Journal of Alloys and Compounds 509 (2011) 6751–6755

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

# Effect of buffer layer annealing temperature on the crystalline quality of $In_{0.82}Ga_{0.18}As$ layers grown by two-step growth method

Xia Liu [a,b], Hang Song [a,*], Guoqing Miao [a], Hong Jiang [a], Lianzhen Cao [a,b], Dabing Li [a], Xiaojuan Sun [a], Yiren Chen [a], Zhiming Li [a]

[a] *Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Dong Nanhu Road 3888 Changchun Jilin Changchun 130033, PR China*

[b] *Graduate school of the Chinese Academy of Sciences, Beijing 100039, PR China*

ARTICLE INFO

*Article history:*
Received 17 November 2010
Received in revised form 5 March 2011
Accepted 18 March 2011
Available online 29 March 2011

*Keywords:*
$In_{0.82}Ga_{0.18}As$
MOCVD
Buffer layer annealing temperature
Crystalline quality

ABSTRACT

$In_{0.82}Ga_{0.18}As$ epilayers were grown by LP-MOCVD on InP substrates with the insertion of $In_{0.82}Ga_{0.18}As$ buffer layers, which were annealed at various temperatures between 490 °C and 630 °C for 5 min in $AsH_3$ ambient. The effect of buffer layer annealing temperatures on the crystalline quality of $In_{0.82}Ga_{0.18}As$ epilayers was investigated by atomic force microscopy, scanning electron microscopy, double-crystal X-ray diffraction, and room-temperature Hall measurement. The characterization results showed that high quality $In_{0.82}Ga_{0.18}As$ epilayers were obtained by optimizing the annealing temperatures of buffer layers. In particular, the $In_{0.82}Ga_{0.18}As$ epilayer with buffer layer annealed at 530 °C showed the best crystalline quality. The changes of crystalline quality of $In_{0.82}Ga_{0.18}As$ epilayers at high and low annealing temperature can be attributed to the recrystallization and reevaporation of the $In_{0.82}Ga_{0.18}As$ buffer layers.



## 1. Introduction

In recent years, there are growing needs for photodetectors covering the short wave infrared (SWIR) band (up to 2.5 μm), the most important applications are spectral imaging including earth observation [1], remote sensing and environmental monitoring, other applications are gas detection, spectroscopy, and night vision [2–4]. Compared with HgCdTe or antimonide materials, the ternary InGaAs material is a good competitor to cover this band [5,6]. Ternary InGaAs materials have the advantage of mature growth and processing technology, and better performance of the photodiodes or arrays can be expected, especially at higher operation temperatures [7]. To obtain a 2.5 μm absorption wavelength, an In-content of 82% is needed. As there is no lattice-matched substrate for $In_{0.82}Ga_{0.18}As$ material, the large lattice mismatch between $In_{0.82}Ga_{0.18}As$ and substrates will result in the misfit dislocations or defects that will destroy the material quality. Many schemes [8–11] have been adopted to solve this problem, in which two-step growth technique was an effective and convenient way [12]. In two-step growth, the low temperature buffer layer is an actively investigated subject. The deposition conditions of buffer layer, such as buffer layer thickness [13] and buffer growth temperature [14] on properties of $In_{0.82}Ga_{0.18}As$ epilayers by the two-step growth method have been reported. However, the report on the effect of buffer layer annealing temperature on $In_{0.82}Ga_{0.18}As$ is rare. For low deposition temperature, there are possibilities that all the chemical reactions do not occur ideally, precursors do not decompose completely and atoms fail to move to equilibrium atomic sites. It is known that thermal annealing can affect the crystal structure, grain size, and surface quality of films, as it can supply sufficient energy for the atoms to move into more suitable positions in the crystal lattice [15]. Therefore, even if low temperature growth of $In_{0.82}Ga_{0.18}As$ buffer is available, annealing treatment is necessary to improve its quality.

