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High Temperature Stability of Electrical and Optical Properties of Bulk GaN:Mg Grown by HNPS Method in Different Crystallographic Directions

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Single crystals of Mg-doped GaN grown by high nitrogen pressure solution method in different crystallographic directions ([0001], $[10\bar{1}1]$, and $[10\bar{1}\bar{1}]$) were investigated in order to determine thermal stability of their electrical and optical properties. Obtained dependences of resistivity, the Hall coefficient and energy shift of Mg-related photoluminescence peak on annealing temperature allow to suggest that incorporation of Mg in GaN is significantly influenced by the direction of the crystallization front.

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1. Introduction

Magnesium is the most important impurity for p-type and semi-insulating GaN. Semi-insulating GaN crystals are widely used as substrates for high frequency high power transistors [1]. Hexagonal GaN:Mg plates grown spontaneously by high nitrogen pressure solution (HNPS) method have extremely high electrical resistivity ($\rho > 10^9$ Ω cm) [2–4] as a result of the compensation between Mg acceptors and O donors, which are always present in the growth chamber. From secondary ion mass spectroscopy (SIMS) measurement it is known that concentration of Mg and O is the same $(2-8) \times 10^{19}$ cm^{-3} within the experimental error. However, electrical properties of these crystals were found to be unstable at high temperatures [3, 4]. This could be explained by the presence of residual hydrogen (although HNPS method, unlike metalorganic chemical vapor deposition (MOCVD) technique, is almost hydrogen-free) that forms Mg–H complexes, which, in turn, are unstable at temperatures above 650 K.

Recent experiments have shown that the concentration of Mg–H complexes in GaN:Mg MOCVD layers strongly increases with the rise of the disorientation angle of a substrate with respect to polar (0001) plane [5]. GaN:Mg crystals grown spontaneously are mostly grown in semipolar $[10\bar{1}1]$ and $[10\bar{1}\bar{1}]$ directions. Therefore, this work is an attempt to clarify the influence of the crystallization direction on the stability of electrical and optical properties of bulk GaN:Mg grown by HNSP method at temperatures up to 900 K.

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2. Experimental

GaN:Mg single crystals were grown by HNPS method in spontaneous [2] and "feed-seed" [6] configurations. Growth was carried out from the solution of nitrogen in liquid gallium with 0.1–0.5% magnesium doping under high pressure (1 GPa). Temperature gradient of about 20 K/cm was applied along the crucible. Accordingly, the temperature at the lower end of the crucible was 1670 K and at the upper end — 1710 K. In spontaneous configuration GaN:Mg crystals grow without seed and other crystals grow on GaN substrates with the orientation of growth surfaces in [0001] and $[10\bar{1}1]$ directions. Typical level of impurities in samples detected by SIMS were Si — *ca.* 10^{18} cm^{-3}, H — *ca.* 10^{17} cm^{-3}, O — $(2-8) \times 10^{19}$ cm^{-3} and Mg — the same as O. Crystals grown spontaneously and in [0001] direction had typical thickness of 100–300 μm. The crystals grown in $[10\bar{1}1]$ direction had thickness *ca.* 10–15 μm that prevented the separation of the substrate.

Measurement of photoluminescence (PL) spectra, temperature dependence of electrical resistivity ($\rho(T)$) and the Hall coefficient ($R_{\rm H}(T)$) were performed for investigated crystals before and after annealing at 850 K during 20 min.

The process of thermal annealing was carried out in air atmosphere. Annealing was performed in electric furnace. The temperature was measured by platinum resistor and stabilized with precision of 0.5 K.

The temperature evolution of the photoluminescence spectra was studied under LGI-21 nitrogen laser excitation at 337 nm emission wavelength with 10 ns pulse duration and power of 1 kW. Luminescence spectra were recorded using a MDR-12 monochromator equipped with the FEU-100 photomultiplier.

The temperature dependence of electrical transport properties was measured in the van der Pauw geometry in temperature range 300–900 K in air atmosphere. Circle shaped Au/Ni contacts with 0.4 mm diameter were created by vacuum evaporation. Equipment description and experimental details of electrical measurements are given in Ref. [7].

