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Cu-doped nitrides: Promising candidates for a nitride based spin-aligner

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ABSTRACT

A spin-aligner that shows ferromagnetism at room temperature is indispensable for spintronic applications. Diluted magnetic semiconductors are prospective candidates for a spin-aligner. We show that Cu-doped group-III nitrides show ferromagnetic behavior at room temperature although Cu is an intrinsic non-magnetic material. Problems with the building of magnetic secondary phases like in Mn- or Gd-doped nitrides are avoided by using Cu. The formation of Cu-group-III metal compounds is observed. However, these compounds will not affect the ferromagnetic properties and 90% of them can be removed by etching with HNO_3 for 5 min.

1. Introduction

Nitride based spintronics is emerging as an interesting alternative to arsenide based spintronics. One reason for the strong interest in using group-III nitrides in spintronics is the long and temperature independent spin-lifetime in InN quantum dots [1,2]. Group-III nitride semiconductors have also additional advantages: these materials have large bandgaps and good thermal and chemical stabilities. For spin injection into quantum dots, a ferromagnetic spin-aligner that yields high spin polarization at room temperature is necessary. The most convenient material for such a spin-aligner would be a ferromagnetic metal. All experiments with a ferromagnetic metal utilized as spin injector into semiconductors showed unsatisfying results for spin injection, efficiency due to a large mismatch in conductivities between the semiconductor and the ferromagnetic metal [3]. An alternative to ferromagnetic metals are diluted magnetic semiconductors (DMS). DMS are conventional semiconductors that show ferromagnetism when doped with transition metal elements. The mismatch in conductivities disappears on using DMS as spin injector for semiconductor based spintronic devices [3].

For group-III nitride based DMS various doping elements are used. The most common dopants are the intrinsic magnetic materials manganese and gadolinium. Especially, theoretical calculations for Mn-doped GaN suggest that the Curie temperature was above room temperature [4]. Further experimental results were published on both Mn- and Gd-doped GaN reporting room-temperature ferromagnetism [5,6]. However, experiments showed the formation of clusters, consisting mainly of the magnetic dopant [7,8]. These two experiments [7,8] lead to the conclusion that the observed ferromagnetism is generated by these clusters and not by the dopants incorporated into the group-III nitride host. Usage of non-magnetic dopants prevented the problems with magnetic clusters. Copper as a non-magnetic transition metal is a promising candidate.

Initial density-functional-theory (DFT) calculations for Cu-doped nitrides by Wu et al. [9] suggested 100% spin polarization of the conduction carriers and a Curie temperature above 350 K. Also, a high total magnetization of 2.0 μ_{Bohr} per Cu atom was calculated. In contrast, DFT calculations by Rosa and Ahuja [10] showed only weak ferromagnetism, making the material unsuitable for spintronic applications. Experimental results were reported for Cu-doped nitride nanowires [11–13], Cu-implanted GaN [14,15] and CVD grown Cu-doped GaN [16]. Initial results for Cu-doped GaN grown by molecular beam epitaxy were reported by our group [17]. All results indicated room-temperature ferromagnetism. For Cu-implanted samples, annealing is necessary to obtain ferromagnetism. The ferromagnetic properties are sensitive to Cu doping levels as well as the method of growth and Cu incorporation.

We report on the preparation and magnetic properties of high quality thin films of Cu-doped GaN and AlN grown on sapphire substrates.

2. Methods

Cu-doped group-III nitrides were grown by plasma assisted molecular beam epitaxy in a RIBER compact 21 system. Commercial one-side polished *C*-plane sapphire with a thickness of 0.33 mm were used for nitride growth as substrates. Because of

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the backside heating in our MBE system and the transparency of the substrates in a wide range from the ultraviolet to the far infrared, the substrates were glued with indium on silicon wafers for better heat transfer and heat coupling. Preliminary outgasing was performed at 130 °C for 60 min before transferring the samples into the growth chamber. After outgasing for the second time at 850 °C for 30 min in the growth chamber, nitridation was carried out for 180 min at 200 °C substrate temperature. Nitridation is essential for growing flat group-III nitride films on sapphire substrates because of the large lattice mismatch. Due to nitridation a few nanometer thin AlN layer is formed on the surface. The lattice mismatch after nitridation is now reduced for GaN to 2.5% and for AlN it is almost 0%. However, a 20 nm thin AlN layer was grown at high temperature on top of the nitridated surface for better nucleation of Cu-doped nitride films. With a growth rate of about 70 nm/h, Cu-doped GaN or AlN was grown for 120 min. Cu was provided from the beginning of the epitaxial layer growth.

