Wet Oxidation of $Al_xGa_{1-x}As$/ GaAs Distributed Bragg Reflectors*

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Abstract: The wet oxidation of AlGaAs with high Al content in a distributed Bragg reflectors (DBR) is studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Some voids distribute along the oxide/ GaAs interfaces due to the stress induced by the wet oxidation of the AlGaAs layers. These voids decrease the shrinkage of the Al_2O_3 layers to 8% instead of the theoretical 20% when compared to the unoxidized AlGaAs layers. With the extension of oxidation time, the reactants are more completely transported to the front interface and the products are more completely transported out along the porous interfaces. As a result, the oxide quality is better.

Key words: wet oxidation; vertical cavity surface emitting laser; distributed Bragg reflectors; Al_2O_3; interface

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1 Introduction

The vertical cavity surface emitting laser (VCSEL) offers various advantages over other light sources, including a symmetrical output beam and ease of manufacturing in the form of two-dimensional arrays. In fact, it has now replacing the standard edge-emitting laser and light emitting diode (LED) in many optical data communications applications. In recent years, advances in VCSELs, such as ultralow thresholds[1] and high efficiencies[2], are attributed to the wet oxidation of high Al composition III-V compounds[3]. The wet oxidation process can proceed laterally (along heterolayers) to create buried apertures that can not only guide electron and hole currents but also provide a lateral refractive index contrast in the active layers of the VCSEL. Furthermore, wet oxidation also forms high refractive-index contrast Al_xO_y/ GaAs Bragg reflectors instead of the usual low contrast AlGaAs/ GaAs DBRs. Compared with the conventional AlGaAs/ GaAs DBR, the oxidized Al_xO_y/ GaAs DBR can increase the mirror band width, elevate the reflectivity of DBR, and reduce the number of pairs in the mirror, which is useful to decrease the growth thickness and growth time of a VCSEL[4~6]. As a result, a VCSEL utilizing oxidized aperture and oxidized DBR demonstrates improved performance, such as high power conversion efficiency, low threshold current, and low threshold voltage[3,5,7].

Although there is a lot of research on the wet oxidation of AlGaAs/ GaAs DBR, most of it about the microstructures and components of the oxides[6,8~10], the porous oxide/ GaAs interfaces (especially their effects) are seldom studied. In this paper, by means of scanning electron microscopy

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(SEM) and transmission electron microscopy (TEM), we investigate the effects of the porous interfaces on the oxide quality of DBR and the contraction of oxidized AlGaAs layers.

2 Experiment

The samples used in this work were grown by molecular beam expitaxy (MBE) on (100) SI GaAs substrates. First, a 200 nm thick undoped GaAs buffer layer was grown. Then a seven-period undoped DBR was grown, each period including a $Al_xGa_{1-x}As$ layer and a GaAs layer. After photolithography and wet etching (H_2SO_4 ∶ H_2O_2 ∶ H_2O = 5 ∶1 ∶1), 136μm-wide trenches spaced 64μm apart were formed. Then, the samples were oxidized in a quartz furnace at above 400 ℃ though water vapor with nitrogen flow, the oxidation time being 12, 20, 40min, respectively. Oxidation, as is well known, proceeds laterally in the $Al_xGa_{1-x}As$ layers of DBR, beginning at the edge defined by chemical etching and proceeding inwards. Specimens from the unoxidized and oxidized samples were prepared for DCXRD and cross-sectional SEM experiments. The oxidized samples for TEM observation were mechanically polished and ion thinned by Ar^+ in standard fashion.

3 Results

The DCXRD rocking curves of the as-grown DBR are shown in Fig. 1. From the measured and simulated curves, we can determine that the Al composition is 0.97 and the thickness of the $Al_xGa_{1-x}As$ layer and GaAs layer in each period is 152.7nm and 70nm, respectively, which are almost in agreement with our design. Moreover, the narrow line width and the large number of satellite peaks indicate that the quality of the as-grown materials is good.

During the wet oxidation, aluminium atoms in AlGaAs layers react with water vapor, probably forming Al_2O_3 with γ, δ, and χ phase in which the

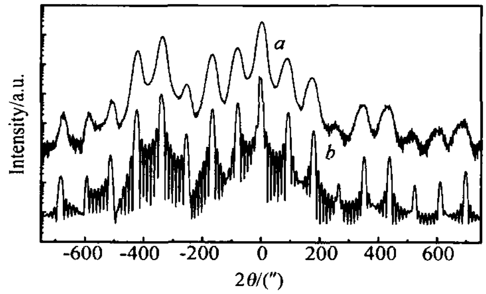

Fig. 1 DCXRD rocking curves of the as-grown $Al_xGa_{1-x}As$/GaAs DBR Curve *a*: the measured curve; Curve *b*: the simulated curve

