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Atmospheric-pressure metal–organic vapor-phase epitaxy of GaAsBi alloys on high-index GaAs substrates

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ABSTRACT

We investigated the growth characteristics and properties of GaAsBi layers grown by atmospheric-pressure metal–organic vapor-phase epitaxy on different GaAs substrate orientations. The surface morphology of GaAsBi alloys was investigated by means of scanning electron microscopy. The structural and optical properties of the alloys were examined using high-resolution X-ray diffraction (HRXRD) and photoreflectance spectroscopy, respectively. HRXRD results show that the GaAsBi growth rate was significantly lower on (1 1 5)A than on (0 0 1), (1 1 1)A and (1 1 4)A GaAs. The highest Bi content was obtained for GaAsBi layers grown on (1 1 5)A GaAs substrates.

1. Introduction

Semiconductor alloys, including semi-metallic compounds such as GaAsBi, are attracting increasing attention [1–15]. The special feature of GaAsBi alloys is the important bandgap reduction, even for small amounts of Bi [5,6,9–12]. Previous studies have revealed the temperature independence of the bandgap energy of GaAsBi [9,16]. These properties have significant potential for the development of heterostructure devices such as semiconductor lasers for communications systems for which the emission wavelength must remain constant under ambient temperature variations [9]. Semiconductor epilayer growth strongly depends on the atomic arrangement of the substrate surface. Therefore, growth of GaAsBi layers on high-index GaAs substrates may lead to improvements in the physical properties of these layers compared to materials grown conventionally on (0 0 1) substrates. Only the Henini group has reported the growth of GaAsBi layers on (0 0 1) and (1 1 3) GaAs substrates [17,18]. Interest in the use of high-index substrates to grow GaAsBi alloys is diverse. For example, in mismatched materials, higher critical layer thickness and longer emission wavelengths can be obtained. In addition, strong built-in piezoelectric fields in non-(0 0 1) strained heterostructures can drastically change their optoelectronic properties.

Here we describe the growth of GaAsBi alloys by atmospheric-pressure metal–organic vapor-phase epitaxy (AP-MOVPE) on different GaAs substrate orientations and compare their physical properties. We used high-resolution X-ray diffraction (HRXRD), scanning electron microscopy (SEM), and photoreflectance spectroscopy (PR) for structural and optical analyses.

2. Experimental details

Two series of GaAsBi alloys were grown on (0 0 1) and (11n) GaAs substrates (n=1, 4, and 5) with different $\frac{[TMBi]}{[TMBi]+[AsH_3]}$ ratios by AP-MOVPE using a horizontal reactor. For each of the series, growth was carried out in a single run on all GaAs substrates. Trimethylgallium (TMGa), trimethylbismuth (TMBi), and arsine (AsH_3) were used as precursors. The growth temperature was 420 °C and the V/III ratio was 9.5, which have previously been used for successful epitaxy of GaAsBi layers on (0 0 1) GaAs [4,19]. The substrate temperature was measured using a thermocouple inserted into the graphite susceptor. Before growth, the substrate was heated under a mixed flow of H_2 and AsH_3 and kept at 650 °C for 10 min to remove the native surface oxide layer. The temperature was then decreased to 420 °C and allowed to stabilize. Then a thick GaAs buffer layer was grown, followed by a GaAsBi epilayer. Sample growth times for $\frac{[TMBi]}{[TMBi]+[AsH_3]}$ ratios of 9×10^{-4} and 68×10^{-4} were 1500 and 3000 s, respectively. HRXRD analyses were performed using a diffractometer with Cu K_α radiation (λ=1.54056 Å) from a Discover D8 (40 kV, 55 mA) high-power X-ray generator. Surface analysis was carried out by SEM. Experimental details for PR measurements were as reported for a previous study [5].