In this paper, the $In_{0.82}Ga_{0.18}As$ epilayers were grown by LP-MOCVD on $In_{0.82}Ga_{0.18}As$ buffer/InP annealed at various temperatures. The effect of buffer layer annealing temperatures on crystalline quality of $In_{0.82}Ga_{0.18}As$ epilayers was investigated and the reasons of the changes in crystalline quality of $In_{0.82}Ga_{0.18}As$ epilayers were also discussed here.

## 2. Experimental

The $In_{0.82}Ga_{0.18}As$ epilayers have been grown on InP (001) substrates by low-pressure metalorganic chemical vapor deposition (LP-MOCVD). The substrate was placed on a graphite susceptor in horizontal reactor with a radio frequency heater. TrimethylIndium (TMIn), triethylgallium (TEGa) and arsine ($AsH_3$) diluted to 10% were used as source materials, respectively. The carrier gas was hydrogen ($H_2$), and the growth pressure was kept at 70 Torr. The growth process was as follows. Before growing InGaAs buffer, the InP substrates were treated at 630 °C to clean the

* Corresponding author. Tel.: +86 431 8462 7073; fax: +86 431 8462 7073.
*E-mail address:* songh@ciomp.ac.cn (H. Song).

0925-8388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2011.03.110

**Table 1**
The annealing parameters of $In_{0.82}Ga_{0.18}As$ samples a, b, c, d, e, and f, respectively.

| Buffer layer samples | a | b | c | d | e | f |
|---|---|---|---|---|---|---|
| Buffer growth temperature (°C) | 450 | 450 | 450 | 450 | 450 | 450 |
| Buffer annealing temperature (°C) | 490 | 510 | 530 | 550 | 580 | 630 |
| Annealing time (min) | 5 | 5 | 5 | 5 | 5 | 5 |

contamination on it. The $In_{0.82}Ga_{0.18}As$ buffer was grown at 450 °C and the thickness was about 100 nm. After growing the buffer layer, the temperature was raised to anneal the buffer layers from 490 °C to 630 °C for 5 min at $AsH_3$ atmosphere. After the thermal treatment, the $In_{0.82}Ga_{0.18}As$ epilayer with the thickness of about 1.4 μm was grown at 530 °C. The schematic diagram of the $In_{0.82}Ga_{0.18}As/In_{0.82}Ga_{0.18}As/InP$ layers structure is shown in Fig. 1. In this study, the growth of the $In_{0.82}Ga_{0.18}As$ epilayers was kept under the same conditions, except for the buffer layer annealing temperatures. The $In_{0.82}Ga_{0.18}As$ epilayers with buffer layers annealed at 490, 510, 530, 550, 580, and 630 °C were named as A, B, C, D, E and F, respectively. The buffer layers, grown under the same conditions as those in samples A, B, C, D, E and F, were named as a, b, c, d, e, and f, respectively. The annealing parameters of buffer layer samples a, b, c, d, e, and f, are shown in Table 1.

The morphologies and surfaces were examined by both atomic force microscope (AFM, Veeco multimode) and field emission scanning electron microscope (SEM, Hitachi S-4800). The crystal structures were investigated by double-crystal X-ray diffraction (DCXRD, Bruker D8). The electrical properties were studied by Hall measurements (Lakeshore 7707) using Van der Pauw technique at room temperature. The Hall data were compiled employing both positive and negative currents and magnetic fields, and the results were averaged in order to compensate various electromagnetic effects.

## 3. Results and discussion

The surfaces of buffer layers after annealing treatment were examined by AFM. As shown in Fig. 2, it is clear that all the annealed buffer layers have the granular surface. The root mean square (rms) roughness values of the buffer layer surfaces can be calculated from AFM measurements. These values of annealed buffer layers are 3.024, 3.419, 4.579, 4.770, 5.823, and 16.233 nm, corresponding to the buffer layer samples a, b, c, d, e and f, respectively. It is found that the surface roughness increases obviously and the grain size become larger after annealing. This phenomenon may be due to that the atoms gain sufficient energy to initiate the coalescence process with the increase of the annealing temperatures [16]. Through the atom migration, small crystallites migrate to larger crystallites, resulting in rougher surface morphology. The cross-section SEM images of the annealed buffer layers at various temperatures were also displayed in Fig. 2. It can be seen that thickness of the $In_{0.82}Ga_{0.18}As$ buffer layers was about 100 nm when the annealing temperature was lower than 530 °C and it decreased when the annealing temperature rose from 530 °C to 630 °C. The reduction of the thickness may be attributed to the reevaporation of $In_{0.82}Ga_{0.18}As$ buffer annealed at high-temperatures.

