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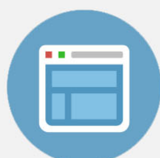
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Kinetics of the reaction of gallium arsenide with molecular chlorine

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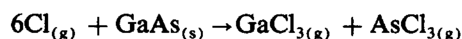
The reaction of Cl_2 with the (100) face of a GaAs single crystal was studied in the temperature range from 25 to 150 °C. The reaction was found to be first order in Cl_2 at low pressures with an activation energy of 23.6 kcal. At pressures above 10 Torr it was found to reach a limiting rate with an activation energy of 14.2 kcal, attributable to the enthalpy of desorption of the $GaCl_3$ product from this surface.

INTRODUCTION

The increasing use of gallium arsenide for monolithic microwave integrated circuits and optoelectronic devices has created an interest in etching techniques for this material.[1,2] For greater automation, increased processing speed, and smaller features dry processing techniques are found to be superior. Hence there have been many attempts to develop new gas phase etching processes.[3–11] In all these techniques it is assumed that the dominant etchant is the chlorine atom produced by the dissociation of a halogen containing precursor. Since the rate constant for the following reaction:



$$6Cl_{(g)} + GaAs_{(s)} \rightarrow GaCl_{3(g)} + AsCl_{3(g)}$$

has not been reported we attempted to measure its value directly by producing chlorine atoms in a microwave discharge in Cl_2 and observing the etch rate downstream from the discharge where the absolute chlorine–atom concentration could be measured.[12] In the course of this investigation[13] we observed that once the inhibiting oxide layer was removed from the gallium arsenide wafer the etching proceeded with an only slightly diminished rate when the discharge which was dissociating the Cl_2 was shut off, i.e., we observed that under certain conditions the etching by Cl_2 was not very much slower than the rate observed when chlorine atoms were present. It was clear that the characteristics of the Cl_2 reaction in this pressure range would have to be established before the chlorine–atom reaction rates were determined.

There have been very few studies of the Cl_2/GaAs interaction. A thermodynamic calculation by McNevin in 1986[14] led her to predict that in the temperature range from 50 to 180 °C the etch rate would be a constant 670 μ min^{-1} at 0.3 Torr of Cl_2. The calculation was based on an assumed constant Cl_2 sticking coefficient of 1 in this temperature range. However, in a molecular beam study of this interaction Balooch *et al.*[15] found that the reaction probability for Cl_2 on GaAs rose from 0.002 at 25 °C to a maximum of 0.5 at 427 °C. In contrast to these observations, Sugata and Asakawa[16] reported no etching of GaAs by Cl_2 (i.e., < 1 Å min^{-1}) at temperatures below 290 °C with a very abrupt rise in the etch rate to 0.2 μ min^{-1} at 330 °C with 2 mTorr of Cl_2. In view of these divergent results there is a need for a more thorough examination of the Cl_2/GaAs reaction as a function of pressure and temperature. In this paper we describe observations made in the temperature range from 25 to 150 °C and pressures from 0.09 to 20 Torr of Cl_2.

EXPERIMENTAL

1 cm^2 chips cut from 3 in. undoped gallium arsenide wafers were etched in a Pyrex reaction tube that could be heated externally between room temperature and 300 °C. The wafers, obtained from Cominco in Trail, British Columbia, Canada were cut and polished to expose the 100 faces of the crystals. These faces were covered with silicon nitride stripes 10 to 50 μ wide and 10 to 50 μ apart, with the stripes running in both the $\langle 0\bar{1}\bar{1} \rangle$ and $\langle 01\bar{1} \rangle$ direction. The chips being etched were pressed with glass springs against a polished silicon heat sink in which a thermocouple was embedded. Prior to insertion in the flow system the sample was washed with dilute HCl to remove the "native" oxide layer. Care was taken to keep the sample under an inert gas until it was introduced into the vacuum system. The thick growth of an oxide layer by exposure to air, especially if the sample is warm, was found to completely inhibit the etching reaction with Cl_2 although the layer could be penetrated by Cl atoms.

The Cl_2 was pumped over the GaAs wafer at a flow rate that exceeded the reaction rate by at least a factor of 50 so that the Cl_2 was not significantly diluted by the gaseous products. The gas was pumped cryostatically with a liquid nitrogen trap backed by a rotary pump. The flow and pressure were separately controllable with needle valves before the reaction chamber and a variable pinhole after the chamber.

