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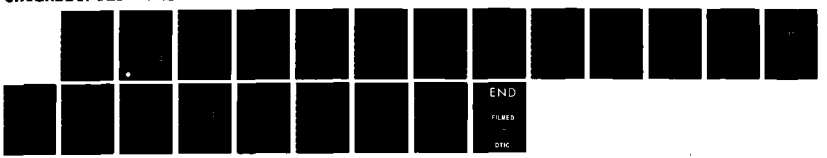

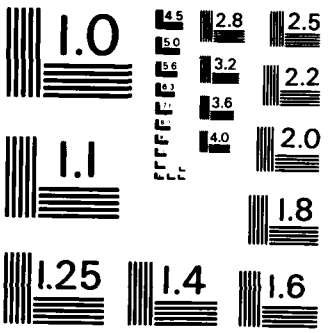

PLASMA DEPOSITION OF SILICON CARBIDE THIN FILMS

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W. D. Partlow, W. J. Choyke, John T. Yates, Jr.,
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

During this reporting period we completed the adaptation of experimental equipment required for the three related areas of the research program: understanding plasma deposition chemistry and physics, characterization of plasma deposited thin films, and surface chemistry of elemental deposition processes.

In the plasma studies area, extensive experiments were conducted on methane plasmas, and experiments were begun on methane-silane plasmas. We achieved significant anisotropy in the deposition chemistry by controlling electrode

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20. Abstract (Cont'd)

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The UHV apparatus for surface chemistry was acquired, assembled, and tested, and initial measurements of the desorption of organic gases were completed.

PLASMA DEPOSITION OF SILICON CARBIDE THIN FILMS

ABSTRACT

During this reporting period we completed the adaptation of experimental equipment required for the three related areas of the research program: understanding plasma deposition chemistry and physics, characterization of plasma deposited thin films, and surface chemistry of elemental deposition processes.

In the plasma studies area, extensive experiments were conducted on methane plasmas, and experiments were begun on methane-silane plasmas. We achieved significant anisotropy in the deposition chemistry by controlling electrode bias and the data are being compared to a theoretical model produced in a collaborative effort by L. E. Kline at Westinghouse R&D Center. We have selected characterization techniques for the thin films produced with these plasmas, and measurements have begun.

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I OVERVIEW

The overall program objective is to understand the fundamental processes of plasma deposition so that properties of the deposited films can be selected by controlling the properties of the plasma and the plasma-substrate interface.

The objectives for this reporting period were:

1. modify the plasma deposition equipment including installation of a quadrupole mass spectrometer;
2. gain an understanding of the reaction chemistry;
3. select and adapt film characterization to include optical as well as other techniques deemed necessary;
4. characterize as-grown samples and develop understanding of processing variables interaction;
5. assemble UHV components of the elementary plasma process experiment.

Objectives 1. and 2. were carried out on the plasma deposition equipment at the Westinghouse R&D Center, objective 5. at the University of Pittsburgh Surface Science Center, and objectives 3. and 4. were shared between Westinghouse R&D and the University of Pittsburgh Physics Department. Research toward the second objectives was also carried out by Dr. L. E. Kline at the Westinghouse R&D Center on a corporate funded research program as a collaborative effort. The research tasks of this program logically subdivide into three categories: plasma studies, thin film characterization, and surface studies. For clarity, we will group our discussions accordingly.

The ongoing progress on this program has been reported in three interim reports submitted September 21, 1984, January 16, 1985, and April 15, 1985. In the present report we will emphasize the overall status and significance of the program, and refer to these earlier reports for description of the details of the program tasks.

II PLASMA STUDIES

In order to carry out a careful study of the influence of deposition conditions on the deposited films, it was necessary to obtain control of these conditions along with suitable diagnostics for characterizing them. A schematic diagram of the experimental plasma deposition reactor is shown in Figure 1. To control the ion bombardment energies, we selected a "powered electrode" configuration, designed and built an elaborate tri-axial, heated electrode shown in Figure 2., and selected operating pressures and frequencies to obtain a wide range of potentials between the plasma and the surfaces on which the films are deposited. Figure 3. shows the measured electrode and floating probe bias voltages for this configuration with 2MHz RF excitation, 0.3 torr pressure. Since the plasma potential is 10-15V above the floating probe potential, we see that we have achieved over 400V average potential between the plasma and the powered electrode, and only tens of volts between the plasma and the grounded electrode. Figure 4. shows that the measured deposition rates are significantly different for substrates placed on these two electrodes. With this control of differential ion chemistry, we are in an excellent position to study its effects via sample characterization. We will discuss our plans for this study in the next section. Thus far, most of our measurements have been on the deposition of carbon from methane plasmas, methane being the majority component of the methane-silane plasmas used for deposition of a-SiC. We have nearly completed our measurements on methane plasmas, and have begun the measurements of methane-silane plasmas.

By measuring the mass spectra of the downstream gases for methane (Figure 5.), we have worked out the mass transport branching for the carbon containing gases and molecular hydrogen, as illustrated in Figure 6. These data are self consistent: carbon lost in the dissociation of methane is found either in the higher hydrocarbons downstream or in the deposited thin films. We compared this data to the

theoretical model of L. E. Kline, which predicts the electron impact neutral dissociation and ionization rates of methane in our plasma conditions. Using the assumption that there is no back reaction of the dissociation products to produce methane, the model predicts downstream methane number density to be only 25% of the input value under conditions where we measure it to be 75%. Chemical kinetics calculations are planned to see if this discrepancy can be explained by gas phase back reactions. The possibility also exists that this is evidence of heterogenious back reactions at the surface. We plan to perform experiments to see if non-uniform gas flow effects can account for the disagreement. It should be pointed out that predictions of these rates within a factor of three with these ab-initio calculations is reasonably good for a first try. We are close to having a well-founded understanding of the methane plasmas, and expect subsequent improvements. Figure 7. shows the ionization and neutral dissociation rate coefficients, and the average electron energy plotted versus electric field/density ratio (E/n) predicted by the model. Typical operating conditions for our plasmas are at E/n values of several hundred to 1000 Townsends, resulting in average electron energies of about 10 electron volts.

