STUDY OF THE MECHANISM OF ELECTRICAL CONDUCTIVITY IN MOLECULAR BEAM-DEPOSITED POLYMER FILMS OF ETHYLENE ON SILICON SUBSTRATES

N. T. Melamed
Optical Devices & Directed Energy Research Group

Final Report for the period
September 15, 1983 to March 14, 1985

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ABSTRACT

The following report describes experiments performed on a molecular beam machine in which mixtures of ethylene and nitrogen, at supersonic speeds, were deposited on substrates of high-resistivity silicon and sapphire held at 4K. At the conclusion of a series of fairly difficult measurements, the results showed that the increases in silicon conductivity that had been seen earlier were due to ion implantation of ethylene, and not to the deposition of a conducting polymer as had been thought earlier.

Cont'd Pg. 1

1. INTRODUCTION

This report describes experiments designed to study what was thought to be the deposition of conducting polymeric films of polyethylene produced by means of a supersonic molecular beam. The original data were obtained by exposing silicon substrates to a high-velocity beam of ethylene gas. Subsequent measurements, using a sapphire substrate, showed that the deposited layers were not conducting. In that sense the results were not particularly rewarding, and for that reason the report presents these results in only the sketchiest form.

Despite the failure to obtain the desired results, there were several offshoots of the work that may have some potential interest. One of these is evidence that ethylene gas molecules striking a surface at very high velocities have a tendency to polymerize. The evidence comes from Auger measurements. Although Auger spectra by their very nature are somewhat equivocal, some sample spectra are shown, together with normalized spectra obtained from other carbon compounds, that indicate that carbon-carbon chains are formed which resemble those of polyethelene, although it is not possible to deduce the lengths of the chains.

A second more certain and potentially more practical result was the observation that ion milling could not only be used to restore a defective bolometer, but could actually be used to improve its performance. This result, while not explicitly discussed in the report, is implied in the data presented in Reference 2. Ion milling was determined to be a simple and easily controlled method for improving the performance of a bolometer.

2. BACKGROUND

During the course of performing measurements on molecular beams of ethylene and ethylene-nitrogen mixtures, we observed a continuous decrease in the sensitivity of the bolometer that was used to detect the beam energy. The method of detection was based on that due to Scoles[1] et al. in which a molecular beam strikes a silicon bolometer held at very low temperatures. The bolometer measures the total energy of a molecule; when several molecules have the same velocity, but a fraction of them has been optically excited, the bolometer measures the change in internal energy due to optical absorption by the molecules striking the detector. The changes we observed were much larger than could be attributed to optical absorption. In addition, the decrease in sensitivity continued as the experiments progressed and appeared to be irreversible.

When the surface of the bolometer was examined, it was found to have a very thin surface layer deposited on it.[2] An analysis of this layer by Auger spectroscopy gave a spectrum, shown in Figure 1, which is characteristic of a polymerized ethylene bond. Repeated measurements showed similar results. Analysis of the thickness of the ethylinic deposit showed it to have a nearly rectangular profile, as shown in Figure 2, characteristic of a surface deposit the thickness of which was about 350 Å. (Note, however, that the silicon does not show a rectangular profile, but the concentration of silicon varies smoothly through the ethylene region.) The results of the Auger spectra indicated that a) the ethylene deposit was polymerized, and b) the ethylene appeared to be a surface layer of finite thickness.

It then remained to explain the loss of sensitivity of the bolometer. A bolometer is basically a temperature-sensitive resistive element. A measurement of the resistance of the bolometer at ~ 4K, after the loss of sensitivity due to the ethylene deposit, showed that its resistance had fallen dramatically due to the surface layer. The

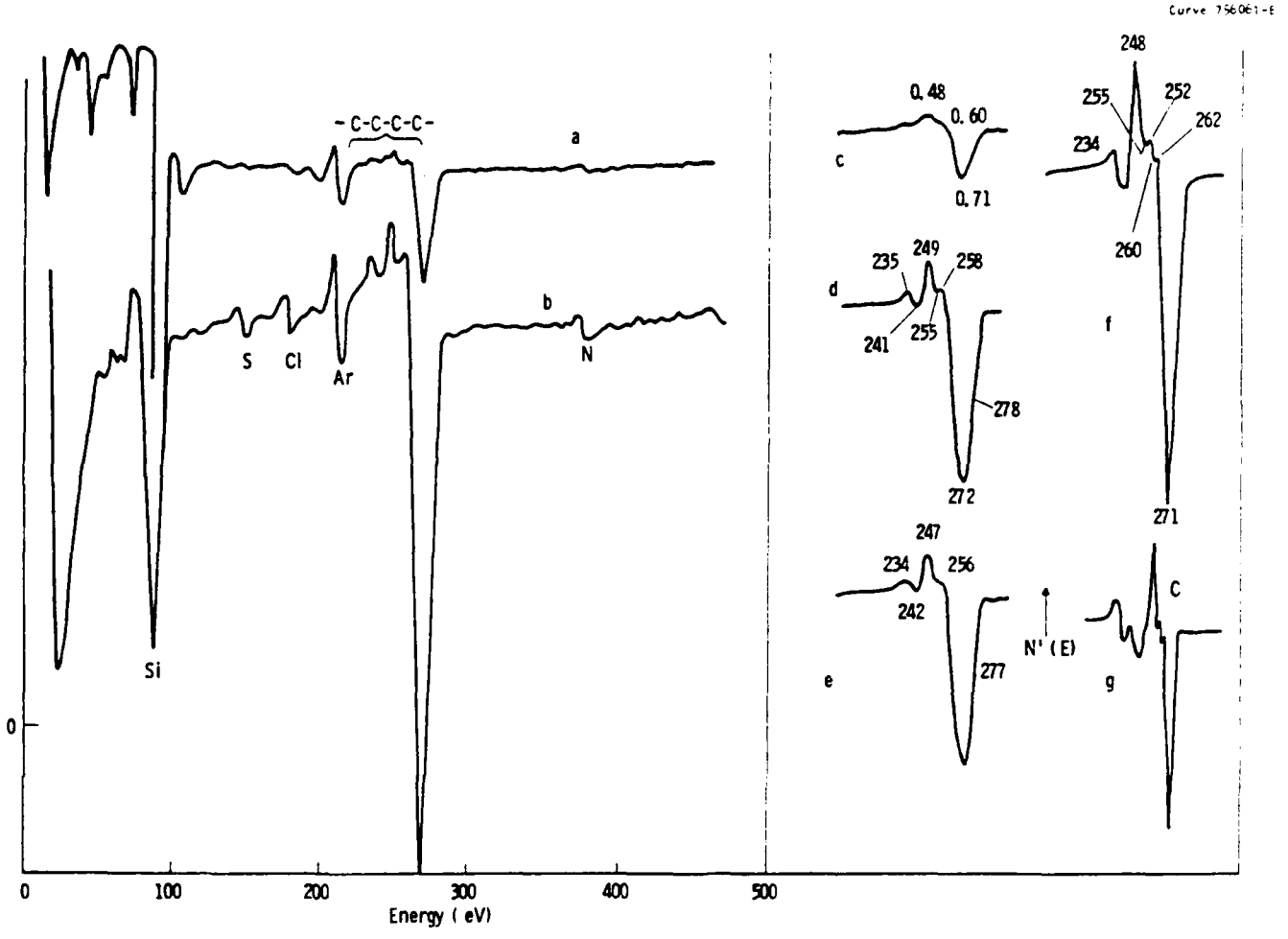


Figure 1. Auger spectra of molecular beam-deposited ethylene: a) ethylene on silicon substrate, b) ethylene on sapphire substrate. Figures c-g are comparison spectra as follows: c) polyethylene, d) sugar on silicon, e) tartaric acid, f) graphite, and g) silicon carbide. Note the similarity of the ethylene-deposited spectra with c in particular, but also with d and e, which also contain -c-c-c- linkages, and the dissimilarity with f and g, having different bonding.

