# Optical properties from amorphous GaN films deposited by a pulsed-laser ablation at room temperature

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# 1. Introduction

The crystalline III-nitride semiconductors have been extensively studied for applications in blue-light emitting diodes, laser diodes and high-power high-frequency electronic devices [1-3]. However, the post-processing at elevated temperature generated crystal defects due to their poor epitaxy on the common substrates, which severely limit the high performance potential of the crystalline films.

Pulsed laser deposition (PLD) which is well known to be a highly energetic deposition technique has been widely used for the film-synthesis of a variety of materials [4]. The high kinetic energies induced by a laser ablation enable to generate the non-equilibrium formation of the meta stable films like the amorphous structure at relatively lower temperature and even at room temperature.

In this study, we present experimental reports on blue-luminescent characteristics of the pulsed-laser deposited a-GaN films at room temperature by controlling the process conditions of laser energy and ambient Ar gas pressure. The structural features and luminescence property of the films were systematically investigated as a function of the pulsed laser energy and ambient Ar gas pressure.

# 2.1 Experimental Procedure

ArF excimer laser (Lambda Physik, LPX110i,  $\lambda$ =193 nm) was used as a laser source in order to transfer the species as energetically as possible. The repetition rate and pulse width of the laser were 10 Hz and 17 ns, respectively. The pulsed laser energies were operated in the range from 34 to 200 mJ/pulse. Laser beam was focused to a laser spot size of ~1×4 mm<sup>2</sup> on a target surface through an UV grade quartz window. The sintered GaN targets were prepared by a spark plasma sintering at 1000 °C in N<sub>2</sub> atmosphere using commercial powders with purity of 99.99% (Kozundo Chemical Ltd.).

The quartz glass substrates were placed near the target at an off-axial position which enables to avoid the large-sized particulates deposition on the film surface.<sup>(15</sup> The target was irradiated with 20,000 pulse. The pressure of the background Ar gas was varied from 1 to 200 Pa. The surface morphology of the deposited films was observed using a field-emission scanning electron microscopy (FE-SEM; Hitachi, S-800, Japan). The crystallinity and physical structure were examined by X-ray diffractometer (XRD; Rigaku, RAD-C, Japan) using Cu Kα radiation and a transmission electron microscopy (TEM; JEOL, JEM 2010, Japan). The surface composition and chemical states analysis were performed with X-ray photoelectron spectroscopy (XPS; PHI, 5600ci) using the monochromated Al Κα source. The optical absorption and the room-temperature photoluminescence spectra were measured with a spectrometer (Shimadzu, UV-2100PC) and a spectrometer with a 0.1nm resolution and using 500 W Xenon lamps as optical excitation source, respectively.

# 2.2 Results and discussion

Figure 1 shows core level X-ray photoelectron spectra of Ga 3d and N 1s for films deposited under Ar pressures lower than 10 Pa. The peak positions in the Ga 3d at 19.9 eV and N 1s at 397.5 eV confirm the existence of GaN, suggesting that the films exhibited the amorphous structures without any crystalline peaks from XRD results. This binding energy is, within the experimental error range, consistent with previously reported XPS studies of a-GaN. A calculation of the [Ga]/[N] ratios were 1.29 in the films deposited at 1Pa and 1.17 at 10 Pa, reflecting the formation of the Ga-rich films.



Fig. 1 Chemical states of a-GaN films deposited at 34 mJ/pu lse under the Ar pressures of 1 and 10 Pa. The peak positio ns shown for gallium (19.9 eV) and nitrogen (397.5 eV) are consistent with previous literature data, indicating no differen ce of the peak positions between 1 and 10 Pa.

