Gallium Nitride: A Novel III-V Semiconductor

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Recently there has been considerable interest in the unique chemical properties of gallium nitride. It is a direct band gap semiconductor with a band gap of 3.39 eV. This large band gap makes gallium nitride a good candidate for the production of blue light-emitting diodes and blue and ultraviolet semiconductor lasers. In addition, the exceptional chemical and thermal stability of gallium nitride could be exploited by its use in high power and high temperature devices [1-6]. The potential utility of gallium nitride-based devices continues to be the driving force behind the ongoing research into the synthesis and properties of this material.

Gallium nitride has two solid state structures, cubic and wurtzite, differing only in their packing sequence. Both forms have closest packed nitrogen layers with gallium occupying half of the tetrahedral holes; the coordination number of both gallium and nitrogen is four. The packing sequence for the cubic form is AcBaCbA, while the packing sequence for the wurtzite form is AcBcA. The wurtzite form is more stable, and cubic gallium nitride can be converted to the wurtzite at high temperatures. The structure of gallium nitride depends upon the method of synthesis: for example, cubic gallium nitride can be grown on a cubic seed crystal [6, 7]. Both gallium nitride structures are very similar to the structure of silicon (Figure 1).

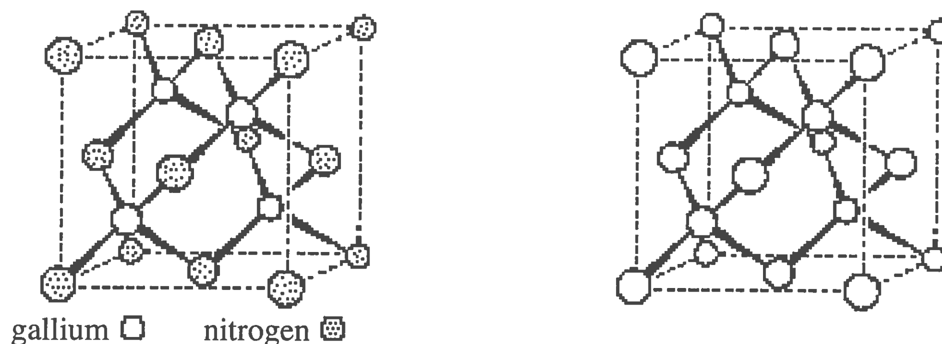

Figure 1. Coordination environment of cubic gallium nitride (left) and of silicon (right).

Solid gallium nitride is stable in air at temperatures exceeding 1000 °C and is impervious to both water and acid attack. The stability of gallium nitride is related to the strength of the gallium-nitrogen bond. Gaseous gallium nitride has a bond strength of approximately 300 kJ/mol compared with a bond strength of 171 kJ/mol for zinc selenide (a semiconductor with a comparable band gap) [8]. The large band gap in gallium nitride translates into fewer electrons thermally promoted to the conduction band of the semiconductor even at high temperatures. Finally, the electron saturation velocity (electron velocity at high power) for gallium nitride has been calculated to be 2.7×10^7 cm/s. Silicon carbide, the current front-runner for high temperature and high power devices, has a smaller electron saturation velocity of 2.0×10^7 cm/s. The high thermal stability and large band gap combined with the superior electronic properties and the ability to produce III-V alloys could make gallium nitride the best choice for high power and high temperature devices [1, 5].

Another potential application of gallium nitride is its use in blue and ultraviolet light emitting diodes and lasers [4-6]. A direct band gap semiconductor such as gallium nitride is needed for efficient light-emitting diodes (LED's). When current flows through diodes constructed from a direct band gap semiconductor, it emits visible light. Gallium nitride diodes

produce blue and blue-green light and can also be used in combination with red and yellow LED's to produce a white LED lamp [9, 10]. These LED's have the potential to replace traditional incandescent light sources. They would have the advantages of greater energy efficiency, smaller size, much longer lifetimes, and greater durability. LED lamps could serve as excellent light sources for accelerated photosynthesis in plants, which would be especially useful for space flight and space station growing systems [11]. Blue and ultraviolet LED's also have applications in medical diagnoses and treatment, such as fluorescent medical imaging and laser surgery [6].

Semiconductor lasers in the blue and ultraviolet range can also be made from gallium nitride. Due to their higher frequency, these lasers should increase the efficiency of fiber optics communication by reducing losses in signal intensity. Another application of gallium nitride semiconductor lasers is in the field of optical data storage [3, 4, 6]. Because of the shorter focal length of the laser beam, it is possible to store more information in a smaller space. Using gallium nitride lasers should result in optical storage measured in the gigabytes per cm^2 range compared with megabytes per cm^2 currently available in optical storage.

