ISSN: 2993-5326

Journal of Applied Surface Science

Short Communication

Gas Etching of Germanium Surface with Water Vapors Contained in Nitrogen-Containing Reagents

I Nakhutsrishvili[1*], Z Adamia[2] and G Kakhniashvili[1]

[1]*Georgian Technical University, Tbilisi*

[2]*Sukhumi State University, Georgia*

[*]Corresponding Author
I. Nakhutsrishvili, Georgian Technical University, Tbilisi, Georgia.

Submitted: 2024, Nov 08; **Accepted:** 2024, Dec 02; **Published:** 2024, Dec 13

Citation: Nakhutsrishvili, I., Adamia, Z., Kakhniashvili, G. (2024). Gas Etching of Germanium Surface with Water Vapors Contained in Nitrogen-Containing Reagents. *J Applied Surf Sci, 2*(2), 01-05.

Abstract

The reactions of nitridation of the surface of single-crystallyne germanium in wet ammonia, in hydrazine and hydrazine-hydrate vapors have been studied. In these processes, nitride is formed - a mixture of the α- and β-modifications of germanium nitride Ge_3N_4. In this case, the relative content of the α-phase increases with the degree of humidity of the gas reagent. The formation of nitride is preceded by the process of etching the surface of germanium with water vapor contained in ammonia and hydrazine. The activation energies of this process are ~46 kcal/mol in the case of ammonia, ~53 kcal/mol in the case of concentrated hydrazine and ~48 kcal/mol in the case of hydrazine-hydrate.

Keywords: Ammonia, Hydrazine, Water Vapor, Gas Etching

1. Introduction

Etching of germanium surface is widely used in semiconductor technology. The most common components of germanium etchants are HNO_3, HF and H_2O_2. Nitric acid is a strong oxidizer of germanium, and hydrofluoric acid dissolves germanium dioxide well. Additives that act as accelerators of the chemical reaction (Br) or retarders ($C_2H_4O_2$) are sometimes added to the main components of the etchant. NH_4OH, H_2O, mixture H_2O_2-NH_4OH-H_2O, HBr, HNO_3-H_2O, HF-HNO_3, HF-HNO_3-CH_3COOH, Cl_2 or CF_4 RF plasma Cl_2-HBr, H_3PO_4-CH_3COOH-HNO_3-H_2O, $N(CH_3)_4OH$ or other alkaline solutions, HF-H_2O_2-CH_3COOH, CH_3CO_3H and others [1-13].

Etching of germanium is mainly used to clean the surface before the technological process. But it can also be carried out by interaction of germanium with gases containing water vapor. In particular, this occurs during the nitridation of germanium with moistened ammonia or hydrazine vapor, which almost always contains a certain amount of water (see below).

2. Experimental

In the experiments, we used plates of single-crystal germanium doped with Sb (concentration of charge carriers $\cong 2\cdot10^{14}cm^{-3}$, resistivity ≅35 Ohmcm, orientation {111}). They were successively degreased in boiling toluene, dried in the air, etched in a liquid etchant HF-HNO_3-CH_3COOH = 1:15:1 for (4-5) min and, washed in running distilled water, followed by drying. Ammonia (freezing point -33.4°C) was purified by passing it through a trap cooled with a mixture of liquid nitrogen and alcohol. Water vapor was then introduced into the reactor at different pressures (pressure of ammonia itself $P_{NH3} \cong 2\cdot10^3$Pa). Commercial hydrazine-hydrate

(50 mol% or 64 wt% N_2H_4) was dehydrated by Raschig's method with modification: before distillation, it was boiled with NaOH in an inert N_2 atmosphere at 120°C for 2 hours [14]. The resulting liquid had a density (at 20°C) of $\rho \cong 1.008$ g/cm^3 and a refractive index of $n_D^{20} \cong 1.471$. The inlet pressure of hydrazine vapors was $P_{N2\ H4} \cong 1.6\cdot10^3$Pa, which increased (1.7÷2.9) times during the process depending on temperature of reaction. Its interval was 650-800oC. In the experiments were used methods of X-ray analysis (diffractometer HZG-4A, CuK_α radiation) and microgravimetry (scales designed by the Institute of Physical Chemistry with a sensitivity of 10^{-6} g). On the germanium surface the scale were formed, where according to X-ray analysis, was a mixture of α- and β-modifications of germanium nitride Ge_3N_4. The kinetics of reactions was studied using the gravimetric method the kinetics of reactions was studied.

