Effects of Thermal Annealing on the Spectral Properties of GaAsBi Alloys Grown by Molecular Beam Epitaxy (MBE)

Ahmed Mohammed Alkaoud

Department of Physics, College of Sciences, Al Imam Mohammad Ibn Saud Islamic University (IMSIU), P. O. Box 90950, Riyadh 11623, Kingdom of Saudi Arabia

Abstract: GaAsBi thin layers of 1 μm thickness were grown by molecular-beam epitaxy on GaAs substrates at a growth temperature of 350 °C. To investigate the effects of the heat treatment on the optical and structural properties of these layers, annealing for a set were carried out at 200 °C and 300 °C for 3 h under a nitrogen gas conditions in a tubular furnace, and another set of layers for 90 s at temperature ranges from 600 to 700 °C in a hydrogen and argon gas mixture. The optical properties such as PL (Photoluminescence) of the as-grown and annealed samples were then characterized. The effect of growth temperature, substrate orientation, nitrogen doping and the annealing effect on the optical properties were presented in full details.

Key words: MBE (Molecular beam epitaxy), thermal annealing, optical properties, PL (Photoluminescence), semiconductors.

1. Introduction

Recently, dilute nitride semiconductors have attracted more attention for applications in electronics [1, 2] and optoelectronics [3, 4], including solar cells. This stems from the observation that small quantities of nitrogen in GaAs modify the conduction band structure and reduce the band gap very significantly, leading to longer wavelength emission [1]. The band gap decreases by approximately 0.1 eV for each percent of N (Nitrogen) in the alloy. However, due to the large difference in atomic size between arsenic and nitrogen, it is difficult to incorporate large quantities of N into the alloy and there is a large miscibility gap in the Ga-As-N materials system. In addition, with increasing N content in the alloy, the optical efficiency decreases. This can be partially restored by post-growth annealing, but these results in an undesirable blue shift in the luminescence. In order to overcome the problem of decreasing optical efficiency with increasing

nitrogen content in GaNAs films, indium is added to provide InGaAsN layers, which can be lattice-matched to GaAs substrates. However, even for InGaAsN the optical efficiency decreases rapidly as the N concentration increases, which restricts the use of InGaAsN in long wavelength needed in telecommunication applications. For growth by PA-MBE (Plasma-assisted molecular beam epitaxy), the presence of In does not influence the incorporation of N in GaAs and theoretical studies indicate that co-alloying of the large In atom with the small N atom does not considerably reduce the total alloy formation energy.

A potential alternative to GaNAs is the GaAsBi system. Bismuth has previously been used extensively for the growth of GaAs by LPE (Liquid phase epitaxy), where it is well known to improve the properties of the layers. It is found that bismuth is not incorporated at high growth temperature in large quantities into all III-V films, due to the large size of the bismuth atom, but it can be used as a surfactant during the growth of III-Vs by MBE to improve the surface morphology. It

Corresponding author: Ahmed Mohammed Alkaoud, assistant professor, research fields: solid state and photovoltaic solar cells. E-mail: aalkaoud@hotmail.com.

has also shown that it is possible to grow GaAsBi alloys at relatively low temperatures by both MOVPE (Metal-organic vapour phase epitaxy) [2]. The GaAsBi alloy system has attracted significant attention due to its potential to realize a temperature-insensitive semiconductor band gap. PL (Photoluminescence) studies of GaAsBi have shown that the temperature variation of PL peak was fairly weak (~ 0.1 MeV/K) compared with that of GaAs. Fluegel et al. [3] also reported that the band gap decreases rapidly with Bi concentration (~ 83 MeV/% Bi); it was suggested that Bi modifies the band structure of GaAs significantly, because of the large bowing parameter ~ 5.6 eV and the large valence band splitting. Recently, GaAsBi alloys have shown a strong enhancement of the spin-orbit splitting energy. This suggests that this material system can be exploited in spintronic applications [3]. GaAsBi alloys have also been proposed as good candidates to fabricate THz emitters and detectors [4].

There is another exciting possibility where the GaAsBiN materials system can be incorporated in multijunction solar cells. Although most of the commercially available solar cells are made from silicon with a maximum efficiency of 27%, III-V triple-junction solar cells hold the record for efficiency of 40.7% (500 sun concentration). They are mainly used for space applications but they are the most important contestant for terrestrial concentrator photovoltaic applications. There is considerable effort to develop solar cells with efficiencies above 30%. It is believed that in multiple band gap cells it might be possible to raise this efficiency to around 50%. The current state-of-the-art for triple junction solar cell, GaInP (1.9 eV)/metamorphic InGaAs (1.3 eV)/Ge (0.66 eV), yields a 1 sun efficiency of 33%. There is a need for 1-1.1 eV cell that if retrofitted to existing GaInP/GaAs/Ge tandems would yield to practical 1 sun efficiencies of about 40% (currently 33%) and concentrated efficiencies $\gg 45\%$ (currently 40.7% under 500 sun). However, there is a lack of 1 eV

material among conventional III-V alloys lattice matched to GaAs or Ge.

