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Scanning Tunneling Microscopy Study of Cr-doped GaN Surface Grown by RF Plasma Molecular Beam Epitaxy

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Abstract:

Cr doped GaN was grown by rf N-plasma molecular beam epitaxy on sapphire (0001) at a sample temperature of 700 ^{o}C. Cr/Ga flux ratio was set to a value from 5% to 20%. Subsequently, scanning tunneling microscopy was performed on these surfaces. Cr incorporates on the GaN surface at 700 ^{o}C at a Cr concentration of 5% and less. By increasing the Cr/Ga flux ratio to 20% in CrGaN, linear nano structures were formed on the surface, which were not observed on the bare GaN surface. The RHEED and STM studies reveal that Cr atoms form 3×3 reconstruction when 0.1 ML of Cr was deposited at room temperature on 1×1 adlayer of Ga on GaN (000-1). Cr substitutes Ga on the surface when deposited at 700 ^{o}C on the MBE grown GaN (000-1) surface for all the experiments, which we have performed, provided the Cr concentration is low (~5%).

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Introduction

For last two decades, spintronics has become a field of wide interest, where not only the charge but also spin degree of freedom of the charge carriers will be manipulated. Successful spin injection into existing semiconductor-based devices at room temperature is still being investigated. Many scientists have predicted that some Nitride Dilute Magnetic Semiconductors (NDMS) can be used as spin injectors at room temperature. According to Sato *et al.*, based on their first-principles calculations in mean field approximation, CrGaN has a stable ferromagnetic state at Cr concentration above 2%, provided Cr substitutes Ga in GaN lattice [1]. Cr incorporation and Cr substitution at Ga lattice site is not an easy task to investigate using bulk techniques. Scanning Tunneling Microscopy (STM) is an important tool to investigate the Cr incorporation and position in the GaN lattice at atomistic scale.

Recently a few results have been reported about the growth and bulk properties of CrGaN. Lee *et al.* have used ion implantation of Cr on Mg doped MOCVD grown GaN on sapphire substrate [2]. Park *et al.* performed the growth of Cr doped GaN single crystal by sodium flux method [3]. There are a few reports about the growth and above room temperature ferromagnetism in CrGaN samples, which were grown on sapphire (0001) by electron-cyclotron plasma-assisted molecular beam Epitaxy (MBE) [4,5,6]. We have recently performed a systematic growth study and have observed the effect of Ga/N flux ratios on the structural and magnetic properties of CrGaN and have found the growth

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conditions, which resulted in above room temperature ferromagnetism [7]. In this paper, we report the *in-situ* STM study of Cr doped GaN and Cr deposition on GaN, to investigate the position of Cr on the GaN surface at atomic level.

Experimental

Growth and depositions were performed in a custom designed ultra high vacuum molecular beam epitaxy (UHV-MBE) chamber where samples can be transferred to the UHV analysis chamber, without exposing them to air, which is equipped with the room temperature STM. Effusion cells are used for Ga and Cr sources while rf-Plasma is used for nitrogen with N_2 as the source gas. Prior to the growth, samples were heated up to 800 ^oC and surface was nitridated with a plasma power of 500 Watts with N_2 flow rate of 1.1 sccm. During the growth background pressure of the chamber was maintained at 9×10^{-6} Torr. Reflection High Energy Electron Diffraction (RHEED) with electron energy of 20 keV was used to monitor the growth.

We have performed three different series of experiments, which can be categorized as: 1) Deposition of fraction of a monolayer of Cr on N-polar GaN (000-1) at 700 ^oC. 2) Deposition of fraction of a monolayer of Cr on 1×1 N-polar GaN (000-1) at room temperature. 3) Deposition of a few monolayers of CrGaN on N-polar GaN (000-1) at 700 ^oC. The details of the experimental procedure for all three experiments are the following:

1) Cr deposition on GaN surface at 700 ^oC:

First Ga-rich N-polar GaN layer was grown on sapphire (0001) at substrate temperature of 700 ^oC. Then growth was stopped and approximately 0.05ML of Cr was deposited on the Ga-rich GaN surface at 700 ^oC. Then sample was transferred to analysis chamber and STM studies were performed on the surface.

2) Cr deposition on 1×1 GaN at room temperature:

First approximately 2500 Å N-polar Ga-rich GaN layer was grown on sapphire (0001) substrate at 700 ^oC. Then sample was annealed to 800 ^oC for 10 minutes to remove all the Ga adatoms from the surface and achieved 1×1 surface when cooled to room temperature. Then approximately 0.09 monolayer (ML) of Cr was deposited at room temperature and subsequently STM studies were performed.