In order to evaluate the effect of annealing on the properties of the $In_{0.82}Ga_{0.18}As$ epilayers, SEM measurement was performed to study the surface morphology of $In_{0.82}Ga_{0.18}As$ materials. Fig. 3(A)–(F) illustrates the planar surface SEM images of $In_{0.82}Ga_{0.18}As$ epilayers with buffer layers annealed from 490 °C to 630 °C, corresponding to the samples A, B, C, D, E and F, respectively. It is evident that the surfaces of the six samples do not appear as three-dimensional (3D) islands, indicating that $In_{0.82}Ga_{0.18}As$ epilayer is in the growth mode of two-dimensional (2D) characteristic [14]. However, the sample C, with the buffer layer annealed at 530 °C, shows that the surface morphology is better than those of other samples. The changes of the surface morphology indicate that the buffer layer annealing temperature is optimized and the optimized annealing temperature is 530 °C. This observation can be explained by the changes of buffer layers after annealing. In the annealing process, both recrystallization and reevaporation possibly occur [17,18]. When the annealing temperature is lower than 530 °C, the recrystallization is dominant. The energy supplied by annealing temperature is favorable for atoms moving into proper sites, resulting in larger grain size and rougher surface. This change of the buffer layer surface is favor of growing $In_{0.82}Ga_{0.18}As$ epilayer, leading to the improvement of epilayer's quality. However, when the annealing temperature is further increased to 630 °C, the reevaporation may be dominant and this process could be proved by the change of the buffer layer thickness displayed in Fig. 2. The thickness of the buffer layer annealed at higher than 530 °C would be thinner than that annealed at lower temperatures. The effect of buffer layer thickness on the quality of the $In_{0.82}Ga_{0.18}As$ epilayer has been reported by Zhang et al. [13]. It indicates that the buffer layer has a critical thickness, smaller or larger than the critical thickness which will have inferior film quality. Therefore, a thinner $In_{0.82}Ga_{0.18}As$ buffer layer will degrade the surface morphology and quality of the following epilayer.

The effect of annealing temperatures on structural quality of $In_{0.82}Ga_{0.18}As$ film was investigated by DCXRD measurements. Fig. 4 shows the full width at half maximum (FWHM) of the $In_{0.82}Ga_{0.18}As$ epilayers with buffer layer annealed as a function of temperatures. The FWHM value of the samples A, B, C, D, E and F are 1320.8, 1180.6, 1060.0, 1432.1, 1812.5 and 2016.3 arcsec, corresponding to annealing temperature of 490, 510, 530, 550, 580 and 630 °C, respectively. It is clear that the sample C has the minimum FWHM value and this value is smaller than that reported by D'Hondt et al. [19]. It is known that the upper limit threading dislocation density can be estimated from the FWHM of XRD signal [20]. Therefore, the $In_{0.82}Ga_{0.18}As$ epilayer with buffer layer annealed at 530 °C has the minimum dislocation density and the best crystalline quality. In our experiments, the growth conditions were all the same but the buffer layer annealing temperature is varied. This indicates that the changes of the FWHM of the $In_{0.82}Ga_{0.18}As$ epilayers are related to the buffer layer annealing temperatures. The selection of the buffer layer annealing temperature can improve the crystalline quality of the $In_{0.82}Ga_{0.18}As$ epilayers.

To further study the buffer layer annealing temperature on the quality of $In_{0.82}Ga_{0.18}As$ epilayers, Hall measurements at room temperature (RT) were performed to evaluate the electrical properties. The Hall measurements were made on the buffers and epilayers with the magnetic field of 2100G to ensure that a low-field approximation is valid. Hall measurement results of samples a, b, c, d, e, f and samples A, B, C, D, E, and F, are shown in Figs. 5 and 6, respectively. All the samples are unintentionally doped n type.

