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LAYER-BY-LAYER DEPOSITION OF GROUP-III NITRIDES BY TWO-STEP CYCLIC PROCESS

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Abstract

Pulsed-Laser-Deposition (PLD) is an attractive alternative to the conventional methods for preparation of films of group-III nitrides. Extremely pure films can be grown by PLD from elemental precursors (Ga, Al, In, N_2). On the other hand, PLD films usually suffer from insufficient nitrogen content and structural imperfection. This work deals with "prove of the principle experiments" on deposition of GaN films by a two-step cyclic process, which is intended to avoid these problems. During the first step, an ultra-thin layer of nitrogen-poor material is deposited by PLD at background N_2 pressure in the range 10^{-3} –10^{-2} mbar. We show that the surface mobility of the film precursors can be varied in this pressure range and hence the film growth mechanism can be controlled. The second step employs intensive N_2-glow-discharge, sustained at pressure of 1 mbar, to incorporate additional nitrogen into the layer. The cycle of two steps is repeated till a film of the desired thickness is obtained. Specific effects of the applied deposition method are demonstrated and discussed.

1. Introduction

The preparation of high quality semiconductor films of group-III nitrides (GaN, AlN, InN and their alloys) is a forefront task of the present technological research because of the attractive applications of such films in "blue and UV" optoelectronic devices. The Pulsed Laser Deposition (PLD) is a promising alternative of the common MO CVD and MBE techniques for preparation of these materials [1-6]. The potential advantages are deposition of extremely clean films at conditions similar to those of MBE, but employing simpler equipment and process operation, as well as, the opportunity for a fast switching between depositions of different III-nitride alloys by simply redirecting the laser beam to different multi-component targets. The common version of PLD is performed by using sintered GaN (AlN, InN) target and highly reactive background atmosphere of NH_4 (typically at 10^{-4} mbar), which is needed to compensate the N-loss from the target. Although, stoichiometric epitaxial films of GaN [1] and AlN [2] have been obtained by this version, it is a compromise because H impurities are not avoided and because it requires the use of sophisticated excimer lasers (the target absorbs in the UV range only). Many attempts have been made to synthesize group-III nitrides by PLD using pure N_2 background gas and metallic targets as material sources [4-6]. Such versions, however, face the problems of nitrogen deficiency and structural imperfection of the obtained films [5]. The problems reflect an inherent conflict of the PLD – efficient nitrogen incorporation can be achieved by operation at high pressure of the N_2 background (~ 0.1 mbar), while the undisturbed transport of the laser ablated species needs low pressure.

This work is focused on synthesis of GaN from elemental precursors (Ga and N_2) by applying a two-step cyclic process, which is intended to establish independent control over the film growth by PLD and the nitrogen incorporation in the film.

2. Approach of the Two-Step Cyclic Process

The process performs a layer-by-layer deposition of GaN film with each sub-layer formed in two steps. During the first step, an ultra-thin layer is deposited by laser ablation of Ga under background N_2 gas atmosphere. In contrast with the common PLD process, this step serves to form a good primary structure of the layer rather than to ensure sufficient nitrogen incorporation in it. Thus, optimal N_2 pressures, which ensure undisturbed transport of the ablated species to the growing surface and favor a superior structure of the primary layer, can be chosen as shown in the next section.

The second step serves to insert additional nitrogen into the last deposited layer by immersing its surface in activated nitrogen (N atoms or/and N^+ ions). For the purpose we have employed a radio frequency glow-discharge, sustained in N_2 at elevated pressure. The duration of this step controls the N-incorporation in the film and has also a favorable effect over the film structure, as the atoms of the surface layer remain mobile during an extended period.

