Enhanced magnetization in erbium doped GaN thin films due to strain induced electric fields

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The ferromagnetic properties of erbium-doped GaN (GaN:Er) epilayers grown by metal-organic chemical vapor deposition were studied. It is found that the different tensile strains produced by the respective lattice mismatch for different substrates used (GaN/Al2O3, AlN/Al2O3, GaN/Si (111), and c-GaN bulk) correlate well with the observed room-temperature saturation magnetization. Under application of a magnetic field, the photoluminescence of the erbium dopant, which causes the ferromagnetism, indicates that the magnetic states of the ions are coupled to the electronic states of the host. These results hold promise for the use of strain to control the magnetic properties of GaN:Er films for spintronic applications. © *2011 American Institute of Physics*. [doi:10.1063/1.3643041]

In order for spintronics to become a practical technology, dilute magnetic semiconductors (DMSs) with room temperature (RT) ferromagnetic (FM) behavior must be developed. Motivated by the theoretical predictions by Dietl *et al.*,[1] III-nitride semiconductors doped with Mn and other transition metals have been widely investigated.[2] While such materials exhibit FM properties and electrical control at RT has been reported,[3] the saturation magnetization (M_S) and the related effective magnetic moment per dopant ion (μ_{eff}) have not reached predicted values. Recent research has also focused on III-nitride semiconductors doped with rare earth (RE) elements.[4] In particular, GaN thin films doped with Gd have been reported to exhibit FM behavior at RT with colossal Ms values.[5] Investigations of GaN thin films doped with other RE elements such as erbium (Er) have also led to FM behavior but with much smaller M_S values.[6] The origin of these magnetic properties is not well understood and especially the role of defects in the thin film is under study.[7,8] Typically, when the RE ion resides in the GaN host, it exists in the trivalent (3+) charge state and intra 4*f* atomic transitions of the RE^{3+} ions lead to optical emissions in spectral regions from ultraviolet to visible to infrared.[9] While different methods have been employed to incorporate Er into GaN thin films, metal-organic chemical vapor deposition (MOCVD) appears to be the most effective in producing high quality samples[10] with a dominant incorporation site.[11–13] Previously, we reported that the MOCVD growth of GaN:Er epilayers on different substrates leads to different photoluminescence (PL) results.[14] The PL intensity was directly correlated with the residual tensile strain due to the lattice mismatch between the GaN:Er film and the particular substrate. Here, we extend that study to report on the effects of strain on the measured FM properties of GaN:Er films. The magnetic data are in close agreement with the PL results and indicate that the strain may be an important factor in optimizing FM properties of RE doped III-N semiconductors.

The GaN:Er epilayers under investigation were grown on GaN/Al_2O_3, AlN/Al_2O_3, GaN/Si (111), and c-GaN bulk substrates using MOCVD and their PL characteristics, crystalline quality, and surface morphology were previously measured.[14] For all templates and substrates, we started out with depositing a thin GaN layer which is then followed by a GaN:Er epilayer with a thickness of ~1 μm. The growth temperature was 1040 °C and the Er concentration was $\sim 6 \times 10^{19}$ cm^{-3}. From θ-2θ x-ray diffraction (XRD) measurements, the biaxial stress parameter δ was estimated for each film. The values of δ are 1.7, 0.7, 0.5, and 0 GPa, for GaN:Er epilayers grown on AlN/Al_2O_3, GaN/Al_2O_3, GaN/Si (111), and c-bulk GaN templates, respectively. The XRD and previous PL data obtained on the same samples[14] indicate that luminescence from GaN:Er epilayers is clearly dependent upon the strain present in the films.

