***Journal of Coating Science and Technology*, 2024, *11*, 1-5**

Journal of Coating Science and Technology
http://www.lifescienceglobal.com/journals/journal-of-coating-science-and-technology

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

Zurab V. Wardosanidze, Irakli Nakhutsrishvili* and Revaz Kokhreidze

Institute of Cybernetics of Georgian Technical University, Tbilisi, Georgia

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.

Received on 27-02-2024
Accepted on 21-08-2024
Published on 04-09-2024

Keywords: Germanium nitride, crystalline modifications, oxynitride films.

https://doi.org/10.6000/2369-3355.2024.11.01

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:

$$3Ge+4NH_3Ge_3N_4+6H_2 \quad (1)$$

and

$$3GeO_2+4NH_3Ge_3N_4+6H_2O \quad (2)$$

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 Ω·cm, orientation {111} or {100}) in the NH_3+H_2O medium at 640-840°C under static vacuum conditions. Germanium plates were etched in a liquid etchant CP-4A ($HF:HNO_3:CH_3COOH$ = 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: $P \equiv P_{H2O}/P_{NH3} \cong 1$, 2.5, 4, and 12.5%. The duration of the

---

*Institute of Cybernetics of Georgian Technical University, Tbilisi, Georgia;
E-mail: iraklinakhutsrishvili52@gmail.com

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

reaction was 2 hours. The obtained nitride was analyzed by X-ray (diffractometer HZG-A, 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 ≅ 630°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≅20%, nitride formation stops).

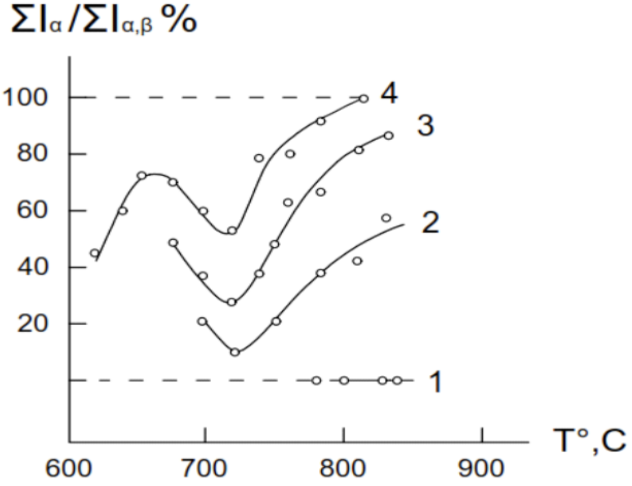
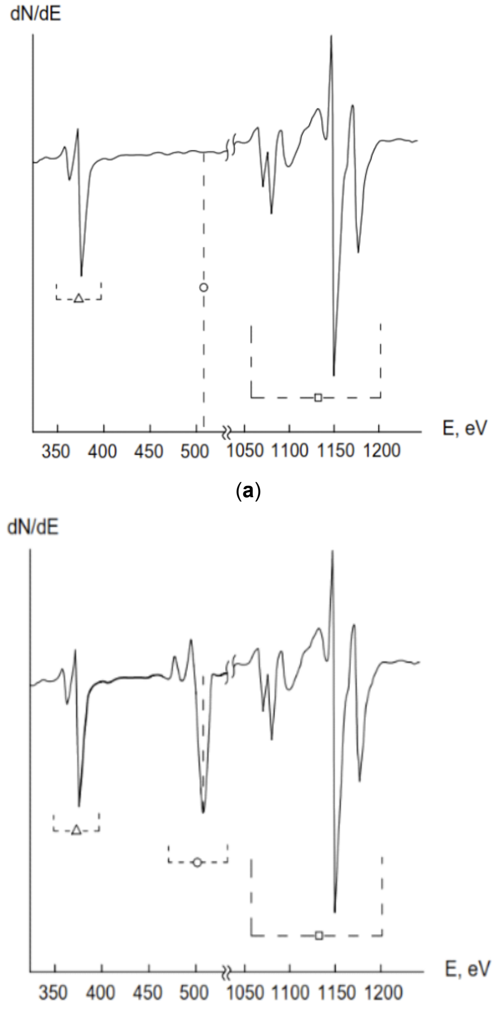


Figure 1: Dependences I ≡ ΣI(α)/ΣI(α,β) on the nitridation temperature of germanium at P≅1 (1), 2.5 (2), 4 (3) and 12.5% (4).

