First-principles calculations for effects of Fluorine impurity in GaN

Jing Lu Mingzhi Gao Jinyu Zhang Yan Wang* Zhiping Yu
Institute of Microelectronics,
Tsinghua University
Beijing, China
wangy46@tsinghua.edu.cn

Abstract—**Fluoride-based plasma treatment has been approved to be an effective technique to make E-Mode GaN-based HEMT by experiments. However, the detailed effect of Fluorine doping in GaN and AlGaN is still unclear and has never been studied theoretically. In this paper, F impurity in GaN material is firstly studied by First Principle Calculations. Sound explanations for the experimental phenomenon are derived from the results and further discuss is presented.**

Keywords-GaN; Defects; F impurity; First-principles calculation

I. INTRODUCTION

GaN-based heterostructure field effect transistors (HEMTs) have been the focus of intense research in the last few years due to their potential high-power applications at RF, microwave, and millimeter-wave frequencies. In spite of their extraordinary performance, GaN HEMTs still lack solid reliability [1]. The effect that most severely limits the RF power performance of AlGaN/GaN HEMTs is the current collapse effect, which originates from trapping effects at the device surface and/or in the buffer layer [2]. The fabrication of E-mode AlGaN/GaN HEMTs is another big challenge. A new technique based on Fluoride-based plasma treatment to fabricate E-mode AlGaN/GaN HEMTs was demonstrated by Chen's group [3]. In addition, it was proposed that the Fluorine doping could decrease the current collapse effect. In this paper, we performed first-principle calculation to investigate the effects of Fluorine impurity in GaN for the first time. Based on the results, some explanations and suggestions were proposed for recent experiments and further development.

II. CALCULATION METHODOLOGY

The calculations were executed on a 32-atom supercell structure (showing in Fig. 1) composed of eight wurtzite GaN unit cells. First-Principles calculations were performed using the GGA (PW91) and ultra-soft core potential. The plane wave cutoff energy was set to 450eV. In order to reduce the defect-defect interaction, Brillouin-zone integrations are carried out using the $4 \times 4 \times 4$ Monkhorst-Pack scheme to avoiding picking up the Γ point as one of the sample points. After structure relaxation, the density of states (DOS) and partial orbital of density of state (PDOS) was calculated keeping the volume of supercell unchanging.

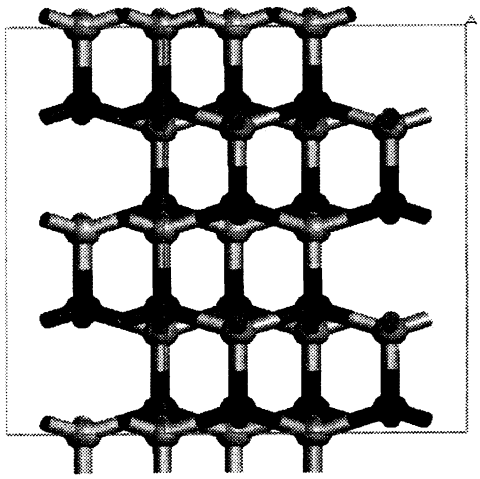

Figure 1. The structure of 32-atom GaN supercell

We considered five kinds of defect in GaN: Nitrogen vacancy (V_N), Gallium vacancy (V_{Ga}), Ga substitution by Fluorine (F_{Ga}), N substitution by Fluorine (F_N), and Fluorine interstitial defects (F_i). The calculation and analysis mainly focus on two aspects, the formation energy and the density of states. The formation energy of a defect or impurity X in charge state q is described as Eq. 1 in Ref [4]:

$$E^f[X^q] = E_{tot}[X^q] - E_{tot}[GaN, bulk] - \sum_i n_i \mu_i + q[E_F + E_v + \Delta V] \quad (1)$$

Where, X indicates the impurity or the defect. $E^f[X^q]$ is the total energy derived from a supercell calculation with X in the cell, and $E_{tot}[GaN, bulk]$ is the total energy for the equivalent supercell containing only bulk GaN. n_i indicates the number of atoms of type i that have been added to (n_i >0) or removed from (n_i <0) the supercell when the defect or impurity is created, and μ_i are the corresponding chemical potentials of these species. q is the charge state of the impurity or the defect. The relative formation energy is a linear function of E_F with respect to the edge of the valence band E_v.