In the current experiments, the magnetic properties of these GaN:Er epilayers were examined using an alternating gradient magnetometer (AGM) and resonant PL spectroscopy combined with an applied magnetic field. The AGM measurements were made at RT with the magnetic field applied both normal to the sample surface as well as parallel to the sample surface. The diamagnetic properties of the substrate and holder were subtracted out and the data normalized to sample volume. Results of these measurements for each GaN:Er sample are presented in Fig. 1. The in-plane hysteretic data, Fig. 1(a), show that the GaN:Er sample grown on the GaN/Al_2O_3 template had the highest saturation magnetization M_S value. This was followed by the sample grown on the GaN/Si (111). The other films displayed either weak or paramagnetic behavior. The out-of-plane hysteretic data, Fig. 1(b), were similar with the M_S value being highest for the GaN:Er layer grown

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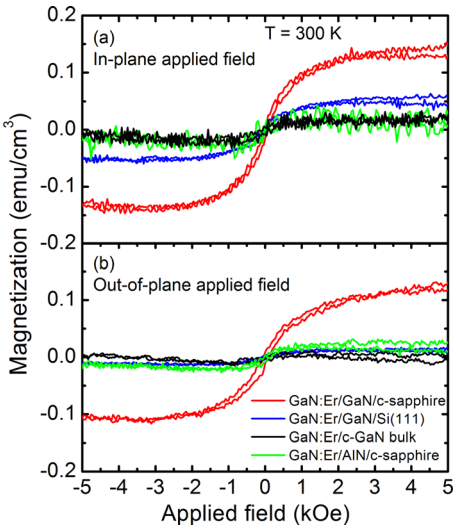

FIG. 1. (Color online) Results of AGM measurements made at RT for GaN:Er epilayers grown on different templates: (a) in-plane hysteretic data and (b) out-of-plane hysteretic data. In either orientation, the saturation magnetization M_S was highest for the GaN:Er sample grown on the GaN/Al_2O_3 template, leading to estimates for the effective magnetic moment of $\mu_{eff} \sim 0.22\ \mu_B$.

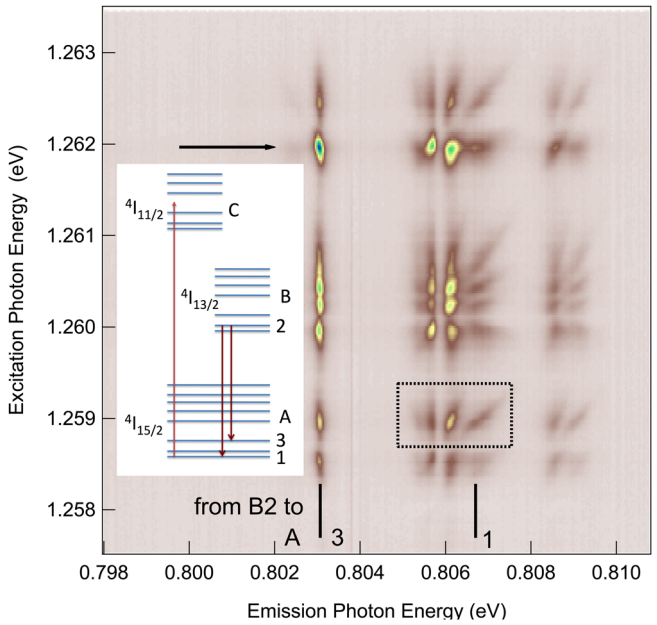

FIG. 2. (Color online) CEES of GaN on sapphire *in-situ* doped with Er. The inset shows a schematic of the excitation and emission transitions. The dotted area indicates the region that is shown in more detail in Fig. 3. The transitions from the levels B2 to A1 and A3 are indicated by vertical lines. The excitation for which the fluorescence line narrowing is small is indicated by a horizontal arrow. This excitation is used for data shown in Fig. 3.

on the GaN/Al_2O_3 template and negligible for the other samples. From the GaN:Er material volume involved in these measurements, an estimate of the effective magnetic moment for the two orientations can be obtained. For the GaN:Er sample grown on the GaN/Al_2O_3 template, the in-plane μ_{eff} was $\sim$0.24 μ_B and the out-of-plane $\mu_{eff} \sim 0.22\ \mu_B$, where μ_B is the Bohr magneton, indicating $\sim$7.2% magnetic activation of Er atoms. Data for the GaN:Er layer grown on the AlN/Al_2O_3 template indicate only weak hysteretic behavior. While the biaxial stress was greatest in this sample, disorder as indicated by the broad XRD spectrum was also very large and may have inhibited magnetic ordering.

