Reactor materials for high purity HVPE GaN growth: a thermodynamic analysis

Vladislav Voronenkov, Natalia Bochkareva, Andrey Zubrilov, Andrey Leonidov, Yuri Shreter
Ioffe Institute, Politehnicheskaya 26, St. Petersburg, 194021, Russia
E-mail: voronenkov@mail.ioffe.ru

Abstract. The chemical resistance of quartz, aluminum oxide, boron nitride, molybdenum, and platinum in the environment of the hydride vapor phase epitaxy of gallium nitride was estimated by chemical equilibrium calculation. The interaction of materials with hydrogen, hydrogen chloride, chlorine, ammonia, and gallium chlorides was analyzed. The conditions in which the use of each material is permissible were determined.

1. Introduction
Hydride vapor-phase epitaxy is today the primary method for producing GaN substrates. The low level of impurity doping is necessary to obtain non-compensated semi-insulating substrates, to achieve high thermal conductivity [1, 2] and to grow drift layers of high-voltage devices. To obtain highly pure epitaxial layers, it is necessary to minimize the level of unintentional doping, in particular, to minimize the emission of impurities from the materials of the reactor. Most of the HVPE GaN growth reactors described in the literature, starting from the pioneering study by Maruska and Tietjen [3, 4], contain quartz parts [5–13]. A significant disadvantage of quartz is its insufficient chemical resistance. During the early development of III-V crystal growth technology, quartz was identified as a source of silicon and oxygen contamination, [14–18], and decomposition of quartz reacting with liquid gallium, hydrogen, and hydrogen chloride was studied [14, 18]. Quartz-related contamination can be significantly reduced by substituting quartz with more chemically resistant materials [17, 19] or by excluding quartz from the hot zone of the reactor [20].

In this paper, the chemical resistance of quartz, aluminum oxide, boron nitride, and molybdenum is estimated by chemical equilibrium calculation.

2. Calculation procedure
Schematic diagram of a conventional HVPE GaN growth system is shown in figure 1. Nitrogen, argon, or hydrogen is used as a carrier gas. Gallium is transported to the growth chamber in the form of gallium monochloride [4] or gallium trichloride [21–23]. Gallium monochloride is obtained by chlorination of gallium [4] or trimethylgallium [24, 25] at a temperature of about 600–800 °C. Gallium trichloride is delivered as vapor from a bubbling evaporator [22] or is formed by the reaction of monochloride and an excess of chlorine [23]. Ammonia is fed through a separate channel and mixed with gallium chloride in the growth zone near the substrate.
Following gases and gas mixtures were chosen to perform comparison of material resistivity in HVPE reactor atmosphere: Hydrogen, which is used as a carrier gas, alone or mixed with nitrogen; HCl, HCl diluted with H₂ and Cl₂ used to obtain gallium chlorides in the boat, to control the supersaturation in the growth process and for dry cleaning of the growth chamber of the reactor; NH₃, the nitrogen precursor; GaCl₃, a gallium precursor in tri-halide HVPE; a mixture of GaCl₃:H₂:HCl in a ratio of 4:4:1 - a typical composition of the products of gallium chlorination carried out in the boat using hydrogen chloride.

To calculate the chemical equilibrium, a hierarchical [26–28], method was used with some modifications to increase the convergence rate [29]. In comparison with the non-stoichiometric methods [30, 31], the hierarchical method shows steady convergence in problems where one or several condensed species and gaseous species with low equilibrium pressure are taken into account in the calculation.

Thermochemical properties of substances from [32–38] were used. No preliminary assumptions were made about the composition of the system; the calculation accounted for all species for which thermochemical data were available in the literature. The total pressure in all the calculations performed was assumed to be 1 bar; ideal gas behavior was assumed.

The interaction of quartz and Al₂O₃ with ammonia was considered in a non-equilibrium condition: the decomposition of ammonia into nitrogen and hydrogen was assumed to be kinetically inhibited; all the ammonia decomposition reactions, except for reactions of ammonia with quartz and Al₂O₃, were excluded from the calculation.
Figure 2. Equilibrium partial pressure of gaseous decomposition products of quartz in hydrogen (a), ammonia (b), hydrogen chloride (c), chlorine (d), gallium trichloride (e), and in a mixture of GaCl:H$_2$:HCl in a ratio of 4:4:1 (f).

