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2004 J. Phys.: Condens. Matter 16 2967

(http://iopscience.iop.org/0953-8984/16/17/023)

J. Phys.: Condens. Matter **16** (2004) 2967–2972 PII: S0953-8984(04)75234-0

# Electrical and optical properties of p-GaN films implanted with transition metal impurities

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Received 21 January 2004
Published 16 April 2004
Online at stacks.iop.org/JPhysCM/16/2967
DOI: 10.1088/0953-8984/16/17/023

**Abstract**
Electrical and optical properties and the spectra of deep hole traps in p-GaN films implanted with high doses ($3 \times 10^{16}$ $cm^{-3}$) of Co, Mn, Fe and Cr and annealed at 700 °C are reported. The dominant deep traps generated by this implantation are of the same type as observed in similar films heavily implanted with protons. The magnitude of the changes in the conductance and transmission of the GaN correlates with the atomic mass of the transition metal ions and the density of primary radiation defects. For fabrication of spintronic devices such as spin-LEDs using implantation of the TM species into the top p-GaN contact layer, the best results should be expected using Cr implantation since this produces both room temperature ferromagnetism and the smallest reduction in conductivity of the p-GaN.

## 1. Introduction

The electrical and optical properties of GaN films doped with transition metal impurities are of great interest because such films have been shown to be magnetic semiconductors with Curie temperature close to room temperature and are potential candidates for use in spintronic devices [1–3]. Also, since many transition metal impurities have been shown to form deep levels near mid-gap in GaN they could be convenient dopants for preparing semi-insulating SI buffer layers for use e.g. in fabricating high electron mobility transistor structures. For example, Fe doped SI-GaN films developed in some laboratories show great promise for such applications [4–6].

Transition metals can be introduced into GaN films by molecular beam epitaxy MBE [7], by metal–organic chemical vapour deposition [8, 9] or by ion implantation with subsequent annealing [10, 11]. In this paper we present the results of electrical and optical studies performed on p-GaN films implanted with high doses of Mn, Co, Fe, Cr. The results of similar studies on undoped n-type films have been reported previously [12, 13]. In n-GaN, transition metals form deep substitutional acceptors with levels near $E_c-(1.4-2)$ eV and more shallow defect complexes in the upper half of the bandgap with levels near $E_c-(0.5-0.6)$ eV. The properties of TM ions in p-type material are also of interest for application in fabricating GaN-based light emitting diodes with the top p-GaN contact layer implanted with Mn [14].

## 2. Experimental details

The 3 $\mu$m thick p-GaN samples were grown by hydride vapour phase epitaxy (HVPE) on sapphire substrates. The samples were doped with Mg and grown in non-hydrogen-containing ambient. Van der Pauw and Hall measurements at room temperature gave the hole concentration and mobility of respectively $4.5\times10^{18}$ cm$^{-3}$ and 3 cm$^2$ V$^{-1}$ s$^{-1}$. Mn, Co, Fe and Cr ions with energy of 250 keV were implanted at 350 °C with a dose of $3\times10^{16}$ cm$^{-2}$ in all cases. The high temperature during implantation prevented the material from undergoing amorphization [15, 16]. The incorporation depth of the ions was 0.2 $\mu$m and the peak volume concentration in the implanted region was close to 3 at.%. All samples were annealed at 700 °C for 5 min in a $N_2$ atmosphere. Electrical characterization included current–voltage ($I$–$V$), current versus temperature ($I$–$T$), capacitance–voltage ($C$–$V$), capacitance versus frequency ($C$–$f$) measurements on Au Schottky diodes prepared by vacuum deposition (the diodes were $0.7\times0.7$ mm$^2$, ohmic contacts were made with In). For deep level studies we used current deep level transient spectroscopy (CDLTS) [17], photoinduced current transient spectroscopy (PICTS) [18] and admittance spectroscopy [19, 20] (i.e. measurement of the temperature dependence of the capacitance $C$ and AC conductance $G$ on temperature for various frequencies). Optical characterization involved room temperature optical transmission measurements using a Hitachi 330 UV–visible spectrophotometer.