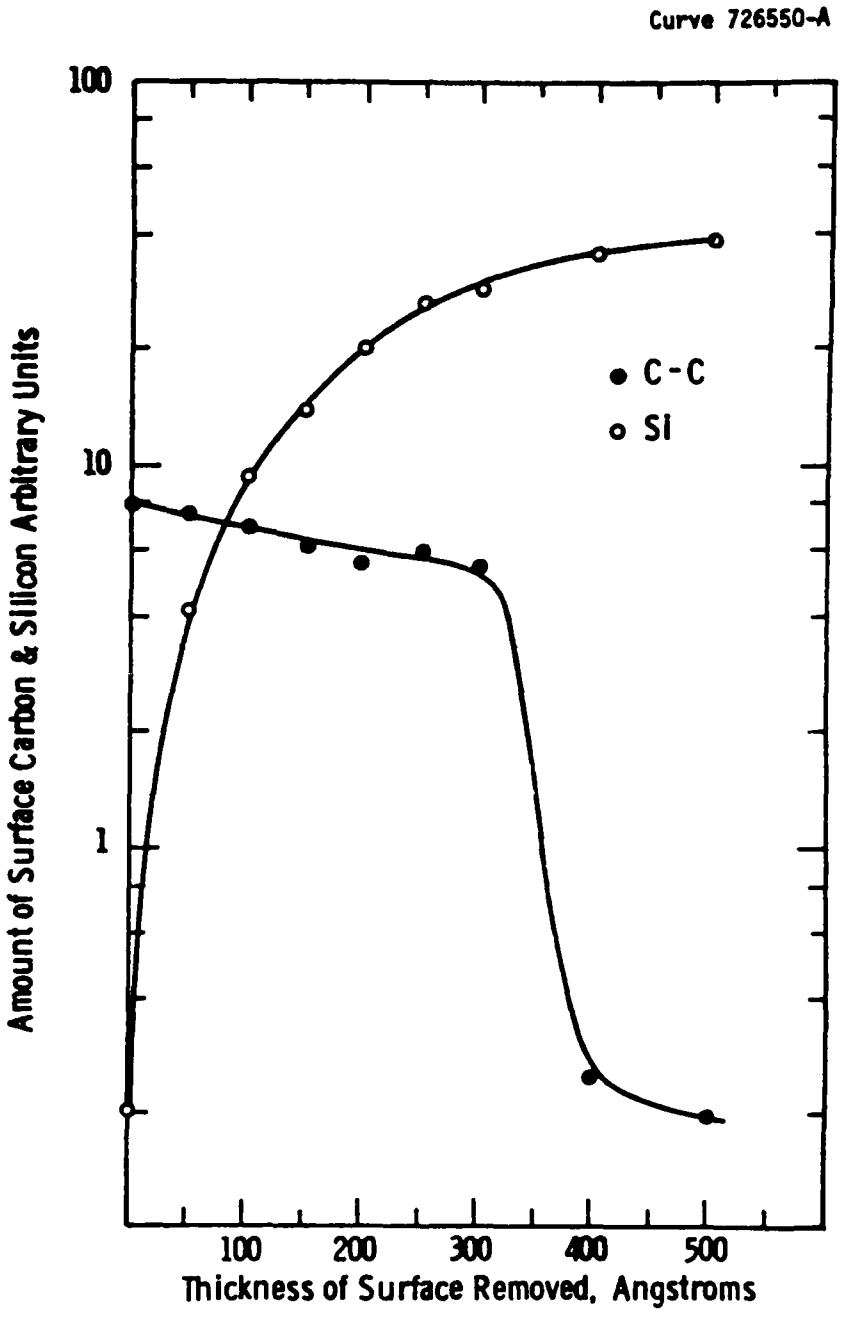


Figure 2. Composition of surface layer (carbon and silicon) as determined by Auger electron spectroscopy following ion milling.

bolometer resistance was measured periodically following the removal by ion milling of incremental layers of the ethylinic deposit. As the ethylene deposit was removed, the bolometer resistance began to increase until the original resistance was restored. These results are shown in Figure 3. (Actually, with still more ion milling the original resistance was exceeded, but for a different reason.) From the electrical measurements and a knowledge of the thickness of the ethylene layer, it was possible to calculate the resistance of the ethylinic layer. The results indicated that the original ethylene layer was ohmic and had a resistance of 28K ohms. The specific resistivity was very low, about 2.7 ohm cm. Such a very low specific resistivity is most unusual, especially for an organic material. Equally important, perhaps, is that ethylene is not known to polymerize without a catalyst, and polythylene has never been known to show any electrical conductivity. These results spurred an effort to examine the molecular beam-deposited films and to discover the cause of the electrical conductivity.

