第 34 卷第 4 期
2015 年 8 月

红 外 与 毫 米 波 学 报
J. Infrared Millim. Waves

Vol. 34, No. 4
August, 2015

文章编号: 1001 - 9014(2015)04 - 0391 - 05

DOI:10.11972/j.issn.1001 - 9014.2015.04.002

# Controllable growth of GaSb polycrystalline thin films based on thermophotovoltaic device

CAI Hong-Kun[1], LI Tao[1], WU Xian-Liang[1], ZHANG De-Xian[1*], NI Jian[2], ZHANG Jian-Jun[2]

(1. Department of Electronic Science and Technology, College of Electronic Information and Optical Engineering, Nankai University, Tianjin 300071, China;
2. The Key Laboratory of Photoelectronic Thin Film Devices and Technology, Tianjin 300071, China)

**Abstract**: GaSb polycrystalline thin films were prepared on ITO substrate with the method of PVD. By controlling substrate temperatures and thicknesses of GaSb films, surface roughness, grain size, electrical and optical properties were investigated. The preferred orientation of GaSb thin films grown on ITO substrate had changed from GaSb (111) to GaSb (220) under specific growth conditions which had never occurred on glass substrates. GaSb thin films with (220) preferred orientation had higher hall mobility because of less grain boundaries and less defects. The thin films after optimization possess, the absorption coefficients over $10^4$ $cm^{-1}$, which is desirable in the application of TPV thin film cells.

**Key words**: GaSb thin films, the crystal orientation, thermophotovoltaic
**PACS**: 81.05. Dz, 81.15. Cd

# 基于热光伏电池 GaSb 多晶薄膜的可控生长

蔡宏琨[1], 李 涛[1], 吴限量[1], 张德贤[1*], 倪 牮[2], 张建军[2]
(1. 南开大学 电子信息与光学工程学院 电子科学与工程系,天津 300071;
2. 天津市光电子薄膜器件与技术重点实验室,天津 300071)

**摘要**:采用物理气相沉积(PVD)法在 ITO 透明导电衬底上制备 GaSb 多晶薄膜.研究了衬底温度及薄膜厚度对 GaSb 薄膜结构特性、电学特性以及光学特性的影响.在一定条件下生长的 GaSb 薄膜择优取向由 GaSb(111)晶向转变为 GaSb(220)晶向,这是在玻璃衬底上生长 GaSb 薄膜没有发现的现象.择优取向改变为(220)晶向的 GaSb 薄膜具有更高的霍尔迁移率.因为这种薄膜材料具有更少的晶粒间界和更少的缺陷.经优化后的 GaSb 薄膜的光学吸收系数在 $10^4$ $cm^{-1}$ 以上,适用于热光伏薄膜太阳电池中.

**关 键 词**:GaSb 薄膜;择优取向;热光伏(TPV)

**中图分类号**:P578.2; TN305.92 **文献标识码**:A

## Introduction

Thermophotovoltaic devices are basically photovoltaic solar cells that utilize the thermal infrared radiation of a heated source to directly generate electric power. System modelling and analysis indicates that low-bandgap (0.25 to 0.7 eV) TPV cells with spectral response extending to the mid-infrared are the best choice for many applications[1-4]. Cody[3] has surmised that a maximum efficiency and maximum power density can be achieved with bandgap between 0.25 and 0.5 eV and with emitter temperatures in the range of 1 000 to 1800℃. These GaSb-based TPV devices share much in common with mid-infrared photodiodes, and the progress in low-bandgap TPV cells has greatly benefited from the development of related technologies for mid-infrared optoelectronics including detectors, light-emitting diodes, tandem solar cells and lasers[5-6].

If GaSb thin films on cheap substrate can be re-

**Received date**: 2014 - 05 - 09, **revised date**: 2015 - 04 - 16 **收稿日期**:2014 - 05 - 09, **修回日期**:2015 - 04 - 16
**Foundation items**:Supported by the National High Technology Research and Development Program of China (2011AA050513), and National Basic Research Program of China (2012CB934201)
**Biography**:Biography: CAI Hong-Kun (1978-), female, Tianjin, Associate professor, doctor, Research area involves semiconductor materials and device. E-mail: caihongkun@nankai.edu.cn
* **Corresponding author**:E-mail: dexianzhang@nankai.edu.cn

placed the GaSb-based materials, the cost of TPV device would be greatly reduced. GaSb thin films have the advantages such as the low deposition temperature, applicable to the cheap and flexible substrate. Current techniques for growing these materials include MOCVD, MBE and LPE. If available, the physical vapor deposition (PVD) that can fabricate these thin film materials, would offer a low cost technique for semiconductor growth. The method of PVD has many advantages, such as using fewer materials and energy, and is also little harmful to the environment[7].

