INFLUENCE OF THE FIRST PREPARATION STEPS ON THE PROPERTIES OF GAN LAYERS GROWN ON 6H-SIC BY MBE

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ABSTRACT

The Gan heteroepitaxy on 6H-SiC is affected by the bad morphology of the substrate surface. We performed a hydrogen etching at 1550°C on the 6H-SiC(0001) substrates to obtain atomically flat terraces. An improvement of the structural properties of GaN grown by MBE on such substrates after deposition of a LT-AlN buffer layer is observed. A value of less than 220 arcsec of the FWHM of the XRD rocking curve, showing a reduced screw dislocations density, is comparable with the best results reported until now for thick GaN samples. Photoluminescence showed a structured near band edge emission spectrum with evidence of the A, B and C free exciton recombinations.

INTRODUCTION

GaN heteroepitaxy calls for a standing improvement in structural material properties to the aim of device application [1]. The best reported laser diodes up to now are based on the epitaxial lateral overgrowth (ELOG) of GaN thick layers on a strip-shaped SiO_2 structured $GaN/Al_2O_3(0001)$ substrate [2]. ELOG is used to reduce the number of threading dislocations originating at the interface with the substrate. SiC is a promising substrate because of the closer lattice match (3.5% mismatch) and thermal expansion coefficent among the commonly available substrates for GaN heteroepitaxy. Despite these positive properties, the quality of GaN grown on SiC is not that extremely better than that of the same material grown on sapphire [3,4], apart from the XRD results reported in Ref. [5]. One possible reason might be the poor surface morphology of the substrate, with defects that might propagate into the epitaxial structure, degrading its quality. Exposing the silicon carbide surface to hydrogen flow at high temperatures is already reported to give rise to large atomically flat terraces and to lead to the disappearance of scratches [6,7]. We decided to perform this treatment on the 6H-SiC wafers, that have been used as substrates for the MBE growth of GaN. For comparison the same growth process was

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considered on SiC substrates wet chemically etched by common procedures. The main interest was then to analyze the influence of this substrate preparation of the use of different buffer layers as well, on the structural and optical properties of GaN.

EXPERIMENT

The deposition of nitride layers on 6H-SiC(0001) Si-terminated substrates (CREE Research Inc.) was carried out in a small VG MBE system, where the active nitrogen was provided by an SVTA RF source operating at 13.56 MHz, 350 W. After thermal annealing up to 800°C in UHV the GaN epitaxy always was performed at 770°C in nearly stochiometric conditions, slightly Ga-rich, after the deposition of a low temperature (LT)-buffer layer (T=550°C -600°C). Prior to insertion into the UHV system some SiC substrates (H*-6H-SiC in the following) were heated up to 1550°C in He flux in a quartz reactor, then a mixture of He:H_2 (7:1) was let flowing for 10 minutes (2 l/min, 1 atm). Surface morphology of these substrates was checked before and after the etching by means of a Digital Instrument AFM in Tapping Mode. Before the introduction in the MBE chamber the as-received substrates were cleaned in a standard way [8], whereas the H_2 etched 6H-SiC substrates were just dipped in a 10% HF solution.
The GaN epitaxial layers were then analyzed by means of XRD, TEM and PL. High resolution and reciprocal space mapping were performed in a Philips XPD1 diffractometer with Cu $K_{\alpha 1}$ and a wavelength resolution $\Delta\lambda/\lambda \sim 10^{-5}$. The TEM analyses were carried out with electron microscopes of the types Philips CM 200 FEG/ST and CM 30 TEM/ST. Plan-view specimens and cross-section samples along the $<1\bar{1}00>$- and $<11\bar{2}0>$-projections were prepared by dimple-grinding and Ar+-ion milling on a liquid-nitrogen cooled sample holder. Two-beam diffraction conditions were applied to identify edge and screw dislocations with the $\vec{g} \cdot \vec{b} = 0$ criterion. The dislocation densities were determined by measuring the specimen volume, which is obtained from the extinction contours and the known extinction lengths for the applied diffraction vectors and the dislocation lengths.
Photoluminescence spectra were measured at 10K using an He-Cd laser for excitation at 325 nm with a power of approximately 10 mW on the sample.

RESULTS AND DISCUSSION

First the SiC surface morphology was analyzed by AFM. The as polished, solvent cleaned 6H-SiC (0001) substrates showed a high density of scratches of different depth (maximum 7 - 8 nm), as is seen in Fig.1a. These features remained unchanged also after the usual chemical etching [8] followed by thermal annealing in UHV. Hydrogen etching of such a surface produces wide atomically flat terraces (Fig. 1b), separated by 15 Å high steps, corresponding to one 6H-SiC unit cell, in good agreement with other results reported in the literature [6,7]. The steps form a regular array and are all seen to lie along the $<1\bar{1}00>$ directions; in contrast with what is stated in Ref. [7] we were not able to see two different set of steps.
Three types of samples have been considered for the present study (Tab. I) and the properties of the GaN epilayers have been compared.