It should be noted that water vapor forms volatile germanium monoxide (Ge+H$_2$O→GeO+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 dependences of the evaporation rate of Ge$_3$N$_4$ and GeO in Arrhenius coordinates are shown in Figure **3**. The activation energies (heats of vaporization) calculated from these dependencies are ~245 (for α-Ge$_3$N$_4$), ~290 (for β-Ge$_3$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 α-Ge$_3$N$_4$ is thermally less stable than β-Ge$_3$N$_4$ and can evaporate at lower temperatures (GeO is even less stable).



(**a**)

(**b**)

Figure 2: Auger-spectrum of: germanium nitride (**a**) and its film (**b**); ∆-N, o - O, □ - Ge.

With the simultaneous evaporation of Ge$_3$N$_4$ and GeO in the “cold” (300÷350°C) zone of the reactor, a film is deposited on substrates Si, Al$_2$O$_3$, 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 (Ge$_x$N$_y$O$_z$). One band appears in the IR spectrum of the films (Figure **4**). Its position changes in the region (780-820) cm^{-1} depending on the temperature of their preparation. This single band, located between bands of Ge$_3$N$_4$ (~750 cm^{-1}) and GeO$_2$ (~890 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.

---

[2] Auger-spectroscopy presents a chemical analysis: each element is characterized by ifs peaks in the Auger-spectrum.
There was an assumption that α-Si$_3$N$_4$ (to which α-Ge$_3$N$_4$ is isostructural) contains oxygen and is an oxynitride (but this has not been proven). However, oxynitrides Si$_2$N$_2$O and Ge$_2$N$_2$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 α-Ge$_3$N$_4$ practically does not affect its crystal structure.

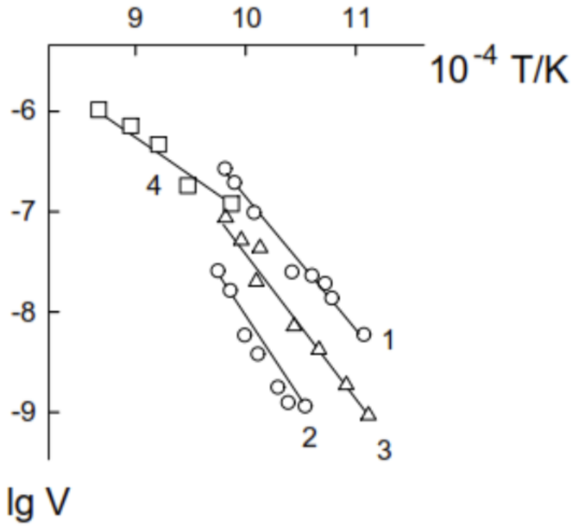


Figure 3: Temperature dependences of α-Ge_3N_4 (1), β-Ge_3N_4 (2), their mixtures with approximately the same content (3) and GeO (4) in Arrhenius coordinates.