We have presented preliminary results of the plasma studies at the IEEE International Conference on Plasma Sciences in Pittsburgh in June, 1985, and will present further results at the Gaseous Electronics Conference in Monterey in October, 1985. We also plan to submit an article on this subject to the Journal of Applied Physics this fall.

III THIN FILM CHARACTERIZATION

The initial characterizarion that we have performed on the films has been weighing uncoated and coated substrates on a microbalance to measure the film weight in order to determine the deposition flux, and thus the mass branching in

the deposition process. Measurements to within about 10 microgram provide film weight measurements to typically 10% accuracy. When combined with reflectometry and ellipsometry measurements, we will have a determination of density along with thickness and refractive index. We think that Raman spectrum measurements on the films will be particularly interesting in determining the influence of deposition conditions on stoichiometry and on the amorphous-glassy-crystalline nature of the films. The Raman spectrometer in the University of Pittsburgh Physics Department has recently become operational, replete with double monochromators, photon counting electronics, cooled photomultiplier detectors, and complete computer interfacing. We have produced samples, and will begin these measurements soon.

IV SURFACE STUDIES

This reporting period has consisted primarily of constructing and testing a dedicated UHV chamber for silicon carbide experiments. The system has been completed, and preliminary experiments on Si(100) surface chemistry have begun.

Apparatus Progress:

A schematic of the apparatus is shown in Figure 8. The apparatus consists of a dedicated UHV chamber operating at a base pressure of $2(10)^{-10}$ Torr base pressure. The chamber has been fitted with a scanning Auger microprobe and a UTI quadrupole mass spectrometer, both of which have been tested and are working satisfactorally. Temperature programming up to 700K is easily achieved by way of radiative heating of the crystal specimen with a 900W quartz-halogen tungsten filament source. Resistive heating of the crystal is also possible by a thermistor controlled power supply. Crystal temperatures are measured by a W-26%-Re vs W-5%-Re thermocouple. A symmetrical collimated molecular beam doser, designed to deposit adsorbate gases in a controlled manor, has been calibrated to supply $1.52(10)^{13}$ molecules/Torr-sec of gaseous species to the crystal. This technique of adsorption on the crystal prevents a major gas load from being incorporated into the ultra-

high vacuum environment, leading to unacceptable levels of residual gases in the system. The flow of gas to the effusion source is controlled by adjusting the pressure behind a 1 micron radius doser aperture. It is possible to dose the crystal with a square pulse of gas by actuating appropriately placed valves in the gas line. Introduction of six species of gas to the system is possible by way of a gas handling system which has been constructed and is now in operation.

Preliminary Experimental Results:

A. Temperature Programmed Desorption

Preliminary experiments have begun to study temperature programmed desorption of propylene on the Si(100) surface. The Si surface was cleaned by 2 kV Ar^+ sputtering, followed by a 1000K thermal anneal to remove the sputter beam damage and volatilize residual argon. Major surface contaminants of C and O were readily removed by this procedure.

A series of thermal desorption spectra for propylene on Si(100) is given in Figure 9. The curves, each corresponding to a different propylene exposure, are displaced slightly for clarity. The propylene pressure changes as observed by the mass spectrometer ion current at mass 42 (the parent peak) is plotted as a function of temperature. The area under each curve is proportional to the propylene coverage. Two well resolved propylene binding states are observed on Si(100), which are found to desorb at temperatures near 200 and 600 respectively. We plan to perform more detailed studies of the adsorption states of propylene on Si(100) by way of a microcomputer controlled data acquisition system, which allows for simultaneous recording of several mass peaks during desorption.

B. Auger Chemical Effects vs. Electron Beam Irradiation

Auger chemical effects have been observed during electron beam irradiation of the Si(100) surface. In particular, the C(272 eV) KLL Auger peak was found to undergo a shape change during continuous application of electron beam current, as

shown in Figure 10. The shape change indicates that the surface C atoms are experiencing a changing chemical environment, and that the irradiation is modifying the propylene surface species. During the irradiation, the focused beam was supplying 1.1 microamps of current in a 0.1 mm spot at 3 kV energy. These results lend optimism to future studies of structural chemistry at silicon surfaces, as it appears possible to induce molecular fragmentation of adsorbed layers on Si by electron beam irradiation.

We believe that electron stimulated surface reactions of this sort can be important fundamental processes in plasma deposition, although the average electron energies and current densities found at surfaces in contact with typical deposition plasmas are much less than those used in these experiments. We expect these studies to determine the role of these reactions.

Figure 1. Schematic diagram of the experimental plasma deposition apparatus.

