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InGaAsPBi grown on InP substrate by gas source molecular beam epitaxy

Fangkun Tian, Likun Ai, Anhuai Xu, Hua Huang and Ming Qi

1 Key Laboratory of Terahertz Solid State Technology, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, People’s Republic of China
2 Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, People’s Republic of China
E-mail: likunai@mail.sim.ac.cn

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Abstract

The effects of growth condition on material quality of quinary alloy InGaAsPBi grown by gas source molecular beam epitaxy (GSMBE) were investigated systematically. It is found that 0.1% of Bi incorporation can play the role of surfactant effects and is beneficial to improve the material quality. The roughness of surface RMS measured by atomic force microscope (AFM) is 0.218 nm. Furthermore, the addition of a small amount of bismuth atoms promotes the binding of phosphorus atoms to group III atoms.

1. Introduction

In the last few years, dilute bismuth has attracted more and more attention because they have the characteristics of large spin–orbit splitting and band-gap reduction [1–6]. It is well known that the isoelectronic energy level of Bi exists in the valence band of most III–V materials since it is the largest and heaviest group V element [3, 6–9]. The small number of Bi substitute As and/or P in the InP, GaAs or InGaAs leads to an unusually narrow band gap due to the valence band cross-over principle [10–13]. Furthermore, dilute bismuth has the advantages of low thermal conductivity, high power factor and insensitive band gap temperature, which is expected to be an excellent thermoelectric material and a promising semiconductor material [14]. The material properties of this band structure will provide more possibilities for optoelectronic and electronic device applications [12, 14–17].

Previously, the research on dilute bismuth alloy mainly concentrate on GaAs-based materials, such as GaAs1−xBix/GaAs or GaN1−xAlxAs1−yBiy/GaAs [11, 18–20]. Feng G etc grew the In1−yGayAs1−xBiy layers with good crystal quality on the InP substrate through molecular beam epitaxy (MBE) for the first time, and its Bi doping amount was up to 2.5%. When the growth temperature was reduced to 260 °C, bismuth incorporation was as high as 6% [10, 21, 22]. In addition, Devenson etc grew the In1−yGayAs1−xBiy layers with up to 7% Bi incorporation through MBE, and studied its optical properties and structural characteristics [23]. Up to now, Zhou etc of our group grew InGaAsBi films by gas source molecular beam epitaxy (GSMBE). The incorporation of bismuth in InGaAsBi alloy was controlled by changing indium gallium beam ratio and bismuth flux, the incorporation rate of bismuth in InGaAsBi alloy was up to about 7.5% [6, 24, 25].

In this paper, we investigated systematically the effects of growth condition including Bi contents, AsH3 pressures and substrate temperature on InGaAsPBi material. It is found that 0.1% of Bi incorporation can play the role of surfactant effects [26–29] and is beneficial to improve the material quality. The incorporation of a small number of Bi atoms can promote the binding of P atoms to III group atoms. The addition of Bi atoms will introduce P-type carriers to compensate for the effect of background N-type carriers on mobility. The band gap of the InGaAsPBi can be well adjusted by controlling III–V ratio reasonably. Controlling the Bi contents in InGaAsBi alloys is very important for optoelectronic and electronic device, high-speed digital device and high-frequency microwave device applications [24] such as HBT (heterojunction bipolar transistor) [30–33], HEMT (high electron mobility transistor) [34, 35] etc.
2. Experiment

2.1. Materials

Materials used in the research were elements indium, gallium, bismuth, P$_2$ and As$_2$. During material growth, elements indium, gallium and bismuth fluxes are controlled by adjusting effusion cell temperatures, respectively. The group V of elements P$_2$ and As$_2$ are produced by cracking phosphorane and arsenane at 1000 degrees Celsius.