3. Results and Discussion

Joint reactions $3Ge+4NH_3 \rightarrow Ge_3N_4+6H_2$ and $Ge+H_2O \rightarrow GeO+H_2$
The interaction of ammonia with germanium has been studied in a fairly large number of works [15-26]. The work found that 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-Ge_3N_4* as well as their mixtures with practically any ratio [26]. It was also shown that during the simultaneous occurrence of nitridation and oxidation reactions of the germanium surface, an amorphous oxynitride ($Ge_xO_yN_z$) film is deposited on the semiconductor (Si, GaAs, InP) substrate located in the cold zone of the reactor.

Foonnote:

*Ge3N4 exists in several crystalline modifications: α-, β- and δ-(hexagonal syngonies), γ-(cubic syngony) [27-29]. Theoretically, t- (tetragonal), m- (monoclinic) and o- (orthorhombic) syngonies of nitride are also considered [30,31]. Among these modifications, only the α- and β-phases are stable at normal pressures and temperatures.

Fig.1 shows kinetic curves of the decrease of the mass of a germanium sample at the initial stage of the process at different degrees of ammonia humidity. It is evident that at the same temperatures, the intensity of the mass reduction is greater, the higher the value of P. This decrease is due to the etching of the germanium surface by water vapor with the formation of volatile GeO (Fig.2). It is also evident that at a fixed P, the etching rate increases with increasing process temperature. (Figures of the etching of surface Ge {111} are shown in the photo - Fig.2.) As for the phase composition of the solid products of reaction, a tendency is observed for a decrease of the relative content of the β-phase in the nitride with increasing P.

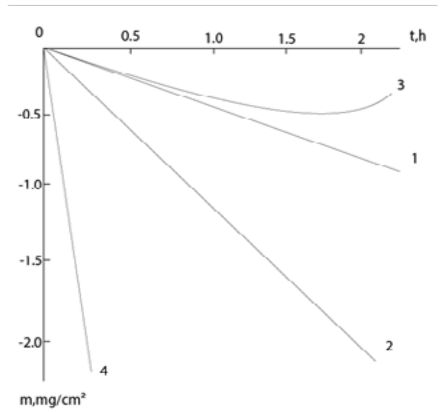

Figure 1: Kinetic Curves of the Change of the Mass of a Germanium Sample for $P \equiv P_{H2O}/P_{NH3}$=0.02 (1), 0.05 (2) at 800°C and 0.1 (3), 0.25 (4) at 700°C.

Figure 2: Typical Etching Figures of the Ge {111} Surface (1x200).

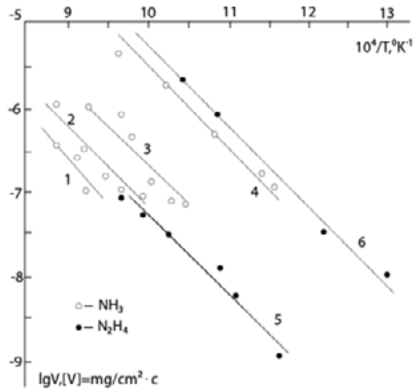

Figure 3: Temperature Dependences of the Etching Rate of the Germanium Surface in Wet Ammonia at P=0.02 (1), 0.04 (2), 0.1 (3), 0.125 (4), in concentrated hydrazine vapors (5) and hydrazine-hydrate (6).

Fig.3 shows the temperature dependences of the etching rate of the germanium surface in Arrhenius coordinates at different degrees of ammonia humidity. The activation energy determined from them lies within the range of 46 kcal/mol, which is in satisfactory agreement with the literature data on the heat of evaporation of GeO (45-55 kkal/mol) [32,33]. Based on all of the above, it can be assumed that the phase composition of Ge3N4 is an indicator of the degree of ammonia humidity.

