

Relative Thermal Stability of A- and B-Modifications of Ge₃N₄

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Abstract

In this article the processes occurring when heating pure α -, β -Ge₃N₄ and their mixtures in a low dynamic vacuum, as well as in hydrogen and water vapor are discussed. Relative thermal stability of pure α - and β -modifications of Ge₃N₄ and their mixtures is studied. In vacuum α -Ge₃N₄ dissociates at temperatures of $T \geq 740^\circ\text{C}$, and β -Ge₃N₄ at $T \geq 780^\circ\text{C}$. At lower temperatures both modifications are sublimated. Sublimation heat of α -Ge₃N₄ is ~ 245 kJ/mol, and of β -Ge₃N₄ is ~ 290 kJ/mol. The predominant thermal stability of β -Ge₃N₄ is also evident in hydrogen and water vapor media.

Keywords: Germanium nitride, α -Ge₃N₄, β -Ge₃N₄, thermal stability, sublimation dissociation.

Introduction

Among the currently known crystalline modifications of germanium nitride (Ge₃N₄) only isostructural α - and β -phases, corresponding to the modifications of silicon nitride Si₃N₄ (Ruddlesden, Popper, 1958, Soignard, McMillan, Henji, Leinenweber, 2004), are stable at normal pressure and temperature (Luo, Cang, Chen, 2014, Cang, Yao, Chen, Yang, Yang, 2016). Both modifications are crystallized in phenacite type structures (Bragg, Claringbull, 1965) with a reduced hexagonal unit cell (Ruddlesden, Popper, 1958). Difference in the reactivity of α - and β -Ge₃N₄ was observed in the work (Ruddlesden, Popper, 1958); when heating the mixture in a nitrogen medium at 820°C, decrease in the α -phase content was observed. At the same time, the content of β -phase increased in the sample and elemental germanium appeared, i. e. in parallel with the dissociation of $\text{Ge}_3\text{N}_4 \rightarrow 3\text{Ge} + 2\text{N}_2$ (1) so called $\alpha \rightarrow \beta$ conversion occurred. This conversion is well studied for Si₃N₄ (Meléndez-Martinez, Dominguez-Rodriguez, 2004, Xu, Wang, Cui, Su, Zhou, 2011). The nitride with predominant content of α -phase was studied in the work (Billy, Labbe, 1971). The temperature limit for the onset of dissociation of the compound, accompanied by the sublimation of germanium, is 780°C. In contrast, according to the data (Lyutaya, Samsonov, Khorpyakov, 1964), in the same nitrogen medium, Ge₃N₄ begins to dissociate at 850°C. In this work the nitride was not separated into crystal modifications. But the values of the unit cell parameters, calculated on the basis of rhombohedral syngony, are very close to the data of the first work on the crystal structure of Ge₃N₄ (Juza, Hahn, 1940). According to the table of intensities of x-ray reflexes given in (Juza, Hahn, 1940), the nitride was β -Ge₃N₄ with traces of α -phase. On the basis of the above results, it is concluded (Billy, Labbe, 1971,

Samsonov, Kulik, Polishchuk, 1978) that from α - and β -modifications of germanium nitride β -phase is more stable.

It should be noted that thin films of the nitride were deposited in the cold zone of the reactor by heating Ge₃N₄ in the range of 700-750°C (Bayractoroglu, Johnson, Langer, Mier, 1980). This indicated the possibility of sublimation of Ge₃N₄, which was subsequently confirmed in the work (Bagratishvili, Nakhutsrishvili, Zhorzholiani, 1992). In these studies, the question of the stability of Ge₃N₄, was not considered from the point of view of the predominance of α or β phase in it. However, the question of dissociation-sublimation of α - and β -Ge₃N₄ requires separate research.