2.2. Experimental procedure

2.2.1. Growth of InGaAsPBi film

All In$_{0.88}$Ga$_{0.12}$As$_{0.27}$P$_{0.37}$ and In$_{0.88}$Ga$_{0.12}$As$_x$P$_{1-x}$Bi$_y$ films were grown on semi-insulating InP (100) substrates by a VG90 gas source molecular beam epitaxy system. Using an infrared radiation thermometer to measure the substrate temperature. The reconstruction of the substrate surface is monitored by in situ reflected high energy electron diffraction (RHEED). Before the growth, samples have been pre-degassed at about 350 °C in the preparation chamber for 2 h to evaporate others volatile species. When the substrate temperature reaches 300 °C inside P$_2$ flux to protect substrate surface and followed by heating to 425 °C for 3 min until the appearance of the (4×2)-(100) In-stable reconstruction. Then 600 nm InGaAsPBi layer is grown by lowering the substrate temperature to 300 °C.

2.2.2. Characterization of InGaAsPBi film properties

The InGaAsPBi materials are investigated by using various characterization techniques. The thickness of InGaAsPBi film was measured by AMBIOS XP-2 Stair Tester. The structural qualities of all films are characterized by a Philips High Resolution x-ray Diffraction (HRXRD) equipped with a four-crystal Ge (220) monochromatic using Cu K$_\alpha$1 ($\lambda = 0.154$ 06 nm) radiation by the same scan parameters along the (004) direction. Atomic force microscopy (AFM) is used to characterize the surface morphology and roughness of the sample. Using Hall measurements to measure room temperature carrier mobility and carrier concentrations of samples. Rutherford backscattering spectroscopy (RBS) is used to measure Bi contents. The He$^{2+}$ beam will be easily scattered after impinging on them. Therefore, these are better methods to measure the concentration of atoms especially for heavy atoms.

| Sample | Ts (°C) | Bi (°C) | PH$_3$ (Torr) | AsH$_3$ (Torr) | $\Delta a/a$ (ppm) | XRD FWHM (°) | Surface roughness (nm) |
|--------|---------|---------|--------------|----------------|-------------------|----------------|-----------------------|
| a1     | 365     | 0       | 660          | 90             | 644               | 43.2           | 1.02                  |
| a2     | 300     | 520     | 660          | 90             | 0                 | 14.4           | 0.351                 |
| a3     | 300     | 530     | 660          | 90             | −1325             | 36             | 0.294                 |
| a4     | 300     | 540     | 660          | 90             | −1828             | 50.4           | 0.223                 |
| a5     | 300     | 550     | 660          | 90             | −1860             | 57.6           | 0.227                 |
| a6     | 300     | 560     | 660          | 90             | −2095             | 75.6           | 0.218                 |

Figure 1. RBS spectrum of the InGaAsPBi film.

Table 1. Series A, the measured properties of InGaAsPBi with different Bi effusion cell temperature.

2. Experiment

2.1. Materials

Materials used in the research were elements indium, gallium, bismuth, P$_2$ and As$_2$. During material growth, elements indium, gallium and bismuth fluxes are controlled by adjusting effusion cell temperatures, respectively. The group V of elements P$_2$ and As$_2$ are produced by cracking phosphorane and arsenane at 1000 degrees Celsius.
3. Results and discussion

3.1. The effect of Bi contents

As shown in table 1, the properties of InGaAsPBi with different Bi effusion cell temperature are measured. The Bi contents of sample a6 is measured shown in figure 1. According to the RBS signal spectrum, the signal separation between Bi signal and other elements is detected in the 400–450 channel, and accurate quantitative analysis could be carried out in this channel. In addition, the peak/step length signal of element Bi was observed at the channel value of about 450, and the Bi content was about 0.1%. In, Ga, As and P elements contents is about 44%, 6%, 8.9% and 41% respectively.