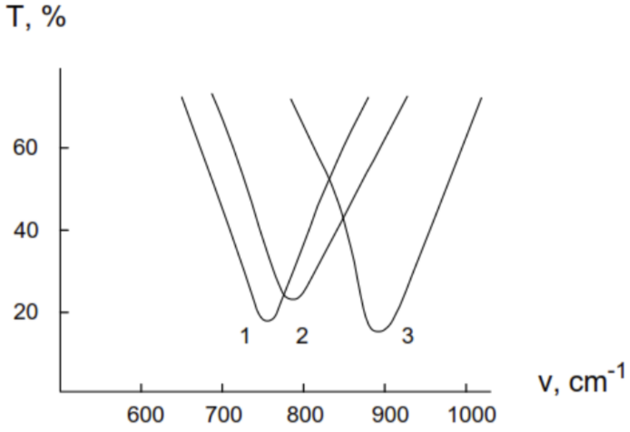


Figure 4: IR absorption spectra of films of nitride (1), oxynitride (2), and dioxide (3) of germanium.

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.

$Ge_xN_yO_z$ films find application in microelectronics as a fermeture layer [20-23].

We have studied the change of the sign of the charge at the interface $Ge_xN_yO_z$-Si with increasing germanium nitridation temperature. Figure **6** shows the temperature dependence of the flat band voltage (V_{FB})[4] in the structure Al-$Ge_xN_yO_z$-Si. As can be seen from this figure, for $Ge_xN_yO_Z$ films obtained 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.

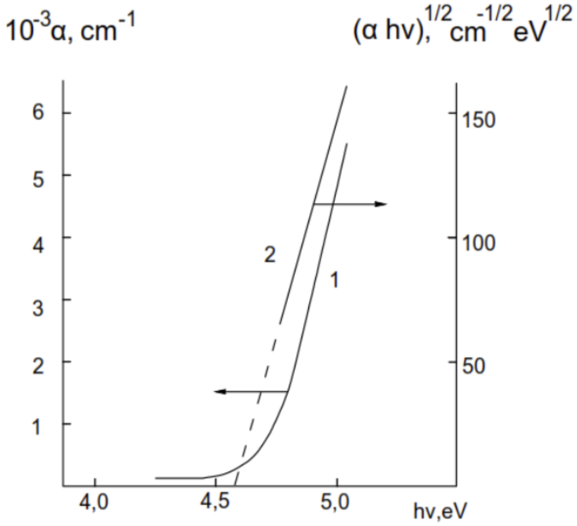


Figure 5: Electronic absorption spectra of $Ge_xN_yO_z$ films in coordinates α – hv (1) and αhv – hv (2).

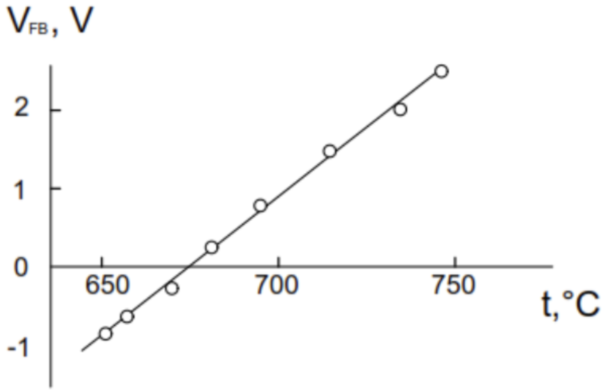


Figure 6: Dependence of the flat band voltage in the Al-$Ge_xN_yO_z$-Si structure on the temperature of preparation of germanium nitride.

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

---

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

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

nitride in the form of pure α- and β-Ge_3N_4, as well as their mixtures with practically any ratio.

2. The formation of germanium nitride in humid ammonia is accompanied by its simultaneous evaporation.
3. Water vapor forms volatile germanium monoxide, which evaporates completely and does not remain in the surface product.
4. Heats of vaporization are: ~245 for α-Ge_3N_4, ~290 for β-Ge_3N_4, ~255 for a mixture with their approximately equal content and ~221 kJ/mol for GeO, respectively.
5. Simultaneous evaporation of germanium nitride and oxide results in the deposition of a film of germanium oxynitride in the cold zone of the reactor.
6. This film is a germanium oxynitride used in microelectronics as a dielectric layer in Metal-Insulator-Semiconductor systems.