Joint reactions $3Ge+2N_2H_4 \rightarrow Ge_3N_4+4H_2$ and $Ge+H2O \rightarrow GeO+H_2$

Hydrazine is widely used in technology and industry, in particular, it is a component of the fuel of space rockets [34-44]. Hydrazine is called "high-purity" when its water content does not exceed 1 mass.% and "ultra-pure" when its water content is a maximum of 0.5 mass.% H_2O. Based on the physical characteristics of the hydrazine we used (see section "Experimental"), it could be concluded that it is 100% N_2H_4, according to the literature data. However, this is not the case, as shown in work, where the preliminary stages of the process of interaction of hydrazine vapor with the surface of germanium were studied in detail [25]. In particular, it has been shown that the physical characteristics of freshly distilled hydrazine do not change for several months. However, the kinetics of its interaction with the germanium surface changes over time - a gradual increase in the etching rate occurs at the same temperature (Fig.3). And in the surface product, the relative content of the phase increases, as in the case of gradual moistening of ammonia (Fig.4). Control experiments were carried out using hydrazine-hydrate, in the vapors of which nitride is no longer formed and only intensive etching of the germanium surface occurs (Fig.3). Thus, here too, all of the above can be considered an indicator of the degree of humidity of the gas reagent.

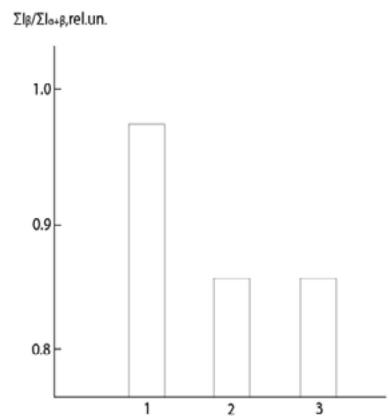

Figure 4: Histograms of the ratio of the intensities of the main X-ray reflections of the α- and β-Ge_3N_4 obtained by nitridation of germanium at 700°C: a process carried out immediately after distillation of hydrazine (1), two weeks after distillation (2), and a month later (3).

4. Conclusion

The reactions of nitridation of the surface of single-crystal germanium in wet ammonia, in hydrazine and hydrazine-hydrate vapors have been studied. In wet ammonia and concentrated hydrazine vapor, nitride Ge_3N_4 is formed, and in the vapor of hydrazine hydrate, nitride is no longer formed the formation of nitride is preceded by the process of etching the surface of germanium with water vapor contained in ammonia and hydrazine. The activation energies of this process are ~58 kcal/mol in the case of ammonia, ~53 kcal/mol in the case of concentrated hydrazine and ~48 kcal/mol in the case of hydrazine-hydrate.