The etch rate could be determined by three independent techniques. A pinhole leading to an E.A.I. model 1100 quadrupole mass spectrometer was placed immediately downstream from the wafer chip being etched. The signal from $GaCl_3$ was found to be too small to measure quantitatively, but the $AsCl_3$ could be monitored quantitatively at mass 181. The vapor pressure above a sample of pure $AsCl_3$ was used to calibrate the mass spectrometer. A second procedure used to determine the etch rate was profilometry. A sample covered with the silicon nitride mask described above was exposed to a fixed Cl_2 pressure for a known length of time and then the etch depth on the wafer chip was measured relative to the mask height with a Tencor profilometer. This method provided the most direct measurement of the etch rate. However, it was susceptible to error if the etch rate was not constant or if there was a significant induction period before the etching began. A method of continuously monitoring the etch rate was provided by laser interferometry. A 0.5 mw HeNe cw laser beam was reflected off the wafer surface on to a photomultiplier. Interference between the 633

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nm radiation reflected from the stationary masked surface and that reflected from the "etching" surface produced a sinusoidal intensity as a function of time. Because the etch rate was faster in the irradiated spot than on the dark portions of the wafer, interferometry was simply used to determine that there was no initiation period and that the etch rate was constant over the period in which the profilometry was used to determine the etch rate. The laser enhancement will be discussed elsewhere.[13]

RESULTS AND DISCUSSION

Our preliminary experiments with the Cl_2/GaAs reaction provided some unanticipated observations. First, great care had to be taken to ensure that the native oxide layer was removed from the wafer surface, and did not reform because of exposure to air. Otherwise, the etching reaction did not occur until the layer was penetrated by Cl atoms or by raising the sample temperature very high. Perhaps a similar surface contamination prevented Sugata *et al.*[16] from observing any etching below 290 °C.

In all our experiments in the temperature range from 75 to 150 °C the surface morphology after etching was rough, with a surface variation of about 2% to 3% of the etch depth. Etching at temperatures above 160 °C produced shiny surfaces but no great change in the percent surface height variation given above. Donnelly *et al.*[5] reported a change from rough to smooth at ~125 °C in a Cl_2 plasma. It is not clear how they judged the surface morphology.

Novel behavior was observed at temperatures below 70 °C when the Cl_2 pressure was greater than 15 Torr. This new phenomenon is illustrated in Fig. 1 where the profile of the etched (100) GaAs surface between two silicon nitride stripes is shown. It can be seen that the etch rate near the stripes is very much greater than it is in the middle of the exposed GaAs area. The etch rate in the middle is consistent with the values obtained at slightly higher temperatures. The etch depth near the edge is anomalously large. The explanation of this accelerated rate became obvious when experiments were performed at 25 °C and 20 Torr of Cl_2. Under these conditions the GaAs was quickly covered with a liquid layer which grew in extent with time until it covered the entire sample. When the liquid was washed away with acetone the etched surface was found to be more irregular than it was in the absence of the liquid layer, and to have been etched an order of magnitude faster than would be expected from measurements at temperatures above 70 °C. It is obvious from these observations that the profile illustrated in Fig. 1 is a result of the accumulation of this "liquid" in the "corners" next to the silicon nitride mask, and the consequent more rapid etch rate under the liquid. The mixture of $AsCl_3$, $GaCl_3$, and Cl_2 has been shown[17] to produce a compound with the formula $GaAsCl_8$ and the structure $AsCl_4^+ GaCl_4^-$ with a melting point of 5 °C. It is quite-probable that this is the identity of the liquid which gathers on the GaAs surface. Since an $AsCl_{3(l)} + Cl_{2(g)}$ mixture is known to be a very good chlorinating agent,[18] it could account for the accelerated etch rate which occurs under the liquid.

