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In-situ Monitoring of AlGaAs Growth by Reflectance Anisotropy Spectroscopy in MOCVD

XU Hua-wei[1,2], ZHANG Jin-long[1], NING Yong-qiang[1*], ZENG Yu-gang[1], ZHANG Xing[1]

(1. *State Key Laboratory of Luminescence and Application*, *Changchun Institute of Optics*, *Fine Mechanics and Physics*, *Chinese Academy of Sciences*, *Changchun* 130033, *China*;
2. *Graduate University of the Chinese Academy of Sciences*, *Beijing* 100039, *China*)

Abstract: The MOCVD growth of $Al_xGa_{1-x}As$ for application in high-power laser diodes was studied by using time resolved reflectance anisotropy spectroscopy (RAS) and normalized reflectance (NR) were studied. Multi-layer $Al_xGa_{1-x}As$ structures with different Al compisition were grown on GaAs (001) substrates. The most suitable photon energy for monitoring the growth process was investigated. The NR and RAS signals at photon energy near the fundamental band gap showed an oscillatory behavior during the growth. The different contribution of surface-induced optical anisotropy and interface-induced optical anisotropy could be distinguished in situ by RAS transient spectra. The intensities of the RAS and NR signals were strongly dependent on the aluminium composition.

Key words: epitaxial growth; metal-organic chemical vapor deposition; reflectance anisotropy spectroscopy;
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1 Introduction

GaAs lattice-matched $Al_xGa_{1-x}As$ epilayers were usually used as active region or DBR pairs in optoelectronic devices such as vertical surface emitting lasers (VCSELs)[1-2] and edge-emitting lasers (EELs). Therefore, it is highly desired to precisely control the aluminium composition, growth rate and the interface of multilayer structure in metal-organic chemical vapor deposition (MOCVD) to ensure high crystalline quality and device properties. In situ reflectance anisotropy spectroscopy (RAS)[3] and normalized reflectance (NR) measurements have been proved a powerful tool for the development of growth processes for optoelectronic device structures[4]. RAS transient spectra[5] can be used to monitor the growth of distributed Bragg reflector and multi-quantum wells. A simple three-phase approach to analyze the optical anisotropies of semiconductor heterostructure was introduced by Yasuda *et al*[6], however, the lattice mismatch between Ⅲ-Ⅴ and Ⅱ-Ⅵ materials could cause strain effect. The upper limit for the thickness of the AlAs/GaAs surface and interface layers could be determined[7], the lattice constants of GaAs and AlAs were nearly the same and therefore lattice matched growth without any additional strain effects can be performed for the growth of $Al_xGa_{1-x}As$ epilayer. Unfortunately, this experimental process was very complicated under unfavorable growth conditions.

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Biography: XU Hua-wei, born in 1982, male, Jilin Province. His work focuses on high power diode laser grown by metal-organic chemical vapor deposition (MOCVD).
E-mail: xuhwciomp@163.com, Tel: (0431)86176335.
*: Corresponding Author; E-mail: ningyq@ciomp.ac.cn, Tel: (0431)86176348

In this paper, the way to establish suitable photon energy for monitoring growth process was described in detail. From the measured RAS transient spectra of $Al_xGa_{1-x}As$ layers, different contribution of surface-induced optical anisotropy and interface-induced optical anisotropy was investigated. At last, it was found that the intensities of the RAS and NR signals were strongly dependent on the aluminium composition.

2 Experiments

The sample was grown on GaAs (001) substrates by a horizontal low-pressure metal-organic chemical vapor deposition (LP-MOCVD) reactor (Aixtron 200/4). The group Ⅲ source materials were trimethylgallium (TMGa) and trimethyaluminium (TMAl) with the temperature of 0 ℃ and 17 ℃, respectively, while pure arsine (AsH_3) was used as for group Ⅴ source with palladium-purified hydrogen as carrier gas. All the epitaxial layers were grown at the same temperature of 710 ℃ with a Ⅴ/Ⅲ ratio of 60. The pressure in the reactor was 13.3 Pa. The scanning electron microscope (SEM) image of multi layer $Al_xGa_{1-x}As$ sample was shown in Fig. 1.