References

1. Han, Y., Li, Y., Song, Y., Chi, C., Zhang, Z., Liu, J., ... & Wang, S. (2018). A comparative study of selective dry and wet etching of germanium–tin (Ge1− xSnx) on germanium. *Semiconductor Science and Technology, 33*(8), 085011.
2. Kim, D. G., Vereecke, G., Puttarame Gowda, P., Wostyn, K., Kim, T. G., Park, J. G., & Altamirano-Sanchez, E. (2023). Investigation of Selective Wet Etching of SiGe Substrates for High-Performance Device Manufacturing. *Solid State Phenomena, 346,* 34-39.
3. Molina, A., Shallenberger, J. R., & Mohney, S. E. (2020). Vapor phase passivation of (100) germanium surfaces with HBr. *Journal of Vacuum Science & Technology A, 38*(2).
4. Kern, W. (1978). Chemical etching of silicon, germanium, gallium arsenide, and gallium phosphide. *RCA Rev, 39*(2), 278-308.
5. Xie, L., Zhu, H., Zhang, Y., Ai, X., Li, J., Wang, G., ... & Radamson, H. H. (2021). Investigation on Ge0. 8Si0. 2-selective atomic layer wet-etching of Ge for vertical gate-all-around nanodevice. *Nanomaterials, 11*(6), 1408.
6. Porret, C., Vohra, A., Sebaai, F., Douhard, B., Hikavyy, A., & Loo, R. (2018). A new method to fabricate Ge nanowires: Selective lateral etching of GeSn: P/Ge multi-stacks. *Solid State Phenomena, 282,* 113-118.
7. Fischer, A. C., Belova, L. M., Rikers, Y. G., Malm, B. G., Radamson, H. H., Kolahdouz, M., ... & Niklaus, F. (2012). 3D Free-Form Patterning of Silicon by Ion Implantation, Silicon Deposition, and Selective Silicon Etching. *Advanced Functional Materials, 22*(19), 4004-4008.
8. Wang, X., Chen, C., Feng, S., Wei, X., & Li, Y. (2017). A hybrid functional first-principles study on the band structure of non-strained Ge1− xSnx alloys. *Chinese Physics B, 26*(12), 127402.
9. Y. J. Lee, F. J. Hou, S. S. Chuang et al., In Proceedings of the (2015) IEEE International Electron Devices Meeting (IEDM), Washington, DC, USA, 7–9 December 2015, 1511–1514.
10. Choi, Y., Cho, C., Yoon, D., Kang, J., Kim, J., Kim, S. Y., ... & Ko, D. H. (2022). Selective Etching of Si versus Si1−xGex in Tetramethyl Ammonium Hydroxide Solutions with Surfactant. *Materials, 15*(19), 6918.
11. Liu, W. D., Lee, Y. C., Sekiguchi, R., Yoshida, Y., Komori, K., Wostyn, K., ... & Holsteyns, F. (2018). Selective wet etching in fabricating SiGe and Ge nanowires for gate-all-around MOSFETs. *Solid State Phenomena, 282*, 101-106.
12. Holländer, B., Buca, D., Mantl, S., & Hartmann, J. M. (2010). Wet Chemical Etching of Si, Si1− x Ge x, and Ge in HF: H2O2: CH3COOH. *Journal of The Electrochemical Society, 157*(6), H643.
13. Xie, L., Zhu, H., Zhang, Y., Ai, X., Wang, G., Li, J., ... & Radamson, H. H. (2020). Strained Si0. 2Ge0. 8/Ge multilayer stacks epitaxially grown on a low-/high-temperature ge buffer layer and selective wet-etching of germanium. *Nanomaterials, 10*(9), 1715.
14. Audrieth, L. F., Ogg, B. A. (1951). The chemistry of hydrazine. John Wiley & Sons, Inc. New York, p. 225.
15. Lee, S., Song, K., & Lim, S. (2024). Control of selective SiGe etching by enhanced formation of hydroxyl radicals and by surface passivation in peracetic acid solution. *Applied Surface Science*, *661*, 160063.
16. Yang, X., Reijerse, E. J., Bhattacharyya, K., Leutzsch, M., Kochius, M., Nöthling, N., ... & Cornella, J. (2022). Radical activation of N–H and O–H bonds at bismuth (II). *Journal of the American Chemical Society, 144*(36), 16535-16544.
17. Wu, Y., Li, M., Luo, X., Wei, C., Deng, Z., Li, X., ... & Sun, P. (2024). Selective separation of zinc from germanium-bearing iron cake via a roasting–leaching process. *Separation and Purification Technology, 337*, 126166.
18. Alguacil, F. J., & Robla, J. I. (2024). Some Recent Advances in Germanium Recovery from Various Resources. *Metals, 14*(5), 559.
19. Ma, B., Li, D., Wang, X., & Lin, K. (2018). Fast and safe synthesis of micron germanium in an ammonia atmosphere using Mo 2 N as catalyst. *RSC advances, 8*(62), 35753-35758.
20. Di, H., Hong, Y., Liang, M., Song, L., Yang, K., & Zhang, L. (2023). Efficient stepwise-purification and mechanism of germanium-containing materials with ammonium. *Arabian Journal of Chemistry, 16*(10), 105119.
21. Wu, Yuangui, Minting Li, Xiaohua Peng, Chang Wei, Xingbin Li, Zhigan Deng, Xingguo Luo, Fu Ye, Bo Yang, and Pu Sun. "Selective extraction of germanium from iron-bearing ammonia leaching residue via low-temperature molten NaOH leaching." *Separation and Purification Technology 353* (2025): 128590.
22. Fireman, M. N., L'Heureux, G., Wu, F., Mates, T., Young, E. C., & Speck, J. S. (2019). High germanium doping of GaN films by ammonia molecular beam epitaxy. *Journal of Crystal Growth, 508*, 19-23.
23. Liu, Y., Ho, L. T. A., Huang, G. Z., Chen, Y. C., Ungur, L., Liu, J. L., & Tong, M. L. (2021). Magnetization Dynamics on Isotope-Isomorphic Holmium Single-Molecule Magnets. *Angewandte Chemie International Edition, 60*(52), 27282-27287.
24. Nakhutsrishvili, I. (2020). Study of Growth and Sublimation of Germanium Nitride Using the Concept of Tedmon's Kinetic Model. *Oriental Journal of Chemistry, 36*(5), 850.
25. Nakhutsrishvili, I., Kokhreidze, R., & Kakhniashvili, G. (2022). Pre-stages of the Formation of Ge3N4 on the Surface of Syngle-crystal Germanium in Hydrazine Vapors. *Oriental Journal of Chemistry, 38*(1).
26. Wardosanidze, Z. V., Nakhutsrishvili, I., & Kokhreidze, R. (2024). Conditions of Formation of α-and β-Modifications of Ge3N4 and Preparation of Germanium Oxynitride Dielectric Films. *Journal of Coating Science and Technology, 11*.
27. Soignard, E., McMillan, P. F., Hejny, C., & Leinenweber, K. (2004). Pressure-induced transformations in α-and β-Ge3N4: in situ studies by synchrotron X-ray diffraction. *Journal of Solid State Chemistry, 177*(1), 299-311.
28. Luo, Y., Cang, Y., & Chen, D. (2014). Determination of the finite-temperature anisotropic elastic and thermal properties

