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This paper reports on the growth of Cr-doped GaN layers by metal organic vapor phase epitaxy (MOVPE) and their characterization for possible spintronic applications. We have used bis (cyclopentadienyl)chromium (Cp_2Cr) to intentionally incorporate chromium (Cr) during GaN layer growth. The effects of the carrier gas, hardware setup, and growth temperature on the growth of Cr-doped GaN were investigated. A linear dependence between mole fraction of Cp_2Cr in the gas phase and incorporated Cr in the solid phase was found. The surface morphology was mostly influenced by carrier gas and growth temperature. A remanent magnetization was observed even above room temperature.

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1 Introduction

In the past decade, research in diluted magnetic semiconductors (DMS) has been an area of great interest. This interest is driven by the desire to utilize the spin of the electron for use in spintronic applications [1, 2]. Feasible spintronic applications require materials with a Curie temperature (T_C) above 300 K. Theoretical calculations predicted that transition metal [3, 4] doping including Cr in GaN should result in room temperature ferromagnetism. Indeed, Mn, Cr, or Gd [6] doped GaN layers exhibit room temperature ferromagnetism. Up to now, Cr-doped GaN layers have only been grown by molecular beam epitaxy (MBE) [7]. Even though metal organic vapour phase epitaxy (MOVPE) is a mature technique for obtaining high quality group III-nitride layers, no growth of Cr-doped GaN layers by MOVPE has been reported. In this study, we investigated the influence of growth parameters on the incorporation of Cr in GaN layers by MOVPE and their structural and magnetic characterizations.

2 Experimental

Cr-doped GaN layer growth was performed on sapphire (0001) substrates by MOVPE in an AIXTRON 200/4 RF-S horizontal reactor equipped with a separation plate in the gas inlet, which allows the separate injection of metal organic (MO) sources and hydride sources into the reactor. Uniquely, we can change the hardware setup regarding the gas inlet between two geometries. The one is the so-called conventional

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inlet in which the ammonia (NH_3) is injected closer to the heated substrate surface through a lower channel and the MO sources through an upper channel. The latter is the so-called inverted inlet because the source gas injection is inverted [8]. We used trimethylgallium (TMGa), NH_3, and bis(cyclopentadienyl)chromium (Cp_2Cr) as Ga, N, and Cr precursors, respectively. A two-step growth procedure was employed for GaN as described in [9]. Three series of samples were grown. In the first series, the influence of the gas inlet on the Cr-incorporation was investigated. The Cp_2Cr flow rate was varied from 0 to 1.021×10^{-7} mol/min. In a second series, the influence of the carrier gas (N_2 or H_2) on Cr-doped GaN layer properties was determined at the highest Cp_2Cr flow rate of 1.021×10^{-7} mol/min. The growth temperature was held constant at 1100 °C, the value used for high quality undoped GaN. For both series a 2 µm thick undoped GaN epilayer was first deposited at the same conditions used for the Cr-doped GaN layer with a thickness of about 500 nm. In the third series, the inverted inlet geometry with optimized flow conditions was used: a mixture of 22% H_2 and 78% N_2. In this series, a 2 µm thick undoped GaN buffer was deposited at 1100 °C. The growth temperature for the successive Cr-doped GaN layer was varied between 900 °C and 1125 °C while the Cp_2Cr flow rate was kept constant at 1.021×10^{-7} mol/min. Growth was monitored by *in-situ* reflectometry combined with emissivity corrected pyrometry (EpiR-M-TT, Laytec). The Cr content in the layer was evaluated by secondary ion mass spectroscopy (SIMS). Scanning electron microscopy (SEM) was used to study the surface morphologies of Cr-doped GaN layers. The structural properties were studied by X-ray diffraction (XRD) using a $\theta/2\theta$ scans. The magnetic properties were investigated using a superconducting quantum interference device (SQUID) by zero field heating (ZFH) and magnetic hysteresis measurements. The samples were heated up to 350 K and a magnetic field of 7 Tesla (*T*) was applied. Then the samples were cooled down to 5 K in the presence of the magnetic field. After a pause of 1 minute at 5 K, the applied magnetic field was switched off. The temperature was increased to 350 K with a constant rate. The magnetic moment was recorded in equal time intervals.

