第25卷第11期 半 导 体 学 报 Vol. 25, No. 11
2004年11月 CHINESE JOURNAL OF SEMICONDUCTORS Nov., 2004

Etch-Pits of GaN Films with Different Etching Methods*

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Abstract: High quality GaN films on (0001) sapphire substrates were grown by a commercial MOCVD system (Thomas Swan Corp.). The etch pits and threading dislocations(TDs) in GaN films have been studied by chemical etching methods such as mixed acid solution (H_3PO_4 : H_2SO_4 = 1 : 3) and molten KOH, HCl vapor etching method, scanning electron microscope (SEM) and transmission electron microscope(TEM). SEM images of the same position of GaN films with HCl vapor etching and wet etching methods show notably different densities and shapes of etching pits. The results indicate that HCl vapor etching can show pure edge, pure screw and mixed TDs, mixed acid solution can show pure screw and mixed TDs and molten KOH wet etching only can show pure screw TDs.

Key words: GaN; EPD; TD
PACC: 4255P; 7360L; 7865P
CLC number: TN304.23 **Document code**: A **Article ID**: 0253-4177(2004)11-1376-05

1 Introduction

The large lattice mismatch(16%) and thermal expansion coefficient mismatch between GaN and sapphire substrate generally cause high-density threading dislocation (TD) in the GaN epilayer[1~3]. TDs are very harmful to electronic and optoelectronic devices, so TD density is a very critical parameter to GaN films. There have been a number of publications on characterization of defects in epitaxial GaN films on (0001) sapphire substrates. Although characterization techniques commonly used are EPD (etch-pits density)[4,5] and TEM[6~9], a careful survey of literature shows that there is considerable discrepancy between the results obtained by EPD with different etching methods. EPD with different etching methods in different samples or different regions of the same sample has been widely studied, however, EPD with different etching methods in the same region of the same sample has been seldom studied, which may give new idea of property of etch-pits with different etching methods.

2 Experiment

In this letter, mixed acid solution (H_3PO_4 : H_2SO_4 = 1 : 3) and molten KOH are used as wet etching media, and HCl is supplied as vapor etching medium. Etch pits and TDs are observed by SEM and TEM, respectively.

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* Project supported by National Natural Science Foundation of China(Nos. 60077022, 60276034), National High Technology Research and Development Program of China(Nos. 2001AA313110, 2001AA313060, and 2001AA313140), and the Opening Project of the State Key Laboratory for Integrated Optoelectronics

Received 23 December 2003, revised manuscript received 21 June 2004

Sample A consisted of 1.3μm GaN layer capped with 2.7μm Si doped n-GaN layer, and sample B consisted of a 0.8μm GaN layer capped with a 1.5μm Mg doped p-GaN layer. Both samples were grown by a low-pressure metal-organic chemical vapor deposition system (Thomas Swan vertical flow reactor) on *c*-plane sapphire substrates with diameter of 50mm. The regular two-step grown technique[2] was applied in this experiment. TMGa and NH_3 were used as Ga and N precursors, respectively. Sample B for SEM were annealed in N_2 at 900℃ for 3min to activate p-type dopant. In order to observe the same position of samples, a mark was made on sample B by FIB (focus ion beam). The etching conditions are 280℃ in mixed acid solution (H_3PO_4 : H_2SO_4 = 1 : 3), 240℃ in molten KOH[10,11] and 600℃ in mixed HCl vapor (N_2 : HCl = 5 : 1)[12], respectively. The SEM observations were performed using JEOL130 microscope, operated at 15~20kV. TEM observations were carried out with Hitachi-9000 microscope operated at 300kV.

