TECHNOLOGICAL PROCESSES FOR THE PRODUCTION OF NWS FROM GALLIUM NITRIDE (GaN) BY CVD METHOD

Abstract. Gallium nitride (GaN) is a III-V semiconductor with a direct zone gap of ~3.4 eV. GaN has important potentials in white light-emitting diodes, blue lasers and field-effect transistors due to its superthermal stability and excellent optical properties, playing major roles in future lighting, in order to reduce the cost of energy and sensors to withstand radiation. The article provides an overview of the authors' research on GaN obtained by the CVD method, which is a much more promising material than other traditional materials. The physical properties are compared to improve the material parameters, the methods of obtaining and the results of the research work of different authors for the creation of light diodes, transistors, microwave electronics.

Keywords: GaN, Gallium Nitride, CVD method, semiconductors, review.

Today, compounds of metals with nitrogen, the so-called nitrides, are of particular interest, among which many have high refractoriness, dielectric and semiconducting properties, the ability to transfer to superconductors at relatively high temperatures, and high chemical stability in various corrosive media. Many of the nitrides have already been successfully used in electronics, nuclear industry, semiconductor and dielectric technology, in space technology, modern machine building, metallurgy, electrical engineering and other industries [1-3]. And it is also possible to use nanocarriers to solve such problems as cancer diseases and one of the directions - creation of antitumor drugs - obtaining structures based on boron nitride [4], which has chemical inertness and high resistance to oxidation. Nanoparticles of hexagonal boron nitride 100-150 nm in size with a smooth and developed surface can be obtained by chemical vapor deposition [5].

Due to their unique properties, the nitrides of metals of the third group (III-N) are very promising for the creation of various semiconductor devices. And one of the elements of the III-group is - gallium nitride (GaN). GaN has long been interested in researchers and developers of semiconductor devices. The heterostructure of GaN and its solid solutions possess physical properties that provide electronic devices based on them, optical, power and frequency characteristics that allow them to be used in various fields of semiconductor electronics.

The main advantage of gallium nitride [6-11] over other common electronics materials is a wide forbidden band of 3,5 eV (1.1 eV for silicon). This means that GaN-transistors operate at higher temperatures and are less sensitive to ionizing radiation (which in the literal sense of the word is vital for space and special electronics). In theory, the operating temperature of GaN devices reaches 500 ° C, in practice it is still equal to 150-200 ° C. The maximum electric field strength for GaN is 3,3 × 10^6 V/cm - this is 11 times greater than that of silicon. And due to the high density of charge carriers GaN-transistors withstand much higher currents. Table 1 shows the comparison of gallium nitride with other semiconductors.
Table 1 - Comparison of the properties of semiconductor materials. The numbers in the table are approximate

<table>
<thead>
<tr>
<th>Material</th>
<th>Bandgap, E (eV)</th>
<th>Electron Mobility (cm²/Vs)</th>
<th>Hole Mobility (cm²/Vs)</th>
<th>Critical Field Ec (V/cm)</th>
<th>Thermal Conductivity (W/m·K)</th>
<th>Coefficient of Thermal Expansion (ppm/K)</th>
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</thead>
<tbody>
<tr>
<td>Si</td>
<td>1.12 300 K</td>
<td>1350</td>
<td>480</td>
<td>2.5 x 10⁵</td>
<td>130</td>
<td>2.6</td>
</tr>
<tr>
<td>AlN</td>
<td>6.2 300 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>InN</td>
<td>1.89 300 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3C-SiC</td>
<td>2.4 300 K</td>
<td>1000</td>
<td>40</td>
<td>2 x 10⁶</td>
<td>700</td>
<td>2.77</td>
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<tr>
<td>6H-SiC</td>
<td>2.86</td>
<td>400</td>
<td>75</td>
<td>24 x 10⁵</td>
<td>700</td>
<td>5.12</td>
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<td>3.25</td>
<td>700</td>
<td>-</td>
<td>318 x 10⁴</td>
<td>700</td>
<td>5.12</td>
</tr>
<tr>
<td>InSb</td>
<td>0.17</td>
<td>77000</td>
<td>580</td>
<td>1 x 10⁵</td>
<td>18</td>
<td>5.37</td>
</tr>
<tr>
<td>InAs</td>
<td>0.354</td>
<td>44000</td>
<td>500</td>
<td>4 x 10⁴</td>
<td>27</td>
<td>4.52</td>
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<tr>
<td>GaSb</td>
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<td>3000</td>
<td>1000</td>
<td>5 x 10⁴</td>
<td>32</td>
<td>7.5</td>
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<tr>
<td>InP</td>
<td>1.344</td>
<td>5400</td>
<td>200</td>
<td>5 x 10⁴</td>
<td>68</td>
<td>4.6</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.424</td>
<td>5800</td>
<td>400</td>
<td>4 x 10⁴</td>
<td>55</td>
<td>5.73</td>
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<tr>
<td>Ge</td>
<td>0.611</td>
<td>3900</td>
<td>1900</td>
<td>1 x 10⁵</td>
<td>58</td>
<td>5.9</td>
</tr>
<tr>
<td>GaP</td>
<td>2.26</td>
<td>250</td>
<td>150</td>
<td>1 x 10⁶</td>
<td>110</td>
<td>4.65</td>
</tr>
<tr>
<td>C (diamond)</td>
<td>5.5</td>
<td>2200</td>
<td>1800</td>
<td>6 x 10⁴</td>
<td>1300</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Figure 1 - Periodic table, where the shaded cells indicate the elements that can be deposited using CVD