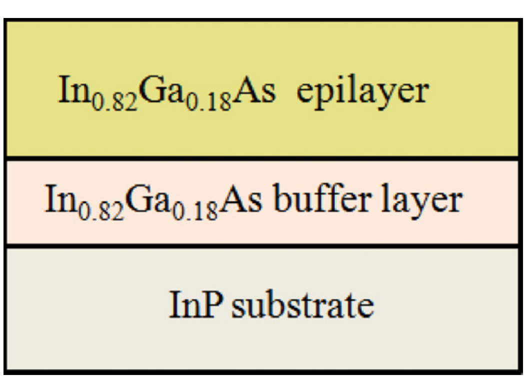


**Fig. 1.** The schematic diagram of the $In_{0.82}Ga_{0.18}As/In_{0.82}Ga_{0.18}As$-buffer/InP layer structure.

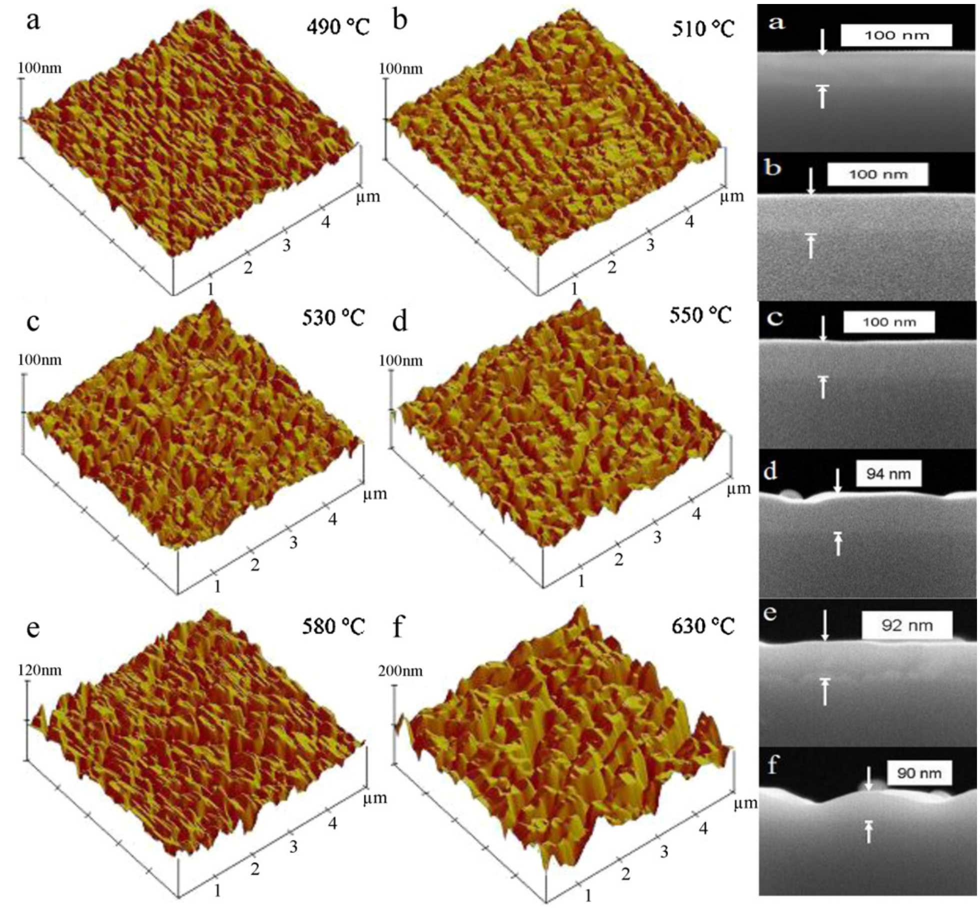


**Fig. 2.** AFM images of $In_{0.82}Ga_{0.18}As$ buffer layers over an area ($5 \times 5 \mu m^2$) and cross-section SEM images of $In_{0.82}Ga_{0.18}As$ buffer layers annealed at various temperatures.

