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THE KINETIC ENERGY OF MOLECULES THAT TRAVERSE  
AN EXCESS ENERGY BARRIER DURING SUBLIMATION

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Raymond W. Mar and Alan W. Searcy

Inorganic Materials Research Division, Lawrence Radiation Laboratory,  
Department of Mineral Technology, College of Engineering,  
University of California, Berkeley, California

ABSTRACT

The flux of molecules that evaporate from a free surface of gallium nitride in vacuo and the corresponding force imposed on the surface were independently measured by the Langmuir and torsion-Langmuir methods. Comparison of the results shows that the kinetic energy of the escaping vapor molecules is that expected for equilibrium with the surface. For gallium nitride, therefore, it is proved that vapor molecules that evaporate by crossing an energy barrier higher than the equilibrium energy of sublimation are not at a higher average temperature than the surface from which they evaporate.

## INTRODUCTION

Condensation under non-equilibrium conditions is often discussed in terms of a schematic plot of potential energy of interaction versus reaction coordinate. Molecules that condense are presumed to possess initial energies equal to or greater than a critical value  $E_C^*$  while molecules with lower energies are reflected.

If free evaporation occurs by traversal of the same barrier in the opposite direction, as must be true under equilibrium conditions, molecules would have to acquire an energy equal to or greater than the sum of the equilibrium energy change for sublimation and of  $E_C^*$ . Molecules would then leave the surface with an average energy  $E_C^*$  in excess of the average energy of molecules that are in thermal equilibrium with the surface. It has been suggested that molecules that evaporate over a barrier of the kind hypothesized may, in effect, have an apparent temperature greater than the surface temperature.<sup>1</sup> Apparently, no experiments have been performed to test this hypothesis. The studies of Kusch et al.<sup>2</sup> for example, demonstrate that the vapor which escapes from the surface of sodium chloride has a Maxwellian energy distribution, but do not address the question at hand; sodium chloride vaporization is impeded by a transmission barrier rather than by an excess energy barrier.

It was the purpose of the present study to obtain the apparent temperature of gallium nitride vapor for comparison with the measured surface temperature by means of simultaneous measurements of the flux of molecules leaving the surface and the pressure which these molecules impart to the surface. The molecular flux is related to the total pressure  $P_T$  through the Hertz-Langmuir equation:

$$P_T = \sum P_i = \sum Z_i (2\pi M_i RT)^{1/2}$$

where  $P_i$  is the partial pressure of species  $i$ ,  $Z_i$  is the number of moles of species  $i$  leaving the surface per unit time per unit area,  $M_i$  is the molecular weight of species  $i$ ,  $R$  is the gas constant, and  $T$  is the temperature of the surface.

The torsion-Langmuir technique<sup>3-5</sup> provides an independent means for calculation of  $P_T$  from the expression:

$$P_T = \frac{2\theta D}{\sum q_j a_j}$$

where  $q_j$  is the horizontal distance from the center of an evaporating surface  $j$  to the center of support,  $a_j$  is the area of surface  $j$ ,  $\theta$  is the angle of twist imparted to a supporting fiber, and  $D$  is the torsion constant of the fiber. Implicit in the usual interpretations of pressures by this technique is the assumption that the escaping vapor is at the temperature of the surface. If the gas temperature were actually higher than the surface temperature, a higher pressure would be calculated than calculated by application of the Hertz-Langmuir equation to the mass flow, and substitution of the pressure measured by the torsion-Langmuir method into the Hertz-Langmuir equation would allow calculation of the temperature that characterizes the translational modes of the vaporizing molecules.

Gallium nitride was selected for study because it is one of very few substances which have been demonstrated to have high apparent enthalpies of activation. Munir and Searcy<sup>4</sup> reported the apparent heat of activation for free surface sublimation by the reaction  $2\text{GaN}(s) \rightarrow 2\text{Ga}(g) + \text{N}_2(g)$  to be  $\Delta H_{1300}^* = 219$  kcal, compared to  $\Delta H_{1300}^0 = 173$  kcal for the equilibrium reaction. If a significant fraction of the excess enthalpy of 46 kcal

were carried off as translational excitation of the vaporizing species the excess kinetic energy should be readily measurable.