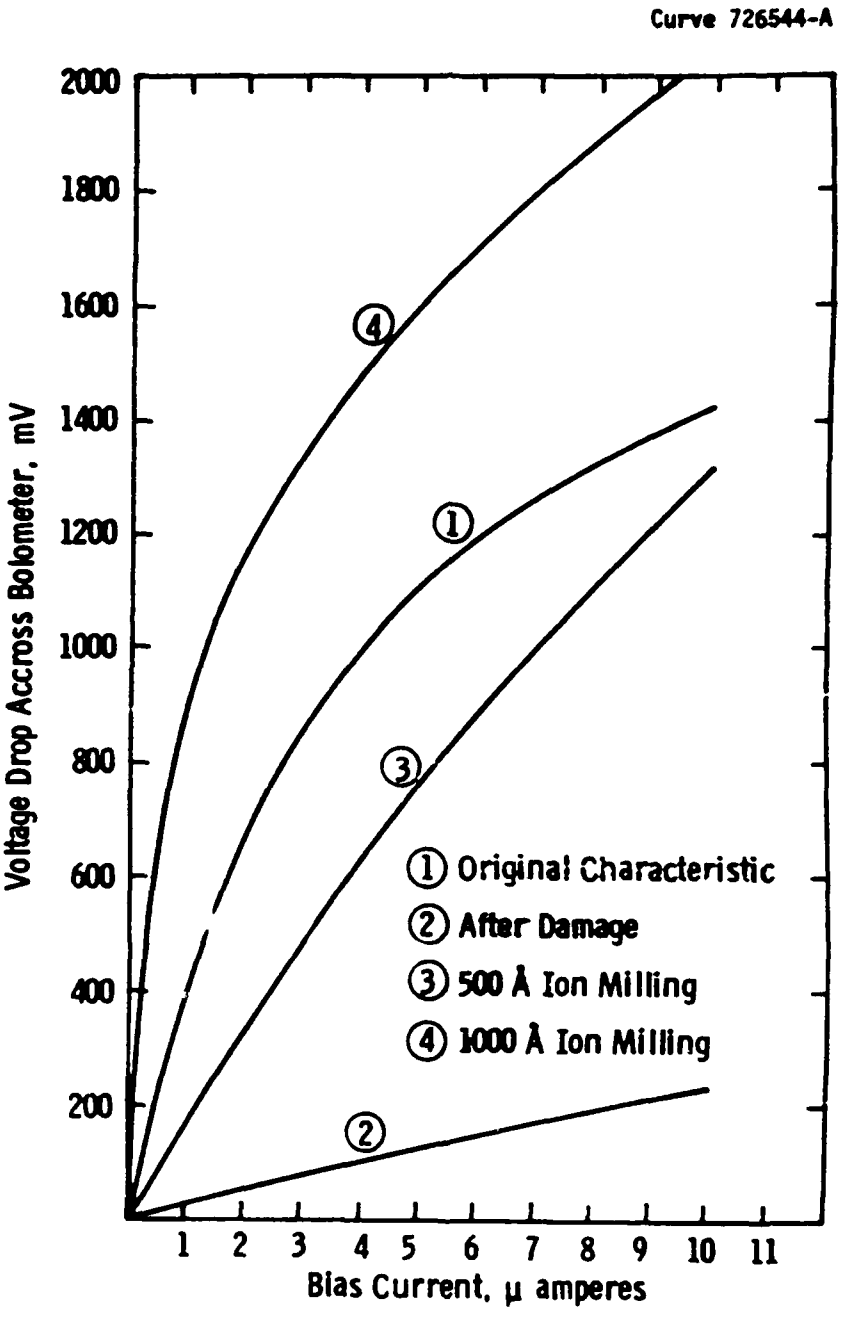


Figure 3. Voltage vs. current characteristics of bolometer before and after ion milling.

3. MEASUREMENTS

3.1 EXPERIMENTAL APPARATUS

The basic equipment used in these experiments consisted of a supersonic molecular beam apparatus, shown in Figure 4. A helium dewar, shown in Figure 5, at the far end of the apparatus contained the target sample. The dewar and the free-flight region of the molecular beam apparatus shared a common vacuum system. The free-flight region extends into the dewar.

The basic design of the supersonic molecular beam apparatus is shown more clearly in Figure 6. The apparatus consists of two separately pumped vacuum chambers. The source gas is fed under pressure into the first vacuum chamber through a tube that terminates on a specially designed nozzle from which the gas emerges. The adiabatic expansion that occurs when the gas leaves the nozzle causes cooling of the internal degrees of freedom of the molecules. In addition, when the difference in pressure within the feed tube (referred to as the stagnation pressure) is sufficiently high that the Knudsen number is less than unity, the gas forms a directed beam whose angular spread diminishes with Knudsen number, and the gas takes on the characteristics of a supersonic jet (i.e., the velocity of the particles exceeds the velocity of sound within the gas). Mach numbers as high as 30 can be obtained. At high Mach numbers the gas particles attain considerable kinetic energy in the longitudinal direction, since much of the internal energy as well as an appreciable portion of the transverse kinetic energy has been converted to longitudinal kinetic energy.

To insure that only molecules or atoms travelling longitudinally within a very small and well-defined solid angle propogate along the beam, skimmers are used. These are essentially supersonic apertures designed to let only the central core of the gas beam pass through, while the off-axis molecules are "skimmed" off without forming a

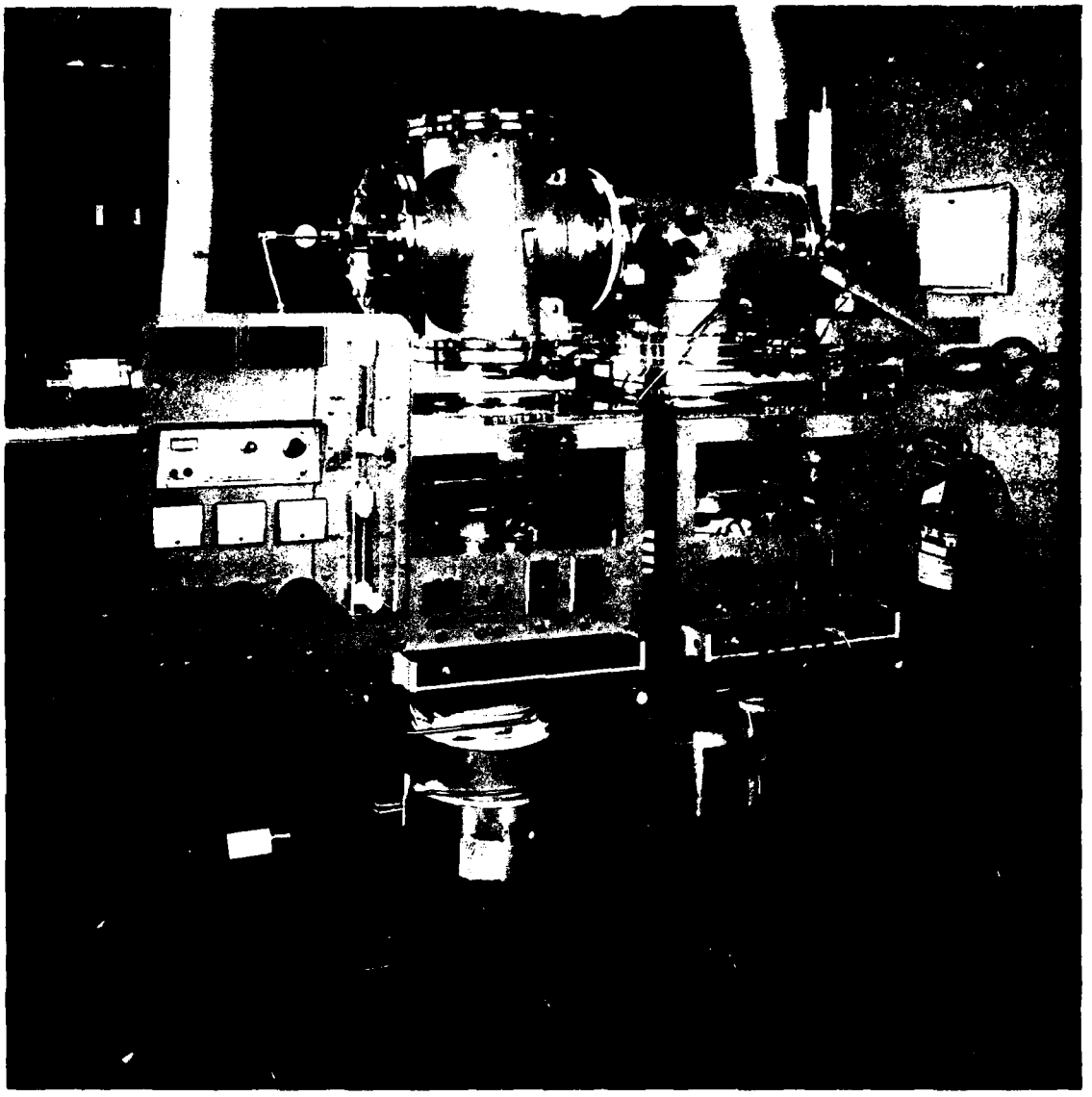


Figure 4. Overall view of supersonic molecular beam apparatus. The chamber on the left is the beam-forming chamber, that on the right is the free-flight chamber. The dewar used is different from the one shown.

