Incorporating Spin Functionality in Non-Polar Optoelectronic Devices

The important role played by Mn valence states in deciding the magnetic properties of non-polar nitrides which was lacking in previous reports related to other transition metal or rare-earth doped non-polar III-nitrides.

Enabling spin polarized current in compound semiconductors would aid in the development of hybrid devices, where logics, communications, and information storages are synergized on a single device. Diluted ferromagnetic semiconductors (DMSs) have been studied for the last 30 years. The applications of such DMSs in optoelectronic devices would generate left or right circularly polarized light which is needed for encrypted communication systems. Gallium nitride (GaN) based optoelectronic devices have achieved great success in the last decade in solid state lighting, but the next challenge for these semiconductors is to develop a spin light emitting diode (LED) or a spin laser. One way suggests that coating with metal oxide nanoparticles could help in creating circularly polarized light. Another alternative way is to design ferromagnetic spin filters which could then be incorporated into existing LED manufacturing technology. Room temperature ferromagnetism has been observed in these semiconductors. This coupled with the strong spin life time could enable the injection of spin polarized carriers into III-nitride based spintronics LEDs by designing appropriate spin filters or spin aligners. Also it would be advantageous if one could incorporate spin filters or spin aligners into such non-polar LEDs to emit circularly polarized light. This would necessitate the development of non-polar diluted magnetic semiconductors.

Typically inducing ferromagnetism in GaN involves doping with transition metal (TM) or rare earth (RE) elements. In most cases, manganese (Mn) is the most preferred dopant. However, based on the valence state of Mn in GaN, one can get ferromagnetic ordering for Mn^{+3} or antiferromagnetic ordering for Mn^{+2}. Thus controlling the valence state of Mn is critical.

To ascertain whether nonpolar nitrides can be transformed into a DMS, Li-Wei Tu (National Sun Yat-sen University) and Cheng-Maw Cheng (NSRRC) studied the physical properties of epitaxial thin films grown by plasma-assisted molecular beam epitaxy (PAMBE), which is a very well established method for the growth of high-quality GaN:Mn thin films and nanostructures.[1] Holistic approach was taken to understand the structural, chemical, magnetic, and transport properties of m-plane GaN:Mn thin films grown on m-plane (100) Al_2O_3 substrates by PAMBE. With high resolution X-ray photoemission spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) conducted at **TLS 08B1** and **TLS 20A1**, the authors found that the Mn doping level governed by the growth temperature was a key role in creating nonpolar DMS. Two growth temperatures were studied. Samples grown at low temperatures (LT) show high Mn content but the Mn is in mixed valence states leading to antiferromagnetic ordering. A high temperature growth (HT), on the other hand, reduces the Mn doping level but leads to homogeneous Mn valence state showing room temperature ferromagnetism.

To identify the valence of Mn doping, the Mn 2*p* core levels for both HT and LT samples were studied by XPS. In HT samples, only two peaks for Mn $2p_{3/2}$ and Mn $2p_{1/2}$ were observed at 641.63 and 657.18 eV, suggesting that the only valence is Mn^{+3} in HT samples. In contrast, in the LT samples, four peaks were observed, two peaks located at 638.52 and 649.35 eV could be attributed to Mn^{+0} valence state, while the remaining two located at 640.95 and 654.05 eV originated from Mn^{+2} valence state. For further confirmation of Mn valence state, X-ray absorption near edge spectra (XANES) were carried out for HT, LT, undoped GaN and standard MnO samples. For the Ga L-edge, there is hardly any change in the line shape implying that the Ga has the same crystal structure for all the three samples. For the N K-edge, the HT and undoped samples show similar features but LT sample show some shoulder peaks as marked by arrows, indicating that the local structure near the nitrogen has changed. Author also compared the Mn L-edge in LT and HT samples to a standard MnO sample. As seen in **Fig. 1(c)**, the Mn L-edge for LT sample matches the MnO signal indicating that the Mn^{+2} is present inside the film. This complements the XPS data indicating that Mn^{+2} is present through the bulk and the surface of LT and HT samples. However, the lack of Mn^{+0} in XANES but the presence in XPS indicates that the surface of LT sample has MnGa alloys precipitates. For HT sample, the signal intensity is very low due to the low doping. The peak position is close to

