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JOURNAL ISSUE: 7
JOURNAL MONTH:
JOURNAL YEAR: July 1996
ARTICLE PAGES: 690-693

ARTICLE AUTHOR:
ARTICLE TITLE: Drozdova, S.V. et al; Activated nitrogen source with an inverted magnetron geometry for molecular beam epitaxy of GaN

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Activated nitrogen source with an inverted magnetron geometry for molecular beam epitaxy of GaN

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(Submitted January 22, 1996; accepted for publication January 29, 1996)
Fiz. Tekh. Poluprovodn. **30**, 1313–1319 (July 1996)

First results are presented on the epitaxial growth of GaN on GaAs (100) substrates using a modified molecular-beam epitaxy apparatus with a plasma-activated nitrogen source that employs an inverted dc magnetron. The principle of operation of the source is based on ionization and activation of the neutral gas in a low pressure dc discharge in crossed electric (up to 4 kV/cm) and magnetic (up to 0.1 T) fields. © *1996 American Institute of Physics.*
[S1063-7826(96)02307-1]

INTRODUCTION

Epitaxial layers and heterostructures based on the nitrides of group-III metals (GaN, AlN, InN, and solid solutions based on them) have been under intense study in recent years as possible elements for creating light-emitting diodes and lasers in the blue and ultraviolet regions of the spectrum, as well as for use in high-temperature electronic devices.[1,2] The primary methods for producing these layers are gaseous phase epitaxy from organometallic compounds and molecular-beam epitaxy.[1,2] Gas sources, as well as plasma-activated nitrogen sources, are used to obtain a flow of nitrogen for molecular beam epitaxy. Two methods for activating the plasma have been most widely used and studied up to now: (a) activation using rf excitation (usually with inductive coupling) and (b) activation using microwave discharges (electron cyclotron resonance).[1]

The purpose of this paper is to study the feasibility of using a fundamentally new type of activated nitrogen source in the form of an inverted magnetron operating at ultralow pressures for molecular-beam epitaxy of the nitrides of group-III metals. Its operating principle is based on the activation of neutral nitrogen in a dc discharge in crossed electric and magnetic fields.[3–5]

The properties of the GaN layers were studied using various methods, including energetic electron diffraction, Auger electron spectroscopy, ellipsometry, and photoluminescence.

EXPERIMENTAL TECHNIQUE

Samples were grown in a modified "Tsna" molecular beam epitaxy system with standard sources for group-III metals and an activated nitrogen source based on a low pressure dc discharge (up to 10^3 Torr) in crossed electric (up to 4 kV/cm) and magnetic (up to $B \approx 0.1$ T) fields. This type of discharge is familiar in an inverted magnetron geometry with a coaxial electrode configuration and a central anode.[5] High purity nitrogen gas was fed to the source from a high-pressure tank. Magnetic discharge pumps with a capacity of 5000 l/s on the "Tsna" system allowed us to use nitrogen flows corresponding to an equivalent flow pressure at a level of 10^{-6}–10^{-5} Torr and, thereby, to grow GaN layers in a standard vacuum configuration for molecular beam epitaxy, i.e., without using an additional turbomolecular or cryogenic pumping system.

The chosen pressures and electric and magnetic fields in the discharge chamber of the source ensured that the electrons were magnetized, i.e., that their drift was along cyclotron orbits and they moved toward the anode mainly as a result of various kinds of collisions. Consequently, in the gap between the anode and cathode a negative volume discharge developed. The main processes leading to ionization and activation of the nitrogen molecules took place there. A discharge in crossed $\mathbf{E}\times\mathbf{B}$ fields can exist in various regimes.[4,5] In the present work, most of the samples were grown with a "vacuum" discharge regime within the volume of the source, for which the distinctive feature is that the spatial distributions of the energy spectrum and electron density are independent of the gas pressure in the discharge vessel over a wide range (10^{-12}–10^{-3} Torr). This means that the flux of activated nitrogen depends linearly on the nitrogen pressure in the source. The pressure in the discharge vessel was controlled by varying the amount of nitrogen entering the vessel with the aid of a SNA-2 piezoelectric leak valve, as well as by using diaphragms of various diameters (1–50 mm) at the outlet of the source.

