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EPITAXIAL CONTROL SYSTEM

Contract No. AF19(604)-8351
Project No. 4608
Task 460804

Scientific Report No. 2

Date of Report - 14 June 1962

Prepared for

ELECTRONICS RESEARCH DIRECTORATE
AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
BEDFORD, MASSACHUSETTS

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AFCRL-62-741

EPITAXIAL CONTROL SYSTEM

BY

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ABSTRACT

A HIGHLY SENSITIVE MASS SPECTROMETER HAS BEEN SELECTED FOR USE IN A VAPOR STREAM ANALYSIS SYSTEM FOR AN EPITAXIAL GROWTH REACTOR. THE INSTRUMENT WILL BE USED TO MONITOR GAS PHASE COMPOSITIONS. PRELIMINARY CALCULATIONS INDICATE THAT IT WILL BE FEASIBLE TO MONITOR GAS PHASE IMPURITIES WHICH WILL YIELD EPITAXIAL FILM RESISTIVITIES OF FROM .001 TO 100 ohm-cm, n AND p TYPE IMPURITIES, AND SILICON COMPOUNDS WILL BE SUBJECT TO CONTINUOUS ANALYSIS. SOME ANTICIPATED PROBLEMS ARE THE LOSS OF SENSITIVITY DUE TO CORROSIVE NATURE OF GASES UNDER INVESTIGATION, INTERFERENCE FROM BACKGROUND GASES, AND UNUSUALLY LOW IMPURITY CONCENTRATIONS IN THE VAPOR SAMPLE.

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I. INTRODUCTION

The vapor phase deposition or epitaxial growth process has been shown to offer capabilities and control in the process of single crystal growth and concurrent doping which are not possible in other processes.

It is possible to grow epitaxial overgrowth structures on silicon and germanium with precise control over layer thickness and impurity content (resistivity). However, it will be necessary to refine this control over thickness and impurity content to within 2% if the full potential of the process is to be realized. All process parameters must be subject to extremely tight control if this is to be accomplished. Furnace geometry, gas flow geometry and reaction temperatures are subject to experimental analysis, and reaction temperatures can be controlled to well within tolerance limits using commercially available controllers. Gas phase composition control, however, presents numerous problems, which are presently under experimental and theoretical investigation.

II. PROGRESS

A. Technical Discussion

The basic problem is that of precisely monitoring and controlling the $SiCl_4$ and dopant gas levels in the hydrogen stream which is fed to the epitaxial reaction tube. It will be necessary to monitor and control gas compositions which will dope the resultant silicon from levels as low as 10 ppb

(100 ohm-cm.) to as high as one part in one hundred (.001 ohm-cm).

At the present time, there are at least three possible methods for monitoring gas phase compositions. These are mass spectrometry, infra-red absorption spectrometry, and gas chromatography. Emission spectrographic procedures have been used to study trace amounts of impurities in $SiCl_4$ in the range 0.8 to 50 ppb (1). Theurer (2) has reported observing characteristic absorption spectra of PCl_3 and BCl_3 in $SiCl_4$ down to levels of 0.01%. Gas chromatography detection limits are generally in the range of .01%, although Ebert (3) has reported detection levels of 0.1 ppm when using combined chromatography and mass spectrometric techniques. Standard mass spectrometric methods with certain refinements should offer the most sensitive and most economical method of monitoring gas phase compositions.

1. Mass Spectrometry

The mass spectrometer is a continuous monitor system with a time response limited only by the design of its gas sampling mechanism. Its output is in the form of an electric current which can readily be used in a control feedback network. The limit of detection in a mass spectrometer is best defined as the least partial pressure which is measureable for a gas component in the ionization chamber of the spectrometer. Characteristically, for most commonly used spectrometers, the limit of detection is 10^{-11} Torr. partial pressure (approx. 10^5 molecules cm^{-3}) which would, under normal operating conditions, correspond to approximately 1 ppm of the majority ambient gas in the spectrometer ion source region.