3 Results and discussion

Figure 1 shows a plan-view SEM image of GaN film etched in molten KOH. The etch pits, as clearly shown in Fig. 1, are all in the similar contrast, and are all well-developed hexagonal with plain edges and {$10\bar{1}1$} facets in different sizes from 0.2μm to 1.8μm (most etch pits in the size of 0.7μm), which means the origin of etch pits is the same (maybe from pure screw TDs). The smallest pit A in size of 0.2μm and the largest pit B in size of 1.8μm are both isolated, moderate pits C1 and C2 in size of 0.7μm and 1.3μm can be seen clearly as the different pits in the overetched area. So it shows that the etch pits are not distributed uniformly and etch pits density is reliable. Figure 1(b) shows clearer SEM micrograph with higher magnification. Through Fig. 1(a) the EPD can be estimated about $4\times10^7/cm^2$. Figure 2 shows a plan-view SEM image of GaN film etched in mixed acid solution. The etch pits are also not distributed uniformly and they are in different sizes from 0.1μm to 0.5μm (most in the size of 0.4μm) with different contrast. The EPD estimated from Fig. 2 is about $5\times10^8/cm^2$, which is one order larger than that in Fig. 1. It shows that there are more origins of etch-pits in Fig. 2 than that in Fig. 1.

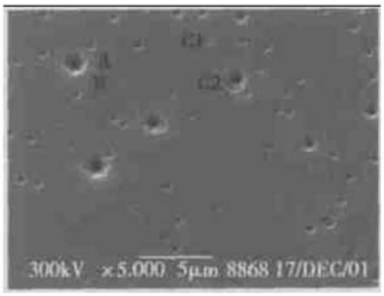

Fig. 1 Plan-view SEM images of sample A, etched in molten KOH (240℃, 13min) The etch-pits density is measured to be $4\times10^7/cm^2$.

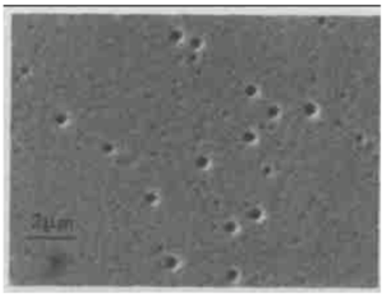

Fig. 2 Plan-view SEM images of sample A, etched in mixed acid solution (H_3PO_4 : H_2SO_4 = 1 : 3) (280℃, 15min) The etch-pits density is measured to be $5\times10^8/cm^2$.

Figure 3 shows a cross-section TEM micrograph of GaN film with $\boldsymbol{g} = 1\bar{1}00$. The GaN template on (0001) sapphire consists of a thick sapphire layer (zone A), a 50nm GaN buffer layer (zone B), a 1.3μm undoped GaN epitaxial layer (zone C) and a 2.7μm Si-doped n-GaN epitaxial layer (zone D). It is highly defective in buffer layer and TDs clearly appear near the interface between buffer layer and GaN epitaxial layer. TDs lines are almost normal to the surface of GaN films owing to the mirror image force between TDs and free surface of GaN film[10]. The inset is a selective area electron diffraction (SAED) pattern of GaN epitaxial layer, which gives the direction of **g** vector[11]. Based on the contrast-invisibility criterion[12], i.e., $\boldsymbol{g}\cdot\boldsymbol{b}=0$ for pure screw dislocations, $\boldsymbol{g}\cdot\boldsymbol{b}=0$ *and* $\boldsymbol{g}\cdot(\boldsymbol{b}\times\boldsymbol{L})=0$ for pure edge dislocations. Here **g**, **b** and **L** stand for the vectors of diffraction beam, Burgers vector and dislocation lines, respectively. In GaN epitaxial film grown on (0001) sapphire substrate **b** parallels $\langle 0001\rangle$ for pure screw dislocations, $1/3\ \langle 11\bar{2}0\rangle$ for pure edge dislocations and **L** parallels $\langle 0001\rangle$ for any TDs[13], so we can conclude that in TEM it is invisible with **g** normal to $\langle 0001\rangle$ for pure screw TDs and parallel to $\langle 0001\rangle$ for pure edge TDs. So in Fig. 3 both pure edge dislocations and mixed TDs ($\boldsymbol{b}=1/3\ \langle 11\bar{2}3\rangle$) could be observed, but they can not be distinguished. Supposing TDs distribute anisotropically, we can get TDs density about $1.837\times10^9/\mathrm{cm}^2$ from Fig. 3.

