



Conditions of Formation of α - and β -Modifications of Ge_3N_4 and Preparation of Germanium Oxynitride Dielectric Films

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Abstract: The binary compound of germanium with nitrogen (Ge_3N_4) is used in various fields of science and technology. Among the experimentally discovered and theoretically predicted crystal modifications of Ge_3N_4 at ordinary pressures and temperatures, only the α - and β -phases of the nitride are stable. There are conflicting data in the literature on the conditions for the formation of these phases. The main methods for obtaining Ge_3N_4 are the nitridation of elemental germanium and its dioxide with ammonia. The present work studied the influence of the degree of humidity of ammonia on the possibility of the formation of pure α - and β -phases and their mixtures. It is shown that it is possible to obtain nitride with practically any ratio of these phases by varying degrees of humidity and the temperature of the process. During the process, the formation of germanium nitride is accompanied by its simultaneous evaporation. Oxidation with water vapors also produces volatile monoxide. Simultaneous evaporation of germanium nitride and oxide results in the deposition of a film of germanium oxynitride in the cold zone of the reactor. This film is a germanium oxynitride used in microelectronics as a dielectric layer in Metal-Insulator-Semiconductor systems.

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1. INTRODUCTION

Nitrides are widely used in various fields of science and technology [1-3]. An important place among these binary compounds is occupied by germanium nitride (Ge_3N_4). Its crystalline form and amorphous thin films are used in micro- and nanoelectronics, photocatalysis, luminescence, energy storage, and others [4-9]. Ge_3N_4 exists in the form of several crystalline modifications: α -, β - and δ - (hexagonal), γ - (cubic) Ge_3N_4 [10-12].¹

Among these modifications, only the α - and β -phases are stable at ordinary pressures and temperatures. The main methods for the synthesis of Ge_3N_4 are the reactions:



and



According to reaction (1), predominantly α - Ge_3N_4 is obtained, and according to (2), β - Ge_3N_4 is obtained. It is noted in the literature that the synthesis of pure α - and β -phases of nitride

is difficult [15]. Since the β -phase is formed in the GeO_2/NH_3 system, it was previously suggested that it is stabilized in the presence of traces of oxygen, oxide, or water vapor (literature data given in [16]). This is contradicted by the data of another earlier work [17], according to which α - Ge_3N_4 is predominantly formed under these conditions. This article considers the influence of the degree of humidity of ammonia on the possibility of obtaining pure α - and β -phases of germanium nitride and their mixtures.

2. MATERIALS AND METHODS

The nitride samples were obtained by nitriding of single-crystal germanium (n-type conductivity, resistivity $35 \Omega \cdot \text{cm}$, orientation {111} or {100}) in the $\text{NH}_3 + \text{H}_2\text{O}$ medium at 640-840°C under static vacuum conditions. Germanium plates were etched in a liquid etchant CP-4A ($\text{HF}:\text{HNO}_3:\text{CH}_3\text{COOH} = 1:15:1$) for 5min and washed in double-distilled water, followed by drying. Commercial ammonia (99.6% NH_3 , 0.2-0.4% H_2O) was purified both by the standard method (passing over CaO and NaOH absorbers) also by freezing in a mixture of liquid nitrogen and alcohol at a temperature of -30°C (freezing temperature of ammonia is -33.4°C). The pressure of ammonia was $2 \cdot 10^3$ Pa. The nitride samples were synthesized under the following conditions: $P_{\text{H}_2\text{O}}/P_{\text{NH}_3} \cong 1, 2.5, 4, \text{ and } 12.5\%$. The duration of the

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¹Theoretically, other synagogues of nitride are also considered [13,14].

reaction was 2 hours. The obtained nitride was analyzed by X-ray (diffractometer HZG-A, $\text{CuK}\alpha$ radiation) and Auger electron spectroscopy (spectrometer LAS-2000).

Infrared (IR) spectra of germanium oxynitride films were recorded on a spectrophotometer UR-20, and electronic absorption spectra - on a quartz spectrophotometer SF-26-A.

3. RESULTS AND DISCUSSION

Figure 1 shows temperature dependencies of the ratio of the intensity of these reflections of the α -phase to the sum of the intensities of the main reflections of both phases. It can be seen from the figure that with increasing P, the lower temperature limit of nitride formation shifts towards lower temperatures. Below the temperature $\cong 630^\circ\text{C}$, nitride is not formed for a sufficiently long period (~ 50 h), and only etching of the germanium surface with water vapor occurs [18]. (The etching process apparently activates the Ge surface for nitriding, and as it increases, this activation intensifies. However, at $P \cong 20\%$, nitride formation stops).

