EVAPORATION AND THERMODYNAMIC PROPERTIES OF SILICON NITRIDE

È. A. Ryklis, A. S. Bolgar, and V. V. Fesenko

Owing to its high chemical stability, excellent high-temperature strength, and semiconductive properties, silicon nitride is used in high-temperature refractories, thermocouple mountings, and various thermistors [1]. Considerable promise attaches to the use of Si₃N₄ by itself, or alloyed with BN [2] or Al₂O₃ [3], as electric insulation materials.

However, little work has been done on the thermodynamic properties of this compound and its behavior in vacuum. Wolf and Alcock [4] studied the evaporation of silicon nitride by the Langmuir method in a vacuum of 10⁻⁴-10⁻⁵ mm Hg at 1000-1500°C with continuous weighing. Disk-shaped specimens of diameter 6 or 3 cm were heated in a resistance furnace. Owing to marked oxidation, Wolf and Alcock [4] did not obtain reliable results. Pehlke and Elliot [5] studied (by the manometric method) equilibrium in the system nitrogen - silicon - silicon nitride in the range 1150-2000 K (the silicon nitride contained 60.01 wt.% Si and 39.94 wt.% N₂). The nitrogen pressures above Si₃N₄, calculated from data of these authors, differed by one to three orders.

We studied the evaporation of silicon nitride obtained by nitriding single-crystal silicon powder in a current of very pure nitrogen at 1723 K; this nitride contained 40.0 wt.% nitrogen and 59.9 wt.% silicon. Owing to the high purities of the initial substances, the impurity contents were not determined.*

The vapor above Si₃N₄ was subjected to mass-spectrometric analysis in an MI-1305 apparatus. The specimens were evaporated from the surface of a tungsten ribbon, heated by passing a current. The experimental procedure is described in detail in [6].† At ionizing electron energies of 24-30 eV, the spectra of the masses obtained in the range 1363-1945 K exhibited only ion peaks of 28 atomic mass units. The recorded peak may be due to either N⁺ or Si⁺ ions. However, the fact that the appearance potential determined from the ionizing efficiency curves (Fig. 1) is equal to the ionization potential of N⁺ indicates that this peak corresponds predominantly to the N⁺ ion. This is partly confirmed by the fact that the ion current intensity remained unchanged when the molecular beam was intercepted by a screen. Evaporation of Si₃N₄ was studied by an integral version of the Knudsen effusion method and by the Langmuir method in a continuous-weighing apparatus [7] in the range 1688-1773 K.

The silicon nitride powder was placed in a molybdenum effusion cell of diameter 12 mm and height 8 mm, placed in a graphite chamber suspended on tungsten wire from the balance arm. We used molybdenum diaphragms with different effusion orifices. Their parameters are given in Table 1.

*We are grateful to M. D. Lyutaya for providing the specimens and analyzing the silicon nitride.

†The mass-spectrometric analysis was performed by S. P. Gordenko and B. F. Fenochkaya.

<table>
<thead>
<tr>
<th>TABLE 1. Effusion Orifice Parameters (d, Orifice Diameter; k, Clausius Coefficient; S, Orifice Area, cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d, cm</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>0.0594</td>
</tr>
<tr>
<td>0.0628</td>
</tr>
<tr>
<td>0.0443</td>
</tr>
</tbody>
</table>

Fig. 1. Ionization efficiency curves of $N_2^+$ and Hg$^+$.  
Fig. 2. Determination of equilibrium values of nitrogen pressures above Si$_3$N$_4$ at 1) 1688, 2) 1710, 3) 1743, 4) 1773°K.

In the case of the Langmuir method the nitride powder was strewn in a molybdenum vessel of height 12 mm and internal diameter 7.7 mm until one third full. The decrease in weight of the specimens due to evaporation was determined by a vacuum electromagnetic balance and recorded automatically by an electron potentiometer. The temperature was measured to within 0.8% by an OMP-043 optical micropyrometer in a pocket in a chamber simulating a black body. The substance was heated by a high-temperature resistance furnace with a graphite heater at a working vacuum of $5 \times 10^{-6}$ mm Hg.

Preliminary experiments revealed that prolonged residence leads to an insignificant decrease in the rate of evaporation of silicon nitride with time at constant temperature. This is also indicated by temperature dependences of the ion-current intensity of $N_2^+$ obtained by a successive series of mass-spectrometric measurements. However, this process is less marked for Si$_3$N$_4$ than for germanium nitride [8]. Note that mixing of the powder in the effusion cell led to restoration of the initial rate of evaporation of the nitride.

After heating in vacuum, the residual powder was subjected to x-ray and chemical analyses, which revealed that it contained nitride and free silicon.

From the mass-spectrometric measurements and x-ray and chemical analyses, we can infer that silicon nitride dissociates as follows:

$$\text{Si}_3\text{N}_4 (\text{sol}) = 3\text{Si} (\text{sol, liq}) + 2\text{N}_2. \quad (1)$$

The observed vapor pressures were calculated by the Hertz-Knudsen formula. An assessment of the experimental errors reveals that the error in the determination of the vapor pressure did not exceed 15%. Table 2 gives the experimental and calculated values.

The effusion experiments revealed that the rate of evaporation of silicon nitride depends on the area of the efflux orifice; therefore the process is not equilibrial and the evaporation coefficient of Si$_3$N$_4$ less than unity. The equilibrium pressures of nitrogen above these compounds were determined by graphical extrapolation of the data to a zero orifice in accordance with the Motzfeldt equation [9]. The results are given in Fig. 2 (each point is the average of four to five measurements). The equilibrium pressures of nitrogen are given in Table 3.

We then calculated by the Clausius-Clapeyron equation the heat of formation of silicon nitride at the average experimental temperature 1740°K; it was 208 ± 4 kcal/mole.