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III. RESULTS AND DISCUSSION

Formation energy can tell if the defect system or impurity system is stable. Fig. 2 displays the line segments that give the overall lowest formation energies of crystal with V_N, V_{Ga}, F_i, F_N, F_{Ga}. The results of V_N, V_{Ga} are approximate to the reported values in Ref [5, 6]. We observed that

1) F_N appears with lowest energy but the most stable charge state transits from +2 to -1 when E_F increasing. Observed from Fig. 3, we can find that in n-type GaN, F_N tends to have lowest energy at -1 charge state and acts as acceptor.
2) In n-type GaN, F_i is with relative low formation energy and it has a stable charge configuration through the band gap. The slope of F_i keeps -1 through band gap, indicating it acts as single acceptor.
3) V_N has higher energy than V_{Ga} in n-type GaN. Thus, V_N would not be present in significant concentration and will not be responsible for the self n-doping of GaN;
4) F_{Ga} is energetically unfavorable.

As an approximation to the AlGaN, we proposed that F_i and F_N act as acceptors in -1 charge state in AlGaN layer of HEMTs which contribute to the under-gate negative charges in E-mode HEMTs.

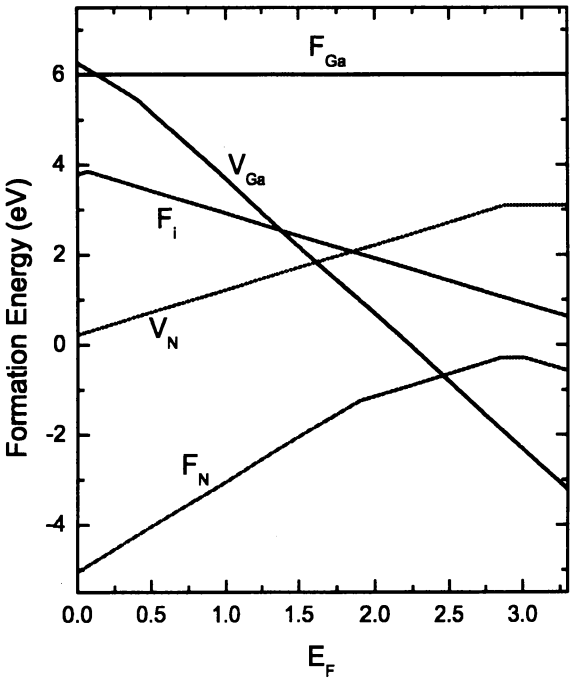

Figure 2. Formation energies as a function of Fermi level (Ga-rich condition is assumed)

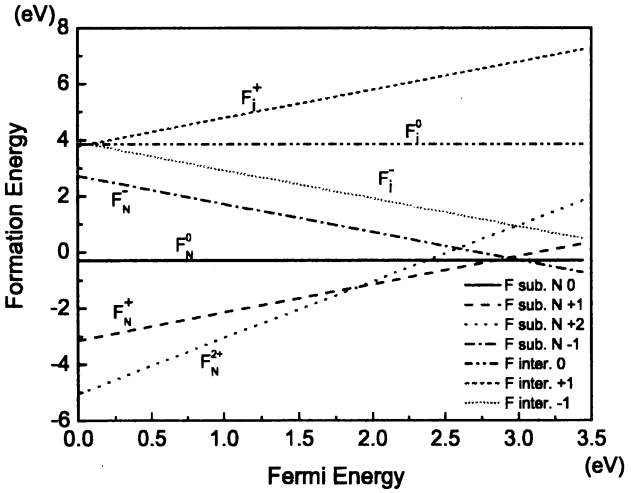

Figure 3. Formation energies of F_i and F_N at different charge states.