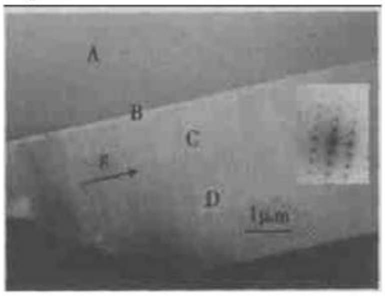

Fig. 3 Cross-section TEM image of sample A with **g** $=\bar{1}100$ The inset is an SAED pattern of sample A. The TDs density is measured to be $1.837\times10^9/\mathrm{cm}^2$.

Figure 4 shows another cross-section TEM micrograph of GaN film with $\boldsymbol{g}=03\bar{3}\bar{2}$. From discussion above, all three types of TDs can be observed in Fig. 4 and the TD density is $1.934\times10^9/\mathrm{cm}^2$ from Fig. 4. Comparing the TD densities measured from Figs. 3 and 4, one can calculate the pure screw TD density to be $9.7\times10^7/\mathrm{cm}^2$, which is similar as EPD in Fig. 1. It can also be verified that etch-pits only generate at pure screw TDs etched in molten KOH. Comparing the TD densities measured from Figs. 2 and 3, it may reveal that mixed acid solution can show pure screw and mixed TDs and the mixed TD density is about $4.6\times10^8/\mathrm{cm}^2$, pure edge TD density is about $1.377\times10^9/\mathrm{cm}^2$.

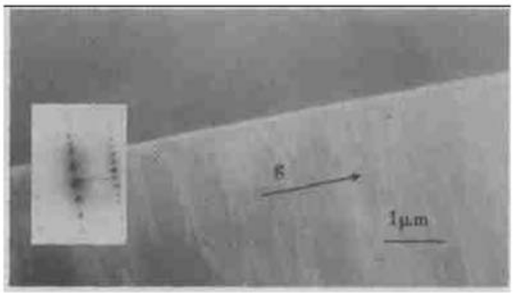

Fig. 4 Cross-section TEM image of sample A with **g** $=03\bar{3}\bar{2}$ The inset is an SAED pattern of sample A. The TDs density is measured to be $1.934\times10^9/\mathrm{cm}^2$.

Sample B was etched in molten KOH for 5min, then in molten KOH for more 5min, then in molten KOH for more 5min, then in mixed acid solution for more than 10min and finally in mixed HCl vapor for more than 10min. Figs. 5(b), (c), (d), (e) and (f) show a plan-view SEM image of same position of sample B described above. In the left region of Fig. 5(a) a black orthogonal mark was made by FIB to track the same position of sample B.

The etch pits, as clearly shown in Figs. 5(b)~(d), are strict hexagonal with plain edges and $\{10\bar{1}1\}$ facets. Through Figs. 5(b)~(d), the etch-pits became bigger with increasing etching time in molten KOH, but the EPD (about $2.0\times10^8/\mathrm{cm}^2$) was not changed which could be revealed by observing the surroundings of pit M. When etched in mixed acid solution for more than 10min, etch pits became bigger and many more small faint etch pits were produced from Fig. 5(e). The EPD was about $2.5\times10^9/\mathrm{cm}^2$. Etched in mixed HCl vapor for more than 10min many more non-hexagonal etch pits were produced through Fig. 5(f). The EPD was about $4.0\times10^9/\mathrm{cm}^2$.

We can confirm that molten KOH can reveal one kind of etch pits with strict hexagonal with plain edges and $\{10\bar{1}1\}$ facets which correspond with pure screw TDs[14], and mixed acid solution can show two kinds of etch pits which correspond with pure screw and mixed TDs, and mixed HCl vapor can show three kinds of etch pits which correspond with pure screw and mixed and edge TDs[15, 16]. So EPD revealed by mixed HCl vapor is the most credible estimation of TDs in GaN films.