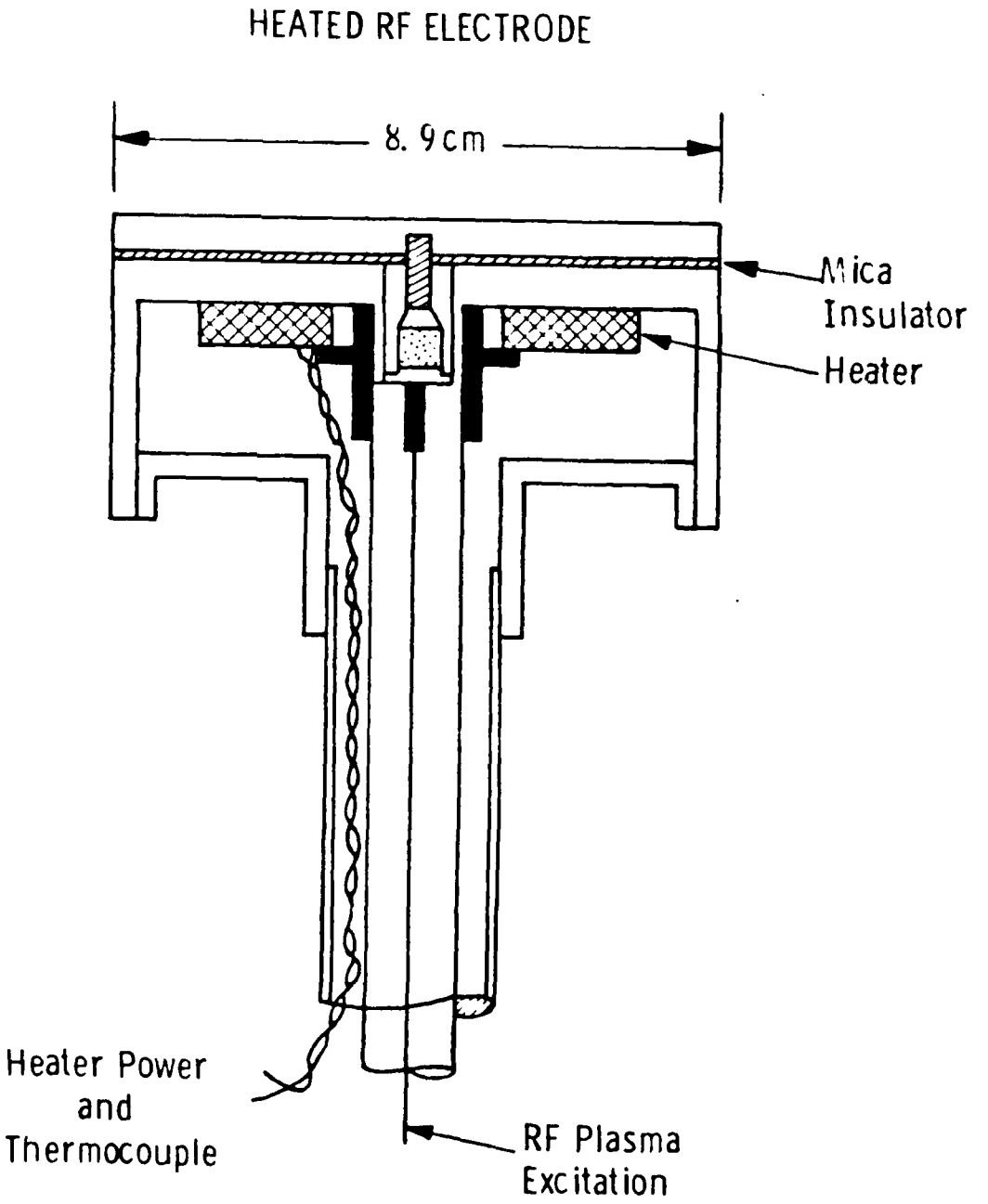

Figure 2. Triaxial electrode for bias potential control.