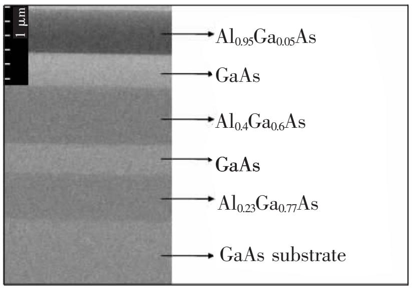

Fig. 1 SEM image of multi layer $Al_xGa_{1-x}As$ sample

The MOCVD reactor was equipped with a standard quartz view-port for in-situ optical measurement. The in-situ measurement was performed with an EpiRAS 200 spectrometer mounted above the normal incidence view-port of the reactor. The schematic optical structure was described in detail in Refs [8-9]. The difference between the complex reflectances of linear polarized light along the two principal axes on the surface was measured. The signals are usually the order $|\Delta r/r| < 10^{-3}$. For the (001) GaAs surface, the RAS signal is given by[8,10]:

$$\frac{\Delta r}{r} = 2\frac{r_{[\bar{1}10]} - r_{[110]}}{r_{[\bar{1}10]} + r_{[110]}} = \mathrm{Re}\left(\frac{\Delta r}{r}\right) + \mathrm{iIm}\left(\frac{\Delta r}{r}\right), \quad (1)$$

Where $r_{[\bar{1}10]}$ and $r_{[110]}$ are the complex reflectances of linear polarized light along the two principal axes $[\bar{1}10]$ and $[110]$ on the $[001]$ surface, respectively, $(r_{[\bar{1}10]} + r_{[110]})/2$ is the averaged reflectance. In this work, only the real part of the spectra $\mathrm{Re}(\Delta r/r)$ will be discussed, since a small residual strain in the reactor window is likely to affect the imaginary part of $\Delta r/r$.

3 Results and Discussion

3.1 Determination of The Photon Energy for In-situ Monitoring of Growth Process

For GaAs (001) surface, the As-rich (4×4) and Ga-rich (2×6) reconstructions (Fig. 2) are predominant under MOCVD growth conditions[11]. All the epitaxial layers were grown at 710 ℃ with a high Ⅴ/Ⅲ radio of 60. Under As-rich environment, the typical c(4×4) reconstruction (minimum at 2.6 eV from As-dimers) was obtained.

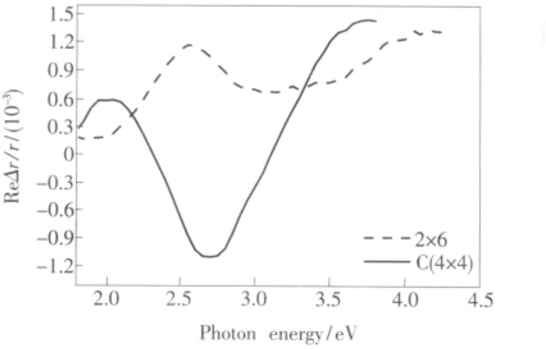

Fig. 2 RAS spectra of GaAs (001) surface reconstruction

When choosing the photon energy for monitoring $Al_xGa_{1-x}As$. A trade-off between surface sensitivity and sensitive to the changes of reflectance has to be considered. The photon energy highly sensitive to NR signal for different aluminium composition could be obtained at about 2.6 eV photon energy as shown in Fig. 3(b). RAS signal is highly sensitive to the composition of $Al_xGa_{1-x}As$ in the photon energy range from 3.5 ~ 3.9 eV as shown in Fig. 3(a). However, high photon energy was not suitable for the calculation of the growth rate and the composition of $Al_xGa_{1-x}As$. Furthermore, photon energy near the bandgap of $Al_{0.95}Ga_{0.05}As$ was needed to get the oscillation in RAS transient spectra. Therefore, a photon energy of 1.9 eV was chosen as a monitoring photon energy for the growth process of $Al_xGa_{1-x}As$ epilayer.

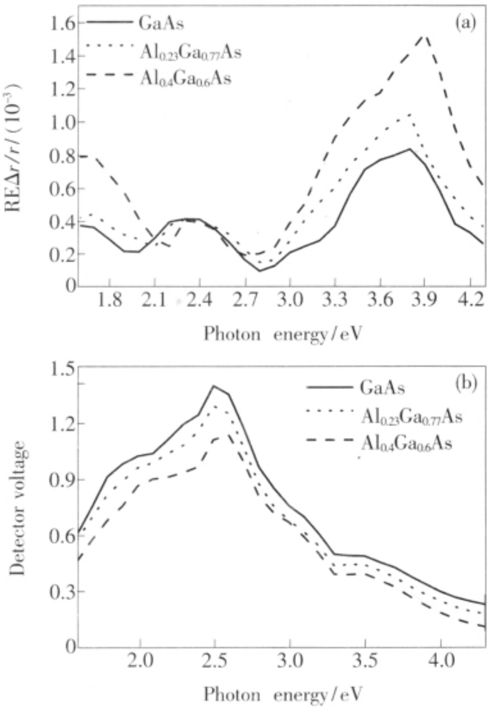

Fig. 3 The spectra were taken at $T = 710$ ℃ with the Al composition $x = 0, 0.23, 0.4$, (a) RAS spectra of $Al_xGa_{1-x}As$; (b) Detector voltage spectra of $Al_xGa_{1-x}As$.

