

**Procedure.** PREPARATION OF EQUIPMENT. The system is connected as shown in Figure 1 except that a variable voltage source is connected between *S* and pin 1. The red and black input jacks to the recorder provide access to the slidewire source. Connections to pins 1 and 2 at the input to the servo amplifier are made through the auxiliary input jacks mounted on the recorder.

The operational amplifier system is warmed up for a half hour before any runs are made. The amplifiers are balanced by adjusting balance pots for each of the amplifiers until the follower output is zero for zero input and the summing point of the integrator is zero after *Sw* has been closed momentarily and then opened. The recorder pen is moved to its maximum displacement to the left and the displacement control is adjusted so that the slidewire source output is zero.

The appropriate reference solution is placed in the reference compartment thermostated at 25.0° C.

The bias  $E_b$  is adjusted so that the minimum elapsed time before the measurement of the most concentrated sample anticipated is completed in about 10 seconds. A bias voltage of about 5 mv. is required for both concentration ranges. The exact value depends upon solution conditions and junction and asymmetry potentials of the cell.

The damping ( $R_1$ ) and sensitivity ( $R_2$  and  $R_3$ ) controls are adjusted in the manner described earlier (2) with a standard glucose solution intermediate in the concentration range of interest. Controls  $R_2$  and  $R_3$  are adjusted until the meter readout is a simple multiple of glucose concentration.

**Measurement Step.** The sample compartment is rinsed with distilled water once between runs. Then 1.00 ml. of composite reagent is added and the stirrer is started; 1.00 ml. of the sample is added and *Sw* is closed momentarily. After the servo begins to respond, the meter reading passes through a maximum. This maximum reading is recorded and used to compute glucose concentration using Equation 4.

#### RESULTS AND DISCUSSION

Results for aqueous glucose samples in the concentration ranges of 2.5 to 25 and 25 to 250 p.p.m. are given in Table I. These data demonstrate relative standard deviations for the method of about 1%. The large negative errors at the lower end of each range result from the fact that significant amounts of glucose are used up before the rate measurement is completed. As pointed out earlier, the reliability of these measurements is also limited by the readability of the meter at the lower end of

the scale. Errors at intermediate concentrations approach 1% for each range.

The response of the system to match the slope of the rate curve is not instantaneous. For a properly damped system 5 to 10 seconds are required for balance. This response time is observed to be independent of the slope of the curve being measured. For high glucose concentrations, iodine is produced rapidly and the slope of the rate curve may decrease significantly before the measurement is completed. Under the conditions described above, this decrease in slope is sufficient to introduce negative errors of the order of 3 to 5% for the upper concentrations of the two ranges investigated here.

These results demonstrate that the measurement method is applicable to response curves with slopes decreasing at moderate rates. Faster response than is attainable with the present system is required for rapidly changing slopes.

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## Infrared Monitoring of Semiconductor Epitaxial Process Gas Streams

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► A gas stream containing a low concentration of a silicon or germanium halide, as in the deposition of semiconductor films by hydrogen reduction, may be monitored continuously by infrared spectrophotometry in the 15- to 35-micron stretching fundamental range. The absorption bands are well suited for quantitative work, and are strong enough so that cells only a few centimeters long are required for halide concentrations of 0.1 to 0.5%. Wavelengths and absorptivities for  $\text{SiCl}_4$ ,  $\text{GeCl}_4$ ,  $\text{SiBr}_4$ , and  $\text{GeBr}_4$  are given.

AN IMPORTANT STEP in the manufacture of many modern semiconductor devices is the epitaxial deposition of a thin film of single-crystal silicon or germanium of controlled resistivity. In a typical silicon epitaxial process, hydrogen at one atmosphere containing 0.1 to 0.4 mole %  $\text{SiCl}_4$  is passed over the

heated Si substrate.  $\text{SiBr}_4$  or  $\text{SiHCl}_3$  may also be used. The rate and uniformity of film deposition are sensitive to concentration (16), and crystal perfection is sensitive to impurities. Close control of the gas composition is thus required.