of Ge3N4: A first-principles study. *Computational Condensed Matter, 1*, 1-7.
29. Feldbach, E., Zerr, A., Museur, L., Kitaura, M., Manthilake, G., Tessier, F., ... & Kanaev, A. (2021). Electronic band transitions in γ-Ge 3 N 4. *Electronic Materials Letters*, *17*, 315-323.
30. Cang, Y., Yao, X., Chen, D., Yang, F., & Yang, H. (2016). First-principles study on the electronic, elastic and thermodynamic properties of three novel germanium nitrides. *Journal of Semiconductors, 37*(7), 072002.
31. Yuping, C., Dong, C., Fan, Y., & Huiming, Y. (2016). Theoretical Studies on Tetragonal, Monoclinic and Orthorhombic Distortions of Germanium Nitride Polymorphs. *Chemical Journal of Chinese Universities-Chinese, 37*(4), 674-681.
32. Inoue, M. (1972). Etching of germanium with water vapor. *Japanese Journal of Applied Physics, 11*(8), 1147.
33. Arslambekov, V. A., Rozhansky, N. V. (1983). Kinetics of interaction of germanium surface with oxygen and evaporation of formed oxides in vacuum. *Surface, 3,* 95-98.
34. Schmidt, E. W. (2001). Hydrazine and Its Derivatives: Preparation, Properties, Applications, 2 Volume Set. John Wiley & Sons.
35. Dang, H., Wu, J., Song, L., & Shi, G. (2024). Exploring the application of hydrazine hydrate in protonic ceramic fuel cells: Strategies and performance improvements. *Journal of Power Sources*, *605*, 234532.
36. Shimizu, T., Yamamoto, K., Pandit, P., Yoshikawa, H., & Higashibayashi, S. (2018). Application of hydrazine-embedded heterocyclic compounds to high voltage rechargeable lithium organic batteries. *Scientific reports, 8*(1), 579.
37. Koech, J. K., Shao, Q., Mutua, F. N., & Wang, Y. (2013). Application of hydrazine hydrate in the synthesis of octa (aminophenyl) silsesquioxane (OAPS) poss.
38. Gerdes, T. W. (2023). A review of hydrazine and its applications. Nova, New York.
39. Pakdehi, S., Shirvani, F., & Zolfaghari, R. (2019). A thermodynamic study on catalytic decomposition of hydrazine in a space thruster. *Archives of Thermodynamics, 40*(4), 151-166.
40. Wilson, M. (2012). Session: LP-10: Spacecraft Engines and Propulsion Systems. 10-13, Tucson, Arison, 97009.
41. Kamble, P., Sinharoy, P., Yevale, P., Ananthanarayanan, A., Banerjee, D., Sugilal, G., ... & Bhattacharya, D. (2020). A comparative evaluation of LHT-9 layered titanates synthesized by reflux and microwave routes for waste treatment applications. *Journal of Radioanalytical and Nuclear Chemistry*, *326*, 209-214.
42. Carlotti, S., & Maggi, F. (2022). Evaluating new liquid storable bipropellants: *Safety and performance assessments. Aerospace, 9*(10), 561.
43. Dzhanelidze, R., Adamia, Z., Loria, L., & Nakhutsrishvili, I. (2024). *Catalytic Decomposition of Hydrazine on Germanium. Georgian Scientists, 6*(1), 227-231.
44. Kakhniashvili, G. Adamia, Z. Nakhutsrishvili, I. (2024). 2nd Edition of Strenuous World Congress on Catalysis, *Chemical Engineering and Technology*, 16-17 April, 2024, London, UK.