Growth of 0.55eV-GaInAsSb Quaternary Alloy Films for a Thermophotovoltaic Device by Liquid Phase Epitaxy

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Abstract: Lattice matched $Ga_{1-x}In_xAs_ySb_{1-y}$ quaternary alloy films for thermophotovoltaic cells were successfully grown on n-type GaSb substrates by liquid phase epitaxy. Mirror-like surfaces for the epitaxial layers were achieved and evaluated by atomic force microscopy. The composition of the $Ga_{1-x}In_xAs_ySb_{1-y}$ layer was characterized by energy dispersive X-ray analysis with the result that $x=0.2$, $y=0.17$. The absorption edges of the $Ga_{1-x}In_xAs_ySb_{1-y}$ films were determined to be 2.256μm at room temperature by Fourier transform infrared transmission spectrum analysis, corresponding to an energy gap of 0.55eV. Hall measurements show that the highest obtained electron mobility in the undoped p-type samples is $512cm^2/(V\cdot s)$ and the carrier density is $6.1\times10^{16}cm^{-3}$ at room temperature. Finally, GaInAsSb based thermophotovoltaic cells in different structures with quantum efficiency values of around 60% were fabricated and the spectrum response characteristics of the cells are discussed.

Key words: GaInAsSb; LPE; thermophotovoltaic; spectrum response
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1 Introduction

Recently, there has been a growing interest in the field of thermoelectric conversion or thermophotovoltaic (TPV) technology due to its large power output, high achievable conversion efficiency, and better spectral match between the source's thermal radiation and photoresponse of the photovoltaic (PV) cells[1,2]. In a practical TPV system, the thermal radiation from a high-temperature body (emitter) is usually distributed from the visible (VIS) to the near infrared (NIR) regions, suppressing the application of conventional bulk or thin film materials like Si- or GaAs-based cells. To match this peculiar spectrum, GaSb and its ternary or quaternary alloys, such as GaInAsSb, have attracted tremendous attention because of their available narrower energy gap and well-defined photoresponse characteristic[3~5].

GaSb was first introduced into the PV community by Fraas when developing mechanically stacked GaAs/GaSb solar cells where a GaSb cell was designed as the bottom cell to convert the residual subband photon from the top GaAs cell. An improvement of energy conversion efficiency of 35% was recorded[6]. So far, many works have investigated the fabrication, properties, and optoelectronic applications of GaSb compound material. However, as for the TPV application, it is theoretically predicted that the optimum TPV cell should have a bandgap near 0.55eV, corresponding to a practical thermal emitter with the operating temperature 1000～1500℃. $Ga_{1-x}In_xAs_ySb_{1-y}$ quaternary alloys, with the features of a wide range of achievable bandgap and eptaxial growth on the commercially-available GaSb wafers with the identical lattice constant, is an optimum candidate for TPV applications[7,8]. Unfortunately, the fabrication of this quaternary film with a narrow energy gap near 0.55eV is challenging with the liquid phase epitaxy (LPE) method due to the existence of the miscibility gap region in the phase diagram[9]. Furthermore, LPE is a well-defined technology for growth III-V group semiconductors as the result of its equilibrium state growth characteristics and because high quality epitaxial layers can be obtained.

In this paper, 0.55eV $Ga_{0.8}In_{0.2}As_{0.17}Sb_{0.83}$ thin films were successfully fabricated on GaSb substrate by the LPE method. Analysis methods such as atomic force microscopy (AFM), X-ray diffraction (XRD), energy dispersive X-ray analysis (EDAX), and Hall measurement were employed to evaluate the quality of the epitaxial films. Then, GaInAsSb based TPV cells with structures of p-GaInAsSb/n-GaSb and p-GaSb/p-GaInAsSb/n-GaSb were fabricated, and the

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quantum efficiencies (QE) of the TPV cell were measured.

2 Experiment

N-type GaSb substrates with carrier concentrations of $1.9\times10^{17}\ cm^{-3}$ were used in this paper. First, the substrates were rinsed successively with tetrachloromethane, acetone, ethanol, and de-ionized water in ultrasonic baths. Before loading into a nitrogen glove box atmosphere, the substrates were etched in a mixture solution of CH_3COOH, H_2O and HF (20 : 9 : 1) to remove the native oxide layer.