3 Results and discussion

Figure 1 shows the concentration of Cr in the layer measured by SIMS as a function of Cp_2Cr flow rate in the gas phase. These SIMS results show that the concentration of Cr in solid phase is linearly dependent on the Cp_2Cr flow rate in the gas phase. It is quite clear that the Cr incorporation efficiency is higher for the inverted inlet than for the conventional inlet. For GaN growth the parasitic reactions are reduced and MO sources access closer to the substrate in the inverted inlet [8]. The enhanced Cr incorporation efficiency may be due to the suppression of parasitic reactions and the closer access of MO sources to the

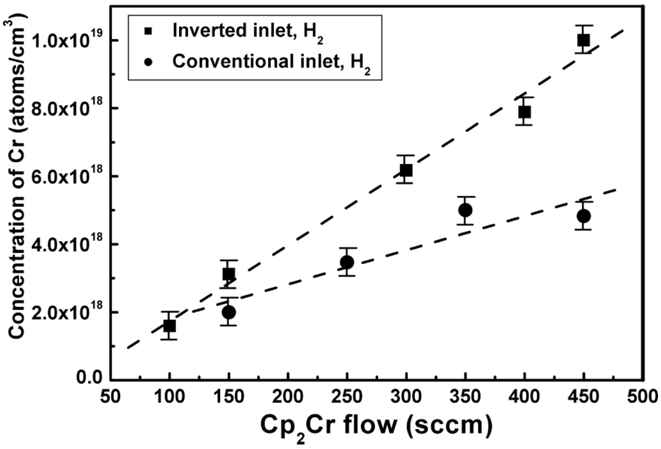
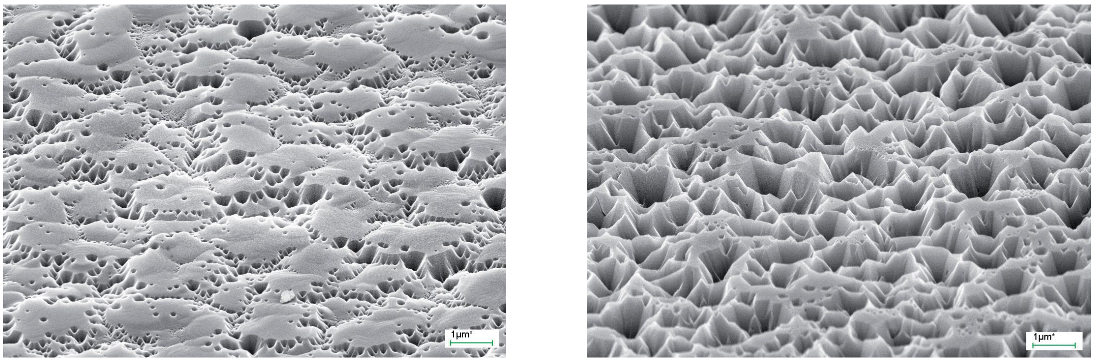


Fig. 1 Concentration of Cr in the layer as a function of Cp_2Cr flow rate in gas phase measured by SIMS. The Cr incorporation efficiency is higher for the inverted inlet than for the conventional inlet.



(a) (b)

Fig. 2 Surface morphologies of the Cr-doped GaN layers with maximum Cp_2Cr flow rate were studied by SEM (a) is grown with pure H_2 and (b) is grown with pure N_2 carrier gas.

substrate. Hence, for this inlet configuration we further studied the influence of the carrier gas on Cr-doped GaN layer growth.

To investigate how the growth was affected by different carrier gases for the inverted inlet, we investigated the surface morphologies of the Cr-doped GaN layers by SEM. It has already been shown for the growth of undoped GaN that different surface morphologies evolve during growth in H_2 and N_2 carrier gases [9, 10]. The surface morphologies of the Cr-doped GaN layers with maximum Cp_2Cr flow rate, 1.021×10^{-7} mol/min, grown in H_2 and N_2 carrier gases are compared in Fig. 2. In H_2 ambient, Cr-doped GaN islands coalesce more than in N_2 ambient probably because of the different chemical reactions. However we need more investigations on these different chemical reactions during Cr-doped GaN growth. From these SEM pictures, we may assume that Cr destroys the 2-dimensional (2-D) lateral growth mode and the 3-D vertical growth is dominant in the N_2 carrier gas. Therefore a certain amount of H_2 carrier gas is needed in order to obtain layers with an improved surface morphology.