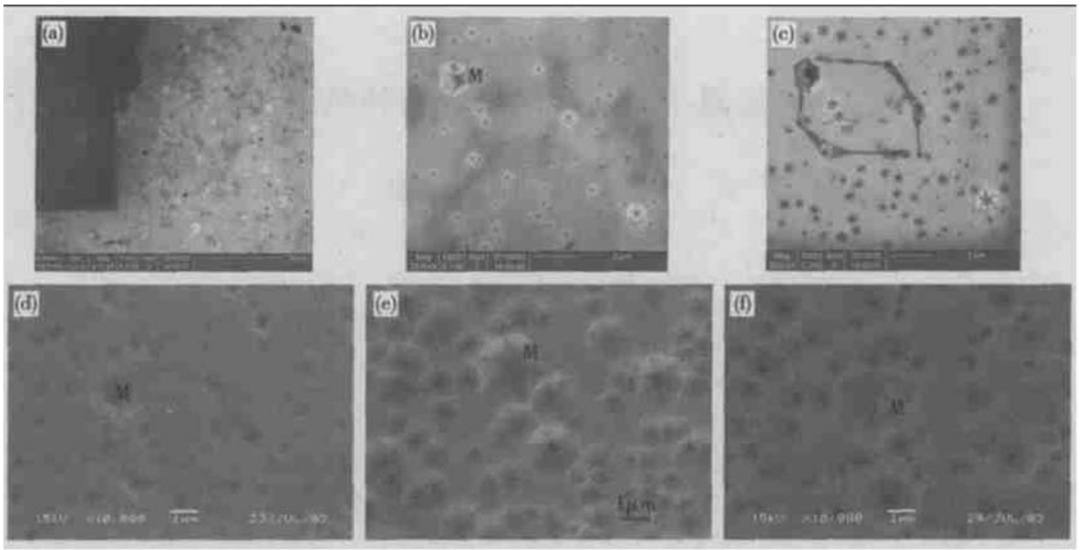

Fig. 5 Plan-view SEM images of sample B etched with different methods In the left region of Fig. 5(a) a black orthogonal mark was made by FIB to track the same etch pit M of sample B.

4 Conclusion

The density and characteristic of etch-pits in GaN films has been studied by wet and vapor etching methods, SEM and TEM. HCl vapor etching can show pure screw, pure edge and mixed TDs, while wet etching by molten KOH only can show pure screw TDs and etching with mixed acid solution can show pure screw and mixed TDs.

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对GaN薄膜不同腐蚀方法的腐蚀坑的研究*

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摘要: 用Thomas Swan公司的MOCVD系统在蓝宝石(0001)面上生长了高质量的GaN薄膜.采用多种化学腐蚀方法,如熔融KOH, H_3PO_4与H_2SO_4混合酸和HCl气相腐蚀法,利用SEM及TEM技术对GaN薄膜中的位错进行了研究.SEM显示在GaN薄膜相同位置处,不同腐蚀法所得的腐蚀坑的形态和密度有明显差别.结果表明HCl气相腐蚀可以显示纯螺位错、纯刃位错和混合位错; H_3PO_4与H_2SO_4混合酸腐蚀可以显示纯螺位错和混合位错;而熔融KOH腐蚀仅能显示纯螺位错.

关键词: 氮化镓; 腐蚀坑密度; 穿透位错
PACC: 4255P; 7360L; 7865P
中图分类号: TN304.23 **文献标识码**: A **文章编号**: 0253-4177(2004)11-1376-05

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* 国家自然科学基金(批准号: 60077022, 60276034), 国家高技术研究发展计划(批准号: 2001AA313110, 2001AA313060和2001AA313140)和集成光电子国家重点实验室开放课题资助项目

2003-12-23收到, 2004-06-21定稿