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Cu-doped GaN grown by molecular beam epitaxy

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Abstract. Cu-doped GaN is a promising candidate for a nitride-based diluted magnetic semiconductor. Theoretical predictions show the possibility of ferromagnetism and high spin-polarization for certain arrangements of Cu atoms in the GaN lattice. Initial experimental results have already indicated ferromagnetism. However, the influence of structural defects on the ferromagnetic order in Cu-doped nitrides is not clear. Hence, the origin of the ferromagnetism is still under debate. We have used density functional theory (DFT) to verify previous theoretical predictions and to investigate the effects of the position of Cu atoms on the ferromagnetic properties. Our DFT calculations show high degrees of spin-polarization, independent of the arrangement of Cu atoms. Additionally, we have investigated the growth of Cu-doped GaN by molecular beam epitaxy. The influence of parameters, such as Cu to Ga ratio and growth temperature, on the structural and magnetic properties will be discussed.

1. Introduction

Group-III nitride semiconductor cover a large bandgap-area and have good thermal and chemical stability. They are therefore interesting for many optoelectronic applications and devices. The possibility to synthesize a diluted magnetic semiconductor (DMS) based on group-III nitrides is in demand for the application area of spintronics. An ideal DMS like a conventional group-III nitride doped with a transition metal, should exhibit ferromagnetism at or above room-temperature. Indeed, theoretical [1, 2] and experimental [3, 4] results show room-temperature ferromagnetism in Mn- and Gd-doped GaN. However, this ferromagnetism could also be caused by clusters of Mn or Gd in the GaN host, because Mn and Gd are intrinsic ferromagnetic elements. The formation of such clusters was already observed experimentally [5, 6].

Copper (Cu) as a non-magnetic transition metal is a promising candidate for overcoming the problem with magnetic secondary phases. Room-temperature ferromagnetism in Cu-doped ZnO was proven theoretically [7] and experimentally [8]. The first density functional theory (DFT) calculations for Cu-doped nitrides by Wu et al. [9] suggested room-temperature ferromagnetism with a 100 % spin-polarization of the conduction carriers and a total magnetization of $2.0 \mu_{\text{Bohr}}$ per Cu atom. DFT calculations for Cu-doped GaN by Rosa and Ahuja [10], showed only a weak ferromagnetism, making the material unsuitable for spintronic applications. The reason could be found in the Cu arrangement in the GaN lattice. Two possible configurations with different Cu-Cu distances have been considered thus far: a "far" configuration (Cu-Cu distance: 5.23 \AA), which is ferromagnetic in accordance with [9], and a "close" configuration (Cu-Cu distance: 3.22 \AA), which is lower in energy and shows only weak ferromagnetism. The first experimental results

were reported on Cu-implanted GaN films [11]. However, the observed magnetic saturation (0.01 to 0.27 μ_{Bohr}) was much lower than predicted by Wu et al. [9] and depended on the annealing temperature. Room-temperature ferromagnetism in Cu-implanted samples was also found by [12]. Yang et al. [12] and Hong [13] concluded, that vacancy-like defects should be considered in order to understand the observed magnetism. Furthermore, room-temperature ferromagnetism was also observed in Cu-doped GaN nanowires [14] which exhibit a single-crystalline and defect-free nature. A much higher magnetic saturation of 0.86 μ_{Bohr} per Cu atom was detected in these nanowires compared to implanted films, but still much lower than theoretically predicted.

2. Methods

DFT calculations were performed using the WIEN2k code [15]. The properties were studied on a $2 \times 2 \times 2$ GaN supercell, with two Cu atoms substituting Ga sites. Other defects such as vacancies or interstitial atoms were not considered. For the calculation of the exchange-correlation potential, the general gradient approximation (GGA) within the PBE scheme [16] was used. A $7 \times 7 \times 4$ \mathbf{k} mesh was used to scan the irreducible Brillouin zone. The convergence criteria was set to 1.4 meV for the total energy. All calculations were obtained for wurtzite GaN with the lattice constants $a = 3.189 \text{ \AA}$ and $c = 5.189 \text{ \AA}$. After structural optimization, a marginal change in the lattice constants was observed. Cu-doped GaN films were grown on *C*-plane sapphire substrates by plasma assisted molecular beam epitaxy in a Riber compact 21 MBE-system. For an improved backside heating in the chamber, the substrates were glued with Indium on Si(001) wafers. After outgasing the substrate in the loadlock chamber, a three-step-growth was performed. First, nitridation of the sapphire surface was made in an activated nitrogen atmosphere with a pressure of 2.4×10^{-5} Torr. Second, a 25 nm buffer layer was grown at low substrate temperature and slightly Al rich conditions. Last, a Cu-doped GaN epitaxial layer followed the buffer layer. This layer was grown at 750 °C thermocouple temperature for two hours. To promote the growth of a high-quality crystalline layer, a slow growth rate of about 70 nm per hour was selected. During growth, reflection high-energy electron diffraction (RHEED) was used to characterize the surface. The structural properties were analyzed with scanning electron microscopy (SEM). X-ray diffraction (XRD) with a Bruker D8 diffractometer yielded information about the crystalline quality and secondary phases. For a characterization of the magnetic properties, a superconducting quantum interference device (SQUID) was used.