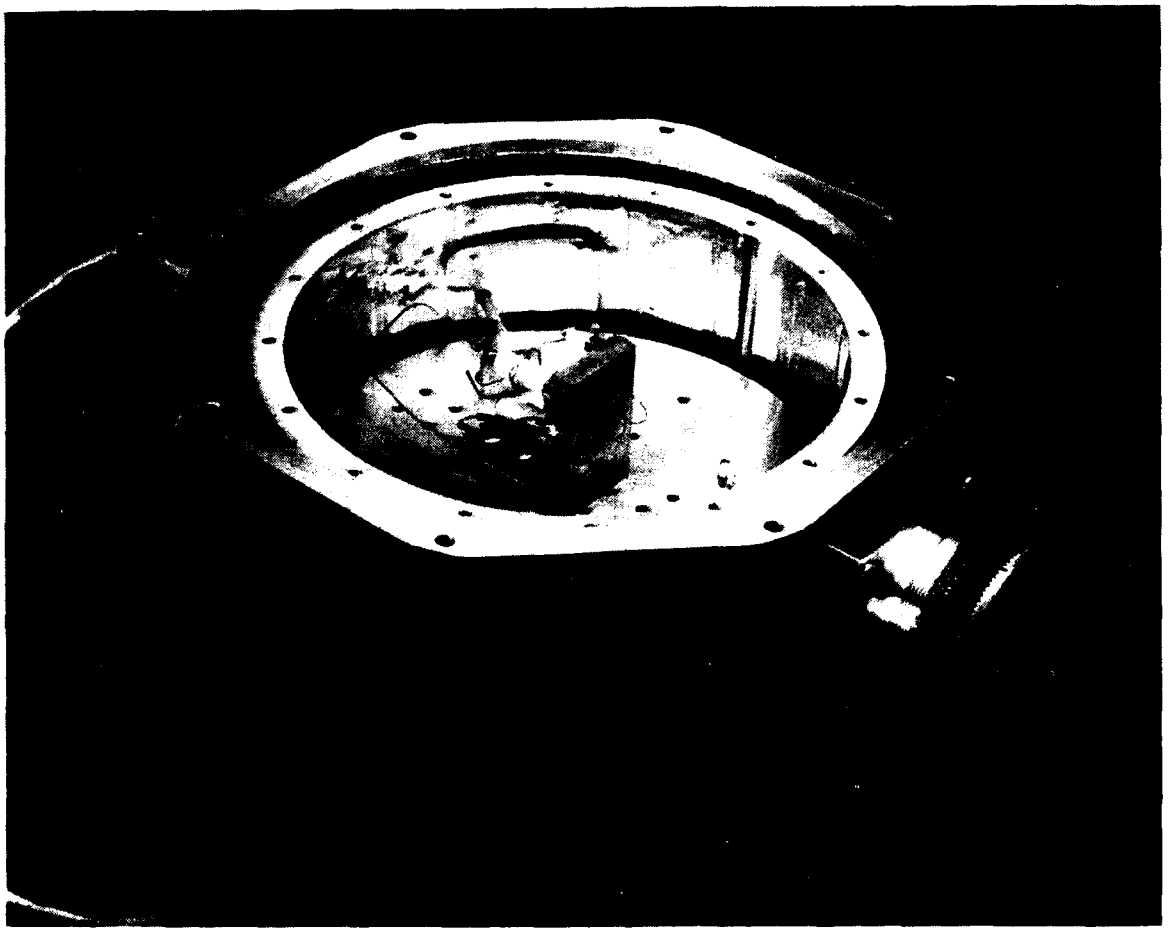


Figure 5. Helium dewar with cover exposed to show sample-mounting block. The sample is mounted in the center of the disc and electrical leads extend out of the dewar through a multi-pin vacuum connector seen on the left.

