[논 문] 한국재료학회지
Korean Journal of Materials Research
Vol. 6, No. 6 (1996)

MOVPE 성장방법으로 corrugated InP 기판위에 성장된 InGaAs/InGaAsP 다층박막의 구조연구

남 산 · 장동훈* · 서경수* · 조경익*
고려대학교 공과대학 재료금속공학부
*한국전자통신 연구소 반도체 연구단

Structural Studies of InGaAs/InGaAsP Multi-quantum well Structure Grown on Corrugated InP by MOVPE

Sahn Nahm, Dong Hoon Jang,*, Kyoung-Soo Suh* and Kyoung-Ik Cho*
Division of Materials and Metallugical Engineering, Korea University, Seoul, 136-1701
**Semiconductor Division, Electronics and Telecommunications Research Institute, Yusong, P.O. Box 106, Daejon, Korea*

초 록 InGaAs/InGaAsP 다층박막을 corrugation이 형성된 InP 기판위에 MOVPE 방법을 이용하여 성장 시킨 후 성장조건에 따른 corrugation 높이의 변화와 석출상에 대하여 투과전자현미경을 이용하여 연구하였다. Corrugation이 형성된 InP 기판을 PH_3 분위기에서 성장온도까지 가열하였을 때 corrugation이 완전히 제거되었다. Corrugation을 보존하기 위하여 InP 기판을 가열할 때 PH_3 및 AsH_3 가스를 동시에 공급해 주었는데 AsH_3 가스의 압력이 높으면(1.8×10^{-2} torr) 많은 양의 As를 포함한 $In_{1-x}As_xP$($x=0.3$)석출상이 격자결함과 더불어 형성되었다. 반면에 AsH_3 가스의 압력이 낮을때는(1.0×10^{-3} torr) corrugation의 높이가 30nm이었고, 적은 양의 As를 포함한 $In_{1-x}As_xP$($x<0.1$)석출상이 격자결함이 없이 형성되었다.

Abstract The InGaAs/InGaAsP MQW structure was formed on the corrugated InP substrate using metal-organic vapor phase epitaxy(MOVPE) and the change of corrugation height and the formation of second were investigated using transmission electron microscopy(TEM). For the sample heated up to growth temperature under the pressure of PH_3, the corrugation formed on InP substrate was completely deformed. In order to preserve the corrugation, both PH_3 and AsH_3 were supplied to the reacotr during the heat up process. However, for the sample heated up with high pressure of AsH_3 (1.8×10^{-2} torr), $In_{1-x}As_xP$ phases with high concentration of As atoms ($x=0.3$) were irregulary formed at the concaved area of the corrugation. Defects were also generated from them. On the contrary, for the sample heated up with 1.0×10^{-3} torr As partial pressure, the height of corrugation was about 30nm and $In_{1-x}As_xP$ phase with low concentration of As atoms($x<0.1$) was formed without defects.

1. Introduction

There is a growing interest in InGaAs/InGaAsP multi-quantum well(MQW) distributed feedback laser diode(DFB-LD) with 1.55 μm wavelength because of its application to high speed optical communication[1,2]. In such system, MQW is grown on corrugated InP substrate since the height of corrigation influences the properties of DFB-LD by changing the coupling coefficient[3]. Therefore, the growth of defect free MQW and controlling of corrugation height are important to obtain DFB-LD with good optical properties. Previously, DFB-LDs have been grown by liquid phase epitaxy[4,5]. However, it was not easy to control the layer thickness and large area uniformity due to the meltback and solution convection in melts. Recently, MOVPE has been widely used to grow laser diode because smoothness of surface, layer thickness and composition can be easily controlled by MOVPE[6, 7]. However, even if there was a report on successful growth of the DFB-LD using MOVPE, corrugation was deformed during the growth procedure and defects were generated at the interface between InGaAs layer and corrugated InP[8]. Moreover, they just have studied the defect structure and suggested possible origin of defects without systemtic study on structural properties[8]. T. Tanbul etal. and W.T. Tsang etal. have sucessfully grown DFB lasers but they have not repoted structural properties of the system [9, 10]. Even if defects and height of grating greatly influence the performance of the lasers, investigations on controlling of corrugation height and defects structure have not been sufficiently carried out.

