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Effect of Substrates on Epitaxial Growth of Group Ⅲ Nitride by PLD

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We have investigated the effect of stress on the structural properties of epitaxial GaN films grown by pulsed laser deposition (PLD) on sapphire and MnO substrates using synchrotron radiation grazing incidence-angle X-ray diffraction (GIXD). The GaN films are compressed in the lateral direction to the surface due to the larger thermal contraction rates of these substrates. The lateral strain in the GaN film grown on the MnO substrate turned out to be much smaller than that expected from the mismatch in the thermal expansion coefficients. This result indicates that the dislocations in the GaN films are mobile during cooling down from the growth temperature under the large stress field.

Key words: pulsed laser deposition (PLD), GaN, MnO, grazing incidence-angle X-ray diffraction, lattice distortion

1. INTRODUCTION

GaN and related nitrides have been regarded as the most promising materials for short wavelength optical devices such as blue light emitting diodes (LEDs) and laser diodes (LDs). GaN thin films have been usually grown by metalorganic chemical vapor deposition (MOCVD) [1,2] or molecular beam epitaxy (MBE) [3,4]. These techniques, however, utilize highly reactive nitrogen sources such as NH_3 or an N_2 plasma, which cause nitridation of the substrate surfaces just before the epitaxial growths. This limits the substrates for the epitaxial growth of GaN only to chemically stable materials. In fact, most of the thin film growths of GaN have been performed on Al_2O_3 substrates in spite of the huge lattice mismatch (approximately 16%) [5].

We have recently shown that the use of the PLD technique for the epitaxial growth of group Ⅲ nitrides is advantageous over the conventional growth techniques because it does not require highly reactive nitrogen sources [6-8]. Since PLD growths proceed in a less reactive N_2 ambient, we can grow nitride semiconductors on substrates vulnerable to chemical attacks. Hence, the use of PLD allows us to grow group Ⅲ nitrides on nearly lattice-matched substrates which have not been used with MOCVD or MBE. Using the PLD technique, we have recently succeeded in the epitaxial growth of high quality GaN films on MnO (1 1 1) [9]. MnO is an attractive material as a substrate for the growth of GaN because MnO (1 1 1) plane has the same symmetry (6-fold rotation) as the GaN (0 0 0 1) plane and the lattice mismatch is as small as 1.6 %. An additional advantage in the use of MnO substrate lies in its high conductivity. This property makes the device fabrication process quite simple because we can make electrodes at the backside of the substrates. To develop high performance optical devices with PLD GaN on MnO, it is necessary to control the strain in the film at the early stage of the epitaxial growth precisely because it is closely related to the formation of defects such as threading dislocations. However, little has been reported about the lattice distortion of the PLD grown GaN epitaxial films.

We have recently shown that generalized grazing incidence-angle X-ray diffraction (G-GIXD) with the synchrotron radiation X-ray source is a powerful tool to investigate the structural properties of the thin compound semiconductor films. This technique allows us to analyze the lattice constants of materials with small volumes both in the lateral and the normal directions to the surface accurately [10–12]. This technique gives lattice constants with an accuracy of 0.001 Å. In this paper, we discuss the structural properties of thin PLD GaN films grown on MnO (1 1 1) substrates using G-GIXD putting special emphasis on the strain caused by the mismatch in the thermal expansion coefficient between GaN and MnO.

2. EXPERIMENAL PROCEDURE

GaN films were directly grown on sapphire (0 0 0 1) and MnO (1 1 1) substrates by PLD. The surfaces of these substrates share the six fold rotational symmetry with the (0 0 0 1) plane of hexagonal group Ⅲ nitrides. After the surface cleaning using ethanol and acetone in an ultrasonic bath, the sapphire and MnO substrates were introduced into the PLD chamber. The base pressure of the growth chamber was $2.0\text{-}4.0\times10^{-9}$ Torr. During the growth, N_2 gas (99.9999% purity) was introduced into the chamber through a variable leak valve and its pressure was kept at 1.0×10^{-1} Torr. The ablated species were ejected with high kinetic energies and deposited onto the substrates that were mounted 5 cm away from the target. The KrF excimer laser (λ=248nm, τ=20ns) with an energy density of 3.0 J/cm^2 was used at pulse repetition rate of 15 Hz. The substrate temperature was set at 700℃. After the deposition, we observed the surfaces of the films with reflection high-energy electron diffraction (RHEED) with a 25 keV electron gun and AFM operated in the tapping mode.