Tab. I – MBE epitaxial structures.

	A	*B*	*c*
Substrate	6H-SiC	6H-SiC	H*-6H-SiC
LT-buffer (thickness)	GaN (10 nm)	AlN (26 nm)	AlN (26 nm)
Epi-layer (~1 μm of thickness)	GaN	GaN	GaN

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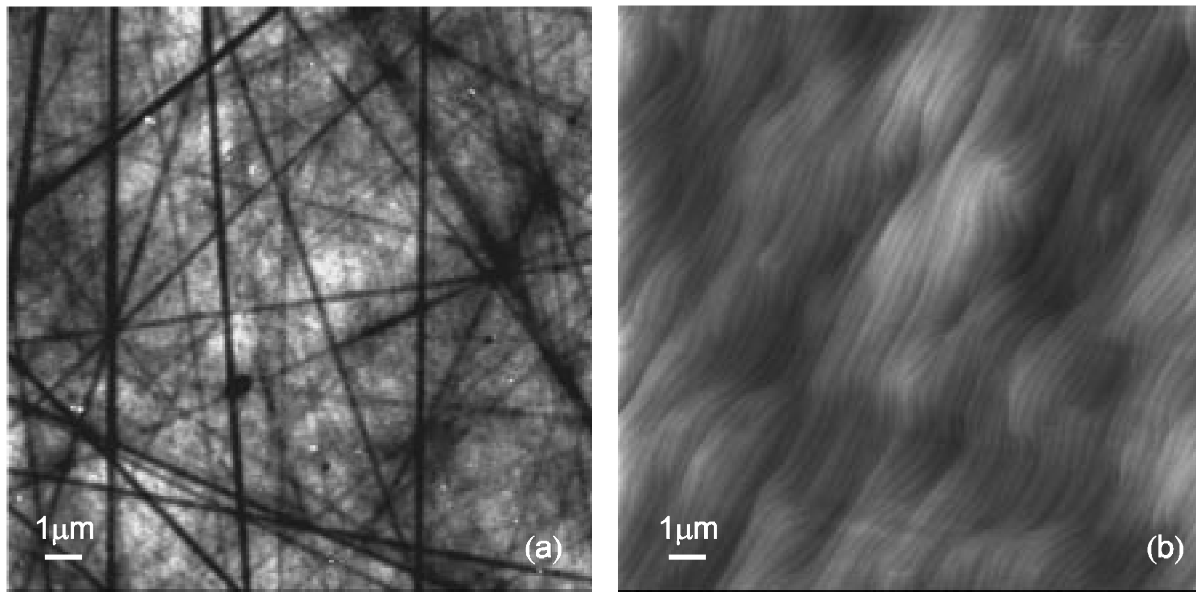

Fig.1 - AFM images of an as-received (a) and of a hydrogen etched (b) 6H-SiC (0001) surface. sample.

The FWHM of x-ray rocking curve of the GaN (0002) reflection (acquired with open detector) decreases from 618 arcsec for the material grown on the GaN buffer to 378 arcsec using the AlN buffer layer instead. A further clear improvement leading to a FWHM of 228 arcsec was obtained by deposition of the AlN buffer/GaN layers on a hydrogen etched substrate.