The distance between the discharge zone in the source and the substrate surface was 80 cm and that between the diaphragm and the substrate surface was 30 cm.

GaN was chosen as the material for studying the capabilities of the source. It was grown on GaAs (100) substrates. Before processing, a substrate was treated in isopropyl alcohol to remove organic contamination, then etched in standard H_2SO_4:H_2O_2:H_2O=4:1:1 etchant with removal of residual oxide in HCl. The surface oxide was removed by heating the substrates to a temperature on the order of 630 °C in a flow of activated nitrogen for 10 min. The temperatures for the growth process were in the range 600–630 °C. The growth of GaN began with the uncovering of a gallium baffle. The growth process lasted 100 min in all the experiments. The

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layer growth was monitored by energetic electron diffraction.

The surface composition was studied by Auger electron spectroscopy in the analytic chamber of a Varian MOD-GEN II system. Etching in an argon flow was used to study the distribution of the composition over the thickness.

Ellipsometry was used to study the thickness and complex refractive index of the grown layers. The measurements were done on an LÉF-3M ellipsometer at a wavelength $\lambda=0.6328$ μm with an angle of incidence of 70°. Quantitative information was obtained from the ellipsometric parameters Δ and Ψ which enter in the expression for the ratio of the complex reflection coefficients R_p and R_s of the sample for the p- and s-components of the optical wave polarization:

$$\rho \equiv R_p/R_s = \tan \Psi \exp\Delta.$$

Photoluminescence data were obtained with a spectroscopic system equipped to vary the sample temperature from 4.2 to 300 K.[7] Photoluminescence was excited by a pulsed N_2 laser with a photon energy of 3.678 eV, a pulse length of 6 ns, and a repetition rate of 1000 Hz. The peak power of the laser radiation was on the order of 3 kW. The spot diameter of the laser light at the sample was ~0.5 mm. The GaN samples were measured at liquid-nitrogen temperature (77 K) and room temperature. The spectral resolution of the spectrometer was better than 1 meV. The radiation was attenuated by means of a series of neutral density filters. The spectral measurements were not corrected for the spectral sensitivity of the photomultipliers and monochromators.

EXPERIMENTAL RESULTS

If a flow of activated nitrogen is directed onto a GaAs substrate located in the molecular beam epitaxy growth chamber and heated to the epitaxy temperature, then a GaN layer can be produced. The reason is that the Ga–N binding energy is substantially higher than that of Ga–As, and the arsenic atoms in the GaAs structure will be actively displaced by nitrogen atoms.[8] In this regard, the first experiments were done without a Ga flow. The GaAs substrate was placed in a flow of activated nitrogen from the source with an equivalent flow pressure of $\sim 10^{-5}$ Torr. The diameter of the exit diaphragm in the source was 50 mm. The electric field in the source was ~3 kV/cm, the current was 10 mA, and the magnetic field was ~0.1 T, which made it possible to maintain the vacuum discharge regime. The energetic electron diffraction pattern changed in the course of holding the substrate in a flow of activated nitrogen and at the end of the process the pattern consisted of a superposition of the diffraction pattern from the GaAs substrate plus some new lines whose positions correspond to the period of the GaN lattice.

Ellipsometric measurements revealed the presence of a surface oxide and, below it, a layer with a refractive index of ~2.5 and a thickness of ~4-5 nm.

Auger electron spectroscopic studies of the samples after nitriding showed that there was a high nitrogen concentration on the surface and that it falls as the sample is etched (Fig. 1). Here the concentration of arsenic increases with depth in the sample, which confirms the model of As atoms being

