Photoresponse investigation of polycrystalline gallium antimonide (GaSb) thin films

Cite as: AIP Advances 10, 035201 (2020); https://doi.org/10.1063/1.5139056
Submitted: 18 November 2019 . Accepted: 13 February 2020 . Published Online: 02 March 2020

Muhammad Shafa, Yi Pan, R. T. Ananth Kumar, and Adel Najar
Photoresponse investigation of polycrystalline gallium antimonide (GaSb) thin films

Cite as: AIP Advances 10, 035201 (2020); doi: 10.1063/1.5139056
Submitted: 18 November 2019 • Accepted: 13 February 2020 • Published Online: 2 March 2020

Muhammad Shafa,1,2 Yi Pan,1,a) R. T. Ananth Kumar,3 and Adel Najar4

AFFILIATIONS
1Center for Spintronics and Quantum Systems, State Key Laboratory for Mechanical Behavior of Materials, Xi’an Jiaotong University, Xi’an 710049, China
2XJTU-YLU Institute for Industrial Innovation of New Materials, Yulin University, Yulin 719000, China
3Department of Physics, Sree Ayyappa College, Chengannur, 689109 Kerala, India
4Department of Physics, College of Science, United Arab Emirates University, Al Ain 15505, United Arab Emirates

a)Author to whom correspondence should be addressed: yi.pan@xjtu.edu.cn

ABSTRACT
Thin films of polycrystalline gallium antimonide (GaSb) were grown on widely available mica substrates using the physical vapor deposition method. The as-grown films contain grains of nano-scale with regular symmetries, as identified by x-ray diffraction and scanning electron microscope analysis. Two-terminal devices with coplanar electrodes were fabricated from the polycrystalline GaSb films; thus, the time dependent photoresponse property of the films was investigated by measuring the current density–voltage characteristics of devices. A significant photoresponse of the device was revealed by the linear dependence of the applied bias. Additionally, the transient behavior of the GaSb thin films was used to optimize growth temperatures of the films. This study shows that polycrystalline GaSb thin films on mica at 500°C are suitable for high photoresponse and low noise IR photodetectors, thus proving to be a low cost solution for IR photodetectors.

© 2020 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5139056

I. INTRODUCTION

III–V semiconductors are widely used in optoelectronic devices that can be applied in optical communications, solid state luminescence, and high efficiency solar cells. Among them, GaSb is an attractive material for infrared devices due to its narrow direct bandgap and high sensitivity.1–3 GaSb thin films respond significantly to a near-infrared region of 2–5 μm, which corresponds to a direct band gap of ~0.7 eV. Due to this noteworthy property of GaSb, it can be used for the fabrication of photonic devices such as photodetectors, laser diodes,2,6 and optical communication devices.7 Thermo-photovoltaic cells synthesized from GaSb thin films are also another promising device. Fabrication of GaSb photodiodes with a high breakdown voltage was reported.8 In the last decade, numerous methods were reported on the growth of GaSb thin films.1–3,10,11 However, the performance of the devices has dramatically reduced as well. In order to find the optimum between cost and performance, we proposed to grow polycrystalline GaSb films on mica substrates, which will dramatically reduce the production cost while maintaining high photoresponse and low noise.

In this paper, we report successful growth of GaSb thin films at diverse temperatures using pure antimony and gallium shots in a furnace tube with mica substrates placed downstream. Time dependent photoresponse devices are fabricated from the grown GaSb films, and the transient behavior of the GaSb thin films are studied in detail. These results indicate that such films grown under optimized conditions are adequate for high photoresponse and low noise IR photodetectors.

II. EXPERIMENTAL

An alumina tube furnace was used for the synthesis of GaSb, as shown in Fig. 1(a). The furnace was thoroughly cleaned as deposition of these thin films were carried out at a base pressure of 10⁻⁶
mbar. Thin films of GaSb were grown on mica substrates, which were thoroughly cleaned with alcohol and acetone several times before mounting in the furnace tube. The precursors, with a purity of 99.999%, were purchased from Alfa Aesar. These high purity gallium ingots with a weight of 0.421 g and 0.415 g of antimony shots were mounted in the central zone of the furnace tube.

Sample growth parameters are optimized by adjusting the gas flow, source temperature, and substrate temperature. The furnace tube was kept at 850 °C for over 180 min. At the end, the furnace tube is allowed to cool down naturally, and a quartz boat containing the samples was taken out. To calculate the influence of substrate temperature while minimizing the deviation of other parameters, three mica substrates were placed at a specific temperature zone with a gradient of ∼500 °C, 300 °C, and 200 °C, respectively. The temperature gradient has been carefully calibrated by a thermocouple.