Theoretical predictions [5] suggest that: (a) Bi and N could compensate for the strong local perturbation each introduces because they are both complementary in size and electronegativity with respect to As, this may potentially improve carrier mobility while preserving the strong bowing of the band gap, (b) co-alloying with Bi and N in GaAs will drastically lower the N concentration required to reduce the band gap of the alloy to 1 eV, (c) the strain compensation due to the size difference between N and Bi also reduces the alloy formation energy, (d) the crystal quality of $\text{GaN}_y\text{As}_{1-x-y}\text{Bi}_x$ is expected to be superior to conventional dilute nitrides of the same wavelength that are lattice matched to GaAs. The theoretically calculated composition to reach the 1 eV band gap of an alloy lattice matched to GaAs is $\text{GaN}_{0.014}\text{As}_{1-x}\text{Bi}_{0.023}$ [6]. For the 1 eV band gap materials lattice matched to GaAs, it is expected that $\text{GaN}_{0.014}\text{As}_{1-x-y}\text{Bi}_{0.023}$, due to the very small N and Bi concentration (N = 1.4%, Bi = 2.3%), will have better optical and transport properties than $\text{Ga}_{1-y}\text{In}_y\text{As}_{1-x-y}\text{N}_x$ alloys (N = 2.8%, In = 8%) [6].

To date, most studies of III-V semiconductor structures have concentrated on the conventional (100)-oriented substrates [7] because of (i) the wide range of growth conditions which result in good epitaxial layer quality, (ii) the well-developed processing technology for this orientation, and (iii) the natural cleavage planes normal to the (100) orientation which are important in fabricating semiconductor devices, such as lasers. However, semiconductor structures are likely to exhibit interesting phenomena which are strongly orientation-dependent because (i) interband transitions involve both the valence band and the conduction band; (ii) growth kinetics depend on the surface orientation (Miller index); (iii) strain depends on the surface index when heterostructures are grown; and (iv) charge or surface polarity depend on the surface index. A new step forward in semiconductor

material engineering involves the growth of epitaxial layers on high index planes, HIPs (High index planes) (i.e. other than (100)) [8]. The high Miller index surfaces, which offer many interesting possibilities, to grow and study the structural, electronic and optical properties of GaAs/(Al, Ga)As heterostructures, quantum dots, dilute nitrides and bismides materials.

Due to the fact that the incorporation of atoms is strongly influenced by the arrangement of dangling bonds on the surface, the use of high Miller index surfaces as substrates for MBE growth of dilute III-V bismides will provide anew degree of freedom for tailoring the band gap in advanced device structures and will offer an additional degree of freedom to develop applications with improved properties with respect to the conventional (100)-grown devices.

Chine et al. have studied the effects of annealing on the photo-reflectance and photoluminescence for GaAsBi layers grown by metal-organic vapor phase epitaxy [9]. They reported that PL measurements below 100 K show a new large band centered at 1.36 eV and depends strongly on bismuth flow.

Zhang et al. suggested that the huge reduction in the band gap was due to a resonant interaction of the Bi impurity state with the valance band, which is similar to the effect of incorporating Nitrogen on the conduction band of GaAs [10].

However, the physics of GaAsBi is still under investigation and not many studies have been reported on the effects of annealing, substrate orientation, method of growth and the Bismuth concentration to improve the spectral properties of such material alloy.

The aim of this research is to grow the GaAsBi layer on (100) and (311)B GaAs substrates and investigate their optical properties before and after annealing to discuss their potential uses in photovoltaic,

optoelectronic, terahertz and spintronic applications.

2. Experiment Methods

Undoped GaAsBi layers were grown by MBE onto semi-insulating (001) and (311)B GaAs substrates at a growth temperature of $\sim 350^\circ\text{C}$ with a growth rate of one monolayer per second using different As to Ga flux ratios. Atomic Ga and Bi were used as group-III and group-V sources respectively, while as in the form of dimmers (As_2) was produced by using a two-zone purpose made cell. The beam equivalent pressure for Ga and Bi was $\sim 9 \times 10^{-7}$ and 1.2×10^{-7} Torr respectively. The As_2 flux was varied from 1.2×10^{-5} to 6×10^{-6} Torr.