The experimental set-up for the G-GIXD measurements was already reported elsewhere [12]. A synchrotron radiation (SR) beam line, BL-3A at the Photon Factory in High Energy Accelerator Research Organization (KEK-PF) was used for the G-GIXD measurements. The wavelength of the X-ray beam was set at 0.9Å. The incidence-angles of the X-ray beam were varied from 0.1 to 0.2 degrees under the total reflection condition of GaN. The sample was mounted onto a 4-circle goniometer [13]. An imaging plate (200x400 mm) on a spherical-type goniometer [14] was used to detect diffraction peaks. The area detector covers a large area and it allows us to detect many diffraction peaks simultaneously. The reciprocal space mapping was taken by a scintillation counter placed on a spherical-type goniometer [15]. Between the sample and the detector, we placed two slits with an opening of 1x1 mm^2.

3. RESULTS AND DISCUSSION

The thickness of the samples used for the measurements was determined to be approximately 200 nm by grazing incidence-angle X-ray reflectivity (GIXR). Using GIXR, we have also confirmed that the reaction between GaN and the substrates did not occur during the growth. Figures 1 (a) and (b) show the RHEED patterns from the GaN on sapphire(0001) and MnO(1 1 1), respectively. The incident directions of the electron beams are sapphire $[1\ \bar{1}\ 0\ 0]$ and MnO $[0\ 1\ \bar{1}]$. These figures show the sharp streaky diffraction patterns, which indicates that high quality GaN films grow epitaxially on these substrates. Assignment of these diffraction patterns leaded us to conclude that GaN (0 0 0 1) grows on these substrates with in-plane alignments of GaN $[1\ 1\ \bar{2}\ 0]$ // sapphire $[1\ \bar{1}\ 0\ 0]$ and GaN $[1\ 1\ \bar{2}\ 0]$ // MnO $[0\ 1\ \bar{1}]$. As seen in these pictures, we observed 3x3 surface reconstructions. This result indicates that the GaN films grown on these substrates have the N-polarity [16].

AFM images of GaN surfaces on sapphire and MnO (1 1 1) are shown in Figs. 2 (a) and (b), respectively. The root mean square (RMS) values for the GaN surfaces on the sapphire and the MnO substrates are as small as 2.81 nm and 2.20 nm, respectively. These results are consistent with the streaky RHEED patterns.

G-GIXD measurements with the imaging plate detector were performed to search the diffraction spots from the film. These measurements revealed that GaN films are hexagonal single crystals and they do not contain the other phases (e.g. cubic phase). Among various diffraction spots detected on the imaging plate, we picked up $1\ 0\ \bar{1}\ 0$ and $1\ 0\ \bar{1}\ 1$ diffraction spots and carried out the reciprocal space mapping for these diffractions using the scintillation counter. Figures 3 (a) and (b) show the typical reciprocal space mappings for the $1\ 0\ \bar{1}\ 0$ and $1\ 0\ \bar{1}\ 1$ diffraction spots, respectively, of GaN grown on MnO(1 1 1). The lattice parameters, *a* and *c*, deduced from the experimental data using the Bragg's law are summarized in Table Ⅰ. One can see that GaN layers are compressed in the lateral directions to the surface. To discuss the structural properties of GaN during the growth, it is necessary to take the lattice contraction of the substrates and the GaN films during the cooling down into account. Temperature dependence of the lattice constant can be estimated with the following equation:

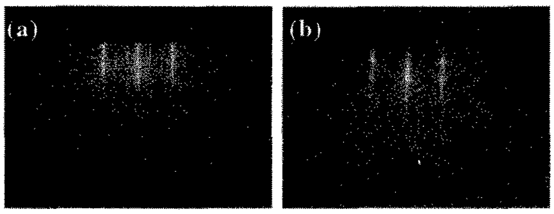

Fig. 1. RHEED patterns of GaN grown on (a) sapphire (0 0 0 1) and (b) MnO (1 1 1) by PLD. The incident direction of the electron beam is GaN $[1\,0\,\bar{1}\,0]$ and 3 × 3 surface reconstructions can be observed for both samples.