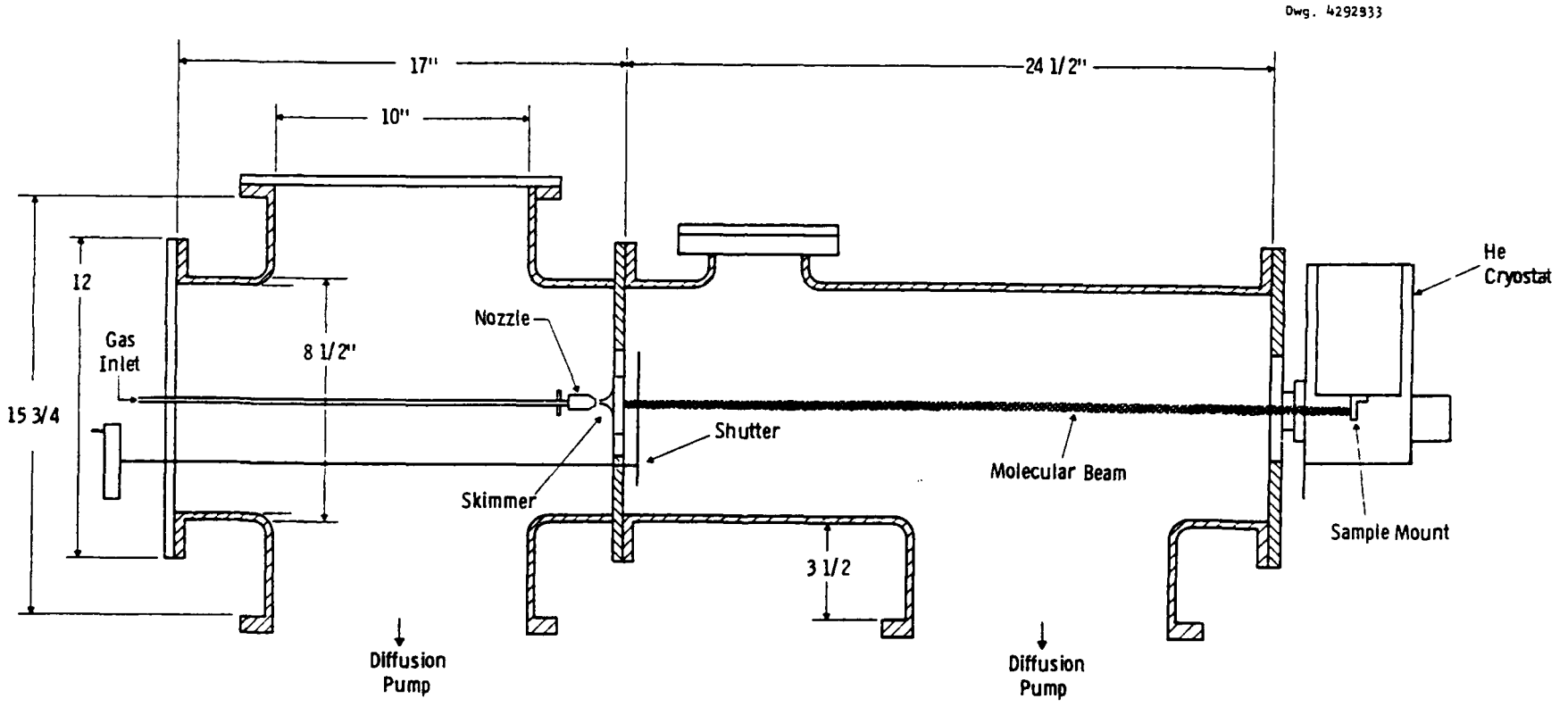


Figure 6. Simplified diagram of the molecular beam apparatus showing the gas inlet tube, the supersonic nozzle, the skimmer, and the sample mount within the He cryostat.

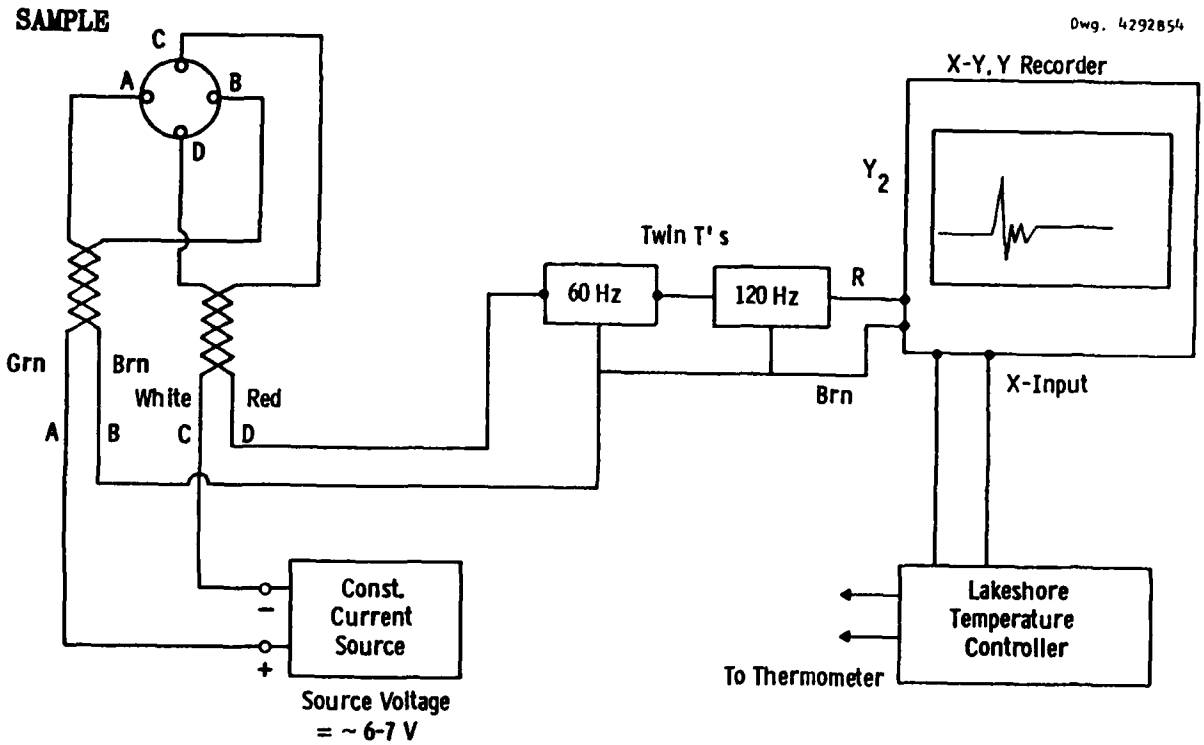
shock wave. The skimmers form the only opening between the beam-forming chamber and the second, or free-flow chamber, which is separately pumped to a vacuum high enough ($<10^{-7}$ torr) to prevent molecular collisions from occurring. In the present experiments, the beam terminates at the far end of this second chamber, where it enters a dewar and strikes the sample mounted at the cooled tip of the cryostat. Since much of the internal energy and the transverse translational energy have been converted to longitudinal translational energy during the expansion, the molecules that strike the sample are kinetically very "hot," i.e., they strike the surface with considerably more average kinetic energy than they would at the stagnation temperature (which in this case was room temperature). Moreover, the process of expansion and skimming narrows the velocity distribution of the particles so that the particle energy distribution is more nearly monoenergetic than a gas which is in thermal equilibrium with its surroundings. This combination of high longitudinal kinetic energy and a narrow energy distribution make possible collision reactions that might not ordinarily occur with gases at thermal equilibrium.

3.2 EXPERIMENTAL DESIGN

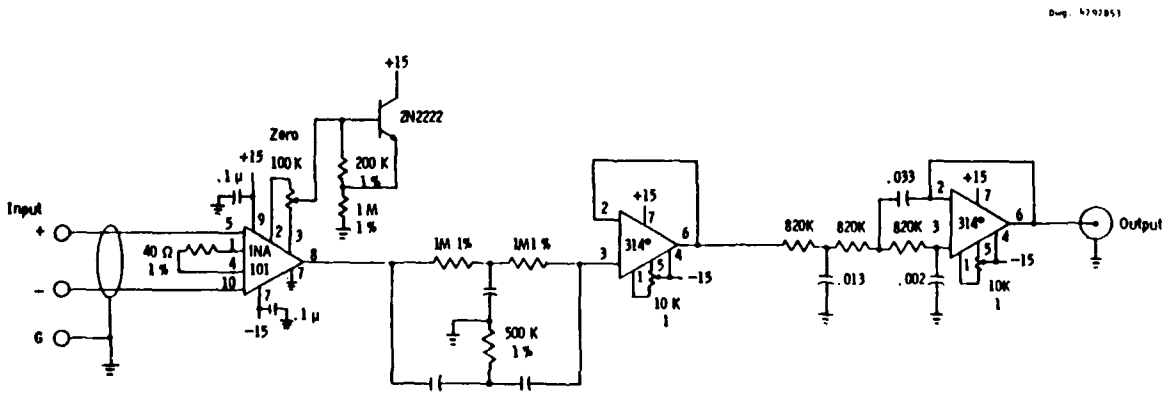
As a starting point for the present experiments, we began by trying to duplicate as closely as possible the circumstances that led to the initial observations. Thus, high-purity silicon discs with electrodes attached were mounted in the liquid helium-cooled dewar and subjected to molecular beams of an ethylene-nitrogen gas mixture.