This control can be accomplished simply and continuously, without risk of contamination, by monitoring the composition of the incoming gas by infrared absorption spectrophotometry. For high sensitivity one must work outside the usual 2- to 15-micron analytical range, but the technique offers several advantages. The method is specific for the metal halide, and indifferent to contaminants such as HCl (from hydrolysis), air, and vapor-phase dopants. It is independent of flow rate. Since only a short absorption path is required, response to concentration changes is virtually instantaneous. Finally, no probe of any kind need be

inserted into the corrosive gas stream and none of the gas is lost by sampling

#### SPECTRA OF THE HALIDES

In this work the infrared spectra of gaseous  $\text{SiCl}_4$ ,  $\text{GeCl}_4$ ,  $\text{SiBr}_4$ , and  $\text{GeBr}_4$  have been studied. The spectra of  $\text{SiCl}_4$  vapor (14) and  $\text{GeCl}_4$  vapor (10) have been published; there are no reports on  $\text{SiBr}_4$  or  $\text{GeBr}_4$  vapors. Raman spectra (3) and liquid spectra for the 2- to 10-micron range (13) are available. These symmetrical tetrahedral molecules have simple spectra; the strongest absorption by far is the  $\nu_3(f_2)$  M-X stretching fundamental. The appearance of these bands for a sample in hydrogen at a total pressure of one atmosphere is shown in Figure 1. Wavelengths of the absorption maxima, in microns, are:  $\text{SiCl}_4$ , 16.1;  $\text{SiBr}_4$ , 20.1;  $\text{GeCl}_4$ , 21.8;  $\text{GeBr}_4$ , 30.3.

The weak absorptions at  $640 \text{ cm}^{-1}$  in  $\text{SiCl}_4$  and  $348 \text{ cm}^{-1}$  in  $\text{GeBr}_4$  are

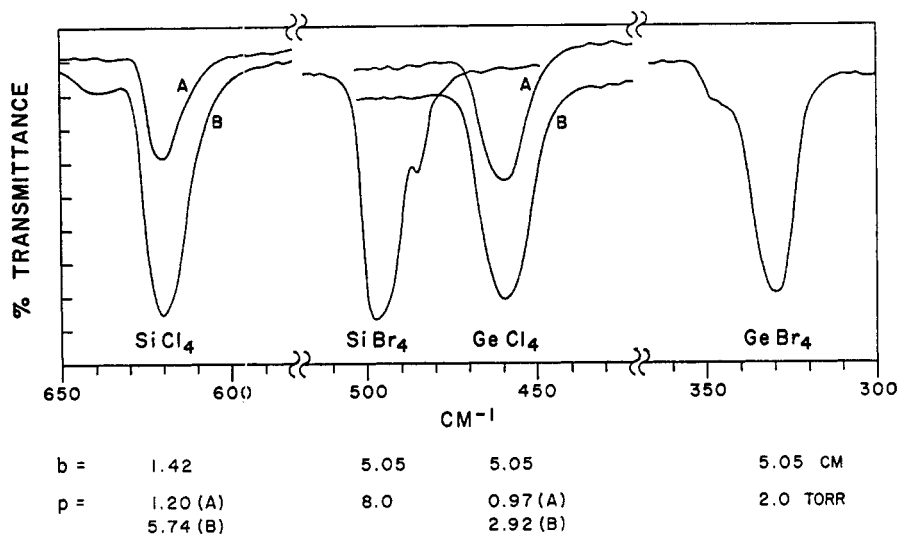


Figure 1. Appearance of the  $\nu_3(f_2)$  absorption bands of silicon and germanium chlorides and bromides in hydrogen, total pressure = 1 atm.

b = path length, p = partial pressure of the halides

probably the  $\nu_1 + \nu_4$  combinations. The weak absorption near 485  $\text{cm}^{-1}$  in  $\text{SiBr}_4$  may be due to  $\text{SiHBr}_3$  impurity, since it is at about the right place for the strong  $\nu_3(e)$  band. At the concentrations used for epitaxial deposition, and with path lengths of only a few centimeters, the absorptions shown in Figure 1 are the only ones detected in the infrared. The simplicity and freedom from interference of the  $\nu_3$  bands make them ideal for quantitative work.

#### EXPERIMENTAL

A Perkin-Elmer Model 221 spectrophotometer with KBr optics was used to scan the 10- to 25-micron region.  $\text{GeBr}_4$  was observed with a Beckman IR-5A spectrophotometer with CsBr optics, scanning 18 to 35 microns. Cells 1 to 5 cm. long were cut from 30-mm. o.d. borosilicate tubing and provided with inlet and outlet tubes with Teflon-plug stopcocks. Cell windows were usually 1-mm. thick silver chloride sheet cemented on with Araldite epoxy resin. (Ordinary alkali halide windows are rapidly fogged by hydrolysis products.) The gas stream flowed through the cell just prior to entering the epitaxial deposition chamber; gas flows were 1 to 5 liters per minute.

