Solubility of Carbon in Silicon and Germanium

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The solubility of carbon in silicon has been measured over the temperature range 1560 to 2900°C. The enthalpy of solution is 59±3 kcal/mol. A phase diagram for the system Si—C is presented, embodying these solubility data as well as the results of other high-temperature experiments with silicon carbide. It is found that SiC possesses a peritectic point at 2830±40°C. These studies were carried out in argon at pressures as high as 35 atmos. Solubilities of carbon in germanium were measured in the temperature range 2780 to 3170°C, at argon pressures up to 55 atmos, and a tentative phase diagram is given.

EXPERIMENTS WITH SILICON

Introduction

Neither the solubility of carbon in silicon at high temperatures, nor the phase diagram of the system Si—C is known. Nowotny et al., in working with the ternary system Mo—Si—C, proposed two possible phase diagrams for the system Si—C. These were for pressures less than one atmosphere and were based on a limited number of experimental points so that a decision between the two could not be made. The solubility of C in liquid Si has been measured by Hall up to 1710°C. Others have found Si as an impurity in natural diamond, although the conditions of formation are of course unknown. We present here some solubility measurements in liquid Si up to 2900°C, and a proposed phase diagram for the system.

Experimental Procedure

The experiments were carried out in a 50-kw graphite resistance furnace heated by 20 v maximum, 60-cy ac. This was enclosed in a water-cooled pressure vessel. Argon at a pressure of 35 atmos was used to reduce the tendency of the silicon to evaporate. The vapor pressure of silicon is about one atmosphere at 2800°C over both Si and SiC. Figure 1 shows the arrangement of the silicon container, heater, and shields which were used above 2000°C. The entire assembly was of graphite and was supported from the current terminals. On the basis of melting point measurements on iridium wires, the temperature variation over the container was believed to be not over ±25°C from the value at the point of measurement. The mounting of the container within the heater tube was such that no current passed through the Si charge. In this way, changes in the state of the Si, and hence in its electrical resistivity, did not affect the temperature distribution.

The Si was du Pont hyperpure grade, ground with a Pyrex mortar and pestle, screened, and leached with HF to remove any glass contamination in the Si from the mortar. The graphite container was filled with 100 mesh Si (about 0.5 g) and closed with a graphite end plug. No carbon was added; the carbon which was

taken into solution by the liquid silicon came from the walls of the container.

After assembly of the furnace, the pressure vessel was evacuated; it was then refilled twice with argon to a pressure of 20 atmos, vented to atmospheric pressure each time, and finally filled to the operating pressure. A manostat maintained the pressure within ±1 atmos.

The length of time that the charge was kept at the operating temperature was a compromise. A long time ensured equilibrium, but for long times the Si loss became excessive with graphite containers. Usually the temperature was kept constant at the desired value for periods of one-half to two minutes. No dependence of the C solubility upon the duration of run was observed. The charge was cooled as rapidly as possible after the run by simply shutting off the power to the furnace. Initial cooling rates of 50°C/sec were typical.

Analysis

The carbon which was in solution in the liquid silicon at high temperatures crystallizes as SiC upon cooling. The Si slug containing the SiC was recovered by oxidizing away the graphite reaction vessel at 1100°C in an O₂ atmosphere. Less than 0.2 mg of SiO₂ was produced by this treatment. The original charge of Si could be accounted for in four portions:

1. Some had reacted with the container, forming a microcrystalline mass of SiC within the pores of the graphite container. Use of a dense graphite (1.90 g/cm³)* for the containers was necessary to avoid excessive losses in this way. This loss occurred mainly during the furnace warmup after the silicon liquified, and in unfavorable cases amounted to over 50 percent of the initial charge.

2. Some remained within the container as elemental Si, frozen into a small slug. This generally ranged from 10 percent to 60 percent of the initial charge of 500 mg, depending on the porosity of the container.

3. Some precipitated as SiC during cooling of the furnace. Most of the SiC was enclosed within the frozen mass of Si, although some may have segregated to the surface of the Si. No free C remained within the piece of silicon, as determined both by microscopic examination and by chemical analysis of the residue which remained after the silicon was removed by etching.

4. Little if any Si was lost by evaporation because of the blanketing effect of the argon and the low porosity of the graphite container.

The SiC from elemental Si containing the precipitated silicon carbide was lightly sandblasted to remove SiC which was formed in the walls of the graphite container and adhered to the surface of the slug. A thin layer of silicon (less than 25 μ) was removed from the slug during the sandblasting. After the sandblasted slug was weighed, the Si was etched away in a mixture of 1 part HF to 3 parts HNO₃. The SiC residue, which was not attacked by the etch, was dried and weighed. The carbon solubility at the operating temperature of the furnace was computed from the ratio of the mass of SiC to the mass of Si in the slug.