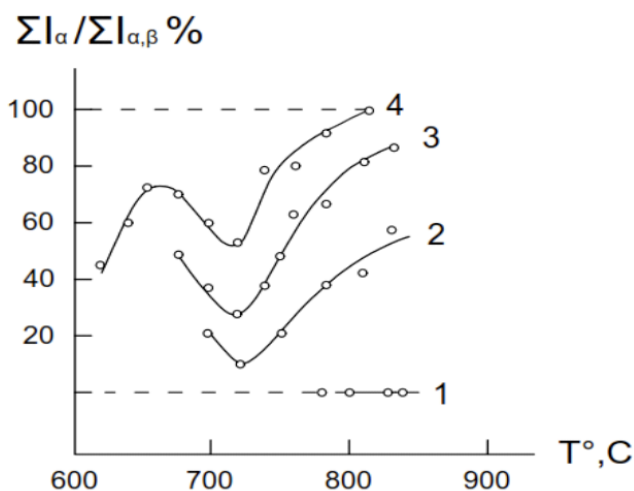


Figure 1: Dependences $I \equiv \Sigma I(\alpha) / \Sigma I(\alpha, \beta)$ on the nitridation temperature of germanium at $P \cong 1$ (1), 2.5 (2), 4 (3) and 12.5% (4).

It should be noted that water vapor forms volatile germanium monoxide ($\text{Ge} + \text{H}_2\text{O} \rightarrow \text{GeO} + \text{H}_2$). However, GeO evaporates completely and does not remain in the surface product. This is confirmed by Auger analysis: only signals of germanium and nitrogen are visible in the spectrum (Figure 2a).²

In the process of germanium nitridation, the nitride also evaporates [18]. The temperature dependencies of the evaporation rate of Ge_3N_4 and GeO in Arrhenius coordinates are shown in Figure 3. The activation energies (heats of vaporization) calculated from these dependencies are ~ 245

²Auger-spectroscopy presents a chemical analysis: each element is characterized by its peaks in the Auger-spectrum. There was an assumption that $\alpha\text{-Si}_3\text{N}_4$ (to which $\alpha\text{-Ge}_3\text{N}_4$ is isostructural) contains oxygen and is an oxynitride (but this has not been proven). However, oxynitrides $\text{Si}_2\text{N}_2\text{O}$ and $\text{Ge}_2\text{N}_2\text{O}$ have a different crystal structure [19]. Due to the sensitivity of Auger-spectroscopic analysis to oxygen, even if there is an oxygen impurity in $\alpha\text{-Ge}_3\text{N}_4$ practically does not affect its crystal structure.

(for $\alpha\text{-Ge}_3\text{N}_4$), ~ 290 (for $\beta\text{-Ge}_3\text{N}_4$), ~ 255 (for a mixture with their approximately equal content) and ~ 221 kJ/mol (for GeO), respectively. From a comparison of these values, it is clear that $\alpha\text{-Ge}_3\text{N}_4$ is thermally less stable than $\beta\text{-Ge}_3\text{N}_4$ and can evaporate at lower temperatures (GeO is even less stable).

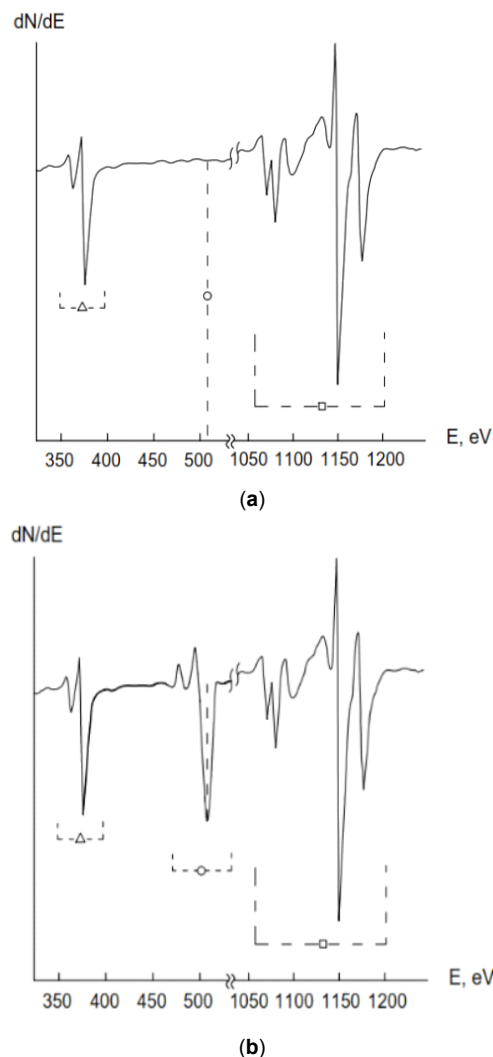


Figure 2: Auger-spectrum of: germanium nitride (a) and its film (b); Δ -N, \circ -O, \square -Ge.