$Ga_{1-x}In_xAs_ySb_{1-y}$ films were grown by LPE using a conventional horizontal graphite sliding-boat system. The starting materials are 6N pure In, Ga, Sb, and undoped polycrystalline GaAs. In the process of growing $Ga_{1-x}In_xAs_ySb_{1-y}$ films, the In-rich solutions with the atom fraction of Ga : In : As : Sb = 0.169 : 0.585 : 0.001 : 0.245 were homogenised and purified for 2h at 800℃. After loading the wafers, the melt was heated to 550℃ for 1h to completely dissolve the growth solutions, then the temperature was decreased to 520℃ at a cooling rate of 0.5℃/min. At 529℃, the substrates were contacted with the melt to grow $Ga_{1-x}In_xAs_ySb_{1-y}$ layers. The growth rates of the GaSb and $Ga_{1-x}In_xAs_ySb_{1-y}$ layers were about 6μm per minute, which is much higher than that of the MOCVD method. So, $Ga_{1-x}In_xAs_ySb_{1-y}$ films with thickness from 0.7 to 40μm can be grown with different growth times in our experiment. GaSb films were also grown by LPE at a temperature of 525℃ with the same growth procedure, and the atomic fraction of the liquid solutions is Ga : Sb = 0.94 : 0.06.

The morphologies of the epitaxial films were evaluated by atomic force microscopy and scanning electronic microscopy (SEM). X-ray diffraction was used to analyze the films' quality. Compositional analyses were characterized by energy dispersive X-ray analysis. The Fourier transform infrared (FTIR) transmission spectrum of $Ga_{1-x}In_xAs_ySb_{1-y}$/GaSb was measured at room temperature using a GaSb substrate as reference. Electrical properties of $Ga_{1-x}In_xAs_ySb_{1-y}$ epitaxial films were examined by Hall measurements. Then, Hall measurements were performed on the sample with In contacts using the Van der Paul method at 300K. For Hall measurements and the XRD analysis of the $Ga_{1-x}In_xAs_ySb_{1-y}$ epitaxial layers grown by LPE, the substrates were removed by grinding in order to eliminate their effects.

The back contact and the front contact grid on the epitaxial p-GaInAsSb /GaSb and p-GaSb/p-GaInAsSb/n-GaSb structure are Au:Ge alloy formed by

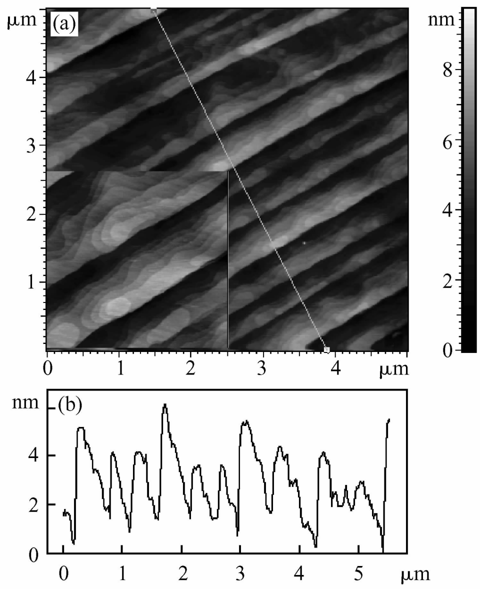

Fig.1 AFM image of GaInAsSb epitaxial film grown by LPE

the magnetron sputtering technique and alloyed at 250℃ for 1min. All TPV cells in this paper are 5mm × 5mm in area. The characterization of the spectrum response and quantum efficiency (QE) was performed at room temperature for all the cells.