Another no less important area is the production of a nanotube of gallium nitride. Thanks to the tubular structure, the material must be significantly more sensitive to environmental influences than the already known nanowires, which opens up prospects for its use in filtration, sensorics, biology, etc.
CVD processes occur at much higher temperatures than PVD processes, typically 300 to 900 °C. This heat is supplied from an oven, radio frequency coil or laser, but it always heats the substrate. Substrates that do not tolerate this temperature should have thin films deposited as a result of the physical form of vapor deposition.

The advantage of substrate temperature in some CVD processes is that they have less waste deposition, especially in cold wall reactors, since only heated surfaces are coated. When using a laser heating system, the process of chemical vapor deposition becomes selective with respect to the laser path; this is a clear advantage over the physical methods of vapor deposition, such as spraying.

In the paper [13] synthesized nanowires and GaN nanotubes by direct reaction of metallic gallium vapor (Ga, 99.99%) with flowing NH₃ in an electric furnace. At different NH₃ flow rates between 50 and 200 centimeters, large-scale nanowires and GaN tubes were formed at a growth temperature of 900 °C on a Si (111) substrate. GaN grown on a Si (111) substrate at 900 °C and at a NH₃ flow rate of 50 cccm, the preferred orientation is growth in the (002) direction. When the flow rate of NH₃ increases to 100 centimeters, the products have a much wider diameter, but, the length is shorter. If continue increasing the NH₃ flow to 200 centimeters, available get nanotubes and nanolayers. Hence, the faster the NH₃ flow rate, the greater the GaN surface tension.

The GaN [14] layers were deposited on the CVD-grown h-BN layers using an organometallic CVD. Trimethylgallium and NH₃ were used as precursors, and the V / III ratio was maintained at 2000-4000 during growth. Before the growth of the GaN layer, the substrate was heated to 1100 °C for 3-20 min only with H₂ gas. The temperature was then lowered to 540-600 °C for the growth of the GaN nucleation layer. After 3 min growth of the GaN nucleation layer, GaN epitaxial layers were grown at a higher temperature in the range 1000-1100 °C. No additional intermediate layers or substrate treatments were used to grow the GaN layer on the growth of CVD h-BN.

![Diagram](image)

**Figure 2 - Growth of GaN films on transferable chemical vapor deposition (CVD) - hexagonal boron nitride (h-BN)**

(a) A schematic illustration of the transfer of h-BN grown by CVD from Ni (111) to amorphous fused quartz substrates and the growth of a gallium nitride (GaN) layer using organometallic chemical vapor deposition (MOCVD). Scanning electron microscopy of field radiation (FE-SEM) images

(b) high-density discrete GaN islands that are almost fused into GaN microstructures several microns in size and (c) fully coalesced GaN films grown on CVD-grown h-BN.
Hopefully, h-BN, grown in CVD, has already discovered many atomic rocks, which allowed to increase the high-density GaN islands, which merged to form a flat homogeneous film. In addition, almost single-crystal GaN layers were grown directly on the growth of CVD h-BN without the use of other single crystal substrates. A clear observation of the high-density GaN epitaxial growth on a large-scale scalable single-crystal CVD-grown h-BN opens the way for new applications of h-BN in the development of a number of inorganic semiconductor devices.

