



Study of Growth and Sublimation of Germanium Nitride Using the Concept of Tedmon's Kinetic Model

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<http://dx.doi.org/10.13005/ojc/360508>

(Received: May 01, 2019; Accepted: September 10, 2020)

ABSTRACT

The paper gives a mathematical model of a thermogravimetric curve for the growth of scale on a metal surface with its simultaneous sublimation is presented and considers the case of the growth-sublimation of scale being preceded by the process of gas etching of the monocrystal surface. The obtained equations are used to describe the kinetic curve of the mass change of a germanium sample when a nitride layer is formed on it in a medium of hydrazine vapors.

Keywords: Tedmon's kinetic, Germanium nitride, Growth and sublimation.

INTRODUCTION

The growth of a scale on the surface of a metal or alloy in the active gas medium is often accompanied by secondary processes limiting its kinetics. In particular, such a process is the sublimation of scale, which leads to the change of the form of the kinetic equations describing the process^{1,2}. The work³ considers the mathematical model of the kinetic dependence of the mass change of the metal (alloy)-scale system in the course of this process. This model uses the equation of the mass gain of the system per unit area (m) due to the active gas, as a starting point.

$$\frac{dm}{dt} = \frac{\frac{k_n}{n}}{m^{n-1} + \frac{k_n}{nk_r}} - v_g \quad (1)$$

Where $n=2$ or 3 ; k_n is the power-law constant; k_r is a rectilinear constant; v_g is the speed

of the system mass reduction due to the gas component of the subliming part of the scale; t is the time. Its integral form is as follows:

$$t = (1+k) \frac{m_{max}^{n-1}}{v_g} \int \frac{dm}{m_{max}^{n-1} - m^{n-1}} - \frac{m}{v_g} \quad (2)$$

Where $k=v_g/k_0$ ($k_0=k_r-v_g$); $m_{max} = (k_n/(nk_r k))^{1/(n-1)}$ is the maximum mass gain of the system at the expense of active gas. By considering expression (2), the total mass change (M) is possible to represent in a parametric form: $M=pm+q(1+k)m_{max}^{(n-1)} \int dm / (m^{n-1} - m_{max}^{n-1})$, where q is the stoichiometric coefficient of conversion of the gas component of the scale into a metallic component. At the same time, $v_m/v_g = q$ (v_m is the rate of mass reduction of the system due to the metallic component of the sublimated part of the scale); $p=q+1=(v_m+v_g)/v_g$ and the parameter is $m=M+v_m t$. For the given values of the index of power n and boundary conditions, solutions of Eq. (2) can



be represented by means of elementary functions. Thus, for $n=2, 3$ and 4 provided $t=0, m=0$

$$t = -(1+k) \frac{m_{max}}{v_g} \ln \frac{m_{max}-m}{m_{max}} - \frac{m}{v_g} \quad (3)$$

$$t = (1+k) \frac{m_{max}}{2v_g} \ln \frac{m_{max}+m}{m_{max}-m} - \frac{m}{v_g} \quad (4)$$

and

$$t = (1+k) \frac{m_{max}}{v_g} \left[\frac{1}{\sqrt{3}} \arctg \frac{\sqrt{3}m}{m+2m_{max}} - \frac{1}{6} \ln \frac{(m_{max}-m)^2}{m^2+m_{max}m+m_{max}^2} \right] - \frac{m}{v_g} \quad (5)$$

Respectively. Explicit expressions of the given type (when $k=0$) are given in a number of works to describe experimental data⁴⁻¹⁰.

In reference 3, Eqs.(3) and (4) were used to describe the thermogravimetric curves of the growth-sublimation of germanium nitride (Ge_3N_4) formed by the interaction of ammonia with the surface of Ge(111) at temperatures of 800-820°C ($3\text{Ge}+4\text{NH}_3=\text{Ge}_3\text{N}_4+6\text{H}_2$). It should be noted, however, that the process of formation-sublimation of the reaction product can be preceded by other processes, for example etching of the surface of a monocrystal¹¹. An example of this is the nitriding of same germanium in hydrazine vapors ($3\text{Ge}+4\text{N}_2\text{H}_4=\text{Ge}_3\text{N}_4+4\text{H}_2$). This part of the paper considers the mathematical model of the kinetic curve (mass change-time) of growth-sublimation of Ge_3N_4 in the medium of vapors N_2H_4 in the presence of the etching process of Ge surface.