3. Results and discussion

3.1. DFT calculations

Our calculations were made for two Cu atoms in the supercell corresponding to a high Cu concentration of 12.5 at.%. The Cu atoms were put on Ga sites. Figure 1 shows the electronic density of states (DOS) for the spin-up and spin-down channels for the "far" configuration (Fig. 1a), corresponding to a Cu-Cu distance of 5.169 \AA , and for the "close" configuration (Fig. 1b), corresponding to a Cu-Cu distance of 2.986 \AA , respectively. For both, a high spin-polarization of about 90 % is observed. For the "far" configuration, we obtain a semiconductor-like DOS for the spin-up channel and a metallic behavior for the spin-down channel. The energy difference between these two spin states is about 600 meV. However, for the "close" configuration, the energy difference is about 300 meV, much lower than for the "far" configuration. There is also a little change in the band arrangement. For the "close" configuration, the spin-up states are more in the valence band and the spin-down states are slightly above zero energy, which corresponds to the valence band edge.

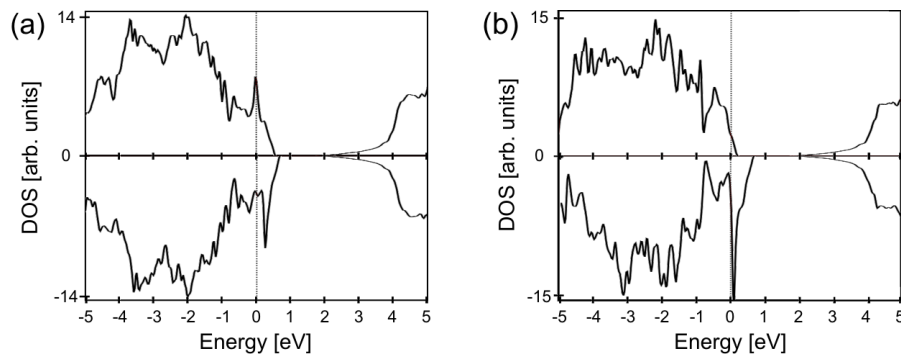


Figure 1. Spin-up (top) and spin-down (bottom) for "far" (a) and "close" (b) Cu arrangement.

3.2. Growth of Cu-doped GaN by molecular beam epitaxy

Aside from the calculations, we investigated the growth of Cu-doped GaN by plasma assisted molecular beam epitaxy. The structural properties of *C*-plane Cu-doped GaN grown on *C*-plane sapphire are presented in Figs. 2 and 3. The surface morphology was imaged by SEM as shown

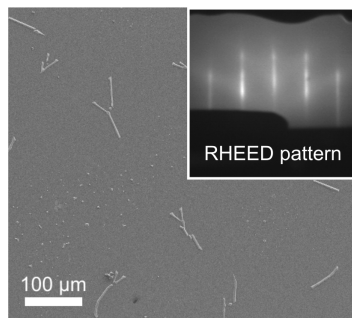


Figure 2. SEM picture and RHEED pattern after growth.