Near stoichiometric condition was achieved with an As overpressure of 8.0×10^{-6} Torr and 1.0×10^{-5} Torr for growth of GaAsBi layers on (001) and (311)B GaAs substrates respectively. The growth details of the GaAsBi epitaxial layers are given in Table 1. More details about the growth conditions are represented in Ref. 7. Fig. 1 shows the GaAsBi layer structure grown on (001) and (311)B GaAs substrates. The nominal thickness of the GaBiAs epilayers is $1\ \mu\text{m}$. To investigate the effect of annealing on the optical and structural properties of these layers annealing heat treatment were carried out at 200 and 300°C for 3 h under N_2 gas conditions in a tubular furnace and at 600 to 700°C for 90 s in a mixture of hydrogen and argon gases. The PL measurements were performed on different samples such as GaAsBi epilayers grown on (100) and on (311)B GaAs substrates. PL spectra were recorded at a room temperature with an excitation of 514.5 nm line from an Ar laser with an excitation power of 100 mW. The signal was measured using an InGaAs detector associated with a standard lock-in amplifier.

Table 1 Details for the growth of dilute GaAsBi epilayers.

Sample	Ms-820 GaAsBi layer grown on (100) substrates	Ms-824 GaAsBi layer grown on (311)B substrates
Growth T ($^\circ\text{C}$)	~ 350	~ 350
As (Torr)	$\sim 8.0 \times 10^{-6}$	$\sim 8.0 \times 10^{-6}$

Bi (Torr)

 $\sim 1.2 \times 10^{-7}$ $\sim 1.2 \times 10^{-7}$

GaBiAs layer($\sim 1 \mu\text{m}$ thick)
Semi-insulating (100) or (311)B GaAs substrate

Fig. 1 Schematic diagram of GaAsBi layer on (100) and (311)B GaAs substrates.

3. Results and Discussion

It is well known that the optical and electronic properties of semiconductor materials are sensitive to the post-growth thermal annealing conditions such as duration of the annealing and temperature. For example, Michel et al. has reported that annealing at temperatures $> 400^\circ\text{C}$ can produce Mn segregation in GaAsMn magnetic semiconductors [6]. This leads to strong structural changes of the samples.

Therefore, a much lower post-growth heat treatment in the range $(200\text{--}300^\circ\text{C})$ was used to investigate for the first time the influence of annealing on the optical and structural properties of MBE grown GaAsBi alloys. In this study the GaAsBi layers were annealed at 200°C for 3 h under inert N_2 gas conditions in a tubular furnace.

Amongst all the as-grown (100) and (311)B samples that we measured only samples Ms820 [(100)] and Ms824 [(311)B] were considered, they showed a very strong PL signal as in Figs. 2 and 3. Fig. 2 shows the effect of annealing on the sample 824 while Fig. 3 shows the difference between the annealing

temperatures for sample 820. This is in agreement with what was reported by Shafi [7] on the GaAs related peak during his studies on Optical Studies of Dilute Nitride and Bismide Compound Semiconductors.

PL measurements were performed on different samples such as GaAsBi epilayers grown on (100) and on (311)B GaAs substrates. The effect of the annealing heat treatment is clearly visible when comparing the PL spectra of the as-grown and annealed samples grown on (100) and (311)B as shown in Figs. 2 and 3 respectively. In addition, a relatively weak GaAsBi emission emerges in the annealed samples labeled Ms820 [(100)] Ms824 [(311)B].

The growth parameters of the samples 820 and 824 are given in Table 1. It is clear that annealing has a strong effect the samples. This may be attributed to the improvement of the surface morphology of the samples as reported by Lemine et al. [11].

For rapid thermal annealing at 600 and 700°C carried out for a short time (90 s), another group of samples were studied, is $\text{GaInN}_{0.02}\text{As}_{0.98}$ double quantum wells grown on different GaAs substrate orientations. The structure of the samples is shown in Fig. 4. Three samples were studied for PL which are 2474 (reference sample), 2486 and 2479. Detailed information about the samples is shown in Table 2.

Fig. 2 PL spectra of sample 820 after annealing at 200 and 300 °C for 3 h.

Fig. 3 PL spectra of sample 824 as annealing and after annealing at 200 °C for 3 h.