EXPERIMENTAL

The initial reagents were germanium plates (with the same pretreatment procedure described in³) and concentrated hydrazine with refraction index $n_D^{20} \approx 1.705$. The inlet pressure of vapor N_2H_4 was $\approx 2 \cdot 10^3 \text{ Pa}$. The temperature interval was 650-800°C. The scale formed on the germanium surface, according to X-ray analysis, was a mixture of α - and β -modifications of Ge_3N_4 . The registration of the sample mass change during the reaction was done on the continuous weighing microbalance mounted in a vacuum installation (the sensitivity of the balance was 10^{-6} g).

RESULTS AND DISCUSSION

Figure 1 shows the most typical thermogravimetric curve of the mass change of a germanium sample in hydrazine vapors obtained at 720°C.

Section OA corresponds to the accumulation of hydrazine and the products of its decomposition on the surface of Ge.

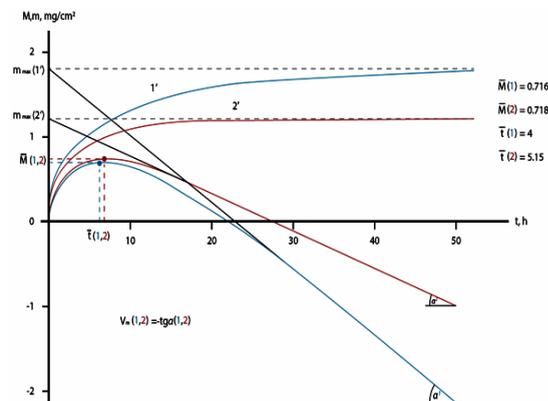


Fig. 1. (1) is the curve of the total mass change of germanium sample in hydrazine vapors $M_{\text{exper.}}(t_{\text{exper.}})$; (2) is the curve of mass gain caused by the active gas plotted according to it; dotted line is the tangent to curve 1 at point O

The abnormally high initial sample mass gain for the adsorption processes can be explained by the presence of highly polarized forms on the surface of germanium capable of accumulating in large quantities due to physical forces¹¹. (We would like to note that in the NH_3 media, no similar initial increments of the germanium sample are observed.) The negative course of the mass change along AC section (the mass of the sample gradually becomes smaller than its initial mass) evidences the presence of etching process of the Ge surface. Later, a mass increase is observed repeatedly (section CD) caused by the gradual growth of the nitride layer. Nitride formation is accompanied by its sublimation (like in case of NH_3)³ as evidenced by the precipitation of an amorphous germanium oxynitride film in the cold zone of the reactor. The sublimation process causes a repeated decrease of mass of the sample (section DF). The rectilinear part of this section (EF) corresponds to the steady state reaction, when the nitride layer reaches its maximum mass (thickness): at this stage, the amounts of the forming and subliming nitride are equalized. The slope of straight line EF corresponds to the rate of mass decrease of the sample due to the metallic component (v_m) of the subliming part of nitride. According to Fig. 1, $v_m = -\text{tg}\alpha \approx -0.047 \text{ mg/cm}^2 \text{ h}$ (for Ge_3N_4 $q = M_{\text{Ge}_3\text{N}_4} / (M_{\text{N}_2\text{H}_4} \cdot 3.886)$; and accordingly, $v_g = v_m / q \approx 0.012 \text{ mg/cm}^2 \text{ h}$).