This paper aims to grow on proper substrates GaSb films with high absorption coefficients, good crystallinity and low defects, which are desirable in the application of TPV thin film cells. ITO ($In_2O_3$:Sn) is one of the most frequently used conducting materials with high transmittance and low resistance[8]. Therefore, the ITO substrate can be used in TPV cells as a window layer and the electrode, meanwhile, it also conducts the electricity generated by incident lights.

## 1 Experiment

In PVD equipment, the substrate is deposited above crucibles, and in the common region the elements evaporated from several sources mix with each other. The substrate is heated by a heater above it, and PID devices control the temperatures of the heater and crucibles. The evaporator sources (Ga and Sb) in the crucibles have a purity of 99.9999%. System vacuum of $10^{-4}$ pa was obtained before the growth of GaSb thin films. We set the temperatures of substrate at a range of 300 ~ 600℃, and temperatures of Ga and Sb crucibles were set at optimized 850℃ and 460℃, separately.

We mainly discussed the structural and electrical properties of GaSb films grown on ITO substrate. By AFM, we can see the roughness of the GaSb films. The thickness of films was measured using a surface profiler (AMBIOS XP-2). The structure of the films was characterized by X-ray diffract spectrum (XRD, Philips PANalytical X' Pert,). Electrical resistivity, mobility and carrier concentration were measured using a Hall automatic measuring system (HL 555DPC). Optical data were investigated by ultraviolet-visible-infrared spectrophotometer (Cary 5000).

## 2 Results and discussion

Substrate's temperature is one of the most crucial technological parameters in growing polycrystalline films. Particle diffusion at surface, adsorption and combination reaction are all deeply affected by the substrate temperature[9]. With the temperature increase, the combinative opportunity increases correspondingly, and the growth rates also rise.

Ga and Sb have different diffusion rates in the growth process, and the diffusion of Sb is far slower than that of Ga[10-11]. When grown under low temperature, samples may contain some pure Sb. Figure1 shows XRD data of GaSb films grown on different temperature, and the thickness of films was control to be 1000nm. We can find some diffraction peaks of pure Sb besides peaks of GaSb at 300℃. In low temperatures (300-330℃), atoms of Ga and Sb have not gain enough energy to form the compounds and transport on the surface to find the fittest position. These atoms will soon be covered by follow-up ones. Meanwhile, these atoms cannot overcome the Ehrlich-Schwoebel (ES) potential barrier to complete the transport in interlamination[10]. So there are many the crystal orientation of Sb, such as Sb (003), Sb (012), Sb(104), Sb(110). Due to the above reasons, the GaSb films grown rapidly have an incompact texture. When the temperature increases, the peaks of Sb decrease, and the content of Sb decreases. The temperature facilitates atoms to overcome ES potential barrier and complete the transport. So, with the temperature increase, the combinative opportunity of GaSb polycrystalline film increases correspondingly. The crystal preferred orientation of GaSb films is GaSb (111).

At temperature 520℃, the preferred orientation of GaSb films grown on ITO substrate changes from GaSb (111) to GaSb (220) (seeing Fig. 1), and it has never occurred on glass substrates. The detailed performance of GaSb film on glass substrate has been described elsewhere[12]. Figure 2 shows XRD data of GaSb films on ITO substrate with different thickness when the substrate temperature is 500℃. The phenomenon of changing preferred orientation is also appeared. The preferred orientation of GaSb films grown on ITO substrate changes from GaSb (111) to GaSb (220) when the thickness of GaSb films is thicker than 2 000 nm. From Figs. 1 and 2, changing preferred orientation of GaSb films is not accidental phenomenon. If we understand the reason of this phenomenon, we can control the growth of GaSb films and use the better properties of GaSb films.