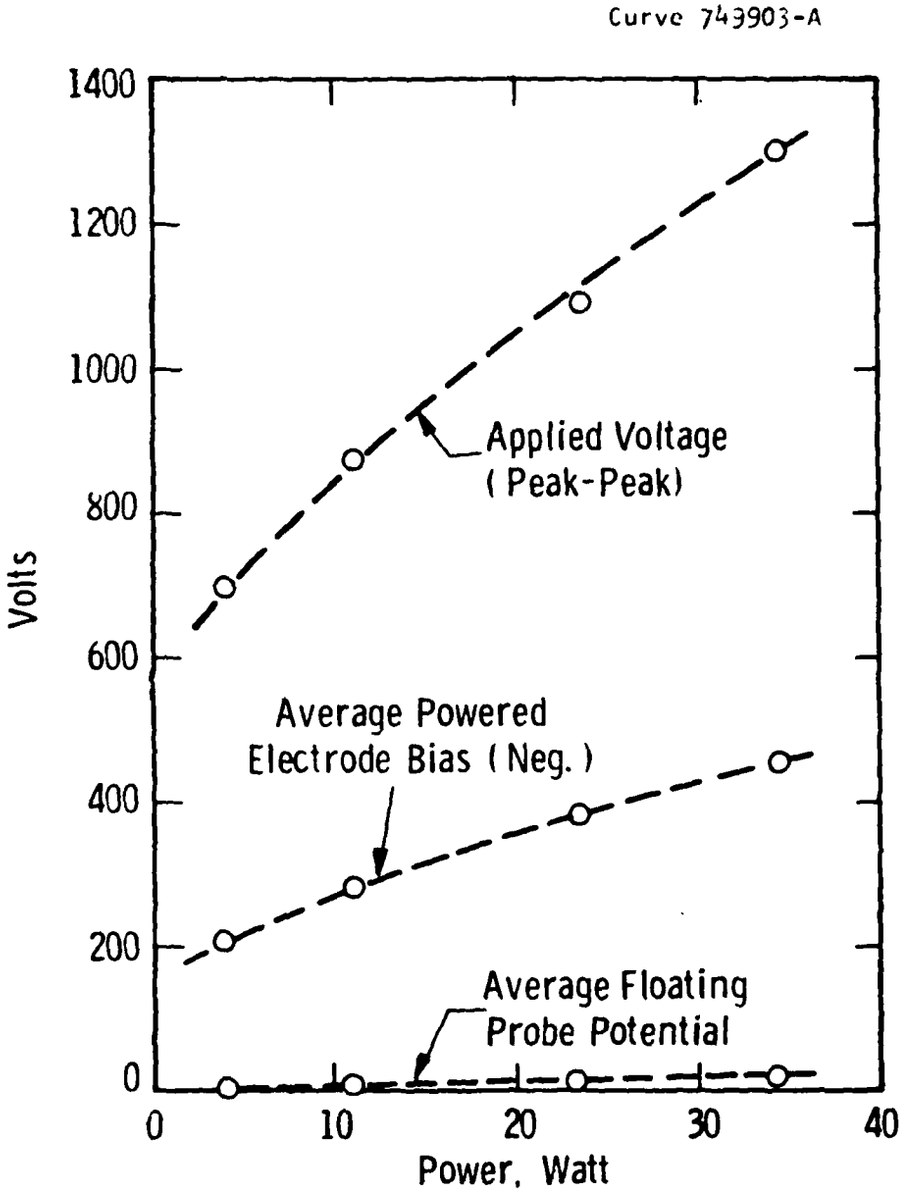

Figure 3. Electrode bias potential, floating probe potential, and peak-to-peak applied voltage of methane plasma, 300mtorr pressure, versus power.

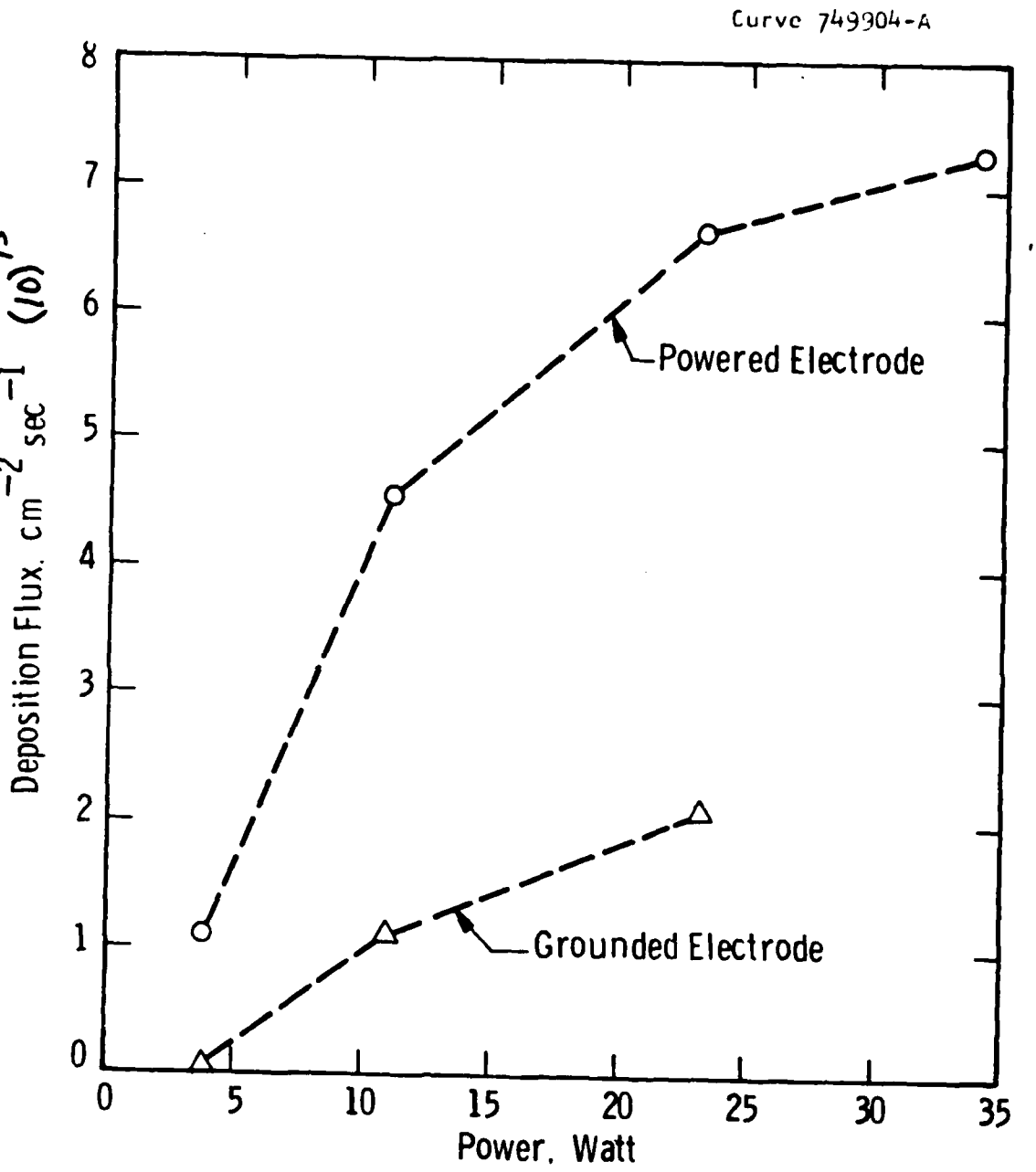

Figure 4. Deposition flux versus power on substrates located on the two electrodes, methane plasma, 300mtorr pressure.