A field emission scanning electron microscope (FE-SEM-JEOL JSM 5800LV) was used to characterize the surface morphology of GaSb thin films at 20 kV. The thickness of the films was measured using a surface roughness tester (210, MITUTOYO). For EDX analysis, an accelerating voltage of 200 kV was used in a JEOL JEM 2010 scanning electron microscope. A Jordan Valley’s D1 Evolution was used for x-ray diffraction (XRD) analysis to reveal the structural quality of the grown films. This diffractometer is equipped with an X-ray source of Cu Kα (λ = 1.5406 Å). A glancing incidence angle of 1.5° was used during the measurement. A Bruker Optics IFS 66V/S Fourier transform infrared (FTIR) spectrometer was used to measure transmission. The UV–Vis spectrophotometer JASCO (V-670) was used to measure the transmission measurement. Conductive graphite paste was applied to electrodes in a co-planar manner, and the electrical measurements of the fabricated device, as shown in Fig. 1(b), were carried out under dark and illuminated conditions with a SAN-EI 3A solar light simulator (XES-301S, 300W) and a Keithley 2400 source meter.

### III. RESULTS AND DISCUSSION

Morphological images obtained by SEM on the GaSb films grown on the mica substrate at three different temperatures are shown in Figs. 2(a)–2(c). The GaSb sample at 200 °C was identified by the presence of a rough surface containing micrometer scale crystals which are detached from each other, as shown in Fig. 2(a), while the inserted zoomed-in image shows a typical isolated crystal. While at a growth temperature of 300 °C [Fig. 2(b)], the film still contains isolated micrometer scale grains but without sharp edges, compared
with the 200 °C samples. The irregular shaped grains are actually composed of nano-scale crystals, as indicated by the zoomed-in image inserted in Fig. 2(b). This is measured by tilting the sample stage during field emission SEM. Figure 2(c) shows the irregular spike like GaSb structures grown on mica at a higher growth temperature of 500 °C. At such a high temperature, the grains are seamlessly connected to each other and form a compact film with much less roughness than the samples grown at lower temperatures. This results in a very smooth surface of GaSb with no out growth at nano-scale with micro-size clusters. The observed surface morphologies of the antimonide films are regular, which may be suppressed by low dimensional growth. Thermal effects on the surface of the thin films are observed, where the size of the GaSb nanoparticles decreases as the growth temperature decreases, which ultimately increases the optical bandgap. The thickness of the film is about 110 nm.

From the EDX analysis, the element ratios are revealed, as shown in Fig. 3(a). At a growth temperature of 500 °C, the quantitative ratios of Ga and Sb contents were found to be close the stoichiometric ratio. However, at a growth temperature of 200 °C, the presence of Sb was found to be excessive, while that of Ga was deficient. At subsequent higher growth temperatures of 300 °C, the Ga content is increasing, while Sb contents are reduced, possibly due to recrystallization. This decrease in Sb concentration vs temperature can be explained as follows: at a lower temperature, the growth zone is away from the source, which reduces the vapor pressure of Sb when compared with Ga. The detected O and Si were due to the formation of native oxides (gallium and antimony oxides) and from the mica substrate at high temperature, respectively. Successful identification of gallium antimonide (GaSb) was also confirmed by XRD measurement for all samples, as shown in Fig. 3(b). A significant Bragg’s peak at 25.28° that corresponds to the GaSb (111) diffraction peak was observed. The diffraction peak observed at 41.88° corresponds to GaSb with the (220) plane which coincides with the standard data (PDF#89-4298, ICSD#044979). These results point toward the existence of well-oriented microcrystall structures. The other unidentified peaks are due to mica substrates, as reported by Munoz et al.

As shown in the upper panel of Fig. 1, co-planar type electrodes were primed for the fabrication of the photodetector. The optical transmission recorded using FTIR and the spectrophotometer is shown in Fig. 4(a). Similar transmission spectra were reported by Qiao et al. The absorption peaks were found in the near-infrared region, around 3000 cm⁻¹ and 3750 cm⁻¹. The lower transmission found in the film grown at 300 °C is due to its higher thickness by the incorporation of excess antimony. The optical bandgap recorded using the Kubelka–Monk function for GaSb thin films under different growing conditions are shown in Fig. 4(b). Bulk GaSb shows a bandgap of 0.725 eV, as reported by Russell et al. At growth temperatures of 200 °C, 300 °C, and 500 °C, the energy gap obtained is found to be about 0.42 eV, 0.38 eV, and 0.35 eV, respectively. These bandgap results are in close agreement with the values measured using FTIR measurement as 3000 cm⁻¹ and 3750 cm⁻¹ correspond to a bandgap energy value of 0.375 eV and 0.465 eV, respectively. These results strongly reveal that growth temperature has a significant effect on the discrepancy of the optical bandgap. As temperature increases, there is enough energy to break some of the weaker bonds, producing certain translational degrees of freedom in the system. This result can be interpreted by assuming the production of surface dangling bonds around the crystallites during the process of crystallization.
The significant modification in the thin films of GaSb may be due to Sb-related states. At the conduction band minimum, the Sb-states persuade a strong band repulsion, which may lead to a reduction in the optical bandgap. Moreover, with increasing growth temperature, the optical bandgap decreases, which shows a red shift, which is a property of semiconductors. There is a distinction between “optical bandgap” and “electrical bandgap.” The optical bandgap is the threshold for photons to be absorbed, while the electrical bandgap is the threshold for creating an electron–hole pair that is not bound together (the optical bandgap is at a lower energy than the electrical band gap). Nonetheless, the excellent structural quality revealed by XRD and optical absorption in the near-infrared region makes GaSb thin films a promising candidate for application in optoelectronics.

