A Flow Method for the Study of Silicon and Germanium Atom Reactions by Direct Spectroscopic Observation

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Summary Free silicon and germanium atoms produced in a microwave-sustained helium plasma are detected downstream from the plasma in their ground states by atomic absorption spectroscopy, and reaction of silicon atoms with silane to produce disilane has been found in the flow system.

THE reactions of silicon atoms have been studied by nuclear recoil techniques[1] and also by thermal evaporation.[2] The chemistry of germanium atoms following nuclear recoil is also under investigation.[3] We report here the generation of silicon and germanium atoms in a flow system under conditions facilitating direct spectroscopic observation of the atomic species which will permit measurement of their reaction rates.

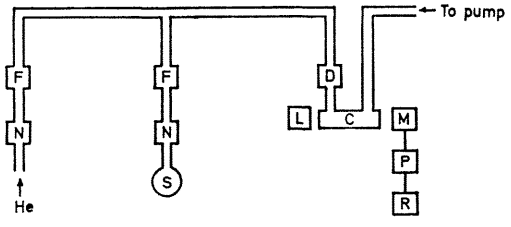

FIGURE. *Atomic absorption discharge flow system. For reaction studies a second substrate inlet has been used in place of the absorption cell.* F = *flowmeter*: N = *needle valve*; D = *discharge*; L = *light-source*; S = *substrate*; C = *absorption cell*; M = *monochromator*; P = *photomultiplier*; R = *recorder.*

Silicon and germanium atoms have been produced by decomposition of silane SiH_4 and germane GeH_4, respectively, in a microwave-sustained helium plasma.[4] A helium stream containing silane or germane in low concentration is passed through the electrodeless microwave discharge in a flow system. A schematic diagram of the apparatus is given in the Figure. The emission spectra of the plasmas have been examined with a 0·5 m Ebert monochrometer in a Jarrell–Ash atomic emission and absorption scanning spectrometer equipped with a type R106 photomultiplier tube. The generation of silicon and germanium atoms within the plasma has been confirmed by observation of emission due to the $^1D \leftarrow {}^1D^0$ (2435·1 Å for Si, 2417·4 Å for Ge) and $^3P \leftarrow {}^3P^0$ (2506·9, 2514·3, 2516·1, 2519·2, 2524·1, and 2528·5 Å for Si, 2592·5, 2651·1 (two unresolved peaks), 2691·3, 2709·6, and 2754·6 Å for Ge) transitions of both silicon and germanium atoms.

Most interesting is the detection of ground state ^3P silicon and germanium atoms *downstream* from the plasma discharge region. An optical cell mounted within 4 cm of the discharge region has been used to take atomic absorption spectra of the gas stream within 1 ms after it leaves the plasma. With silicon and germanium hollow-cathode atomic emission line light sources, strong absorption of the 2516 and 2651 Å resonance lines by silicon and germanium atoms, respectively, is observed. Atomic transition lines of other atoms lying near the silicon and germanium resonance lines are absorbed weakly or not at all, indicating that the absorption of silicon and germanium resonance radiation is by the atomic species Si and Ge. In both cases the transition observed is $^3P \rightarrow {}^3P^0$. The absorption data are given in the Table. There is no absorption of the silicon or germanium resonance lines when silane or germane is passed through the flow system *without* a discharge. Also, there is no absorption with a discharge but without silane or germane being passed through it. Thus the absorbing species are shown to be decomposition products of silane and germane, respectively.

The application of this discharge-flow-spectroscopic technique to reaction studies has just begun. Injection of

silane *downstream* from the discharge region into a helium stream containing silicon atoms leads to the production of disilane, previously observed as a reaction product of recoiling silicon atoms in silane.[1] The formation of disilane in the discharge flow system is *not* due to the reactions of hydrogen atoms produced along with silicon atoms in the dissociation of silane.† There is a negligible yield of disilane when molecular hydrogen is passed through the discharge producing hydrogen atoms, and then silane is injected downstream from the plasma. In future applications, the attenuation of silicon and germanium atom concentrations will be monitored directly by atomic absorption spectroscopy as a function of the concentration of reaction substrate introduced between the plasma region and the optical cell. Hence direct rate studies on silicon and germanium atom reactions should be feasible.[5]

In view of the interest in the mechanism of silane decomposition by pyrolytic,[6] photolytic,[7] and discharge methods,[7d] and the continuing controversy about the relative importance of silylene SiH_2 and silyl radicals SiH_3 as reactive intermediates, it is of interest that the total disruption of silane molecules into silicon atoms has been demonstrated in the present experiments. Spectroscopic observation of silane and germane decomposition products under a variety of conditions in a flow system gives promise for the elucidation of the mechanisms of several synthetically useful and mechanistically interesting reactions. Circulation of silane through an electric discharge has become a standard method for the synthesis of disilane and higher silanes,[8] but the reaction mechanisms remain to be determined. The present results suggest the involvement of silicon atoms.

TABLE

Attenuation of atomic emission lines due to absorption by decomposition products of silane and germane

Substrate	Helium flow rate (ml/min at STP)	Substrate feed rate (ml/min at STP)	Flow system pressure (Torr)	Wavelength[a] (Å)	ΔI[b] (%)
SiH_4	2724	7·6	36	2516	70
				2483	5
				2428	5
				2795	4
GeH_4	2720	10·4	33	2651	20
				2483	0
				2795	0
				2801	0
				2320	0

[a] Hollow cathode light sources were used with cathode materials and wavelengths as follows: Si 2516, Ge 2651, Mn 2795, 2801, Fe 2483, Au 2428, Ni 2320.

[b] The photomultiplier amplification was adjusted to give a full scale reading I_0 on an auxiliary recorder with no substrate passing through the plasma. ΔI is the decrease in transmitted intensity observed upon passing the substrate through the plasma.

We thank the United States Atomic Energy Commission for financial support.

(*Received, June 7th*, 1971; *Com.* 925.)

† Until data correlating the disappearance of silicon atoms with the appearance of disilane become available it can be argued that some other dissociation product of silane besides silicon or hydrogen atoms is responsible for disilane formation. Ring and his co-workers[7d] have suggested that in a silent electric discharge silane is dissociated to silylene SiH_2 which inserts itself into the silicon–hydrogen bonds of undecomposed silane. Under the more vigorous conditions of the microwave-sustained discharge used in our experiments, complete dissociation of silane to silicon atoms is believed to occur. Certainly no silane survives the discharge, and no stable volatile silicon hydrides emerge unless a trapping reagent such as silane is injected downstream.

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