GaN ON 6H-SiC -- STRUCTURAL AND OPTICAL PROPERTIES


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ABSTRACT

Recent progress in the growth of high quality 6H-SiC single crystal leads to an ideal substrate material for GaN epitaxial films. Nearly matching lattice constants of wurzite GaN to 6H-SiC in the hexagonal plane can reduce strain effects at the interface. We employed the sublimation sandwich method to grow single crystal layers at reasonable growth rates with free carrier concentrations of 2x10^{17} cm^{-3}. Very sharp x-ray diffraction peaks of the GaN (0002) plane are obtained indicating the high quality of this system (\Delta(2\theta) < 0.1 degrees). These findings are directly reflected in the optical properties. The photoluminescence is dominated by a single sharp exciton line, impurity related donor acceptor transitions are seen with very weak intensities. However, at lower energies the internal luminescence transitions of the 3d transition metal ions Fe and V are observable. The incorporation of Fe is confirmed by electron paramagnetic resonance.

INTRODUCTION

The potential of GaN as a blue light emitter is intimately connected to the substrate material used in the epitaxial growth [1]. One of the key issues is lattice matching, but also the difference in thermal expansion and conductivity of substrate and epitaxial layer has to be taken into consideration. Growth of GaN on 6H-SiC offers distinct advantages over the commonly used substrate sapphire [2]. The lattice mismatch is 3.5 % only and this should reflect in the structural and optical properties of the layers. This has been demonstrated quite recently [2]. Molecular beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD) are the techniques to achieve GaN layers of high crystalline quality [4,5]. The sublimation growth technique is an alternative method. It achieves very high growth rates typically 300 \mu \text{m} per hour and offers a great freedom in doping. The potential of this technique is best demonstrated by the growth of SiC epitaxial layers on various polytypes of SiC substrates, having outstanding quality [6,7]. In this report we present results from photoluminescence and X-ray reflection measurements of GaN layers grown on 6H-SiC using the sublimation growth technique [8]. The structural and optical properties are compared to samples grown by MBE and MOVCD.

EXPERIMENTAL DETAILS

The GaN epilayers are grown from metallic Ga and activated ammonia on SiC. The substrates of the 6H polytype (6H-SiC) have been grown by the LELY method and are oriented in the [0001] plane. The growth of the GaN layers is performed using a modification of the sandwich method as originally described in Ref.[8]. The quartz reactor contains several deposition cells
in a row that share the same gas stream of ammonia. Each cell consists of a pair of Ga source and SiC substrate separated by a gap of 5 mm. The heating is performed by a high frequency generator on a graphite rod. The surface of this rod is covered by a layer of SiC to prevent the evaporation of C into the reactor volume. The gradient of the resulting temperature field across the narrow gap is perpendicular to the surface of the substrate. Through this gap ammonia flows with a speed of 25 to 50 l/min. Under these conditions there is an efficient mass transport of Ga vapor and activated nitrogen towards the substrates. Prior to deposition the 6H-SiC substrates are etched in molten KOH. At growth temperatures between 1170 and 1270 °C single crystal layers of GaN are obtained at a growth rate up to 300 mm/h. These GaN layers showed n-type conduction, the electron mobility ranged from 30 to 80 cm²/Vs.

The GaN epitaxial layers were characterized by temperature dependent photoluminescence in the spectral range from 3.5 to 0.5 eV using a grating monochromator or a Fourier Transform spectrometer. Standard absorption or reflection measurements were performed to determine the free electron concentration. For further details see Ref.[7]

EXPERIMENTAL RESULTS

For the X-ray diffraction the Cu Kα line was used. The sample was oriented along a high symmetry axis in the basal plane. One hence expects reflections from the planes perpendicular to the c-axis [0001] as shown in fig.1. At 34.5 degrees the GaN (0002) reflection occurs with a half width of 6 minutes. X-ray reflection data for GaN grown on sapphire using MBE or MOCVD are of the same order. At 73 degrees the second order of the (0002) reflection is seen. Simultaneously the reflections from the 6H-SiC can be observed in first order (0006) and in second order (000 12). Measuring the backside of the sample, i.e. the substrate, a reversed intensity ratio for GaN and SiC reflections is found. A matching of the lattice constant cannot be observed since mainly reflections from the c-axis are seen. However, within the deformation potential model a change of the lattice constant a within the plane is directly connected with changes in c. For the analysis the following lattice constants were used: SiC a=3.0806 Å, c=15.1173 Å and GaN a=3.186 Å and c=5.176 Å, accordingly the lattice mismatch amounts to 3.5 %.