γ-Al_2O_3 phase is dominant. In general, some hydroxyl phases besides Al_2O_3, such as $Al(OH)_3$ and AlO(OH), are also obtained[8~11]. The structures of AlGaAs and GaAs are both zinc blend, while that of γ-Al_2O_3 is spinelle. Since the volume per Al atom in $Al_{0.97}Ga_{0.03}As$ is significantly larger than that in γ-Al_2O_3, there should theoretically be 20% linear contraction of the γ-Al_2O_3 layer along the growth direction compared with the as-grown AlGaAs layer[9]. As a result, the shrinkage would produce stress that can greatly affect the mechanical and optical properties of oxidized DBR, such as delamination or small fracture of the oxide films after complete oxidation[10]. The interfaces of the oxide/GaAs layers can not stand so great a stress and ultimately fissure. Figure 2 is the TEM images of the sample oxidized for 20min. From Fig. 2(a), we can see that the oxidized $Al_{0.97}Ga_{0.03}As$ region is well confined by a convex-shape oxidation front. We can also clearly observe the voids. Figure 2(b) indicates that these voids (as pointed to by arrows) primarily distribute along the side interfaces between the Al_2O_3 and unoxidized GaAs layers. In turn, these voids release the stress induced by the wet oxidation of the AlGaAs layers. As a result, the oxide layers can not shrink as much as the expected 20%. In our experiments, the oxide layers only shrink about 8% along the growth direction.

Figure 3 shows cross-sectional SEM images of DBR as-grown, oxidized for 12, 20, and 40min, respectively (the dark layers are unoxidized and oxi-