The first series of quantitative experiments were performed at 91 °C to determine the order of the reaction with respect to Cl_2. The results are shown in Fig. 2 which gives the etch rate as a function of the chlorine pressure. The reaction clearly displays a saturation effect, i.e., the rate increases with increasing Cl_2 pressure at low pressures, but becomes independent of Cl_2 above 10 Torr. Such behavior is characteristic of a two step reaction in which the first step has a Cl_2 dependence and the second does not. The most general formulation of such a two step mechanism is given by Eqs. (1) and (2),

$$S_f + Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S_c, \quad (1)$$

$$S_c \xrightarrow{k_2} S_f + \text{product}, \quad (2)$$

where S_f represents a free surface site which can react with Cl_2 to produce a surface–bound intermediate S_c where the subscript c is used to indicate that the site is covered and

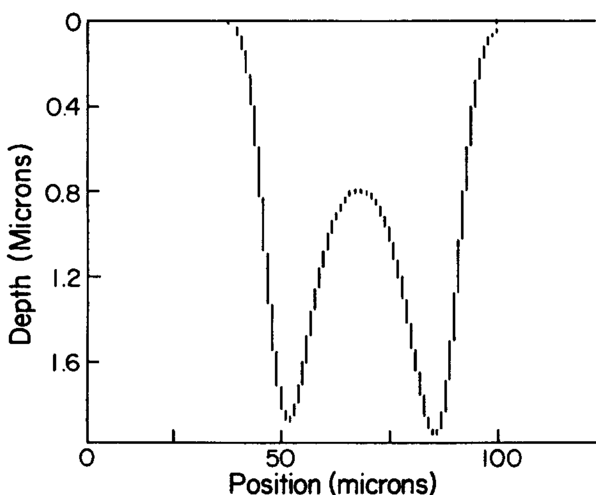

FIG. 1. Profile of etched (100) GaAs surface between two silicon nitride masked areas. $T = 66$ °C, $P_{Cl_2} = 15.5$ Torr. Flow = 50 times etch rate.

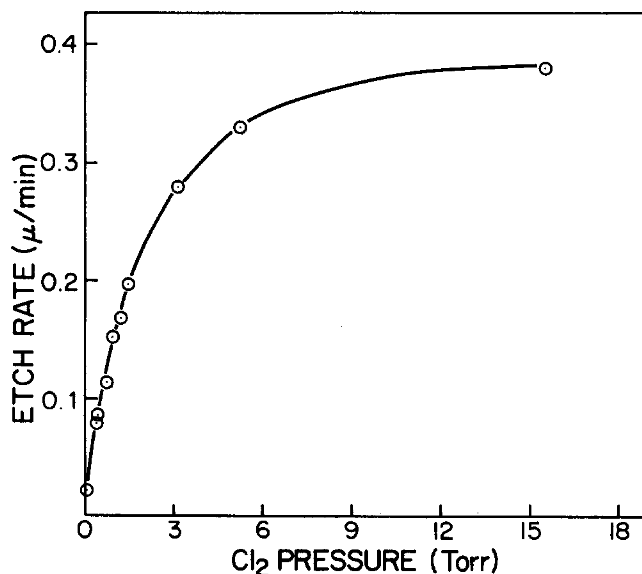

FIG. 2. The etch rate of (100) GaAs by Cl_2 as a function of the pressure of Cl_2 at 91 °C.

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hence cannot react with Cl_2 until a product molecule is desorbed to reexpose S_f. Under these circumstances $S_c + S_f = S_0$, where S_0 is the total number of surface sites available for reaction, and the rate law governing the steady state etch rate (ER) of such a surface is given by Eq. (3):

$$\mathrm{ER} = \frac{[k_1/(k_{-1}+k_2)]P_{Cl_2}}{[k_1/(k_{-1}+k_2)]P_{Cl_2}+1} k_2. \quad (3)$$

To simplify the expression we write the rate constant ratio $k_1/(k_{-1}+k_2) = K_{ss}$, a constant governing the steady state concentration of the intermediate S_c. Equation (3) becomes

$$\mathrm{ER} = \frac{K_{ss}P_{Cl_2}}{K_{ss}P_{Cl_2}+1} k_2 \quad (4)$$

or in its "straight line" form

$$\frac{1}{\mathrm{ER}} = \frac{1}{k_2} + \frac{1}{K_{ss}k_2}\frac{1}{P_{Cl_2}} \quad (5)$$

which predicts that a plot of 1/ER vs $1/P_{Cl_2}$ should be a straight line with slope $= 1/K_{ss}k_2$ and intercept $1/k_2$. Such a plot is presented in Fig. 3 for the data obtained at 91 °C. The values of k_2 and $K_{ss}k_2$ extracted from the straight line are listed in Table I together with the values obtained at several other temperatures from similar data. To determine the activation energies for k_2 and $K_{ss}k_2$ these constants were assumed to fit the Arrhenius equation ($AE^{-E^*/RT}$). The Arrhenius plots for these two constants are given in Fig. 4. Within experimental error the plots are linear and the straight lines yield the following values for k_2 and $K_{ss}k_2$:

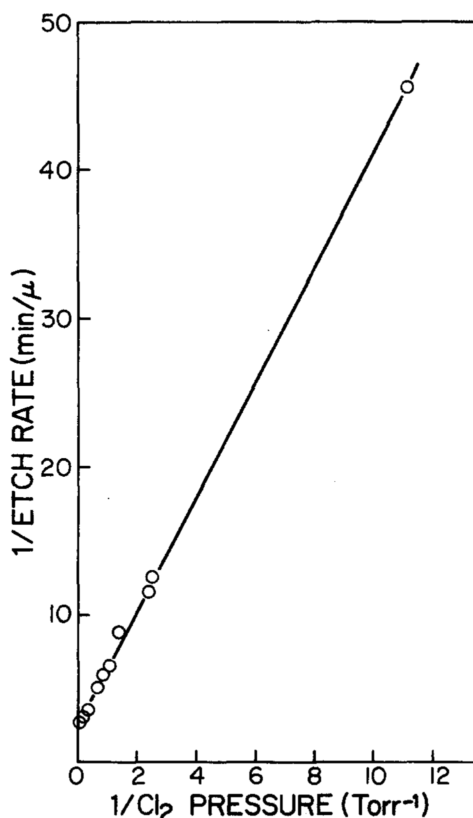

FIG. 3. A plot of the reciprocal GaAs etch rate vs the reciprocal pressure of Cl_2 at 91 °C.

TABLE I. Experimental values of k_2 and $K_{ss}k_2$ obtained at several temperatures.

T (°C)	k_2 (μ min^{-1})	$K_{ss}k_2$ (μ min^{-1} Torr^{-1})
76	0.20(±0.01)	0.056(±0.005)
91	0.39(±0.01)	0.26(±0.03)
126	2.3 (±0.1)	4.5(±0.5)
142	5.0 (±0.3)	12.0(±1.4)

$$k_2 = 1.5\times10^8 e^{-14\,200/RT} \mu \text{ min}^{-1}, \quad (6)$$

$$K_{ss}k_2 = 3.4\times10^{13} e^{-23\,600/RT} \mu \text{ min}^{-1} \text{ Torr}^{-1}, \quad (7)$$

where E^* is in units of calories.

To assess the compatibility of the assumed mechanism with these values for A and E^* we should consider two circumstances under which K_{ss} assumes a simpler form.

Case I: $k_{-1} \gg k_2$, i.e., the concentration of the intermediate species S_c is determined principally by the equilibrium constant $K_a = k_1/k_{-1}$. The rate law then becomes reminiscent of the "Langmuir isotherm"[19] and would be expected to prevail when Cl_2 is relatively weakly bound to S_f in step (1). Such a mechanism has been proposed for the etching of silicon[20] and germanium[21] by bromine. The basic requirement of a mechanism of this form is that the activation energy of $K_{ss}k_2$ (now $K_a k_2$) be *lower* than that for k_2 by an amount equal to the enthalpy of adsorption of Cl_2 on the surface as represented by step (1) in the mechanism. For the Cl_2/GaAs reaction this mechanism clearly fails the test since $K_a k_2$ has an activation energy 9.4 kcal *higher* than k_2.