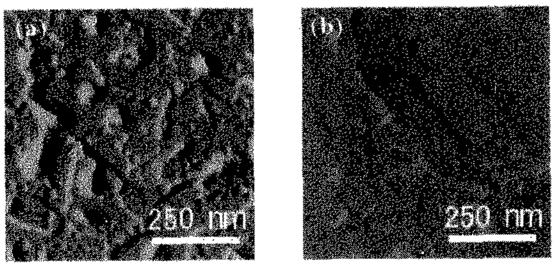

Fig. 2. AFM images of GaN grown on (a) sapphire (0 0 0 1) and (b) MnO (1 1 1).

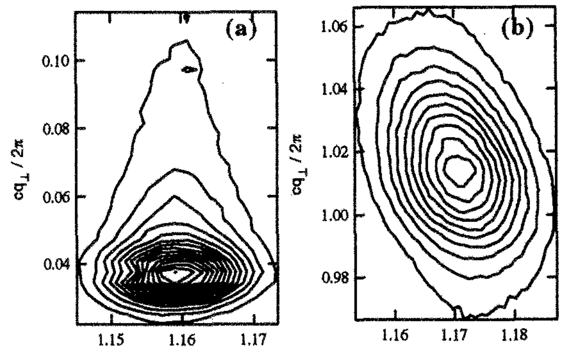

Fig. 3. Reciprocal space mappings for (a) $1\ 0\ \bar{1}\ 0$ and (b) $1\ 0\ \bar{1}\ 1$ GaN diffraction spots on MnO(1 1 1).

$$\frac{dl}{dt} = \alpha\, l_0, \tag{1}$$

where l_0 and l denote the lattice constants at 0 ℃ and *t* ℃, respectively. α is the thermal expansion coefficient and those for GaN, sapphire, and MnO are 5.59×10^{-6} K^{-1}, 7.50×10^{-6} K^{-1}, and 3.45×10^{-5} K^{-1}, respectively [17, 18]. It should be noted that the thermal expansion coefficient for MnO is much larger than those for the other materials. If we assume that the strains in the GaN epitaxial layers on these substrates are fully relaxed at the growth temperature and the thermal contraction solely determines the strains in the films at room temperature, room temperature in-plane lattice constants of GaN are calculated to be 3.181 Å and 3.125 Å on sapphire and MnO, respectively [19]. The fact that the experimental value for GaN on sapphire is quite close to the calculation suggests that the introduction of misfit dislocations during the growth

Table I . Lattice constants and strains of the group III nitride films measured by G-GIXD. The lattice constants, *a* and *c*, of bulk GaN are 3.185 Å and 5.19 Å, respectively.

	Lattice constant (Å)		Strain (%)	
Sample	*a*	*c*	*a*	*c*
GaN/sapphire	3.182	5.099	−0.099	−1.760
GaN/MnO	3.177	5.068	−0.240	−2.355

releases the strain in the GaN film almost completely and that the stress during cooling down is too small to make the dislocations mobile. On the contrary, considerable difference exists between the experimental data and the calculated value only in the case of GaN on MnO. This indicates that the dislocations are mobile at low temperatures and the annihilation and formation of dislocations occur even in the process of the cooling down under the large stress field caused by the large thermal contraction rate of the MnO substrate.

As can be seen in Table I, we have also found that the GaN films on sapphire and MnO is compressed in the normal direction to the surface in spite of in the lateral compressions. These phenomena cannot be explained by the simple theory of the lattice mismatch and indicate that the conventional Poisson ratio cannot be applied for the surface of GaN films. These results for the GaN surface region are possibly related to the existence of the point defects and their preferential piling-up [20]. Further study is necessary to clarify this phenomenon.

4. CONCLUSIONS

GIXD measurements have revealed that the PLD GaN films on sapphire and MnO are compressed in the lateral direction to the surface due to the larger thermal contraction rates of these substrates. The lateral strain in the GaN film grown on the MnO substrate turned out to be much smaller than that expected form the mismatch in the thermal expansion coefficients. This result indicates that the dislocations in the GaN films are mobile during cooling down from the growth temperature under the large stress field.

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