Recently, General Electric's Power Tube department marketed a low cost mass spectrometer which is called "The General Electric Partial Pressure Analyzer Model 514." The instrument has an extremely high sensitivity of 10^{-13} to 10^{-16} Torr. partial pressure. It can be used with a recorder, or with an oscilloscope display to view transient phenomena. The spectrometer consists of a Nier-type electron bombardment ion source; a 90° sector, 5 cm radius magnetic analyzer; and a 10-stage electron multiplier ion detector entirely enclosed in a glass-metal envelope. The entire package can be baked-out at temperatures up to 450°C. Its volume is approximately 400 cc. Its usable mass range is from 2 to 200 AMU (automic mass units). The spectrometer is supplied with a complete control unit which consists of an emission regulated power supply with automatic mass scan, an electron multiplier power supply, and a Kiethley micro-microammeter to measure the multiplier output current. The instrument is also supplied with a 3000 gauss permanent sector magnet and yoke. A removable cylindrical metal shield is provided for the ion detector. Figure 1 is a photograph of the mass analyzer, and Figure 2 is a typical spectrum of the instrument. This instrument will be incorporated in the vapor stream analysis system.

FIGURE 1

PARTIAL PRESSURE ANALYZER

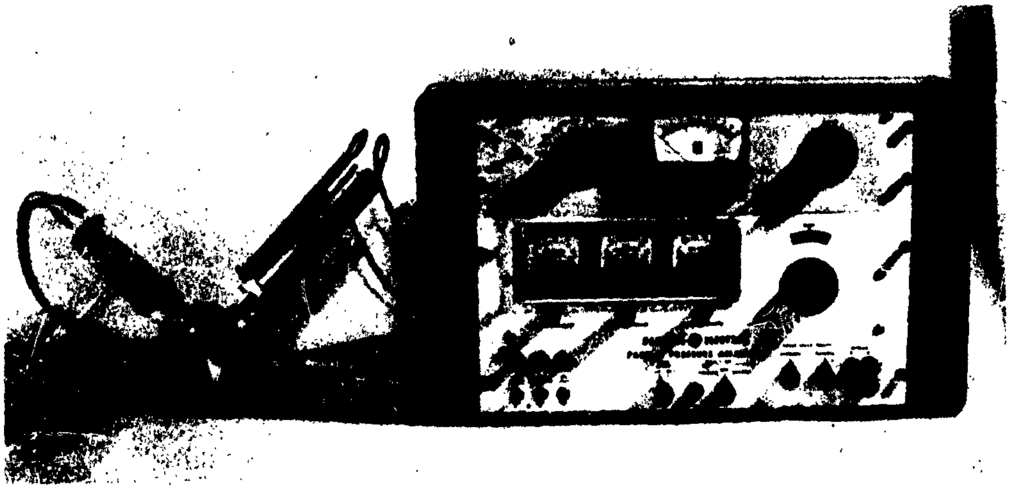
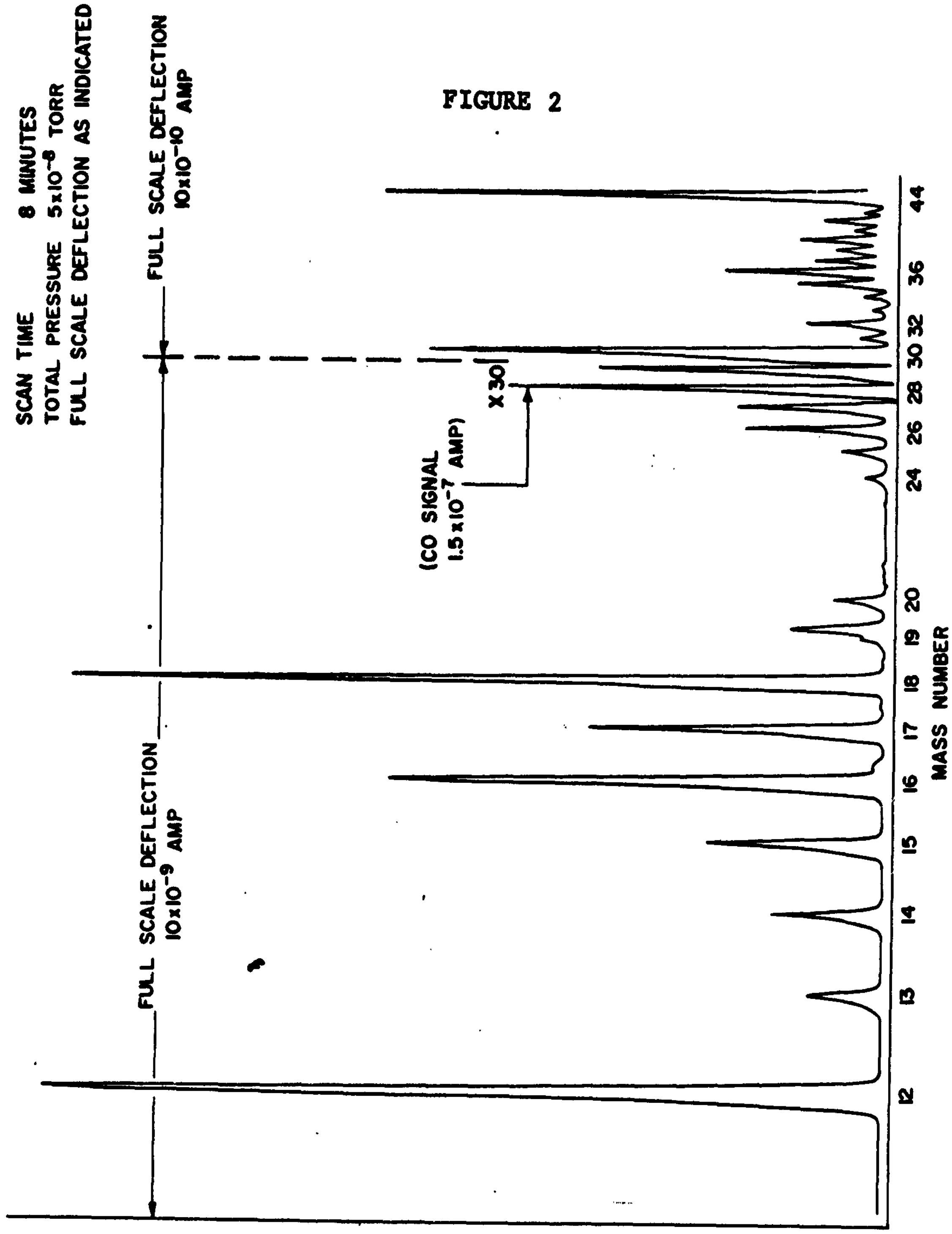


