第 29 卷　第 7 期
2008 年 7 月

半　导　体　学　报
JOURNAL OF SEMICONDUCTORS

Vol. 29　No. 7
July, 2008

Defect Cluster-Induced X-Ray Diffuse Scattering in GaN Films Grown by MOCVD*

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Abstract: High-resolution X-ray diffraction has been employed to investigate the diffuse scattering in a (0001) oriented GaN epitaxial film grown on sapphire substrate. The analysis reveals that defect clusters are present in GaN films and their concentration increases as the density of threading dislocations increases. Meanwhile, the mean radius of these defect clusters shows a reverse tendency. This result is explained by the effect of clusters preferentially forming around dislocations, which act as effective sinks for the segregation of point defects. The electric mobility is found to decrease as the cluster concentration increases.

Key words: X-ray diffuse scattering; GaN; defect cluster
PACC: 7870; 6855; 7850G
CLC number: TN304　**Document code**: A　**Article ID**: 0253-4177(2008)07-1242-04

1 Introduction

In recent years, group III-nitrides have attracted much attention because of their potential for high-temperature and high-power electronic devices. Due to lack of appropriate substrate, high density dislocations ($10^8 \sim 10^{10} \mathrm{cm}^{-2}$) will be generated in group III-N epitaxial layers. Various structural investigation methods, such as X-ray diffraction (XRD), transmission electron microscopy (TEM), and Rutherford back-scattering (RBS)/channeling techniques were used to investigate the effect of the threading dislocations on the structural properties of III-nitride epitaxial layers. Among these methods, XRD is a well-established technique to analyze crystal lattice perfection. The density of screw and edge dislocations can be characterized by the half widths of diffraction peaks of X-ray Bragg reflection. Although the obtained structural parameters are instructive for the material growth and device design, it is still not enough to determine the crystal perfection. In addition to the threading dislocations, the effect of point defects on structural quality can not be neglected. The X-ray diffuse scattering technique, i. e., Huang diffuse scattering, is applicable for studying point defects, dislocation loops, and small defect clusters in metals[1,2] and semiconductors[3~5]. However, few reports about X-ray diffuse scattering of GaN films are available at present. In this study, we will focus on an investigation of the broad tail of the X-ray rocking curve, which is induced by the diffuse scattering of a large number of defect clusters in GaN film grown on sapphire substrate, as well as the relationship between defect clusters and photoelectric properties. It is found that the carrier mobility decreases as the cluster density increases in GaN films.

2 Theoretic basis of diffuse scattering from point defects

The defect-induced distortions in a crystal lattice gives rise to X-ray diffuse scattering[6]. A review of diffuse scattering of defects has been given by Krivoglaz[7] and Dederichs[8,9]. In addition, experimental results have shown that X-ray diffuse scattering in the vicinity of the Bragg reflection can be used to investigate point defects[1,5,10]. Here we will outline those parts of the theory that are relevant to the understanding of our experimental measurements. If point defects aggregate into a cluster, a statistical distribution of clusters will be formed in the lattice. Under

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* Project supported by the National Natural Science Foundation of China (Nos. 60506001, 60476021, 60576003) and the State Key Development Program for Basic Research of China (No. 2007CB936700)

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Received 29 February 2008, revised manuscript received 19 March 2008

the assumption of a linear superposition of the displacements of the point defects in a cluster of radius R_{cl}, the diffuse scattering is proportional to the density C_{cl} and the square of relaxation volume V_{rel} of defect clusters[8,11]. Depending upon the magnitude of $\boldsymbol{q}$ deviated from the Bragg position, where $\boldsymbol{q}$ is defined as $\boldsymbol{q} = \boldsymbol{k} \pm \boldsymbol{h}$ (where $\boldsymbol{k}$ is the scattering vector and $\boldsymbol{h}$ is the reciprocal-lattice vector), one may distinguish two regions of diffuse scattering. First, at small $\boldsymbol{q}$, the displacement field is away from the defect centers and scattering function $S(\boldsymbol{K})$ has q^{-2} dependence. The scattering is Huang diffuse scattering (HDS). Second, at larger $\boldsymbol{q}$ values, diffuse X-ray scattering from strongly distorted regions of the lattice falls off like $\boldsymbol{q}^{-4}$ according to a generalized form of the Stokes-Wilson (SW) approximation[8].

3 Experiment

All the investigated samples were grown by metal-organic chemical vapor deposition (MOCVD) (Thomas Swan Scientific Equipment 3 × 2 CCS-MOCVD with a vertical quartz reactor) on *c*-axis sapphire substrate. The growth of GaN epitaxial layer takes the conventional two-step method with H_2 carrier gas under low reaction pressure at the temperature of 1040℃. The group-III precursor used for the growth of GaN layers was trimethyl-gallium. Diffuse X-ray scattering measurements were performed with a Bede D1 high-resolution X-ray diffractometer (HRXRD), using a conventional sealed X-ray tube and Cu $K\alpha_1$ radiation. The rocking curve (ω scan) was taken to study the X-ray diffuse scattering in GaN films. The full width at half maximum (FWHM) of the ω scan for the symmetric (0002) and skew symmetric $(10\bar{1}2)$ reflections of GaN films was used to characterize the density of screw-type dislocation and edge-type dislocation, respectively. The density of threading dislocation was obtained using the following expression[12,13]: $\boldsymbol{D} \approx \beta^2/(4.35 \times \boldsymbol{b}^2)$ (where $\boldsymbol{b}$ is the Burgers vector of the threading dislocation; and β is the FWHM of the rocking curve). In addition, the optical and electrical properties of GaN samples were investigated using Hall and photoluminescence (PL) measurements at room temperature.