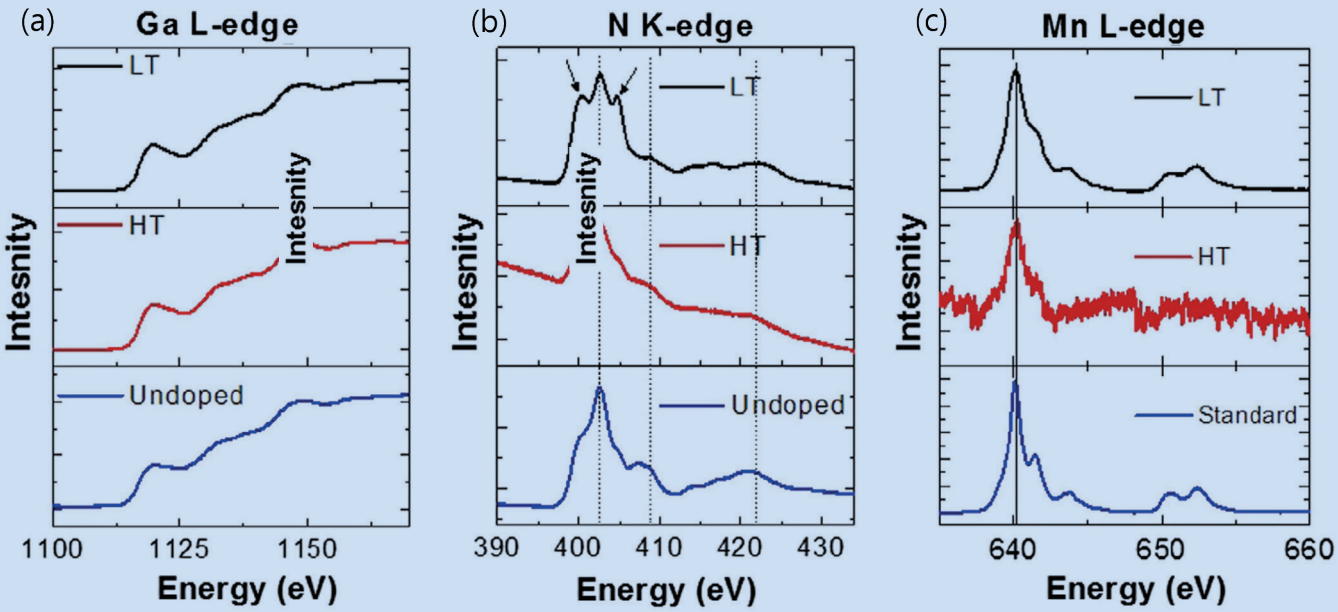

Fig. 1: (a)–(c) XANES for the Ga, N, and Mn regions. [Reproduced from Ref. 1]

the standard sample, yet the overall shape is not the same suggesting this peak to be slightly different from Mn^{+2}. Comparing the result of magnetization for both HT and LT samples, HT samples from the MBE growth method shows that magnetizations in samples are an order of magnitude higher. In LT sample, it has a much wider hysteresis. As mentioned the wider hysteresis would indicate a hard ferromagnetic material, but the moment is two orders of magnitude lower than that of HT sample suggesting it is from the secondary phase. The origin of this small moment could be due to the small uncompensated ferromagnetic phase which is typically present in the MnGa alloy, as observed from XPS result.

In summary, Tu *et al*., demonstrated room temperature ferromagnetism in nonpolar, m-plane manganese doped gallium nitride (m-GaN:Mn) epitaxial thin films. These were synthesized using plasma-assisted molecular beam epitaxy on nonpolar, m-plane sapphire (Al_2O_3) substrates. Tu points out that the doping level of Mn plays a key role in stabilizing the valence state of Mn ions thereby influencing the magnetic and transport properties. Chemical characterization by XPS and XAS affirms homogeneous valence state Mn^{+3} in lightly doped samples, while higher doping levels cause a heterogeneous Mn^{+0} and Mn^{+2} mixed valence states. Magnetic measurements indicate that films with low doping levels show the signature of room temperature ferromagnetism, while films with higher doping show antiferromagnetic/spin glass behavior besides the presence of MnGa alloys. The findings suggest the possibility of incorporating spin functionality in non-polar optoelectronic devices. The impact of this work highlights the important role played by Mn valence states in deciding the magnetic properties of non-polar nitrides which was lacking in previous reports related to other transition metal (TM) or rare-earth (RE) doped non-polar III-nitrides. (Reported by Cheng-Maw Cheng).

This report features the work of Li-Wei Tu and his collaborators published in Appl. Surf. Sci. ***473****, 693 (2019).*

TLS 08B1 BM – AGM
TLS 20A1 BM – (H-SGM) XAS
- *X-ray Absorption Spectroscopy*
- *Materials Science, Condensed-matter Physics*

Reference

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