The major source of error in this procedure was the separation of the SiC formed by reaction with the container from that formed by reaction with dissolved carbon. It is felt that the experiments done in graphite gave a lower limit to the solubility of C in Si, because some dissolved SiC which was segregated to the surface during cooling may have been lost in sandblasting. Because only a thin layer was removed it is believed that at least 90 percent of the SiC is retained in the slug. Also, from the reproducibility of experiments one concludes that this loss was not serious.

* We are indebted to R. L. Shenard, of the National Carbon Company Research Laboratories, for some samples of a suitable high-purity graphite.

**Fig. 1.** Graphite resistance furnace (axial cross section).

**Fig. 2.** The solubility of C in Si as a function of temperature.
Two of the measurements at temperatures below 2000°C were made in the same furnace, but with a different heater and an Al₂O₃ container (see Fig. 2). This change was necessary because a larger melt (10-20 g) was needed to dissolve a measurable amount of carbon. In the latter experiments, a weighed crystal of SiC was included in the melt, and its weight loss was used to determine the solubility. As a check, the SiC content of the Si melt was also found. About 2/3 of the SiC which was dissolved from the crystal was recovered. The total amount of SiC lost from the crystal was 5-10 mg. These experiments in ceramic containers were done in order to provide a comparison with those carried out in graphite. These data are upper limits to the solubility, because all the SiC lost from the weighed piece was considered to have gone into solution even though some redeposition of SiC on the walls of the container may have occurred during the run. The agreement between the measurements performed in Al₂O₃ and those performed in graphite is good, as can be seen from Fig. 2.

A measurement of the solubility at the Si melting point was made by W. C. Dash. This was performed in vacuum using a pedestal technique. A vertical bar of Si, clamped at the bottom, was heated at the top until a portion melted. Then a carefully weighed crystal of SiC of about 4.1 mg was inserted from above into the melt and sank until it rested at the liquid-solid interface. After about 10 min the melt was refrozen. The Si which surrounded the SiC crystal was removed by etching and again the SiC crystal was weighed. The weight loss and the mass of Si in the melt enabled the solubility to be found. The carbon solubility in liquid silicon at the melting point is 3.0±0.3x10⁻⁸ A/cm².

Temperature Measurement

All temperature measurements were made with a Leeds & Northrup type 8622-C optical pyrometer which had been recently standardized. Calibration errors are known to within ±2°C on the low-temperature (L) scale. Correspondingly the higher temperature scales have at most a ±10°C error. Measurements of transmission through the sight tube window of the furnace were made separately using a tungsten strip lamp inside the furnace as a source, with the window alternately in place and removed. This allowed an accurate correction to be made for transmission losses. During operation the surface of the Si container was visible at the bottom of a hole in the heater tube two diameters deep. The rough walls of the hole and the high emissivity of graphite both tended to make the hole equivalent to a blackbody. The temperature drop across the wall of the Si container was found as a function of temperature by direct measurement on an empty container which had a hole through to the interior. This hole was so positioned that both internal and surface temperatures could be measured at the same time. A useful check on the pyrometer was obtained from a plot of heater current vs absolute temperature squared. Above about 1700°C this plot was linear, indicating that radiation was by far the most important mechanism of energy loss.

As a final test, the melting points of Ir (2454°C) and Mo (2622°C) were measured, care being taken to avoid contact between the metal and carbon. We obtained 2446°C and 2634°C, respectively.

Pyrometry errors may be estimated as follows: setting and calibration errors on the instrument, ±10°C; window transmission uncertainty, ±20°C; and error in the temperature drop across the reaction container wall, ±10°C.

Results

The solubility of C in Si as a function of temperature is given in Fig. 2. Some curvature may be noted at concentrations of five atom percent and more, presumably because the solution is nonideal. We find the solubility to be about 1/5 of that reported by Hall. Recent experiments by J. H. Racette of this laboratory, in a fused quartz apparatus similar to that used by Hall, indicate that this discrepancy was most likely due to the presence of sufficient oxygen in the melt in Hall's experiment to remove much of the dissolved carbon as CO or CO₂. The oxygen presumably came from the quartz (SiO₂). In that case the carbon solubility would have appeared to be too high because the SiC crystal placed in the melt continuously lost carbon. Racette's


7 J. H. Racette (private communication).
experiments show an apparent increase in solubility as the duration of the experiment is increased.

The linear portion of the curve below 1A% carbon has a slope corresponding to an enthalpy of solution of 59 kcal/mole, as calculated from the expression

$$x = \exp\left(\frac{\Delta H}{R}\left[\frac{1}{T} - \frac{1}{T_m}\right]\right).$$  \hspace{1cm} (1)

In this equation, $x$ is the fractional atomic concentration of carbon in silicon at temperature $T$, $\Delta H$ is the enthalpy of solution, $R$ is the gas constant per mole, and $T_m$ is the temperature intercept at unit carbon fraction obtained by extrapolation of the linear portion of the solubility curve. Depending on how the line is drawn through the data points, $\Delta H$ may vary ±3 kcal/mole.