The evaporation of significant concentrations of gaseous gallium nitride molecules from free surfaces of gallium nitride, which has been reported,<sup>6</sup> could obscure the significance of the measurements, but a recent mass spectrometer study has not confirmed the presence of significant concentrations of these molecules.<sup>7</sup> The latter study, which was made with surfaces prepared in the same manner as those used in this study, confirms dissociation to the elements as the only significant free surface sublimation reaction.

#### EXPERIMENTAL

Gallium nitride powder was purchased from Research Inorganic Chemical Co. The powder was yellow, which suggests an oxygen content of the order of 1%.<sup>7</sup> Munir and Searcy have shown that oxygen should not concentrate at the surface of gallium nitride during sublimation.<sup>4</sup> Wafers about 0.75 cm in diameter and 0.02 to 0.06 cm thick were formed by cold pressing to  $1.5 \times 10^6$  psi. A description of the pressing equipment and procedures has already been given.<sup>4</sup> The wafers were gray and metallic in appearance. Those that had cracks or that appeared under microscopic examination to be inhomogeneous were discarded.

The experimental techniques, apparatus, and graphite cell used to obtain torsion-Langmuir pressures have been described in an earlier publication.<sup>5</sup> In this study temperatures were read by means of an optical pyrometer focused on a black body hole in the bottom of the cell.

Prior to each run, the assembly was outgassed by slowly heating to

1000°K and holding until the background pressure dropped below  $7 \times 10^{-9}$  atm. The furnace voltage was then increased to a predetermined value and held there for the duration of the run. The background pressure remained below  $7 \times 10^{-9}$  atm during a run. Runs of 800 to 2500 seconds duration were made at constant temperatures in the range 1225° to 1335°K.

Once the constant temperature had been established, angular deflections from which torulon-Langmuir pressures could be calculated were recorded at approximately ten minute intervals. The weight losses from which Langmuir pressures could be calculated were obtained in three ways: 1) from the assembly weight loss minus the weight loss of the cell and parts; 2) from the GaN wafer weight loss, and 3) from the difference in weight loss between the sample cell and an identical dummy cell which was subjected to an identical heating schedule for each run.

It took approximately 2 to 3 minutes for the temperature to increase and stabilize to within  $\pm 2^\circ$  from the time at the end of the outgassing. The total weight loss incurred during the heating and cooling periods has been estimated to be less by at least three orders of magnitude than the weight loss sustained during the steady state run, so end effects were neglected.

Because leakage in random directions through the cell walls might significantly increase the mass flow from the wafers, while having a lesser effect on the torque, samples were heated in a cell which had no orifices. These wafers showed negligible losses in weight.

Dimensions and correction factors<sup>8,9</sup> for the orifices which were used to define the area of surface from which sublimation occurred are presented in Table I. The condensation coefficient of gallium nitride is so low that the probability is negligible that a molecule which has once evaporated will be reincorporated into the surface even if collisions



with the orifice cause it to return. An effective Clausing factor of unity must apply to the mass flow equation.

On the other hand, the force correction factor is not unity since the distribution of molecules that escape through the orifice will be distorted and non-cosine. A close approximation to the correction for the effect of the channel on the force exerted by the escaping molecules should be the ratio of the normal Clausing correction factor to the normal force of effusion correction factor for an equilibrium vapor. This correction neglects the fact that the molecules that are returned to the gallium nitride surface at least once after collision with the walls of the orifice may not strike with uniform radial distribution. As a consequence, their angular distribution on re-evaporation may be slightly different from that assumed in our approximation. The error in calculated force must be negligible for orifices such as those used here which return only about 20% of the vapor molecules to the sample surface as a result of orifice wall collisions.

#### RESULTS AND DISCUSSION

The weight loss pressures are presented in Table II where it is seen that values obtained by the three methods are in good agreement. Torsion-Langmuir pressures are compared with the averaged weight loss pressures in Fig. 1. These averages were usually slightly higher than the torsion-Langmuir pressures, but agreed within the probable reliability of the data.