Case II: $k_{-1} \ll k_2$, i.e., the backreaction in step (1) does not occur at a significant rate. The rate law then becomes

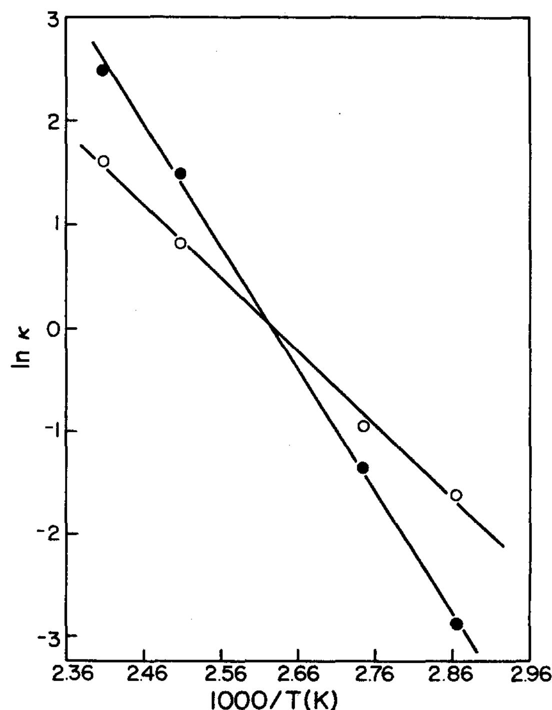

FIG. 4. An Arrhenius plot of k_2 (open circles) and $K_{ss}k_2$ (closed circles).

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$$\mathrm{ER} = \frac{k_1 P_{\mathrm{Cl}_2}}{(k_1/k_2) P_{\mathrm{Cl}_2} + 1} \quad (8)$$

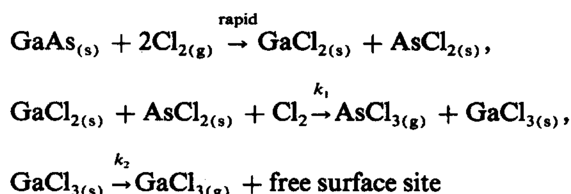
and $K_{ss} k_2$ in Table I is equal to k_1 and can thus have a value unrelated to k_2. In view of the magnitude of the activation energy for k_2 (14.2 kcal) an obvious possibility is that this reaction is the desorption of $GaCl_3$ which is the least volatile component. The heat of vaporization $GaCl_3(1)$ is 11.4 kcal mol^{-1} [14] and the heat of sublimation of $GaCl_3(s)$ is 18 kcal mol^{-1}. It is therefore not unreasonable to postulate that the heat of desorption of $GaCl_3$ from a partially chlorinated GaAs surface is 14.2 kcal mol^{-1}. Donnelly *et al.*[5] rejected this possibility because the rate of evaporation which they calculated from vapor pressure data exceeded the observed etch rate by several orders of magnitude. However, in their plasma etching experiments where both Cl atoms and molecules are present, they obtained an activation energy of 10.5 kcal for the etch rate, compared with the 14.2 kcal obtained in the present work. Moreover, they were working at a Cl_2 pressure of only 0.30 Torr and may have been below the high pressure limit where desorption is rate controlling. Converting the units of k_2 to those conventionally used for first order reactions we obtain

$$k_2 = 8.6 \times 10^9 e^{-14\,200/RT} s^{-1}. \quad (9)$$

The preexponential is very close to that obtained for the desorption of krypton from charcoal[22] and hence is consistent with a simple desorption process that has an activation energy of 14.2 kcal. This intepretation of k_2 is also consistent with the conclusions reached by Balooch *et al.*[12] in their modulated molecular beam study of the Cl_2/GaAs interaction. From their inability to detect a $GaCl_2^+$ signal at 300 K in ion-assisted Cl_2 etching while $AsCl_3$ could be detected at their modulation frequency they concluded that the formation of a $GaCl_3$ "scale" limited the etch rate. From a very small $AsCl_3$ signal at 300 K in the thermal reaction they estimated a value of $\sim 0.4\ s^{-1}$ for k_2. This is very close to the value predicted at 300 K by Eq. (9) obtained in this work.

