Preparation of gallium nitride (GaN) and related compounds by plasma immersion ion implantation and rapid thermal annealing

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Abstract

Recent advances in the preparation of gallium nitride (GaN) and related compounds have promised the production of a blue semiconductor laser, a device that has long been desired for by the consumer electronics market. Conventional preparation involves growing GaN thin films on lattice-mismatching sapphire or silicon carbide using metal–organic chemical vapor deposition (MOCVD). In this article, we present an alternative method to produce a lattice-matching substrate for subsequent GaN growth, and to possibly synthesize device-grade GaN and related materials, like InN and InGaN, by plasma immersion ion implantation (PIII) followed by rapid thermal annealing. Our novel approach uses a broad ion-impact energy distribution and multiple implant voltages to form a spread-out nitrogen depth profile and an amorphous surface layer. This approach circumvents the retained-dose limitation and low nitrogen content problems associated with ion beam implantation at fixed energy. Based on our Raman study, the resulting structure after PIII and rapid thermal annealing is strained and contains some GaN, possibly in crystal form. The process still needs to be refined to make device-quality materials, but the present materials should suffice as a substrate on which lattice-matching GaN layers can be grown directly by MOCVD. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The wide band-gap semiconductor based on the nitride compounds of the III–V group has attracted much attention because of the potential applications in optoelectronics in the visible spectrum [1] and high-temperature electronic devices [2]. At present, the majority of the commercial GaN-based devices use sapphire as the substrate. Although the inherent 15% lattice mismatch with GaN makes sapphire an unlikely substrate for high quality crystal growth, it has been found that a sequence of ultra-thin GaN buffer layers can be grown at low temperatures to confine the cracks to a narrow region [1]. On the surface of this ‘transition’ layer, high quality GaN can be grown at normal temperatures for device applications. Using this idea, it is possible that good quality GaN growth can be achieved if a surface that contains a thin layer of polycrystalline GaN can be prepared. Nitrogen ion implantation into a Ga-containing surface followed by an annealing process is a possible approach that can result in the formation of a GaN buffer layer.

Pertaining to the formation of GaN via ion implantation, several groups have so far reported results on
their exploratory experiments [2–7]. From their TEM results, Lin et al. showed that in GaAs, the heavily N⁺-implanted surface contained nano-size crystals of cubic- and hexagonal-GaN after annealing at 850°C [4]. Kuriyama et al. also recently demonstrated that N⁺-implanted GaAs exhibits photoluminescence in the blue region, thus further confirming the prospect of producing functional GaN by ion implantation [5]. The group led by Sealy [6,7] adopted an alternative approach. They implanted Ga into Si₃N₄ and found from Auger measurement that when the starting layer was nitrogen-rich, the final material contained GaN. The basic rationale associated with these experiments is that the Ga–N bond strength is stronger than that of Ga–As or Si–N, and it should be energetically favorable for the formation of GaN if the two constituent atoms are available and in adequate proximity. While there is strong experimental evidence confirming the generation of GaN, at least in the form of small crystals, the theoretical work carried out by Stumm and Drabold [8] revealed even more encouraging findings. They showed that amorphous GaN in fact possesses no deep mid-bandgap traps. They further argued that any form of amorphous GaN could be utilized as electronic materials. In particular, the low-density type shows special promise.

The aforementioned studies employ conventional ion beam implantation at a fixed ion energy. The retained-dose problem limits the proper formation of GaN, as each Ga–As has to be replaced by a Ga–N bond. The fixed energy implant further prevents the formation of a continuous GaN layer. Plasma immersion ion implantation (PIII) circumvents the retained-dose limitation and multiple implants with different energy values are quite easy to accomplish by PIII, by simply varying the magnitude and pulse shape of the sample bias during implantation. Thus, the choice of PIII as the implantation technique has several advantages over conventional beam-line ion implantation. First of all, PIII is a low-cost process, particularly suited to large wafer processing. The successful demonstration of GaN-coated wafers that are compatible with industrial production equipment and at affordable costs is certainly very attractive. Secondly, PIII is versatile in terms of varying the ion energy and energy spread during implantation. It is possible to tailor the nitrogen concentration along the depth direction by varying the ion energy and/or voltage pulse shape to improve the crystal quality of the GaN layer. Thirdly, the nitrogen plasma can provide a better supply of radicals that are essential to the formation of Ga–N bonds. Last but not least, in situ doping can be easily implemented by mixing the nitrogen gas with a dopant gas, e.g. hydrogen sulfide, metal–organic compounds, and so on.