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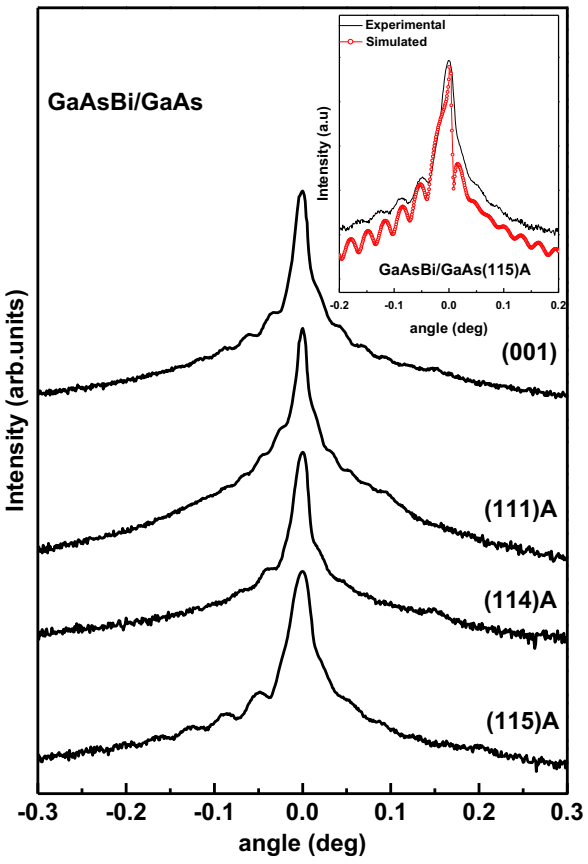

Fig. 1. HRXRD ω/2θ patterns for dilute GaAsBi layers grown on (0 0 1), (1 1 1)A, (1 1 4)A, and (1 1 5)A GaAs substrates with $\frac{[TMBi]}{[TMBi]+[AsH_3]} = 9 \times 10^{-4}$. The inset shows experimental and simulated HRXRD patterns for a GaAsBi layer grown on a (1 1 5)A GaAs substrate.

3. Results and discussion

Fig. 1 presents ω/2θ diffraction patterns for GaAsBi layers with low Bi content grown simultaneously on different GaAs substrates with $\frac{[TMBi]}{[TMBi]+[AsH_3]} = 9 \times 10^{-4}$. We chose (1 1 5), (0 0 4), (1 1 1), and (0 0 4) GaAs reflections for layers grown on (1 1 5)A, (1 1 4)A, (1 1 1)A, and (0 0 1) GaAs substrates, respectively. For all layers, slight broadening is evident for the substrate peak due to diffraction by the GaAsBi layer. In addition, the HRXRD patterns clearly display pronounced Pendellösung fringes originating from interference within the GaAsBi layers, indicating smooth and coherent interfaces. They also suggest that the GaAsBi layers are pseudomorphic and their thickness can be deduced from the Pendellösung oscillation periods [4]. The differences in layer thickness (Table 1) indicate variation in the growth rate with substrate orientation. This behavior is consistent with the kinetics of vapor-phase epitaxy. For homoepitaxial growth of GaAs/GaAs(*hkl*) at 750 °C, the maximum growth rate was obtained for growth on a (1 1 1)A substrate orientation [20,21]. The high (1 1 1)A growth rates indicate the ease of arsenic addition to the growing surface. Fujii et al. found that the rate of AlGaAs growth by MOVPE is independent of the (11*n*) GaAs substrate polarity [22]. However, a significant polarity effect for (11*n*) orientation was identified for GaAs growth in other studies [21,23–25]. To quantify the surface orientation dependence for GaAs growth at low temperature, we grew GaAs layers on the same substrate orientations and under the same experimental conditions with $\frac{[TMBi]}{[TMBi]+[AsH_3]} = 9 \times 10^{-4}$. All samples were characterized by SEM. Fig. 2 shows SEM images of GaAs layers grown simultaneously on different GaAs substrates

Table 1
Layer thickness determined by HRXRD, bandgap energy E_g and internal electric field strength F_{int} obtained from PR analysis, and Bi island density according to SEM for the study samples.