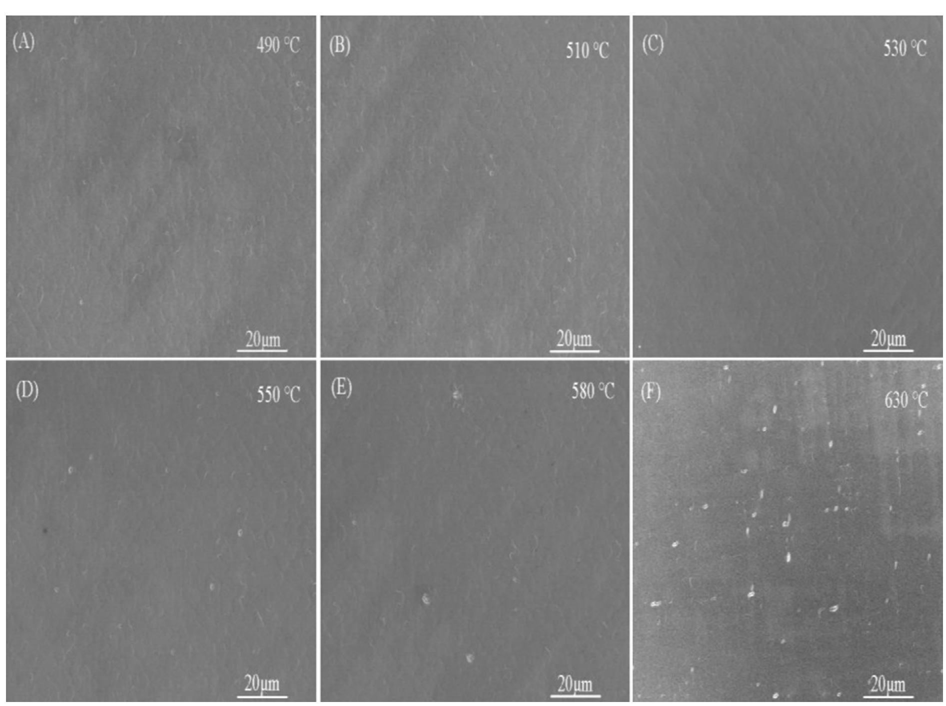


**Fig. 3.** SEM images of $In_{0.82}Ga_{0.18}As$ epilayers grown on InP with different buffer layer's annealing temperatures.