Since optical measurements prove that the thin films of GaSb are active in the infrared regime, they can also act as photodetectors, as illustrated in Fig. 1. Current density–voltage (J–V) characteristics of three photodetectors are measured at room temperature with different growth temperatures under illumination as well as under dark conditions, as shown in Figs. 5(a)–5(c). Good ohmic contacts are shown for the three photodetectors, based on the linear dependence of the bias voltage with current curves. A significant difference between dark current and photocurrent for the GaSb films grown at a lower temperature was observed. On the other hand, a significant photoresponse was observed for the film grown at 500 °C whose surface morphology shows leaf-like textures. Moreover, for the film grown at 500 °C, a distinct improvement in the photocurrent has been observed upon illumination. This improved performance of the photodetector device fabricated from the films grown at higher temperature might result due to the high crystalline quality. Although these deficiencies in the contents measured by EDX will lead to poor performance of the devices, it can be optimized by controlling growth conditions. It is also observed that excess of Sb will contribute to dark current instead of photocurrent.

Figures 6(a)–6(c) show the transient behavior of the GaSb thin films. The grown thin films at 200 °C, 300 °C, and 500 °C demonstrate a significant photoresponse under dark and illuminated conditions. However, transient response was achieved by applying high dark current. Dark current corresponds to the density of the surface.
FIG. 6. Time dependent photosresponse devices fabricated from GaSb films grown at (a) 200 °C, (b) 300 °C, and (c) 500 °C at different bias voltages, where illumination is switched on and off for 30 s (where red, blue, and brown curves represent a bias voltage of 4 mV, 40 mV, 400 mV, respectively).

state, which is much higher, making thin films more conductive. At zero bias voltage, there is no response from the thin films, which is the property of photoconductive devices. The bias voltage linearly depends on the on/off ratio that can be improved with better time dependence of photo-generated carriers. Trap states in GaSb thin films are responsible for the poor response time that enhances the performance of the devices ultimately. The surface states slow down the transient response due to trapping/detrapping of photoexcited carriers. For example, trap states of holes related to oxygen at the surface of GaSb can prolong photoresponse. An inferior signal to noise ratio is observed for the detector fabricated from the thin films grown at low temperature, which is consistent with J-V and EDX measurements. It is expected that passivation of surface states can decrease rise and decay time and hence improve on/off ratios.

IV. SUMMARY AND CONCLUSIONS

The physical vapor deposition technique was used to grow GaSb thin films on mica substrates. Depending on the growth conditions, GaSb grown films are uniformly covered with nano- or micro-crystalline textures. XRD analysis exhibited the excellent quality of the GaSb thin films, while a distinct absorption peak in the near-infrared region was observed by FTIR. Absorption peaks of 3000 cm$^{-1}$ corresponding to the near-infrared region revealed limited mica absorption. Bandgap calculations showed a red shift because of the decrease in the bandgap with an increase in growth temperature. A prototype infrared photodetector was fabricated based on these results. It can be concluded that improved response time, signal to noise ratios, and photocurrent can be obtained by increasing growth temperatures for the thin films. Surface passivation and reduction in trap states may improve the performance of the device. The best crystalline quality and optical absorption observed show that GaSb is an excellent candidate for applications in the optoelectronics industry in the future. The technique proposed in this paper can be a superlative alternative to low cost near-infrared technology.

ACKNOWLEDGMENTS

M. Shafa and Y. Pan acknowledge the support from the National Key R&D Program of China (Grant No. 2017YFA0206202), the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB30000000), and the National Natural Science Foundation of China (Grant No. 11704303).

REFERENCES

23 M. H. C. Delia et al., Nat. Sci. 6, 963–967 (2014).