$\frac{[TMBi]}{[TMBi]+[AsH_3]}$	Substrate	Layer thickness (nm)	Growth rate (nm/s)	E_g (eV)	F_{int} 10^5 (V/m)	Bi island density (cm^{-2})
9×10^{-4}	(0 0 1)	210 ± 8	0.145 ± 0.004	1.402	30	8.8×10^5
	(1 1 1)	234 ± 5	0.162 ± 0.002	1.408	145	1.2×10^8
	(1 1 4)	261 ± 5	0.181 ± 0.002	1.410	75	1.2×10^8
	(1 1 5)	165 ± 9	0.114 ± 0.004	1.406	70	2.8×10^6
68×10^{-4}	(0 0 1)	30 ± 3	0.010 ± 0.001	1.340	–	1.6×10^6
	(1 1 1)	61 ± 8	0.021 ± 0.002	1.340	175	1.4×10^7
	(1 1 4)	76 ± 6	0.025 ± 0.002	1.362	132	5.6×10^6
	(1 1 5)	25 ± 4	0.008 ± 0.001	1.335	163	1.5×10^7

at 420 °C. There are pronounced differences in surface morphology among the sample. The GaAs surface for (0 0 1) and (1 1 1)A GaAs substrate orientations is smooth. The surface morphology for (1 1 4) and (1 1 5) samples is not smooth, but shows regular faceting. The growth rate for the layers was determined for a typical growth region, corresponding to the thickness most often observed in a cross-sectional SEM image. The results show that the relative growth rate decreases in the order (1 1 1)A > (1 1 4)A ~ (1 1 5)A > (0 0 1). Data on the growth rate and thickness for all the GaAs layers are listed in Table 2. It should be noted that the growth rate obtained for the (1 1 4)A sample is not as accurate because of the rough surface morphology. The decrease in growth rate in the kinetic-limited growth regime at lower temperature (420 °C) using TMGa can be attributed to incomplete decomposition of TMGa and AsH_3. At this lower temperature, the decomposition rate for TMGa and AsH_3 is less than 20% [26,27]. Pyrolysis of TMGa furnishes many methyl groups and/or Ga-methyl groups that reach the surface. Furthermore, the amount of atomic hydrogen from AsH_3 decomposition is very small, but the hydrogen needs to desorb from the TMGa the methyl groups, which are bound quite strongly. Thus, adsorbates cover a good part of the surface and hinder further precursor attachment.

Unusual growth-rate anisotropy can be observed for our GaAsBi/GaAs(*hkl*) heterostructures. Fig. 3 shows the growth rate of GaAs and GaAsBi layers as a function of substrate orientation. The growth rate is lower for GaAsBi than for GaAs at the same temperature. It is known that use of Bi as a surfactant and a low growth temperatures decrease the growth rate and change surface parameters such as adatom diffusion, the surface structure, and the sticking coefficient [21,28]. The maximum GaAsBi growth rate was obtained on (1 1 4)A GaAs and the minimum on (1 1 5)A GaAs. To verify these results, experiment were repeated under the same conditions. The results were reproducible within a maximum growth rate variation of ~1%. The growth-rate anisotropy can probably be explained in terms of the surface free energy for different crystal orientations. For these orientations, the surface coverage is different because each (11*n*) surface is formed via a different number of steps. A low sticking coefficient may be responsible for atom desorption, leading to lower incorporation [29]. The difference in growth rate between GaAs and GaAsBi may be due to the surfactant properties of Bi. Disparities in the growth rate may also be attributable to diversity in the kink site density for different surfaces. The amplitude of the Pendellösung fringes in HRXRD patterns is greater for the (0 0 1) and (1 1 5)A samples, indicating apparently higher surface quality. This is confirmed by SEM observations (Fig. 4). For the (0 0 1) and (1 1 5) layers, the surface contains few Bi islands. Results for the Bi island density deduced from SEM analysis are listed in Table 1. The results differ somewhat from those observed in our previous study [29] on the