Gallium nitride and indium nitride nanotubes [15] were grown using a hot wall chemical vapor deposition (CVD) system. NWs GaN were synthesized by the metal-catalyzed (Ni or Fe) growth of VLS on alumina or oxidized silicon substrates. This process included a solid gallium source (either metallic Ga, or metallic Ga in combination with Ga$_2$O$_3$), heated to temperatures between 800 and 1100 °C, in ammonia flowing at a rate of 2 centimeters to 100 centimeters. This process consistently produced nanowires with similar structural and electrical properties for similar growth parameters, having a high crystalline quality (Table 2).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Growth 1</th>
<th>Growth 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature °C</td>
<td>800</td>
<td>950</td>
</tr>
<tr>
<td>Ammonia Flow sccm</td>
<td>100</td>
<td>2</td>
</tr>
<tr>
<td>Substrate</td>
<td>Si/SiO$_2$</td>
<td>Si/SiO$_2$</td>
</tr>
<tr>
<td>Gallium Source</td>
<td>Ga$_2$O$_3$</td>
<td>Ga$_2$O$_3$</td>
</tr>
<tr>
<td>Pressure</td>
<td>1 atm</td>
<td>1 atm</td>
</tr>
<tr>
<td>Metal Catalyst</td>
<td>Ni</td>
<td>Fe</td>
</tr>
</tbody>
</table>

Both types of nanowires exhibit large carrier concentrations with decreasing mobility with increasing free carrier concentrations, which is consistent with a transport in which dispersion of impurities predominates. In the case of nanowires of gallium nitride, using the feedback between the parameters of growth and electrical characteristics, it was possible to reduce (increase) the concentration of carriers (mobility) by one order. In addition, simple theoretical estimates and annealing experiments show that nanowires of gallium nitride are highly compensated.

Epitaxial layers [16] were grown on an AlX2400G3-HT instrument of MOC-hydride epitaxy. Sources of gallium, nitrogen and dopants (trimethylgallium (TMGa), NH$_3$ and bis-cyclopentadienyl magnesium (Cp$_2$Mg), respectively) were delivered to the reactor with a hydrogen stream. 0.5 μm p-GaN epitaxial layers were grown on 2°-Al$_2$O$_3$ (1000) substrates with a pre-deposited i-GaN 2 μm buffer layer. Doping-impurity consumption was 5.4 · 10$^{-7}$ mol / min. The temperature and growth rate of GaN were the same for all samples. Two methods were used for post-growth thermal annealing. Some of the samples were annealed at 800-1000 °C in an epitaxy reactor for 7 min under a nitrogen atmosphere. Other samples were annealed at 1000 °C in an IR-heated unit with rapid thermal annealing at different times from 0.5 to 3 min. Heating to specified temperatures was 5-7 s. The annealing atmosphere was nitrogen at a pressure of 0.1 atm. The same pressure was used for all samples. A significant change in the electrophysical properties of the p-GaN: Mg samples as a result of a change in the annealing temperature. The main observation is a significant (approximately 20-fold) increase in the hole concentration in the samples annealed at 1000 °C, compared to those that were annealed at 800 °C, which is probably due to the higher activation of the acceptor.

In the paper [17] talks about the approach to the synthesis of straight and smooth GaN nanowires with catalyzed NiO by the CVD method. The nanorbeters were deposited on a substrate from a LaAlO$_3$ monolayer without the use of a template. Before deposition, the substrate was immersed rapidly in a solution of ethanol Ni (NO$_3$)$_2$ and then heated at 900 °C in a long quartz tube in an Ar flow for 2 hours (h) to decompose Ni (NO$_3$)$_2$ into NiO nanoparticles. Then, the growth of the nanoparticles GaN was carried out in a long quartz tube at 920-940 °C in a NH$_3$ stream for 5-20 min. The synthesized GaN nanowires had a diameter of 10-40 nm and a maximum length of about 500 μm. And also in work [18] it was demonstrated that using a sapphire substrate it is possible to fabricate long nanowires of GaN using the CVD method. Using gallium and ammonia metals as sources of Ga and N, GaN nanowires were deposited on a sapphire substrate at 900 °C using a nickel catalyst. The wires they had prepared had a length of several hundred micrometers and diameters from 30 to 150 nm.
The paper [19] describes the photocatalytic activity of GaN nanowires and they have a good ability to photodegrade the organic dye at various pH values even with strong acidity and alkalinity. In addition, the photocatalytic activity of GaN nanowires was compared with the photocatalytic activity of TiO₂ and ZnO nanowires. It was found that the surface area of GaN nanowires was an order of magnitude lower than that of TiO₂ nanowires; the photocatalytic activity of GaN nanowires was slightly higher. Compared to ZnO nanowires, ZnO nanowires were performed better than GaN nanowires at pH 7.0, but in a strong pH range, for example, pH 2.3, the photocatalytic activity of ZnO nanowires rapidly decreased from 70% to 33%, whereas nanowires of GaN increased by 60%.