The structural characteristics of Cr-doped GaN layers were investigated by XRD using $\theta/2\theta$ scans (not shown here). Neither additional peaks were observed nor a peak shift relative to the GaN/sapphire peak positions. There are no additional phases to be seen that have the same crystal orientation as the substrate and the original GaN layer. Nevertheless the sensitivity of the XRD investigations may not be sufficient since the additional phases may be present as a small fraction in the layer. Additionally the contribution of the undoped GaN buffer layer may be dominant, so that structural changes may not be observable. Therefore, other characterization methods such as transmission electron microscopy (TEM) still need to be carried out.

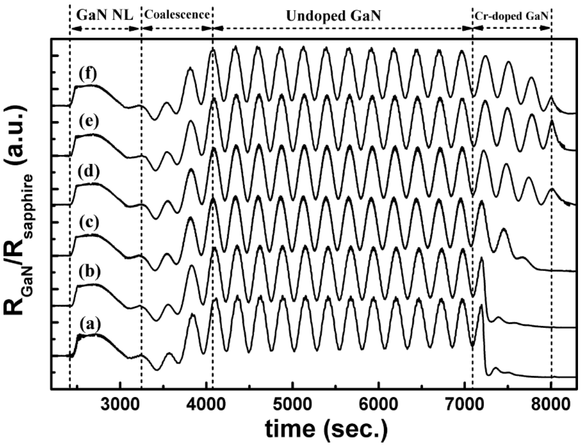
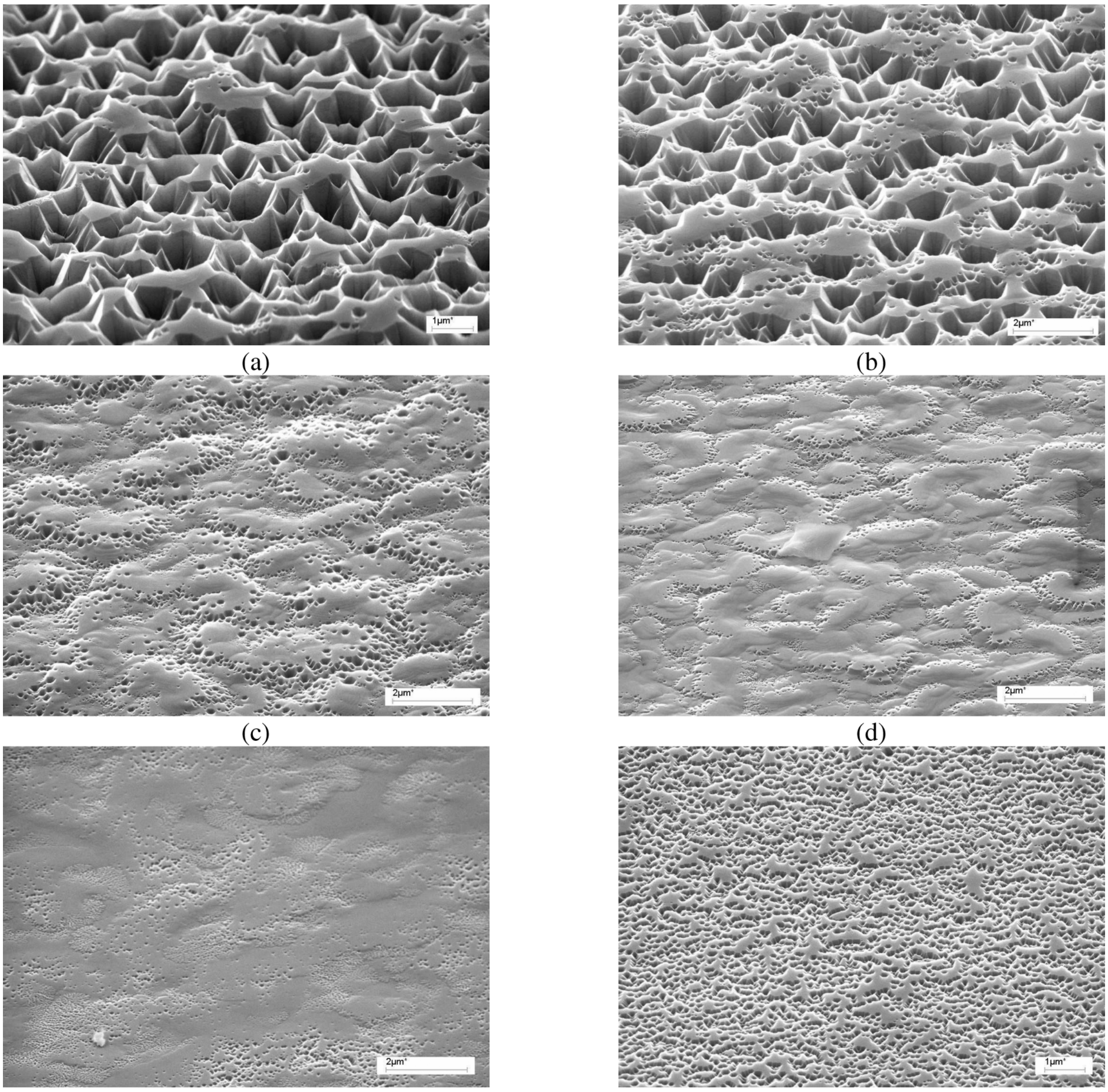