Figure 2 shows the HRXRD swing curve of samples a1–a6. The relatively narrow and tall diffraction peaks correspond to InP diffractions and the relatively broad peaks correspond to InGaAsP and InGaAsPBi epilayers. It can be clearly seen that the mismatch between the diffraction peaks of InGaAsPBi and InP increases with the Bi contents increasing. The incorporation of a small number of Bi atoms promotes the binding of P atoms to III group atmos. Therefore, InGaAsPBi epilayers peaks moves from left to right cause the lattice constant to decrease. According to the table 1, the full width at half maximum (FWHM) of the InGaAsPBi epitaxial peaks gradually becomes wider with the increasing of Bi contents. The FWHM of sample a2–a6 is 14.4s, 36s, 50.4s, 57.6s, 75.6s respectively. If the Bi contents is properly controlled, the lattice constant of InGaAsPBi will match InP.

For samples of series A, the surface morphology of the sample was characterized by the AFM tapping mode. As shown in table 1 and figure 3, the root-mean-square (RMS) roughness in different Bi contents of the
InGaAsPBi epilayer. According to the figure 3, The RMS of sample a and sample b are 1.02 nm and 0.351 nm respectively. The RMS roughness decrease significantly with the increasing of Bi contents owing to the Bi surfactant effects.

Using Hall measurements to measure room temperature electrical properties of samples and reveal n-type. Figure 4 reports the variation of the carrier mobility and density as a function of the Bi contents, which possesses an electron concentration of $10^{17}$ cm$^{-3}$. Comparing to the sample a1 the electron mobility of sample a2 increased significantly after incorporation of Bi. It is owing to the Bi surfactant effects improve mobility of electrons. Because Bi incorporation introduces p-type carriers and compensate the background n-type carriers resulting in mobility decreases. The electron mobility decreases with the Bi contents increasing, which means that the intrinsic free electrons are compensated. When Bi is incorporated into InGaAsP isolated Bi atoms and

![Figure 4](image)

**Figure 4.** Hall mobility and Concentrations of electrons in different Bi contents for InGaAsP and InGaAsPBi samples.

| Sample No. | $T_s$ (°C) | Bi (°C) | $PH_3$ (Torr) | $AsH_3$ (Torr) | $\Delta a/a$ (ppm) | XRD FWHM ($\theta$) | Surface roughness (nm) |
|------------|------------|---------|--------------|----------------|--------------------|---------------------|------------------------|
| b1         | 300        | 540     | 660          | 80             | $-2381$            | 43.2                | 0.248                  |
| b2         | 300        | 540     | 660          | 90             | $-1828$            | 50.4                | 0.223                  |
| b3         | 300        | 540     | 660          | 100            | $-999$             | 39.6                | 0.232                  |
| b4         | 300        | 540     | 660          | 110            | $-657$             | 46.8                | 0.428                  |
| b5         | 300        | 540     | 660          | 120            | 668                | 57.6                | 0.159                  |
| b6         | 300        | 540     | 660          | 130            | 1632               | 64.8                | 0.172                  |

![Figure 5](image)

**Figure 5.** HRXRD (004) $\omega$–$2\theta$ scans for InGaAsPBi epilayers on InP with different $AsH_3$ pressures.
Figure 6. The surface morphology of the InGaAsPBi samples on InP with different AsH₃ pressures.

Figure 7. Hall mobility and Concentrations of electrons in different AsH₃ pressures for InGaAsPBi samples.

Figure 8. HRXRD ω-2θ scans for InGaAsPBi epilayers on InP with different substrate temperature.
pairs or clusters of Bi will induce Bi-related acceptor states that compensate the intrinsic free electrons [6, 15, 37].