3. Deposition System and Experimental Details

The experiments have been carried out in UHV deposition system. To achieve the needed fast and repeatable changes of the process conditions, a computer conducts all system actuators (gas & vacuum valves, laser, R.F. generator). The design of the reactor chamber is shown in figure 1. The substrates are fixed “face down” on a grounded Mo holder. The holder can be heated up to 1200^oC. In front of the holder is placed a R.F. counter-electrode at 3 cm distance. A Mo crucible is mounted within the R.F. electrode and filled with Ga (99.9999 % purity) serving as ablation target. A Q-switched

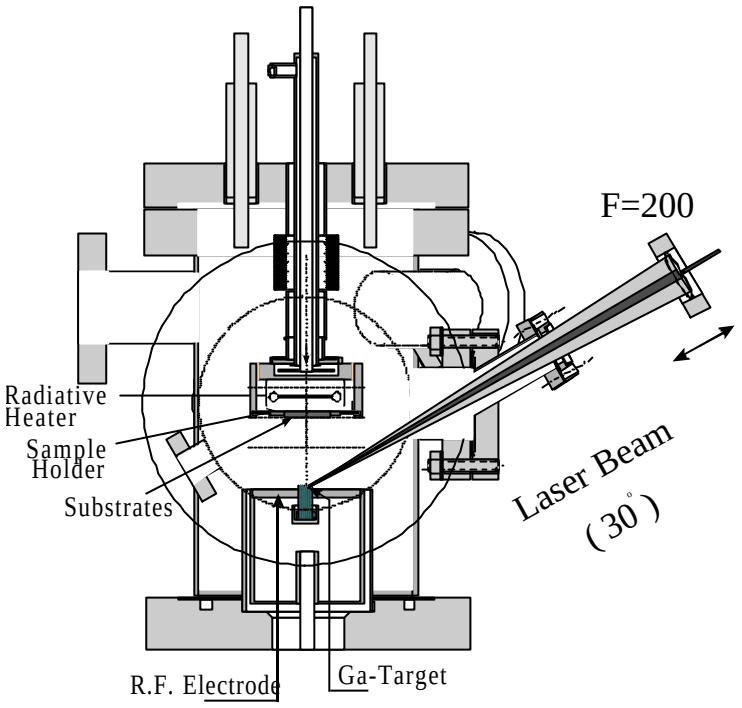

Figure 1. The reactor chamber used for performing the two-step cyclic process

Nd:YAG laser, operating at 1064 nm wavelength with variable pulse energy of up to 20 mJ and pulse duration 5 ns, is used to ablate the target. The laser beam is focused on the target to elliptical spot of size 200 x 400 μm, which result in a beam fluency of 15 J/cm^2. The chamber is pumped by turbo-drag pump trough a butterfly valve and cut-off valve. Pure nitrogen (99.999 %) is introduced either via mass-flow-controller or via a buffer volume, which can be pre-filled with certain quantity of gas. The pressure during I-step is adjusted by controlling the conductance of the vacuum line (butterfly valve) and the gas flow. The choice of optimal conditions for execution of this step is described in the next section. The fast increase of the pressure, needed for carrying out the II-step, is achieved by injection of N_2 from the buffer volume into the closed chamber. During the second step R.F. power is applied to the counter-electrode, producing capacitively coupled glow-discharge in front of the substrates. All samples for this work were deposited on quartz substrates at temperature of 300^{o}C.

4. Results and Discussion

4.1. Optimization of Pulsed Laser Deposition as a First Step of the Cycle

To optimize the process conditions during the first step we investigated the electric currents, which flow between the Ga target and the sample holder after the laser shot. Figure 2 shows an example of such time-resolved currents, measured at zero, negative and positive voltage applied to the target in vacuum. The positive sign of the current corresponds to positive charge flowing from the target to the sample holder. Fast negative and slower positive components can be distinguished in the figure. The first one can be associated with electrons and the second one with Ga ions – both originating from the plasma plume initiated by the laser shot. Note that electrons and ions are reaching the substrates even when no bias is applied (electrodes are short-circuited). With applying negative bias to the target (retarding for the ions) the ion component is decreasing fast and vanishes at voltages as low as -0.2-0.3 V. Thus, one can conclude that the initial energy of the Ga ions in our experiment is low - of the order of 0.25 eV (effective ion temperature ~ 3000 K). In contrast, the electron current needs about