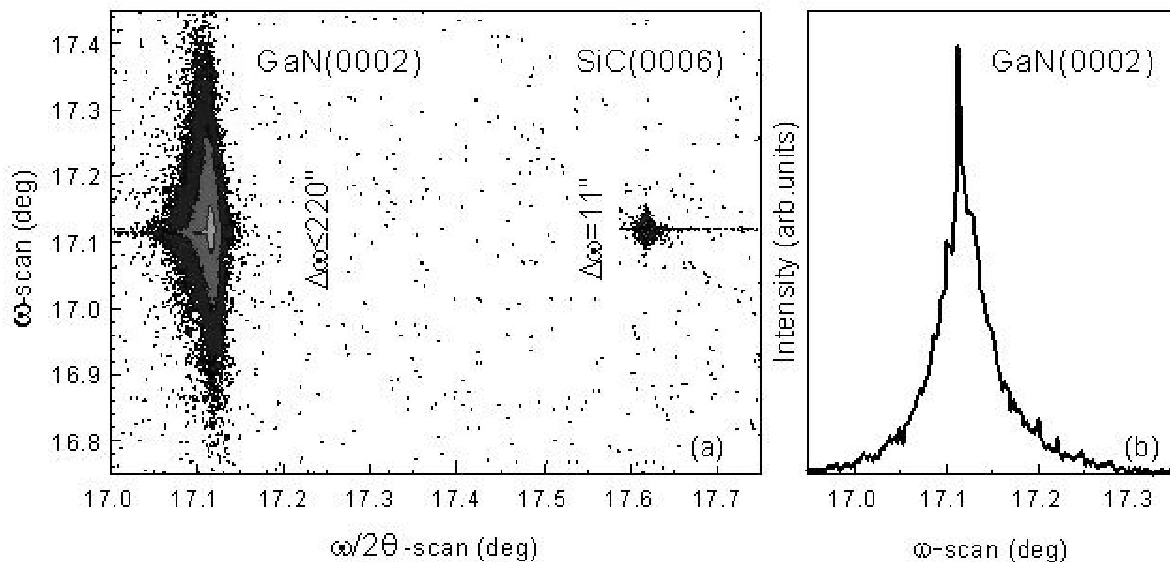

Fig. 2 - (a) Reciprocal space map of the sample *c* in the region of the GaN (0002) and SiC(0006) reflections. (b) ω-scan rocking curve of the GaN (0002) reflection.

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For this last sample we performed also measurements in the triple axis diffraction mode. A series of ω-2θ scans taken for different offset values of ω gives the reciprocal space map reported in Fig. 2a. Small lattice constant variations are observed, as shown by the FWHM of 35 arcsec in a direction parallel to the diffraction vector. In the perpendicular direction the reciprocal lattice point of GaN shows a broadening with a FWHM of less than 220 arcsec. This is due to microscopic tilts of the layer and is an indication of a low number of screw and mixed dislocations, that are the ones distorting the (0002) planes, as pointed out in Ref. [9]. The ω-scan line shape gives evidence of a peak with a FWHM of around 90 arcsec, superimposed on a broader one (Fig. 2b). This might be due to a well aligned and extended grain probably in the upper part of the epi-layer, where the dislocation denstity decreases.

The TEM analysis yielded a screw dislocation density N_{screw} of 4.4×10^{9} cm^{-2} and an edge and mixed dislocation density N_{edge} of 9×10^{9} cm^{-2} for the GaN on the hydrogen-etched substrate. Slightly higher values of $N_{screw} = 7.5\times10^{9}$ cm^{-2} and $N_{edge} = 1.5\times10^{10}$ cm^{-2} were obtained for the sample *b*. However, error margins of ± 50 % can occur due to the uncertainties of the specimen volume determination. HR-TEM measurement on sample *c* revealed an atomically abrupt interface between the SiC substrate and the AlN buffer layer, which also corresponds to a flat GaN surface (RMS ~ 5 nm), as proved by AFM results, not reported here. Furthermore a flat GaN surface morphology is of obvious relevance for the growth of complex heterostructures.

PL measurements were performed on the three samples in Tab. I and the results are shown in Fig.3. The spectra of the samples grown on the AlN buffer (*b* and *c*) layer show predominantly near band edge (NBE) emission. In the spectrum of sample *a*, grown on a GaN buffer, the most intense emission is centered at 3.389 eV, to be assigned to the first LO-phonon replica of the free exciton, estimated at 3.458 eV. Higher phonon replicas are also observed. As can be seen in the

