CHAPTER 3
INVESTIGATIONS ON COBALT AND CARBON CODOPED GALLIUM NITRIDE

3.1 INTRODUCTION

The dilute magnetic semiconductors (DMSs) provide both ferromagnetic and semiconducting properties and are unique type of promising materials in the emerging field of spintronics. The III–V (GaAs, GaN, etc.) and II–VI (ZnTe, ZnO, etc.) compound semiconductors when doped with transition metal have attracted considerable attention in spintronic applications (Cui et al 2006, Kronik et al 2002, Ogawa et al 1999, Weng et al 2006). Among the III-nitride semiconductors, GaN with wide band gap energy of 3.39 eV is one among the most promising material for information processing with short wavelength optics (Kudrnovsky et al 2004). Therefore, detailed investigations on the ferromagnetism of GaN based DMSs is of great importance. GaN doped with Mn or Cr shows ferromagnetism with high Curie temperature and their band structures are much more suitable for spin injection than those of TM-doped GaAs (Wang et al 2005). Ferromagnetism is predicted in Cu doped GaN using DFT calculations with a transition temperature $T_c$ of 350K without forming any precipitate (Wu et al 2006). The stable configurations of Cr dimer and nitrogen vacancy in GaN shows ferromagnetism driven by double exchange mechanism (Li et al 2010, Wu et al 2003). DFT calculations support the Mn/C-codoping in the GaN matrix which is energetically favorable and the C-codoping strongly enhances the
preference of the ferromagnetism coupling over the anti-ferromagnetism coupling between the two doped Mn sites. Experimentally synthesized Mn/C-codoped GaN shows that carbon doping favors the N sites over the Ga sites (Wang et al 2008). The ferromagnetism in carbon doped GaN is due to spin-orbital overlapping of C2p with Ga 3d orbital and second nearest neighbor nitrogen p orbital (Yu et al 2010). Mn dimer in GaN with one of the Mn at interstitial site is energetically favorable with antiferromagnetic behavior showing 3.7 $\mu_B$ per supercell of 32 atoms (Liu et al 2007). In case of GaN thin film, Mn dimer couples antiferromagneticity, but as the concentration of codopant carbon atom increases, the orbital coupling becomes ferromagnetic and this may be due to hole carrier introduced by C (Wang et al 2007). We have shown from DFT calculations and experimental results that lower percentage of Co in GaN is suitable for spintronic applications (Munawar Basha et al 2011). There are only very few literature on Co dimer doped GaN (Hong and Wu 2003) and there is no report on carbon codoped with Co in GaN. Detailed theoretical calculations have been carried out to evaluate the electronic and magnetic properties based on Tight Binding Linear Muffin-tin Orbital (TB-LMTO) method within density functional theory of cobalt dimer in GaN and on the effect of Co dimer via carbon in GaN. In addition, synthesis of Co and C codoped GaN is carried out and extensively studied for their structural optical and magnetic properties. The theoretical and experimental results have been correlated and presented.

3.2 METHODS OF CALCULATION

Theoretical calculations based on the density functional theory are performed by means of TB-LMTO method. The local density approximation (LDA) parameterized by Barth and Hedin was used for the exchange and correlation potential. GaN crystallize in the wurtzite structure with lattice
constants \( a = 3.188 \text{ Å} \) and \( c = 5.189 \text{ Å} \) (Lagerstedt and Monemar 1979). A supercell containing 72 host atoms in wurtzite structure of GaN has been employed. The dopant site of substitutional Co dimer and carbon is indicated in Figure 3.1. Spin polarized scalar relativistic calculations are performed to obtain the total energy, density of states (DOS) and magnetic moment. 144 K points in the irreducible part of the Brillouin Zone was used to calculate the total density of states by means of tetrahedron method (Stokes et al 1987).