3. Results

PL spectra for all as-grown and annealed samples are presented in Fig. 1. All spectra are similar and exhibit strong blue emission peaked in the range 3.0–3.2 eV. From the comparison of obtained PL spectra for crystals before and after annealing one can see that for crystals grown in [0001] direction PL spectra are unchanged. However, for crystals grown spontaneously and on substrate in $[10\bar{1}1]$ direction, an increase in blue emission intensity and 50 meV red shift are observed after annealing.

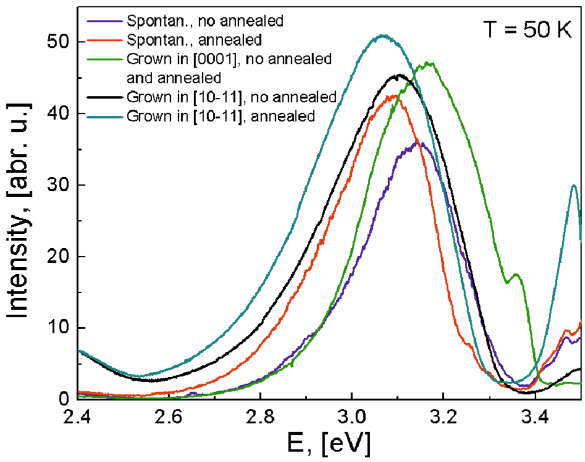

Fig. 1. PL spectra of GaN:Mg crystals measured at 50 K. Green line — spectrum for GaN:Mg crystal grown in [0001] direction (spectra before and after annealing are identical); black line — PL spectrum of crystal grown in $[10\bar{1}1]$ direction before annealing; cyan line — PL spectrum of crystal grown in $[10\bar{1}1]$ direction after annealing; blue and red lines — PL spectra of crystal grown spontaneously before and after annealing, respectively.

Temperature dependences of resistivity $\rho(T)$ for GaN:Mg crystals grown in [0001] direction and grown spontaneously before and after annealing are shown in Fig. 2 and Fig. 3. It has to be noted that we do not present here $\rho(T)$ values for GaN:Mg crystals grown on substrate in $[10\bar{1}1]$, since it was impossible to distinguish between the resistivity contribution of the substrate and the crystal.

In case of GaN:Mg grown in [0001] direction we have examined two samples, grown at different temperatures (Fig. 2). $\rho(T)$ dependences before and after annealing are identical, therefore no traceable changes due to the annealing are visible in Fig. 2. Activation energies (E_a) estimated from the plots in Fig. 2 were 0.9 and 1.4 eV for the sample grown at 1670 K and 1710 K, respectively. It should be noted that conductivity type for GaN:Mg crystals grown in [0001] direction (particularly for the sample grown at 1710 K) as determined from R_H measurements is electronic.

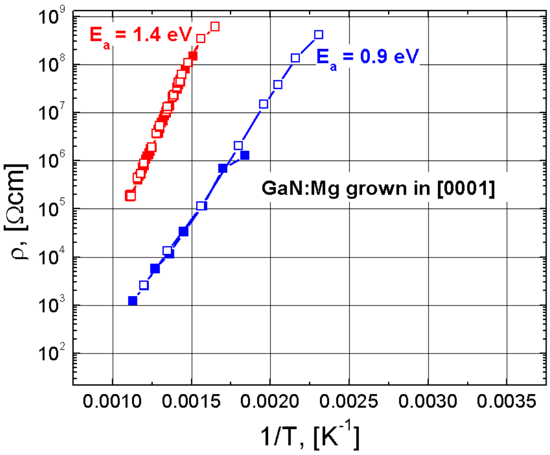

Fig. 2. $\rho(T)$ dependencies for two samples of GaN:Mg grown in [0001] direction. Solid rectangles correspond to $\rho(T)$ points measured before annealing, open rectangles corresponds to $\rho(T)$ points measured after 20 min annealing at $T = 850$ K. Red curve — the sample with growth temperature of 1710 K; blue curve — the sample with growth temperature of 1660 K.