Eq. (2) for any $n > 1$, assumes convexity of the corresponding graph $m(t)$ along the positive direction of the ordinate axis. Therefore, the considered mathematical model can be applied by choosing a new coordinate system (t, m) with

the origin at the second inflection point (O) on the experimental curve $M_{\text{exper.}}(t_{\text{exper.}})$ (Fig.1). The values of characteristic parameters of the process determined in this new system of coordinates are: $m_{\text{max}} \cong 0.092$ mg/cm², $K_0 \cong \text{tg}\beta \cong 0.129$ mg/cm² h (respectively, $k_0 = K_0 + v_m \cong 0.176$ mg/cm² h, $k = v_g/k_0 \cong 0.069$), the coordinates of the point of maximum (point D) $\bar{t} \cong 0.57$ min $\cong 0.95$ h, $\bar{M} \cong 0.018$ mg/cm². By substituting the values of k, m_{max} and v_g in Eq. (2), we obtain:

$$t = 88.347 \int [1 - (10.870m)^{n-1}]^{-1} dm - 82.645m \quad (6)$$

Where m in mg/cm², t in hours.

To determine the exponent n , we use formula^{3,12}:

$$n = \frac{\lg[(1-qk)(\bar{M} + v_m \bar{t})/pm_{\text{max}}]}{\lg[(\bar{M} + v_m \bar{t})/m_{\text{max}}]} \quad (7)$$

This formula is an analog of formula derived in 6, which in our designations of experimentally determined quantities is as follows:

$$n = \frac{\lg[(\bar{M} + v_m \bar{t})/pm_{\text{max}}]}{\lg[(\bar{M} + v_m \bar{t})/m_{\text{max}}]} \quad (8)$$

By substituting the experimental values in Eqs.(7) and (8), we obtain: $n \cong 5.9$ and 5.1 , respectively. (In the first part of the work, for the nitriding of germanium with ammonia, the values $n \cong 2.2$ and 3.3 were obtained. This made it possible to describe the corresponding thermogravimetric curves with Eqs. (3) and (4). In our case, with the aim of selecting the appropriate equation to describe dependence of $m(t)$, constructed based on the curve $M_{\text{exper.}}(t_{\text{exper.}})$, we give all the graphs for $n=2, 3, 4$ and 5 in Eq.(6) for the boundary conditions $t=0, m=0$, see Fig.2, curves (1-4).

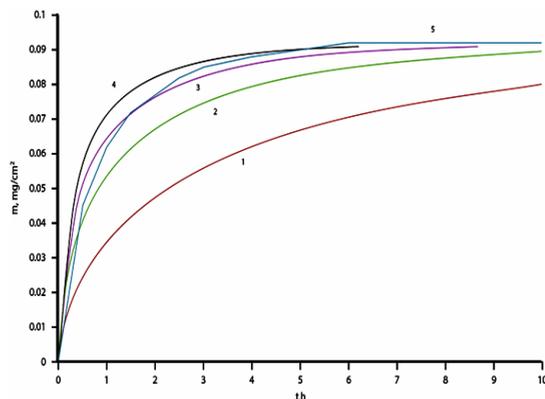


Fig. 2. Graphs of Eq. (2) when (1) $n=2$, (2) $n=3$, (3) $n=4$, and (4) $n=5$; (5) is curve 2 in Fig.1.

It also shows dependence $m(t)$ from Fig.1 (curve 5). The fact that this graph is saturated on top of all calculated curves is not unexpected: the thermogravimetric experiment is performed with a certain accuracy, and the exit of curve 5 on the ordinate $m_{\text{max}} \cong 0.092$ mg/cm² is observed for ~ 6 h (in (t, m) coordinate system); while theoretically, $m \rightarrow m_{\text{max}}$ as $t \rightarrow \infty$. Fig. 2 shows that curve 3 (constructed from $n=4$) is the closest to curve 5. In this connection, it should be noted that value n in Eqs. (7) and (8) change significantly with relatively small changes of the parameters included in them. For instance, if in Fig.1, artificially increasing the slope of the EF line by 20%, then changing the value v_m will change the values of v_g , m_{max} and k_n (k , respectively). Then, for the same values of \bar{t} and \bar{M} in Eqs.(7) and (8), we obtain $n \cong 4.3$ and 3.7 , respectively. Thus, gaining values $n > 4$ from formulae (7) and (8) should be associated with the error in measuring the experimental values. Moreover, when the equation corresponding to $n=5$ lacks physical meaning.