Fig. 3 *In-situ* reflectometry transients. The Cr-doped GaN layer was grown at (a) 1125 °C, (b) 1100 °C, (c) 1050 °C, (d) 1000 °C, (e) 950 °C, and (f) 900 °C.



(a) (b)
(c) (d)
(e) (f)

Fig. 4 Surface morphologies of the Cr-doped GaN layers grown at different temperatures were observed by SEM. Layers grown at (a) 1125 °C, (b) 1100 °C, (c) 1050 °C, (d) 1000 °C, (e) 950 °C, and (f) 900 °C.

Usually, the growth temperature is one of the most important parameters for the growth of GaN layers [11]. It was already shown that growth temperature influences drastically the quality of Mn or Fe doped GaN layers grown by MOVPE [12, 13]. Therefore, we varied the growth temperature only in the Cr-doped GaN growth regime from 900 °C to 1125 °C. Figure 3 shows the *in-situ* reflectometry transients. At 1125 °C the oscillations vanished as soon as the Cp_2Cr source was opened. It means that the 2-D growth was destroyed. However, by decreasing the growth temperature of Cr-doped GaN layers, the oscillations were maintained. It means that the surface morphologies were improved in comparison with the one of Cr-doped GaN grown at temperatures higher than 1050 °C. Even though the oscillation amplitude and overall intensity were still reduced in comparison with the undoped GaN, the oscillations for the layer grown at 950 °C have shown the highest overall intensity and the highest amplitude of all the Cr-doped GaN layers.

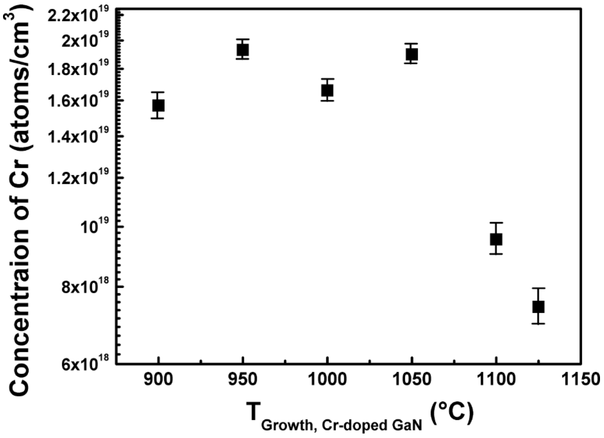


Fig. 5 Concentration of Cr in the layer as a function of the temperature at Cr-doped GaN growth regime measured by SIMS.

The surface morphologies of the Cr-doped GaN layers grown at different temperatures were investigated by SEM and correlated with the *in-situ* results. In Fig. 4, we can see how the surface morphology was influenced by the growth temperature. The surface morphology was significantly improved at lower temperatures. It means that the 2-D lateral growth mode has been promoted during Cr-doped GaN growth. However, the surface is roughened again at 900 °C. We can conclude that for obtaining Cr-doped GaN layers with good morphology it is necessary to grow at temperatures higher than 900 °C and lower than 1050 °C.

