SYMPOSIUM K

Morphological and Compositional Evolution of Heteroepitaxial Semiconductor Thin Films

April 24 – 27, 2000

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* Invited paper

selected-area diffraction patterns through the employment of the Laue curcle.

K5.25
STRUCTURE AND OPTICAL CHARACTERISTICS OF AlN AND AlGaN ALLOYS THIN FILMS. Janis Jansons, Maris Springis, Ivar Tale, Aris Veispals, Institute of Solid State Physics, University of Latvia, Riga, LATVIA; Hans-Joachim Fitting, Heinrich Stolz, Physics Department, Rostock University, Rostock, GERMANY.

The AlGaN alloys hold promise for developing ultraviolet photo-detectors, MESFET, MODFET, bipolar transistors, light-emitting diodes and laser diodes. Native and introduced defects strongly influence their optical and electronic properties. The optical properties of mono crystalline AlN and AlGaN thin films grown by MOVPE on saphire substrates were investigated by transmittance, reflectance, photoluminescence and cathodoluminescence measurements. Epitaxial films were deposited in two step process, with a low temperature buffer layer. The structure of films was tested by X-ray diffraction and scanning microscope techniques. The excitonic absorption edge of AlGaN alloys continuously shifts from 3.43 eV to 6.2 eV by increase of the Al content in alloy. An additional absorption slope, distinct from the Urbach tail and caused by defects was observed even at Al concentration of some percent. The structured absorption tail below the band edge was detected in films ranging in Al concentration above 55%. The photoluminescence and cathodoluminescence spectra in the whole Al concentration range are represented by exciton related luminescence bands peaked close to the band gap. In films ranging in Al concentration above 60% new luminescence bands peaking in spectral range 2 - 4.5 eV occur. Introduction of oxygen in film results in considerable increase of these luminescence bands. It can be expected that principial presence of deep defects in AlGaN alloys at high concentration of Al can be an important problem in development of electronic and optoelectronic devices.

K5.26
ANALYSIS OF STRUCTURAL PROPERTIES OF AlGaN EPILAYER WITH VARIATION OF AlN MOLAR FRACTION. Je Won Kim, Young K. Park, Seong-Il Kim and Yong Tae Kim, Korea Institute of Science and Technology, Semiconductor Materials Laboratory, Seoul, KOREA; In-Hoon Choi, Korea University, Dept of Materials Science, Seoul, KOREA.

AlGaN alloy is a very attractive material to use in UV photo-detectors, high electron mobility transistors, and field-effect transistors, based on AlGaN/GaN heterostructures, holding promise for high power and high-temperature electronics device applications. In order to achieve the bandgap engineering in the heterostructures of $Al_xGa_{1-x}N$, it is essential to investigate the dependence of structural properties of AlxGa1-xN as a function of AlN molar fraction (x) and achieve the better control of AlN composition without a compositional fluctuation in depth of the epilayer. In this work, the structural properties of $Al_xGa_{1-x}N$ epilayers grown on (0001) sapphire by molecular beam epitaxy (MBE) with variation of AlN molar fraction is characterized by Auger electron spectroscopy (AES) and atomic force microscopy (AFM).

K5.27
A THEORETICAL STUDY ON DOMAIN BOUNDARIES IN EPITAXIAL WURTZITE GaN FILM. Shaoqing Wang, Hengqiang Ye, Laboratory of Atomic Imaging of Solids, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, PR CHINA.