It should be noted, however, that none of the curves presented in Fig.2 correspond totally to the "true" mass gain of germanium sample, since it is obvious that the growth of the nitride layer will occur well before the occurrence of second inflection point (O) on experimental curve $M_{\text{exper.}}(t_{\text{exper.}})$ (the same process is also observed in the control experiments). To estimate the value of this initial "hidden" mass gain (m_0), we can solve Eq. (2) for $n=4$ with boundary conditions $t=0, m=m_0$. This solution is shown by the following expression:

$$t = (1+k) \frac{m_{\text{max}}}{v_g} \left[\frac{1}{\sqrt{3}} \arctg \frac{2\sqrt{3}m(m-m_0)}{m+2m_{\text{max}}} - \frac{1}{6} \ln \frac{(m_{\text{max}}-m)^2(m_0^2+m_{\text{max}}m_0+m_{\text{max}}^2)}{(m_{\text{max}}-m_0)^2(m^2+mm_{\text{max}}+m_{\text{max}}^2)} \right] - \frac{m-m_0}{v_g} \quad (9)$$

Time shift between (5) and (9):

$$t_0 = (1+k) \frac{m_{\text{max}}}{v_g} \left[\frac{1}{6} \ln \frac{(m_{\text{max}}-m_0)^2}{m_0^2+m_0m_{\text{max}}+m_{\text{max}}^2} - \frac{1}{\sqrt{3}} \arctg \frac{\sqrt{3}m_0}{m_0+2m_{\text{max}}} \right] + \frac{m_0}{v_g} \quad (10)$$

Thus, m_0 can be determined by an approximate solution of transcendental Eq.(10) by considering the values of experimentally calculated indices. Assuming that in the study process, the environs of the first inflection point (B) corresponds to the onset of nitride formation, the time shift between the two inflection points (t_0) can be estimated with value $|t_0| \cong 11.5 \pm 1.5$ min $\cong 0.192$ h (Fig.1). Eq.(10) gives the value $m_0 \cong 0.030$ mg/cm². This value is $\geq 30\%$ of the "observed" mass gain m_{max} , which

cannot be ignored when studying the process by the thermogravimetric method.

Dependence $m(t)$ constructed from Eq. (9) is shown in Fig.3 (curve 1). This figure also shows the extrapolation of curve 1 in the negative direction of the ordinate axis (curve 2). In new coordinate system (\bar{t}, \bar{M}) , this curve can be considered as the "true" kinetic dependence of the mass gain of a germanium sample in hydrazine vapors.

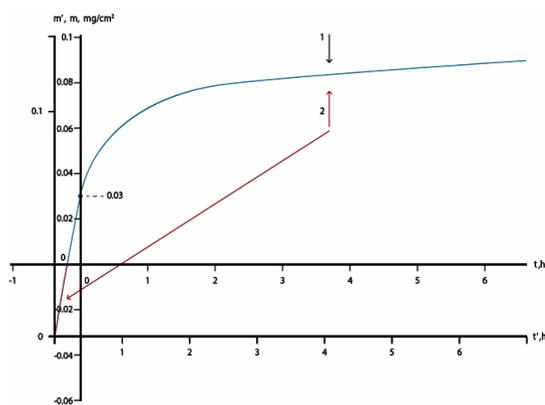


Fig. 3. Ggraphs of Eq.(9') for (1) $m \geq 0$ and (2) $m > -0.037 \text{ mg/cm}^2$. (On site $m \geq 0$, curve 2 coincides with curve 1.)

From Eq.(1) that graphs kinetic dependences $m(t)$ must have the top at the point with ordinate $\bar{m} \equiv m_{(dt/dm=0)} = (-k_n/nk_r)^{1/(n-1)} = m_{\text{max}} k^{1/(n-1)}$ for even values of n ; and as for the odd values, no such point exists for them (in this case, \bar{m} is a complex number). For $n=2$ $\bar{m} = -km_{\text{max}}$, and in case $n=4$ $\bar{m} = m_{\text{max}}(-k)^{1/3}$. Fig. 4. shows the graphs of Eqs.(3) and (5) for different values of parameter k (in nondimensional coordinates).