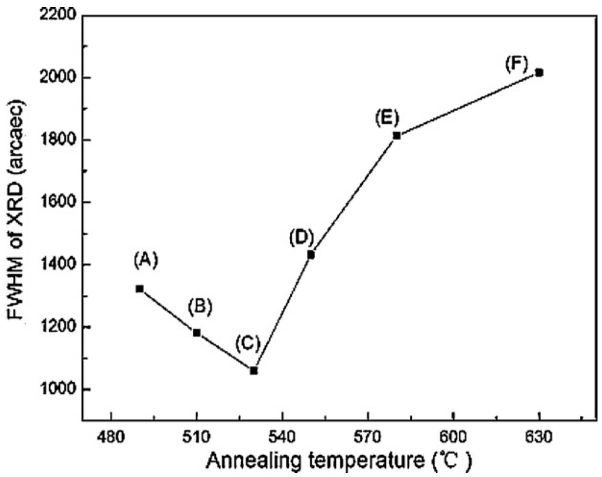


**Fig. 4.** The XRD FWHM of the $In_{0.82}Ga_{0.18}As$ epilayers as a function of thermal annealing temperatures.

From Fig. 5, the values of buffers mobility was 65.6, 70.7, 76.5, 61.2, 53.3, 45.4 $cm^2$/Vs, corresponding to the samples a, b, c, d, e, and f, respectively. The carrier concentration of buffer layers was about $\sim 10^{17}$ $cm^{-3}$. It can be seen that the quality of buffer layers is bad. The mobility of buffer layers is very sensitive to the annealing temperature, which can also reveal the recrystallization and reevaporation of the buffer layers in the annealing process. Fig. 6 displays the results of Hall measurement of the whole layer structure, including the buffer layers and epilayers. As the parallel conduction in the heavily defected buffer layer is known to be present, it can really affect the behavior of the mobility as well as the concentration. This phenomenon has been reported in InGaAs [21], InSb [22], and InAs [23]. However, the further investigation for parallel conduction and transport properties is outside the scope of this paper and will be discussed carefully in future work. In this paper, as the layer structure consists of two layers, a simple two-layer model [24] is used to determine the RT mobility and carrier concentration of the $In_{0.82}Ga_{0.18}As$ bulk layer. It should be noted that the use of two-layer model is only for charactering the samples. The electron mobility and concentration of the $In_{0.82}Ga_{0.18}As$ epilayer can be denoted by $\mu_1$ and $n_1$, $\mu_1$ and $n_1$ can be extracted from experimental Hall mobility ($\mu$) and concentration ($n$) using the formulae listed in [24]:

$$\mu_1 = \frac{\mu^2 n - \mu_2^2 n_2}{\mu n - \mu_2 n_2} \quad (1)$$

$$n_1 = \frac{(\mu n - \mu_2 n_2)^2}{\mu^2 n - \mu_2^2 n_2} \quad (2)$$

By inserting the measured electron mobility and concentration of the $In_{0.82}Ga_{0.18}As$ films ($\mu$ and $n$) and the buffer layers ($\mu_2$ and $n_2$) into Eqs. (1) and (2), the corresponding electron mobility and concentration of the $In_{0.82}Ga_{0.18}As$ epilayer ($\mu_1$ and $n_1$) can be obtained.

The values of $In_{0.82}Ga_{0.18}As$ mobility and carrier concentration versus the buffer layer thermal annealing temperature are displayed in Fig. 7. It is found that the values of bulk $In_{0.82}Ga_{0.18}As$ are higher than those of measured $In_{0.82}Ga_{0.18}As$ films. The buffer layer annealing temperature can strongly influence the carrier concentration and mobility of $In_{0.82}Ga_{0.18}As$ epilayer. The lowest carrier concentration and highest mobility measured at room temperature is $2.9 \times 10^{16}$ $cm^{-3}$ and 5369.8 $cm^2$/Vs, which occur at buffer layer thermal annealed at 530 °C. This can also be explained by the changes of buffer layers after thermal annealing. In the epilayers, the residual misfit dislocations that act as scattering center can reduce the carrier mobility [25]. When the annealing temperature is lower than 530 °C, the crystalline quality of buffer layer is improved by the recrystallization and the amount of dislocations which could go through in the epilayers will be reduced. Therefore, the mobility will increase with increasing the buffer layer annealing temperature from 490 °C to 530 °C. When the annealing temperature is higher than 530 °C, the crystalline quality of buffer layer is deteriorated by the reevaporation and the buffer layer thickness is decreased. This would increase the amount of dislocations in the epilayers and degrade the crystalline quality of $In_{0.82}Ga_{0.18}As$ epilayers. This result indicates that the thermal annealing process does reduce the amount of dislocations

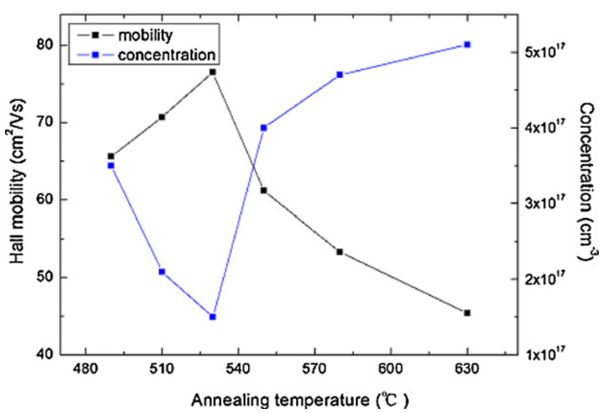


**Fig. 5.** The dependence of Hall mobility and carrier concentration of $In_{0.82}Ga_{0.18}As$ buffer layers on annealing temperatures.