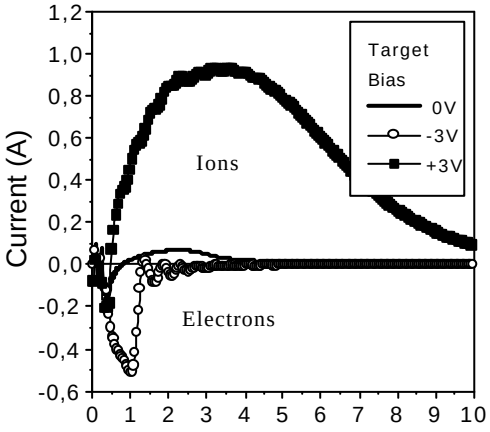

Figure 2.
Time resolved currents between the target and the substrate holder at different voltage polarities.

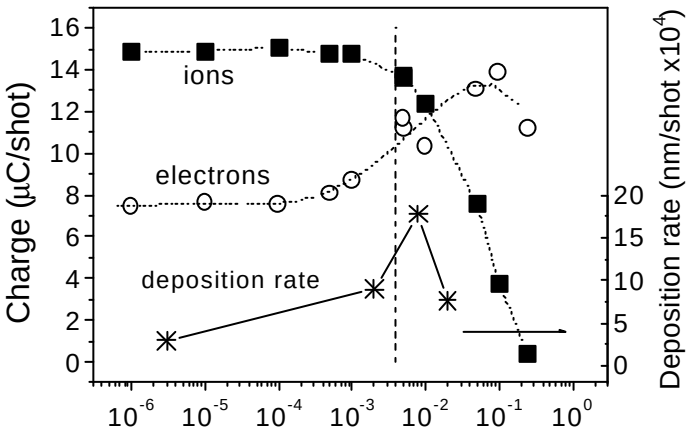

Figure 3.
Charge collection experiments (acceleration voltages +/-30 V) and film growth rate vs. background N_2 pressure

+15 V retarding (positive) voltage to be suppressed. Hence, we conclude that the electrons are emitted from the plume at high energies (`~ 15 eV or 10^5 K).

Figure 3 shows the charges (integrated areas below current curves), collected at high voltages, after laser ablation at various background N_2 gas pressures. At such voltages, the charges of opposite signs are sharply separated and all accelerated carriers arrive at the substrate holder without recombination. Note that when no voltage is applied, almost the same number of Ga species (both neutral and ionized) reaches the substrates, although only a few of them can be detected as ion current after the recombination with electrons on the way. Thus, the high-voltage collection of ions gives a measure of the total amount of Ga species reaching the substrate at the actual conditions of a film deposition experiment. Figure 3 reveals that about 15 μC per shot are collected in vacuum. On the other hand, the same conditions of laser ablation result in Ga film deposition rate of about 0.003 Å/shot. The comparison of these values (in number of Ga particles per cm^2 per shot) shows that less than 1/4 of the arriving Ga atoms are deposited. In other words, the laser ablated Ga has a very low “sticking” ability. This can be explained by the high surface mobility of Ga, which could slow down the thermalization of the energetic ad-atoms on the film surface. Thus, they can be reemitted back into the vacuum before significant condensation occurs.

As can be seen in Fig. 3, the collected charges of both kinds do not vary from high vacuum up to a critical pressure, at which the mean free path of the gas molecules approaches the distance between the electrodes (indicated by a dashed line on the figure). The beginning of the interaction between the plasma plume and the background N_2 manifests as an increase of the collected electron charge because of the rise of an additional e-current peak at shorter times of flight. This increase can be interpreted as originating from secondary electrons, emitted during breakdown of the N_2 molecules

(producing reactive N atoms and/or ions). The e-charge reaches maximum at pressures as high as 0.1 mbar (25-50 mean free paths between the electrodes) and then fall down due to the rising scattering and recombination. On the other hand, the collected ion charge begins to decrease immediately after the mean free path reaches the inter-electrode distance. This can be explained by the significant scattering of the large Ga ions during their transport to the substrates.