The  $\text{GeCl}_4$  absorption lies only 3 microns from the transmission limit of silver chloride. To provide a horizontal baseline for the spectrophotometer trace, it is advisable to insert a compensating pair of windows into the reference beam. Cell windows which have been used with  $\text{SiCl}_4$  streams should not be used for  $\text{GeCl}_4$ , because even the thinnest  $\text{SiO}_2$  coating gives absorption bands which overlap the  $\text{GeCl}_4$  460- $\text{cm}^{-1}$  band.

For  $\text{GeBr}_4$  at 30.3 microns, a cell with 25-mil thick polyethylene windows was used.

Calibration of the absorption bands and testing for validity of Beer's law

were carried out using an all-glass apparatus designed to produce gas streams of controlled composition. Pre-purified hydrogen was first saturated by passing it through a gas-washing bottle containing the appropriate liquid halide. The bottle was jacketed for cooling when the more volatile halides were employed. The gas then passed through a thermostated trap whose temperature could be regulated to  $\pm 0.1^\circ \text{C}$ . in the range from room temperature to  $-70^\circ \text{C}$ . Finally the gas was warmed to room temperature and passed through the spectrophotometer cell and out to the atmosphere. Calibration was at about 750 torr total pressure and  $25^\circ \text{C}$ .; the result is independent of small variations in the total pressure but a simple gas law correction is required if monitoring is done at other than the calibration temperature.

This system requires knowledge of the vapor pressures of the halides at

Table I. Summary of Data for Infrared Monitoring

Compound	Absorption maximum, $\text{cm}^{-1}$	Absorptivity, $25^\circ \text{C}$ ., $\text{cm}^{-1} \text{ torr}^{-1}$
$\text{SiCl}_4$	621	0.104
$\text{GeCl}_4$	460	0.046
$\text{SiBr}_4$	498	0.022
$\text{GeBr}_4$	330	0.061
$\text{SiHCl}_3$	600	0.026
$\text{GeHCl}_3$	449	0.044

low temperatures. Standard reference works apparently include many extrapolated data since the original papers have no experimental measurements below  $0^\circ \text{C}$ . For  $\text{SiCl}_4$  (6, 7, 11), the expression used was:

$$\log p (\text{torr}) = A - \frac{B}{t + C}$$

where  $A = 6.97287$ ,  $B = 1200$ ,  $C = 236$ . For  $\text{GeCl}_4$ , the vapor pressures recommended by Stull (15) and Kelley (8) have been used: a good approximation in the range  $-15^\circ \text{C}$ . to the freezing point is  $\log p (\text{torr}) = -1965/T + 8.611$ . It should be noted, however, that these authors depend on original data published many years ago (9), and these data are not in good agreement with their smoothed curve below  $-15^\circ \text{C}$ . Redetermination of the vapor pressure curves of all the pure halides is much needed.

For  $\text{SiBr}_4$ , the measurements of Pohland (12) are available; for  $\text{GeBr}_4$ , see (2, 4, 15).

#### RESULTS

Plots of  $\log I_0/I$  vs. the product of halide partial pressure and cell length—i.e., the number of halide molecules in the absorbing path—were good straight lines. The slopes of these plots are the absorptivities of the bands. Table I

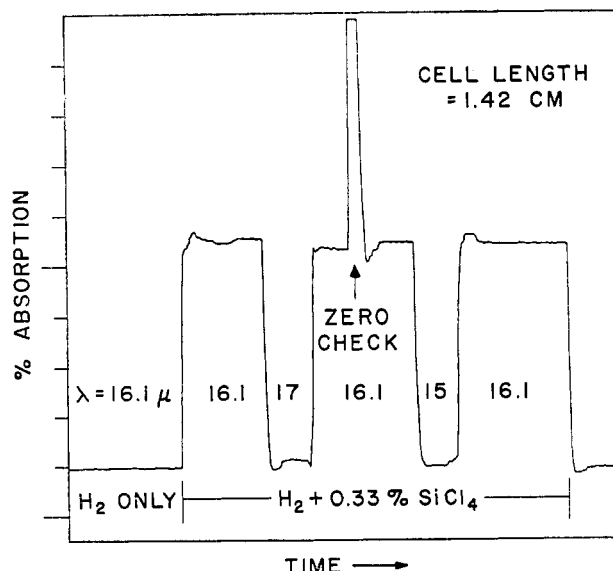


Figure 2. Recorder trace of infrared monitoring of gas supply to a silicon epitaxial deposition apparatus

summarizes results.  $\text{SiHCl}_3$  and  $\text{GeHCl}_3$  have not been studied, but estimates for the  $\nu_3(e)$  band have been made from published spectra (5, 10). Absorptivities vary somewhat with the spectrophotometer (1), and for precise work each instrument should be calibrated. The constants given in the table will allow choice of the optimum cell length, however. Furthermore, for film deposition it is often more important to observe whether the reactant concentration remains constant than to know its exact value.