The fact that the magnetic properties are induced by rare earth ions coupled to the GaN host offers the unique possibility to relate the spectroscopic properties of the ions, which reflect their local environment, with the magnetic hysteresis data. To this end, we use combined excitation emission spectroscopy (CEES) which has been proven to be a powerful tool to identify the different incorporation sites and the variation of their environment.[12] This is shown in Fig. 2 for a GaN:Er sample grown on the GaN/Al_2O_3 template. The CEES data were obtained at T = 4 K using liquid He-flow cryostat by scanning a 980 nm external cavity laser in the spectral region of the $^4I_{15/2}$–$^4I_{11/2}$ transition and record the resulting emission around 1.5 μm corresponding to the transition between the $^4I_{13/2}$–$^4I_{15/2}$ state. The resulting 2D-data set is depicted as an image plot. Despite the multitude of transition peaks in our measurements, all transitions can be accounted for by taking thermally excited states into consideration.[12,13] The corresponding level scheme is shown as an inset of Fig. 2. There is clear evidence of fluorescence line narrowing (FLN), which is reflected in excitation/emission features that are tilted in our CEES image (e.g., the right most feature within the dotted square in Fig. 2). The differences in spectra that are manifested that way are most likely related to modifications of the intrinsic strain fields across the sample. For our work here, we use the distance between the emission transitions from levels B2 to A1 and B2 to A3, as a measure for this strain.[12] In Fig. 3(a), we compare a small region of our CEES data for two samples grown on different substrates. The image plot represents a zoomed representation of the same data as in Fig. 2 for the sample grown on the GaN/Al_2O_3 template, while the contour lines indicate the data for a sample grown on bulk c-GaN. We clearly see how different the spectral features are both in position as

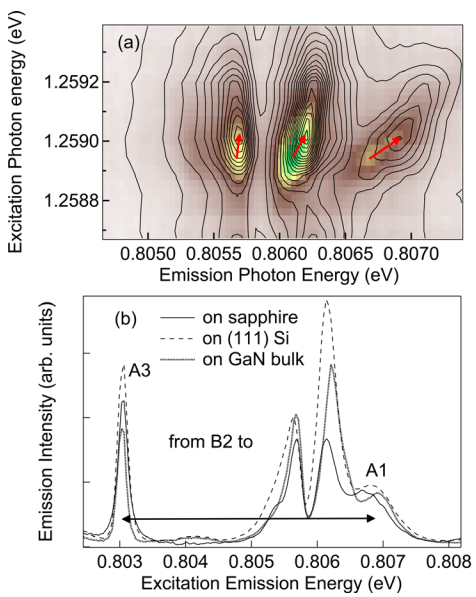

FIG. 3. (Color online) (a) Excerpt of CEES for samples grown on sapphire (image) and on bulk GaN (black contour lines) for an area that shows pronounced fluorescence line narrowing. Arrows indicate the shifts of the maxima of the respective lines between samples. (b) Emission spectra taken for layers grown on three different substrates excited at a transition for which little fluorescence line narrowing occurs (see arrow in Fig. 2). The arrow indicates the splitting between the A1 and A3 levels, which characterizes the strain.