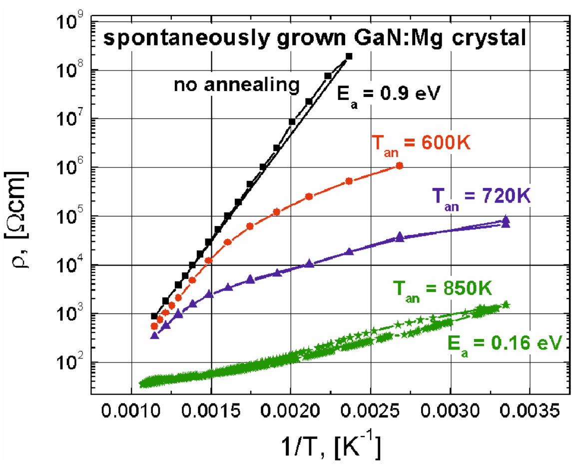

Fig. 3. Evolution of $\rho(T)$ dependences of GaN:Mg sample before and after annealing with temperature.

Typical behavior of $\rho(T)$ dependence of spontaneously grown GaN:Mg crystal before and after annealing at different temperatures is shown in Fig. 3. In this case, the resistivity is drastically decreased after the final stage of annealing (green curve in Fig. 3). The value of E_a changed from 0.9 to 0.16 eV. After annealing these crystals had *p*-type conductivity. Hole concentration at room temperature as determined from the Hall coefficient measurements was 1×10^{15} cm^{-3}.

It is worth mentioning that resistivity and activation energy changes occur also at intermediate annealing temperatures as follows from the analysis of blue and red curves in Fig. 3.

4. Discussion

The analysis of high temperature stability of optical and electrical properties of GaN:Mg crystals grown in [0001] direction in comparison with the same properties of crystals grown in semipolar direction suggests that incorporation of Mg–H complexes is dependent on the direction of the crystallization front. It should be taken into account that the concentration of hydrogen in growth chamber used in HNPS method is too small for Mg–H complexes to incorporate in GaN:Mg during the growth on (0001) surface in significant amount. This observation is consistent with earlier reports [7], where the incorporation of Mg–H complexes in MOCVD GaN:Mg layers was shown to be dependent on the substrate orientation.

The hole concentration measured in GaN:Mg crystals grown spontaneously confirmed recently reported data that suggests that these crystals show *p*-type conductivity. The concentration of Mg–H complexes, created during growth from residual hydrogen determine the stability of electrical properties at high temperature.

Observed behavior of electrical properties can be interpreted within the model, which assumes three impurity states: O-related shallow donor ($E_{\mathrm{a}} = 0.03$ eV), Mg-related shallow acceptor ($E_{\mathrm{a}} = 0.16$ eV) and deep acceptor ($E_{\mathrm{a}} \approx 1$ eV above valence band). The latter can have different values of E_{a} depending of growth conditions, especially growth temperature [8]. For crystals, grown in semipolar direction (spontaneously or on GaN substrate) the situation is the following: prior to annealing, O donors are fully compensated by Mg acceptors and deep acceptors and residual electrically inactive Mg–H complexes are present; after the annealing Mg–H complexes dissociate and Mg-related acceptors appear accordingly, decreasing the resistivity. For crystals, grown in polar direction [0001] the situation is similar to the case of not annealed GaN:Mg crystals, grown in semipolar direction, but Mg–H complexes are absent and this ensures high temperature stability of resistivity.

5. Conclusions

Single crystals of Mg doped GaN were grown by high nitrogen pressure solution method in different crystallographic directions and their electrical and optical properties were examined before and after annealing.

It was shown that electrical and optical properties of spontaneously grown GaN:Mg crystals are considerably less stable at high temperatures than those of GaN:Mg grown in [0001] direction. Based on optical and electrical data it can be suggested that the dissociation of Mg–H complexes is the key process that affects the stability.

Model of three impurity states, explaining the changes in resistivity is proposed.

Acknowledgments

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