FIGURE 2



Spectrum Showing Resolution from 32-44 AMU

2. Vacuum System

The mass spectrometer maximum operating pressure is a 10^{-5} Torr. Therefore, it will be necessary to incorporate a vacuum pumping section. In order to minimize background peaks which arise from organic O-rings or pump fluids, the vacuum pumping system will utilize a 9 lps electronic pump, stainless steel plumbing, and copper gaskets. Figure 3 shows a schematic diagram of the vacuum pumping system and mass spectrometer tube. All parts and plumbing are off-the-shelf items from the "Ultek" Corporation. Ultek parts are used because of ease in alignment. The system will be roughed out to less than 10 microns with a mechanical pump. A molecular sieve trap will be used in the roughing line to prevent oil from backstreaming into the system from the mechanical pump. The electronic high vacuum pump will be capable of reducing the pressure in the spectrometer to 10^{-10} Torr.

3. Vapor Sampling System

Since the mass spectrometer typically operates at 10^{-5} Torr., and the epitaxial gas stream is atmospheric or slightly above, it will be necessary to reduce the pressure of the gas sample by a factor of 10^{8} before it is fed into the spectrometer ion source region. A system of valves, expansion chambers, and differential pumping will be used to lower the sample pressure. The proposed vapor sampling system that is to be incorporated is shown schematically in Figure 4.