Figure 3. Equilibrium partial pressure of gaseous decomposition products of sapphire in hydrogen (a), ammonia (b), hydrogen chloride (c), chlorine (d), gallium trichloride (e), and in a mixture of GaCl:H$_2$:HCl in a ratio of 4:4:1 (f).

Chemical equilibrium analysis does not allow to determine the exact amount of impurities emitted by the materials of the reactor since the reaction kinetics is not taken into account. However, this analysis allows estimating the upper limit of contamination caused by the decomposition of the materials of the reactor.

The following was chosen as an arbitrary criterion for chemical resistance of the material: the
Figure 4. Equilibrium partial pressure of gaseous decomposition products of boron nitride in inert gas (a), hydrogen (b), hydrogen chloride (c), chlorine (d) gallium trichloride (e), and a mixture of GaCl:H₂:HCl in a ratio of 4:4:1 (f).

total pressure of the decomposition products should not exceed 10⁻⁶ bar, which corresponds to a contamination level of 1 ppm.

The substances that were considered in the calculations are listed in table 1.

3. Results and discussion

The results of the chemical equilibrium calculations performed are shown in the figures 2 – 6. For the sake of clarity, the graphs show the partial pressures of only those material decomposition products that introduce impurities to the growth process.

3.1. Quartz (SiO₂)

In a hydrogen atmosphere, quartz can be considered resistant at temperatures up to 1000 °C. The main decomposition products in the high-temperature region are H₂O and SiO, the partial pressure of which reaches 10⁻⁴ at a temperature of 1300 °C (figure 2a).

With ammonia, quartz reacts to a large extent to form solid silicon oxynitride and water vapor (figure 2b).

In hydrogen chloride, the main products of quartz decomposition are silicon tetrachloride and water vapor, the partial pressure of which exceeds 10⁻⁴ bar already at a temperature of 600 °C (figure 2c).

In chlorine, quartz meets the chosen criterion of chemical resistance at temperatures below 600 °C; the main decomposition products are silicon tetrachloride and oxygen (figure 2d).

The main products of the reaction of quartz with gallium trichloride are the same as in the reaction with chlorine, but the partial pressure of decomposition products is approximately three orders of magnitude lower (figure 2e).

In a mixture of hydrogen GaCl and chlorine hydrogen, the chemical resistance criterion is satisfied at T<650 °C. In the low-temperature region, the main decomposition products are H₂O and SiCl₄, in the high-temperature region – H₂O and SiO (figure 2f).
Figure 5. Equilibrium partial pressure of gaseous decomposition products of molybdenum in hydrogen chloride (a), gallium trichloride (b), and a mixture of GaCl:H₂:HCl in a ratio of 4:4:1 (c).

3.2. Aluminum Oxide (Al₂O₃)

Compared with quartz, aluminum oxide is significantly more resistant in hydrogen (figure 3a) and somewhat more resistant in ammonia, in the reaction with which aluminum nitride is formed (figure 3b). However, in the atmosphere of chlorine, hydrogen chloride, GaCl₃ and a mixture of GaCl:H₂:HCl, the equilibrium pressures of decomposition products are even higher than that above quartz under similar conditions (figure 3c,d,e,f). Experimental studies of Al₂O₃ decomposition [39–41] show a kinetically limited but observable etching rate.

3.3. Boron Nitride (BN)

In hydrogen, BN meets the criterion of resistance at temperatures below 1200 °C (figure 2a). In ammonia, BN is inherently resistant. With chlorine, BN reacts completely over the entire temperature range, BCl₃ is the main decomposition product (not shown). In pure hydrogen chloride, BN is unstable, decomposing into BCl₃, N₂ and H₂, but diluting the HCl with hydrogen (figure 4c) or hydrogen:nitrogen mixture (figure 4d), shifts the reaction equilibrium and significantly reduces the decomposition of BN.

BN is less resistant than Al₂O₃ and quartz in GaCl₃ ambient (figure 4e), but more resistant than Al₂O₃ and quartz in a mixture of GaCl:HCl:H₂ (figure 4f).

