Crystal Perfection in GaP Films Heteroepitaxially Grown on GaAs by Low-pressure Metalorganic Chemical Vapor Deposition*

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Abstract

The crystal perfection in GaP epitaxial layers was stuided by the use of double crystal X-ray diffraction, backscattering spectrometry and Raman scattering techniques. GaP films grown on GaAs by low-pressure metalorganic chemical vapor deposition were used as the samples. By means of the morphology and the full-width at half maximum of X-ray diffraction peak for the GaP epilayers, the growth temperature and Ⅴ/Ⅲ ratio were optimized. In addition, the residual stress and strain of a GaP epilayer were calculated, based on Raman scattering measurement.

Key Words: GaP, Heteroepitaxy, Raman spectroscopy, Backscattering spectrometry

1. Introduction

The crystal perfection for Ⅲ-Ⅴ group semiconductor materials heteroepitaxially grown by metalorganic chemical vapor deposition (MOCVD) was found to be a sensitive function of growth factors, including precursors, substrate, temperature, pressure, flow rate and reactor design *etc*.[1] In order to obtain high quality epilayer with optoelectronic properties, it is necessary to optimize these growth factors. In comparison with Si and GaAs, GaP could make good high-temperature semiconductor devices because of its large band gap and low depletion region generation-recombination current[2]. However, because some important physical chemistry properties of GaP, such as lattice constant and thermal expansion coefficient, differ from that of GaAs, the GaP epilayer grown on GaAs by MOCVD usually does not present "mirror-like" but "frost-like" morphology, and these exist internally a great deal of defects[3]. This pa-

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per presents the preliminary study of the crystal perfection of GaP films heteroepitaxially grown by low-pressure MOCVD using the optimized growth temperature and III/V ratio.

2. Experimental

MOCVD epitaxial growth was performed in a horizontal, cold-wall, low-pressure reactor with an RF heated graphite susceptor. Trimethylgallium (TMG), phosphine (PH_3) and arsine (AsH_3) were used as the precursors. TMG was kept at −10 ℃. The GaP epilayers were grown on n-type GaAs substrates (Si-doped, $n \sim 10^{18}$ cm^{-3}) with an orientation of about 3° off (100) towards [110]. Before growing epilayers, the GaAs substrates were processed in a H_2 atmosphere at 375 ℃ for 4min to remove adsorbed water, and then in a $AsH_3 + H_2$ atmosphere at 820 ℃ for 6 min to remove the natural oxides. A two-step growth method was introduced for the heteroepitaxial growth of GaP on GaAs. First, an about 0.3 μm thick GaAs buffer layer was grown at 700 ℃. Then, the GaP epilayers were grown in a temperature range from 700 to 780 ℃ with a [PH_3]/[TMG] ratio from 10 to 80. The total thickness of the GaP epilayers was about 2μm. The chief growth conditions for GaP on GaAs substrate are summarized in Table. 1.

Table. 1 Heteroepitaxial growth factors for GaP on GaAs

Growth temperature ℃	Reactor pressure Pa	H_2 flow rate dm^3/min	V/III ratio	PH_3 flow rate cm^3/min	TMG flow rate cm^3/min
710~780	1.2×10^4	2.5	10~80	10~80	20

The surface morphology and the growth rate for the GaP epilayer were investigated with scanning electron microscopy (SEM). Double crystal X-ray diffractometry using Cu $K\alpha_1$ radiation was used for the measurement of the full-width at half maximum (FWHM) and the lattice constant of the epilayers. Laser Raman spectroscopy was used for the characterization of the residual stress and strain in the GaP epilayers. Raman spectra measurements were conducted in the backscattering geometry using the 488 nm line of an Ar^+-ion laser operated at 50mV power. The beam was focused to a spot size of approximately 1 mm^2. Backscattering spectrometry for 2.1 MeV ^4He ions was used for the characterization of the crystal perfection in the GaP epilayers. The scattering angle (θ_0) was chosen as 165°.

3. Results and Discussion

The surface morphology of the GaP epilayer on GaAs substrate could not only characterize the crystal perfection, but also present the dependence of the crystal perfection on the growth conditions. Under the condition of a constant V/III ratio it was illustrated by SEM that a given temperature in the range from 710 to 780 ℃ affected the morphology of GaP on GaAs by low pressure MOCVD. The results show that the higher the temperature is, the better the surface morphology for the GaP epilayer[4]. On the other hand, at 780 ℃ the effect of V/III ratio in the range

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from 10 to 80 upon the surface morphology of GaP epilayer was also investigated by SEM. The results showed that the best surface morphology was observed when V/III= 20[4].

In comparison with GaP perfect crystal, the GaP films heteroepitaxially grown on GaAs by MOCVD always increased the FWHM of the X-ray diffraction peak because of the residual stress and strain. So the FWHM for the GaP epilayer could be used to characterize the crystal perfection. It was found that the results of $\omega \sim 2\theta$ measurement for (400) plane were in good agreement with that from the surface morphology by SEM.