3 Results and discussion

3.1 GaInAsSb film quality

Mirror-like surfaces for the $Ga_{1-x}In_xAs_ySb_{1-y}$ films were successfully achieved by LPE at an appropriate growth condition in our experiment. AFM was employed to evaluate the surface morphology. From Fig. 1(a), the texture like grooves and terraces are observed in the AFM image, which is quite similar with Mejia's result[10]. In each terrace there are many observable growth striations, which mean good growth quality for the epitaxial layers. The "S" shaped growth striations can be more clearly observed in the inset picture in Fig. 1(a). The height profile for the line shown in Fig. 1(a) is shown in Fig. 1(b). The steps detailed in the profile image in Fig. 1(b) represent the terrace heights that are between 4 and 6nm with widths around 0.6μm. The average roughness of the surface is 4.3nm. Good surface morphology for the very thick epitaxial films was not achieved in this work.

The composition of the epitaxial layers was determined using EDAX with the result that $x=0.2$, $y=0.17$. The rocking curve of the $Ga_{0.8}In_{0.2}As_{0.17}Sb_{0.83}$ (400) reflection was carried out initially to characterize the quality of the epitaxial layer. As seen in Fig. 2, the $Ga_{0.8}In_{0.2}As_{0.17}Sb_{0.83}$ film exhibits good quality

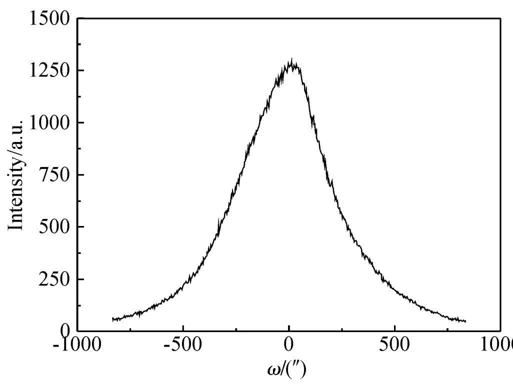

Fig. 2 Rocking curves of the $Ga_{0.8}In_{0.2}As_{0.17}Sb_{0.83}$ film

values. The FWHM of the peak is 0.13°, which is smaller than that of epitaxial 0.55eV GaInAsSb film grown by MOCVD[11].

The Fourier transform infrared transmission spectrum of the sample measured at room temperature is shown in Fig. 3. Defining the cutoff wavelength as the mid-transmittance wavelength, the absorption edges of the $Ga_{0.8}In_{0.2}As_{0.17}Sb_{0.83}$ film can be determined to be 2.256μm at room temperature. Transmission spectra recorded at room temperature show a shift in the absorption edge towards the low energy side for $Ga_{0.8}In_{0.2}As_{0.17}Sb_{0.83}$ in comparison to GaSb, as shown in Fig. 3. For a direct energy gap semiconductor, the absorption coefficient (α) of $Ga_{1-x}In_xAs_ySb_{1-y}$ can be described as $\alpha = A(h\nu - E_g)^{1/2}$, where α is the absorption coefficient in cm^{-1}, ν is the incident photon frequency, and A is a constant depending on the electron and hole effective masses and the optical transition matrix element. Therefore, based on the calculation of αd (d is the film thickness) from the FTIR transmission results, the calculated room temperature energy gap was 0.55eV for the $Ga_{0.8}In_{0.2}As_{0.17}Sb_{0.83}$/GaSb film corresponding to an absorption edge of 2.25μm, which is consistent with the former definition.

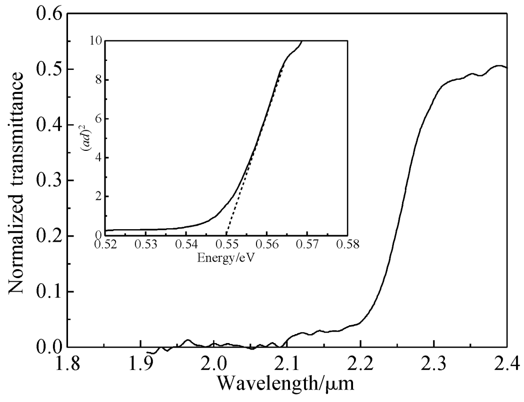

Fig. 3 Fourier transform infrared transmission spectra at room temperature of the $Ga_{0.8}In_{0.2}As_{0.17}Sb_{0.83}$ film Inset shows the corresponding for linear fitting.