## 3. Results and discussion

### *3.1. I–V and I–T measurements*

The $I$–$V$ characteristics at 400 K of the diodes are shown in figure 1. Virgin diodes showed low reverse current which increased approximately exponentially with voltage, due to the high level of acceptor doping and prominent tunnelling component in the current. The forward characteristics showed an ideality factor ∼2 and a very slight temperature dependence of the forward current with an activation energy of 0.18 eV. At forward biases higher than $-1$ V the current was determined by the series resistance of the p-GaN film.

After implantation all the diodes showed increased reverse and forward current, most probably due to the high density of defects in the implanted region and even more prominent tunnelling via these deep defects than in the virgin sample. In fact, the $I$–$V$ characteristics after implantation are essentially ohmic due to this introduction of defects. For all implanted samples the temperature dependence of the conductivity at temperatures below room temperature was of the Mott type, i.e. proportional to $\exp[-(T_0/T)^{1/4}]$, where $T_0$ is the characteristic temperature [21–23]. For temperatures above 300 K the temperature dependence was approximately exponential. The activation energy in this region was about 0.07 eV (i.e. much lower than the Mg ionization energy) for the virgin sample and 0.12–0.15 eV for implanted samples. It seems reasonable to assume that, in the virgin sample, the conductivity at high temperature is of the hopping $\varepsilon_2$ type as in some other (e.g. p-InSb) heavily doped semiconductors [23, 24]. For implanted samples the data indicate increased compensation but with the current still flowing via the same impurity band. The compensation was strongest for

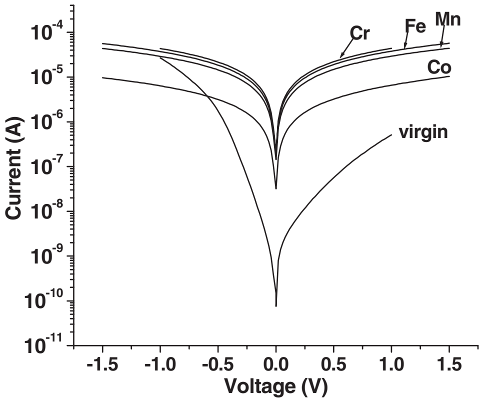


**Figure 1.** 400 K *I–V* characteristics of the p-GaN Schottky diodes made on the virgin sample and on the samples implanted with Co, Cr, Mn, Fe.

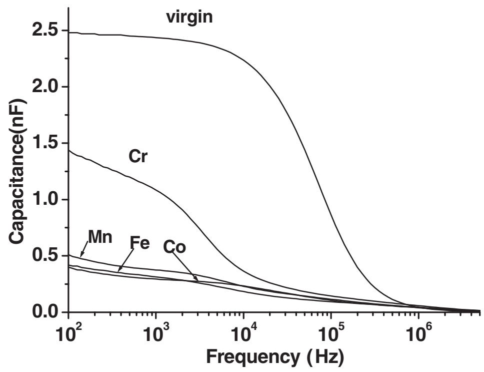


**Figure 2.** 400 K *C–f* characteristics for the virgin sample and the samples implanted with Co, Cr, Mn, Fe.

Co and the weakest for the Cr. These results correlate with the atomic masses of the implanted species and indicate that the heavier ions create more radiation damage that is not completely removed by the 700 °C annealing.

### 3.2. $C$–$f$, $C$–$V$ and $C/G$–$T$ measurements

Figure 2 compares the 400 K $C$–$f$ characteristics of the virgin and implanted p-GaN Schottky diodes. The low frequency capacitance value on the plateau strongly decreases after the implantation and the roll-off frequency in $C$–$f$ curves corresponding to the transition from the low frequency plateau in $C$–$f$ to the high frequency values decreases after the implantation due to the increased series resistance of the diodes [19, 20]. As with the forward current measurements, the magnitude of the series resistance increase is the highest for the Co implanted sample and the lowest for Cr implanted sample. $C$–$V$ measurements at frequencies corresponding to the low frequency plateau gave the net acceptor concentration for the virgin sample as $4 \times 10^{18}$ cm$^{-3}$. For implanted samples this value decreased considerably. It was the lowest ($2.1 \times 10^{17}$ cm$^{-3}$) for the Co implanted sample, the highest ($1.2 \times 10^{18}$ cm$^{-3}$) for the Cr implanted sample and in between for Fe ($6.1 \times 10^{17}$ cm$^{-3}$) and Mn ($5.3 \times 10^{17}$ cm$^{-3}$). A plausible explanation is that the acceptors present in the virgin material are compensated by implantation-related donor-type defects [25, 26].