FIGURE 3

VACUUM PUMPING SYSTEM AND MASS SPECTROMETER

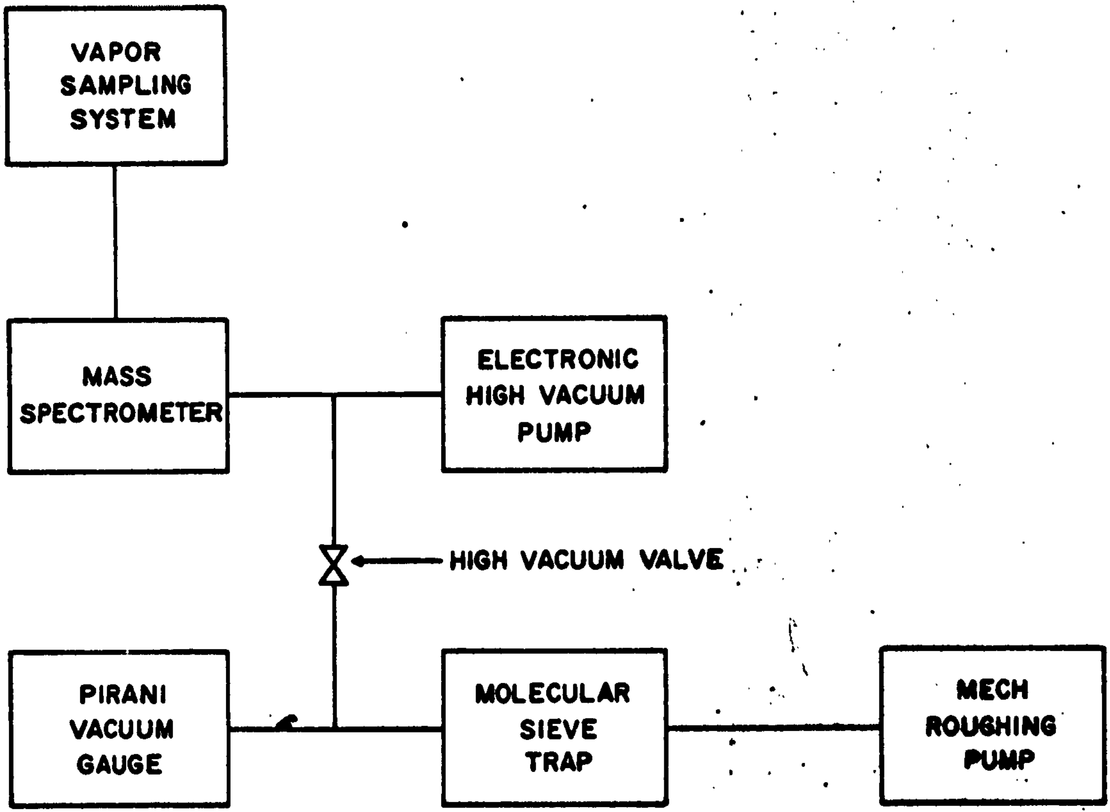
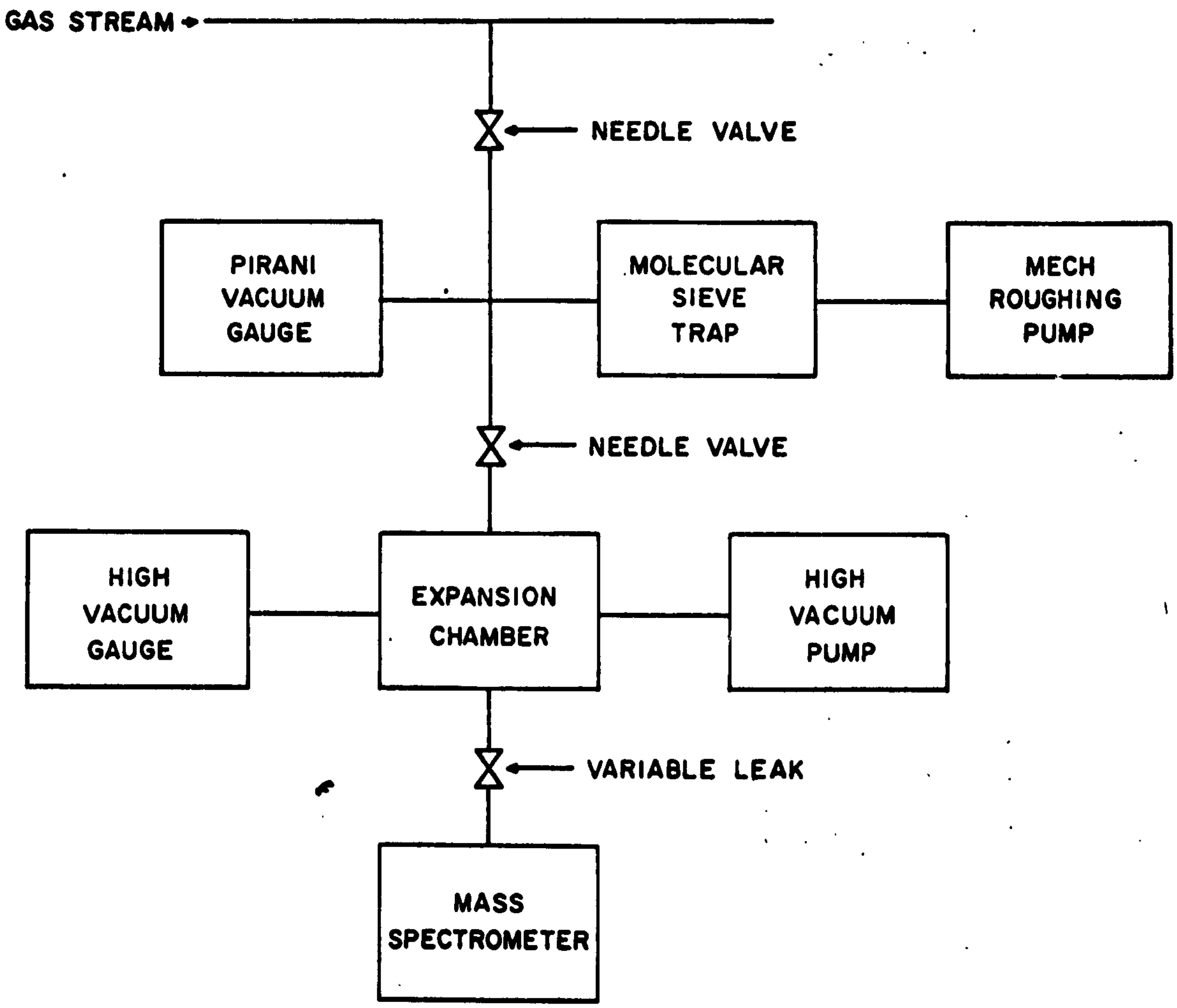