Before the potential of gallium nitride-based devices can be realized, reliable and cost-effective methods for the production of electronics-quality epitaxial crystals of gallium nitride must be found. There are two main methods that have been used to produce epitaxial layers of gallium nitride, molecular beam epitaxy (MBE) and chemical vapor deposition (CVD). MBE employs a highly energetic atomic or molecular beam that is directed towards a heated substrate in an ultrahigh vacuum chamber . CVD utilizes chemical precursor vapors deposited onto a heated substrate, where subsequent surface reactions take place to produce the desired epitaxial layer. CVD is preferred in industry because it is more conducive to large scale production and is currently the only technique employed in industrial production of gallium nitride-based devices [6].

Several problems in the production of gallium nitride prevented its commercial usage before 1992 [5]. One of the problems was the unintentional intrinsic n-doping of gallium nitride that resulted from nitrogen vacancies in the lattice. This was alleviated by using an excess of the nitrogen precursor. The biggest problem was the inability to produce electronics-quality p-doped gallium nitride. This precluded the development of gallium nitride diodes since they require p-doped as well as n-doped materials. This was solved when it was learned that hydrogen impurities were interfering with p-doping. Subsequently, it was found that the use of low-energy electron beam irradiation as well as thermal annealing could drive off this hydrogen, producing good p-doped material. A third problem was the lack of a substrate that was a good lattice match. Sapphire is the substrate most commonly used since it is widely available and easy to clean. However, it has a large lattice mismatch that causes considerable strain on the deposited gallium nitride, resulting in a large number of defects. This problem was solved by using a sacrificial gallium nitride buffer layer on the sapphire in order to deposit relatively defect-free gallium nitride [12, 13, 14]. Because these problems have been overcome, gallium nitride LED's are now currently in the marketplace.

Unfortunately, these solutions also have several drawbacks. The chemicals used as precursors are quite reactive, which renders them difficult to purify. The usual precursors, ammonia and trimethylgallium, are safety and health hazards especially under the conditions used for CVD. The high temperatures that are required make sharp junctions used in many devices more difficult to achieve and also preclude the formation of cubic gallium nitride. Although nitrogen vacancies have been reduced, they are still high. Consequently, gallium nitride must be heavily doped in order to produce high quality p-doped material [5,6].

One possible solution currently being pursued by chemists is the use of single-source CVD precursors. This involves using only one precursor with a gallium-nitrogen bond already present. These reagents are typically safer and easier to handle, while still sufficiently

unstable to decompose at lower temperatures in CVD. Stoichiometry control would be inherent, virtually eliminating the problem of nitrogen vacancies that are caused by gallium-nitrogen bond formation being the rate limiting step [15]. The potential also exists for reduced impurity incorporation [16].

The first single-source precursor studied was the adduct $(CH_3)_3Ga{\bullet}NH_3$ [17]. This approach was unsuccessful since there was a large loss of the 1:1 stoichiometry due to breaking of the gallium-nitrogen bond in the decomposition process. The next attempt utilized a precursor with a strong two-center, two-electron Ga-N bond (triethyl gallium azide) [18]. These produced gallium nitride with a good 1:1 stoichiometry, but the material was polycrystalline. The most recent examples of single-source precursors contain more than one gallium-nitrogen bond $(Me_2N)_2GaN_3$[19]. These have been shown to produce epitaxial films, but the carbon impurity incorporation is still far too high for use in electronic devices. One class of future gallium nitride precursors might be homoleptic gallium silylamides with the formula $Ga(N(SiR_3)_2)_3$ (R=alkyl) [20]. By themselves they would be expected to decrease the carbon content since the carbon atoms are farther from the gallium atoms. Precedence also exists which suggests that deposition with these precursors could be achieved close to atmospheric pressure. If this were possible, then using a large excess of ammonia might generate high quality gallium nitride films [21]. Although gallium nitride formed from single-source precursors has yet to achieve the purity required for most electronic applications, single-source precursors have been used to produce high purity gallium arsenide. It is possible that a suitable single-source precursor for gallium nitride could also be developed.

The unusual properties of gallium nitride as well as the recent developments in synthesis have allowed gallium nitride-based technologies to be industrially produced and become more than just a laboratory novelty. The difficulties that keep gallium nitride from realizing its full potential are being investigated intensively. Judging from the progress that has been made so far, it does not seem unreasonable to expect gallium nitride to become a widely used semiconductor in the future.

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