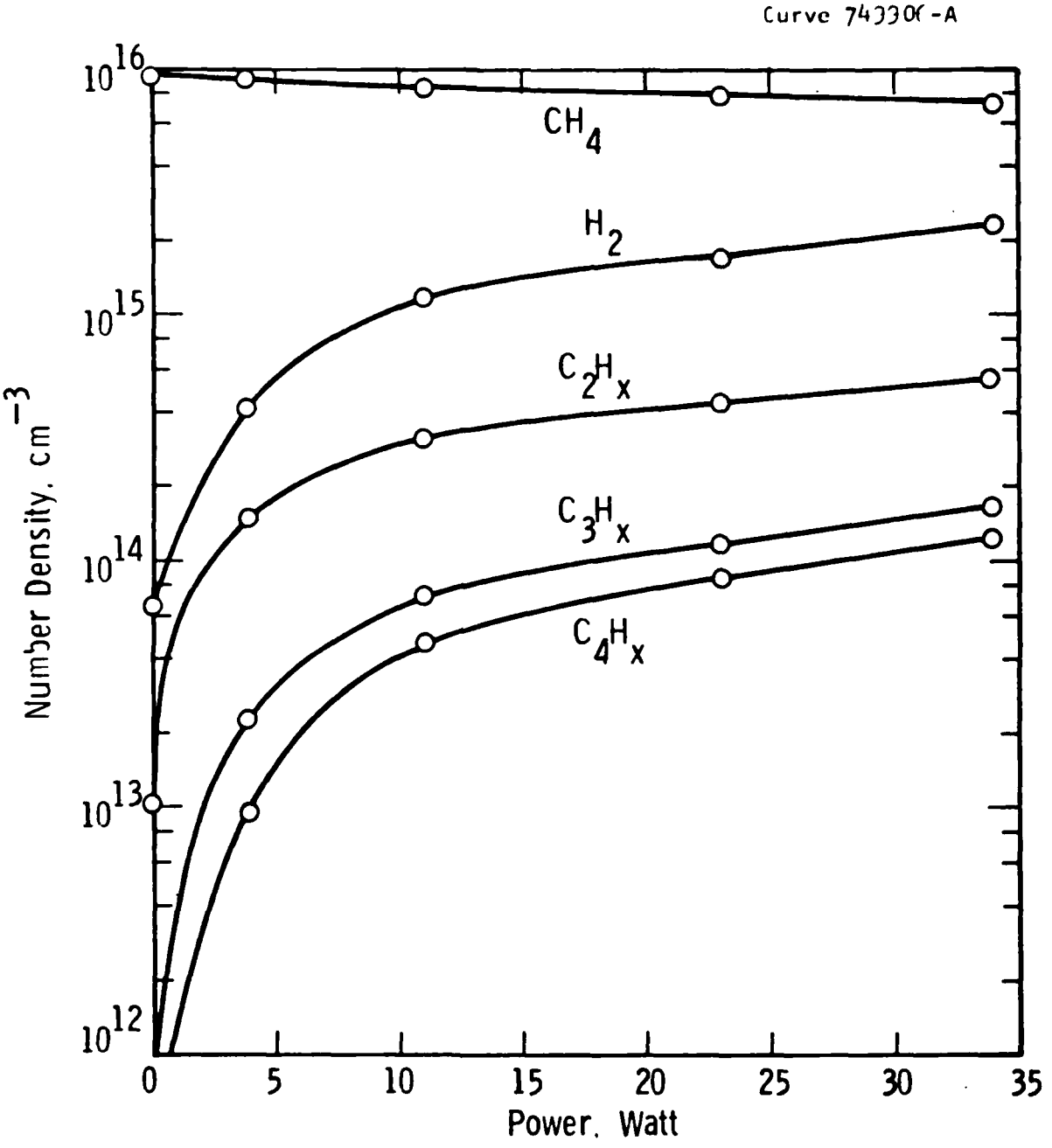

Figure 5. Downstream partial pressures of product species from the plasma measured with the mass spectrometer.