### 3.2. The effect of AsH$_3$

As shown in table 2, the InGaAsPBi samples with different AsH$_3$ pressures. According to the figure 5 the HRXRD $\omega$-2$\theta$ scans of samples b1–b6. It is obvious that InGaAsPBi epilayers peaks moves from right to left with AsH$_3$ pressure increasing. As the AsH$_3$ pressure reaches 120 Torr the epitaxial peaks move the left side of the substrate peak. It is mean that transformed from tensile strain to compressive strain and the lattice constant increase. Continuing to increase the AsH$_3$ pressures, the lattice constant increase. FWHM of samples decreases at first and then increases and reaches the minimum value of 39.6s when the pressures of AsH$_3$ is 100 Torr.

From the figure 6, comparing to the AFM images at different AsH$_3$ pressures it is found that the RMS roughness value of sample b5 is 0.159 nm, which is the best. Comparing to others samples, the RMS roughness value of sample b4 become larger signifcantly. As shown in figure 7, the electron mobility and electron concentration are optimized under different AsH$_3$ pressures. It is clear that the sample b3 has better electrical properties.

### 3.3. The effect of substrate temperature

As shown in table 3, InGaAsPBi samples with different substrate temperature. The HRXRD $\omega$-2$\theta$ scans of samples c1–c6 are shown in figure 8. It is obvious that the mismatch among diffraction peaks of InGaAsPBi and InP increases as the temperature decreasing. InGaAsPBi epilayers peaks moves from left to right with the substrate temperature decreasing. It is means that the lattice constant decrease. Because Bi atoms easily incorporated at lower growth temperature, the incorporation of a small number of Bi atoms can promote the binding of P atoms to III group atoms. This conclusion is consistent with the lattice constant decrease due to the increase of Bi contents.

The RMS roughness versus the different substrate temperature of the InGaAsPBi epilayer is shown in figure 9. Comparing to the AFM images at different substrate temperatures, it is found that the RMS roughness

### Table 3. Series C, the measured properties of InGaAsPBi with different substrate temperature.

| Sample No. | Ts (°C) | Bi (°C) | PH3 (Torr) | AsH3 (Torr) | $\Delta a/a$ (ppm) | XRD FWHM (s) | Surface roughness (nm) |
|------------|---------|---------|------------|-------------|-------------------|--------------|------------------------|
| c1         | 280     | 540     | 660        | 90          | $-1983$          | 75.6         | 0.387                  |
| c2         | 290     | 540     | 660        | 90          | $-1816$          | 36.0         | 0.227                  |
| c3         | 300     | 540     | 660        | 90          | $-1828$          | 50.4         | 0.270                  |
| c4         | 310     | 540     | 660        | 90          | $-1456$          | 43.2         | 0.280                  |
| c5         | 320     | 540     | 660        | 90          | $-881$           | 97.2         | 0.308                  |
| c6         | 330     | 540     | 660        | 90          | $-112$           | 72.0         | 0.320                  |

Figure 9. The surface morphology of the InGaAsPBi samples with different substrate temperature.
value of sample c2 is 0.227 nm. This the surface quality is the best. The incorporation of a small amount of Bi act as a surfactant effects and improve the material quality.

Bi atoms can’t easily be incorporated if the substrate temperature too high, such as sample c6. On the contrary, if the substrate temperature too low, the surface migration of Bi will be limited, leading to a local increase in Bi contents and the formation of Bi related metallic droplets is easy, such as sample c1.

4. Conclusions

In summary, we have investigated the material quality of quinary alloy InGaAsPBi epilayers grown on InP substrates by gas source molecular beam epitaxy. The effects of growth condition including Bi flux, AsH3 pressures and temperature of substrate on material components, surface morphology and electrical characteristics were studied systematically. It is found that 0.1% of Bi incorporation can play the role of surfactant effects and is benefit to improve the quality of the material. The incorporation of a small number of Bi atoms can promote the binding of P atoms to III group element. The band gap width of the InGaAsPBi can be well adjusted by controlling III–V ratio reasonably. It is considered as the excellent semiconductor materials can be applied potential optoelectronic and electronic device.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

ORCID iDs

Fangkun Tian https://orcid.org/0000-0002-3450-1239

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