Growth of $Ga_xIn_{1-x}As_{1-y}Sb_y$ Alloys by Metalorganic Chemical Vapor Deposition

LI SHUWEI,† JIN YIXIN, ZHOU TIANMING, ZHANG BAOLIN, NING YONGQIANG, JIANG HONG, and YUAN GUANG

Chang Chun Institute of Physics, Academia Sinica, 130021 Chang Chun, P.R. China

The quaternary GaInAsSb alloy system with direct band gaps adjustable in wavelength from 1.7 to 4.3 μm, which may provide the basis for emitters and detectors over this entire region, was studied. Alloys of GaInAsSb were grown lattice-matched on GaSb substrates by metalorganic chemical vapor deposition using a conventional atmospheric pressure horizontal reactor. The properties of the GaInAsSb alloys were characterized by single crystal x-ray rocking curves, the double crystal x-ray rocking curves, the photoluminescence and infrared absorption. A preliminary study of the capabilities of scanning electron acoustic microscopy in the characterization of GaInAsSb alloy has been made, some observations are briefly compared with scanning electron microscopy.

Key words: GaInAsSb, metalorganic chemical vapor deposition (MOCVD), scanning electron acoustic microscopy (SEAM)

INTRODUCTION

III-V antimonide compounds have several important applications including optical communications employing fluoride-based fibers,[1] laser radar exploiting atmospheric transmission windows, and remote sensing. The quaternary GaInAsSb alloy system with direct band gaps adjustable between 1.7 and 4.3 μm was grown lattice-matched on GaSb, InP, and InAs substrates which may provide the basis for emitters and detectors over this entire region. GaInAsSb alloys grown by liquid phase epitaxy (LPE) were firstly reported in 1976.[2] There is a miscibility gap for GaInAsSb alloy grown by equilibrium growth techniques such as LPE so it is difficult to grow GaInAsSb alloys in the miscibility gap by LPE. The metastable GaInAsSb alloys with compositions in the miscibility gap can be grown by using nonequilibrium techniques such as molecular beam epitaxy (MBE)[3] and metalorganic chemical vapor deposition (MOCVD).[4] Scanning electron acoustic microscopy (SEAM) was developed in 1980 and has been mainly used in the last years in the characterization of thermal, elastic, and pyroelectric properties on a microscale resolution.[5] The observation by SEAM is especially useful for nondestructive analysis of materials for optics and electronics.

(Received April 5, 1995; revised July 21, 1995)

EPITAXIAL GROWTH

The alloys of GaInAsSb were grown on GaSb substrates by MOCVD using a conventional atmospheric pressure horizontal reactor.[6] The sources of Ga, In, Sb, and As were trimethylgallium (TMGa), trimethylindium (TMIn), trimethylantimony (TMSb), and arsine (AsH_3) diluted to 10% in hydrogen, respectively. TMGa, TMIn, and TMSb were held at −14, 16, and −10°C, respectively, by using temperature baths and carried by Pd-diffused hydrogen into the reactor. The substrates were n-GaSb (Te-doped) oriented 2–3° off (100) toward <110>. GaSb was cleaned by degreasing

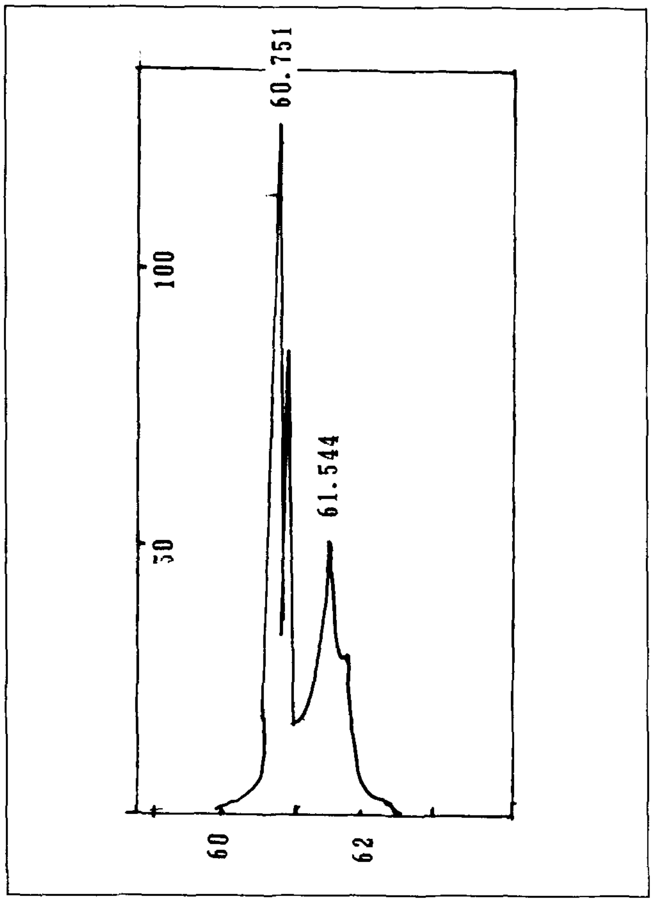

Fig. 1. The single crystal x-ray diffraction pattern.

in solvents and deionized water. It was then chemically polished by a solution of HNO_3:HCL:CH_3COOH = 0.2:2:20 for 15 min, rinsed with deionized water, blown with dry nitrogen and then put into the reactor. The growth temperature was between 560 and 610°C.