In this work, InGaAs/InGaAsP MQW structures were grown on the corrugated InP substrate by MOVPE and the change of corrugtion height and defect structure with the variation of AsH_3 partial pressure were studied using TEM. Furthermore, the formation of the $In_{1-x}As_xP$ second phase at concaved area of corrugation were also investigated.

Experimetal Details

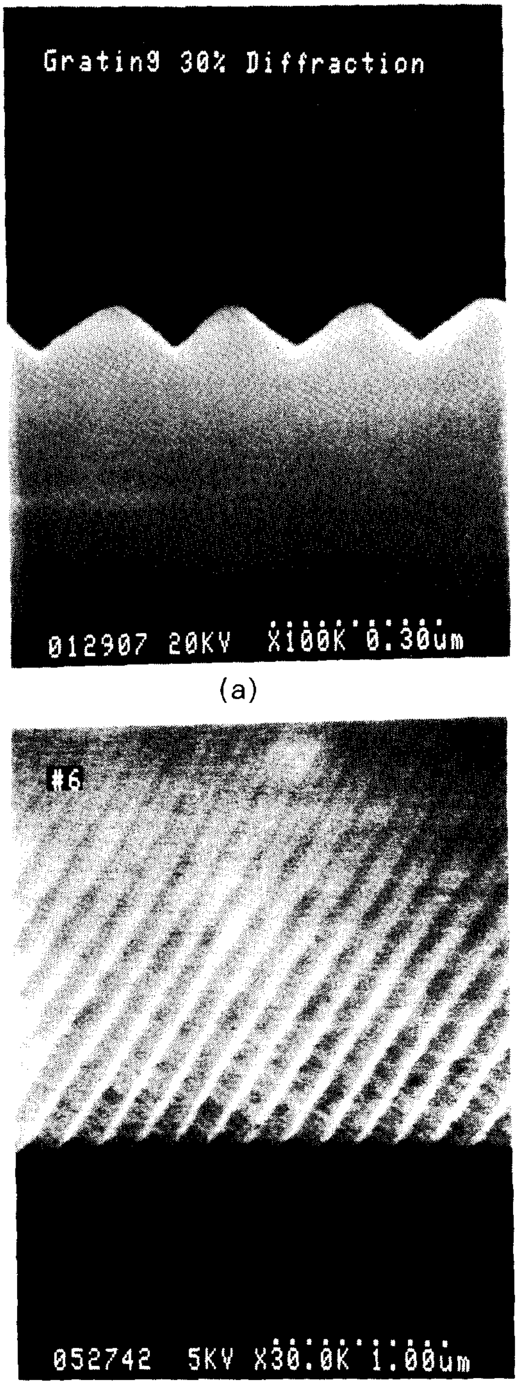
First order grating with the pitch of 238nm on InP substrate was prepared by holographic exposure and wet chemical etching. The lattice matched InGaAs layer and InGaAs/InGaAsP MQW layers were grown on the corrugated InP substrate using MOVPE. The heat up conditions of samples are listed in table 1. and the detailed growth condition will be described in elsewhere[9]. The cross sectional TEM samples were prepared by mechanical grinding and subsequent ion milling. Ion milling using Ar ion was carried out at liquid nitrogen temperature to prevent the formation of In islands and the damage induced during the ion milling[10]. During the first stage of ion milling, the energy of the ions was 4 KeV with glancing angle of 15 degrees and during the later stage of ion milling, even lower energy 3 KeV with 12 degrees of glancing angle was used to minimize the damage. Philips CM20 T/STEM was used to observe samples and composition analysis was carried out using EDX(Energy Dispersive X-ray) system attached in TEM.