Pressures measured in this work were many orders of magnitude below the calculated equilibrium pressures, but were consistently higher by an order of magnitude than those measured by Munir and Searcy<sup>4</sup> in a similar apparatus and with samples prepared in the same manner. The difference

is not the result of differences in measurements, since the equilibrium pressures of tin measured in the two apparatuses were in satisfactory agreement.

The kinetics of surface reactions can be, of course, strongly influenced by small changes in concentration of surface impurities. And, in particular, Blank and Searcy<sup>10</sup> have shown that the free surface sublimation rate of magnesium nitride is depressed by background pressures of nitrogen or argon gas which are comparable to the measured sublimation pressures. The nominal background pressure in the apparatus of this research was about an order of magnitude lower than that in the research of Munir and Searcy.<sup>4</sup> Probably the higher sublimation rate in the present study results from a decreased concentration of impurities on the sample surface.

The rates of sublimation tended to increase with time as indicated by the torsion-Langmuir data of Fig. 1. The changes in pressures ranged from negligible amounts to as much as 20% for two of the runs. Two additional runs for which results are not included in Table II or Fig. 1 showed more rapid increases in torsion-Langmuir pressures, by a factor of 1.4 in 400 sec and by a factor of 5 in 2700 seconds. Examination of the surfaces revealed that both samples were cracked. The increases in surface area due to the cracks were not alone great enough to cause the measured increases in pressure. But the cracks may have become regions of concentration of free gallium, or at least of gallium-rich gallium nitride. Munir and Searcy<sup>4</sup> noticed evidence of a change in composition around cracks after free surface sublimation. Schoonmaker et al.<sup>11</sup> report that gallium catalyzed gallium nitride sublimation.

The lesser increases in pressure with time shown by some of the runs may reflect simply small increases in effective area with time as the surface roughened and receded from the orifice or may reflect the influence of small changes in composition on the sublimation rate.

The estimated systematic error in determination of the ratio of the Hertz-Langmuir pressures to the apparent total torsion-Langmuir pressures is 10% for the six runs made with crack-free samples. The average ratio measured experimentally is  $1.100 \pm .036$  where  $.036$  is the standard deviation from the mean.

The apparent vapor temperature is the same as the measured sample temperature to within the estimated errors, and the direction of the small deviation is opposite to that which would result from excess kinetic energy in the vapor. By contrast, if the 46 kcal excess enthalpy of activation reported by Munir and Searcy were equilibrated among rotational, vibrational, and translational modes of the vapor molecules, the apparent temperature of the vapor would exceed the surface temperature by more than  $3000^\circ$  and the pressure ratio would be many orders of magnitude less than unity.

We conclude that no significant fraction of the excess enthalpy can be accounted for as excess translational energy of the vaporizing species. The excess energy must either be dissipated to the solid or must be present as unequilibrated internal energy of excitation of one or both of the vaporizing species. We plan to attempt to test the second possibility by comparing the appearance potentials of gallium and nitrogen beams from free surface sublimation with those from equilibrium vapor.

We cannot conclude, of course, that because gallium nitride vapor does not show excess kinetic energy upon free surface sublimation that no materials will do so. The experimental method illustrated here should be applied to other suitable materials. We believe, however, that while substances which evaporate over an excess enthalpy barrier may have excess internal energy, they will not have excess kinetic energy at least until a subsequent process, such as a collision, causes equilibration.

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Table I. Graphite cell dimensions

Orifice	radius cm	Channel length cm	correction factor		
			normal	applic- able to this study.	
A	.1529	.1090	torsion -	.798	1.1076
			wt. loss-	.7418	1.0
B	.1521	.1141	torsion -	.7879	1.1078
			wt.loss -	.7318	1.0

Table II. Weight loss pressures.