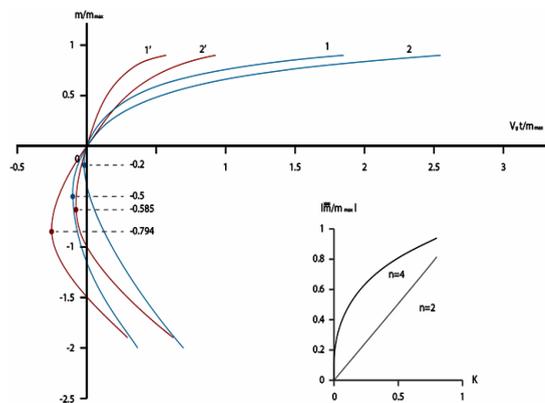


Fig. 4. Graphs of Eqs.(3) and (5) when (1, 1') $k=0.2$ and (2, 2') $k=0.5$ with rated (dimensionless) coordinates. (m/m_{max} is considered as an argument, and $(v_g t)/m_{\text{max}}$ -as a function.) In the block: dependence of correlation \bar{m}/m_{max} module on coefficient k

As value $|\bar{m}|$ increases with an increase of value k , it can be assumed that "hidden" mass gain $m_0 \sim k$; and that in this case, $m_0 = -\bar{m}$. This assumption can be justified by the fact that for low values of rectilinear constant k_r (and consequently, for high values of parameter $k = v_g/k_0 = v_g/(k_r - v_g)$), the kinetic control of the process will be quite visible. And with the predominance of diffusion control (at high values of k_r), the model in question will assume all the low values of m_0 . Therefore, Eq. $m_0 = -\bar{m}$ will probably have a physical justification. In this connection, we can add that in the past, we empirically deduced a similar equality in the study of the oxidation of the structural (Al_2O_3 forming) chromium alloys in air¹³. (In this case, the secondary process, which changes the form of the initial parabolic equation, is not the sublimation of the scale, but the decrease of the effective area of reaction due to the formation of diffusion barriers from the oxides of the doping elements of the alloy.)

CONCLUSION

The above equations can be used to describe thermogravimetric curves of the growth-sublimation of scale, when this process is preceded by gas etching of the metal(alloy) surface. According to its, we can determine the initial "hidden" mass gain, which is not directly revealed on thermogravimetric curves. This approach can also be used for parabolic and cubic processes. In this case, solutions of Eq. (2) for $n=2$ and 3 provided $t=0, m=m_0$ will be:

$$t = -(1+k) \frac{m_{\text{max}}}{v_g} \ln \frac{m_{\text{max}} - m}{m_{\text{max}} - m_0} - \frac{m - m_0}{v_g} \quad (11)$$

and

$$t = (1+k) \frac{m_{\text{max}}}{2v_g} \ln \frac{(m_{\text{max}} + m)(m_{\text{max}} - m_0)}{(m_{\text{max}} - m)(m_{\text{max}} + m_0)} - \frac{m - m_0}{v_g} \quad (12)$$

respectively.

Time shift between Eqs.(3) and (11)

$$t_0 = (1+k) \frac{m_{\text{max}}}{v_g} \ln \frac{m_{\text{max}} - m_0}{m_{\text{max}}} + \frac{m_0}{v_g} \quad (13)$$

between Eqs.(4) and (12):

$$t_0 = (1 + k) \frac{m_{max}}{2v_g} \ln \frac{m_{max} - m_0}{m_{max} + m_0} + \frac{m_0}{v_g} \quad (14)$$

By calculating values k_0, v_g, m_{max} and t_0 from the experimental data, "hidden" mass gain m_0 can also be identified by using approximate solutions of Eqs.(13) and (14).

ACKNOWLEDGEMENT

Author thanks the leader engineer of the Institute of cybernetics Omar Tkheselashvili for useful participating of discussing of the article.

Conflicting interest

There is no conflicting interest in this study.

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