Research On Mg Doping in Nitride Semiconductor Materials

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Abstract. Summarized the achievements of various model research directions in nitride Mg doped semiconductors in this thesis. Due to the Internal properties of Mg acceptors which resulting the low ionization rate of acceptor, and the low hole mobility in heavily Mg doped nitrides, the conductivity of Mg doped nitrides is limited. At present, research is divided into three categories of models, one is a new type of polarization model. This model adopts a built-in electron polarization ionization acceptor dopant in the bulk uniaxial semiconductor crystal, and provides an attractive solution for the problem of P-type and n-type doping in broadband gap semiconductors. The other two are the traditional thermal activation model. There are mainly ultra-high-pressure-annealing (UHPA) and multicycle rapid thermal annealing (MRTA) respectively. Both of these schemes can activate more Mg impurities, resulting in higher conductivity in nitrides. The principles, advantages and disadvantages, and future development prospects will be explained of these three models in this thesis.

Keywords: Three models, UHPA, MARTA, polarization, priciple.

1. Introduction

Nitride-based materials is a very potential direct wide bandgap optoelectronic semiconductor material [1], which has undergone significant development in the past 20 years. Since then, many researchers have begun to pay attention to it because the III-nitride material has obvious advantages in the application of LED full-color display, Solid-state lighting and other aspects. The continuous improvement of lighting efficiency has driven a revolution in lighting and other cutting-edge applications. A few years ago, Cree announced the successful development of a 303Im/W high-power white LED, indicating another milestone in optoelectronic semiconductor materials development [2]. In 2017, Isamu Akasaki, Hiroshi Amano and Shuji Nakamura won the Nobel Prize in Physics because they invented efficient blue light-emitting diodes, which made bright and energy-saving white light sources possible [3].

At present, the most commonly used acceptor dopant in nitrides is Mg, mainly because Mg impurities have a relatively smaller activation energy of approximately 160-200meV compared to other II or III group metals, while Al, which is also a metal, has an activation energy of up to 600meV. However, there is a problem that has persisted is P-type nitride layer’s high resistivity. Even though the required activation energy for Mg is 160meV, this is several times the heat energy at room temperature, and the activation energy of the acceptor increases with the expand of the band gap. Therefore, due to the high energy required for the activation of Mg impurities, the thermal activation efficiency at room temperature is very low, and it becomes increasingly problematic in high bandgap nitride layers[4]. The current theoretically achievable value is 13.12meV (based on 8.2% of the 160 meV acceptor level). But the actual activation rate is 1% or lower[5]. In the past 20 years, polarization model and thermal activation model have been devoted to how to reduce the activation energy required by Mg impurity and improve the conductivity.

The advantages and disadvantages, working principles, and challenges faced by three models that have made significant contributions to improving conductivity in Mg doped nitride semiconductors are provided a detailed description in this article. Three modules are:

① Polarization model, ② Multicycle rapid thermal annealing (MRTA) model, ③ Ultra-high-pressure-annealing (UHPA) model. And also has a discussion on whether there is a better model in the future for improving the conductivity of Mg doped nitride semiconductors.

A very common phenomenon in broadband gap semiconductor dopants is lattice relaxation. Figure 1[6] provides a detailed comparison of the detachment of MOCVD and MBE growth. The results indicate that the reason for the full system photoconductivity (PPC) effect of P-GaN using both methods is due to Mg impurities. The reason for H passivation may be due to the non-equilibrium of its dark conductivity during the growth of P-GaN using MOCVD method.

After preparing Mg doped samples with different concentrations using metal organic chemical vapor deposition method, the electrical properties of P-type Mg doped GaN and the relationship between the properties of electrical Mg doped GaN and doping level were studied through temperature dependent Hall effect measurement. The research is shown in Figure 2[7]. To Concluded, With the increase of doping level, many heavy doping effects were observed, including an increase in impurity conduction and compensation degree. However, this development compensation seems to have other effects, such as a significant decrease in acceptor activation energy and a decrease in hole mobility.