Working Methodology

The nitride was obtained by nitriding of single-crystal germanium (n-type conductivity, resistivity ~ 35 $\Omega\cdot\text{cm}$, orientation {111}) in the NH₃+H₂O medium at 800-820°C under static vacuum conditions. The duration of nitriding was 2 hours. – 2 hours. The ammonia pressure was $P_{\text{NH}_3} = 2.0 \cdot 10^{-3}$ Pa; The test samples were synthesized under the following conditions: Sample N1 - $P \equiv P_{\text{H}_2\text{O}} / P_{\text{NH}_3} \cong 1.5\%$, 820°C (pure β -Ge₃N₄); sample N2 - $P \cong 3\%$, 800°C; sample N3 - $P \cong 12.5\%$, 800°C (the nitride with a phase composition close to that studied in (Billy, Labbe, 1971); sample N4 - $P \cong 12.5\%$, 820°C (pure α -Ge₃N₄).

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Results

The processes occurring when heating pure α -, β - Ge_3N_4 and their mixtures in a low dynamic vacuum ($\sim 10^{-4}$ Pa), as well as in hydrogen ($P_{\text{H}_2} \cong 2 \cdot 10^3$ Pa) and water vapor ($P_{\text{H}_2\text{O}} \cong 2.4 \cdot 10^3$ Pa) are discussed. In the vacuum α - Ge_3N_4 dissociates at temperatures of $T \geq 740^\circ\text{C}$, and β - Ge_3N_4 at $T \geq 780^\circ\text{C}$. At lower temperatures they sublime. Sublimation heat of α - Ge_3N_4 is ~ 245 kJ/mol, and of β - Ge_3N_4 is ~ 290 kJ/mol.

Line diagrams of α - and β - Ge_3N_4 basic X-ray reflections are shown in Fig. 1.

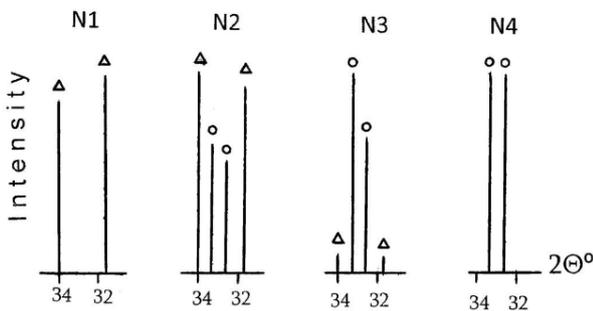


Figure 1. Line diagrams of the studied samples: \circ - α - Ge_3N_4 , Δ - β - Ge_3N_4 .

Sample N1 was a continuous coating densely grown on the Ge surface with thickness of ~ 0.3 μm ; samples N2-4 were easily removable from the germanium surface loose coatings. For the sample N2 $I \equiv I(\alpha)/I(\alpha,\beta) \cong 40\%$. (Samples of Ge_3N_4 with $I < 40\%$ were layers whose mechanical removal from the surface of germanium gradually became difficult.)

It was previously shown (Bradley, Munro, Whitfield, Remy, Pauleau, 1976, Nakhutsrishvili, Mogilyanskii, 1994), that depending on the composition of the gaseous medium and the process temperature, it is possible to obtain nitride with practically any ratio of α - and β - Ge_3N_4 in it. For clarity, this is demonstrated in the form of graphs in Fig. 2 according to the data (Nakhutsrishvili, Mogilyanskii, 1994).

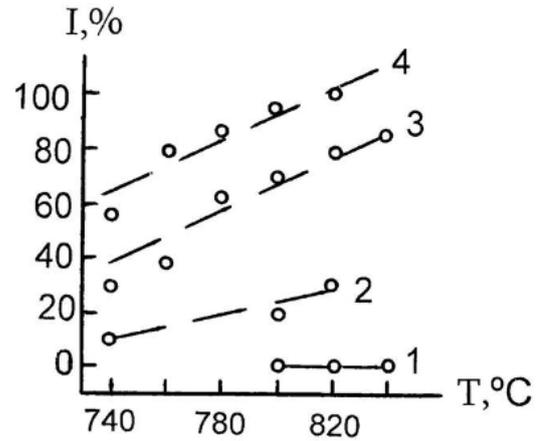


Figure 2. Dependences $I \equiv I(\alpha)/I(\alpha,\beta)$ on the nitriding temperature of germanium at $P=1.5\%$ (1), 3% (2), 10% (3) and 13.3% (4).