GaN attracts extensive research interests both in science and in industry for its potential use in the manufacture of photoelectric devices. This paper reports our attempt for a molecular dynamics study on various domain boundary structures in Wurtzite GaN. The domain boundaries can be classified into two types along {1-100} and {11-20} planes in Wurtzite GaN, respectively. Our research results show that the domain formation energies of (1-100) and (11-20) boundaries are significantly different. The latter ones have general quite higher formation energies than the formers. All the like-atom bonding domain boundaries have higher formation energies than their counterparts of unlike-atom bonding domain boundaries in both of GaN (1-100) and (11-20) interfaces. There will be more (1-100) rather than (11-20) domain boundaries in Wurtzite GaN from the viewpoint energetically. This conclusion is in accordance with the usual experimental observations that most grain boundaries are (1-100) boundaries. All the unlike-atom bonding domain boundaries can form stable atom configurations. The atom positions are regular and symmetrical at the boundaries. While most of the like-atom bonding domain boundaries are unstable. The atom positions are irregular and lack of symmetry at the boundaries. A simple way to differ these domain boundaries can be that the atomic images by unlike-atom boundaries will be clearly distinguishable regular-arranged image patterns while the images of like-atom boundaries will contain many irregular patterns and be serious blurred by experiment of high-resolution electron microscopy. We found one exceptional (1-100) like-atom bonding boundary. Its domain formation energy is not quite high. The boundary configuration is stable and there is no serious lattice distortion. It can not be easily observed by high-resolution electron microscopy.

K5.28
X-RAY PHOTOELECTRON SPECTROSCOPY EVALUATION OF SURFACE CHEMICAL STATES OF GaN, InGaN AND AlGaN HETEROEPITAXIAL THIN FILMS GROWN ON SAPPHIRE BY MOCVD. K. Li, Institute of Materials Research and Engineering, SINGAPORE; A.T.S. Wee, J. Lin, National Univ of Singapore, Dept of Physics, SINGAPORE; Z.C. Feng, S.J. Chua, Institute of Materials Research and Engineering, SINGAPORE.

The surface chemical states of MOCVD grown GaN, AlGaN and InGaN, and the influence of different dopants have been studied with x-ray photoelectron spectroscopy (XPS). The results show that for most of the samples the N 1s peak can be deconvoluted into a dominant GaN peak at the binding energy of about 397.2 eV and a small N-H peak at the binding energy of about 398.5 eV, while Ga 3d can be deconvoluted into three peaks, ie, elemental Ga at 18.5 eV, GaN at 19.7 eV, and Ga_2O_3 at 20.4 eV. Si-doping appears to change the surface oxidation property of GaN by causing a change of intensities in the relative components of the Ga 3d peak. Compared with Si doping, the influence of Mg-doping appears to be larger. In addition to a change in the component intensities, Mg-doping also causes the N 1s and Ga 3d peaks to broaden. The ternary AlGaN sample shows the surface segregation of aluminum. For the undoped InGaN, surface indium deficiency is observed. Due possibly to trapped N-H and Ga-CH intermediate species at grain boundaries, the Zn doped InGaN sample shows a relatively larger N 1s peak at 398.78 eV and an additional Ga 3d peak at 21.4 eV respectively.

K5.29
FORMATION OF GALLIUM NITRIDE (GaN) TRANSITION LAYER BY PLASMA IMMERSION ION IMPLANTATION AND RAPID THERMAL ANNEALING. Dixon T.K. Kwok, Aaron H.P. Ho, X.C. Zeng, Chung Chan and Paul K. Chu, Department of Physics and Material Science, City University of Hong Kong, Hong Kong, CHINA; S.P. Wong, Department of Electrical Engineering, Chinese University of Hong Kong, Hong Kong, CHINA

Recent advances in the preparation of gallium nitride (GaN) and related compounds have promised the commercial production of blue semiconductor light emitting devices. Typical preparation of GaN involves growing the materials on sapphire or silicon carbide using metal-organic chemical vapor deposition (MOCVD). The lattice mismatch between GaN and the substrate makes it difficult to achieve high quality crystal. In this work, we will describe a novel process to synthesize a device-grade GaN buffer layer by plasma immersion ion implantation (PIII) of nitrogen ions into a III-V semiconductor substrate followed by rapid thermal annealing. This thin surface layer of GaN can then be used for either direct device fabrication or as a lattice-matched template for further epitaxial growth of GaN. PIII offers the advantage of high efficiency and highly uniform beam density over a large area, which are particularly important for commercial and large wafer processing. PIII can be performed at low energy implantation thereby favoring the formation of thin layers. We will present our characterization results acquired by photoluminescence, Raman scattering, x-ray diffraction, Hall mobility and carrier concentration measurements.