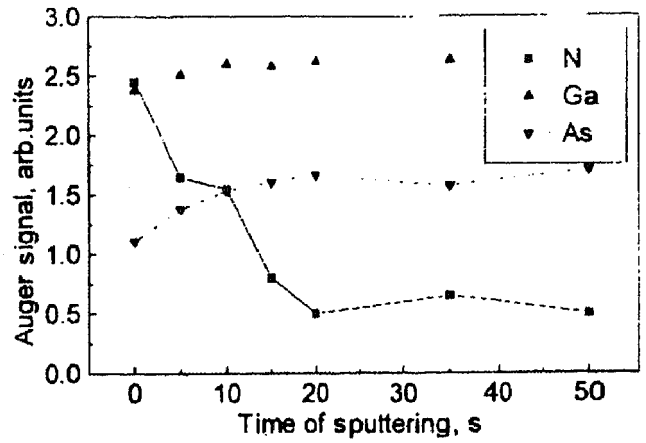

FIG. 1. Auger profile of sample G-5 obtained by nitriding a GaAs surface. The voltage $U=3.5$ kV, current $I=10$ mA, and magnetic field $B\approx 0.1$ T.

displaced by N atoms. Given the rate of etching, the thickness of the formed layer is on the order of 10 nm.

Another group of experiments was conducted with a nitrogen flow of the same magnitude and with a gallium flow corresponding to an equivalent pressure on the order of 10^{-8} Torr. In the first experiments the diameter of the diaphragm was 50 mm. Several minutes after the process began, the energetic electron diffraction pattern was observed to change: additional lines, which can be associated with the growth of GaN, appeared at the completion of the process, the sample surfaces were coated with droplets of gallium with a diameter of order 1 μm and a density of $\sim 3-4\times 10^5$ mm^{-2}.

Further experiments were conducted with smaller diameters of the source exit diaphragm. Using a diaphragm with a diameter of 5 mm at the source outlet made it possible to increase the discharge current to 100 mA and lower the concentration of Ga droplets because of an increase in the flow of activated nitrogen as the pressure in the discharge vessel increased in the "vacuum" regime.

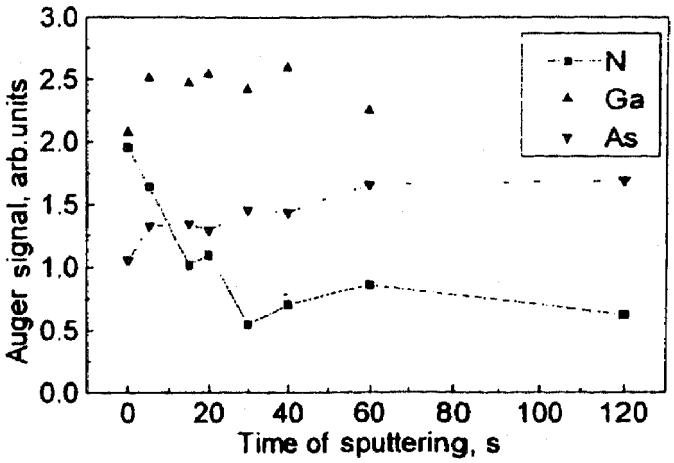

FIG. 2. Auger profile of a sample grown with a Ga flux at 10^{-8} Torr. Voltage $U=2.1$ kV, current $I=6$ mA, and magnetic field $B\approx 0.1$ T.