3) Cr doped GaN growth at sample temperature of 700 ^oC:

Ga-rich N-polar GaN layer (~ 2500 Å) was grown on sapphire (0001) substrate at a sample temperature of 700 ^oC. Cr/Ga flux ratio was set to ~ 5% and Cr shutter was opened without stopping the growth. The growth was stopped after ~ 3 monolayer of CrGaN were grown. Then surface was studied with *in situ* STM. In the second experiment in this series, approximately 4 ML of CrGaN were grown on MBE grown GaN (000-1) and Cr/Ga flux ratio was set to ~ 20% and surface was studied with STM.

In addition to these experiments, we have also grown thick CrGaN samples on sapphire (0001) at 700 ^oC for measuring the bulk properties including magnetic and structural properties.

Results and Discussions

Ga-rich N-polar GaN (000-1) Surface

First we studied the N-polar Ga-rich GaN (000-1) surface using STM to observe the difference between GaN (000-1) and Cr-doped GaN surfaces.

Shown in Figure1 are the STM images of 3×3 and 6×6 reconstructions on the N-polar GaN surface and their schematic atomic models. These images of 3×3 and 6×6 reconstructions were acquired at sample bias of +1.5V and +2V respectively with the tunneling current of 0.08nA. Some areas of the sample surface contain 3×3 and some areas contain 6×6 reconstructions. These reconstructions are commonly observed on the N-polar GaN surface and have been reported previously [8,9,10]. These reconstructions are observed after the growth and after cooling the sample to below 300 °C. At higher temperatures Ga adatoms are in motion randomly and do not form a periodic 3×3 or 6×6 reconstructions but at lower temperature after the growth these adatoms arrange themselves in 3×3 and 6×6 ordering. In case of 3×3 reconstruction, Ga adatoms are apart from each other by a distance three times the distance between Ga atoms of the underlying Ga adlayer. The 6×6 reconstruction consists of ring-like structures where each ring consists of 6 Ga adatoms and each two adjacent Ga adatoms in the ring form a dimer. These ring-like structures have a periodicity of 6×6 as is evident from the schematic atomic model.

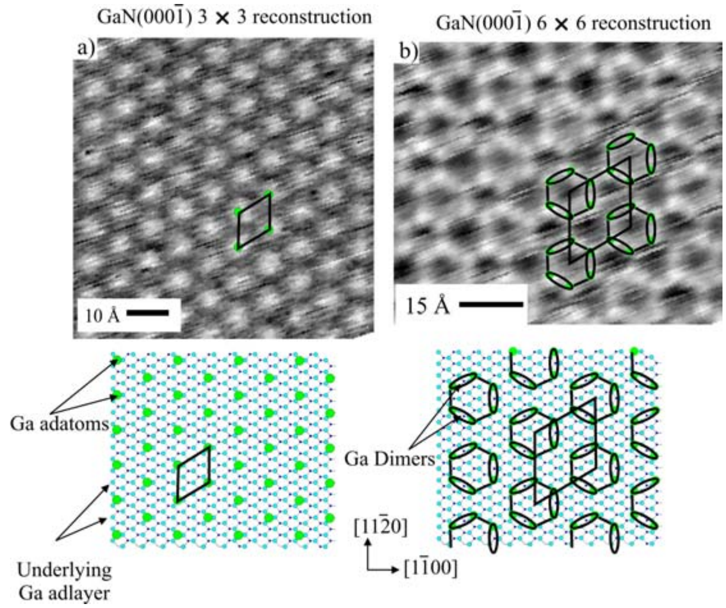

Figure 1: STM images of GaN (000-1) surface. a) 3×3 reconstruction image acquired at V_S = +1.5V and I_t = 0.08nA and schematic atomic model b) 6×6 reconstruction image with schematic model superimposed on the STM image [V_S = +2V; I_t = 0.08nA] and schematic atomic model.

Cr deposition on GaN (000-1) at T_s = 700 °C

In this experiment, approximately 0.05ML of Cr

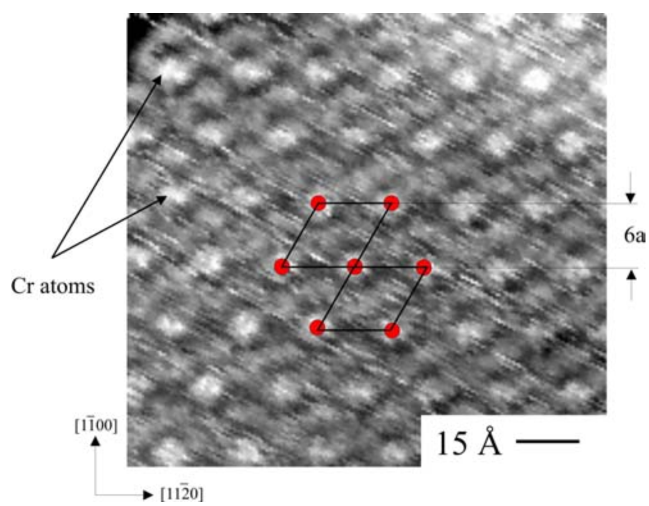

Figure 2: STM images of high temperature Cr deposited GaN (000-1) surface, 6×6 reconstruction image where Cr atoms are apparent in the image [V_S = -1.5V; I_t = 0.08nA].