4 Results and discussion

Figure 1 shows rocking curves (ω scan) around the (0002) reflection in the GaN films. The symmetrical part of the diffuse scattering intensity curves is described by $I = [I(+q) + I(-q)]/2$, where I is the average intensity change measured at equal q on either side of the center of the Bragg peak. Figure 2 shows the symmetric intensity of the diffuse scattering on a double logarithmic plot for (0002) reflection from three GaN samples. These curves indicate that there are two regions of linear behavior with different slopes, corresponding to $I \propto q^{-2}$ and $I \propto q^{-4}$, respectively. This suggests that the HDS region (I_H) for smaller q values and the SW scattering (I_{SW}) for larger q values are observed. Therefore, it is possible to determine the average radius R_{cl} of the clusters from the crossing point q_0 of the two straight lines, i.e., the q^{-2} dependence line of the HDS and the q^{-4} dependence line of the SW scattering, as shown in Fig. 2. Thus, $q_0 \approx 1/R_{cl}$. In fact, this method has been widely used for experimental estimate of defect cluster sizes[3,10,11].

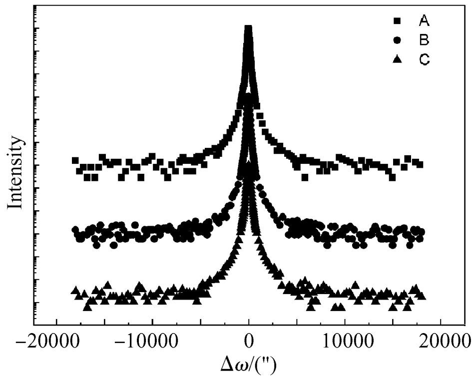

Fig. 1　Rocking curves around the (0002) XRD reflection in three GaN films

Furthermore, for $q > q_0$, the diffuse intensity decreases faster and then follows a relation of $I_{sw}(q)$-q^{-4}. It finally becomes less than the thermal diffuse scattering intensity I_T, which decreases slowly in

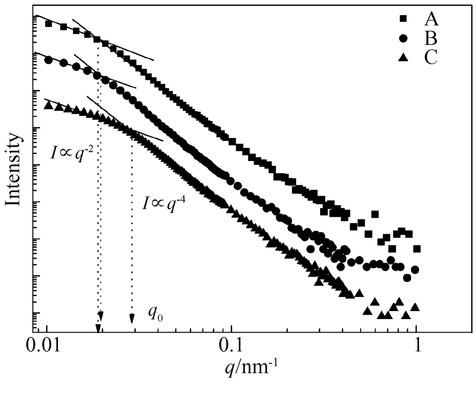

Fig. 2　Log-log (intensity versus q) plots of the symmetric part of the scattered intensity close to (0002) reflection for three samples　The data points (squares, circles, triangles) correspond to the ω scan intensity near the (0002) reflection of samples A, B, and C, respectively. The measured curves are fitted by 2 straight lines with 2 different slopes shown by solid lines corresponding to $I \propto q^{-2}$ and $I \propto q^{-4}$, respectively. The intersections of the two solid lines, q_0, are shown by the arrows.

Table 1 Results of HRXRD, PL, and Hall measurements

Sample	Screw dislocation density /cm^{-2}	Edge dislocation density /cm^{-2}	Cluster radius /nm	Cluster concentration /cm^{-3}	FWHM of NBE peak /meV	I_0/I_{YL}	Carrier mobility /(cm^2/(V·s))	Carrier concentration /cm^{-3}
A	7.2×10^7	3.1×10^8	52	9×10^{12}	28	1.6	700	6.8×10^{16}
B	6.8×10^7	2.2×10^8	51	1×10^{13}	31	1.7	600	1.1×10^{17}
C	1.1×10^8	6.3×10^8	35	4×10^{13}	28	0.5	150	1.3×10^{17}

analogy to I_H.[4] The intensity of the thermal diffuse scattering $I_T(q_T)$ can be used as an internal reference to scale the Huang intensity. Thus, one can obtain an expression for determining cluster concentration C_{cl} from Eq. (1)[3,14].

$$\frac{I_H(q_H)}{I_T(q_T)} = \frac{C_{cl}(\Delta V)^2}{k_B T/E} \times \frac{|q_T|^2}{|q_H|^2} \times \frac{\Pi(\boldsymbol{m},\boldsymbol{n})}{\widetilde{K}(\boldsymbol{m},\boldsymbol{n})} \qquad (1)$$

where k_B is the Boltzmann constant, T is the sample temperature, E is the Young modulus, ΔV is the change in the volume of the crystal produced by a single defect cluster, q_H is the wave vector in the HDS region, q_T is the analogous value in the thermal diffuse scattering region, and $\Pi(\boldsymbol{m},\boldsymbol{n})$ and $\widetilde{K}(\boldsymbol{m},\boldsymbol{n})$ are dimensionless factors of order 1 that depend on the unit vector $\boldsymbol{m}$ and $\boldsymbol{n}$, and on the elastic constants of the matrix. The ratio of $\Pi(\boldsymbol{m},\boldsymbol{n})$ to $\widetilde{K}(\boldsymbol{m},\boldsymbol{n})$ is of order 1. Thus, the corresponding defect cluster concentration C_{cl} can be estimated from the value of I_H/I_T.