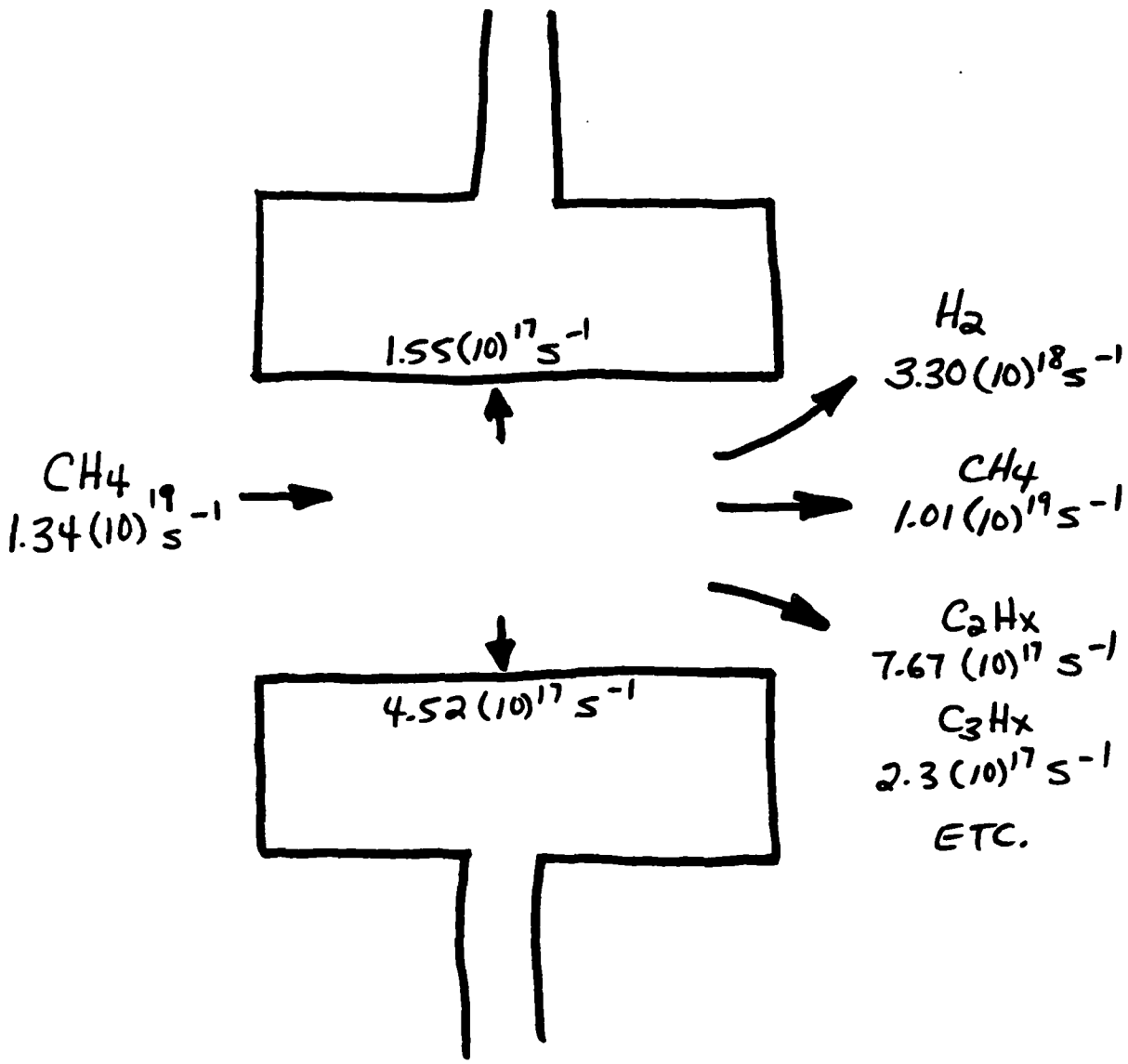

Figure 6. Schematic showing mass transport branching of carbon containing species and of molecular hydrogen.

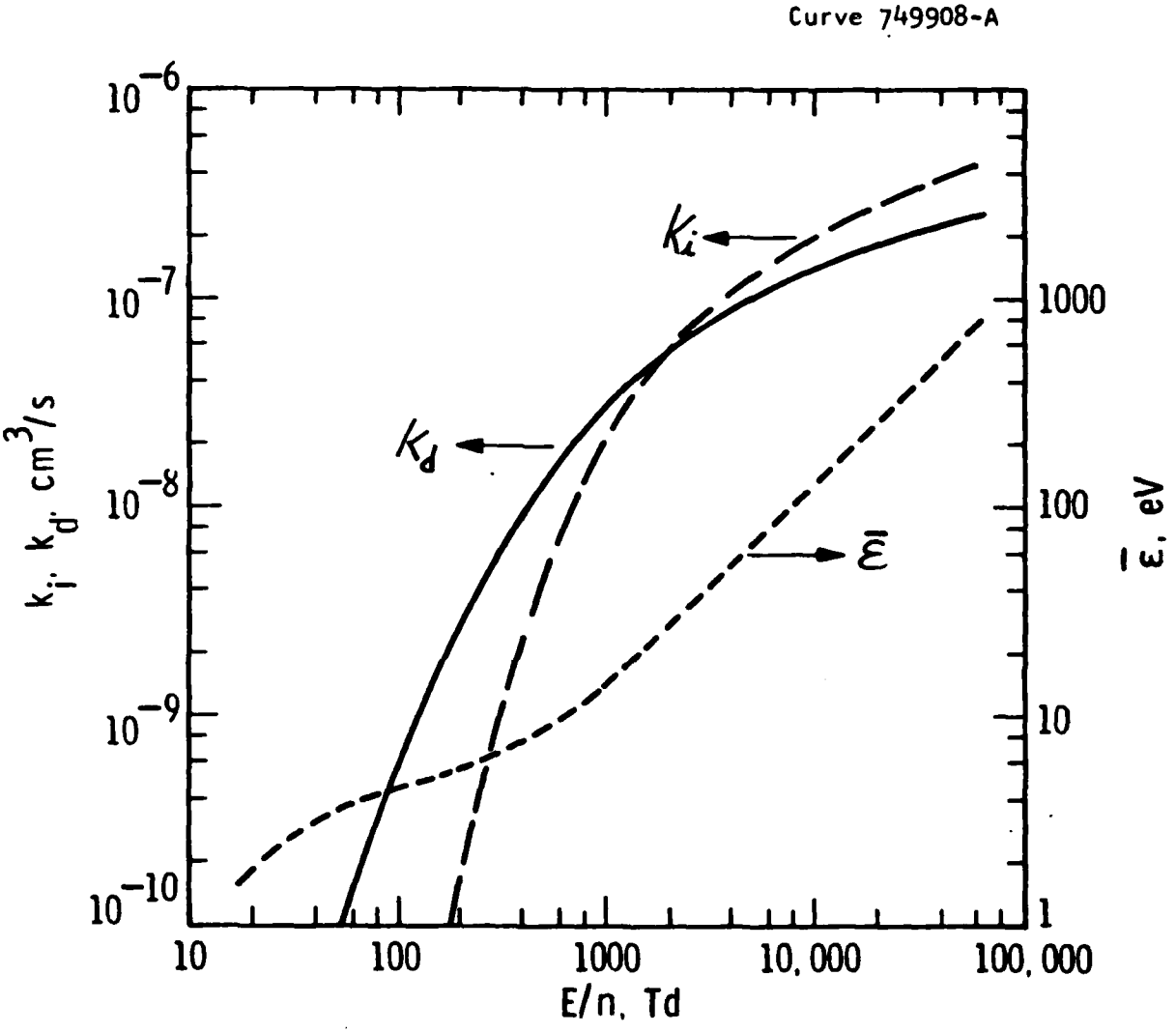

Figure 7. Neutral dissociation rate coefficient [k_d], ionization rate coefficient [k_i], and average electron energy [$\bar{\varepsilon}$] versus E/n predicted by the theoretical model.