By the method reported by Moon et al.[7] we obtained the energy-composition relation for $Ga_xIn_{1-x}As_{1-y}Sb_y$

$$Eg(x,y) = 0.359 + 0.48x - 0.78y - 0.398\,xy + 0.6\,x^2 - 0.596\,y^2 + 0.185\,x^2 y + 0.054\,xy^2. \quad (1)$$

The single-crystal x-ray diffraction pattern of a GaInAsSb epilayer on a GaSb substrate in Fig. 1 shows good crystallinity. Figure 2 shows the double-crystal x-ray rocking curve of the (400) diffraction of a GaInAsSb epilayer on a GaSb substrate. The full width at half maximum (FWHM) of 5 arc-min shows the high crystalline quality of the GaInAsSb epilayer.

Photoluminescence measurements of GaInAsSb epilayers were carried out at 72K excited by the 0.5145 nm line from an argon ion laser with a power of 100 mW. Figure 3 shows the photoluminescence spectra of two GaInAsSb epilayers. The peak wavelengths are 1.966 and 2.136 μm and FWHM are 26 and 30 meV, respectively. This indicates that the epilayers have high quality. Figure 4 is an infrared absorption spectrum of a GaInAsSb epilayer at 300K. The compositions of GaInAsSb epilayers were directly determined by electron microprobe. The energy gaps of GaInAsSb alloys were determined by photoluminescence or infrared absorption spectra. The values of Eg measured by photoluminescence and infrared absorption are in good agreement with the values of Eg calculated from the Eq. (1). The metastable GaInAsSb alloys with compositions in the miscibility gap were successfully grown by metalorganic chemical vapor deposition.

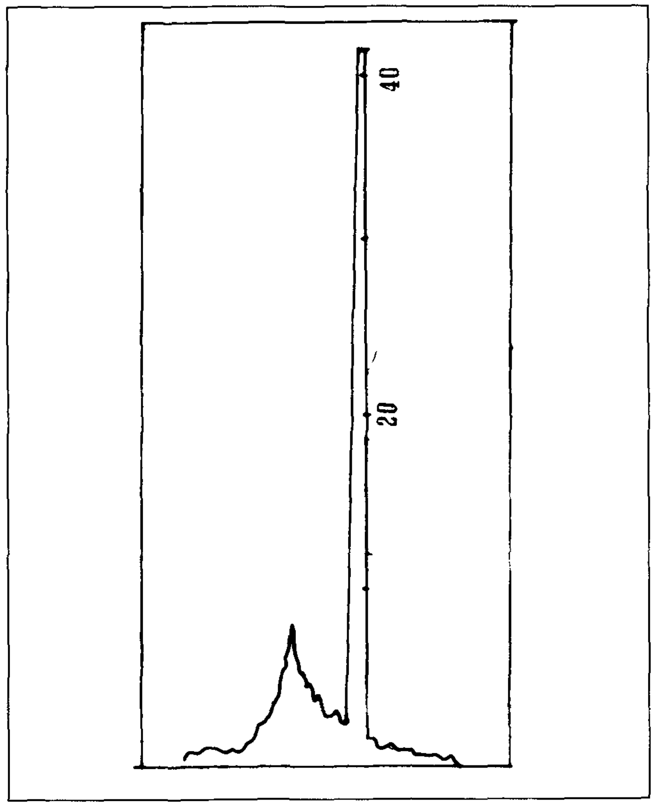

Fig. 2. The double crystal x-ray rocking curve.

EXPERIMENTAL OF SCANNING ELECTRON ACOUSTIC MICROSCOPY

Scanning electron acoustic microscopy (SEAM) observations were performed in a system constructed using conventional scanning electron microscopy (SEM) to which several newly designed parts a flexible plug-in beam blanking system, an opto-electric coupler and a spring loaded and metal shielded PZT electron-acoustic signal detector were attached. It has been successively reported as a new experimental tool for the study of polarization, phase transition, subgrain boundaries, and domain structure in polar materials and nondestructive observation of internal phenomena in many other materials and devices.[8,9]