The DOS comparison between perfect crystal, crystals with V_N and F_N at neutral state is shown in Fig. 4. From Fig. 4, we found that V_N introduces deep defect densities in band gap, which is about 0.5eV above the GaN valence band maximum (VBM). Besides, defect densities also can be observed near the conduction band minimum (CBM). The DOS of F_N shows the deep defect density introduced by V_N is flattened and the defect density near CBM is also decreased. Fig. 5 presents the DOS comparison between different charge states of F_N. Little difference can be observed between different charge states, even though F_N^{-1} is proved to be the most stable charge state in n-type GaN.

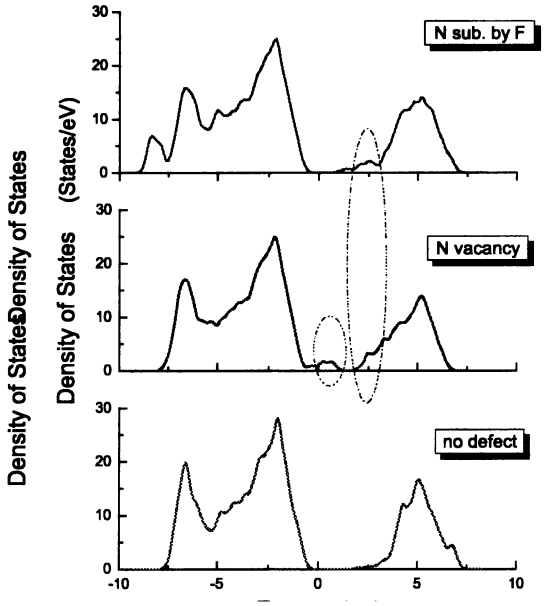

Figure 4. DOS comparison between perfect crystal and crystal with neutral V_N and F_N.

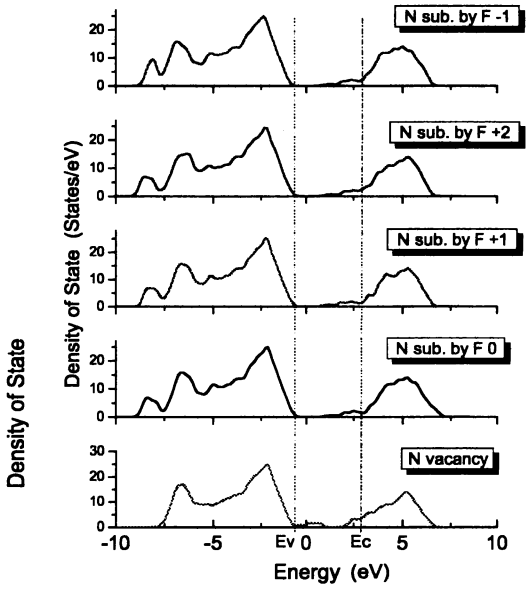

Figure 5. DOS comparison between crystal with V_N and F_N in different charged states.

Fig. 6 and Fig. 7 show the PDOS of V_N and F_N systems respectively. The deep defect densities in V_N are mainly introduced by Ga atom near N vacancy and which easily forms a Ga-F bond with the near F impurity atom.