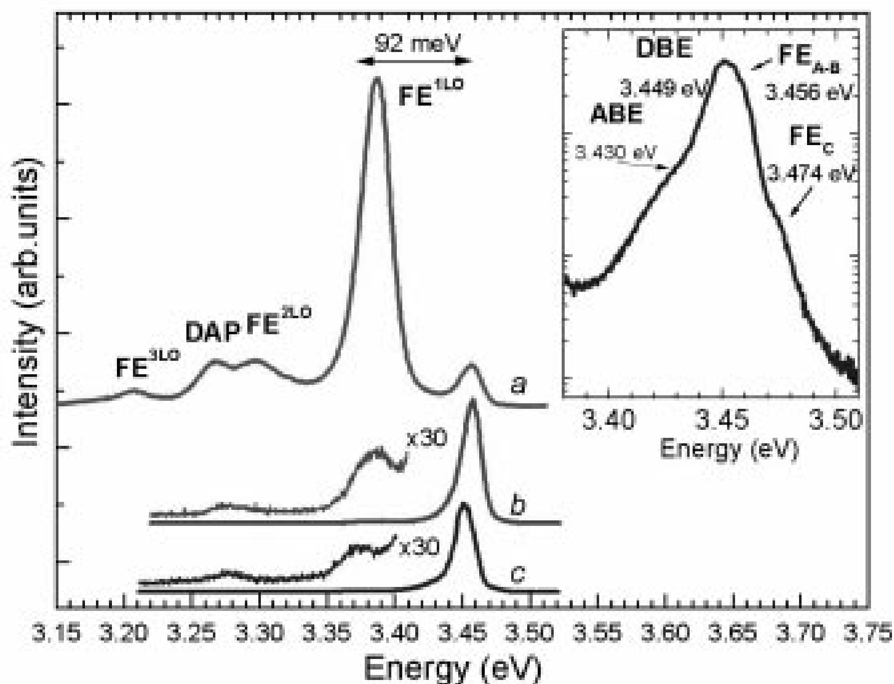

Fig. 3 - Photoluminescence spectra at 10K for the three GaN samples. In the inset just the NBE region is reported for the sample *c* using a logarithmic scale for the intensity.

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inset the NBE peak for the sample *c* consists of the superposition of a dominant donor bound exciton at 3.449 eV and A and B excitons at 3.456 eV. A shoulder at higher energies is attributed to the C exciton, whereas on the low energy side some contribution from an acceptor BE is identified. The same features are also measured on sample *b* slightly shifted to higher energies due to a different state of strain. These emissions persist up to room temperature. For the relaxed GaN "bulk" material several values are reported for the position of the free exciton, ranging from 3.469 eV [10] to 3.499 eV [11]. Whatever energy location we choose as reference for relaxed GaN, the emissions of our samples are downshifted, indicating the presence of biaxial tensile stress. This is commonly interpreted in terms of the difference in the thermal expansion coefficients of GaN and SiC.

If compared to analogous spectra (GaN on SiC) by Monemar *et al.* [12], in our case the FE_{A-B} emissions shift to lower energies. This is assigned to a higher state of strain in our GaN epi-layers. From the HR-XRD analysis of sample *c* we could extract, for the strain perpendicular to the basal plane, a value close to – 0.11%, the one predictable if one takes into account the difference in the thermal expansion coefficients of GaN and SiC. Monemar reported an axial strain of - 0.07% which was determined in GaN layers grown by MOVPE on 6H-SiC without a buffer layer. This difference must be assigned to a different defect structure, which influences the release of the strain.

Worth noting is that the two samples grown with the same buffer layer on differently treated SiC showed similar spectra, though the different density of screw dislocations, that could be inferred from the XRD measurements. In fact, the only effect to be expected is a reduction of the optical efficiency. Screw and mixed dislocations are predicted to have deep defect states in the gap [13] and indeed some CL studies related them to non-radiative recombination centers [14]. We did not register a big difference in the optical efficiency of the two samples.

Concerning the phonon replicas we note that samples grown on different buffer layers exhibit a substantial variation of the phonon-replica intensity: Actually it is well known that in polar materials the strong exciton-phonon coupling leads to important polaron corrections to the polariton wavefunctions. The recombination rate of the dressed polariton (zero-phonon line) or of its phonon replicas depends on the actual density of scattering centers available in the crystal, resulting in a sample-dependent intensity ratio of the luminescence lines. This might be related to existence of grains of high crystalline quality in the sample *a*, whereas the dominant no phonon excitonic emission in the two samples *c* and *b* let us suppose the presence of other defects, acting as scattering centers, connected to the different growth mechanism on the LT-AlN or to the diffusion of impurities from the buffer. The density of threading dislocations, does not seem to play such a big role in the scattering of the exciton polaritons promoting the no-phonon line.

CONCLUSIONS

We proved that the growth of GaN on SiC substrates results in better structural quality when using a LT- AlN buffer instead of a LT GaN-buffer, at least for the growth conditions we used. The FWHM of the XRD ω-scan becomes lower. A big difference is also seen in the PL properties: a LO-phonon replica dominates the spectrum of the sample grown on the GaN LT-buffer whereas the NBE emissions become dominant by using an AlN buffer. A further clear improvement in the structure of GaN has been achieved by using a hydrogen etched substrate with atomically flat terraces. The ω-scan FWHM of 220 arcsec we obtained for this GaN layer is comparable with the best value for MBE GaN reported so far [4]. However it must be noticed that in that case the epilayer was nucleated on a thick HVPE GaN on SiC. The narrow broadening of the symmetrical reflections in the rocking curve is usually associated with a low number of screw and mixed dislocations. Taking into account that those defects are probably

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non-radiative recombination centers and also considering the role of TDs in generating V-defects in QWs structures, the reduction of the density of screw dislocations can be considered a promising result. Preliminary AFM results showing a reduced surface roughness are also encouraging.

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