3.4. Molybdenum (Mo)

The main product of the interaction of molybdenum with hydrogen chloride is molybdenum tetrachloride MoCl₄, the concentration of which substantially depends on the hydrogen content in the gas phase [38]. When diluting the hydrogen chloride with hydrogen, in a 1:1 ratio, the equilibrium pressure of MoCl₄ decreases below 10⁻⁶ bar (figure 5a).

In gallium trichloride, molybdenum is unstable (figure 5b). On the contrary, in a mixture of GaCl:H₂:HCl, the equilibrium pressure of decomposition products is below 10⁻⁹ over the entire temperature range (figure 5c).

3.5. Platinum

Platinum reacts with chlorine to form volatile chlorides of PtCl₂ and PtCl₃, the equilibrium pressure of which exceeds 10⁻⁵ bar in the entire considered range (figure 6a). When diluting chlorine with an inert gas in the ratio of 1:10, the equilibrium pressure of platinum chlorides decreases, but remains above 10⁻⁶ bar at temperatures above 700 °C (figure 6b). In hydrogen chloride, platinum is stable over the entire temperature range considered (figure 6); in a mixture of hydrogen chloride and hydrogen, the equilibrium pressures of platinum chlorides decrease to negligibly small values (figure 6d). Platinum is also stable in GaCl₃ at temperatures up
Figure 6. Equilibrium partial pressure of gaseous decomposition products of platinum in Cl₂ (a), Cl₂ diluted with an inert gas in a ratio of 1:10 (b), hydrogen chloride (c), a mixture of HCl:H₂ in a ratio of 1:1 (d), gallium trichloride (e), and a mixture of GaCl:H₂:HCl in a ratio of 4:4:1 (f).

Table 2. Materials chemical resistance calculation summary: (+) total vapor pressure of decomposition products < 10⁻⁶ bar, material is considered to be chemically resistant, (—) total vapor pressure of decomposition products > 10⁻⁶ bar.

|            | SiO₂  | Al₂O₃ | BN     | Mo   | Pt   |
|------------|-------|-------|--------|------|------|
| H₂         | (+) T<1000 °C | (+) T<1300 °C | (+) T<1200 °C | (+) | (+)  |
| NH₃        | (—)   | (—)   | (+)    | (—)  | (—)  |
| HCl        | (—)   | (—)   | (—)    | (—)  | (—)  |
| HCl:H₂     | (—)   | (—)   | (+)    | (-)  | (+)  |
| Cl₂        | (+) T<600 °C | (—)   | (—)    | (—)  | (—)  |
| GaCl₃      | (+) T<1100 °C | (+) T<900 °C | (—)   | (—)  | (—)  |
| GaCl:HCl:H₂| (—)   | (—)   | (+), T<700 °C | (+)  | (+)  |

to 1080 °C (figure 6e), and in a mixture of GaCl:H₂:HCl over the entire temperature range (figure 6f).