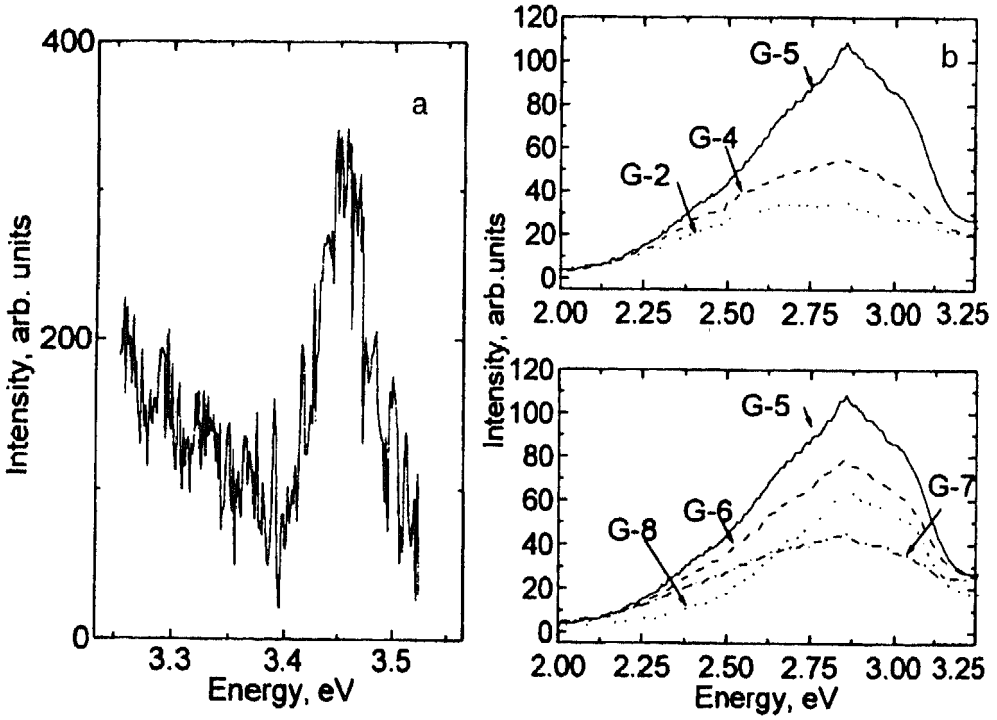

FIG. 3. Photoluminescence spectrum of sample G-5 at 77 K obtained by nitriding a surface and of samples G-2, G-4, G-6, G-7, and G-8 grown in a flux of N and Ga: (a) near the band-band transitions and (b) at lower energies.

When the diameter of the diaphragm was reduced to 1 mm, a transition to a "plasma" discharge regime became possible. The fluxes of activated nitrogen in this regime made it possible to reduce the density of Ga droplets to 5×10^4 mm^{-2}.

The properties of the fabricated layers were studied after removal of the gallium droplets from the surface.

Ellipsometric studies demonstrated the presence of a surface oxide and, under it, of a layer with a refractive index of ~2.5 and a thickness of ~4–10 nm, depending on the parameters of the growth process. The distribution of the composition with depth in the layer obtained by Auger electron spectroscopy is shown in Fig. 2. A high concentration of N is observed on the surface, but the As line intensity is observed to be high at the same time. This is because the diameter of the Auger electron spectroscopy spot encompassed segments with the grown layer, as well as segments of the GaAs surface that were uncovered after removal of the Ga droplets. This discontinuity in the layer made it impossible to observe a sharp substrate-epitaxial layer interface boundary in the Auger electron spectroscopy profile. The thickness of the GaN layer estimated from the Auger electron spectroscopy data is of order 10–15 nm.

Photoluminescence spectra of these samples contain lines corresponding to a band-band transition of GaN (Fig. 3a). The intensity of this photoluminescence line, however, is low, possibly because of the small thicknesses of the layers. At energies below the width of the bandgap there is a broad photoluminescence line (Fig. 3b) which appears to consist of a superposition of four peaks with energies of order 2.4, 2.6, 2.8, and 3.0 eV. This line is quite broad and is difficult to characterize in detail. Since the films were produced with an excess of Ga, however, we may assume that this line originates mainly in intrinsic point defects of the lattice such as nitrogen vacancies V_N or antistructural Ga_N defects. This assertion, however, is not well supported. All that we can say is that this long wavelength line is caused by defects in the GaN layer. Further studies are presently under way.

CONCLUSION

GaN layers can, therefore, be grown on GaAs substrates by molecular beam epitaxy using a plasma activated nitrogen source with an inverted magnetron configuration in which nitrogen is ionized and activated in a dc discharge in crossed electric and magnetic fields with various excitation regimes for the discharge. We have been able to observe radiative recombination in these layers experimentally, both from point defects or impurities in the GaN and at energies close to the width of the band gap in GaN. The efficiency of the active nitrogen source, however, must be enhanced greatly in order to improve its prospects for growing GaN device structures.

The authors thank the Royal Society of Great Britain (P826) and INTAS (94-2608) for financial support of this work.

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Translated by D. H. McNeill