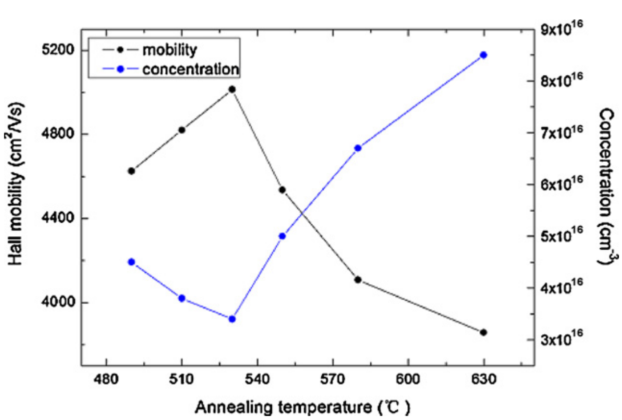


**Fig. 6.** The measured Hall mobility and carrier concentration of $In_{0.82}Ga_{0.18}As$ layer structure as a function of buffer layer annealing temperatures.

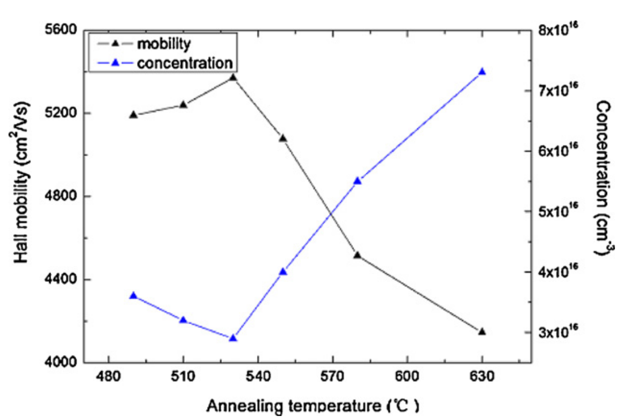


**Fig. 7.** The deduced mobility and carrier concentration of $In_{0.82}Ga_{0.18}As$ epilayers with buffer layers annealed at different temperatures.

in the $In_{0.82}Ga_{0.18}As$ epitaxial layers. From Fig. 7, we found that the $In_{0.82}Ga_{0.18}As$ epilayer with buffer layer thermal annealed at 530 °C has the best electrical property.

In order to obtain high quality $In_{0.82}Ga_{0.18}As$ epilayer, various annealing temperatures of buffer layers were employed to improve the crystalline quality of $In_{0.82}Ga_{0.18}As$. From the results of SEM, XRD and Hall measurements, there exists an optimum annealing temperature of buffer layer for the growth of $In_{0.82}Ga_{0.18}As$ epilayers. That is, the $In_{0.82}Ga_{0.18}As$ epilayer with buffer layer thermal annealed at 530 °C has the best crystalline quality. Our work shows a simple way on how to get high quality epilayers in the growth of InGaAs on InP substrate and the results obtained from this paper will become the basis of studying the InGaAs epilayers with different thicknesses and material compositions.

## 4. Conclusions

In summary, we have studied the effect of the thermal annealed $In_{0.82}Ga_{0.18}As$ buffer layer on the crystalline quality of the $In_{0.82}Ga_{0.18}As$ epilayers. Several different temperatures have been studied to obtain the optimum annealing conditions. It is found that the epilayer's quality is strongly dependent on the buffer layer thermal annealing temperatures. The $In_{0.82}Ga_{0.18}As$ epilayer shows the best crystalline quality when the annealing temperature is 530 °C. Two different processes may have strong influence on the crystalline quality of $In_{0.82}Ga_{0.18}As$ epilayers. One is the recrystallization which is dominant at lower annealing temperatures and the other is the reevaporation process which is dominant at higher annealing temperatures.

## Acknowledgments

This work was supported by the National Natural Science Foundation of the China under Grant Nos. 50632060 and 50972141.