Admittance spectroscopy data are shown in figure 3 for the virgin sample. Two major steps in capacitance (peaks in $G/\omega$) correspond to two closely spaced acceptors with different capture cross sections. For the implanted samples such measurements are difficult because of the high leakage current that contributes to the conductivity values measured at low frequencies. As a result the peaks in conductance appear as steps. In order to alleviate this problem we subtracted the DC conductance from the measured values [20]. Admittance spectra of the Co implanted sample showed a peak activation energy of 0.17 eV and hole capture cross section of $1.3 \times 10^{-19}$ cm$^2$, i.e. similar to the high temperature peak of the virgin sample. Similar results were obtained for the Fe implanted sample, as shown in figure 4. The spectra for the Cr and Mn implanted samples were qualitatively similar to those of the Fe implanted sample. These results suggest that the implantation decreases the net number of acceptors forming the space charge region through compensation, but these are still the same Mg-related centres with ionization energy of 0.15–0.16 eV as in the virgin sample. The nature of the two acceptor centres often

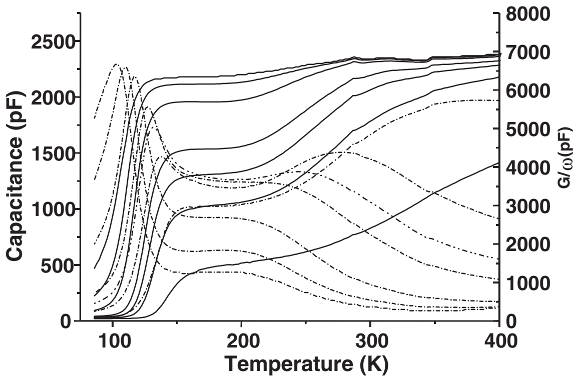


**Figure 3.** Capacitance (left axis, solid curves) and $G/\omega$ (right axis, dashed curves) dependences on temperature for various frequencies obtained for the virgin sample for frequencies of 300, 500, 1000, 5000, 10 000, 50 000 Hz. The lowest frequency spectrum is at the left and the highest frequency one at the right of the figure. The peak on the left has an activation energy of 0.15 eV with capture cross section $3 \times 10^{-15}$ cm$^{-2}$ while the peak on the right has an activation energy 0.17 eV and cross section $1.2 \times 10^{-19}$ cm$^{-2}$.

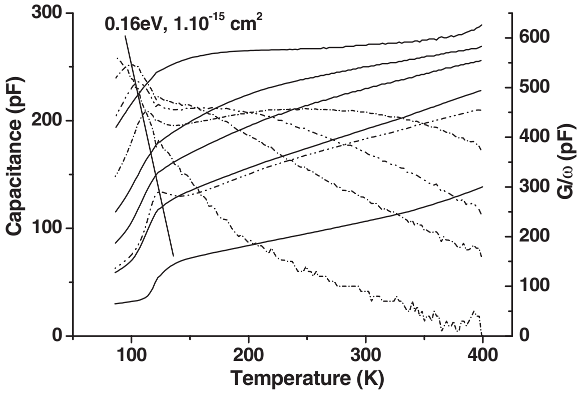


**Figure 4.** Capacitance (left axis, solid curves) and $G/\omega$ (right axis, dashed curves) dependences on temperature for various frequencies obtained for the Fe implanted sample after subtracting the low frequency conductance; the measurement frequencies were 1, 3, 5, 10, 50 kHz for the curves going top to bottom on the figure.

detected in admittance spectra of p-GaN(Mg) Schottky diodes [24] is not well understood. One possibility is that these are due to Mg and some other acceptor species (e.g. carbon). Note also that in each case, the admittance peaks shift with frequency as expected for deep traps with significant de-trapping times.

