we believe that it is associated with a Si impurity. By examining CVD diamond samples deposited under different conditions and on different substrates, we were able to eliminate this feature by eliminating sources of Si that can be transported into the deposition reaction. This is demonstrated by the three spectra shown in Figure 11; diamond deposited on tungsten, on AlN with silicon fixturing in the reactor, and on a silicon substrate.

We evaluated the use of the CL technique on the amorphous materials that we deposited with the RPCVD technique. The cathodoluminescence in the spectral range of 350 to 800 nm of several RPCVD-deposited thin films, and also of a diamond-like carbon film that we deposited in a conventional glow discharge,²⁴ are shown in Figure 12. The spectra of these amorphous materials, taken at 77K with 20 keV excitation, have very broad features and show only a weak dependence on composition or deposition temperature, and even on deposition technique. We were discouraged that these weak features would not provide much information about the RPCVD films. We therefore devoted most of the CL effort to the studies of CVD diamond coatings.

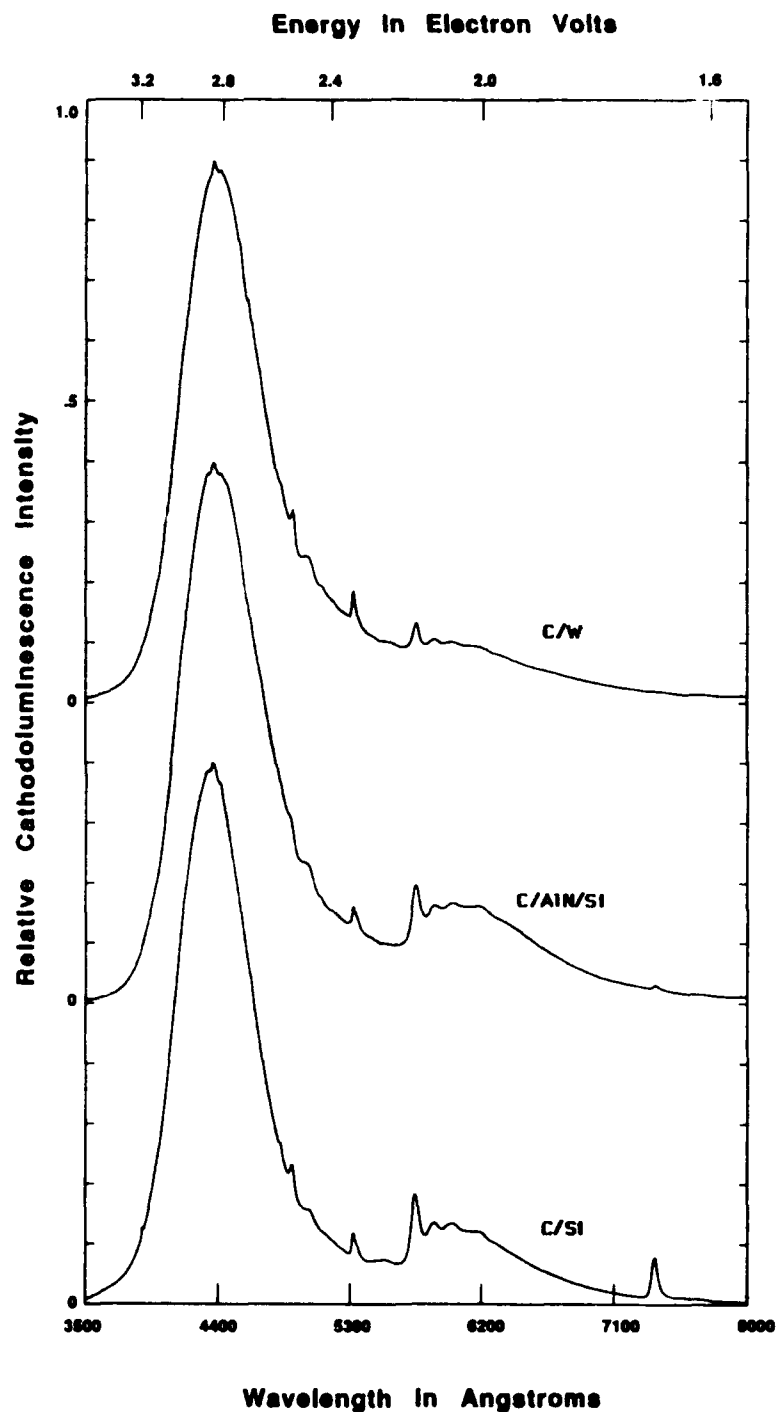


Figure 11. CL spectra of CVD diamond deposited on three substrates with different possibilities for transport of silicon into the process. Upper: W substrate only; middle: AlN substrate, Si fixturing; lower: Si substrate.