1D GaN NWs were prepared in a reaction chamber with an air hot reaction with a hot temperature [20]. The growth of 1D GaN was carried out at a growth temperature of 1000 ° C for 1 hour using a Ga₂O₃-NH₃ system. NH₃ at a flow rate of 130 cm³ min⁻¹ was used as the reaction gas and the carrier gas. The substrate was located in the center of the furnace with a series of crucibles mounted on Ga₂O₃. In each experiment, Ga₂O₃ powder was loaded with 0.2 g. For the growth of NW, 100-oriented Si substrates coated with sputtered Au were used. The phase formation of CVD-GaN was analyzed by X-ray diffraction.

Figure 3 - (a) FESEM images of GaN nanowires synthesized by the CVD method at 1000 ° C on Au / Si substrates for 1 hour with the Ga₂O₃-NH₃ system and (b) magnified image

Figure 4 - The TEM, SAED and HRTEM images of GaN nanowires grown at 1150°C: (a) TEM and SAED images, and (b) HRTEM images

For the fabrication of GaN nanowires [21] CVD was used. The main materials are powdered Ga₂O₃ (99.99%), a crystal of NiCl₂ · 6H₂O (99.9%) and NH₃ (99.999%). Thin film of NiCl₂ was formed by the immersion method. Unpolished substrate Si (1 1 1) n-type after ultrasonic cleaning was immersed in the NiCl₂ · 6H₂O ethanol solution with a concentration of about 2%, and dried at 100 ° C. The second step
was to manufacture GaN nanowires in a conventional tube furnace with Ga₂O₃ as a gallium source and NH₃ as a source of nitrogen. When the furnace is increased to a certain temperature (1050 °C, 1100 °C and 1150 °C), 3 g of Ga₂O₃ Si substrate and placed inside a quartz tube in a horizontal tube furnace, and the distance between them was 1 cm, with Ammonia 800 ml min-flow rate 1 was passed into the oven for 40 minutes at a certain temperature. After the ammonia, the gas flow Ar (99.999%) was introduced into the tube for 5 minutes to wash the residual NH₃. After the reaction, the samples were lamellar-light yellow on the surface of the substrate. As the reaction temperature increases, the number of nanowires grows, and the quality improves. Nano drives start to emerge at 1100 °C and at 1150 °C have the highest crystallinity with a smooth and clean surface.

HRTEM shows that the distance between crystals nanowires grown at 1150 °C, corresponds to the (1 0 0) Distance between the crystals of hexagonal GaN monocrystal and that the direction perpendicular to the growth of GaN nanowires (1 0 0).

For the growth of Mn-doped GaN-wires [22] used the metal Ga (purity 99.99%) and powder of Mn (≥99%), with high purity N₂ (99.999%) as the carrier gas and NH₃ (99.999%) as the reaction gas. For the growth of GaN wires, a substrate of a silicon substrate (100) was used. While the temperature of the tube furnace was increased to reach reaction temperature N₂ (99.999%), NH₃ (99.9995%) and HCl gases (N₂, 10 mole%) were injected. The heating rate was 5 °C/min, and the holding time was 1 hour. During this time, the temperature and the total flow were regulated in the ranges 950-1400 °C and 490-625 centimeters, respectively. As the amount of Mn doping increases, the light-emitting wavelength increases to 700 nm (red), the maximum. Moreover, even when the experiment was carried out with the same ratio of the Ga metal to the Mn powder, the light emitting wavelength was 644.4 nm while maintaining the temperature at 1300 °C.

Carina B. Maliakkal, Azizur Rahman and others [23] were grown GaN NWs using as precursors (Figure 3) organometallic chemical vapor deposition (MOCVD), nickel catalyst and trimethylgallium (TMGa) and ammonia (NH₃).