The basic experimental objective was to measure the resistivity (and possibly the Hall effect) of the deposited ethylene layers as a function of various deposition conditions. From these data, the nature of the conductivity might be determined.

Since measured resistance is very much a function of sample and electrode geometry, a four-probe method was used, based on a technique described by Van der Pauw.[3] The method consists of applying four electrode leads to the sample approximately equally spaced along the sample perimeter. Labelling these contacts A to D as shown in Figure 7a,



(a)



(b)

Figure 7. Van der Pauw sample geometry and connections: a) basic electrical circuit for measuring sample resistivity; b) high-gain, high-impedence preamp that replaced the Twin-T's in circuit a.

a constant current is applied to two adjacent contacts, say A and C, and the voltage is measured between contacts B and D. A second similar measurement is taken by indexing the current and voltage terminals by one electrode in either direction, for example, to AD and BC, respectively. Under these conditions, the true value of resistivity, ρ, can be determined independently of sample shape or electrode position from Equation 1, where d is the sample thickness and f is a parameter that depends on the ratio $R_{AC,BD}/R_{AD,BC}$.

$$\rho = \frac{\pi d}{\ln 2} \left(\frac{R_{AB,CD} + R_{BC,DA}}{2} \times f \times \frac{R_{AC,BD}}{R_{AD,BC}} \right) \qquad (1)$$

For the present measurements, the constant current source initially used was a Lake Shore Cryotronics model CCS-EXB. The 4.2K resistivity of the high-resistivity Si substrate samples forced us eventually to replace this current source with a Kiethley Model 225 constant current source capable of current control as low as 1 namp and a Kiethley Model 610 electrometer in series with it to monitor the current.

Voltage measurements were obtained with a specially designed homemade voltage preamplifier (shown in Figure 7b) with a very high impedance input, a gain of 100 or 1000, and a low impedance output. The amplifier was mounted directly over the terminal block of the dewar, to minimize noise pickup, and had a switch for indexing the sample electrode terminals as required by Equation 1. Heavy filtering at 60 and 120 Hz provided by the preamplifier essentially eliminated noise due to ac pickup. Temperature was measured by means of a Lake Shore Cryotronics temperature controller, model DRC-70C.

All of the data were recorded on a Hewlett-Packard Model X-Y,Y recorder. For measurements of resistance versus time during deposition runs, the output of the voltage amplifier was recorded as the ordinate with time as the abscissa. For measurements of voltage and current versus temperature, the voltage and current values were applied to the Y_1 and Y_2 recorder terminals, respectively, while temperature drove the

abscissa. Different color pens enabled us to distinguish the voltage from the current traces.

3.3 SAMPLE PREPARATION

A major requirement for the success of the Van der Pauw method is to insure true ohmic contacts. In order to accomplish this, we had to develop a protocol for sample and contact preparation.

Sample discs one-quarter inch in diameter were machined from a thin wafer of high-resistivity silicon. (The sample area was chosen to insure uniform coverage by the molecular beam.) Contact preparation proceeded as follows:

1. The samples were etched in a solution of HF and glacial acetic acid.

2. The samples were waxed to a glass slide, and a 5000 Å layer of aluminum was sputtered on one surface.

3. After removing the discs from the slides, four dots of Apiezon wax were placed on the locations where the electrodes were desired. The wax acted as a resist for the subsequent etch.

4. The unprotected aluminum was etched away in a mixture of phosphoric, nitric, and acetic acids.

5. The Apiezon wax was completely removed, exposing the protected aluminum dots.

6. The sample discs were heated in a hydrogen furnace for five minutes at 650°C and cooled for two hours to allow the aluminum to alloy with the silicon, but not to allow it to diffuse too deeply into the silicon.

7. Indium dots were then alloyed to the Al-Si functions, and copper leads were bonded to the contacts.

The sample discs, with leads attached, were mounted inside the helium cryostat using standard heat sinking techniques, the thermometer was attached, and the leads connected. The dewar was mounted on the molecular beam machine, and the system was evacuated.

Subsequently, sapphire was used as a substrate. For the sapphire discs, contacts were made by evaporating chromium on one-quarter-inch sapphire discs, masking the desired contact points with Apiezon as in step 3 above, dissolving in acid the unwanted chromium, and bonding wires to the chromium contacts with indium.

Considerable time and effort was needed to develop successful techniques for making suitable contacts on both the silicon discs and the sapphire to which leads could be applied. Even after the technique was developed, not all of the samples were satisfactory, due to the high sensitivity of the methods to small variations in preparation conditions.

3.4 MOLECULAR BEAM DEPOSITION

Once the sample was mounted in the dewar, the dewar was attached to the molecular beam machine, and the entire molecular beam apparatus was evacuated to $< 10^{-6}$ torr; the dewar was cooled to 4.2K by transferring liquid He to it, and ethylene deposition was begun. To provide for a very cold high-velocity beam, nitrogen gas was added to the ethylene.[4] A typical procedure was to use a mixture having equal pressures of nitrogen and ethylene gas. With the shutter following the expansion nozzle in the beam closed to prevent the beam from reaching the sample, the gauge pressures of the two gases were each adjusted to 45 psi. The flow rates of each gas were then adjusted to provide 500 torr in the stagnation region, for a total stagnation pressure of 1000 torr. The shutter was then opened, and the supersonic molecular beam was allowed to strike the sample.

Deposition typically continued for about 1000 seconds. Measurements of the voltage across one pair of electrode contacts was monitored during the deposition. It was not possible to interchange electrodes during deposition, in the manner described in Section 3.1

above, because of transients and long electrical relaxation times that occurred during the contact changes, and the relatively short deposition times.

Once deposition was terminated, measurements of resistivity versus temperature were recorded. During deposition, the temperature of the sample remained essentially constant at 4.2K. To warm the sample, a very small measured flow of He gas at room temperature was admitted into the liquid He compartment of the dewar. Once the He had fully evaporated, the temperature rose fairly evenly and slowly until about 100K was reached, after which the rate of temperature rise began to noticeably diminish. To obtain measurements from 100K to room temperature, warming had to proceed through the night, with room temperature being barely reached by the next morning.

Since it was only possible to make measurements with only one set of electrode positions during one temperature run, the sample had to be cooled back to 4.2K by the addition of fresh liquid He in order to take the two sets of measurements required of Van der Pauw's method. This was typically done the following day, and the warning process was repeated for the new contact positions.

Because of the long sample preparation and setup times, and the time required for each warming cycle, measurements on a single sample took about a week or longer, from sample preparation to measurement.

4. EXPERIMENTAL RESULTS

4.1 SILICON

4.1.1 Resistivity Versus Deposition Time

Changes in resistivity during deposition were monitored with most of the samples. In general the signals were extremely noisy (for reasons that are probably associated with the deposition process); the early results seem to indicate a stepwise change in the resistivity of the sample probes as a function of deposition time, which led us to think that some form of layering or reorientation may occur during deposition. We later concluded that the more probable explanation is that it was due to a measurement artifact associated with a lack of sufficient compliance in the current source. When the sample current was monitored during deposition with a Kiethley Model 610 electrometer, as was done in later measurements, we noted that, because of the extremely high intrinsic resistance of the Si samples, at times the current itself did not remain constant during the early portions of the deposition. This variation in current could account for the apparant stepwise change in resistance. Although we intended to examine this phenomenon in greater detail to determine the cause of the stepwise resistance changes, time did not permit us to do so.