4. Conclusion
The chemical resistance of quartz, aluminum oxide, boron nitride, molybdenum and platinum was estimated using chemical equilibrium analysis. Summary data on the durability of the materials studied are given in the table 2. None of the materials studied is chemically resistant to all gases involved in the HVPE process. An individual selection of material for each part of the reactor is necessary to minimize the decomposition of materials and to reduce the associated impurity contamination.
References
[1] Slomski M, Paskov P P, Leach J H, Muth J F and Paskova T 2017 Phys. Status Solidi B 254 1600713
[2] Jezowski A, Churiukova O, Mucha J, Suski T, Obukhov I A and Danilchenko B A 2015 Mater. Res. Express 2 085902
[3] Tietjen J J and Amick J A 1966 J. Electrochem. Soc. 113 724–728
[4] Maruska H P and Tietjen J J 1969 Appl. Phys. Lett. 15 327–329
[5] Safvi S, Perkins N, Horton M, Matyi R and Kuech T 1997 J. Cryst. Growth 182 233 – 240
[6] Tavernier P R, Etzkorn E V, Wang Y and Clarke D R 2000 Appl. Phys. Lett. 77 1804–1806
[7] Dam C, Grzegorczyk A, Hageman P, Dorsman R, Kleijn C and Larsen P 2004 J. Cryst. Growth 271 192 – 199
[8] Segal A, Kondratyev A, Karpov S, Martin D, Wagner V and Ilegems M 2004 J. Cryst. Growth 270 384 – 395
[9] Monemar B, Larsson H, Hemmingsson C, Ivanov I and Gogova D 2005 J. Cryst. Growth 281 17 – 31
[10] Richter E, Hennig C, Weyers M, Habel F, Tsay J D, Liu W Y, Breckner P, Scholz F, Makarov Y, Segal A and Kaeppeler J 2005 J. Cryst. Growth 277 6 – 12
[11] Williams A D and Moustakas T 2007 J. Cryst. Growth 300 37 – 41
[12] Fujito K, Kubo S, Nagaoka H, Mochizuki T, Namita H and Nagao S 2009 J. Cryst. Growth 311 3011 – 3014
[13] Amilusik M, Sochacki T, Lucznik B, Bockowski M, Sadovyi B, Presz A, Dziecielewski I and Grzegory I 2013 J. Cryst. Growth 380 99 – 105
[14] Cochran C N and Foster L M 1962 J. Electrochem. Soc. 109 149–154
[15] Stearns R I and McNeely J B 1966 J. Appl. Phys. 37 933–934
[16] Greene P D 1973 J. Phys. D: Appl. Phys. 6 1550–1554
[17] Callaghan M, Patterson E, Richards B and Wallace C 1974 J. Cryst. Growth 22 85 – 98
[18] Weiner M E 1972 J. Electrochem. Soc. 119 496–504
[19] Long G and Foster L M 1959 J. Am. Ceram. Soc. 42 53–59
[20] Fujikura H, Konno T, Yoshida T and Horikiri F 2017 Jpn. J. Appl. Phys. 56 085503
[21] Nickl J, Just W and Bertinger R 1974 Mater. Res. Bull. 9 1413 – 1420
[22] Lee H and Harris J J S 1996 J. Cryst. Growth 169 689–696
[23] Hirasaki T, Asano K, Banno M, Ishikawa M, Sakuma F, Murakami H, Kumagai Y and Koukitu A 2014 Jpn. J. Appl. Phys. 53 05FL02
[24] Kumagai Y, Murakami H, Seki H and Koukitu A 2002 J. Cryst. Growth 246 215 – 222
[25] Kryliouk O, Reed M, Dann T, Anderson T and Chai B 1999 Mater. Sci. Eng., B 66 26–29
[26] Villars D S 1959 J. Phys. Chem. 63 521–525
[27] Colonna G and D’angola A 2004 Comput. Phys. Commun. 163 177–190
[28] Colonna G 2007 Comput. Phys. Commun. 177 493–499
[29] Voronenkov V 2015 Epitaxial growth of bulk gallium nitride layers: technological parameters optimization (in russian). Ph.D. thesis
[30] Gordon, Sanford and McBride, Bonnie J 1976 Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations. Interim Revision, March 1976 Tech. rep. NASA Lewis Research Center
[31] Smith W R 1980 Industrial & Engineering Chemistry Fundamentals 19 1–10
[32] Gurvich L V and Veyts I 1990 Thermodynamic Properties of Individual Substances: Elements and Compounds vol 2 (CRC press)
[33] Chase M W (ed) 1998 NIST-JANAF Thermochemical Tables, Fourth Edition (American Chemical Society)
[34] Przhevalskii I, Karpov S Y and Makarov Y N 1998 MRS Internet J. Nitride Semicond. Res. 3 1–16
[35] Zinkevich M and Aldinger F 2004 J. Am. Ceram. Soc. 87 683–691
[36] Schafer H 1980 Z. Anorg. Allg. Chem. 469 123–127
[37] Schonherr E, Wojnowski M, Rabenau A and Lacher S 1988 J. Less Common Met. 137 211–286
[38] Quill L (ed) 1950 Chemistry and Metallurgy of miscellaneous materials: Thermodynamics
[39] Reti F, Bertoti I, Mink G and Szekely T 1987 React. Solid. 3 329 – 336
[40] Akiyama K, Araki T, Murakami H, Kumagai Y and Koukitu A 2007 Phys. Status Solidi C 4 2297–2300
[41] Akiyama K, Ishii Y, Murakami H, Kumagai Y and Koukitu A 2009 J. Cryst. Growth 311 3110 – 3113