3.3 EXPERIMENT

Pure Gallium (5N) and cobalt metal along with graphite powder was taken in an alumina boat and kept inside the horizontal quartz tube (Senthil Kumar and Kumar 2002). The experimental details are as described in the previous chapter. Nitrogen gas is allowed to flow from the beginning of the experiment. Upon attaining the growth temperature (\( \sim 1223 \text{ K} \)) ammonia gas is allowed to flow for 8 hours and then the system is slowly cooled to room temperature under the flow of nitrogen. The synthesized sample is etched with hydrofluoric acid and nitric acid in order to remove the un-reacted metal, the final product is dried and then pulverized to a fine powder. Structural investigations have been carried out using XRD (D8 Brucker AXS) and Transmission Electron Microscope (TEM) studies. Micro-Raman analysis (LabRam HR 800) is carried out to study the vibrational properties of the samples. Magnetic properties of the samples have been carried out using superconductor quantum interface device (SQUID) measurements.

3.4 RESULTS AND DISCUSSIONS

3.4.1 Electronic and magnetic properties of Cobalt and Carbon co-doped GaN

It has been reported earlier that for thermodynamically stable system, the transition metal atom prefers the substitution site rather than the
interstitial site in the host GaN (Sanyal and Mirbt 2005). Here we studied the Co and C in GaN system for CoGa$_{35}$N$_{36}$, (CoGa$_{35}$N$_{35}$C), Co dimer in GaN (Co$_2$Ga$_{34}$N$_{36}$) and Co dimer via carbon in GaN (Co$_2$Ga$_{34}$N$_{35}$C) have been investigated.

![Diagram of Co dimer in GaN](image)

**Figure 3.1** Schematic diagram of Co dimer in GaN (A) via Carbon (B) via Nitrogen

A single Co replacing Ga corresponds to a cobalt concentration of 2.77 % in GaN. The system shows a magnetic moment of 4.0 $\mu_B$. Most of moment comes from Co atom. The nearest nitrogen and gallium atom also induced small amount of moment. The density of state (DOS) plot in Figure 3.2 show that 3d orbital of Co appears at the highest occupied level in case of majority spin and there is no dopant energy level above the fermi level and hence it shows the half metallic character. For the minority spin there is an energy level which arises due to the Co dopant at Fermi level and it is metallic. The 3d electron of Co coupled with 2p electron of nearest nitrogen
atom forms the tetrahedral bonding. The remaining excess 3d electron gives rise to spin polarization in the system.

Carbon in the same supercell has been introduced by removing one nitrogen atom such that it forms a bond with Co. Co in tetrahedral bonding with surrounding nitrogen atom, gives the possibility of Co-C bonds with smaller and larger distances.

![DOS plot for 2.7 % Co doped GaN](image)

**Figure 3.2 DOS plot for 2.7 % Co doped GaN**

For both the cases, the system is ferromagnetic but total magnetic moment is drastically reduced to 1.00 $\mu_B$ with Co inducing 0.77 $\mu_B$, while C induces -0.03 $\mu_B$ for smaller distance and 0.02 $\mu_B$ for larger distance. The DOS plot in Figure 3.3 shows clearly the 3d band of Co is at the $E_F$ in spin up state giving rise to metallic character and is half metallic for spin down case.
Figure 3.3  DOS plot of 2.7 % Co and C codoped GaN with Co-C smaller bond distance

Next two Ga atoms have been replaced by Co atoms which correspond to 5.5 % Co concentration in GaN system to form a dimer via nitrogen atom such that the distance with two cobalt is same and is shown in Figure 3.1. The calculated spin-polarized density of states is shown in Figure 3.4A. The total magnetic moment is 3.99 $\mu_B$ per supercell. Here the moment contribution from each Co is 1.46 $\mu_B$. The remaining moment come from the nearest neighbors Ga and N atoms. The system is ferromagnetic with half metallic character. The occupied 3d states of the Co-Co dimer hybridize with the top of the valence band, whereas the unoccupied 3d orbital, mix with the bottom of the conduction band. The presence of Co further splits the spin-up 3d band of Co into two separated states namely occupied states at the Fermi level and empty states far above the Fermi level. The spin-down splitting shows that the occupied state is well below the Fermi level. The d-d orbital of cobalt atoms overlap via nitrogen atom which indicates that the double
exchange interaction mechanism is responsible for the observed ferromagnetism in the system.