In fig.2 we show the low temperature photoluminescence results. In this particular sample the donor bound exciton recombination at 3.47 eV [10] is rather weak and the luminescence is dominated by the impurity related transitions (donor-acceptor or band-acceptor) around 3.26 eV. Not shown in fig. 2 is the deeper luminescence band at 2.2 eV which according to other groups is related to intrinsic defects [11]. The ratio of exciton to donor-acceptor pair recombination can be taken as a measure of the quality of the samples. In the best ones it was 30:1 and the donor bound exciton had a line width of 4 meV thus comparable to MBE or MOCVD grown layers. A second transition with rather strong intensity is seen 100 meV below the exciton line. It is not a phonon replica of the 3.47 eV line. The temperature dependence of this line could be followed up to 40 K, where the intensity had decreased beyond detection limit. The activation energy is 5 meV which points to excitonic behavior. In a recent publication [12] it was reported that the 3.37 eV line appeared after hydrogen passivation of the Mg acceptors in GaN. If this is true the recombination could be explained by exciton recombination at neutral acceptor hydrogen complexes. Another less intense line appears at 3.31 eV. Its temperature dependence allows to distinguish whether it is an independent transition or a phonon replica of the 3.37 eV line. From 5 K up to 30 K its intensity decreases
more or less linearly being reduced by 30% at 30 K. At higher temperatures it merges into the transition centered around 3.26 eV and could not be followed any more. Assuming band acceptor transitions which is plausible for the high carrier density of 4x10\(^{17}\) cm\(^{-3}\) a binding energy of 190 meV is calculated (the band gap of GaN at low temperatures is 3.5 eV). Such a shallow acceptor level has to our knowledge not been reported before. The acceptor binding energies in GaN span a very wide range from 220 meV down to 800 meV (Mg, Zn) [1]. In Zn doped GaN [13] four Zn related acceptor levels have been observed, the shallowest one being 340 meV above valence band. Zn belongs to the group II acceptors amongst Be, Mg and Cd. Since the epitaxial layers were undoped and the group II acceptors are no common trace impurities we disregard them as the source of the 3.31 eV line. On the other hand Zn is sometimes used as a dopant and may remain in the reactor. The group IV elements C, Si and Ge are also shallow acceptors in III-V compounds, possibly also in GaN. Carbon doped GaN as well as GaN implanted with C have been investigated earlier [11,14]. In the implantation study [14] no near band gap luminescence due to C could be found, only the deep center at 2.2 eV appeared. Doping with C [11] enhanced this particular luminescence and it was concluded that the recombination is between a shallow donor level and a deep acceptor complex involving C as a constituent. We can speculate that C induces also a shallow level but more experiments are needed to clarify the role of C in GaN.

The recombination at 3.26 eV is often observed in undoped GaN. The zero phonon line is followed by up to 4 phonon replicas with average energies of 92 meV. The peak positions agree well with values reported by Khan et al.[15]. They studied the influence of Si on the photoluminescence of GaN and concluded that the 3.26 eV donor acceptor recombination is due to Si as unintentional dopant. The intensity of the luminescence was proportional to the amount of Si in the sample. For GaN on SiC grown at temperatures around 1100 °C Si can evaporate from the substrate and diffuse into the epilayer. The amphoteric character of Si is well established in GaAs and it points that Si shows a similar behavior in GaN.