With the simultaneous evaporation of Ge_3N_4 and GeO in the "cold" ($300 \pm 350^\circ\text{C}$) zone of the reactor, a film is deposited on substrates Si, Al_2O_3 , GaAs, or InP. X-ray analysis shows this film is amorphous (continuous background on the X-ray pattern). Auger-spectrum shows (along with germanium and nitrogen signals) an oxygen signal (Figure 2b). Thus, the film is germanium oxynitride ($\text{Ge}_x\text{N}_y\text{O}_z$). One band appears in the IR spectrum of the films (Figure 4). Its position changes in the region $(780\text{--}820)\text{ cm}^{-1}$ depending on the temperature of their preparation. This single band, located between bands of Ge_3N_4 ($\sim 750\text{ cm}^{-1}$) and GeO_2 ($\sim 890\text{ cm}^{-1}$), excludes separate nitride and oxide phases. The shift of the IR band towards lower frequencies is associated with a decrease in the oxygen content in the film as the temperature rises.

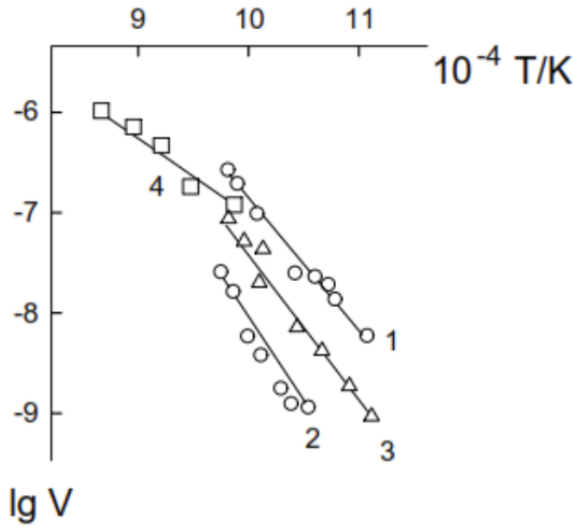


Figure 3: Temperature dependences of α - Ge_3N_4 (1), β - Ge_3N_4 (2), their mixtures with approximately the same content (3) and GeO (4) in Arrhenius coordinates.

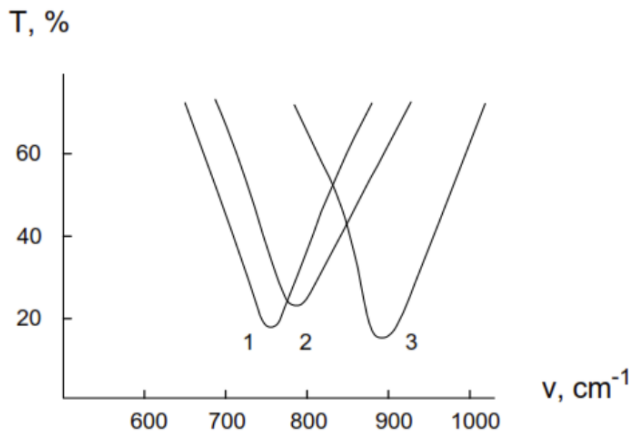


Figure 4: IR absorption spectra of films of nitride (1), oxynitride (2), and dioxide (3) of germanium.

Figure 5 shows the electronic spectra of germanium oxynitride films in different coordinates. They can be used to calculate the band gap.³ Depending on the temperature, values of E_g (4.1-4.7) eV were obtained, which corresponds to a dielectric.

$\text{Ge}_x\text{N}_y\text{O}_z$ films find application in microelectronics as a fermature layer [20-23].

We have studied the change of the sign of the charge at the interface $\text{Ge}_x\text{N}_y\text{O}_z$ -Si with increasing germanium nitridation temperature. Figure 6 shows the temperature dependence of the flat band voltage (V_{FB})⁴ in the structure $\text{Al-Ge}_x\text{N}_y\text{O}_z$ -Si. As can be seen from this figure, for $\text{Ge}_x\text{N}_y\text{O}_z$ films obtained

³The band gap is calculated using the known dependence $\alpha h\nu - (h\nu - E_g)^2$, where α is the absorption coefficient, h is Planck's constant, and ν is the frequency.

⁴The flat band voltage characterizes the charge built into the dielectric at the interface with the semiconductor.

below 675°C , $V_{FB} < 0$, and above 675°C $V_{FB} > 0$. This means that in the first case, the boundary region of the dielectric with the semiconductor is charged positively, and in the second, negatively. It is known that MIS (Metal-Insulator-Semiconductor) structures based on germanium nitride films are characterized by positive values of the flat band voltage, and those based on oxide films have negative values. All this allows us to conclude that the dielectric film is enriched with oxygen in the first case, which is gradually removed with increasing temperature. Oxygen rediffusion is detected by direct Auger-spectroscopy analysis.