FIGURE 4

VAPOR SAMPLING SYSTEM



This particular section will be subject to considerable experimental investigation in order to determine optimum operating parameters.

4. Operational Parameters

There are three major considerations to be made to determine the feasible operating range of the vapor analysis system. First, the identity of the various elements and compounds which are likely to be encountered in the investigation, such as dopant, matrix, or background molecules; second, the range of concentrations (partial pressure) of the impurities which will be subject to control; third, the concentration of silicon or germanium in the vapor streams. The elements and compounds which are likely to be subject to control are found in Table I. Typical backgrounds are listed in Table II.

From the Tables, it is obvious that several real problems immediately come into the picture. First, Si and N_2 fall together, and N_2 is quite often one of the major background peaks. Also, Diborane has a major peak at 28. Gallium and Germanium have intermixed major peaks, while phosphorous and oxygen may become confused. Thus, considerable work will be needed to avoid background interference with measurements.

5. Impurity Concentration in Gas Stream

Calculations have been made to determine the concentration of dopant gas in the stream to the

TABLE I
CONTROLLABLE VAPOR STREAM CONSTITUENTS

Compound or Element	Chemical Composition	AMU	% Abundance
Silicon	Si	28	92
		29	5
		30	3
Silicon Tet	$SiCl_4$	170	100
Germanium	Ge	70	21
		72	27
		73	7.8
		74	37
		76	7.8
Germanium Tet	$GeCl_4$	214	100
Boron	B	10	18
		11	82
Diborane	B_2H_6	26	18
		28	82
Phosphorous	P	31	100
Phosphine	PH_3	34	100
Arsenic	As	75	100
Arsine	AsH_3	78	100
Antimony	Sb	121	57
		123	43
Stibine	SbH_3	124	57
		127	43
Gallium	Ga	69	60
		71	40
Aluminum	Al	27	100
Indium	In	113	4
		115	96

TABLE II

TYPICAL BACKGROUND GASES

Compound or Element	Chemical Composition	AMU	% Abundance
Chromium	Cr	50 52 53	5 84 10
Manganese	Mn	55	100
Iron	Fe	54 56	6 92
Cobalt	Co	59	100
Nickel	Ni	58	100
Copper	Cu	63 65	69 31
Zinc	Zn	64 66 68	49 28 19
Nitrogen	N_2	28	100
Oxygen	O_2	32	100
Carbon	C	12	100
Carbon Dioxide	CO_2	44	100
Water Vapor	H_2O	18	100

epitaxial reactor. An example was chosen as 0.5 ohm-cm. n and p type silicon from typical process development data. Here, for simplicity, we will assume that all gases are ideal. In p-type doping, each gas molecule contains 2 dopant atoms, while for the n-type gases there is one dopant atom per molecule.