Figure 2 shows an actual monitoring trace from an epitaxial silicon deposition using 0.33%  $\text{SiCl}_4$  in  $\text{H}_2$ . This was made by a Perkin-Elmer KBr Infracord with a slave recorder; the spectrophotometer scan clutch was disengaged so that a chosen wavelength could be observed continuously. The reference beam was attenuated with a screen to bring the transmittance to about 95% with only

hydrogen in the cell. The fast response to the introduction of  $\text{SiCl}_4$  is evident. The instrument zero may be checked during operation by closing a shutter in the sample beam. Measurement at 15 or 17 microns gives no signal, as shown. In ordinary operation the spectrophotometer remains set on the absorption maximum.

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## Activation Analysis of High Purity Materials

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► Samples of high purity beryllium, aluminum, and iron have been analyzed for trace amounts of 62 possible elemental impurities by measuring the gamma activities of radionuclides produced by neutron activation. Ten elements are determined by nondestructive techniques after bombarding a portion of the sample for 10 seconds and making a rapid measurement of the short-lived radionuclides that are induced. A second portion of the sample is activated for 20 minutes and analyzed for the gamma-emitting radionuclides of chlorine, bromine, and iodine. Forty-nine elements can be determined in a third portion of the sample after a 16-hour irradiation. The induced radionuclides are divided into six groups by a series of rapid chemical separations and each gamma activity is identified, counted, and compared with that of a standard radionuclide.

STRINGENT SPECIFICATIONS are currently being placed on many materials used in the construction of nuclear reactors. These specifications have created a renewed demand for methods of determining trace amounts of essentially all naturally occurring elements. Although much of this demand can be met with currently available methods, many elements cannot be determined readily with the

desired sensitivity by any method amenable to routine use.

The techniques of activation analysis and gamma spectrometry have become very useful for the determination of micro or submicro amounts of most elements (2, 4). In this paper a method is described in which trace amounts of 62 elements in certain matrices can be determined by neutron activation analysis.

The inherent sensitivity of neutron activation analysis is dependent on the accuracy with which the induced gamma-emitting nuclides can be identified and measured. Many elements can be detected with extremely high sensitivities—i.e.,  $10^{-9}$  gram—after being subjected to a flux of  $10^{12}$  n./sq.cm./sec. for several hours. Most elements, however, have sensitivities that do not differ by more than a factor of 100,  $\sim 10^{-7}$  to  $10^{-6}$  gram. Consequently, the bulk of the gamma energies are easily masked when multiple activities are induced by neutron activation. This interference is especially serious when the major elemental constituents of a sample are converted into gamma-emitting nuclides. Partial resolution of gamma energies can be obtained by variation of the experimental conditions used, such as irradiation and decay times. This approach is not practical when a sample contains even trace amounts of such common elements as Na, Al, Mn, Cu, or Br because these

elements become highly radioactive during neutron bombardment and, subsequently, overshadow the activities of other nuclides.

Several proposals (1, 3, 7, 8) have been reported wherein instrumental resolution of gamma energies has been simplified by postirradiation chemical treatment of the sample. The purpose of this paper is to extend these techniques and present a flexible method which can be used to determine 10 p.p.m. or less of essentially all of the naturally occurring elements that form gamma-emitting nuclides when bombarded by reactor neutrons. "Non-destructive" and "chemical" procedures have been combined to achieve this goal, and the resulting method is a compromise of possible conditions selected for maximum scope, sensitivity, simplicity, and accuracy.

#### EXPERIMENTAL

**Neutron Activation.** Two reactor facilities were used for the activation of samples. An air-cooled facility with a flux of  $\sim 8 \times 10^{11}$  n./sq. cm./sec. was used to irradiate 1-gram samples in polyethylene bottles for 20 minutes and 16 hours. A pneumatic facility with a flux of  $\sim 6 \times 10^{13}$  n./sq. cm./sec. was used to activate 1- to 100-mg. samples for 10 seconds. For these latter irradiations, the samples were sealed in high purity polyethylene tubing and placed in a polyethylene "rabbit."