In-situ reflective high energy electron diffraction (RHEED) provided information on growth. Scanning electron microscopy (SEM) revealed the surface morphology of the group-III nitride films. The structural properties were determined by X-ray diffraction (XRD). Energy dispersive X-ray spectroscopy (EDS) yields information on the composition of the layer and the Cu incorporation in the film. Magnetic properties were monitored using superconducting quantum interference device (SQUID) magnetometry.

3. Results and discussion

The supply of Cu during epitaxial layer growth has the effect that islands are formed on the surface, which can be clearly seen in Fig. 1. For both Cu-doped GaN (Fig. 1a) and Cu-doped AlN (Fig. 1c), slightly metal rich conditions are chosen in order to ensure flat film growth. The same amount of Cu was provided for both samples. The higher amount of islands on Cu-doped AlN (Fig. 1c) can be ascribed to slightly more Al-rich conditions during growth, ending in a higher amount of group-III metal being on the surface. Most of the islands show a rectangular shape. Arborescent thin stripes are observed only for Cu-doped GaN (Fig. 1a) when the Cu to Ga beam equivalent pressure ratio (BEP) is higher than 2.0% at 790 °C substrate temperature. Getting more information on the island composition, element specific EDS measurements were performed. Their results (not shown here) indicate a Cu content in the island of about 60%; the remaining 40% can be ascribed to Ga or Al. Other elements are not found in these islands. In the film near the islands the Cu signal was below the detection limit of our EDS setup. *In-situ* RHEED measurements indicate a smooth surface for Cu-doped GaN (Fig. 1b) and Cu-doped AlN (Fig. 1d).

A high crystalline quality of Cu-doped GaN (Fig. 2) and AlN (Fig. 3) is found in the XRD spectra. The full width at half maximum (FWHM) of the (0 0 0 2) peak is calculated around 160 arcsec for both materials. A shift in this peak for GaN and AlN due to Cu incorporation is not observed. Due to AlN buffer layer growth, the AlN (0 0 0 2) peak appears also for Cu-doped GaN (Fig. 2). Additional peaks around $\theta=22.4^\circ$ can be found in both XRD spectra. These peaks are assigned to the Cu-metal (metal=Al and Ga) compounds on the surface. For Cu-doped GaN (Fig. 2), only one peak is allocated at $\theta=22.4^\circ$. However, a second single peak is detected around $\theta=49.2^\circ$.

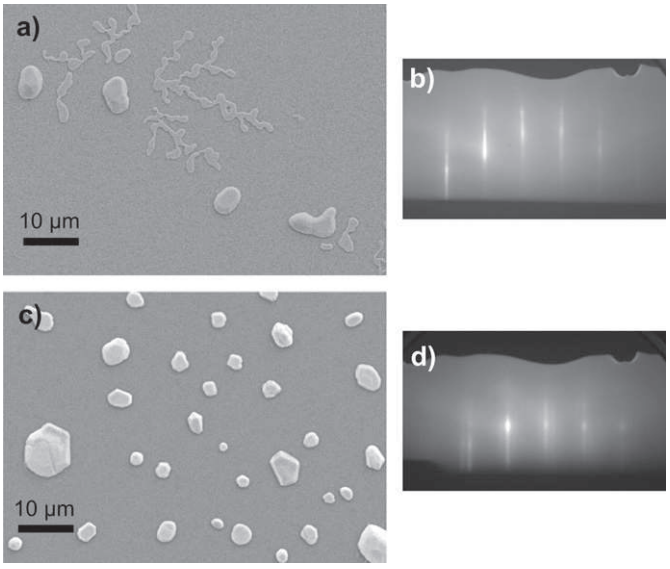

Fig. 1. (a) Typical surface for slightly metal rich grown Cu-doped GaN and (c) AlN. The surface is covered by islands. EDS measurements show that the islands consist of Cu and Ga or Al. The film adjacent to the islands is flat, which can also be expected from the streaky RHEED patterns for (b) Cu-doped GaN and (d) AlN.

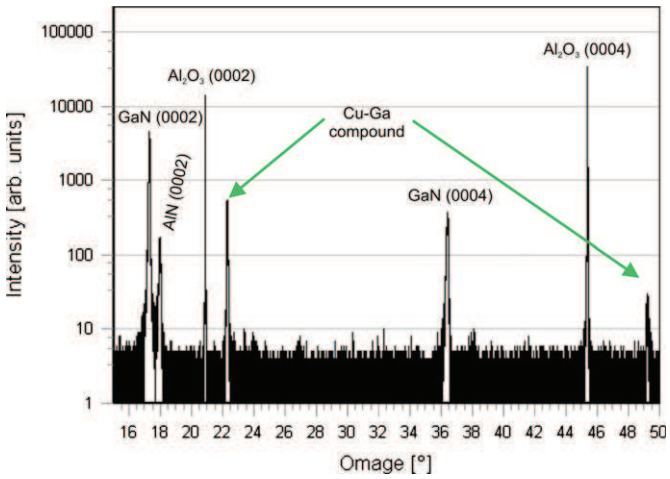

Fig. 2. XRD spectra of Cu-doped GaN show no shift in peak position due to Cu incorporation compared to pure GaN. The full width at half maximum (FWHM) of the GaN (0 0 0 2) peak is about 160 arcsec. The observed AlN (0 0 0 2) peak can be ascribed to the AlN buffer layer. The Cu–Ga compounds on the surface give some additional single peaks at 22.4° and 49.2°.