APPENDIX

Ge_3N_4 can be obtained also by nitridation of elemental germanium in hydrazine vapor: $3Ge+2N_2H_4 \rightarrow Ge_3N_4+4H_2$. Dehydration of hydrazine (pre-boiling with NaOH in an inert N_2 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% N_2H_4. Nevertheless, in such hydrazine vapor at 700°C, we obtained β-Ge_3N_4 along with traces of a-phase. When the refractive index was ≅1.463 (~ 5 mass% H_2O), pure α-Ge_3N_4 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-Ge_3N_4 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-Ge_3N_4.

REFERENCES

[1] Lin Y, Zhang Sh. Reactive DC magnetron sputtering induced the formation of amorphous CuN films embedded nanocrystalline WC phase. Journal of Coating Science and Technology 2016; 3: 23-28. https://doi.org/10.6000/2369-3355.2016.03.01.3

[2] Hsu Ch-H, Liu H-T, Huang W-Ch, Lin M-R. Effect of post-heated TiN coating on pitting corrosion of austenitic stainless steel. Journal of Coating Science and Technology 2015; 2: 93-99. https://doi.org/10.6000/2369-3355.2015.02.03.4

[3] AK, Savin SS, Poklonskaya ON, Trofimov NS. Growth of Si-doped polycrystalline diamond films on AlN substrates by microwave plasma chemical vapor deposition. Journal of Coating Science and Technology 2015; 2: 38-45. https://doi.org/10.6000/2369-3355.2015.02.02.1

[4] Mallem K, Jagadeesh Chandra, SV, Ju M, Dutta S, Ramana CHVV, Hussain Sh. Q, Park J, Kim Y, Cho Y-H, Cho E-Ch, Yi J. Influence of ultra-thin Ge_3N_4 passivation layer on structural, interfacial, and electrical properties of HfO_2/Ge Metal-Oxide–Semiconductor devices. Nanosciience Nanotechnology 2020; 20: 1039-1045. https://doi.org/10.1166/jnn.2020.16934

[5] Ma Y, Wang M, Zhou X. First-principles investigation of β-Ge_3N_4 loaded with RuO_2 cocatalyst for photocatalytic overall water splitting. Energy Chemistry 2020; 44: 24-32. https://doi.org/10.1016/j.jechem.2019.09.013

[6] Huang Z, Su R, Yuan H, Zhang J, Chen F, Shen Q, Zhang L. Synthesis and photoluminescence of ultra-pure α-Ge_3N_4 nanowires. Ceramics International 2018; 4: 10858-10862. https://doi.org/10.1016/j.ceramint.2018.03.137

[7] Kim Sh, Hwang G, Jung J-W, Cho S-H, Cheong JY, Shin S, Park S, Kim I-D. Fast, scalable synthesis of micronized Ge_3N_4 @C with a high tap density for excellent lithium storage. Advanced Functional Materials 2017; 7: 1605975. https://doi.org/10.1002/adfm.201605975

[8] Maggoini G, Carturan S, Fiorese L, Pinto N, Caproli F, Napoli DR, Giarola M, Mariotto G. Germanium nitride and oxynitride films for surface passivation of Ge radiation detectors. Applied Surface Science 2017; 393: 119-126. https://doi.org/10.1016/j.apsusc.2016.10.006

[9] Yayak YO, Sozen Y, Tan F, Gungen D, Gao Q, Kang J, Yagmurcukardes M, Sahin H. First-principles investigation of structural, Raman and electronic characteristics of single layer Ge_3N_4. Applied Surface Science 2022; 572: 15136. https://doi.org/10.1016/j.apsusc.2021.151361

[10] Soignard E, McMillan PF, Hejny C, Leinenweber K. Pressure-induced transformations in α- and β-Ge_3N_4: In situ studies by synchrotron X-ray diffraction. Solid State Chemistry 2004; 177: 299-311. https://doi.org/10.1016/j.jssc.2003.08.021