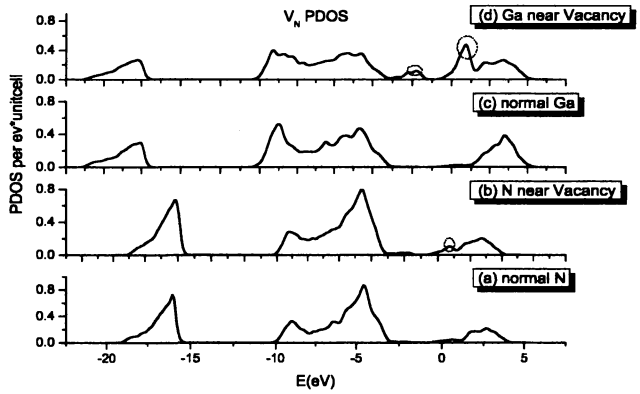

Figure 6. PDOS of crystal with V_N

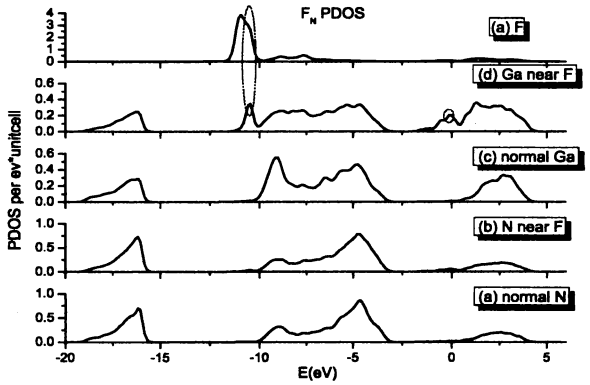

Figure 7. PDOS of crystal with F_N

The DOS presented in Fig. 8 shows that F_i does not induce any defect density in the band gap. The PDOS of F_i was shown in Fig. 9. We can see F is easy to get an electron from the nearest host atom (Ga or N).

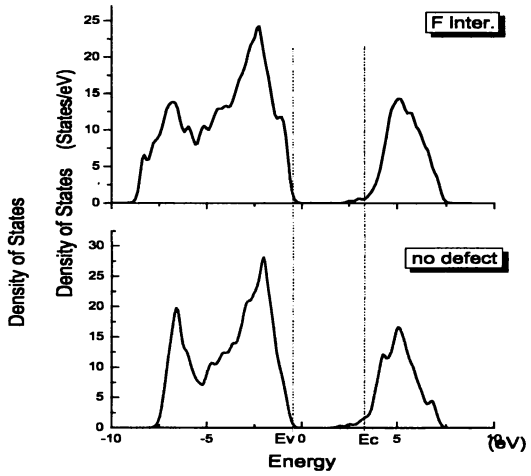

Figure 8. DOS comparison between perfect crystal and crystal with F_i.

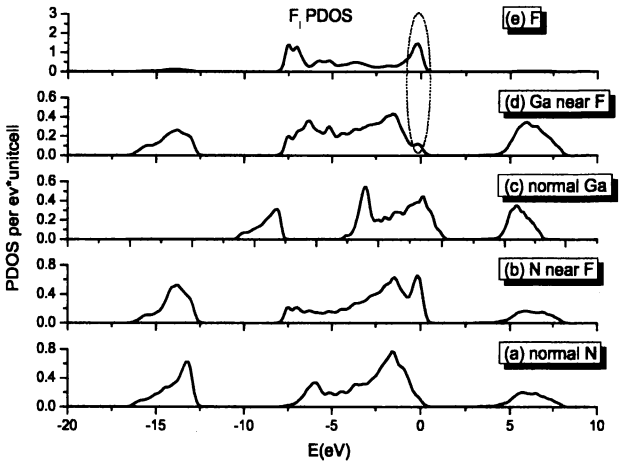

Figure 9. PDOS of crystal with F_i

In Fig. 10, the DOS comparison between neutral V_{Ga} and F_{Ga} is presented. V_{Ga} also induces a deep defect level near the VBM. F_{Ga} decreases the defect DOS induced by V_{Ga} but introduces a new deep level. However, F_{Ga} is with high energy formation, so its effect is inconsiderable. From Fig. 11, we can see the deep state density is introduced by N atom near the Ga vacancy. When F atom is added, it tends to get a electron from the nearby N atom (Shown in Fig. 12).