was deposited on Ga-rich grown GaN surface at sample temperature of 700 ^{o}C. Shown in Figure 2 is the room temperature STM image of the surface. This image was obtained at a sample bias of -1.5V and tunneling current of 0.08nA. This reconstruction is a 6×6 ring-like reconstruction which appears similar to the GaN (000-1) 6×6 reconstruction except one of the protrusions in the 6 atoms ring appears brighter than the others. As this unusual effect was not observed in the GaN 6×6 reconstruction so it can be inferred that this brighter protrusion is due to Cr atom, which is substituting Ga position in this 6×6 arrangement.

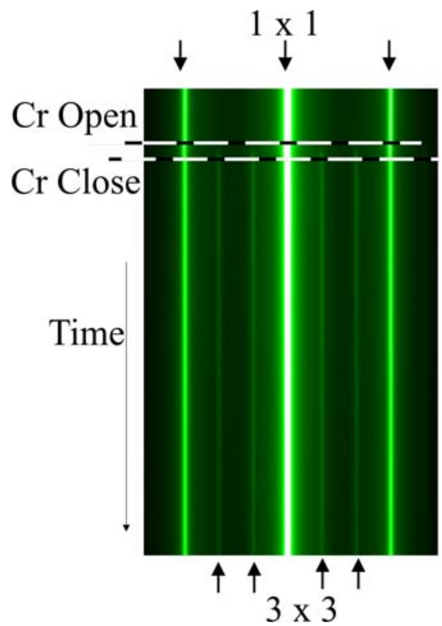

Figure 3: RHEED scan of 1×1 GaN surface and Cr deposition at room temperature.

Room Temperature Cr deposition on GaN (000-1)

In this experiment approximately 0.09ML of Cr was deposited on 1×1 GaN adlayer at room temperature.

Shown in Figure 3 is the RHEED scan acquired in real time. As it can be seen from the RHEED pattern that before the Cr shutter was opened there were only 1×1 streaks of the GaN (000-1) surface. These streaks are due to the 1×1 Ga ad-layer on the GaN surface. Then Cr shutter was opened for a very short time to deposit approximately 0.09 ML of Cr. As it can be seen that during the Cr deposition 3×3 streaks appear and these streaks stay on the surface even after the Cr shutter was closed.

This is a direct evidence that this 3×3 reconstruction was formed by Cr atoms. Thus it can be inferred that Cr substitutes Ga atoms at least on the GaN surface.

The 3×3 reconstruction was observed when Cr deposition was performed at room temperature and disappears when temperature is increased (above 100 ^{o}C). Moreover, this 3×3 reconstruction is irreversible; because when the temperature is reduced to room temperature then this reconstruction is not recovered. On the other hand, if we deposit more Cr then 3×3 appears again. So this is in a metastable state: when temperature is increased then either the Cr atoms form themselves into 1×1 reconstruction or simply accumulate and form clusters.

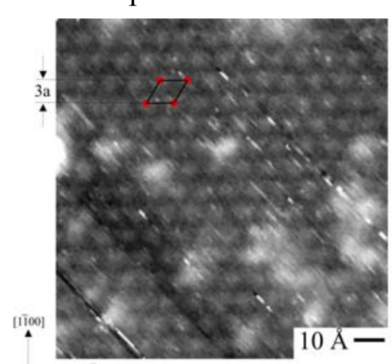

Figure4: STM images of room temperature Cr deposited GaN (000-1) surface, 3×3 reconstruction image of the surface. [V_S = -1V; I_t = 0.09nA]

STM studies were performed on the surface. Shown in Figure 4 is the STM image of the Cr deposited GaN (000-1) surface. This image clearly shows 3×3 reconstruction. The image was obtained at a sample voltage of -1V and tunneling current was set to 0.09nA. This image is a clear proof in the real space of the 3×3 reconstruction observed in the RHEED pattern. Some bright spots on the surface can be attributed to some impurities, which were deposited on the surface in the growth chamber, as the Cr deposition was performed at room temperature.