In the course of these experiments it seemed worthwhile to explore as much of the phase diagram of the system Si-C as was accessible. Attempts were made to melt SiC in graphite containers similar to those used for the solubility experiments. The ambient pressure was well in excess of the decomposition pressure in all experiments. A transformation of some originally light green, type 6H, hexagonal, 120-mesh, SiC grain to a markedly different structure occurred at temperatures of 2830±40°C and above. The SiC found after the transformation was cubic, as analyzed by x-rays. Heating to lower temperatures resulted only in a sintering together of the grains without any gross structural change. This experiment was repeated with cubic SiC grain as the initial charge. It decomposed at the same temperature, and the SiC found after the transformation was also cubic. From this, and from evidence gained from other experiments with SiC at elevated temperatures, we conclude that SiC decomposes without congruent melting, resulting in a silicon-rich liquid in equilibrium with graphite at temperatures from 2830°C to at least 3160°C. The liquid composition at this latter temperature is approximately 50 atom percent carbon. When the liquid resulting from the decomposition of SiC is cooled below the decomposition temperature, the Si reacts with the dissolved and suspended carbon to form the cubic SiC found by x-ray analysis.

Experiments have also been performed in which cubic SiC grains have been heated in graphite tubes in this furnace to temperatures slightly below 2830°C. At the end of a run lasting several minutes the original cubic SiC is still present although slightly sintered together. Other experiments have been conducted in this apparatus in which both cubic and hexagonal crystals of SiC have been grown side by side from the vapor phase at temperatures of 2600°C. These growing experiments lasted several hours. It is therefore concluded that cubic SiC is stable at these temperatures and does not readily transform into hexagonal SiC in contrast to the conclusions of Baumann. However, it should be noted that the conditions in the present experiments are not the same as those found in commercial SiC furnaces.

Difficulty was encountered in attempting to extend the solubility measurements above 3000°C. Even the high-density graphite containers would not hold liquid silicon at these temperatures. Furthermore the interpretation of the chemical analysis became difficult because the sample after cooling to room temperature usually contained silicon carbide, silicon, and carbon in a carbon container.

The phase diagram shown in Fig. 3 incorporates the
findings described above, the melting point of carbon given by Basset,\textsuperscript{9} and the melting point of silicon given by Pell.\textsuperscript{10} It confirms the general features of the diagrams proposed by Nowotny \textit{et al.}\textsuperscript{1} and quoted by Hansen.\textsuperscript{11} Note that in Fig. 3 the ambient pressure is assumed to be high enough that solid or liquid phases are always present. This will be at least 108 atm for pure carbon at 3730°C, since this is the vapor pressure over carbon at the triple point.\textsuperscript{9} At lower temperatures the required pressure will be less. With a pressure of 35 atm a temperature of about 3400°C can be reached.\textsuperscript{4}

\textbf{EXPERIMENTS WITH GERMANIUM}

The solubility of carbon in germanium has apparently not been previously reported. Using the furnace shown in Fig. 1, we have heated Ge in graphite containers to temperatures between 2780°C and 3170°C and have analyzed the results. The upper temperature limit of 3170°C was set by the requirement that the germanium evaporation rate be kept low with a maximum argon pressure of 55 atm. At temperatures below 2780°C the amount of carbon dissolved in the limited volume of liquid germanium was too small to measure accurately. The Ge had been previously zone refined; the containers were machined from spectroscopic graphite with a density of 1.7 g/cm\textsuperscript{3}.

The samples were recovered by cracking apart the graphite containers. The germanium did not adhere to the graphite, and was in the form of a shiny slug. After weighing, the slug was etched in a mixture of one part HF in three parts HNO\textsubscript{3}. The residue was partly precipitated graphite in the form of small flakes and partly Ge. Apparently the etch was unable to leach all the Ge from the graphite flakes because of the hydrophobic nature of graphite. The residue was therefore roasted in Cl\textsubscript{2} at 1000°C in a quartz crucible to remove the Ge by the formation of volatile GeCl\textsubscript{4}. After the remainder of the residue was weighed, it was then burned in O\textsubscript{2} at 1000°C to form CO\textsubscript{2}. No evidence of GeO or GeO\textsubscript{2} was found after the oxidation, indicating that the residual Ge had indeed been removed from the graphite.

The results are shown in Fig. 4. If the solubility line were extrapolated to the melting point of Ge, the concentration of C in the liquid would be about 10\textsuperscript{8} atoms per cm\textsuperscript{3}. This is probably a lower limit. The carbon-germanium system is nonideal and such an extrapolation is inaccurate. This extrapolated solubility is a factor of about 10\textsuperscript{10} less than the carbon concentration in liquid silicon at its melting point. No evidence of compound formation between carbon and germanium was found up to temperatures of 3170°C. The C—Ge phase diagram therefore appears to be quite simple, and a tentative sketch is shown in Fig. 5. A simple eutectic point probably exists very slightly below the melting point of Ge at 937°C.\textsuperscript{12} This is qualitatively similar to the C—Pb and C—Sn systems as deduced from the solubility studies of C in Pb and in Sn at temperatures up to 2300°C.\textsuperscript{13}

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