Run	Temp. °K	Duration sec	P <sub>I</sub>	P <sub>II</sub>	P <sub>III</sub>	torsion pressure
1	1334	803	(2.33)10 <sup>-5</sup>	(2.06)10 <sup>-5</sup>	(2.36)10 <sup>-5</sup>	(2.05)10 <sup>-5</sup>
2	1276	1178	(3.96)10 <sup>-6</sup>	(4.64)10 <sup>-6</sup>	(3.98)10 <sup>-6</sup>	(3.40)10 <sup>-6</sup>
3	1310	1140	(1.15)10 <sup>-5</sup>	(1.14)10 <sup>-5</sup>	(1.15)10 <sup>-5</sup>	(9.38)10 <sup>-6</sup>
4	1299	1560	(1.11)10 <sup>-5</sup>	(1.20)10 <sup>-5</sup>	(1.10)10 <sup>-5</sup>	(1.03)10 <sup>-5</sup>
5	1251	2445	(4.39)10 <sup>-6</sup>	(4.60)10 <sup>-6</sup>	(4.34)10 <sup>-6</sup>	(4.13)10 <sup>-6</sup>
6	1260	2400	(2.29)10 <sup>-6</sup>	(2.52)10 <sup>-6</sup>	(2.21)10 <sup>-6</sup>	(2.47)10 <sup>-6</sup>

P<sub>I</sub> = Pressure calculation from wafer weight loss

P<sub>II</sub> = Pressure calculation from total weight loss--dummy cell at loss

P<sub>III</sub> = Pressure calculation from total weight loss--experimental cell at loss

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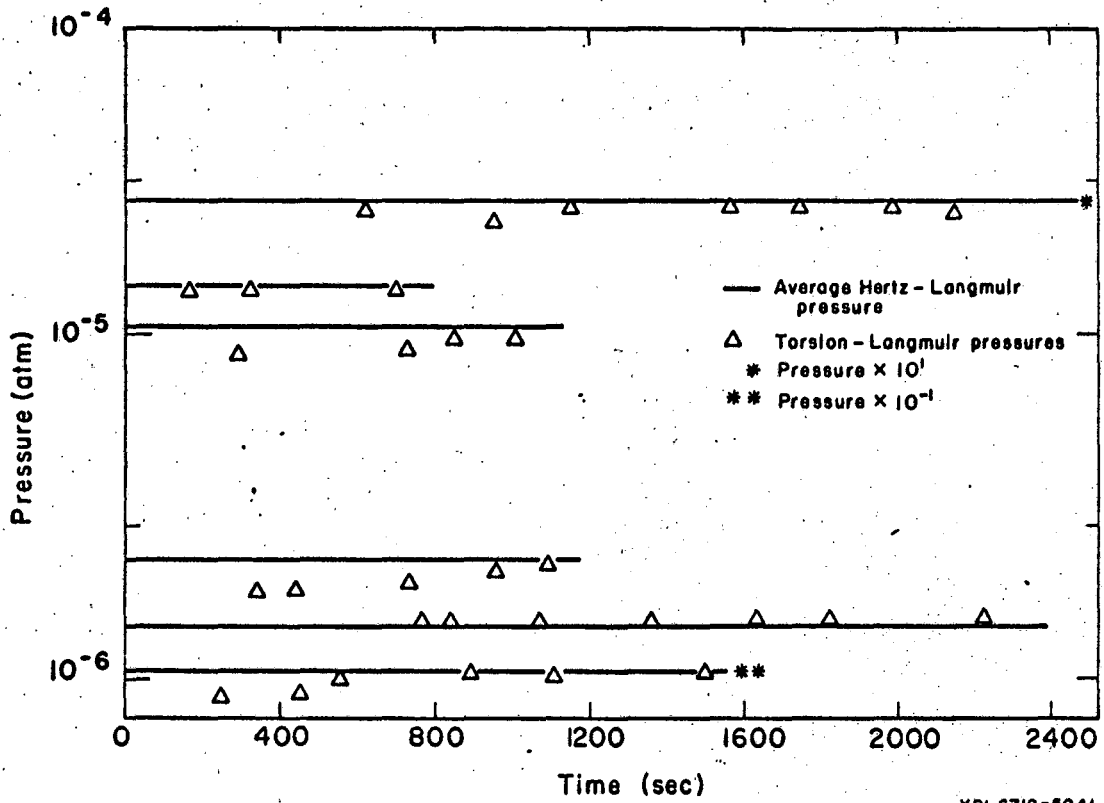


Fig. 1 Comparison of average Hertz-Langmuir pressures with torsion-Langmuir pressures.



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