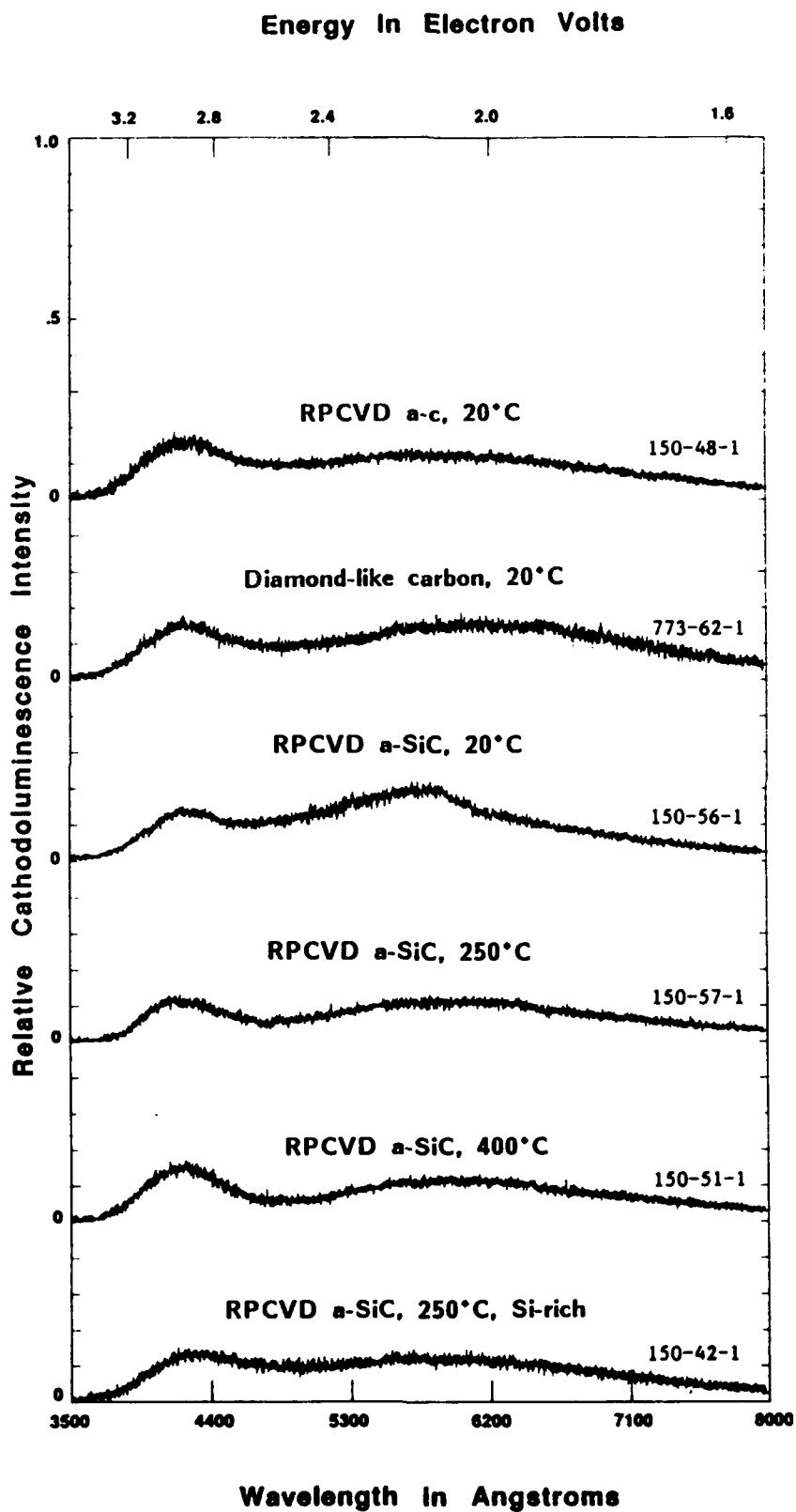


Figure 12. CL spectra of several RPCVD-deposited films and a diamond-like carbon film for comparison.

6. SUMMARY OF PROGRAM ACCOMPLISHMENTS

We have developed an understanding of important issues that are associated with the RPCVD technique, in particular the control of charged species in the reaction zone. Utilizing this understanding, we deposited and characterized a wide range of films in the Si-C composition series and also heterostructures. Key processes of importance to deposition were studied with a newly developed quantitative desorption technique, and new information about surface processes was obtained. A UHV, cryogenic cathodoluminescence facility was built and tested. The cathodoluminescence spectra provided little information about amorphous films, but were very valuable for characterizing CVD diamond coatings, giving new insight on the nature of defects and impurities in this material.

Technical articles published, or planned to be published, in technical journals are references 13, 18, 20, and 23. Reference 12 is published as a paper in a conference proceedings, and references 11, 19, 22, and 23 were presented as conference papers.

6. ACKNOWLEDGMENTS

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