5% and 20% Cr-doped GaN (000-1)

Shown in Figure 5 is the zero field cooled (ZFC) and field cooled (FC) data of CrGaN sample acquired by superconducting quantum interference device (SQUID). This sample was about 600nm thick and the Cr/Ga flux ratio was set to about 2.13%. Both ZFC and FC curves are distinctly apart from each other, which is an indication of ferromagnetic behavior. The FC curve has been extrapolated to qualitatively imagine the Curie temperature, which appears to be much higher than room temperature. The highest Curie temperature recorded for CrGaN is above 900K [11].

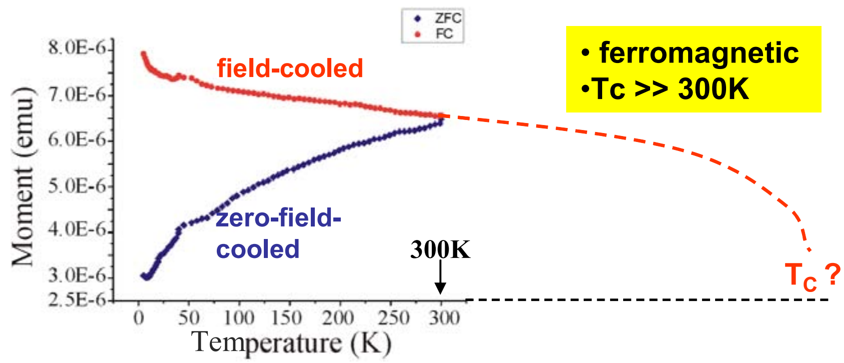

Fig. 5: SQUID result for thick CrGaN sample. The dashed curve is shown to qualitatively imagine the Curie temperature.

A sample grown under the same growth conditions but with a Cr/Ga flux ratio of 5% exhibits similar magnetic properties. A detailed description on the acquisition and analysis of magnetic properties of CrGaN bulk samples can be found in our previous work [7].

For STM studies a few monolayers thick CrGaN samples were grown at Cr/Ga flux ratio of approximately 5% and 20% at substrate temperature of 700 °C. Shown in Figure 6 are the STM images of the 5% and 20% Cr-doped GaN surface acquired at sample bias of +1V and –1V respectively with tunneling current of 0.08nA. The STM image of 5% Cr-doped surface shows 3×3 arrangement of atoms. This STM image appears similar to the GaN surface shown in Figure 1 except there are some bright protrusions, which can be attributed to the Cr atoms. These Cr atoms appear at

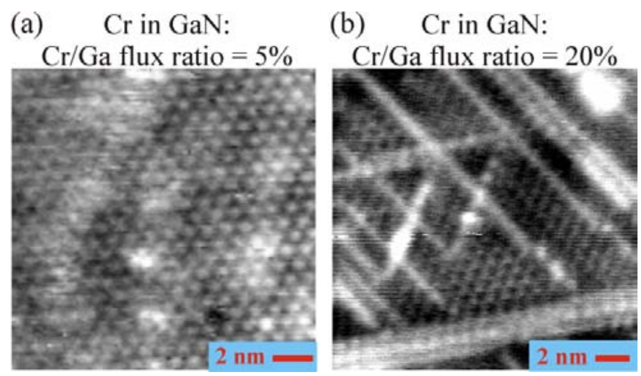

Figure 6 STM images of 5% Cr-doped GaN (000-1) surface, showing 3×3 reconstruction with apparent substitutional Cr atoms [V_S = +1V; I_t = 0.08nA] STM images of 20% Cr-doped GaN (000-1) surface, showing Cr nanowires [V_S = -1V; I_t = 0.08nA]

the position of Ga atoms. This means that at least on the surface Cr occupies Ga lattice site in CrGaN growth.

For the case of 20% Cr-doped GaN surface, Cr segregation can clearly be seen on the surface. It can be interpreted as Cr atoms arrange themselves in linear features, forming Cr nanowires along the high symmetry lines. The area between these nanowires consists of atoms having 3×3 periodicity. In this study we could not determine conclusively that whether this 3×3 reconstruction observed on the surface was also formed by Cr atoms or Ga atoms. But the linear features formed on the surface are definitely a result of higher Cr concentration, as these features are not observed on the bare GaN surface regardless of the Ga/N flux ratio. It can be seen from the STM image that most of the Cr nanowires consist of single Cr atoms aligned linearly. Most of the Cr atoms forming these nanowires are commensurate with the perfect 3×3 reconstruction but some are displaced about a single lattice constant from the perfect 3×3 reconstruction. Most of these nanowires are several hundred Angstroms long.

Conclusion

It has been found that Cr substitutes Ga site at least on the surface during CrGaN growth when Cr/Ga flux ratio is kept 5% and below. At higher Cr/Ga concentration of 20% during CrGaN growth, Cr starts to form nano linear features. When Cr was deposited on the 1×1 GaN surface then Cr forms 3×3 reconstruction on the surface.

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