GaAs
Al _{0.35} Ga _{0.65} As
GaAs
4 nm In _{0.36} Ga _{0.02} As _{0.98} QW
GaAs
7 nm In _{0.36} Ga _{0.02} As _{0.98} QW
GaAs
Al _{0.35} Ga _{0.65} As
GaAs Substrate
(100), (311)A, (311)B

Fig. 4 A schematic of the In_xGa_{1-x}As_{1-y}N_y double QW's structures.

As reported by Michel et al. [6] and Zhang et al. [10], introducing nitrogen into GaAs lattice by substituting As atoms creates localized energy states near the conduction band edge which leads to a huge band gap bowing that affects the electrical and optical properties of the materials. However, it also occupies the non-substitutional sites in the lattice of GaAs (i.e. the nitrogen atoms may incorporate in locations other than the group V lattice sites) leading to formation of N-related defects that can degrade the optical quality of the crystal and decreasing the optical efficiency and carrier lifetime. In order to recover this behavior it is common practice to subject the material to appropriate thermal treatment to improve optical properties of nitrogen-containing III-V compound semiconductors. The effect of post-growth RTA (Rapid thermal

annealing) on band gap in GaInN_{0.02}As_{0.98} DQW (Double quantum wells) grown on different GaAs substrate orientations namely (100), (311)A, (311)B is systematically investigated by PL under various excitation intensities and at various temperatures. RTA up to 600 °C improves the PL intensity for all planes but with different order of magnitude. Thermal annealing has strong effect on the electrical of optical properties of the samples, which were also investigated.

No PL peaks were observed for all the samples. Different annealing conditions were performed on the samples in order to see the effect of annealing temperature and duration. Table 3 presents the annealing conditions.

After annealing the samples in 5% H₂ and Ar for 90 s at 600 °C an enhancement of the PL intensity is observed for sample 2479 as shown in Fig. 5. From the figure, it is clear that the influence of annealing temperature on the improvement of the peak. All the peaks have the same wavelength (1,104 nm = 1.12 eV) with same patterns. There is another small peak at 1,157 nm (1.07 eV) which decreases as we raise the temperature.

Samples 2474 and 2486 didn't give any peaks before and after annealing. This may be due to very low

nitrogen content incorporated during the MBE process.

Table 2 Sample specification: InGaAsN DQW structures.

Sample	N ₂	T _g (QW) °C	Pressure	
MBE 2474	no	450	-	DQW 9 and 4 nm on 1/4 of 2 inch ² 100
MBE 2486	low	450	1.9E-4 mbar/300 w	DQW 9 and 4 nm on 2 inch ² 100
MBE 2479	high	435	2.3E-4 mbar/350 w	DQW 9 and 4 nm on 2 inch ² 100

Table 3 The annealing condition for the three samples.

Sample	Annealing temperature (°C)	Duration (s)	Ambient gas
2474	600	90	5% H ₂ and Ar
2474	600	30	N ₂
2474	700	30	N ₂
2479	600	90	5% H ₂ and Ar
2479	600	30	N ₂
2486	600	90	5% H ₂ and Ar
2486	600	30	N ₂

Fig. 5 PL graph for annealing sample 2479 in 5% H₂ and Ar₂ for 90 s at 600 °C.

Fig. 6 PL graph for annealing sample 2479 in nitrogen at 600 °C.

Fig. 7 PL graph for annealing sample 2479 in nitrogen at 700 °C.

Fig. 8 PL graph for annealing sample 2479 in different conditions.

Annealing sample 2479 in a nitrogen atmosphere at 600 and 700 °C showed a peak as demonstrated in Figs. 6 and 7. It is clear that the PL peak starts to decrease as the annealing temperature increase. Comparing the result of the three annealing conditions at 13 K showed that annealing the samples for 90 s gives better peak appearance as shown in Fig. 8. This enhancement in the PL peak may have resulted from the improvement of the structure and morphology of the MBE grown layers, due to the rapid thermal annealing.

4. Conclusions

The effect of thermal annealing for a time period of 2-3 h and at temperature range (200-300 °C) was investigated for the as-deposited GaAsBi alloys grown by MBE onto (100) GaAs and (311)B substrates in a nitrogen gas ambient and in a mixture of 5% H₂ and Ar gases.

The thermal annealing in a nitrogen atmosphere at a temperature of 600 to 700 °C for 90 s showed an improvement in the optical properties of the sample 2479 as shown in Figs. 6 and 7.

After annealing the samples in 5% H₂ and Ar gas mixture for 90 s at 600 °C, an enhancement of the PL intensity is observed for sample 2479 as shown in Fig. 5.

This showed that rapid thermal annealing at high temperature improved the optical properties of these layers with a clear PL peak enhancement in both various gas ambient mixtures.

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