Results and discussion

Figures 1(a) and 1(b) show the cross sectional and plane view scanning electron microscopy (SEM) images of first order gratings formed on InP(001) sibstrate, respectively. They were made by holographic exposure and chemical wet etchings. The shape of gratings is triangular and they were formed along the [-110] direction as shown in Figs. 1(a) and 1(b). The height and wavelength of grating are 100nm and 238nm, respectively. Figure 2 shows the cross sectional SEM image of sample 1. As shown in this figure, the corrugation was completely deformed. The deformation of corrugation can be explained as follow. At elevated temperatures, some decomposition takes

Table 1. Heat up conditions of each sample.

	PH3 pressure(torr)	AsH3 pressure(torr)	heat up time	growth temperature
sample 1	5.67×10^{-1}	0	5 min	630℃
sample 2	5.67×10^{-1}	1.8×10^{-2}	5 min	630℃
sample 3	5.67×10^{-1}	2.4×10^{-3}	5 min	630℃
sample 4	5.67×10^{-1}	1.0×10^{-3}	5 min	630℃



(a)

(b)

Fig. 1. (a) Cross sectional and (b) plane view SEM images of InP substrate after the formation of first order grating. The height of grating is 100nm and the wavelength is 238nm.

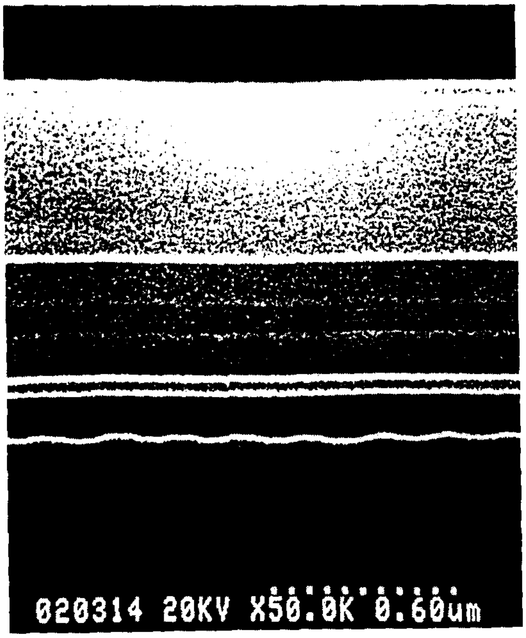
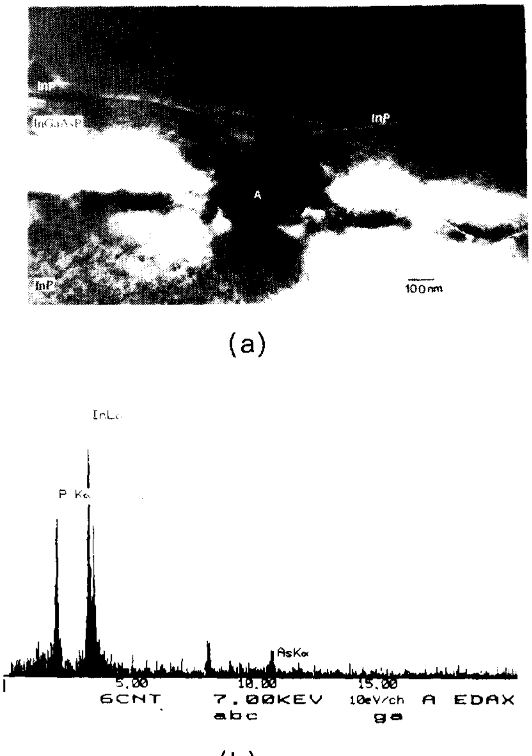


Fig. 2. SEM image of sample heated up to the growth temperature(630℃) under PH$_3$(5.67×10^{-1} torr). The corrugation was completely deformed.

place at the surface of InP corrugation and free In atoms are generated[11]. The concentration of free In atoms are higher in convexed area compared to concaved area because of the high surface energy in convexed area indicating low binding energy in decomposition process. Therefore, the free In atoms in convexed area diffuse into the concaved area, where the concentration of In atom exceeds that of equilibrium In atom. As a results, In atoms in concaved area recombined with P atoms in vapor and formed InP crystal. This process continues until corrugation was completely deformed as shown in Fig. 2 and at this point the surface energy of concaved region is the same as that of convexed region.

