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HIGH RESISTIVITY GaN SINGLE CRYSTALLINE SUBSTRATES

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High resistivity 10^4-10^6 Ω cm (300 K) GaN single crystals were obtained by solution growth under high N_2 pressure from melted Ga with 0.1–0.5at.% of Mg. Properties of these crystals are compared with properties of conductive crystals grown by a similar method from pure Ga melt. In particular, it is shown that Mg-doped GaN crystals have better structural quality in terms of FWHM of X-ray rocking curve and low angle boundaries. Temperature dependence of electrical resistivity suggests hopping mechanism of conductivity. It is also shown that strain free GaN homoepitaxial layers can be grown on the Mg-doped GaN substrates.

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1. Introduction

GaN crystals grown from diluted solutions in liquid gallium, under high nitrogen pressure of 10–20 kbar and temperature 1400–1700°C (high nitrogen pressure solution method), are always highly conductive [1]. Typical free electron concentration is 3–6 × 10^{19} cm^{-3}. The main native donors are nitrogen vacancies, also some oxygen can be present substituting nitrogen in the crystal lattice. Structural and optical properties of these crystals are strongly influenced by the presence of the native point defects and free carriers. In particular the fundamental absorption edge is shifted due to the Burstein–Moss effect and a strong free carrier absorption dominates an infrared part of the spectrum. Also the Raman scattering is modified by the free electrons and in particular, the LO mode which should be active in GaN is not detected in the samples grown from the pure gallium solution. The lattice constants of the conductive, bulk GaN crystals are slightly bigger than those of undoped homoepitaxial layers of low concentration of free electrons which leads to a certain small value strains.

2. Crystal growth

The GaN crystals were grown by high nitrogen pressure solution method from the solution in liquid gallium containing 0.1–0.5at.% of Mg. Before the growth conditions were achieved, the growth solution was homogenized at temperature of 1100°C for several hours. Then the temperature was increased up to the growth conditions. The time of the growth was varied in the range of 40–150 hours.

Crystals in the form of hexagonal platelets reaching dimensions up to 8 mm were found in the cooler part of the crucible. The crystals were transparent, colorless or slightly orange.

Some of the crystals were prepared for homoepitaxial growth. One of the hexagonal surfaces of platelets were polished mechano-chemically by the procedure described in [2]. Homoepitaxial GaN layers were deposited by metalorganic chemical vapor deposition (MOCVD) by standard procedures used up to now for the conductive GaN substrates [3].

3. Morphology of GaN:Mg crystals

The crystals grown from the solutions containing Mg were hexagonal platelets similar to the platelets grown without an intentional doping. It shows that Mg impurity does not influence the relative growth rates in significant degree and therefore the form of hexagonal platelets is obtained at the conditions typical of the growth of the undoped crystals. However, one observes that the platelets with Mg are generally thicker which suggests that Mg impurity accelerates the growth in c-direction.

4. Free carriers

Although the morphology of GaN crystals grown with and without an intentional doping is very similar, their physical properties differ very substantially. The comparison of electrical properties for both types of crystals is given in Table I. The increase in electrical resistance in GaN:Mg crystals is related to drastic

TABLE I

Electrical properties of GaN crystals.

Crystal	Conductivity type	Resistivity ρ [Ω cm] at 300 K	Carrier concentration [cm^{-3}]
GaN — undoped	metallic	10^{-1}	$3\text{–}6 \times 10^{19}$, n-type
GaN — Mg doped	hopping?	10^{4}–10^{6}	–

decrease in free carriers concentration. The temperature dependence of resistivity for these samples is typical of hopping conductivity (Fig. 1). Also the optical absorption data indicate that the free carrier concentration in the Mg-doped GaN is very low. Figure 2 compares the optical absorption of both undoped and Mg-doped pressure grown GaN crystals. The free carrier absorption which dominates the low energy part of the absorption spectra for the undoped GaN disappears completely for crystals grown from Mg containing solutions.

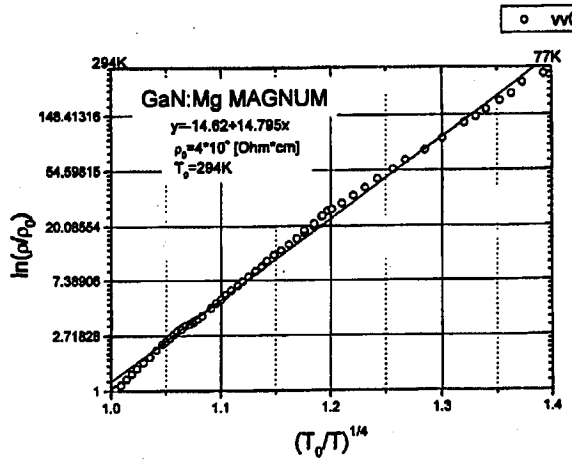

Fig. 1. Temperature dependence of resistivity of GaN crystal grown from Ga+Mg solution at high N_2 pressure.