Intrinsic GaSb films grown on ITO substrate are always p-type, which means majority carriers are hole carriers. Some researchers attribute p-type conductivity to the $V_{Ga}$ $Ga_{Sb}$ acceptors[13-15], but some others hold a different view that $Ga_{Sb}$ antisite defects are the cause of the p-type conductivity[16-17]. In this paper, GaSb thin films are p-type semiconductor.

Figure 3 shows the curves of hall concentration and mobility when temperature changed from 330℃ to 560℃. Hall concentration always show a high value (around$10^{20}$ $cm^{-3}$) when films were grown at low temperature. This high concentration is attributed to the high density of $V_{Ga}$ $Ga_{Sb}$ or $Ga_{Sb}$ because of different diffusions of Ga and Sb at low temperatures. Then hall concentration decreases to a relatively stable level (around $10^{18}$ $cm^{-3}$) when temperature reaches above 480℃. Our measured hall concentration are compared favorably with those from previous results[12], indicating good quality of the grown layers. In such conditions, films always have relatively low defects and high quality. Contrary to hall concentration, hall mobility shows a rising trend when temperature increases to 520℃ and then drop when temperature reaches 560℃. Hall mobility increase because of the improved structure of GaSb thin films. Special attention should be paid to the film with GaSb (220) preferred orientation has the higher hall mobility (51.2 $cm^2/V \cdot S$) than that of film with GaSb (111) preferred orientation. In figure 4, the same result is also appeared.

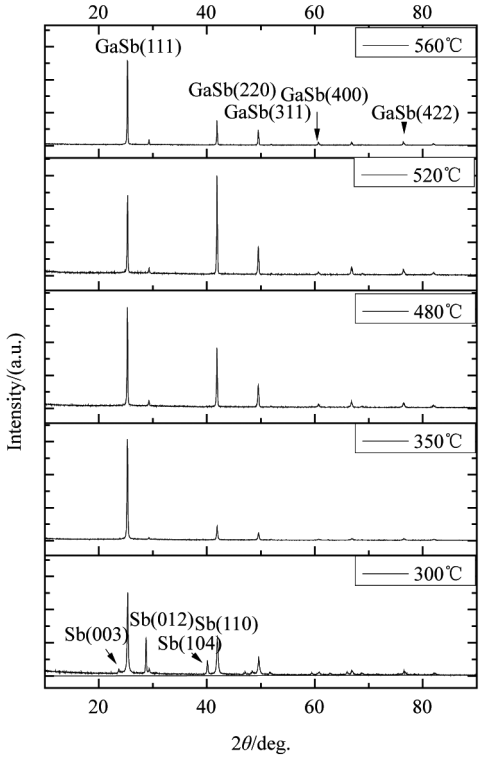


Fig. 1　The XRD spectra of GaSb thin films deposited on ITO substrate as a function of the substrate temperature (changing from 300℃ to 560℃)

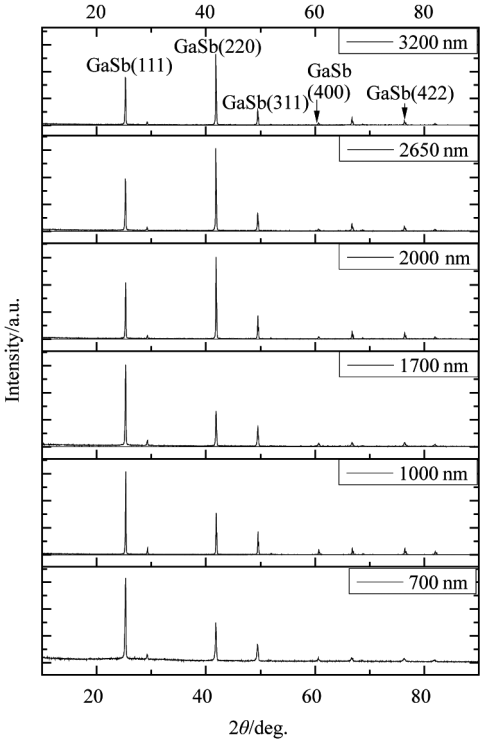


Fig. 2　The XRD spectra of GaSb thin films deposited on ITO substrate as a function of thin films thickness (changing from 700nm to 3 200 nm)