In order to preserve the height of corrugation, the mixture of AsH$_3$ and PH$_3$ are introduced into the reactor during the heat up process of the samples. For sample 2 grown with high pressure of AsH$_3$, the height of corrugation was well preserved. However, second phases(marked A in Fig. 3(a)) were irregulary formed at the concaved area of corrugation and defects were generated from them as



(a)

(b)

Fig. 3. (a) TEM bright field image of sample heated up to 630℃ with $PH_3(5.67\times10^{-1}$ torr) and $AsH_3(1.8\times10^{-2}$ torr) and (b) EDS from the second phase formed at the concaved area of corrugation.

shown in Fig 3(a). According to EDX analysis as shown in Fig. 3(b), the second phase at concaved area is $In_{1-x}As_xP$(x is about 0.3) without Ga atom. Since the Ga atoms were not detected in the second phases, they are expected to be formed during the heat up process by the recombination of excess In atoms with both P and As atoms. Moreover, the growth rate of InGaAsP layer on $In_{1-x}As_xP$ is lower than that on InP substrate resulting in the failure of planarization of InGaAsP layer grown on corrugated InP substrate(see the area indicated by arrow in Fig. 3(a)).

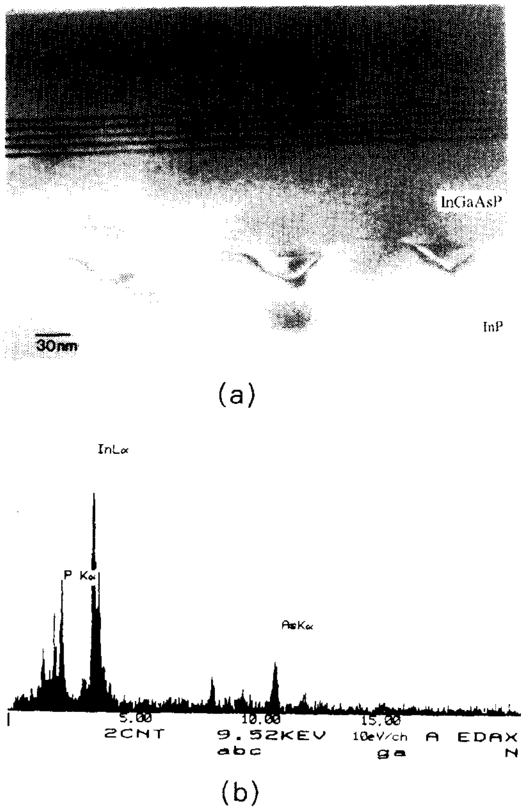
Figure 4 shows a TEM bright field image of sample 3 taken under(004) two beam condition. Second phases were regulary formed at the concaved area of corrugation but defects were not found in the system. The height of corrugation was measured as 60nm. According to the EDX ananlysis, second phase is $In_{1-x}As_xP$ phase and x is approximately 0.18. The growth rate on of InGaAsP is considered to be same on both Inpand $In_{1-x}As_xP$ phase resulting in flat InGaAsP surface. However, some region indicated by arrow in Fig. 4, growth rate of InGaAsP on $In_{1-x}As_xP$ is still lower compared to that on InP layer. Even if defects were not found in the samples grown with AsH_3 partial pressure below 2.4×20^{-3} Torr during the heat-up time, strain is present between the $In_{1-x}As_xP$ second phase and InP substrate(see the dark and white contrast below second phase indicated by arrow heads in Fig. 4). The strain is due to the lattice mismatch between $In_{1-x}As_xP$ phase and InP substrate.