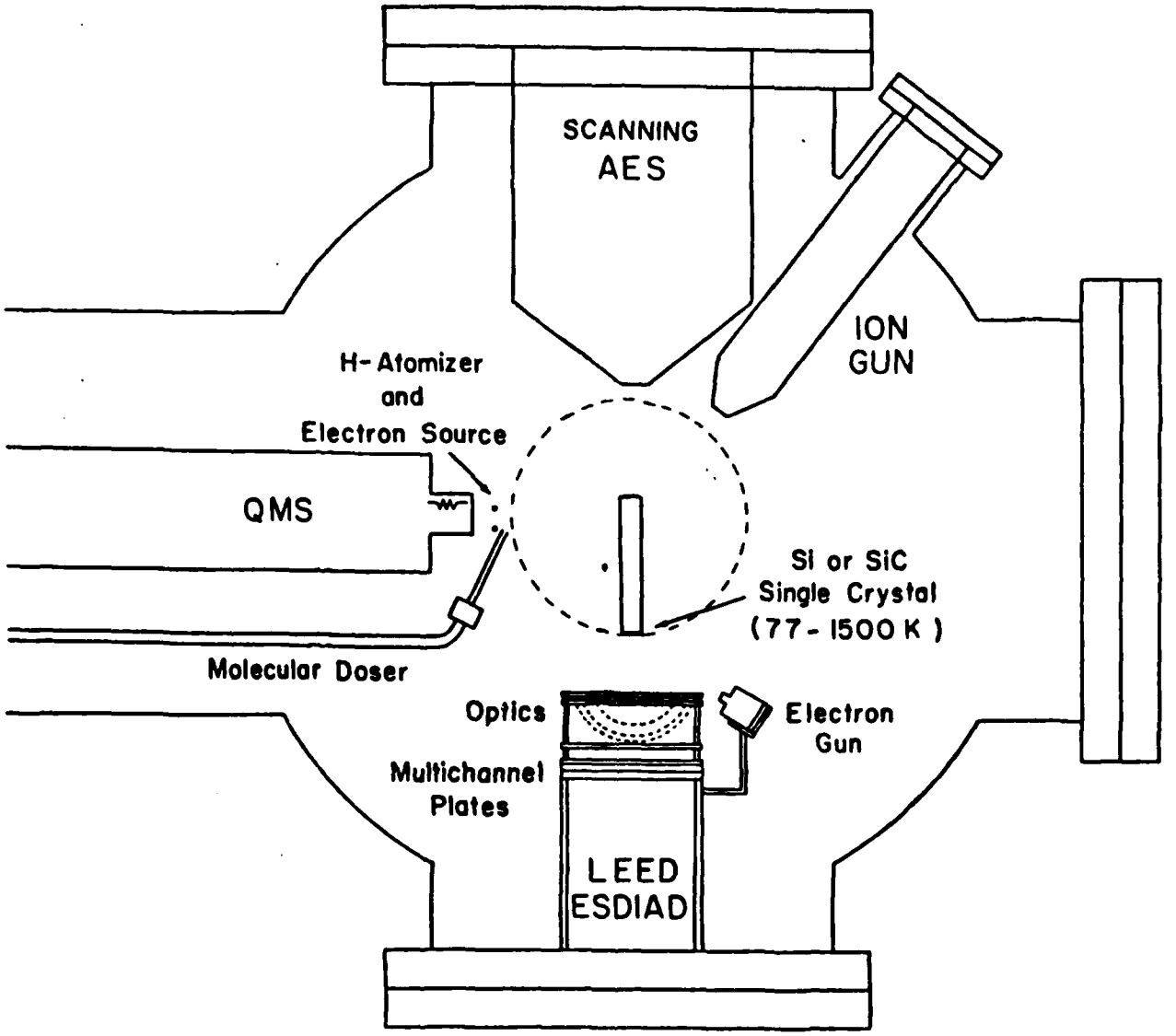

Figure 8. The experimental system constructed for study of semiconductor surfaces.