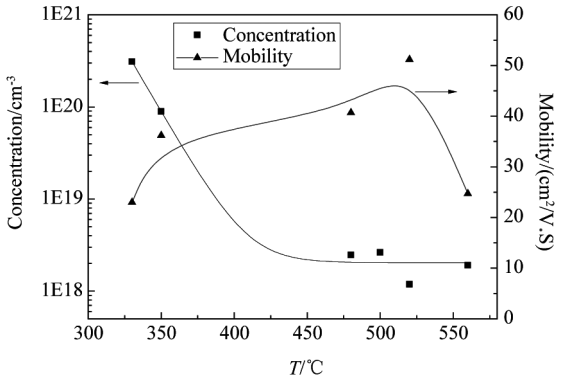


Fig. 3　The hall concentration and hall mobility of GaSb thin films deposited on ITO substrate as a function of the deposition temperature

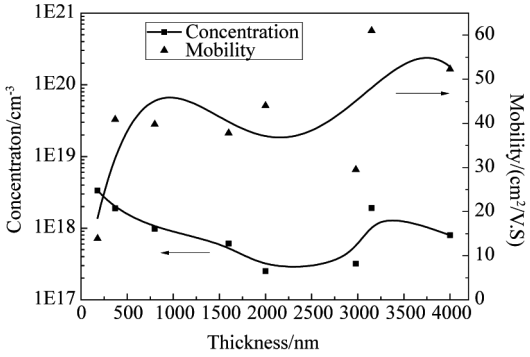


Fig. 4　The hall concentration and hall mobility of GaSb thin films deposited on ITO substrate as a function of the film thickness

Figure 4 shows the hall parameters of films with different thicknesses from 200nm to 4000nm with the substrate temperature at 500℃. We can see that hall concentration also comes to a steady value (around $10^{18}$ $cm^{-3}$) with different thickness. The hall mobility shows a rising trend and can be divided into three regions. The hall mobility increases quickly for thickness thinner than 1000nm. Then it changes slowly when thickness is changed between 1000nm to 2000nm. Finally it increases quickly when thickness is above 2000nm. When the preferred orientation of GaSb films changs from GaSb (111) to GaSb(220), the hall mobility of films reaches the high level, the same phenomenon as in the Fig. 3. So we can draw the conclusion that the films with GaSb (220) preferred orientation have higher hall mobility and have the better structure than that of film with (111) orientation. The crystalline grains of films grow bigger with increasing substrate temperature and film thickness (seeing Fig. 5), so the hall mobility of films is increasing. The crystalline grains begin to extrude with each other when they reach some condition. These phenomenon are easy appeared in films with GaSb (111) preferred orientation because the growth direction of GaSb (111) is in the inclined direction to the substrate. So it can be infered that there are more grain boundaries and defects in the films with GaSb (111) preferred orientation.

From FWHM of XRD data, we calculated the grain

sizes of the films (seeing Fig. 5). Grain sizes of GaSb increases along with the rising temperatures and thickness, and the crystalline grains of GaSb (220) are always bigger than that of GaSb (111). These results demonstrate again that the crystalline grain of GaSb (220) can be easy to grow bigger because its growth direction is in parallel with the substrate and has less grain boundaries. From Fig. 5, the grain sizes of GaSb (111) reach saturation at different temperature and thickness, but the crystalline grain of GaSb (220) has a rising trend under different thickness.

Figure 5 also shows surface roughness of GaSb films grown at different temperatures measured AFM (seeing Fig. 6). At 330℃, GaSb film has a relatively large value in surface roughness compared with other samples, due to the high growth rate. The substrate temperature didn't give enough energy to the precursor of GaSb, so they are quickly piled up (seeing Fig. 6(a)). With the increasing temperature, the surface of films are even, and the grain on the film surface are growing bigger (seeing Fig. 6(b), (c), (d)). So the roughness of GaSb films increases from the minimum value (14.75nm) at 480℃ to 62.11nm at 540℃. When the temperature increases, larger grain size leads to larger surface roughness.