For a transparent layer, the reflectance is a periodic function of the thickness at the monitoring photon energy. The growth rate can be determined from the oscillation period. Therefore the NR transient spectra show oscillation characteristic if the layer thickness d satisfies the requirement $d > \lambda$. The refractive index n and $\lambda/2n$ at the growth temperature of 710 ℃ was obtained from Refs [12], as shown in Table 1. The layer thickness of our sample should be over 100 nm in order to get the oscillation characteristic in NR transient spectra.

Table 1 Refractive index n of $Al_xGa_{1-x}As$ for $x = 0, 0.23, 0.4, 0.95$ at the growth temperature of 710 ℃

Material	n	)
GaAs	3.810	85.56
$Al_{0.23}Ga_{0.77}As$	4.152	78.52
$Al_{0.4}Ga_{0.6}As$	3.765	86.59
$Al_{0.95}Ga_{0.05}As$	3.267	99.79

3.2 Determination of The Different Contribution of Surface-induced Optical Anisotropy and Interface-induced Optical Anisotropy

The RAS signal is mainly caused by the optical anisotropy of the surface reconstruction. However. the optical anisotropy of the interface reconstruction also contributes to the RAS signal when the distance of the interface to the surface are smaller than the penetration depth of the incident light. Our sample (Fig. 1) is specifically designed to study the interface-induced optical anisotropy between $Al_xGa_{1-x}As$ and GaAs layer. $Al_{0.95}Ga_{0.05}As$ has a significantly higher bandgap than GaAs. Therefore, the interface-induced optical anisotropy of $Al_{0.95}Ga_{0.05}As$/GaAs interface can be easily detected because the incident light penetrates into $Al_{0.95}Ga_{0.05}As$ layer more deeper at the photon energy of 1.9 eV. Moreover, the lattice constants of GaAs and $Al_{0.95}Ga_{0.05}As$ are almost the same and therefore lattice matched growth without any strain effects is realized. In this work, we select the time-resolved mode in order to get the whole growth process information.

Time-resolved RAS is measured at a photon energy of 1.9 eV (652 nm) where the penetration depth of $Al_{0.95}Ga_{0.05}As$ layer is very large because the photon energy is near the bandgap of $Al_{0.95}Ga_{0.05}As$. The RAS signal shows a significant oscillatory behavior (Fabry-Perot-like oscillations) which is not observed in the growth process of GaAs epilayers as shown in Fig. 4. For smaller bandgap such as $Al_{0.25}Ga_{0.75}As$ or $Al_{0.4}Ga_{0.6}As$ layers, the oscillations damp out faster than that of $Al_{0.95}Ga_{0.05}As$ layer as the thickness increases. This is due to the fact that the penetration depth of light for these layers are smaller than the thickness. The RAS oscillations are mainly caused by the GaAs/$Al_xGa_{1-x}As$ interface reconstruction and can be interpreted as the real information of the interface-induced optical anisotropy. The RAS value is the same during and after the oscillations (dash-dotted line in Fig. 4), so there is no defects formation in the GaAs/$Al_xGa_{1-x}As$ interface which can contribute to the interface-induced optical anisotropy. Therefore, from the RAS transient spectra, we can analyze the different contribution of surface-induced optical anisotropy and interface-induced optical anisotropy. Furthermore, a comparison of the RAS of the AlGaAs layers during and after the oscillation gives information on defect formation.

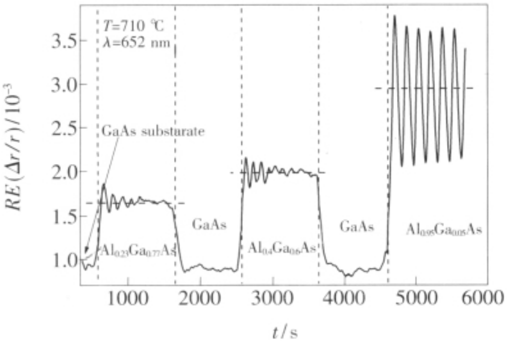

Fig. 4 Time-resolved reflectance anisotropy spectroscopy (RAS) taken at 1.9 eV during the growth of $Al_xGa_{1-x}As$ with increasing aluminum composition

We need to pay attention to that the oscillation are not comparable to RAS/RHEED monolayer growth oscillations which occur on a time scale of seconds[13], moreover, RAS/RHEED oscillations can not be observed at such a high temperature. And it is different with doping-induced RAS oscillations, because we do not intentionally dope in the growth of all the epilayers.