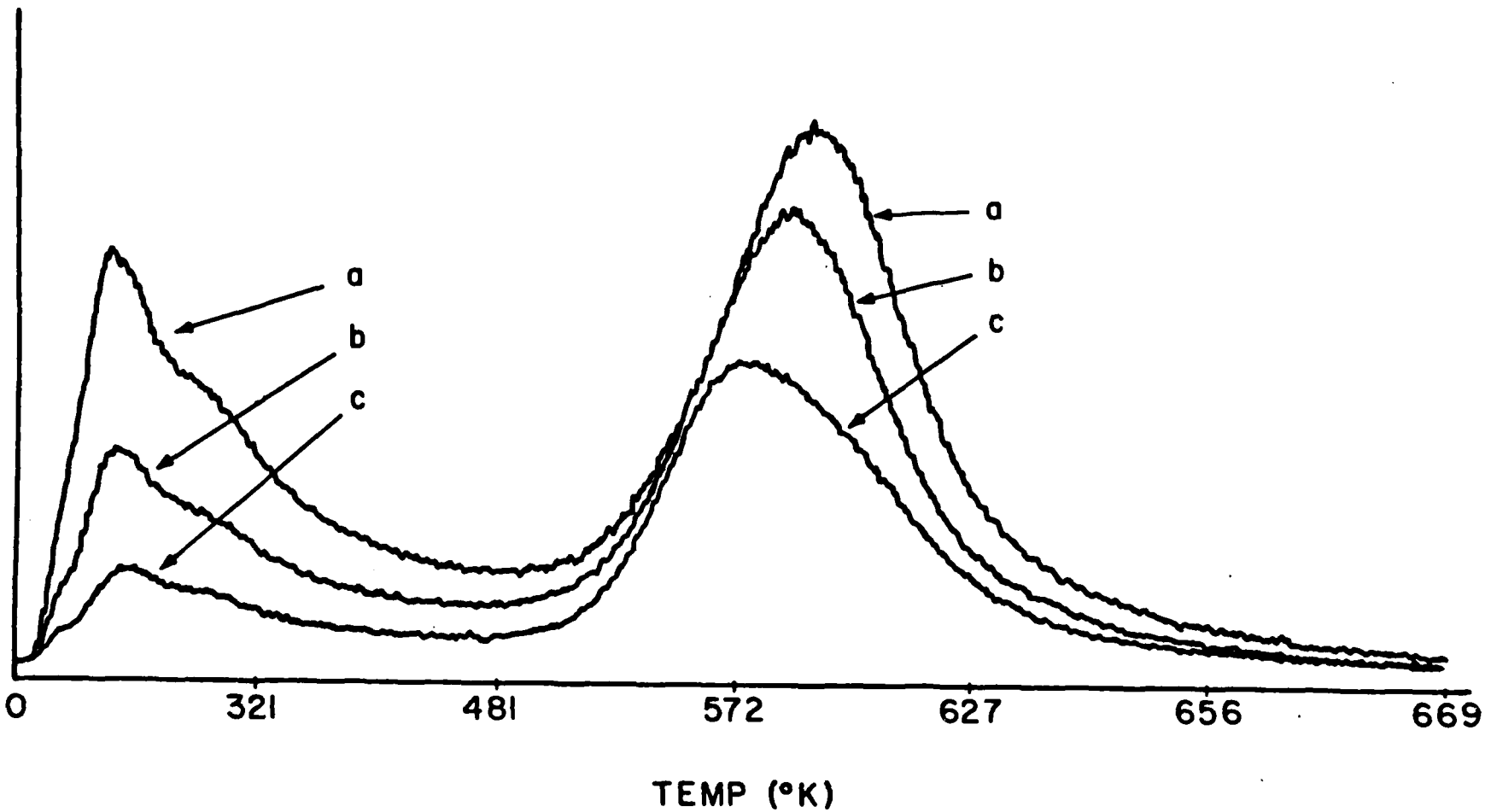

Figure 9. Thermal desorption of propylene (C_3H_6) on Si(100). Two well-resolved binding states are observed to desorb at temperatures near 200 K and 600 K respectively. Curves indicated correspond to molecular exposures of (a) 5.0 X 10^{15} (b) 2.7 X 10^{15} (c) 1.4 X 10^{15} molecules of propylene.

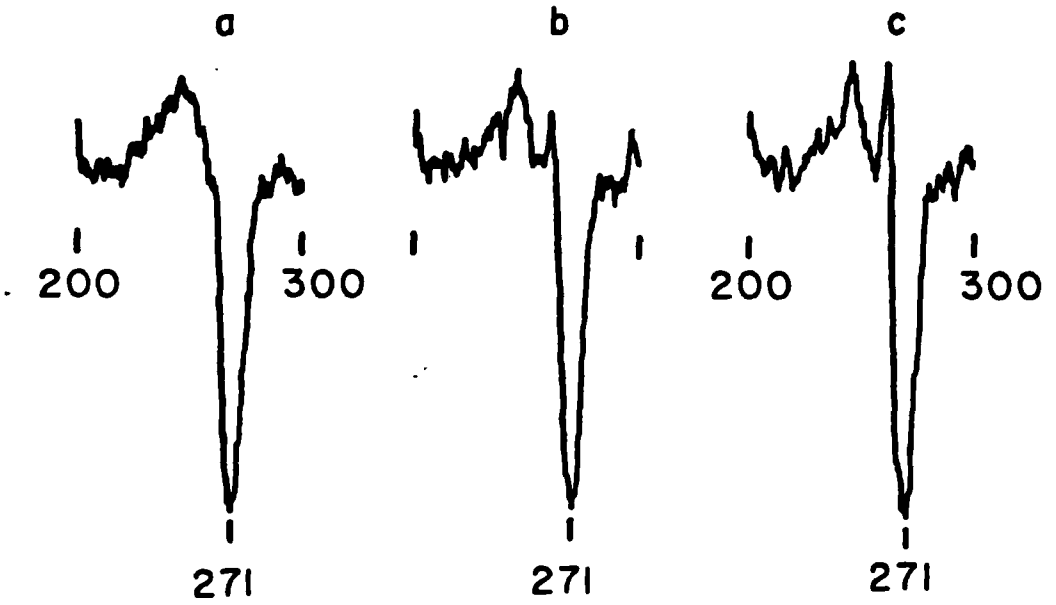

Figure 10. Auger chemical effects during electron beam irradiation. During the irradiation, the focused beam was supplying 1 microamp of current in a 0.1 mm spot at 3 kV. Drawings indicate the C(272) Auger peak shape after (a) 2 minutes (b) 6 minutes (c) 16 minutes of irradiation.

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