When two cobalt in GaN forms a dimer with one at smaller distance (1.946 Å) with nitrogen compared to the other at 1.952 Å, the system shows an overall magnetic moment of 4 \( \mu_B \). The Co-N with smaller distance induces a magnetic moment of 1.58 \( \mu_B \). The other with larger distance have a magnetic moment of 1.34 \( \mu_B \). The nitrogen atom which forms a dimer with Co shows a moment of 0.053 \( \mu_B \). From DOS plot shown in Figure 3.4B for majority spin it is clear that the impurity band is well above the Fermi level with filled valence band and is metallic.

\[ \text{Figure 3.4 DOS plot for 5.5 \% Co doped GaN forming Co dimer via N} \]

(A) equal Co-N distance (B) unequal Co-N distance

In case of minority spin there is empty level at the top of the valence band and a well defined gap is observed at Fermi level indicating insulator behavior. Hence the system is half metallic with ferromagnetism. It is therefore, concluded that for cobalt dimer with both equal and unequal
distance the system is half metallic and ferromagnetic, only the induced magnetic moment by each cobalt atoms is different. The total magnetic moment per supercell is not reduced significantly as the Co concentration increases. For 2.7% concentration of Co doped GaN (monomer), the contributions to the total magnetic moment also come from the neighboring N and Ga atoms, whose magnetic moments are parallel to that of Co$_{Ga}$. For 5.5% Co doped GaN (dimer), the effective magnetic moment per Co atom is reduced. This may be due to the contribution from antiferromagnetism coupling between Co dimer. Hence the net magnetic moment of a Co dimer is close to that induced by a Co$_{Ga}$ monomer alone.

Next a cobalt dimer is formed via carbon giving rise to Co concentration of 5.5% and carbon of 2.7%, keeping the distance between carbon and two cobalt atoms as to be the same. The system shows metallic character and ferromagnetic with magnetic moment of 2.95 $\mu_B$, each cobalt induces a magnetic moment of 1.09 $\mu_B$ and carbon with -0.11 $\mu_B$. From DOS plot in Figure 3.5 (A) it is clearly observed that the bands of Co and C are lying at the Fermi level and overlaps with the bottom of conduction band in both the spin state. The two Co atoms forming a dimer are too far apart (3.027Å) to allow significant direct overlap of the unpaired electron wave functions, thus instead of a substantial direct exchange mechanism, it is possible to have a Co-Co indirect exchange interaction mediated by the C atom.

This can be confirmed by the magnetic moment of -0.11 $\mu_B$ for the mediated C atom. Partial density of state (PDOS) plot in Figure 3.5 (B) shows the overlap of Co 3d and C 2p states at $E_F$ in the majority spin state.
Figure 3.5(A) DOS plot for 5.5 % Co and 2.7 % C doped GaN forming Co dimer via C with equal Co-N distance

Figure 3.5(B) PDOS plot for 5.5 % Co and C doped GaN forming Co dimer via C with same distance (i) for Co-3d (ii) C-2p state
There is no overlap of C 2p with Co 3d state in minority spin. For Co dimer via carbon with non equivalent Co-C distance, the induced magnetic moment is 3 $\mu_B$. The Co magnetic moment is 0.98 $\mu_B$ for the smaller Co-C distance (1.949Å) whereas it is 1.22 $\mu_B$ for larger Co-C distance (1.964Å). The system is ferromagnetic with semiconductor character. The carbon plays an important role in changing the electrical properties which depends upon their bonding with Co dimer. There is only change in the magnitude of magnetic moment in the system for dimer forming via Nitrogen or carbon, but for all the cases the system is ferromagnetic. Thus Co codoped GaN with C is a suitable candidate for spintronic application with control over their electrical and as well as their magnetic properties.