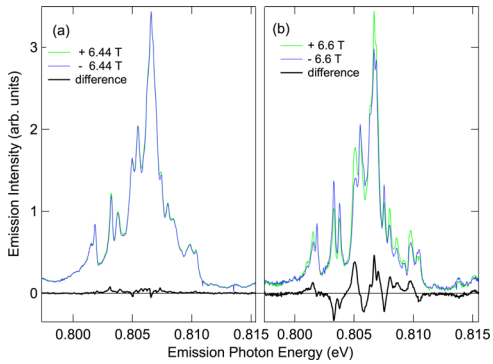

FIG. 4. (Color online) Emission spectra of Er ions in GaN under the application of a magnetic field parallel and anti-parallel to the growth axis of the layer grown on (a) GaN bulk and (b) sapphire excited at the spectral position indicated in Fig. 2. Emission difference spectra clearly demonstrate the changes brought about by the residual strain in the layer grown on sapphire.

well as the extent of the features. In particular, the tilted feature is shifted from one sample to another indicating the same incorporation site but with different strain environments for the two samples. Arrows indicate the shifts of the maxima. This finding becomes even more apparent if we take spectra for an excitation transition that has no FLN, which leads to wider emission lines that reflect the average splitting of A1 and A3 in their emission maxima. In Fig. 3(b), we compare three samples grown on GaN/Al_2O_3 template, GaN/Si (111) template, and on bulk c-GaN. While the peaks for the transition between the levels B2 and A3 are almost identical, the transition to A1 is shifted dramatically giving rise to a sample dependent splitting of the A1 and A3 levels (indicated by an arrow in Fig. 3(b)), which is correlated to different average strain fields. It should be noted that the values of these shifts vary in a similar way as the magnetization shown in Fig. 1.

Moving to our spectroscopic studies under the application of magnetic fields up to 6.6 T obtained in a Janis magnet cryostat. Fields were applied parallel and antiparallel to the growth direction of the doped c-GaN layer. In Fig. 4(a), we show the emission spectra for a sample grown on c-GaN. It shows a rather complicated splitting compared to the zero-field spectrum in Fig. 3. The splitting and the relative strength of the peaks are independent of the direction of the magnetic field. This generally expected behavior is changed dramatically for the sample grown on sapphire, see Fig. 4(b). In this case, the relative strength of the transitions is quite different for the two anti-parallel field directions, while the splitting still remains independent of the direction. Apparently, in this sample, the magnetic states of the Er ion are dependent on the growth direction. Such coupling between growth direction and magnetic field states can be provided by the electric polarization that is induced by the lattice mismatch through the piezoelectric effect. The resulting strain induced electric fields are drastically different when a layer is grown on c-GaN or on a GaN/Al_2O_3 template. The electric field breaks the symmetry, which is then reflected in the dependence of transitions strength on the field direction. This clearly demonstrates a coupling of the Er^{3+}-states to the host. The changes in relative transition strength are most pronounced for transitions that are also shifted most significantly for different strain environments.

The results of these experiments provide strong evidence that FM behavior of GaN:Er epilayers grown by MOCVD is directly proportional to the stress in the thin films induced by lattice mismatch with the substrate. Hysteretic data from such films are in general agreement with optical emission intensity taken in PL measurements and with the strain-induced spectral shifts found in our CEES measurements. In addition, PL spectra taken in the presence of an applied magnetic field indicate the magnetic states of the Er ion are coupled to the electronic states of the host. The strongest effect is observed for states that are also most sensitive to strain. This correlation suggests that the coupling of the magnetic states to the host can be modified by strain. While these results apply to stress produced through lattice mismatch, strain may be introduced through other means (e.g., applied electric fields) leading to eventual active control of ferromagnetism. The presented data and the apparent coupling of strain and magnetic properties may set the foundation for understanding the origin of PL and ferromagnetism not only for Er-doped GaN, but also for other RE doped III-N semiconductor films. Finally, we should mention that our results demonstrate the coupling between the strain-induced electrical polarization and the RE-ion induced magnetization and, hence, resemble the coupling phenomena observed in multiferroics.[15]

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