SESSION K6: INTERDIFFUSION AND SEGREGATION

Chair: David E. Jesson
Wednesday Morning, April 26, 2000
Salon 1/2 (Marriott)

8:30 AM *K6.1
INTERACTIONS, INTERDIFFUSION AND SEGREGATION IN QUANTUM DOT ENSEMBLES. Rosa Leon, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA.

Statistically non-interacting quantum dot ensembles can be achieved by raising surface energies during growth [1]. This also produces large concentration variations in simultaneous growths of InGaAs quantum dots (QDs) by step edge nucleation control on vicinal GaAs [001]. These QD surface density variations radically affect their optical properties. Strong strain interactions between QDs in dense ensembles are seen to blue-shift emission energies, narrow inter-sub-level transition energies, shorten luminescence decay times for excited states, and increase inhomogeneous photoluminescence broadening [2]. These effects are compared to recent results obtained in QDs after InGaAs/GaAs interfacial compositional disordering [3]. Different

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FORMATION OF GALLIUM NITRIDE (GaN) TRANSITION LAYER 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 made possible the production of blue semiconductor laser. Conventional preparation involves growing GaN thin films on lattice-mismatching sapphire using metal-organic chemical vapor deposition (MOCVD). In this article, we describe an alternative method to produce a lattice-matching strained layer in GaAs for subsequent GaN growth by plasma immersion ion implantation (PIII) followed by rapid thermal annealing. Our novel approach uses 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 and low nitrogen content problems associated with ion beam implantation at fix 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.

INTRODUCTION

The wide band-gap semiconductor based on the nitride compounds of the III-V group has attracted much attention because of their 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 substrates. Although the inherent 15% lattice mismatch with GaN makes sapphire an unlikely substrate for high quality crystal growth, it has been found that one can grow a sequence of ultra-thin GaN buffer layers 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 temperature 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 so far have 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 [3]. Kuriyama et al. recently also demonstrated that N^+-implanted GaAs exhibits photoluminescence in the blue region, thus further confirming the prospect of producing functional GaN by ion implantation [4]. The group led by Sealy [5,6] adopted an alternative approach. They implanted Ga into Si_3N_4 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 done 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 material. 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 energies 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 for 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 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.

EXPERIMENT

Nitrogen was implanted into GaAs substrate by plasma immersion ion implantation (PIII) [9]. The plasma mainly consisted of N_2^+ ions. The GaAs sample was biased at three different voltages of 40, 20, and 10 kV with an implant dose of 8 x 10^{16} cm^{-2}, 5 x 10^{16} cm^{-2}, and 3 x 10^{16} cm^{-2}, respectively. The use of multiple energies 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 five minutes 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 minutes. 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 20mW.

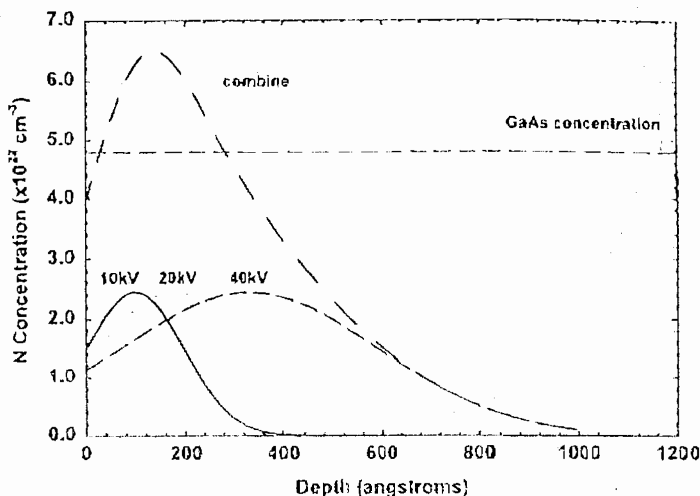

Figure 1: Nitrogen depth profile in the PIII GaAs sample simulated by TRIM. The implanted nitrogen concentration at the peak is higher than the arsenic concentration in GaAs.