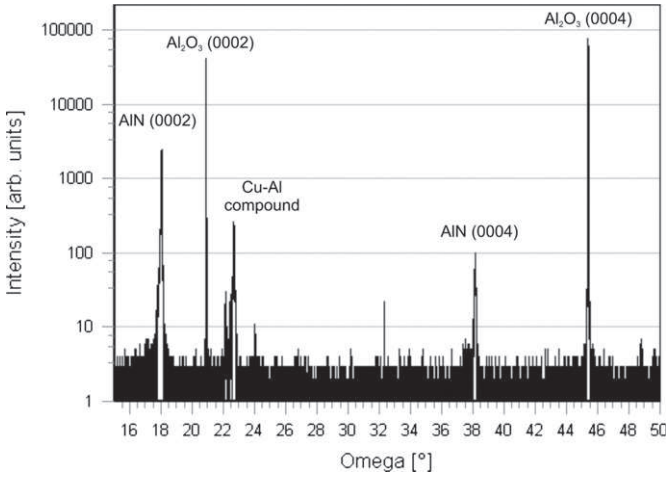

Fig. 3. XRD spectra of Cu-doped AlN. The FWHM of the AlN (0 0 0 2) is in the same order as for GaN. Cu–Al compounds show similar signature in the spectra like Cu–Ga compounds.

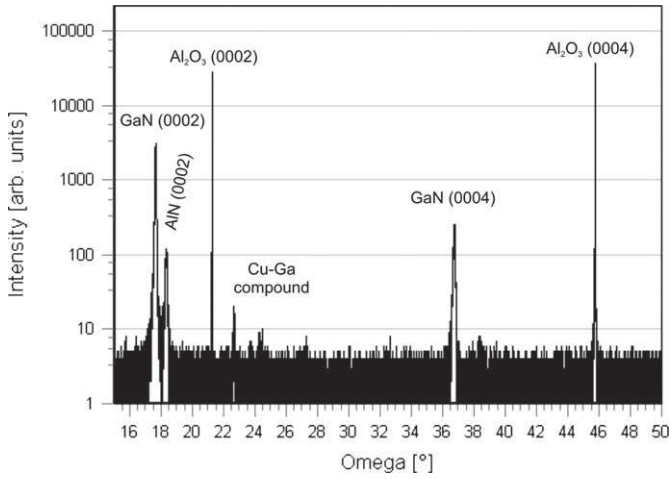

Fig. 4. XRD spectra of Cu-doped GaN after etching with HNO_3 for 5 min. The Cu–Ga compound peak at 22.4° is strongly reduced and the peak at 49.2° disappears. The position and width of the GaN and Al_2O_3 peaks did not change after etching. Therefore, etching acts only on the compounds and has no effect on GaN.

For further applications of these diluted magnetic semiconductors, it would be very nice to get rid of these islands. Removing these islands can easily be done by wet chemical etching, if there is a suitable acid to etch the islands. Chemical etching is very convenient for group-III nitrides because they are very stable. Etching with HNO_3 for 5 min was performed on the Cu-doped nitrides. The results for Cu-doped GaN are detected by XRD and shown in Fig. 4. Compared to Fig. 2, the right Cu–Ga peak (49.2°) disappears completely after etching. Over 90% of the counts for the major peak of the Cu–Ga compounds at $\theta = 22.4°$ is lost. The same results are also obtained for Cu–Al compounds in Cu-doped AlN (not shown here).

As the Cu-metal compounds have no influence on magnetic properties because of their metallic character, the SQUID measurements are performed on non-etched samples. Fig. 5a shows the magnetization M versus the magnetic field H for Cu-doped GaN, measured at 10 K and at room temperature. A small hysteresis can be clearly seen for both temperatures. The magnetic remanence of 0.1 emu/cm^3 and a coercive field of 5 mT at 290 K are found for Cu to Ga BEP ratio of 1.2%. The temperature dependent magnetization of this sample is shown in Fig. 5b. For a magnetic field of 50 mT the decrease in magnetization up to a temperature of 400 K is measured. Magnetization M decreases to about 1.13 emu/cm^3 at 400 K. This equates to a decrease of less than 10% in magnetization when compared to the magnetization at the lowest temperature in our setup of about 10 K. The Curie temperature of Cu-doped GaN is therefore expected to be much higher than 400 K. This makes Cu-doped GaN a promising candidate for a nitride based spin-aligner. In contrast, Cu-doped AlN shows only diamagnetic behavior (Fig. 5c). No ferromagnetic behavior is found for Cu to Al BEP ratios from 1.0% to 4.0%.