In most instances, however, there was a monotonic decrease in sample resistance as a function of deposition time, as shown in Figure 8, and the current (as recorded by the horizontal line labelled 10 na) remained essentially constant throughout the deposition. These measurements, while not subject to easy analysis because the voltage probe positions were not interchanged, indicate a decrease in voltage across the probes of about a factor of 30, from 13 volts to 0.45 volts, during 1900 seconds of deposition. The change in resistance across these contacts cannot be determined from these measurements alone

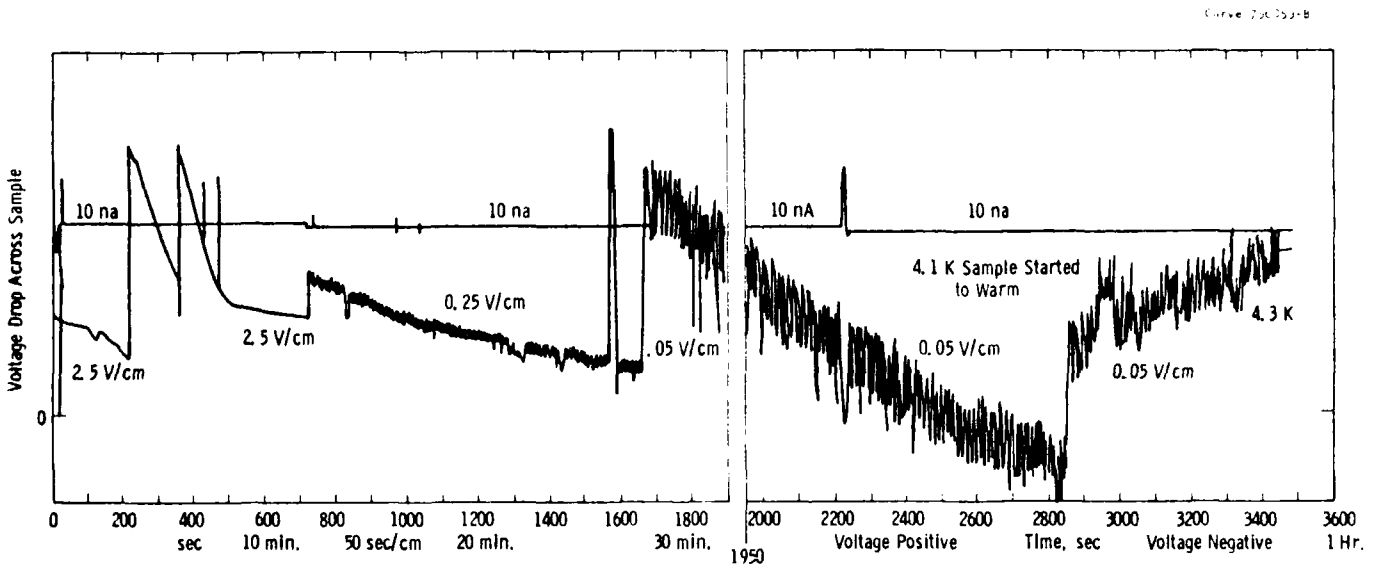
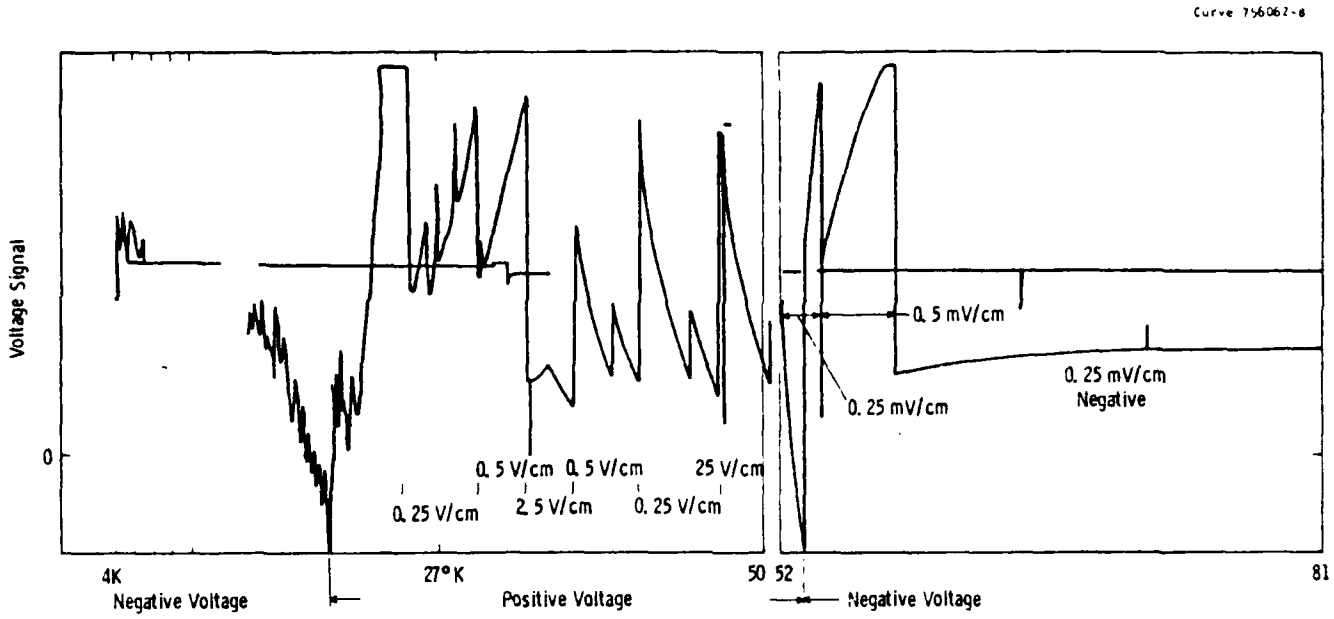
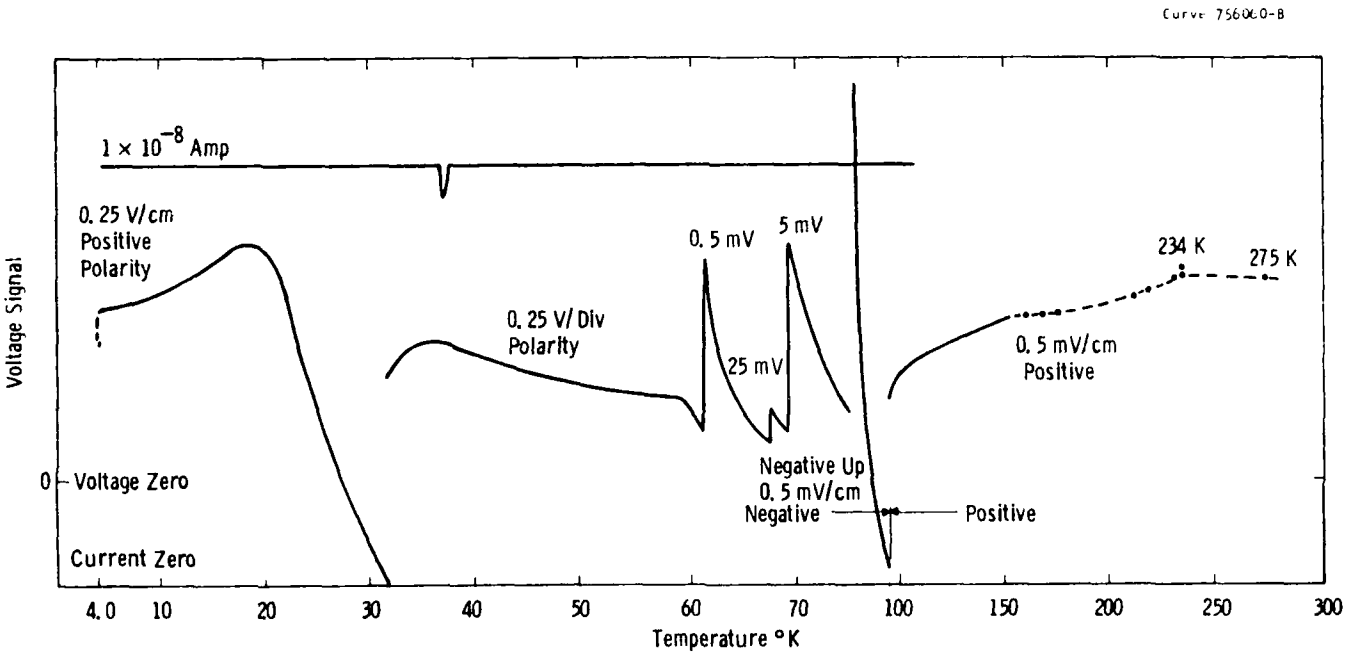