2. Experimental

Nitrogen was implanted into a GaAs substrate by plasma immersion ion implantation (PIII) [9]. The plasma consisted mainly of N⁺ ions. The GaAs sample was biased at three different voltages of 40, 20 and 10 kV with an implant dose of 8 \times 10^{16}, 5 \times 10^{16} and 3 \times 10^{16} cm⁻², respectively. The use of multiple energy values ensures a relatively broad distribution of nitrogen and more effective surface amorphization. After implantation, a highly saturated nitrogen-doped GaAs layer was formed within 400 Å from the surface, as depicted in Fig. 1. The depth profile was simulated by TRIM [10]. After implantation, the GaAs substrate was pre-etched by diluted HF (15%) acid for 5 min to remove the surface oxide and a mixture of bromine (2%) and methanol (98%) to clean the top surface. The GaAs wafer was then rapid thermal annealed at 850°C for 2 min. The Raman spectra were acquired by a micro-Raman system (Reinshaw Raman 2000) with excitation at 514.5 nm (Ar laser) and at a resolution of 1 cm⁻¹. The laser power was 20 mW.

3. Results and discussion

The Raman spectra of the GaAs substrate before PIII, after PIII, and after PIII and rapid thermal annealing (RTA) are displayed in Fig. 2a,b,c. Fig. 2a shows the Raman spectrum of the GaAs after etching, and the GaAs-type feature peaks at 268 (TOₓ) and 292 (LOᵧ) as well as the broad band at 525 cm⁻¹ (2TOₓ;Γ, LOᵧ;Γ + LAᵧ;L) are clearly seen [11]. The relative intensity of TOₓ is greater than that of LOᵧ, revealing that the GaAs substrate has been disordered and has many dislocations. The Raman spectrum of the implanted GaAs is depicted in Fig. 2b. All the GaAs-type feature peaks displayed in Fig. 2a are absent. A very
Fig. 2. Raman spectra of the GaAs substrate: (a) before PIII; (b) after PIII; and (c) after PIII and rapid thermal annealing (RTA).

A broad peak with 100 cm$^{-1}$ half width at 232 cm$^{-1}$ is seen. The high background intensity shows that the surface layer is fully damaged after PIII implantation and an amorphous surface layer is formed. After rapid thermal annealing, several sharp peaks are seen in Fig. 2c, including the GaAs-type feature peaks at 268, 292, and 525 cm$^{-1}$, like the ones shown in Fig. 2a. The two peaks at 507 (2TO; Γ) and 533 cm$^{-1}$ (LO$_2$; Γ + LA$_2$; L) are the GaAs-type TO$_2$ and LO$_1$ peaks modified by shifts arising from the strain-compensated lattice. After re-crystallization of the nitrogen-implanted surface layer by RTA, many nitrogen atoms are inserted into and occupy lattice sites, and the surface layer is strained. The vibration mode of the GaN bonds in the GaAs-type lattice at 417 cm$^{-1}$ [11] can be observed in Fig. 2c. The weak Raman intensity reveals that only a small amount of GaN, possibly in small crystal form, has been generated. It appears that under the adopted conditions, the implanted nitrogen atoms do not replace all the As atoms. The surface layer remains essentially a GaAs-type structure, and the nitrogen atoms mainly generate a strained surface GaAs layer. By controlling the annealing condition, for example by carrying out solid phase epitaxy re-growth at 850°C, a larger amount of GaN should form, replacing the GaAs bonds. Based on our Raman data, even though the strained structure created is not good enough for direct device fabrication, it can be used as the substrate with a built-in lattice-matching top buffer layer for further growth of GaN by MOCVD and other techniques.

4. Conclusion

We have demonstrated for the first time the use of nitrogen plasma-immersion ion implantation to generate a strained surface layer in GaAs, permitting subsequent lattice-matching GaN film growth by conventional techniques, such as MOCVD. In order to broaden the nitrogen in-depth distribution and the thickness of the surface amorphous layer, we used multiple implantation energy values by changing the pulsing voltage. This is easily implemented in PIII, but quite time consuming by conventional beam-line ion implantation. Our Raman spectra show that GaN, possibly in small crystal form, is generated in GaAs by PIII and rapid thermal annealing. We suggest that by using solid phase epitaxy, a surface layer with a higher GaN content can be obtained.

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References