Table 1 Electrical parameters of the $Ga_{0.8}In_{0.2}As_{0.17}Sb_{0.83}$ related epitaxial flims

Epitaxial layer	Type	N_a/cm^{-3}	$\mu/(cm^2/(V \cdot s))$
GaSb	p	1.7×10^{17}	774
GaInAsSb	p	6.1×10^{16}	512
GaInAsSb:Zn	p	2.1×10^{17}	606
GaInAsSb:Te	n	2.4×10^{17}	7325

For the application of $Ga_{0.8}In_{0.2}As_{0.17}Sb_{0.83}$ quaternary alloy in TPV cells, determining the electrical properties of the film is essential. Therefore, Hall measurements were carried out for the $Ga_{0.8}In_{0.2}As_{0.17}Sb_{0.83}$ films. Table 1 presents the electrical properties of the $Ga_{0.8}In_{0.2}As_{0.17}Sb_{0.83}$ films and the GaSb films. The electron mobility of the undoped $Ga_{0.8}In_{0.2}As_{0.17}Sb_{0.83}$ film grown was $512cm^2/(V \cdot s)$ with a carrier concentration (n-type) of $6.1\times10^{16}cm^{-3}$. Zn atoms and Te atoms are used in the LPE growth process to form p-type and n-type $Ga_{0.8}In_{0.2}As_{0.17}Sb_{0.83}$ films, with carrier concentrations of $2.1\times10^{17}cm^{-3}$ and $2.4\times10^{17}cm^{-3}$, respectively. The mobility of the $Ga_{0.8}In_{0.2}As_{0.17}Sb_{0.83}$ films of either p-type or n-type are much higher than the GaInAsSb films with a close solid composition grown by MOCVD[12].

3.2 GaInAsSb TPV cells

Both GaInAsSb and GaSb TPV cells are fabricated in this paper. The structure of GaSb cells are simple pn-junctions in which no window layers were fabricated because of the low surface recombination rate for p-type GaSb[7]. GaInAsSb based TPV cells were fabricated in two structures of p-GaInAsSb/n-GaSb and p-GaSb/p-GaInAsSb/n-GaSb. Figure 4 shows a cross section SEM image of the GaSb/$Ga_{0.8}In_{0.2}As_{0.17}Sb_{0.83}$/GaSb structure grown by LPE. The growth rates of $Ga_{0.8}In_{0.2}As_{0.17}Sb_{0.83}$ layers are about 6μm per minute, as mentioned above. But high growth rates also create difficulties in obtaining very thin epitaxial layers. In Fig. 4, the thickness of each epitaxial layer

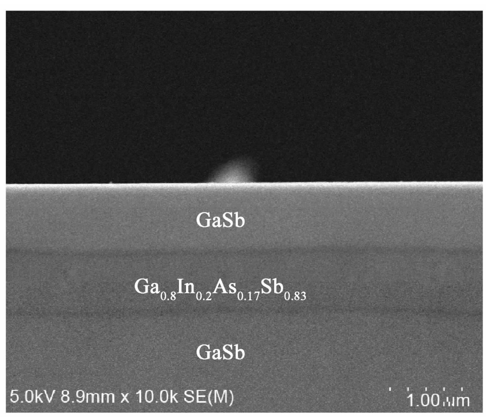

Fig. 4 SEM image of GaSb/$Ga_{0.8}In_{0.2}As_{0.17}Sb_{0.83}$/GaSb epitaxial layer grown by LPE

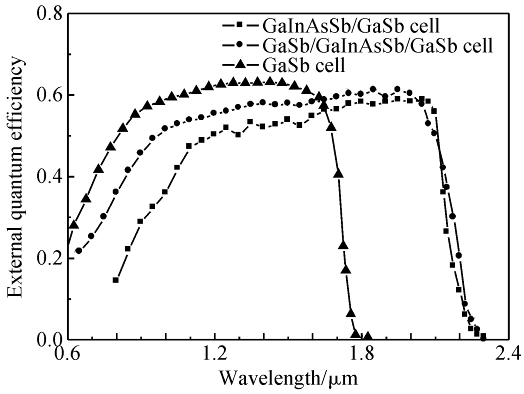

Fig. 5　External quantum efficiencies of GaSb and GaInAsSb based TPV cells

is 0.7μm with a growth time of less than 10s.