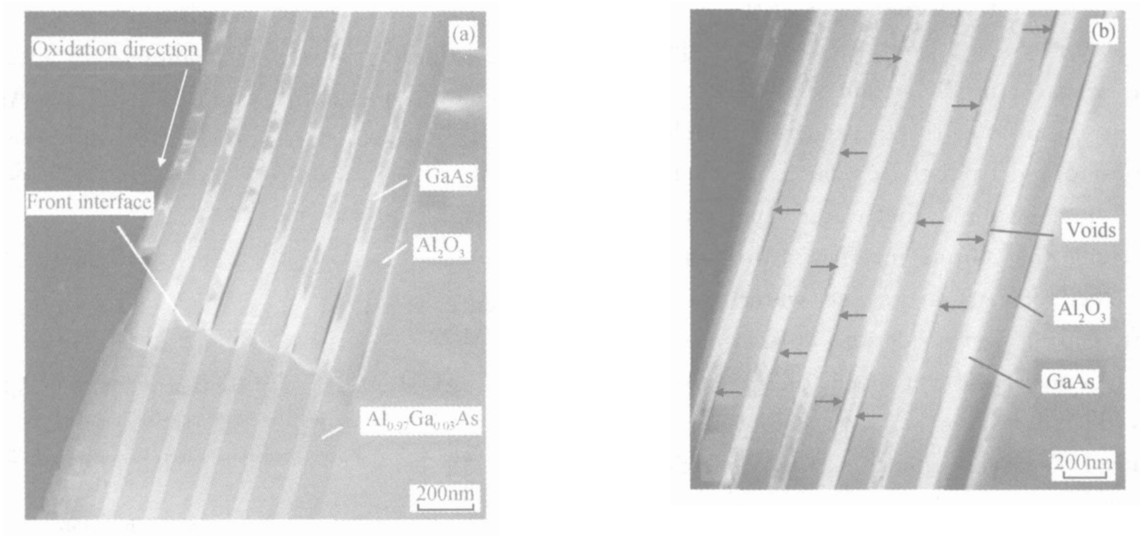

Fig. 2　Cross-sectional TEM image of DBR oxidized for 20min

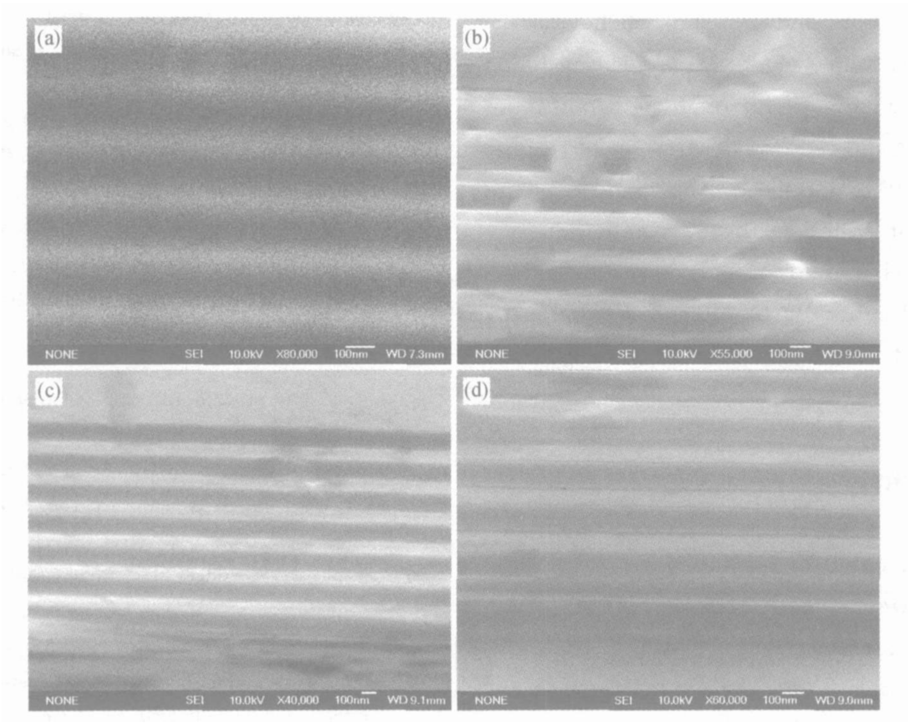

Fig. 3　Cross-sectional SEM images of DBR　(a) As-grown; (b) Oxidized for 12min; (c) Oxidized for 20min; (d) Oxidized for 40min

dized AlGaAs and the bright layers are GaAs). We can see that the longer the oxidation time is, the better the oxide quality and the smoother the oxide/ GaAs interface. In the process of oxidation, the reactions are as follows[8]:

$$AlGaAs + H_2O \rightarrow Al_2O_3 + AsH_3 + Ga$$

$$AlGaAs + H_2O \rightarrow AlO(OH) + AsH_3 + Ga$$

$$AlGaAs + H_2O \rightarrow Al(OH)_3 + AsH_3 + Ga$$

$$Ga + H_2O \rightarrow Ga_2O_3 + H_2$$

$$AsH_3 + H_2O \rightarrow As_2O_3 + H_2$$

$$As_2O_3 + H_2 \rightarrow As + H_2O$$

As shown above, the interfaces of the oxide/ GaAs layers are porous and they can serve as channels to transport reactants and products. When the oxidation front propagates inwards in $Al_{0.97}Ga_{0.03}$-As layers, the reactants (such as H_2O) have to be transported to the front interface and the products (such as AsH_3, As_2O_3 and As) are transported out. The voids along the oxide-semiconductor interfaces are in favor of the transport of the chemical species to and from the oxidation front. If the oxidation time is so long that water vapor can fully diffuse along the porous interfaces, the reactions between the AlGaAs layers and water are more complete. During wet oxidation, arsenic atoms in the AlGaAs layers are converted to AsH_3, As_2O_3, and As, which can serve as main volatile species for the removal of arsenic elements from the oxidized films[8]. We anticipate the residual arsenic element in the oxides to be as little as possible because high residual arsenic can deteriorate the capabilities of VCSEL, such as *C-V* and transport behavior[10]. Consequently, continued oxidation or heating helps these arsenic products to be remove through the porous interfaces and reduces the content of residual arsenic. In our experiments, the quality of the DBR oxidized for 40min is the best and that oxidized for 12min is the worst. Therefore, the oxidation time should generally be kept long enough to complete the wet oxidation of the high Al content layers.

4 Conclusion

The porous oxide/ GaAs interfaces and their effects during wet oxidation of $Al_{0.97}Ga_{0.03}As$/ GaAs DBR are studied. The TEM images show there are some voids along the oxide/ GaAs interfaces due to the stress induced by the wet oxidation of the AlGaAs layers. These voids decrease the shrinkage of the Al_2O_3 layers to 8 % instead of the theoretical 20 % compared with the as-grown AlGaAs layers. The SEM images show that with the extension of the oxidation time the quality of the oxide layers is better in that the diffusion of water in the oxide layers is more complete. In addition, the removal of volatile products, such as AsH_3, As_2O_3, and As, is more sufficient through the porous oxide/ GaAs interfaces, which benefits the capabilities of the VCSEL.

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$Al_xGa_{1-x}As/GaAs$ 分布布拉格反射镜的湿法氧化 *

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摘要: 对垂直腔面发射激光器(VCSEL)的 $Al_xGa_{1-x}As/GaAs$ 分布布拉格反射镜(DBR)进行了高温湿法氧化. 由于 $Al_xGa_{1-x}As$ 层的氧化产生了应力而导致 $Al_2O_3/GaAs$ 界面处出现了孔洞. 这些孔洞反过来又缓解了应力而使氧化层的厚度只收缩了 8 %而不是理论上的 20 %. 并且,随着氧化时间的延长,湿法氧化反应中的反应物和产物沿着多孔界面在氧化物中的传输越充分,从而使 AlGaAs 层的氧化进行的越完全,氧化质量就越好.

关键词: 湿法氧化; 垂直腔面发射激光器; 分布布拉格反射器; Al_2O_3; 界面

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