Table 1 presents the density of screw and edge threading dislocations for GaN films, the mean radius R_{cl} and the density of defect clusters C_{cl}, and the results of Hall and PL measurements. It is found that the mean defect cluster radius decreases as the dislocation density of the samples increases. Meanwhile, the density of defect clusters seems to have a slight ascending tendency. As shown in Table 1, the cluster size (35nm) is the smallest and the cluster density (4×10^{13} cm^{-3}) is the highest for sample C, which has the highest screw and edge dislocation density in the investigated samples.

The lattice matrix may be distorted by point defects in the crystal. Therefore, in general there will be a long-range interaction between point defect and dislocations. Dislocations provide sites for the segregation of point defects. The accumulation of impurities or native defects at the dislocation lines is usually referred to as a "Cottrell atmosphere"[15]. We think that the same mechanism is valid for wide band gap group III-N materials. In view of the presence of a high density of dislocations ($10^8\sim10^{10}$cm^{-2}) in GaN epilayers grown on sapphire, it is reasonable to assume that the dislocation lines are suitable sites for the segregation of point defects like the nitrogen vacancy, oxygen[16] and carbon impurities, and their complexes. Therefore, we suggest that the defect clusters observed in GaN samples are related to the threading dislocations, and the density of defect clusters increases as the density of threading dislocations increases. Actually, both edge and screw dislocations may form defect clusters around them. As first reported by Chern *et al*., an open core type of nanopipes, 5～25nm in diameter were observed in nominally undoped GaN films grown by MOCVD, which contained threading dislocations with Burgers vectors 〈0001〉 (screw dislocations)[17]. The point defect species such as Ga interstitials and the impurities or its complexes may segregate around dislocations to form clusters. It seems that the stress fields of dislocation represented by the observed HDS are large enough and the point defects thus can be trapped in the vicinity of dislocation lines. Table 1 shows that the defect cluster concentration increases as the density of the threading dislocations increases. On the contrary, the cluster radius decreases at the same time. There seems to be a balance of the magnitude between cluster size and concentration. This result can be understood if the total concentration of point defects in these GaN films is assumed to be nearly a constant.

The Hall and PL results measured at room temperature are listed in Table 1. The carrier mobility decreases as the defect cluster concentration increases and as the cluster size decreases. However, a reverse dependence is observed for the carrier concentration in the investigated samples. Thus, statistically a lower defect cluster density may be related with a higher carrier mobility and a lower carrier concentration. In other words, the mobility is improved as the cluster size increases. As for the optical property of the measured GaN samples characterized by PL, it seems that there is not a remarkable correlation between the PL properties and the defect clusters in GaN samples. The FWHM of near-band-gap (NBE) luminescence peak is almost the same for all three samples, as shown in Table 1. However, sample C which has a higher defect cluster concentration, displays a lower ratio of I_0/I_{YL}, i.e., the ratio between the intensity of NBE luminescence peak I_0 and the intensity of yellow luminescence peak I_{YL}.

5　Conclusion

In summary, the defect clusters in GaN films grown by MOCVD are observed by the method of diffuse scattering using HRXRD. A fundamental correlation is found between the density of threading dislocations and the cluster density. The experimental results are explained based on a suggestion that the dislocations act as an ideal sink for the accumulation of the point defects, i.e., the dislocations play a role of "scavengers" for the point defects in the GaN films. Furthermore, with increasing cluster size and a corresponding decrease of the cluster density, the carrier mobility is improved.

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MOCVD 生长的 GaN 薄膜中缺陷团引起的 X 射线漫散射研究*

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摘要： 采用高分辨 X 射线衍射对在蓝宝石(0001)面生长的 GaN 外延膜的漫散射进行了研究.结果表明，GaN 薄膜中存在缺陷团，其浓度随着穿透位错密度的增加而增加，其平均半径呈相反趋势.基于位错是点缺陷的聚集区，缺陷团优先在位错附近形成的效应对结果进行了解释.同时发现电子迁移率随缺陷团浓度的增加而减少.

关键词： X 射线漫散射；GaN；缺陷团
PACC： 7870；6855；7850G
中图分类号： TN304　　**文献标识码：** A　　**文章编号：** 0253-4177(2008)07-1242-04

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* 国家自然科学基金(批准号：60506001，60476021，60576003)和国家重点基础研究发展规划(批准号：2007CB936700)资助项目

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2008-02-29 收到，2008-03-19 定稿