3.5 CHARACTERISATION OF COBALT AND CARBON CODOPED GaN

3.5.1 X-ray Diffraction Analysis

Experiments have been carried out to study the effect of Co and C in GaN. Figure 3.6 shows the X-ray diffraction pattern of synthesized 2.7 % Co doped GaN, 2.7 % Co and 2.7 % C codoped GaN and 5.5 % Co and 2.7 % C codoped GaN powder samples recorded using D8 Brucker AXS X-ray diffractometer with Cu K$_\alpha$ source. The observed XRD pattern confirmed that doped GaN crystallize in the wurtzite structure. There is no secondary phase formation on doping with Co and C. The sharp intensity peaks indicate the well crystallised nature of the synthesized powder.
Figure 3.6 XRD for (A) 2.7 % Co doped GaN (B) 2.7 % Co and 2.7 % C doped GaN (C) 5.5 % Co and 2.7 % C doped GaN

3.5.2 Transmission Electron Microscope

Transmission electron microscope (TEM) uses a high energy electron beam which transmits through a very thin sample to image and analyze the microstructure of test materials with atomic scale resolution. The systematic representation of TEM is shown in Figure 3.7. The electrons are focused with electromagnetic lenses and the image is observed on a fluorescent screen and stored in digital storage systems. The electrons are accelerated at 200kV electrons to have a wavelength of 0.025Å. The resolution of the optical microscope is limited by the wavelength of light and that of the electron microscope is limited by aberrations inherent in
electromagnetic lenses to about 1-2 Å. The transmission electron microscope is used to characterize the microstructure of materials with very high spatial resolution. Information about the morphology, crystal structure and defects, crystal phases, composition and magnetic microstructure can be obtained by a combination of electron-optical imaging.

Figure 3.7  Schematic diagram of transmission electron microscopy assembly

Figure 3.8 represents the Transmission electron microscope (TEM) images with corresponding diffraction pattern of Co and Co codoped with C in GaN. The image A reveals the well dispersed nature of Co in GaN with diffraction ring (Das and Pal 2007) from (100) and (110) plane of h-GaN phase indicating there is no phase change.
There is a Co cluster formation for 5.5 % Co doped GaN as observed from the diffraction pattern, whereas no other phase is present in Co codoped with C in GaN as confirmed from TEM images along with well formed diffraction pattern of wurtzite GaN. This reveals that dopant is incorporated in the GaN lattice. Also Co does not act as a catalyst for any nanostructure growth through VLS mechanism.
3.5.3  Micro Raman Spectroscopy

Micro-Raman spectroscopy is based on the inelastic scattering of photons from a surface being irradiated by monochromatic light, which provides information on the spatial distribution of physical properties of semiconductors that are sensitive to crystalline quality, microstructure, strain, alloy composition and free carrier density. Only photons from a narrow spectral domain are sent to the Charge Coupled Detector mosaic and each pixel receives those coming from a given area of the sample. The laser source is often built-in, but light coming from an external excitation source can also be used. In the “macro”-configuration, the beam section is ~1mm² but the laser spot can be reduced to ~1 µm in diameter by using the high-magnification microscope objectives.

![Figure 3.9 Micro Raman spectra of Co, Co and C codoped GaN](image)

Figure 3.9 Micro Raman spectra of Co, Co and C codoped GaN
The intensity of the signal thus reveals the presence and location of any substances with a strong Raman signal in the selected spectral window (Bergman and Robert 1996, Gouadec and Colomban 2007).

Figure 3.9 shows the micro Raman spectra of Co and C doped GaN. The well defined E\(_2\) (high) mode which mainly relates to stress in the system is observed at 567 cm\(^{-1}\) for 2.7 % Co doped GaN. For pure GaN it is generally observed at 568 cm\(^{-1}\). The shift to lower value indicate that a stress is created in the lattice, this is due to the fact the small ionic radii difference between Co and the host Ga atom causes the shift in E\(_2\) (high) peak. A\(_1\) (TO) and A\(_1\) (LO) peaks have also been observed. The peak at 416 cm\(^{-1}\) is related to acoustic overtone. For Co and C codoped GaN samples E\(_2\) (high) peaks shift to still lower value indicating that more stress is developed as the doping percentage increases. Raman peaks between 620 to 650 cm\(^{-1}\) may arise due to a defect that arises during synthesis. We did not observe local vibrational modes (LVM) (Gao et al 2009) which arises due to isolated transitional metal in GaN. This clearly indicates that there is no agglomeration of transition metal atom in GaN. The doped Co atom accurately occupies the host Ga site.