[11] LuoY, Cang Y, Chen D. Determination of the finite-temperature anisotropic elastic and thermal properties of Ge_3N_4. Computat Condens Matter 2014; 1: 1-7. https://doi.org/10.1016/j.cocom.2014.08.001

[12] Feldbach F. *et al*. Electronic band transitions in γ-Ge_3N_4. Electronic Mater Lett 2021; 17: 315-323. https://doi.org/10.1007/s13391-021-00291-y

[13] Cang Y, Yao X, Chen D, Yang F, Yang H. First-principles study on the electronic, elastic, and thermodynamic properties of three novel germanium nitrides. Semiconductors 2016; 37(7): 072002. https://doi.org/10.1088/1674-4926/37/7/072002

[14] Cang Y, Chen D, Yang F, Yang H. Theoretical studies of tetragonal, monoclinic, and orthorhombic distortions of germanium nitride polymorphs. Chem Chinese Universities 2016; 37(4): 674-681.

[15] Paszkowicz W, *et al*. High-pressure study of α and β polymorphs of germanium nitride. Synchrotr Rad Natural Sci 2007; 6(1/2): 28-29.

[16] Samsonov GV, Kulyk OP, Polyshchuk VS. 1978. Obtain and methods of analysis of nitrides. Kiev, Naukova Dumka 320.

[17] Remy JC, Pauleau Y. Conditions of formation of alpha and beta phases of germanic nitride. Inorg Chem 1976; 15(9): 2308-2310. https://doi.org/10.1021/ic50163a068

[18] Nakhutsrishvili I. Study of growth and sublimation of germanium nitride using the concept of Tedmon's kinetic model. Oriental J Chem 2020; 36(5): 850-854. https://doi.org/10.13005/ojc/360508

[19] Billy M, Labbe JC. Sur la thermolyse du nitrure de germanium. Compt Rend Acad Sci Paris ser C 1971; 813-816.

[20] Bayraktaroglu B, Johnson RL, Langer DW, Mier MG. Germanium (oxy) nitride-based surface passivation technique as applied to GaAs &InP. Phys. MOS Insulators, Nort. Carolina, USA 1980; 301. https://doi.org/10.1016/B978-0-08-025969-7.50043-9

[21] Bagratishvili GD, Dzhanelidze RB, Kurdiani NI, Saksaganskii OV. MIS structure GaAs-Ge_3N_4-Al. Phys Stat Sol (a) 1976; 36: 73-79. https://doi.org/10.1002/pssa.2210360107

[22] Pinto N, *et al*. Thermally induced irreversibility in the conductivity of germanium nitride and oxynitride films. Materials Sci in Semiconductor Process, 2018; 74: 57-63. https://doi.org/10.1016/j.mssp.2017.10.006

[23] Sze SM, Li Y, Ng KK. Physics of Semiconductor Devices. Wiley & S., N.-Y., USA 2021; 944.

[24] Audrieth LF, Mohr PH. The chemistry of hydrazine. Chem Eng 2010; 26(51): 3746-3749. https://doi.org/10.1021/cen-v026n051.p3746

[25] Sato J, Saito N, Yasmada Y, Maeda K, Takata T, *et al*. RuO_2 –loaded β-Ge_3N_4 as a non-oxide photocatalyst for overall water splitting. J Am Chem Soc 2005; 127(12): 4150-4151. https://doi.org/10.1021/ja042973v

[26] Lee Y, Watanabe T, Takata T, Hara M, Yoshimura M, Domen K. Effect of high-pressure ammonia treatment on the activity of Ge_3N_4 photocatalyst for overall water splitting. J Phys Chem B 2006; 110(35): 17563-17569. https://doi.org/10.1021/jp063068v

[27] Maeda K, Domen K. New non-oxide photocatalysts designed for overall water splitting under visible light. J Phys Chem C 2007; 111: 7851-7861. https://doi.org/10.1021/jp070911w