Figure 5 shows the SEM and SEAM images of a GaInAsSb layer. The comparison of SEM and SEAM images shows that both techniques provide different information. The image in Fig. 5a shows pyramidal hillocks parallel with the <110> axis. In-situ SEAM images in Fig. 5b and 5c show these hillocks formed during the growth proress. A hypothesis has been made that GaInAsSb has a face centred cubic Bravais lattice so there is no piezoelectric coupling for the

<100> crystal orientation of substrate and epilayer.[10] The thermoelastic coupling is the main signal generation mechanism in GaInAsSb epilayers. By introducing the values of specific heat C and thermal conductivity K in the equation of the value of the thermal decay length $d = (2\ K/fC\rho)^{0.5}$ (ρ is the density and f the frequency) the values of 9.2 and 10.6 μm for d at 456 and 341 KHz, respectively, are obtained.[8] Thus, the features emerging at low frequencies would be situated deeper in the sample.

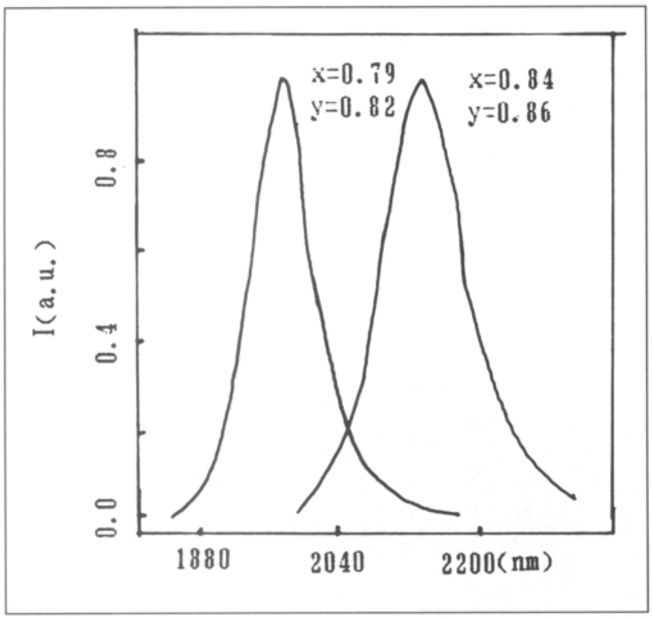

Fig. 3. The PL spectra of $Ga_xIn_{1-x}As_{1-y}Sb_y$ alloys at 72K.

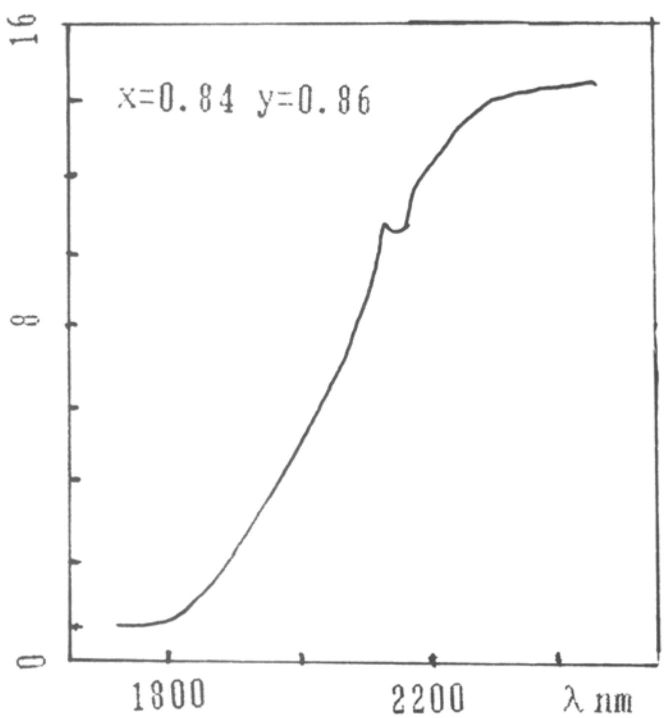

Fig. 4. The infrared absorption spectrum of $Ga_{0.34}In_{0.16}As_{0.14}Sb_{0.36}$ alloy at room temperature.

CONCLUSIONS

GaInAsSb alloys have been successfully prepared by atmospheric pressure-MOCVD using TMGa, TMIn, TMSb, and AsH_3 as source materials. The results of single crystal x-ray diffraction, double crystal x-ray rocking curves, photoluminescence spectra, and in-