Figure 4 - Growth of GaN-NWs: (a) GaN NWs obtained by growing in medium N₂, (840 °C and 150 torr with a flow of 1 cm³ of NH₃ and a TMGa stream of 2.5 ecm). (b) droplets containing gallium and nickel obtained by growing in an H₂ atmosphere under similar growth conditions. (c) nickel-catalyzed unsteady GaN NW obtained by rowing under the same conditions (840 °C and 150 torr with a flow of 1 cm³ of NH₃ and a flow of 2 mcm TMGa) in (c) the plane of the c (d) plane and (e) sapphire substrates r-plane [26]. The pressure of 150 torr in medium N₂ and ~840 °C, with low precursor flow rates and V-III ratio, was optimal for growing thin, not oblique GaN NW.
So, several technologies of the process of growth of GaN obtained by the CVD method were compared. These methods show the progress in the production of GaN. The best way to synthesize nanowires and GaN nanotubes is the direct reaction of metallic gallium Ga vapor with a flowing NH₃ gas. By choosing a gas flow of hydrogen nitride and temperature, it is possible to obtain thinner or thicker nanowires and nanotubes.

For semiconductor nanowires, cylindrical geometry and strong two-dimensional retention of electrons, holes and photons make them particularly attractive as potential building blocks for nanoscale electronics and optoelectronic devices [20]. The use of GaN nanowires has been demonstrated by researchers in the following areas: photoelectric devices, light emitting diodes (LED), field effect transistors (FET), lasers, photocatalysts and nano-generators.

The future, GaN will play an increasingly important role in the use of nitride-based semiconductor devices, through the introduction of homoepitaxy and the structure of the device, replacing heteroepitaxy and the currently used device structure. The bulk GaN substrate will grow rapidly over several years, with larger sizes, higher quality and lower cost. To implement mass production and wide application of volumetric GaN substrates, a combination of different growth methods is a possible solution.

REFERENCES


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К. Аскарұлы¹, Н.К. Манабаев²

К.И.Сәтбәев атындағы Қазақ ұлттық техникалық қызмет университеті, Алматы, Қазақстан

CVD ЭДІСІ АРҚЫЛЫ ГАЛЛИ НИТРИДДЕН NWs – АЛУДЫҢ ТЕХНОЛОГИЯЛЫҚ БАРЫСЫ

Аннотация. Галли нитриді, зоналық санылдау тіке ~3,4 эВ және (GaN) III-V (АдВ₃) кластерді жарықтық откізілген болып табылады. GaN өзінің аса жоғары температурада тұрғығы және оптикалық қасиеттеріне байланысты зыңғай жарықтық шығармаларды құрама, құз тәріздер мен даярламалы транзисторларда көлдану үшін қалай кезеңге сәуеленуге қарсы, энергияның, құралымдарының басының тығындығынан көрсетеді. Макросхем дәстүрлі материалдарының толқында болашағы, және бірінші CVD әдісімен алынған GaN - ті зерттєрдегі авторлардың жұмысына шолу келтіріледі. Материалдардың параметрлерін және транзистордың, жұмысқа келеді және АЖК электроника сияқты көлдану үшін материалдарды алу процестерін, физикалық қасиеттерін және ол түрлі авторлардың қызметінің әсерін салыстыру құралдарын көрсетіп жатады.

Түпін сөздер: GaN, галли нитриді, CVD әдісі, жарықтық откізіліш, шолу.

К. Аскарұлы¹, Н.К. Манабаев²

Қазақстан национальный исследовательский технический университет
им. К.И.Сатпаева, Алматы, Қазақстан

ТЕХНОЛОГИЧЕСКИЕ ПРОЦЕССЫ ПОЛУЧЕНИЯ NWs
ИЗ НИТРИДА ГАЛЛИЯ CVD МЕТОДОМ

Аннотация. Нитрид галлия (GaN) представляет собой полупроводник III-V с прямым зонным зазором ~3,4 эВ. GaN имеет важные потенциалы в белых светозащитных диодах, синих лазерах и полевых транзисторах из-за его сверхгерманической стабильности и превосходных оптических свойств, играя главные роли в будущем освещении, чтобы снизить стоимость энергии и датчики, чтобы противостоять иллюминации. В статье приводится обзор исследовательских работ авторов по GaN полученных CVD методом, которые гораздо более перспективных материалов, чем другие традиционные материалы. Сравниваются физические свойства для улучшения параметров материала, методы получения и результаты исследовательских работ разных авторов для создания светодиодов, транзисторов, СВЧ электронике.

Ключевые слова: GaN, Нитрид галлия, CVD метод, полупроводники, обзор.

Information about authors:
Askaruly Kydy/R - PhD doctoral student of the 1st academic year for the specialty of 6D072300 - "Technological Physics", the Department of "Technical Physics and Materials Science", Satbayev University. kaskaruly@gmail.com,
Manabaev Nurlan Kasenovich - PhD doctor, the Department of "Technical Physics and Materials Science", Satbayev University. infopresskz@gmail.com

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