SIMS measurements were used to explore the effect of the growth temperature on Cr incorporation efficiency in the layers. Figure 5 shows the concentration of Cr in the layer as a function of the growth temperature. The Cr concentration was increased by reducing the growth temperature below 1050 °C. For the layers grown at temperatures above 1050 °C, the Cr concentration is lower than 10^{19} atoms/cm^3. Below 1050 °C, the Cr concentration is nearly constant at around 1.8×10^{19} atoms/cm^3. The slight differences in the Cr concentration may be due to the roughness of the layers.

Finally, we evaluated the magnetic properties. The ZFH measurements were carried out for the best two Cr-doped GaN layers, which were grown at 950 °C and 1000 °C. For reference an undoped GaN layer was also considered. The origin of the non-zero magnetic moment in the undoped GaN at low temperature might be due to metallic impurities contained in the sapphire substrate. These results indicate that our Cr-doped GaN layers exhibit remanent magnetization above room temperature. Also these two

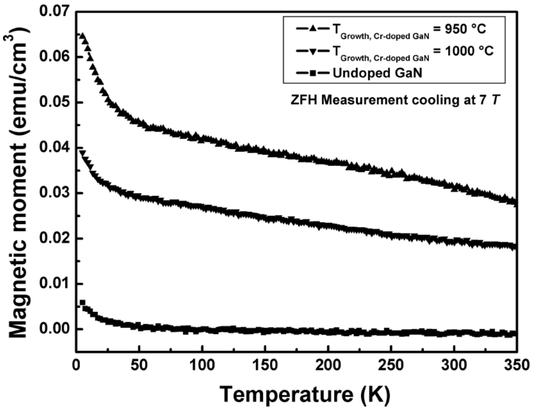


Fig. 6 ZFH measurements performed with two Cr-doped GaN layers, which were grown at 950 °C and 1000 °C. They show remanent magnetization above room temperature.

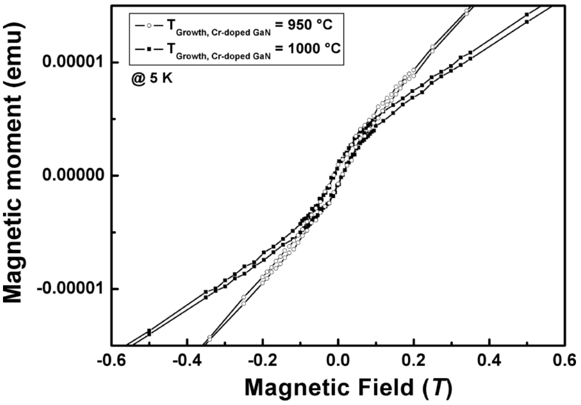


Fig. 7 Magnetic moment versus magnetic field curves at 5 K with external magnetic field perpendicular to the *c*-plane.

Cr-doped GaN layers show a clear hysteresis loop in Fig. 7. The magnetic contributions of the undoped GaN and sapphire substrate were subtracted. The origin of this remanent magnetization still needs to be studied in more detail.

4 Conclusions

Cr-doped GaN layers were grown by MOVPE on sapphire (0001) substrates. The effects of different hardware setups, carrier gases, and growth temperatures on the Cr-doped GaN layers were studied systematically. The use of the inverted inlet results in a higher Cr incorporation efficiency than the use of the conventional inlet. Significantly different surface morphologies were observed for N_2 and H_2 carrier gas due to the changed growth mechanism. Relatively low temperatures, which are below 1050 °C for Cr-doped GaN layer growth in comparison to the undoped GaN growth temperatures help to improve the surface morphology and to increase the Cr incorporation efficiency. However, the temperature should be above 900 °C in order to obtain a good surface morphology. Based on the overall results, we can conclude that the carrier gas and growth temperature affect the surface morphology of Cr-doped GaN layers very strongly. The two Cr-doped GaN layers grown at 950 °C and at 1000 °C show remnant magnetization above room temperature as well as a clear hysteresis loop at 5 K. However, the origin of this remanent magnetization still needs to be clarified.

These results demonstrate the growth of Cr-doped GaN layers by MOVPE for spintronics for the first time. In future we still need to optimize the growth parameters for Cr-doped GaN layers with the aim to increase the Cr incorporation in the GaN layers and hence to improve their magnetic properties.

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