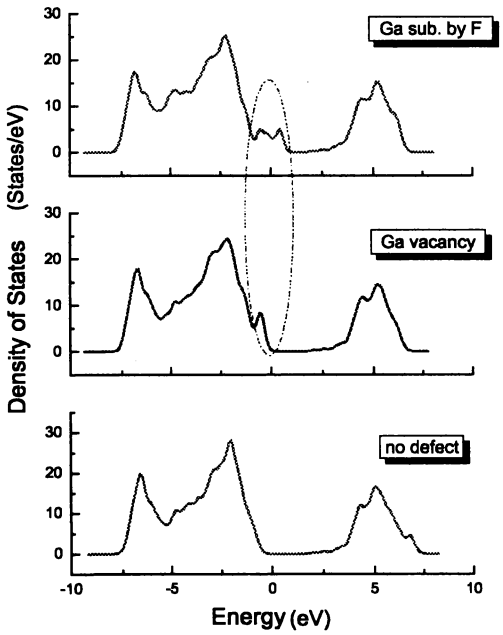

Figure 10. DOS comparison between perfect crystal and crystal with neutral V_{Ga} and F_{Ga}.

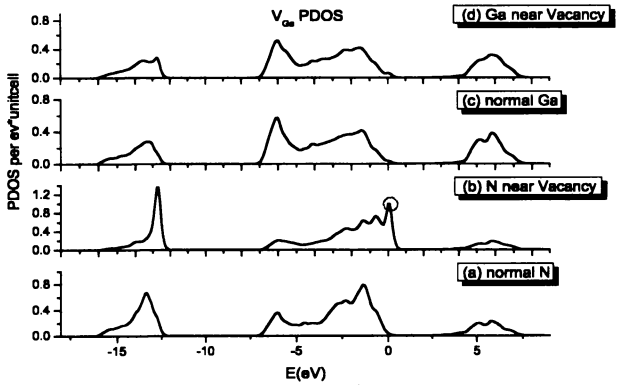

Figure 11. PDOS of crystal with V_{Ga}

From the discussion above, we can safely conclude that the F impurity can decrease the deep state density induced by point defects such as V_N and V_{Ga} in GaN material without introduce any new deep level in the band gap. Many works have been done to demonstrate that the current collapse effect is due to deep defect levels in AlGaN surface and in GaN bulk. So it is reasonable to deduce that F impurity decreases the deep defect densities in band gap in GaN and AlGaN layers which will be helpful for reducing the current collapse effect.

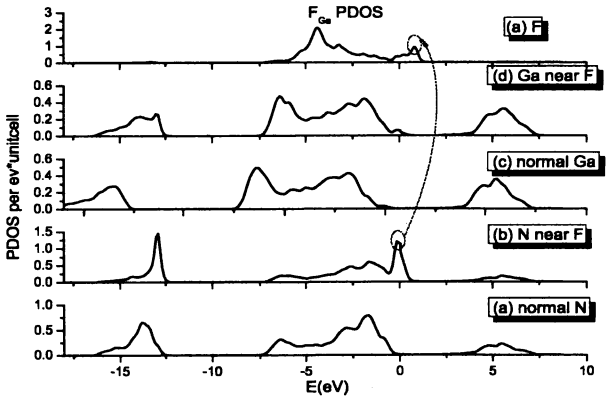

Figure 12. PDOS of crystal with F_{Ga}

IV. CONCLUSION

The effects of Fluorine impurity in GaN was firstly theoretically studied by First Principle calculation. From the calculation results we conclude that :

- Fluorine atom may mainly exist as F_N and F_i in n-type GaN and act as acceptors which may be major contribution to positive threshold voltage shift in the E-mode HEMTs.
- From the DOS study, it was proposed that the Fluorine impurity will decrease the defect density in band gap which is helpful for reducing the current collapse effect and enhancing the device's performance.

All these results build up a good base for studying the effect of introducing Fluorine in AlGaN.

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