The external quantum efficiencies of the TPV cells are measured by a spectrum response measurement system. Figure 5 shows the external QEs of TPV cells with values near 60%, which are close to the results of Wang[13]. Compared with the GaSb cell, the QE curves of the GaInAsSb cell shift remarkably toward long wavelengths with an absorption edge near 2.2μm. This fits well with the result of the FTIR transmission spectrum. Thus, the GaInAsSb cells with lower energy gaps are more suitable than GaSb cells when the radiator is working at a relatively low temperature, for example, 1200℃. The QE value of a p-GaInAsSb/n-GaSb cell in short wave length is lower than that of a p-GaSb/p-GaInAsSb/n-GaSb cell with the same emitter layer thickness. This contributes to the higher surface recombination rate of p-GaInAsSb alloy than of p-GaSb alloy because photons with a short wavelength always show a high absorption coefficient and are always absorbed near the surface of the material. A high surface recombination rate would make the photo-generated carrier recombine quickly. The p-GaSb layer also played the role of the window layer, which is beneficial to the collection of photo-generated carriers.

The *I-V* characteristics of the TPV cells are difficult to evaluate because of the lack of a standard light source. Moreover, there is no well-accepted criterion for the *I-V* measurement of light sources in the TPV community. In our experiment, the best short circuit current density and open circuit voltage for the GaSb homo-junction cell and p-GaSb/p-GaInAsSb/n-GaSb cell are 54 and 71mA/cm^2, 0.35 and 0.26V, respectively, under a Halogen lamp with a color temperature of about 3000℃. The fill factors of the two cells are 0.64 and 0.61, respectively.

4 Conclusion

Smooth $Ga_{0.8}In_{0.2}As_{0.17}Sb_{0.83}$ epitaxial films were successfully grown on n-type GaSb substrates by the LPE method. AFM analysis showed that groove- and terrace-like surface morphology with an average roughness of 4.3nm was observed. The FWHM of the rocking curve of the films exhibits the high quality of the films. The absorption edges of the $Ga_{0.8}In_{0.2}As_{0.17}Sb_{0.83}$ films were determined to be 2.256μm at room temperature by the Fourier transform infrared transmission spectrum corresponding to the energy gap 0.55eV. The electrical property of the $Ga_{0.8}In_{0.2}As_{0.17}Sb_{0.83}$ films either p-type or n-type are measured through the Hall effect and showed good results. Two kinds of GaInAsSb TPV cells, p-GaInAsSb/n-GaSb and p-GaSb/p-GaInAsSb/n-GaSb, were fabricated using $Ga_{0.8}In_{0.2}As_{0.17}Sb_{0.83}$ composition. The quantum efficiency measurement of the TPV cells show that the QE curves of the GaInAsSb cell shift remarkably toward long wavelength comparing with GaSb cells. The QE value of the p-GaSb/p-GaInAsSb/n-GaSb cell is higher than that of the p-GaInAsSb/n-GaSb cell, especially in the short wavelength region.

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液相外延法制备 0.55eV-GaInAsSb 四元合金薄膜及其在热光伏器件中的应用

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摘要： 利用液相外延法(LPE)在 n 型 GaSb 衬底上成功制备了用于热光伏电池的 $Ga_{1-x}In_xAs_ySb_{1-y}$ 四元合金薄膜. 通过原子力显微镜对薄膜的表面形貌进行了分析评价. X 射线能谱(EDAX)分析表明四元合金薄膜的成分为 $x=0.2$, $y=0.17$. 红外傅里叶变换透射谱分析表明,其室温下的吸收截止波长为 2.256μm,对应禁带宽度为 0.55eV. 室温下的霍尔测试结果表明外延膜具有良好的电学性能,其非故意掺杂的薄膜表现为 p 型,载流子浓度为 $6.1\times10^{16}\ cm^{-3}$,迁移率为 $512cm^2/(V\cdot s)$. 又进一步利用 $Ga_{1-x}In_xAs_ySb_{1-y}$ 薄膜制备了不同结构的 GaInAsSb 基热光伏电池,光谱响应测试表明其量子效率可达 60%.

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