### 3.5.4 Magnetic Studies using SQUID

SQUID magnetometer uses the properties of electron-pair wave coherence and Josephson junctions to detect very small magnetic fields with resolutions up to \(\sim 10^{-14}\) kG or greater. The central element of a SQUID is a ring of superconducting material with one or more weak links called Josephson’s junctions and is discussed in last chapter.

Figure 3.10 shows the magnetization curve of 2.7 % Co doped GaN, 5.5 % Co and 2.7 % C codoped GaN and 2.7% Co and C codoped GaN as a function of magnetic field at 10K. The plot clearly shows magnetic hysteresis. The magnitudes of measured magnetic moment per cobalt atom
are 2.06 $\mu_B$, 1.55 $\mu_B$ and 1.01 $\mu_B$ respectively. All samples exhibit well saturated M-H cure with finite coactivity.

![M-H loop measurement for 2.7% Co doped GaN, 2.7% Co and C codoped GaN and 5.5% Co and 2.7% C codoped GaN](image)

**Figure 3.10** M-H loop measurement for 2.7% Co doped GaN, 2.7% Co and C codoped GaN and 5.5% Co and 2.7% C codoped GaN

No lateral shift of hysteresis loop indicates the absence of spin glass behavior. These findings prove the strong presence of ferromagnetic ordering in the synthesized samples. The theoretical calculations of magnetic moment per Co for 2.7% Co doped GaN, 5.5% Co and 2.7% C codoped GaN and 2.7% Co and C codoped GaN atom are 2.57 $\mu_B$, 2.2 $\mu_B$ and 0.77 $\mu_B$ respectively. The difference in magnetic moment value may be due to the fact that the synthesized sample is poly-crystalline i.e, shorter lattice order. These parameters are not included during theoretical calculations. Table 3.1 shows
the experimental and theoretical values of magnetic moments which shows that both the results are in close agreement. Lesser percentage of Co in GaN is suitable for DMS based spintronic applications. Carbon plays a lesser role in magnetic moment, but it helps in avoiding metal agglomeration in the system.

Table 3.1 Theoretical and experimental magnetic moments values of Co atoms

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Concentrations</th>
<th>Magnetic moment ($\mu_B$)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TB-LMTO</td>
</tr>
<tr>
<td>CoGa$<em>{35}$N$</em>{36}$</td>
<td>Co=2.7 %</td>
<td>2.57</td>
</tr>
<tr>
<td>Co$<em>2$Ga$</em>{34}$N$_{35}$C</td>
<td>Co=5.5 % C =2.7 %</td>
<td>2.2</td>
</tr>
<tr>
<td>CoGa$<em>{35}$N$</em>{35}$C</td>
<td>C =2.7 %</td>
<td>0.77</td>
</tr>
</tbody>
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3.6 CONCLUSIONS

In this chapter we discuss about the observed ferromagnetism in 2.7 % cobalt doped GaN has been discussed as that, when one Gallium is replaced by cobalt in a 3x3x2 supercell the system is half metallic with a magnetic moment of 4.0 $\mu_B$. When Co is bonded with one carbon, the system becomes metallic with reduced magnetic moment. When Co dimer is introduced via nitrogen which corresponds to the Co concentration of 5.5 % the magnetic moment is 3.99 $\mu_B$ and the system is half metallic. When Co is bonded via nitrogen with unequal distance the system is still half metallic with a magnetic moment of 4.0 $\mu_B$. When Cobalt dimer is formed via carbon, the moment becomes 2.95 $\mu_B$ and it shows metallic character. For dimer via carbon with unequal distance, the moment is 3.0 $\mu_B$ and the system becomes semiconductor. For higher percentage of cobalt dopant the system shows
metallic character. C and Co doped GaN samples have been synthesized experimentally, XRD and TEM confirmed no secondary phase formation. Micro Raman spectra indicate there is no agglomeration of TM in GaN and the magnetic results are correlated with the theoretical studies. Thus lesser percentage of Co in GaN is necessary for use in DMS based spintronic application. Carbon plays lesser role in magnetic moment, but it helps in avoiding metal agglomeration in the system.