For 0.5 ohm-cm. n-type doping, there are:

$$5.2 \times 10^{10} \text{ atoms cm}^{-3}$$

and for p-type, there are

2.4×10^{11} atoms cm^{-3} in the gas stream.

For an ideal gas at standard conditions, there are

$$2.7 \times 10^{19} \text{ molecules cm}^{-3}$$

Therefore, in the gas stream, we have a dopant gas partial pressure of approximately 10^{-5} Torr. If we were to sample the gas stream and pump it down to the maximum operating pressure of the spectrometer (10^{-5} Torr.), the corresponding dopant gas partial pressure would be 10^{-13} Torr. The result does not account for any possible lack of efficiency or selectivity in the sampling system.

Thus, at 0.5 ohm-cm., we are at the lower limit of detection for the spectrometer when using straight gas dilution techniques. Consequently, to monitor the vapor stream at 100 ohm-cm., the spectrometer would have to detect a partial pressure of 10^{-15} Torr.

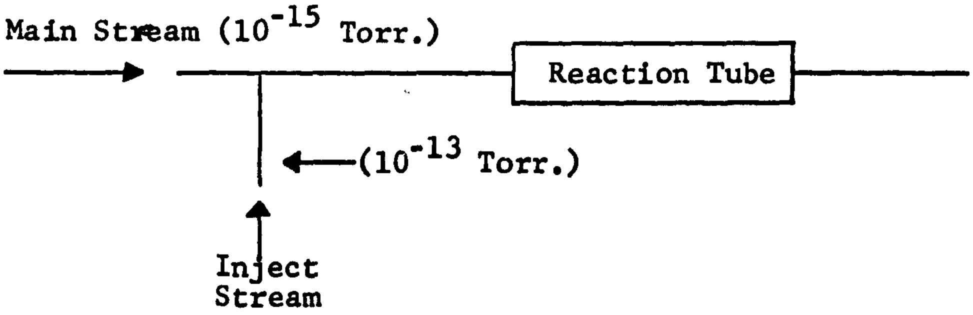
Since 100 ohm-cm. is a reasonable resistivity, some engineering is in order to bring the gas stream concentrations to within the spectrometer's ball park.

To complete the picture, 0.001 ohm-cm. would correspond to 10^{-9} Torr.

The partial pressure of the $SiCl_4$ in the reduced pressure sample is approximately 10^{-8} Torr.

There are two techniques which will be developed for this system in order to concentrate the dopant gas.

By selecting a point in the system other than the main stream, the partial pressure at 100 ohm-cm. can be as high as 10^{-15} Torr.



Sampling at side stream points would mean that an extremely complex sampling system would have to be used in order to monitor both matrix and dopant atoms, or several spectrometer tubes would be needed for a single system.

A second method could be modelled after that reported by Ebert(3) in which the major carrier gas (H_2) is pumped off after freezing the sample at liquid nitrogen temperatures. This process would mean that batch sampling would be necessary in lieu of continuous sampling.

B. Equipment Order

During the last period, the sampling system was designed, and components were selected and ordered for delivery by October 1, 1962.

III. FUTURE WORK

A. Theoretical

Further calculations will be made in order to estimate operating parameters of the spectrometer. Special efforts will be made to determine what types of ions will actually be under investigation, i.e., Si or $SiCl_4$ or $SiCl_3$, etc. Certainly a wide range of molecular species will be observed which will also have a marked effect on the spectrometer's sensitivity.

B. Experimental

Such practical problems as system ability to handle corrosive gases will be investigated and it may be that the ion multiplier dynode surfaces will be strongly effected by the sample gases.

The system will be assembled and debugged. The sampling system will be subject to considerable development effort. The entire system will be mounted in a console arrangement for ease of operation. Automation will be used where feasible, especially in a batch sampling set-up.

A systematic investigation of the working range of the spectrometer for a variety of dopant gases will be carried out.

Eventually, feedback techniques for process control will be investigated.

IV. CONTRIBUTING SCIENTISTS AND ENGINEERS

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