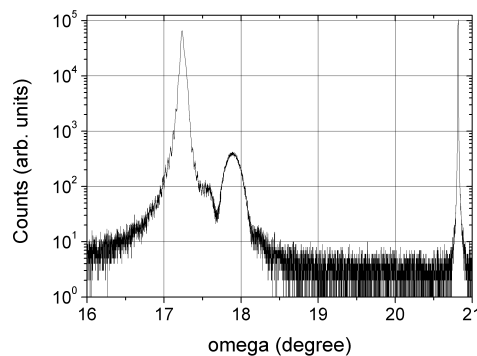


Figure 3. ω - 2θ scan.

in Fig. 2. Needle-shaped islands are visible on top of the film. The RHEED pattern (inset in Fig. 2) indicates a flat surface of the Cu-doped GaN. Energy dispersive x-ray spectroscopy (EDX) was used to determine the composition of these islands. They have an average height of about 100 nm and contain a high amount of copper and gallium, both in a concentration of about 50 %. Efforts to etch them away with 30 % HCl or 65 % HNO₃ were not successful. No Cu could be detected in the layer using EDX. XRD measurements indicated no secondary phase in Cu-doped GaN. Figure 3 shows a strong peak at an angle of $\omega = 20.82^\circ$ corresponding to the *C*-plane of the sapphire substrate. The full width at half maximum (FWHM) is about 0.0092° . The peak at 17.23° is the *C*-plane peak (0002) of the GaN. The FWHM of GaN (about 0.0389°) is broader but still reasonable for GaN. The lower quality of the GaN can have two reasons. First, the growth of Cu-doped GaN can be optimized with regard to the nitridation, the buffer and the epitaxial layer. A second reason for the lower quality could be the dopant. Cu may cause defects, that give rise to a lower crystalline quality. A third peak is observed at 17.89° in Fig. 3. This peak is due to the AlN buffer layer and a thin AlGa₃N layer between the buffer and epitaxial layer, because the peak is shifted by to lower angles with respect to the pure AlN *C*-plane peak.

3.3. Magnetic properties

The magnetic properties were measured by SQUID magnetometry for samples with varying Cu to Ga beam equivalent pressure (BEP) flux ratio. The growth was investigated for samples with BEP flux ratios from 0.9 % to 4.8 %. Figure 4a) presents the magnetization at room

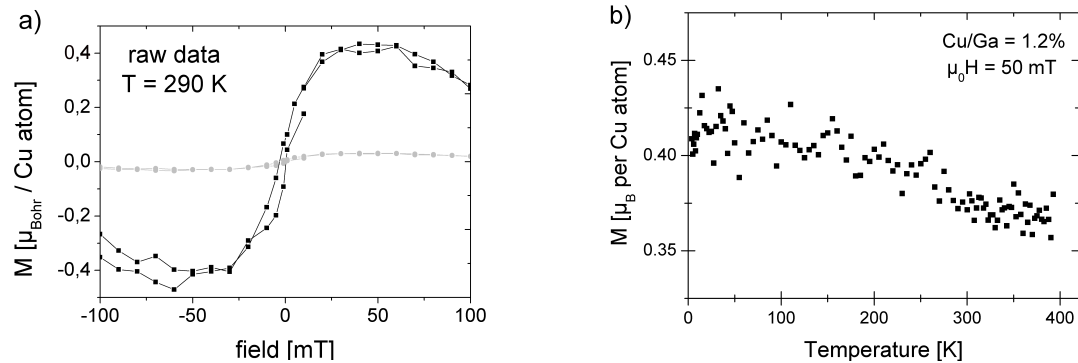


Figure 4. a) Nominal magnetization as a function of external field for BEP flux ratios of 1.2 % (black) and 4.8 % (grey). The negative slope of $M(H)$ at large fields is due to the diamagnetic contribution of the sapphire substrate. b) Magnetization as a function of temperature.

temperature as a function of external magnetic field for two different Cu to Ga BEP flux ratios. The magnetic saturation is getting lower for a higher flux ratio. For the sample with a flux ratio of 1.2 %, the nominal magnetic saturation is calculated to $0.42 \mu_{\text{Bohr}}$ per Cu atom, although the real moment may be much larger considering the large amount of Cu in the islands on the film. The reduced magnetic saturation for higher ratios is attributed to the higher Cu allocation, because there was no change in other parameters. Fig. 4b) shows the magnetization as a function of temperature, measured up to 400 K. The magnetization decreases slowly with increasing temperature. Therefore, the Curie temperature is expected to be far above 400 K.

We presented DFT calculations on Cu-doped GaN containing 12.5 % Cu atoms. All calculations show a high degree of spin-polarization. A ferromagnetic behavior at room-temperature was also observed in epitaxially grown Cu-doped GaN. For a higher Cu to Ga BEP flux ratio, the saturation magnetization decreases.

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