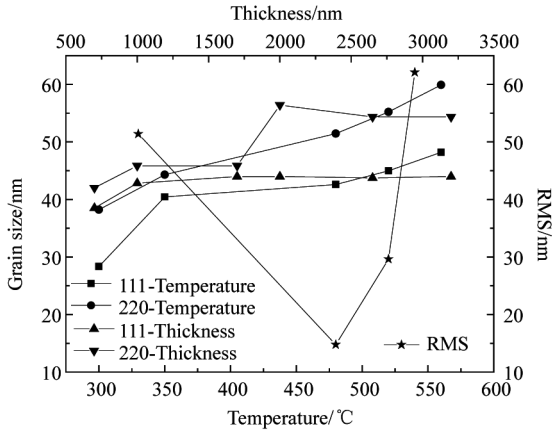


Fig. 5 Grain size and roughness (RMS) of GaSb thin films deposited on ITO substrate as a function of the substrate temperature and films thickness

High optical properties of GaSb films are crucial to TPV cells, and in this paper we investigate the transmission and reflection of two samples with the same thickness of 700nm. The absorption coefficient α, is written as,

$$\alpha = \frac{1}{d}\ln\left[\frac{(1-R)^2}{T}\right] \quad , \quad (1)$$

where, $d$ is the thickness of sample. $T$ and $R$ stand for transmission and reflection rates, separately.

Figure 7 shows the α curves of GaSb films grown at different temperature. α achieves a high value over $10^4$ $cm^{-1}$ at a large range from 0.6eV to 3.2eV. It indicates a superb optical absorption property for TPV thin film cells. Meanwhile, rising temperature may promote light absorption to some extent, and it benefits from the improvement of GaSb crystallinity.

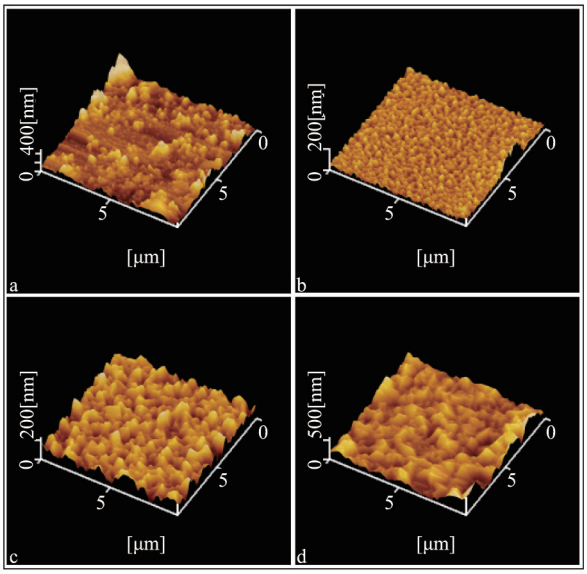


Fig. 6 AFM profiles of GaSb thin films deposited on ITO substrate at different temperature (a) at 330℃, (b) at 480℃, (c) at 520℃, (d) at 540℃

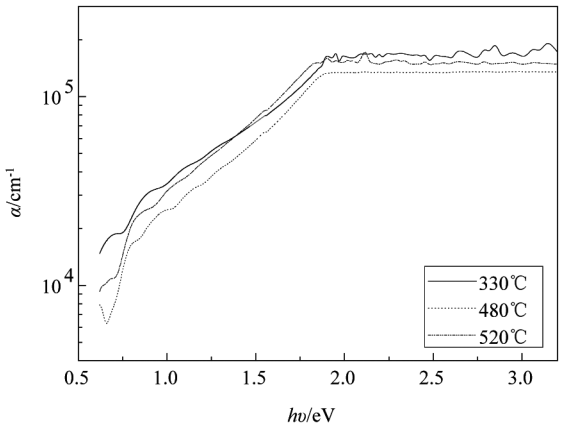


Fig. 7 Absorption coefficient (α) of GaSb thin films deposited on ITO substrate as a function of the substrate temperature

## 3 Conclusion

GaSb polycrystalline thin films with different thickness were prepared on ITO substrate at different temperature. The preferred orientation of GaSb thin films grown on ITO substrate has been changed from GaSb (111) to GaSb (220) when the substrate temperature reaches 520℃ and films thickness exceed 2000nm. This phenomenon had never occurred on glass substrates. GaSb thin films with (220) preferred orientation had high hall mobility because of less grain boundaries and less defects. The grain sizes of GaSb (220) are always bigger than that of GaSb (111). The growth direction of GaSb (220) is parallel with the substrate, this it has more space to growth. The thin films after optimization possess

the hole concentration of $1.18 \times 10^{18}$ $cm^{-3}$ and hall mobility of 51.2 $cm^2/V \cdot S$. Meanwhile, the absorption coefficients of films can be over $10^4$ $cm^{-1}$, which is desirable in the application of TPV thin films cells.

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