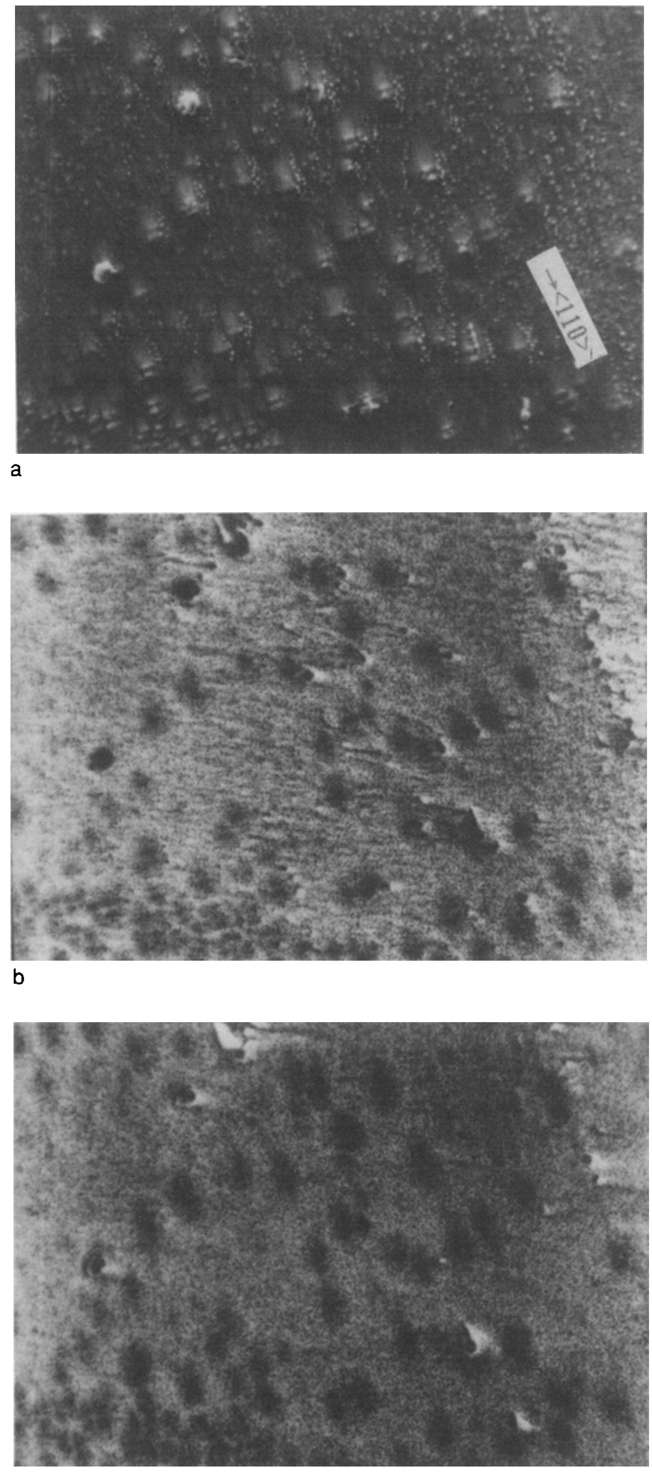

Fig. 5. The GaInAsSb alloy images: (a) the SEM image, (b) the SEAM image f = 456 KHz, and (c) the SEAM image f = 341 KHz. (mag x200)

frared absorption spectra indicate that high quality GaInAsSb alloys are obtained. The experimental results of SEAM indicates that SEAM reveals internal information about the specimen. Electron acoustic imaging by SEAM has definite advantages as compared with secondary electron imaging.

ACKNOWLEDGMENTS

The authors wish to thank Jiang Fuming, Yin Qingrui, and Zhang Bingyang of Shanghai Institute of Ceramics Academia Sinica for the SEAM image. This work was supported by the National Advanced Material Committee of China under grant 863-715-01-02-02.

REFERENCES

1. S. Shibata, M. Horiguchi, K. Jinguji, S. Mitachi, T. Kanamori and T. Manabe, *Electron. Lett.* 17 (2) 775 (1981).
2. R. Sankaran and G. Antapas, *J. Cryst. Growth* 36 (2) 198 (1976).
3. W.T. Tsang, T.H. Chin, D.W. Kisker and J.A. Pitenberger, *Appl. Phys. Lett.* 48 (3), 283 (1985).
4. M.J. Cherng, H.R. Jen, C.A. Larsen and G.B. Stringfellow, *J. Cryst. Growth* 77, 408 (1986).
5. M. Urchulutegui, J. Piqueras and J. Llopis, *J. Appl. Phys.* 65 (7), 1 (1989).
6. Zhou Tiamning, Zhang Baolin, Jin Yixin, Jiang Hong and Ning Yongqiang, *Rare Metals* 11 (3), 1190 (1992) (in Chinese).
7. R.L. Moon, G.A. Antypas and L.W. James, *J. Electron. Mater.* 3 (3), 635 (1974).
8. M. Urchulutegui and J. Piqueras, *J. Appl. Phys.* 69 (5), 15 (1991).
9. F. Dominguez-Adame and J. Piqueras, *J. Appl. Phys.* 66 (5), 15 (1989).
10. D.L. Smith, *Solid State Comm.* 57 (12), 919 (1986).