CONCLUSION

From the magnitude of the preexponential for k we would surmise that the process described by reaction (1) is a complex one involving more than one step. It is therefore possible that the rate-controlling reaction is preceded by a step in which rapid partial chlorination occurs to satisfy the "free valences" of Ga and As without breaking the bonds holding these atoms to the surface. Such a step has been proposed by Repinski and co-workers[20,21] in their studies of the halogenation of group IV semiconductors. Although we have no direct evidence for such a process, we include it in the following complete mechanism, which is consistent with our data:



$$GaAs_{(s)} + 2Cl_{2(g)} \xrightarrow{\text{rapid}} GaCl_{2(s)} + AsCl_{2(s)},$$

$$GaCl_{2(s)} + AsCl_{2(s)} + Cl_2 \xrightarrow{k_1} AsCl_{3(g)} + GaCl_{3(s)},$$

$$GaCl_{3(s)} \xrightarrow{k_2} GaCl_{3(g)} + \text{free surface site}$$

with

$$k_1 = 3.4 \times 10^{13} e^{-(23.6 \pm 2) \times 10^3/RT} \mu\ \mathrm{min}^{-1}\ \mathrm{Torr}^{-1}$$

and

$$k_2 = 1.5 \times 10^8 e^{-(14.2 \pm 1.7) \times 10^3/RT} \mu\ \mathrm{min}^{-1}.$$

The first step is a very rapid chlorination of all "dangling bonds" on the gallium arsenide surface to form surface bonded dihalides ($AsCl_{2(s)}$ and $GaCl_{2(s)}$). The second step which is rate controlling at low pressure produces easily vaporized $AsCl_3$ and a surface bound $GaCl_3$ which covers the surface at high Cl_2 pressures, limiting the etch rate to that determined by the rate of vaporization represented by the third step in the above mechanism.

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[1] Y. Tarui, Y. Komiya, and Y. Horada, J. Electrochem. Soc. Solid State Sci. **118**, 118 (1971).
[2] R. Matz, J. Lightwane Tech, **LT-4**, 726 (1986).
[3] G. Smolinsky, R. P. Chang, and T. M. Mayer, J. Vac. Sci. Technol. **18**, 12 (1981).
[4] G. A. Lincoln, V. Efremow, and W. J. Piatcentrini, J. Vac. Sci. Technol. **19**, 1390 (1981).
[5] V. M. Donnelly, D. L. Flamm, C. W. Tu, and D. E. Ibbotson, J. Electrochem. Soc. Solid State Sci. Technol. **129**, 2533 (1982).
[6] D. E. Ibbotson, D. L. Flamm, and V. M. Donnelly, J. Appl. Phys. **54**, 5974 (1983).
[7] E. L. Hu and R. E. Howard, J. Vac. Sci. Sci. Technol. B **2**, 85 (1984).
[8] A. E. Geissberger and P. R. Clayton, J. Vac. Sci. Technol. A **3**, 863 (1985).
[9] C. I. H. Ashby and R. M. Biefield, Appl. Phys. Lett. **47**, 62 (1985).
[10] S. C. McNevin and G. E. Becker, J. Appl. Phys. **58**, 4670 (1985).
[11] M. W. Geis, N. N. Efremow, and G. A. Lincoln, J. Vac. Sci. Technol. B **4**, 315 (1986).
[12] E. A. Ogryzlo, Can. J. Chem. **39**, 2556 (1961).
[13] J. H. Ha and E. A. Ogryzlo. (to be published).
[14] S. C. McNevin, J. Vac. Sci. Technol B **4**, 1216 (1986).
[15] M. Balooch, D. R. Olander, and W. J. Siekhaus, J. Vac. Sci. Technol. B **4**, 794 (1986).
[16] S. Sugata and K. Asakawa, J. Vac. Sci. Technol. B **5**, 894 (1987).
[17] B. Demerican and W. Brockner, Z. Naturforsch. Teil A **38**, 811 (1983).
[18] *Halogen Chemistry*, edited by Victor Gutman (Academic, New York, 1967), Vol. 2, p. 154.
[19] D. F. Eggers, N. W. Gregory, G. D. Halsey, and B. S. Rabinovitch, *Physical Chemistry* (Wiley, New York, 1964), p. 733.
[20] L. L. Sveshnikova, S. M. Repinskii, and B. Posado, Surf. Phys. Chem. Mech. **8**, 134 (1982) (in Russian).
[21] V. M. Elieev, S. M. Repinski, and L. L. Sveshnikova, Inorg. Mater. **17**, 9 (1981) (translated to English).
[22] E. A. Moelwyn-Hughes, *Physical Chemistry* (Pergamon, London, 1961), p. 954.

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