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 Figs. 2, 3, and 4, respectively. Fig. 2 shows the Raman spectrum of the GaAs after etching, and the GaAs type feature peaks at 268 (TO_1) and 292 (LO_1) as well as the broad band at 525 cm^{-1} ($2TO_1:\Gamma$, $LO_1:\Gamma+LA_1:L$) are clearly seen [11]. The relative intensity of TO_1 is greater than that of LO_1 revealing that the GaAs substrate has been disordered and have many dislocations. The Raman spectrum of the implanted GaAs is depicted in Fig. 3. All the GaAs type feature peaks displayed in Fig. 2 are absent. A very 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 has been formed. After rapid thermal annealing at 850°C for 2 minutes, several sharp peaks can be observed in Fig. 4, including the GaAs type feature peaks at 268 (TO_1) and 292 (LO_1) as well as the broad bands at 507 ($2TO_1:\Gamma$) and 533 cm^{-1} ($LO_1:\Gamma+LA_1:L$. The intensity of TO_1 is higher than that of LO_1 revealing that the GaAs substrate has been disordered. 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. 4. 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.

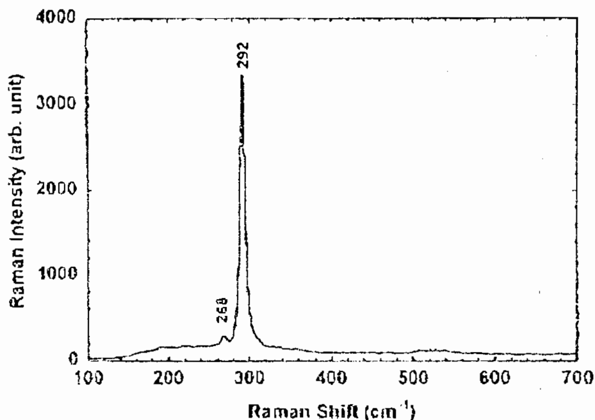

Figure 2: Raman spectrum of the GaAs substrate before PIII (integrated for 10 scans), showing the GaAs type feature peaks at 268 (TO_I) and 292 (LO_I) cm^{-1}.

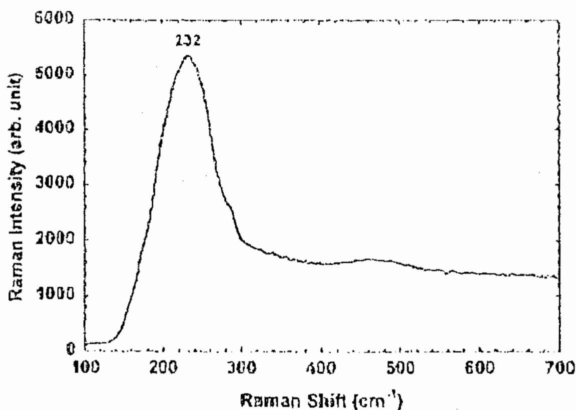

Figure 3: Raman spectrum acquired by integrating 10 scans from the GaAs substrate after nitrogen PIII.

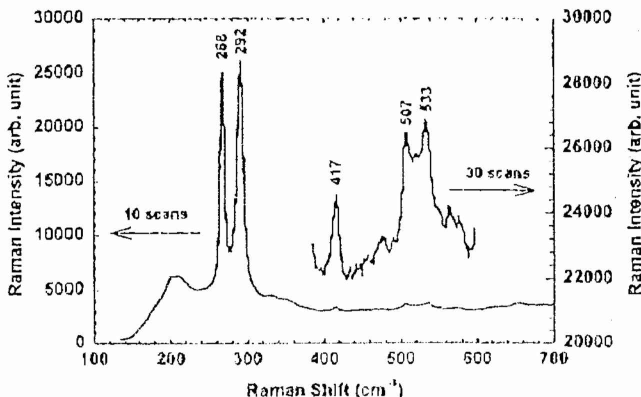

Figure 4: Raman spectrum acquired by integrating 10 scans from the GaAs substrate after nitrogen PIII and RTA at 850ºC for 2 minutes.

CONCLUSION

We have demonstrated the use of nitrogen plasma immersion ion implantation (PIII) 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 use multiple implantation energies by changing the pulsing voltages. 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.

ACKNOWLEDGMENTS

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