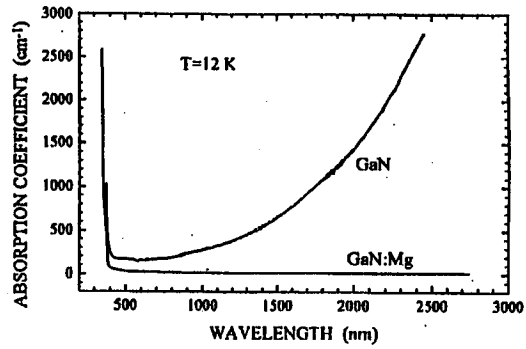

Fig. 2. Optical absorption spectra for GaN crystals grown from pure Ga and Ga+Mg solutions at high N2 pressure.

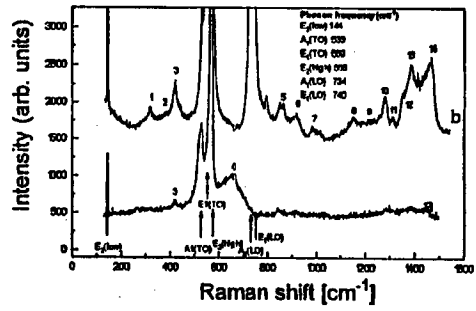

Fig. 3. Raman spectra for pressure grown GaN crystals: *a* — crystal grown from pure Ga solution, *b* — crystal grown from Ga+Mg solution.

The absence of free electrons in GaN:Mg crystals is also reflected by the changes in Raman scattering spectra (Fig. 3). In particular, a very strong peak corresponding to the LO phonon is observed in contrast to the undoped crystals where this peak is not visible at all, due to the interaction with free electrons. Compared to the Raman spectra of the undoped crystals, a number of additional peaks is visible in the Raman spectra for GaN:Mg samples, which are analysed in more detail in [4].

5. Structure of GaN:Mg crystals

The structure of the crystals was investigated by X-ray diffraction methods. Table II summarizes the data characterizing crystal structure of both highly conductive (grown from pure Ga solutions) and non-conductive (grown from Ga+Mg alloys) crystals. It was observed [5] that the lattice constants for undoped GaN bulk crystals vary slightly for different crystals as well as for different areas of the individual crystals. This is caused by the differences in free electron concentration and can lead to certain strains in the crystals. For the Mg-doped crystals there is no influence of free electrons on crystal structure and therefore the lattice parameters are uniform for individual crystal and constant for different samples. Elimination of the strains in the GaN:Mg crystals is the reason for the improvement of their structure. The rocking curves are narrower and no low angle boundaries are observed even for 8 mm single crystalline GaN:Mg platelets. The strains in the undoped GaN crystals are very small but their presence can more adequately explain wider rocking curves than for the Mg-doped samples.

TABLE II

Lattice parameters for GaN crystals and homoepitaxial layers.

Sample	a [Å]	c [Å]	FWHM X-ray rocking curve
GaN undoped, bulk	3.1881–3.1890	5.1856–5.1864	30″–40″
undoped homoepitaxial GaN on undoped GaN bulk	3.1881	5.1844	30″–40″
GaN:Mg, bulk	3.1876	5.1846	20″– 30″
undoped homoepitaxial GaN on GaN:Mg bulk	3.1876	5.1846	20″–30″

The undoped homoepitaxial GaN layers grown on GaN:Mg substrates are practically strain free and are the best available standard for unstrained GaN. Lattice constants of the substrate and homoepitaxial layer are perfectly identical.

6. Mg content in the crystals

The presence of Mg in GaN crystals grown from the solutions in Ga+Mg alloys has been detected by photoluminescence (PL) measurements. The PL spectra

are very typical of Mg-doped GaN layers grown commonly by vapor phase methods, i.e. MOCVD. These data indicate that at least a part of Mg contained in the crystals are in the same configuration in the crystal lattice as in the MOCVD hetero- and homoepitaxial layers. The concentration of Mg in GaN:Mg bulk crystals can be evaluated from the structural data. Both theoretical [6] and experimental [7] data show that Mg atoms incorporated into the GaN crystal lattice in high concentration (of order of 10^{19} cm^{-3}) have to increase both a and c lattice constants significantly. The observed effect that the lattice constants of the undoped homoepitaxial layers and Mg-doped GaN substrates are identical indicates that the amount of Mg in the considered crystals is probably of the order of 10^{18} cm^{-3}. This suggests the strong influence of the Mg impurity on the crystallization mechanisms especially on the formation of the native point defects during the growth.

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