The surface morphology and compositional analysis of the deposited films revealed that the Ar pressure of 10 Pa was found to be most suitable for the deposition of the stoichiometric films with the smooth surface. In order to investigate the effect of a laser energy on the film characteristics, the a-GaN films deposited at 34, 100 and 200 mJ/pulse, respectively under the same pressure condition were examined taking into account the microstructure and stoichiometry. From the X-ray diffraction patterns and HR-TEM micrographs, the a-GaN film deposited at 100 mJ/pulse exhibits typically an amorphous structure, very similar to that for the film at 34 mJ/pulse. When laser energy increased to 200 mJ/pulse, low intensity of broad crystalline peak appeared around the scattering angle of  $2\theta=35^{\circ}$ . This behavior could be clearly confirmed from the HR-TEM analysis. The a-GaN film deposited at 34 mJ/pulse shows a diffuse background scattering which points to a significant amount of amorphous phase, similar to the diffraction patterns reported in reference on a-GaN films grown at 200~300  $^{\circ}$ C.

On the other hand, the a-GaN film deposited at 200 mJ/pulse exhibits a two phase microstructure that consists of GaN nanocrystallites with a diameter of about 10 nm embedded in an amorphous matrix. The diffraction pattern has clearly discrete two rings, corresponding to lattice plane spacings d=0.24 and 0.27 nm. These spacings were well consistent with the calculated spacings d(0111) and d(0110) of the hexagonal GaN.

In addition, there was no difference of the binding energies of Ga 3d and N 1s between these films and the measured [Ga]/[N] ratio were 1.17 for the film at 34 mJ/pulse, 1.16 at 100mJ/pulse and 1.05 at 200 mJ/pulse. An increase of laser energy was found to lead to an enhancement of crystallinity and stoichiometry of the films, as compared with that of the films at relatively lower laser energies. Generally, high kinetic energy of the ejected species generated by a laser ablation cause the increase of the surface mobility, which allows the atoms to diffuse over the surface. As a result, the promotion of the atom diffusivity on the surface could cause the formation of film as well as fine crystallites due to the enhancement of the atomic bonding and this bonding nature restains the reevaporation of nitrogen atoms with volatility higher than that of gallium which can be induced by ion bombarding.

Figure 2 presents the photoluminescence (PL) spectra of the a-GaN films deposited at 34 mJ/pulse and 200 mJ/pulse measured at room temperature. Consistent with the optical band gap estimated from the absorbance, both the films exhibits the blue emission peak at ~2.8 eV. This value is in quite good agreement with the optical band gap of a-GaN calculated from ab initio molecular dynamics as well as blue luminescence shown in the a-GaN deposited by compound source molecular beam epitaxy. In particular, the a-GaN film deposited at 200 mJ/pulse exhibited the relatively stronger luminescence intensity, indicating that two Gaussian bands of the emissions at 3.4 and 3.7 eV in inset of Fig. 2 could be attributed to the presence of the nanocrystals observed in the HR-TEM images. The trap states in the band gap which can be generated from negative defects of Ga or N vacancy are severely limited in the stoichiometric composition, leading to the formation of the clean band gap. In addition because the band gap energy depends strongly on the atomic density in a-GaN, an increase of laser energy might enhance the bonding between Ga and N, raising the possibility that the bonding characteristic may affect the emission process.



Fig. 2 The room temperature photoluminescence spectra for a-GaN films deposited at various laser energies under the Ar gas pressure of 10Pa. The luminescence intensity is considerably high in the films at 200 mJ/pulse.

### 3. Conclusions

The blue light emitting a-GaN films were fabricated without substrate heating using a laser ablation of a GaN target. The a-GaN films with the smooth surface could be deposited at various laser energies under 10 Pa, in particular the almost stoichiometric composition of GaN<sub>0.95</sub> was achieved at high laser energy of 200 mJ/pulse. The subgap absorption observed in the films deposited at lower laser energies decreased effectively with increasing to 200 mJ/pulse while the luminescence efficiency significantly increased, suggesting that the stoichiometric composition allows the clean band gap to form. It is worthy to note that our observation of the blue luminescence in the a-GaN films deposited by the pulsed laser ablation technique at room temperature is the first experimental evidence consistent with the recent theoretical results, strongly supporting that this approach should be a very promising technique as the extremely low temperature process suitable for various device application of the multilayer structure and the deposition on low-melting substrate.

#### References

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