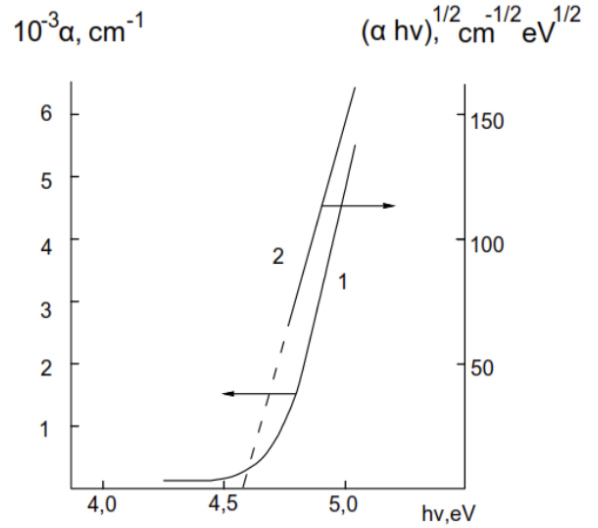


Figure 5: Electronic absorption spectra of $\text{Ge}_3\text{N}_2\text{O}_2$ films in coordinates $\alpha - h\nu$ (1) and $\alpha h\nu - h\nu$ (2).

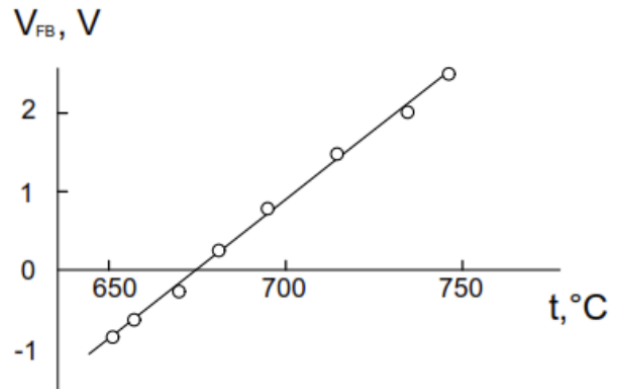


Figure 6: Dependence of the flat band voltage in the $\text{Al-Ge}_x\text{N}_y\text{O}_z$ -Si structure on the temperature of preparation of germanium nitride.

In conclusion, we note that the issue of regulating the sign of the charge at the dielectric-semiconductor interface is of great practical importance for the implementation of open (transistor with a built-in channel) and closed (transistor with an induced channel) type MIS transistors.

CONCLUSION

1. By varying the degree of humidity of ammonia and the temperature of the process, it is possible to obtain

nitride in the form of pure α - and β -Ge₃N₄, as well as their mixtures with practically any ratio.

- The formation of germanium nitride in humid ammonia is accompanied by its simultaneous evaporation.
- Water vapor forms volatile germanium monoxide, which evaporates completely and does not remain in the surface product.
- Heats of vaporization are: ~245 for α -Ge₃N₄, ~290 for β -Ge₃N₄, ~255 for a mixture with their approximately equal content and ~221 kJ/mol for GeO, respectively.
- Simultaneous evaporation of germanium nitride and oxide results in the deposition of a film of germanium oxynitride in the cold zone of the reactor.
- This film is a germanium oxynitride used in microelectronics as a dielectric layer in Metal-Insulator-Semiconductor systems.

APPENDIX

Ge₃N₄ can be obtained also by nitridation of elemental germanium in hydrazine vapor: $3\text{Ge} + 2\text{N}_2\text{H}_4 \rightarrow \text{Ge}_3\text{N}_4 + 4\text{H}_2$. Dehydration of hydrazine (pre-boiling with NaOH in an inert N₂ atmosphere at 120°C for 2 hours + Rashig's method [24]) is a rather time-consuming procedure. An explosion is also possible.

The water content in hydrazine is estimated by the density, freezing point, or refractive index of the mixture. But the literature data about the first two parameters are somewhat different. This is due to the difficulty of measuring the physical characteristics of pure hydrazine.

The refractive index of distilled hydrazine was $n_d^{20} \cong 1.471$. According to the literature this corresponds to 100% N₂H₄. Nevertheless, in such hydrazine vapor at 700°C, we obtained β -Ge₃N₄ along with traces of α -phase. When the refractive index was $\cong 1.463$ (~ 5 mass% H₂O), pure α -Ge₃N₄ was obtained at 750°C.

In the introduction, it was mentioned that one of the fields of application of germanium nitride is photocatalysis. In particular, the catalytic properties of β -Ge₃N₄ have been studied in the process of water decomposition [5, 25-27]. The authors of the present article are currently working on studying the photocatalytic properties of α -Ge₃N₄.

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