In particular, to obtain pure β - Ge_3N_4 , high vacuum is not required - variation of the water vapor content in the reaction medium is sufficient. However, ultrahigh vacuum conditions are of significant importance in the technological process of obtaining nitride films during the sublimation of Ge_3N_4 - nonstoichiometric films of germanium oxynitride can precipitate in a low vacuum.

The products of phase transformation of the initial samples were examined by X-ray diffractometry (diffractometer HZG-4A, $\text{CuK}\alpha$ radiation); change of their mass in the process of thermal annealing was studied by microgravimetry (vacuum microbalance of the IFC design with sensitivity of ~ 10 g).

The experiments have shown that the diffractograms of samples N1 and N2 do not undergo changes when heated in vacuum up to $\sim 780^\circ\text{C}$, and for the samples N3 и 4 - up to $\sim 740^\circ\text{C}$. At higher temperatures, the elemental germanium begins to appear on the diffractograms, which indicates the onset of the reaction (1). Fig. 3 shows temporary dependence of the intensity ratio of elemental germanium main reflex to the sum of the intensities of the main reflexes of α -, β - Ge_3N_4 and Ge ($I' \equiv I(\text{Ge})/I(\alpha,\beta,\text{Ge})$).

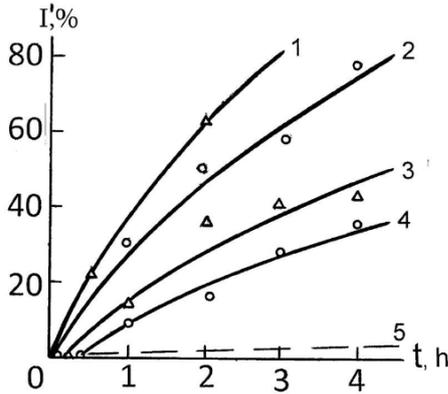
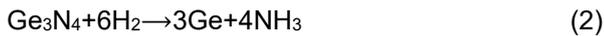
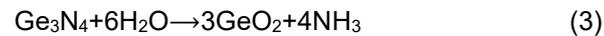


Figure 3. Time dependences $I' \equiv I(\text{Ge})/I(\alpha, \beta, \text{Ge})$ in vacuum at 820°C (1-3) and in hydrogen at 600°C (4,5): 1 – sample N4; 2 and 4- sample N3; 3 and 5 – sample N2.

It can be seen in Fig. 3 that at the same temperature (820°C), the dissociation process proceeds more rapidly on samples with a predominant content of α - Ge_3N_4 . Similar situation was observed in hydrogen medium, in which at temperatures $\geq 600^\circ\text{C}$ nitride is reduced to elemental germanium:



as well as in water vapor, where at temperatures $\geq 900^\circ\text{C}$ the nitride is oxidized to the dioxide:



Thus, according to the data of (Juza, Hahn, 1940), where an almost pure nitride of β - Ge_3N_4 phase was studied, temperature limit of the onset of reaction (2) is 700°C. In our experiments in hydrogen on samples N2 and 3, the elemental germanium reflexes already appeared at 600°C (Fig. 3). As it can be seen from the Fig. 3, for the sample N3 during 4-hour process $I' \sim 35\%$. And for the sample N2 for 10 hours this ratio was almost an order of magnitude lower. In water vapor at 950°C for 0.5 h, sample N3 was completely oxidized to GeO_2 , and in the diffractogram of sample N2 under the same conditions only weak GeO_2 reflexes were observed. It should be noted that in the experiments carried out in the above media (vacuum, H_2 , H_2O) in the range of 600-900°C, no significant change was observed on the samples of all types with respect to the intensities of the main x-ray reflexes of α - and β - Ge_3N_4 . However, at the temperatures coupled with the reactions (1), (2) or (3), their total intensity was decreased due to detection of germanium reflexes. Thus, in these media no $\alpha \rightarrow \beta$ transition was observed for Ge_3N_4 .