Figure 8. Voltage vs. deposition time for constant deposition rate. The sample resistance is proportional to the voltage. Deposition continued for ~2800 sec (~ 47 min), after which deposition was stopped and the sample began to warm. Note that the voltage kept dropping during deposition, indicating a drop in resistance.



(a)



(b)

Figure 9a,b. Voltage signals as a function of temperature for ethylene deposited on Si substrate for the two different current-voltage probe positions, as dictated by the Van der Pauw method.

because of the way the electrodes are connected, but the magnitude of the resistance change should be as large or larger.

4.1.2 Resistivity Versus Temperature

As described earlier, resistivity versus temperature plots were obtained on a number of samples by allowing the samples to warm following completion of the ethylene deposition. Each sample had to be measured twice, with the electrode connections indexed for the second measurement. The results of a typical sample are shown in Figure 9a,b for the two positions 1) and 2) of electrode connections as required by the Van der Pauw method. As can be seen, the R versus T behavior in each case is quite complex, involving large changes in voltage (as shown by scale changes in the figures) with the voltage showing occasional changes in polarity. Such behavior is apparently not unusual for measurements of this type. The behavior was most complex from 4K to about 25K. Above 25K the resistivity, as deduced from the measurements, diminished rapidly with increasing temperature. The current was also monitored and can be seen on the curves as the nearly constant horizontal line. A complete analysis of the data was not performed in light of the results indicated below. However, the data clearly indicated the presence of appreciable electrical conductivity even at or near liquid He temperatures.

Since the purpose of these experiments was to determine whether or not a conductive ethylinic polymer was being produced, two other sets of measurements were performed. One of these involved a set of electrical measurements on silicon samples under conditions nearly identical to those above, except that no ethylene was deposited on them. No meaningful measurements of voltage or current could be obtained at very low temperatures since the samples behaved as though they had nearly infinite resistivity. These are exactly the results expected of high-resistivity silicon at low temperatures, where all of the carriers are frozen out. They contrast sharply with the rather pronounced conductivity seen in samples subjected to ethylene deposition.

4.2 SAPPHIRE

A second and similar set of measurements was performed on sapphire discs in place of silicon both with and without ethylene deposition. The results were fairly conclusive: there was no evidence of any conductivity under any of the conditions of ethylene deposition, even for extended time periods and with variations of gas mixtures.

5. CONCLUSIONS

The negative results obtained with ethylene deposition on sapphire indicates quite conclusively that the ethylene deposits are not themselves conducting. Since an increase in conductivity at 4.2K does occur with silicon substrates, in contrast to silicon on which no ethylene was deposited, several possible explanations are possible: One is that silicon acts as a catalyst to produce a conductive polymer, whereas sapphire does not. Such an explanation is very unlikely because silicon is not known to be a catalyst for polymerization. A more reasonable explanation for the occurrence of conductivity in silicon at the very low temperatures (where no conductivity from silicon itself might be expected) is that at these very high Mach numbers ($M > 5$), ethylene implantation takes place, and a surface layer of relatively high conductivity is produced on the silicon wafer due to the heavily implanted ethylene molecules. Evidence for this can be deduced from Figure 2, which shows that although ethylene forms the dominant surface layer and has a fairly sharp demarcation as far as thickness is concerned, the presence of some silicon is seen at all depths including those nearest the surface, indicating that the ethylene may indeed be imbedded in the silicon to a varying degree.

Auger measurements taken on both the surface of the silicon wafers and on a sapphire wafer gave essentially similar patterns to those originally obtained and shown in Figure 1. These indicate that a form of ethylene polymerization may, in fact, occur on the surface of either substrate as a result of the high-energy molecular collisions. Thus, the action of a supersonic jet on ethylene gas appears to produce some level of polymerization, although the size of the polymeric molecules and the mechanism of their formation is not known. These results are interesting and merit some further investigation.

We conclude, therefore, that the results, while disappointing in terms of their original purpose, are not without some merit. In particular:

1. They reinforce the original finding that the deterioration of a bolometer subjected to a supersonic jet of ethylene is due to ethylene deposition on or into the surface. It is probable that other simple organic compounds introduced into a jet at high Mach numbers could have a similar effect, and therefore places a limit on the usefulness of bolometers for measuring the internal energy of cold molecules.

2. The evidence indicates that some form of polymerization takes place on both silicon and sapphire substrates. Since the two substrates are so very different, both chemically and physically, the results suggest some generality to this conclusion. The effect merits further study.

3. Evidence for ion implantation of ethylene into silicon by a supersonic nozzle jet seems fairly clear.

4. Means for making finely tuned bolometers under controlled conditions are suggested. The ion implantation may be a novel means for making silicon bolometers, and the ion planing used to remove portions of the surface for analyses suggests a means for trimming bolometers to the desired V/I characteristics.

6. ACKNOWLEDGMENTS

The author wishes to thank Dr. J. D. Feichtner for having participated in the early deposition measurements; Dr. J. Schruers for performing the Auger spectroscopy; and Dr. S. Sinharoy for assisting in the interpretation of the Auger spectra. Thanks are also due to G. Madia for assisting with the measurements.

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