Most previous researchers in photoluminescence investigations concentrated on the spectral range from the band gap region down to 1.5 eV. They thus missed the characteristic internal luminescence lines of the 3d transition metal elements in the near infrared. Baur et al. [16] were the first to report on infra red luminescence of the iron acceptor in undoped epitaxial GaN layers. We confirm their results and show the presence of vanadium in addition. In fig.3 the luminescence spectrum from 11000 cm\(^{-1}\) to 7000 cm\(^{-1}\) is shown. In order to achieve the high resolution a Fourier Transform spectrometer was used. Three prominent zero phonon lines (ZPL) are seen at 10480, 9629 and 8450 wave numbers followed by phonon replicas. The transition at 10480 cm\(^{-1}\) corresponds to the internal \(\text{Fe}^{3+}\rightarrow6\text{A}\text{l}(S)\) recombination of \(\text{Fe}^{3+}\) on Ga site, the \(3d^5\) configuration [16]. The origin of the ZPL at 9628.8 cm\(^{-1}\) deserves further investigations. In ref. [16] it is tentatively assigned to the \(\text{Cr}^{4+}\rightarrow\text{A}_2\text{F}(F)\) transition of \(\text{Cr}^{4+}\). The iron acceptor level has been determined to be 2.6 eV above valence band [17]. According to the Langer Heinrich rule [18] the energy levels of the transition metal elements can be used as a measure of the band offset. Knowing the energy level of \(\text{Fe}^{3+}/2+\) in GaAs and in GaN allows to conclude where the energy level position of other 3d elements will be. It predicts for Chromium the \(3+/2+\) level to be located around 0.6 eV below conduction band. In n-type material the \(\text{Cr}^{2+}\) charge state will be present and excitation will start from the \(2+\) charge state, i.e. \(\text{Cr}^{2+} \rightarrow \text{Cr}^{3+} + e_{\text{cb}}\). So the internal luminescence of \(\text{Cr}^{3+}\) is expected to be seen. For an internal transition of a 3d element the 9628.8 cm\(^{-1}\) line has an unusual temperature dependence, it can be seen up to 150 K whereas the other lines disappear around 80 K. Also
hardly any broadening of the line is observed. The full width at half maximum is below 1 cm\(^{-1}\) and thus narrow enough to perform Zeeman spectroscopy and to conclude about spin and hence charge state of the impurity. These experiments are currently underway.

The third line at 8450 cm\(^{-1}\) is attributed to the internal luminescence of V\(^{3+}\) on Ga site. The internal luminescence of V\(^{3+}\) in III-V semiconductors is a well known feature [19]. V\(^{3+}\) has the 3d\(^2\) configuration the identical configuration as Cr\(^{4+}\) mentioned above. In each compound GaAs [20], GaP [20] and InP [21] the luminescence of V\(^{3+}\) is dominated by a ZPL ("cold" line) and a "hot" line 10 to 15 wave numbers at higher energies. This line appears at higher temperatures (>8 K). The identical behavior is seen on the 8450 cm\(^{-1}\) line. More details will be presented in a forthcoming publication [9]. The three ZPLs were strongest when illuminating the sample with above band gap light, but also could be seen under the excitation of the green line of an Ar ion laser (514 nm). All three impurities hence are electrically active inducing energy levels in the band gap of GaN. The high free electron concentration did not allow to perform magnetic resonance experiments which could clarify which impurity in what charge state is present. We could however compensate the layers by fast neutron irradiation. For a dose around 10\(^{18}\) n/cm\(^2\) the layers became transparent in the infrared. In the electron paramagnetic resonance (EPR) experiments the Fe\(^{3+}\) resonance [17] was seen meaning that the Fermi level is at least 1 eV below conduction band. It also shows that by neutron irradiation acceptors probably Gallium vacancies are formed in an amount to compensate the action of Nitrogen vacancies, the shallow donors, in GaN.

CONCLUSION

GaN grown on 6H-SiC by the sandwich sublimation technique has excellent crystalline and optical properties comparable to MBE and MOCVD grown layers. The residual impurities acting in GaN on SiC as shallow acceptors are tentatively assigned to Si and C. The presence of three 3d transition elements with their characteristic luminescence bands between 1.3 and 1 eV in GaN is shown.

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REFERENCES:

18. For a compilation of data see A. Zunger, Solid State Phys. 39, 275 (1987)