### *3.3. PICTS and CDLTS deep level spectra measurements*

The PICTS spectrum of the virgin sample with an optical injection pulse provided by a deuterium light illumination pulse showed two peaks with activation energies of 0.3 and 0.6 eV. For all TM implanted samples the photosensitivity was negligibly small due to the very high density of defects. For current transient deep level spectroscopy the effect of the series resistance is greatly alleviated [17]. Although such spectra lack quantitative information

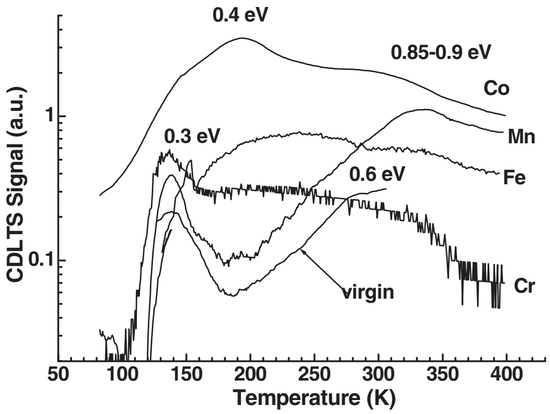


**Figure 5.** Current DLTS spectra obtained for the virgin sample and for the samples implanted with Cr, Co, Fe, Mn; reverse bias of 0.5 V, forward bias pulse of −3 V, 5 s long, $t_1/t_2 = 150\,\text{ms}/1500\,\text{ms}$.

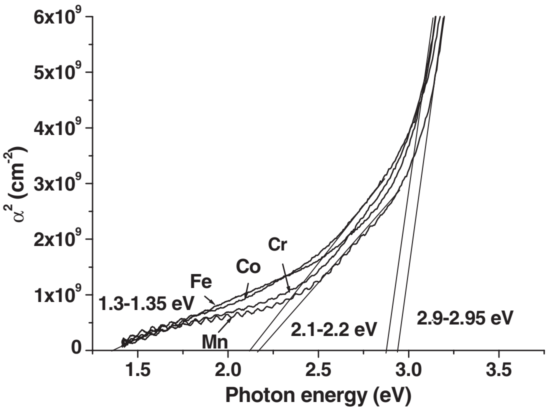


**Figure 6.** Absorption coefficient $\alpha^2$ versus photon energy plots.

on the densities of deep centres the spectra could be measured for all samples and a qualitative comparison of the deep level spectra was possible. The results are presented in figure 5. The virgin sample shows the same two peaks as observed in the PICTS spectrum. With current DLTS these centres can only be hole traps [17] (in PICTS both electron and hole traps can be recharged and give rise to peaks in the spectra because of the optical excitation used [18]). The 0.3 eV hole traps have been reported in proton implanted p-GaN or Mn implanted p-GaN layers in GaN/InGaN-based light emitting diodes [14, 21]. In the high temperature portion of the spectra all TM samples but the Cr implanted sample show hole traps with energy of 0.85–0.9 eV instead of 0.6 eV. These traps are also introduced by high dose proton implantation into p-GaN [21] and are most probably due to native defects. For the Cr implanted sample these defects are not detected, probably because of the overall lower density of defects compared to other implanted species.

### *3.4. Optical transmission*

The virgin sample did not show any strong defect absorption bands. In contrast, the implanted samples showed very strong absorption in the extrinsic region. Figure 6 shows the squared absorption coefficient $\alpha^2$ versus photon energy [27]. Three defect bands can be clearly seen: the A1 defect band with the threshold energy of 1.3–1.35 eV, the A2 defect band with the threshold energy of 2.1–2.2 eV and the A3 defect band with the threshold energy of 2.9–3 eV.

## 4. Summary and conclusion

In none of the samples did the Fermi level shift from the Mg acceptor band where it is pinned in the virgin samples. The amounts of increase in the series resistance and decrease in the diode capacitance and in the hole concentration were highest for Co and the lowest for Cr. This correlates with the mass of implanted ions and the number of radiation defects generated. Even after the 700 °C annealing, the electrical properties are dominated by the radiation damage introduced upon implantation and not by the properties of the TM ions incorporated. The main deep levels introduced are the 0.3 and 0.9 eV hole traps, as was also the case with similar p-GaN films implanted with protons [22]. A clear conclusion is that doping during epitaxial growth is a superior method for incorporating the transition metals into GaN, especially for structures such as spin light emitting diodes in which the transport of polarized carriers is critical.

## Acknowledgments

The work at IRM was supported in part by a grant from the Russian Foundation for Basic Research (Grant 01-02-17230). The authors would like to thank Mrs E F Astakhova for preparing the Schottky diodes. The work at UF is partially supported by ARO and NSF.

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