	MOCVD	MBE
Hydrogen	rich	largely free
Impurities	Mg, H	Mg
Complexes	Mg–H	largely free
Dark conductivity	nonequilibrium	normal
PPC	small	large
Capture barrier (meV)	55	129
Implications	lattice relaxation about Mg (or Mg–H)	lattice relaxation about Mg

Fig.1 The growth data of Mg impurities in P-type GaN in MOCVD and MBE

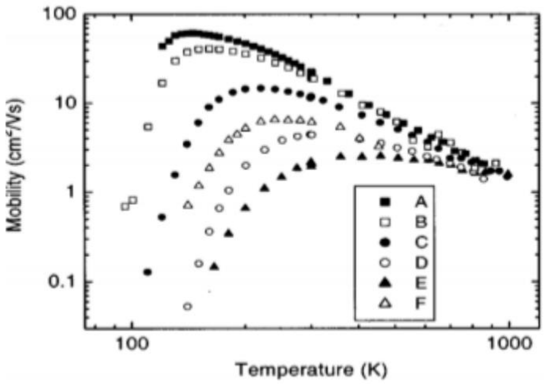

Fig. 2 Temperature-Mobility Function of Mg-doped GaN Samples

2. Principles of three categories of models

2.1. Polarization model

The energy required to activate the hole of thermal activation process is high, which result low efficiency in doping P-type semiconductors using thermal activation models[8]. The Polarization-doping model uses a new model, which uses a built-in electron Polarization-ionization acceptor dopant in the bulk uniaxial semiconductor crystal, demonstrating that P-type doping can also be carried out efficiently and not affected by temperature successfully. The mechanism is shown in Figure 3[4]. Compared to the Thermal activation model, the conductivity efficiency of P-type doped semiconductors has been greatly improved with the Polarization-Induced doping model. The following diagram is a schematic diagram of polarization induced p-type doping. The charge dipole plates in each crystal cell generate a net unbalanced polarized charge, which leads to the bending of the electric field and valence band in. Field ionization generates energy bands and smooth valence band edges without any potential barriers in hole flow.

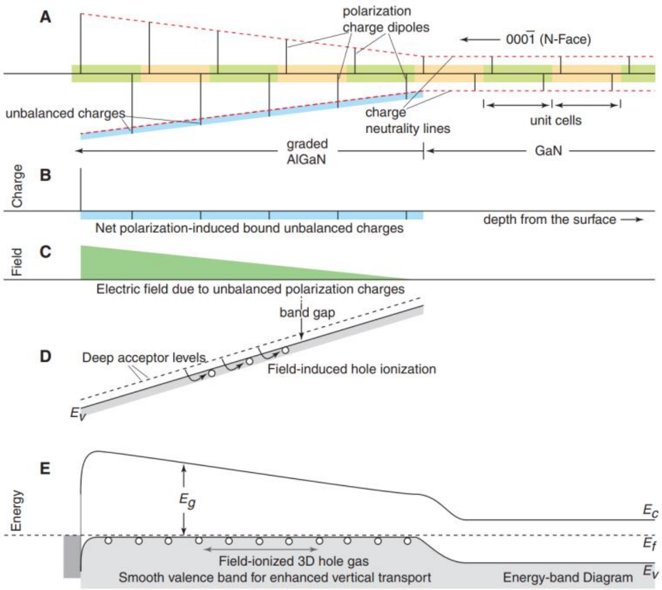

Fig.3 (A) Charge Dipole Sheet (B) Unbalanced Polarized Charge (C) Electric Field Bending, (D) Valence Band Bending, (E) Energy Band Graph E_f: Fermi level, E_c: Edge of conduction band, E_v: Price Band Edge, E_g: bandgap.

2.2. Multicycle Rapid Thermal Annealing (MRTA)

The thermodynamics of GaN at high temperatures is unstable, and in its device technology, the low activation rate of uncompensated Mg acceptor has become a tough problem. If high-temperature rapid thermal annealing (RTA) technology and co-injection technology are used, the actual activation rate is 1% or lower[9]. Although magnesium is a relatively deep acceptor, it is still far below the theoretically achievable value (based on 8.2% of the 160meV acceptor level).