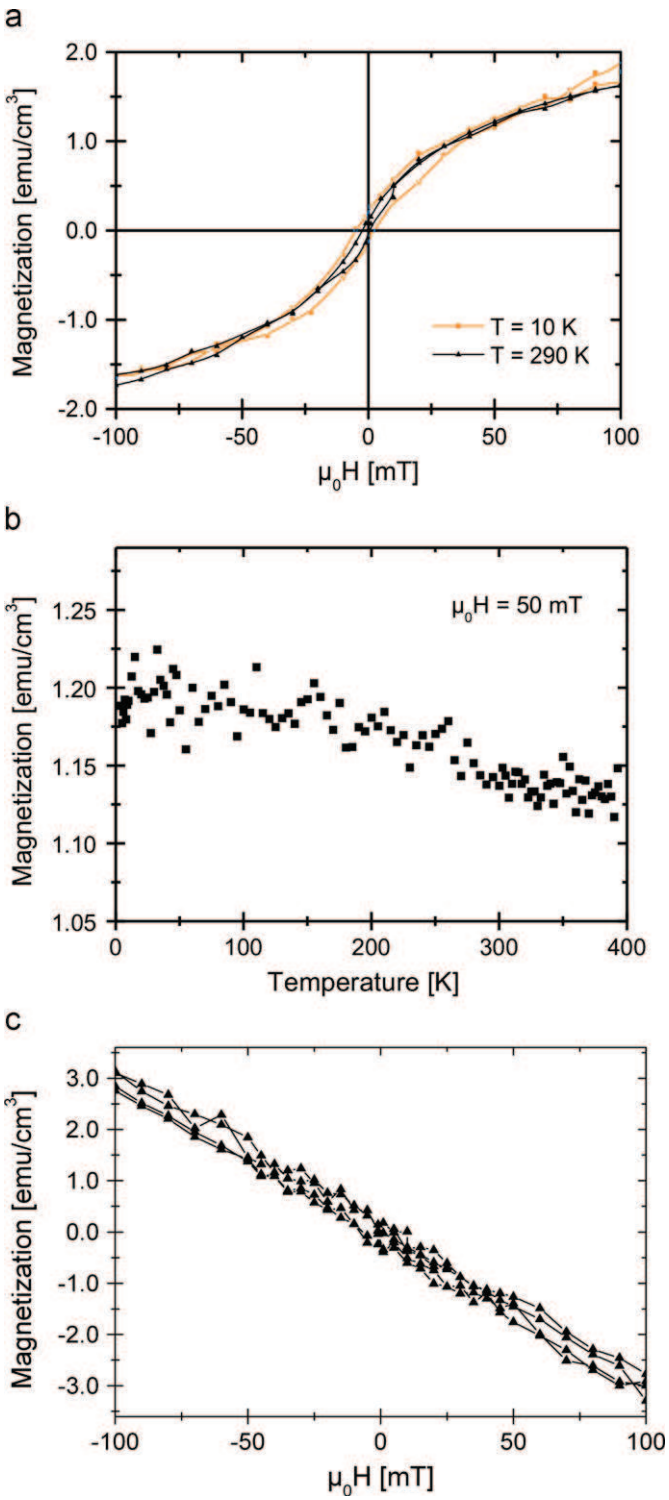

Fig. 5. (a) M–H curve for 1.2% nominal Cu-doped GaN at room-temperature. A small hysteresis loop is visible. The temperature dependence of magnetization for this sample is given in (b). Even at a temperature of 400 K the decrease in magnetization is lower than 10% compared to the magnetization at 10 K. No ferromagnetic behavior was found for Cu-doped AlN. Only diamagnetic behavior was detected (c).

4. Conclusions

Our experimental results show that Cu-doped GaN and AlN can be easily grown by molecular beam epitaxy. The Cu supply has no influence on the crystal properties of GaN and AlN, although Cu is incorporated in the film. Islands consisting of Cu and Ga or Al are formed on the surface. After etching the samples for 5 min with HNO_3, 90% of the islands are removed. Because of the intermetallic character of the islands, in addition to the fact that Cu is being an intrinsic non-magnetic material, the islands have no influence on magnetic properties in contrast to Mn- or Gd-doped nitrides. Diamagnetism is found for Cu-doped AlN in all our samples with a nominal Cu doping from 1.0% to 4.0%. In contrast, Cu-doped GaN shows a clear ferromagnetic behavior even at 400 K. Therefore, Cu-doped GaN is a promising candidate for a nitride based spin-aligner.

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