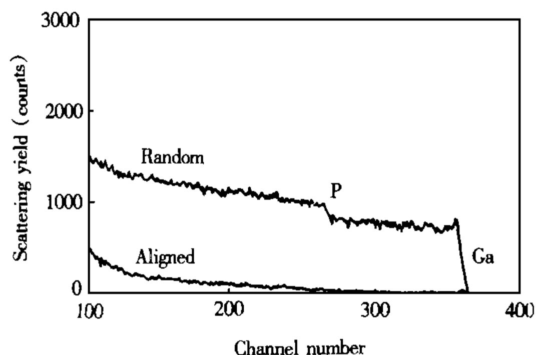

Fig. 1. Random and (100)-aligned spectra for 2.1 MeV ^{4}He ions incident on GP12.

Fig. 1 shows the random and (100)-aligned backscattering spectra for 2.1 MeV ^{4}He ions incident on the GaP epilayer grown at 780℃ and V/III= 20, signed GP12. The ratio of the heights of two spectra taken in the near surface region for aligned and random orientation is referred to as the minimum yield χ_{min}. In the near surface region of a perfect crystal, the value for the minimum yield lies in the range of 1 to 3×10^{-2} for low-index axial direction[5]. For a GaP epilayer with lattice disorder or polycrystalline, the dechanneled particles can interact with the nondisplaced host lattice atoms and give a much higher backscattering yield than that of the channeled particles, so it causes the χ_{min} increased. On the basis of the two heights of two spectra taken in the near surface region for GP12, the χ_{min} was calculated. The result, $\chi_{min} < 2\times 10^{-2}$, showed that the GaP epilayer on GaAs characterized the perfect crystal in the thickness of about 1μm and the incident range for megaelectron volt ^{4}He ions on GaP.

The Raman spectra from the sample GP12 was shown in Fig. 2. The residual stress and strain in the GaP epilayer could be evaluated using the LO-phonon peak shift. The LO-phonon peak for the heteroepitaxially grown GaP layer was shifted by 0.4cm^{-1} towards a lower wave number than that for GaP substrate. The LO-phonon peak shift to a lower wave number indicates that the epilayer is subject to tensile stresses. According to Cerdeira *et al*[6], the LO-phonon peak shift due to the stress in (001) films with zincblende structure is calculated by the following equation[6,7]

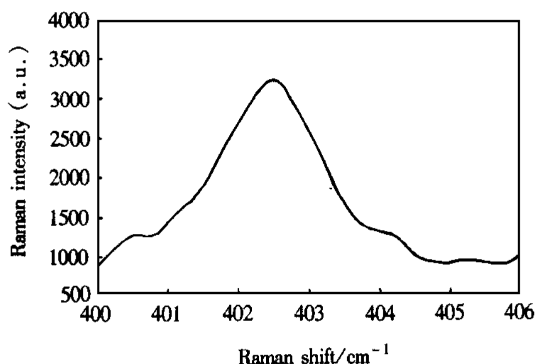

Fig. 2. Raman spectra from GP12.

$$\Delta\omega = \frac{p + 2q}{3\omega_0}(S_{11} + 2S_{12})X -$$

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$$\frac{p-q}{3\omega_0}(S_{11}-S_{12})X \qquad (1)$$

where p and q refer to the parameters related to the elastic coefficients, S_{11} and S_{12} the elastic compliances and X the stress. ω_0 represents the frequency in the absence of stress and is equal to the GaP bulk frequency in Eqn. (1). The value of ω_0 measured for the GaP substrate was 402.9 cm^{-1}. The other parameters used in Eqn. (1) are as follows[7~9]

$$\frac{p+2q}{6\omega_0^2}=-1.07 \qquad (2)$$

$$\frac{p-q}{2\omega_0^2}=0.53 \qquad (3)$$

$$S_{11}=0.967\times 10^{-12}dyn^{-1}.cm^2 \qquad (4)$$

$$S_{12}=-0.295\times 10^{-12}dyn^{-1}.cm^2 \qquad (5)$$

From the LO-phonon peak shift, $\Delta\omega$, the stress is obtained. Furthermore, the strain parallel to the growth surface (ε_{xx}) and the perpendicular one (ε_{yy}) are calculated as follows

$$\varepsilon_{xx}=(S_{11}+S_{12})X \qquad (6)$$

$$\varepsilon_{yy}=2S_{12}X \qquad (7)$$

In terms of the above mentioned procedures and measured result of $\Delta\omega$, the values of ε_{xx} and ε_{yy} for the sample GP12 were determined as follows

$$\varepsilon_{xx}=5.32\times 10^{-4}$$

$$\varepsilon_{yy}=-4.67\times 10^{-4}$$

4. Conclusion

The crystal perfection and residual stress and strain in GaP layer grown on GaAs (001) substrate by low-pressure MOCVD have been investigated by using back-scattering spectrometry and Raman scattering measurements. The result of back-scattering spectrometry showed that the value of the minimum yield, χ_{min}, was in the range of a perfect crystal. As indicated that the crystal characterization for the GaP film near the epilayer was similar to that of a perfect crystal. The residual stress and strain of the epilayer were calculated from the result of LO-phonon peak shift. The degree of strains was small. It could be demonstrated that although there exists a big lattice mismatch (3.6%) between GaP and GaAs, it is possible to grow GaP epilayer with nearly perfect crystal characterization by MOCVD.

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