According to the references and the experimental data, there is no regularity in the variation of the dissociation energy of Ge_3N_4 as a function of its phase composition (these values lie in

the range of ~ 375 -460 kJ/mol (Billy, Labbe, 1971, Bagratishvili, Nakhutsrishvili, Litvinenko, 1980). As for the heat of sublimation, a value of ~ 250 kJ/mol was obtained for a nitride with a predominant content of α -phase (Bagratishvili, Nakhutsrishvili, Zhorzholiani, 1992). We performed experiments on the free evaporation of pure α - and β - Ge_3N_4 in a dynamic vacuum directly from the germanium source. The temperature interval was 630-760°C, where the decomposition of the nitride can be neglected. A rectilinear decrease in the mass of the samples was observed (Fig. 4a, b), which corresponds to the sublimation of the compound during the isothermal process.

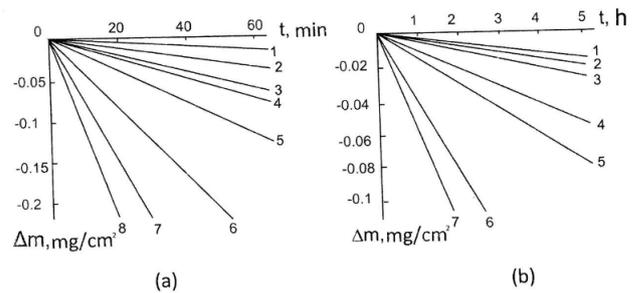


Figure 4. (a) - the decrease in the mass of α - Ge_3N_4 in vacuum at 635°C (1), 655°C (2), 675°C (3), 695°C (4), 720°C (5), 730°C (6), 745°C (7) u 755°C (8); (b) - the decrease in the mass of β - Ge_3N_4 at 680°C (1), 695°C (2), 705°C (3), 725°C (4), 735°C (5), 750°C (6) u 760°C (7).

It is noticeable that this process is much more intensive in the case of α - Ge_3N_4 (compare mass changes and time intervals in Fig. 4a, b). Fig. 5 shows the temperature dependence of the sublimation rates of α - and β - Ge_3N_4 .

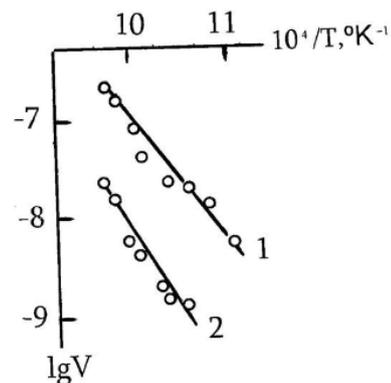


Figure 5. Temperature dependences of the sublimation rate of α - Ge_3N_4 (1) and β - Ge_3N_4 (2) in Arrhenius coordinates ($[V]=\text{g}/\text{cm}^2 \cdot \text{sec}$).

Conclusion

It can be concluded that for approximately equal temperatures, sublimation rate of α - Ge_3N_4 is on average an order of magnitude higher than for β - Ge_3N_4 . The apparent activation energy determined from the dependence (1) gave the value of ~ 245 kJ/mol to the sublimation heat of α - Ge_3N_4 ; and for β - Ge_3N_4 (dependence (2)) a somewhat higher value was obtained: ~ 290 kJ/mol.). Thus, the above experimental results support the conclusion that of the two stable α - and β - crystalline modifications of Ge_3N_4 the β -phase is more stable. This point of view can also be justified by comparing the structures of α - and β - Ge_3N_4 . Theoretical aspects of the problem are to be considered separately.

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