Multicycle rapid thermal annealing (MRTA) can solve this problem effectively, which has been proven to have electrically active acceptors and can achieve longer annealing times at high temperatures. It is the first time of P-type conductivity observed that there is no co-doping enhancement in Mg injected samples, and up to 8% activation of Mg injected GaN can be achieved, which is close to theoretical values. Figure 4[10] shows the optical images of GaN samples. Figure 5[10] shows the measured data in MRTA over a period of 40 cycles. The experimental results indicate that MRTA technology is a feasible GaN annealing ion implantation method. This technology improves the stability of the material at the temperature required for activating injected impurities, thereby prolonging annealing time and increasing activation and hole mobility. This technology will also be used to enhance the activation of Mg in doped gallium nitride during the growth process, as well as to enhance the activation of other dopants. In addition, the MRTA method can also be applied to the annealing of other unstable materials.

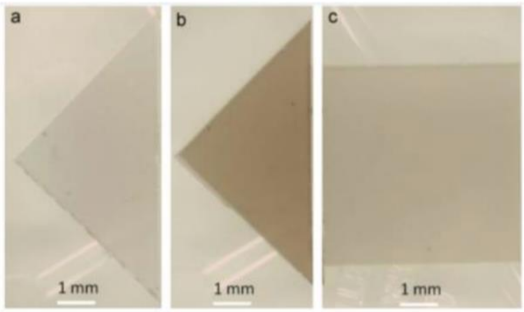

Fig.4 Optical images of GaN samples: (a) as grown before the implantation, (b) after the implantation, (c) after the first step of annealing at 1050 1C for 1 h-apparent.

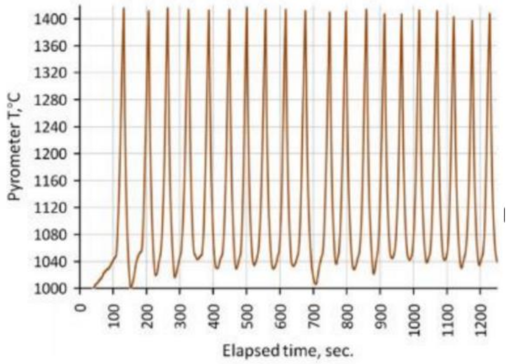

Fig.5 Temperature cycle diagram during MRTA.

2.3. Ultra-high-pressure-annealing (UHPA)

Diffusion of Mg implanted co-epitaxial GaN layers in environmental nitrogen was researched by observing the distribution of Mg and H ions in GaN at different ultra-high-pressure annealing (UHPA) temperatures and durations[11]. At a temperature of 1573K, Mg exhibits an inactive state, mainly due to Mg segregation and ID (continuous leakage current) phenomenon in the bottom region of the box shaped injection profile. On the contrary, at temperatures above 1673 K, Mg atoms are generated at the binding site between Mg receptors and H atoms, which reduces the accumulation of Mg in holes. During the heating stage, the diffusion of Mg and H ions significantly increased in the sample injected with Mg, indicating the existence of defect assisted diffusion mechanisms.

3. Conclusion

The main principle of the polarization induction model is that positively polarized charges induce the formation of a mobile 3D electron gas. These 3D electron gases are significantly different from electron gases formed by doping with donor impurities: the charge carriers of 3D electron gases are generated by effective electrostatic fields through field ionization, rather than those generated by thermoelectric ionization in shallow and donor doped layers. Therefore, they do not need to be doped with impurities and are not affected by thermal activation energy. At the same time, they do not have ionizing impurity scattering, so the obtained 3D electron gases have higher conductivity than doped impurity layer gases with the same carrier concentration. In addition, because the polarized charge is spatially distributed, the changes in the edge of the band are smooth, and there is no sudden change in the potential barrier for hole flow in any direction. These properties are unique advantages of polarization models.As for MRTA, this technology improves the stability of the material at the temperature required for activating injected impurities, thereby prolonging the annealing time and increasing activation and hole mobility. The temperature for ordinary thermal annealing is around 1573K. This method cannot estimate the activation ratio: (acceptor number/Mg atomic number) because the free hole concentration is too low. UHPA was conducted in a N2 environment of 1673K and 1GPa. At this temperature, the thermal decomposition of mg injected GaN is suppressed, resulting in a decrease in free hole concentration and a difference between epitaxial in-situ mg doped GaN. Therefore, for mg atoms, H atom may be a good indicator.

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