## References

[1] R.W.M. Hoogeveen, R.J. vander A, A.P.H. Goede, Infrared Phys. Technol. 42 (2001) 1–16.
[2] M.A. di Forte-Possion, C. Brylinski, J. Cryst. Growth 124 (1992) 782–791.
[3] S.L. Murray, F.D. Newman, C.S. Murray, D.M. Wilt, M.W. Wanlass, P. Ahrenkiel, R. Messham, R.R. Siergiej, Semicond. Sci. Technol. 18 (2003) s202–s208.
[4] Y.G. Zhang, Y. Gu, K. Wang, A.Z. Li, C. Li, Semicond. Sci. Technol. 23 (2008) 125029.
[5] A. Rogalski, Infrared Phys. Technol. 43 (2002) 187–210.
[6] J. Kaniewski, J. Muszalski, J. Piotrowski, Phys. Status Solidi (A) 201 (2004) 2281–2287.
[7] M.J. Cohen, G.H. Olsen, Proc. SPIE 1946 (1993) 436–443.
[8] R.U. Martinelli, T.J. Zamerowski, P.A. Longerway, Appl. Phys. Lett. 53 (1988) 989–991.
[9] M. Wada, H. Hosomatsu, Appl. Phys. Lett. 64 (1993) 1265–1267.
[10] Z.C. Zhang, S.Y. Yang, F.Q. Zhang, B. Xu, Y.P. Zeng, Y.H. Chen, Z.G. Wang, J. Cryst. Growth 247 (2003) 126–130.
[11] D.S. Kim, S.R. Forrest, M.J. Lange, M.J. Cohen, G.H. Olsen, R.J. Menna, R.J. Paff, J. Appl. Phys. 80 (1996) 6229–6234.
[12] T.M. Zhang, G.Q. Miao, Y.X. Jin, J.C. Xie, H. Jiang, Z.M. Li, H. Song, Microelectr. J. 38 (2007) 398–400.
[13] T.M. Zhang, G.Q. Miao, Y.X. Jin, S.Z. Yu, H. Jiang, Z.M. Li, H. Song, J. Alloy. Compd. 458 (2008) 363–365.
[14] T.M. Zhang, G.Q. Miao, Y.X. Jin, S.Z. Yu, H. Jiang, Z.M. Li, H. Song, J. Alloy. Compd. 472 (2009) 587–590.
[15] T. Sasaki, K. Arafune, H.S. Lee, N.J. Ekins-Daukes, S. Tanaka, Y. Ohshita, M. Yamaguchi, Physica B 376–377 (2006) 626–629.
[16] A.Z. Simoes, A.H.M. Gonzalez, M.A. Zaghete, J.A. Varela, B.D. Stojanovic, Thin Solid Films 384 (2001) 132–137.
[17] C.F. Lin, G.C. Chi, M.S. Feng, J.D. Guo, J.S. Tsang, J.M. Hong, Appl. Phys. Lett. 68 (1996) 3758–3760.
[18] C.R. Kim, J.Y. Lee, C.M. Shin, J.Y. Leem, H. Ryu, J.H. Chang, H.C. Lee, Solid State Commun. 148 (2008) 395–398.
[19] M. D'Hondt, I. Moerman, P. Van Daele, P. Demeester, IEE Proc. Optoelectron. 144 (1997) 277–282.
[20] F. Xiu, Z. Yang, D. Zhao, J. Liu, K.A. Alim, A.A. Balandin, J. Cryst. Growth 286 (2006) 61–65.
[21] D.R. Mace, M. Pepper, R. Grey, J. Phys.: Condens. Matter 4 (1992) L487–l494.
[22] T. Zhang, M. Debnath, S.K. Clowes, W.R. Branford, A. Bennett, C. Roberts, L.F. Cohen, R.A. Stradling, Physica E 20 (2004) 216–219.
[23] L. Botha, P. Shamba, J.R. Botha, Phys. Status Solidi (c) 5 (2008) 620–622.
[24] D.K. Schroder, Semiconductor Material and Device Characterization, Third ed., IEEE Press, New Jersey, 2006.
[25] T.M. Zhang, G.Q. Miao, H. Jiang, Y.X. Jin, S.Z. Yu, H. Song, Z.M. Li, Mater. Sci. Semicond. Process. 12 (2009) 156–160.