The amount of strain is expected to be reduced by decreasing the AsH_3 partial pressure during the heat up process. Figure 5(a) shows the TEM bright field image of sample heated up with AsH_3 pressure of 1.0×10^{-3} Torr. The $In_{1-x}As_xP$ second phases were also formed in concaved area of corrugation as shown in this figure. However, according to the EDX analysis shown in Fig. 5(b), the concentration of As atom in $In_{1-x}As_xP$ phase was decreased($x<0.1$) and there is no evidence of strain. Moreover, the corrugation with the height of 30nm is well preserved without defects and the surface of InGaAsP layer grown on corrugated InP is flat with nicely formed InGaAs/InGaAsP MQW. Above results show that second phase is formed during the heat up process and the composition of second phase and corrugation height depend on the AsH_3 partial pressure. Therefore, it can be suggested that coulping coefficients for the grating in the DFB-LD the system can be controlled by the AsH_3 partial pressure during heat up process.

Conclusions

For the sample heated up to the growth temperature with the flow of PH_3, corrugation formed on InP substrate was completely de

Fig. 4. TEM bright field image of sample heated up to 630℃ with $PH_3(5.67\times10^{-1}$ torr) and $AsH_3(2.3\times10^{-3}$ torr).



(a)

(b)

Fig. 5. (a) TEM bright field image of sample heated up to 630℃ with $PH_3(5.67\times10^{-1}$ torr) and $AsH_3(2.3\times10^{-3}$ torr) (b) EDS from the second phase formed at the concaved area of corrugation.

formed. Because of the difference of curvature across the surface of the corrugation, many free In atoms are generated at the convexed area of corrugation and diffuse to the concaved area, where excess In atoms recombine with P atoms in vapor forming InP crystal. In order to prevent the corrugation from the thermal deformation, both PH_3 and AsH_3 were supplied during the heat up of the sample. However, for the sample heated up under high pressure of $AsH_3(1.8\times10^{-2}$ torr), $In_{1-x}As_xP$(x is about 0.3) was irregulary formed in the concaved area of corrugation with defects even if the height of corrugation was preserved. The height of corrugation and concentration of As in $In_{1-x}As_xP$ phase were reduced with the decrease of AsH_3 partial pressure during the heat up procedure. For the sample grown with 1.0×10^{-3} torr, the height of corrugation was about 30nm and concentration of As atom in $In_{1-x}As_xP$ phase is low($x<0.1$). Defects were not observed in the system. Our results indicated that the height of corrugation and the concentration of $In_{1-x}As_xP$ therefore the coupling coefficients of system can be controlled by the AsH_3 partial pressure during the heat up process.

References

1. Y. Suematsu, 12th International Semiconcuctor Laser Conference, Paper A1, September, 1990, Davos, Swizerland.
2. K. Uoni, A. Murata, S. Sano, R. Takeyari, IEEE Phonics Technol. Lett. 4, 657 (1992).
3. K.Y. Matsui, Optical and Quantum Electronics 24, 719 (1992)
4. K. Utaka, S. Akiba, S. Skai, and Y. Matsushima, Electron. Letters 17, 961 (1981)
5. T. Matsuoka, H. Nagai, Y. Itaya, Y. Noguchi, Y. Suzuki, and T. Ikegemi, Electron. Letters 18, 27 (1982)
6. M. Razeghi, R. Blondeau, K. Kaymiezski, M. Krahowski and B. deCremoux, Appl. Phys. Letters 45, 784 (1984).
7. M. Oishi, M. Nakao, Y. Itaya, K. Sato and Y. Imamura, IEEE, J. Quantum Electron. QE-23, 822 (1987).

8. K. Sato, M. Oishi, Y. Itaya, M. Nakao, and Y. Imamura, J. Cryst. Growth, 93, 825 (1988).
9. D.H. Jang, J.S. Kim, K.H. Park, S. Nahm, S.W. Lee, J.K. Lee H.S. Cho, H.M. Kim and H.M. Park, accepted to be pubilished in Appl. Phys. Lett..
10. R. Alani, J. Jones, and D. Swann, Mat. Res. Soc. Symp. Proc. Vol 199, 85 (1990)
11. Z.L. Liau and H.J. Zeiger, J. Appl. Phys. 67(5), 2434 (1990)