3.3 Composition Dependence of RAS and NR

A clear change in the energy position of the main peak (at about 3.8 eV) can be seen in Fig. 3(a). The energy position of the main peak shifts to higher energies as the aluminium composition increases. This dependence can be correlated to the aluminium dependence of the E_1 feature in the band structure[14].

The difference of the RAS level increases with aluminum compositions as shown in Fig. 4, dependence is related to the surface stoichiometry. From this difference, an estimation of the composition can be obtained. However, RAS signal is very sensitive to surface properties, therefore an absolute composition determination should based on a bulk related effect.

Fig. 5 shows the NR transient spectra during growth of $Al_xGa_{1-x}As$ structures at a photon energy of 1.9 eV in a single run. The NR signal shows a significant dependence on the aluminium compositions in $Al_xGa_{1-x}As$ layer, and the amplitude of the Fabry Perot oscillations increase with increasing aluminium compisition, due to the larger difference of the refractive index between GaAs and $Al_xGa_{1-x}As$. The oscillation of epilayer with high aluminium composition decayed more slowly than that of the low composition, due to the decrease of the absorption coefficient with the increase of aluminium composition[15].

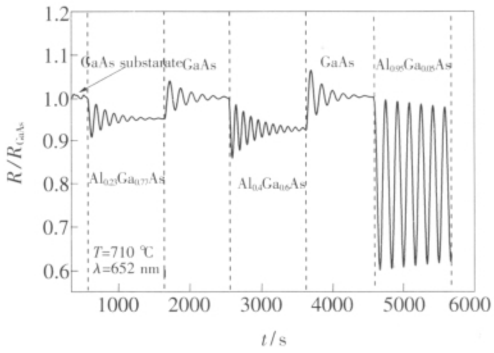

Fig. 5 Time-resolved normalized reflectance (NR) measurement during growth of $Al_xGa_{1-x}As$ structures at 1.9 eV

4 Conclusion

We have intensively studied the growth of $Al_xGa_{1-x}As$ by using time resolved RAS and NR. The most suitable photon energy of 1.9 eV was chosen for in situ monitoring. The different contribution of surface-induced optical anisotropy and interface-induced optical anisotropy could be distinguished in situ with RAS transient spectra. With high bandgap of $Al_xGa_{1-x}As$, an oscillation similar to Fabry-Perot oscillation appeared in RAS transient spectra. Our work suggests that RAS oscillations are originated from the interface-induced optical anisotropy. A comparison of the RAS level of the AlGaAs layers during and after the oscillation can give us the information of defect formation. The difference of the RAS level increases with aluminum compositions, which is related to the surface stoichiometry. The oscillation for epilayer with high aluminium composition decayed more slowly than that of the low composition in the NR transient spectra, resulted from the decrease of the absorption coefficient with the aluminium composition.

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RAS 在线监测 AlGaAs 的 MOCVD 生长

徐华伟[1,2]**，张金龙**[1]**，宁永强**[1*]**，曾玉刚**[1]**，张 星**[1]

（1. 中国科学院 激发态重点实验室 长春光学精密机械与物理研究所，吉林 长春 130033；
2. 中国科学院 研究生院，北京 100039）

摘要：通过瞬态反射各向异性谱和瞬态反射谱在线监测和研究了 $Al_xGa_{1-x}As$ **的生长过程，利用金属有机化合物汽相淀积技术在** GaAs（001）**衬底上生长了多层** $Al_xGa_{1-x}As$ **结构。选择最**

适合在线监测生长过程的探测光能量，在此探测光能量处所得到的反射各向异性谱和反射谱的信号在生长过程中有很明显的振荡行为产生。研究发现，通过瞬态反射各向异性谱可以很好地分辨出由表面引起的光学各向异性和由界面处引起的光学各向异性，能够得到界面处形成缺陷的信息，并且发现了反射各向异性谱和反射谱的信号随着铝组分的不同而发生有规律的变化。

关 键 词： 外延生长；金属有机化合物汽相淀积；反射各向异性谱；

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作者简介： 徐华伟(1982－)，男，吉林白山人，主要从事高功率半导体垂直腔面发射激光器的外延生长的研究。
E-mail：xuhwciomp@163.com，Tel：(0431)86176335

*：通讯联系人；E-mail：ningyq@ciomp.ac.cn，Tel：(0431)86176348