An important result, shown in Fig. 3, is that the film deposition rate increases sharply after the start of the gas phase interaction, reaching maximum at a pressure corresponding to 2-3 mean free paths between the target and the substrates. One can interpret this event as originating from the enhanced "sticking" of the arriving species due to the formation of Ga:N complexes within the gas phase. The variation of deposited film morphology, shown in Figure 4, is in agreement with such explanation. The transition from smooth surface to grainy and finally mountain-like structure is an evidence for rising "sticking" (i.e. decreasing surface mobility) of the film precursors.

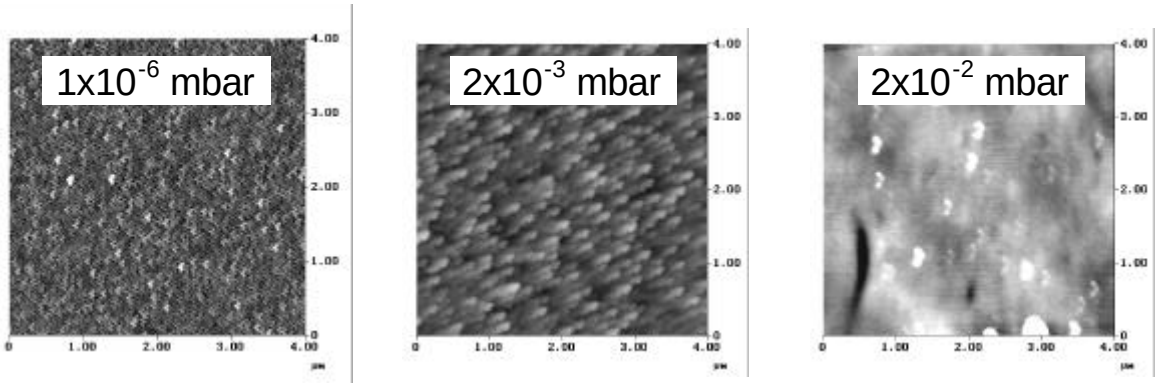

Figure 4.
AFM images of samples, prepared by PLD at the indicated background N_2 pressures.

Figure 5 shows that the nitrogen incorporation in the film begins to occur in the same pressure range. The films, deposited above 10^{-3} mbar, tend to clear optically in contrast with the metallic Ga films deposited in vacuum. A trace of absorption edge in the UV region just emerge at pressures as high as

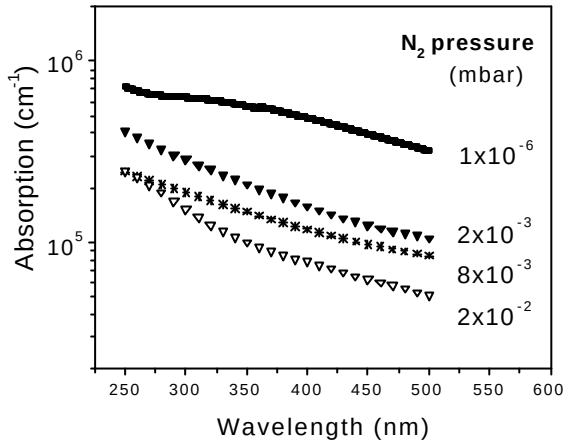

Figure 5.
Optical absorption of samples, prepared by PLD at the indicated N2 pressures.

$2x10^{-2}$ mbar. However, the deposition rate drops at this pressure, indicating that the transport of Ga:N species to the growing surface is already disturbed. On the other hand, all films, deposited up to this pressure, have a significant rest absorption in the visible region, which is a sign of severe nitrogen deficiency. In spite of that, we chose N_2 background pressures from the 10^{-3}-10^{-2} mbar range as optimal for performing the first step of the cycle because a primary layer of better structure can be grown at higher rate. The nitrogen deficiency at this stage is not critical, as the missing nitrogen has to be restored during the second step of the cycle.

4.2. Full Cycle

We have carried out a "prove of the principle" experiment by alternating PLD (I-step) and Plasma Nitrogenation (II-step) in 250 full cycles. Each first step is performed by applying 200 laser shots on the Ga target at N_2 background pressure of $8x10^{-3}$ mbar, which results in deposition of 0.4 nm thick nitrogen-poor layer. During the second step the N_2 pressure is raised to 1 mbar and R.F. power of 15 W is applied between the target and the sample holder. This results in a bright glow discharge in front of the substrates. The duration of this N-plasma treatment is fixed at 20 seconds in the present work. At the end of the cycle the chamber is pumped down to 10^{-5} mbar before the next I-step begins.

The effects of the plasma treatment can be seen in Figures 6 and 7. The extended background optical absorption clears out and a distinct semiconductor absorption edge in the UV region appears in the films prepared by the full cycle. The edge, seen in Fig. 6, is rather broad due to an extended Urbach tail. This is not surprising, as the samples for this study have been deposited on amorphous quartz substrates at temperature as low as 300^{o}C. Thus, the films obtained are obviously amorphous. In spite of this fact, Figure 6 demonstrates the conversion of the Ga-rich film, prepared by PLD at low N_2 pressures, into GaN film as a result of the application of the two-step cyclic process. Another effect of the complete cycle is the formation of a rather smooth film instead of the grainy structure, obtained in the first PLD step as can be seen in Fig. 7. To further investigate the potential of the deposition process, introduced in this work, we are currently carrying out experiments on epitaxial growth of GaN on lattice matching substrates at elevated temperatures.

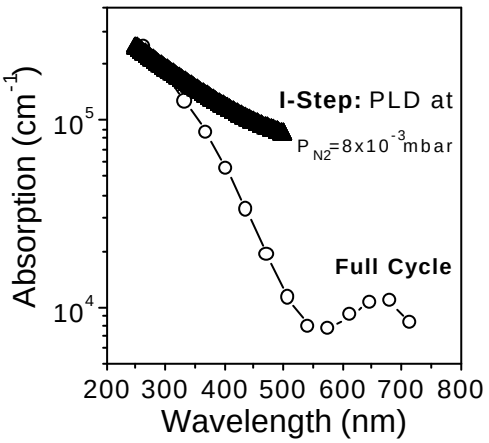

Figure 6.
Optical absorption of samples, prepared as indicated.

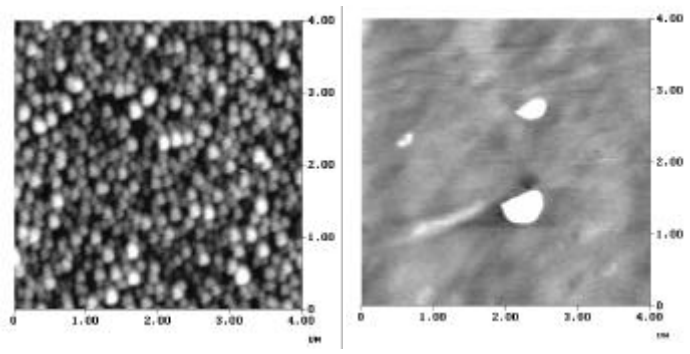

Figure 7.
AFM images of samples, prepared by: a) PLD (I-step only) at 8x10^{-3} mbar N_2 background pressure and b) applying a full cycle with the same I-step.

5. Conclusions

We introduced a new technique for preparation of GaN films from elemental precursors (Ga, N_2), which is based on alternation of Pulsed Laser Deposition (PLD) and N-plasma nitrogenation steps. In

contrast with the usual PLD, this technique allows to control independently the structure and the nitrogen content of the growing film. We have shown that optimal condition for performing the first step is to operate PLD at low pressure of the N_2 background gas in $10^{-3} – 10^{-2}$ mbar range. Hence, the film deposition rate is maximized and a primary film with improved structure is grown from species with enhanced surface mobility. A proven advantage of applying N-plasma in the second step is that enough nitrogen can be inserted in the primary film independently of the conditions of its growth during the first step. The growth interruption during the second step favors the formation of smooth GaN films. The "prove of the principle experiments", presented in this work, justify the further attempts to prepare high-quality films of group-III nitrides by the proposed process.

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