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A simple method for growth of very smooth and ultra-thin GaSb films on GaAs (111) substrate by MOCVD

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Abstract:

We present a simple thermal treatment with antimony source for the MOCVD growth of thin GaSb films on GaAs (111) substrates for the first time. The properties of the as-grown GaSb films are systematically analyzed by scanning electron microscopy, atomic force microscopy, X-ray diffraction, photo-luminescence (PL) and Hall measurement. It is found that the as-grown GaSb films by the proposed method can be as thin as 35 nm and have a very smooth surface with the root mean square roughness as small as 0.777 nm. Meanwhile, the grown GaSb films also have high crystalline quality, of which the FWHM of the rocking-curve is as small as 218 arcsec. Moreover, the good optical quality of the GaSb films has been demonstrated by the low-temperature PL. This work provides a simple and feasible buffer-free strategy for the growth of high quality GaSb films directly on GaAs substrates and the strategy may also be applicable to the growth on other substrates and hetero-growth of other materials.

Keywords: GaSb on GaAs; MOCVD growth; smooth; infrared.

Introduction:

Antimonide based compound semiconductors have many attractive applications in infrared lasers, detectors, and high-speed electronic devices due to its wide range of electronic band gaps, unique band-structure alignments, and high electron mobility.[1-8] Moreover, as a member of the 6.1 Å family, GaSb is also an important substrate material, for example, for the growth of type II superlattice infrared lasers and detectors.[9-11] Although significant progress have been made in the fabrication technology of GaSb substrates in the past few years, the quality of currently commercially available GaSb substrates still cannot meet the technical requirements for the "epi-ready" substrates, due to the non-optimized oxide layer as well as the large amount of macroscopic defects on the surface. On the other hand, compared with GaSb substrates, GaAs substrates offer many advantages, such as, low cost, better quality, availability of large diameter and high resistivity.[12-14] Furthermore, GaAs substrate is more transparent than the GaSb substrate in the long wavelength range, which makes a thin layer of relaxed GaSb grown on GaAs a good alternative to bulk GaSb substrates for fabricating photodetectors using the most convenient design with illumination from the back side.[15,16] However, suffering from the large lattice constant mismatch (~ 7.8%), it is always problematic to grow high-quality GaSb materials directly onto GaAs substrate because the large lattice constant mismatch between them will gives rise to a high misfit dislocation density ($10^9 cm^{-2}$) at the GaSb/GaAs interface,[17-19] which is deleterious to the electrical and optical properties, and thus to the performance of the devices made of them.[1,20] To address this problem, many growth techniques have been proposed to accommodate strain and reduce the dislocation density, including strained superlattice, step and continuously graded thick metamorphic buffer layer, low-temperature nucleation technique, and interfacial misfit dislocations (IMF) growth mode,[21-24] which however will inevitably increase the growth complexity and extend the growth time. Therefore, it is of great importance to develop a simple, feasible and even buffer-free method to obtain high quality GaSb film directly on GaAs substrates. So far, great efforts have been devoted to the growth of GaSb on GaAs (001) substrates. There were also reports on growth of GaSb on GaAs(111) by molecular beam epitaxy.[25,26]

In this paper, we show that ultra-thin GaSb films with mirror-like morphology, very small roughness, good crystalline quality and good optical quality can be grown directly on GaAs (111) substrates via metal-organic chemical vapor deposition (MOCVD) by employing a simple antimony thermal treatment. The mechanism for this method is also discussed in details.

Experimental details:

The GaSb samples were grown using a horizontal low-pressure MOCVD system (Aixtron, AIX200). Trimethylgallium (TMGa) and trimethylantimony (TMSb) were used as the metal-organic sources in the growth. High purity (99.999%) hydrogen gas was used as the carrier gas. Commercial epi-ready semi-insulating GaAs (111) wafers were used as substrates. Before growth, a small amount of TMSb source (with flux of ~ 9.5×10^{-6} mol/min) was introduced into the reactor when the substrate temperature was larger than 300 ^{o}C. Then the GaAs substrate underwent a thermal treatment inside the MOCVD reactor at 600 ^{o}C for 10 min under H_2 and TMSb sources environment. After that, the substrate temperature was lowered to 500 ^{o}C for the growth of GaSb film. During the growth, the pressure of the

MOCVD reactor was kept at 100 mBar. The total H_2 flow during the whole process was kept at 3 slm.

The surface morphologies of the GaSb films were analyzed by a scanning electron microscopy (SEM) and an atomic force microscopy (AFM). The AFM was performed onto the surface of GaSb films with a scanning probe microscope (Shimadzu SPM-9500J2) in ambient atmosphere in non-contact mode over square areas of 2 μm × 2 μm with a silicon tip. The scan resolution is 512 pixels × 512 pixels and the scan rate is 1.000 Hz. The structural information of the GaSb films was examined by the X-ray diffraction (XRD) measurements using a Bruker D8 Discover system. The PL measurements were carried out under the excitation of a 1064 nm Nd: YAG laser. A compressor with continuous helium flow is used to realize low temperatures. A liquid-nitrogen cooled MCT detector and lock-in amplifier were used to detect the PL signal. The electrical properties of the GaSb films grown on GaAs substrates were studied by Hall measurements using the Van der Pauw method over a wide temperature range from 80 K to 400 K.

Results and discussion:

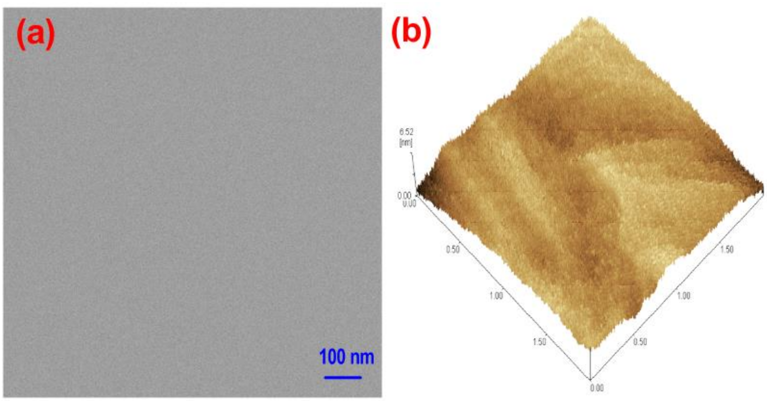

Fig. 1 SEM image (a) and AFM image (b) of the GaSb film grown on GaAs (111) substrates by the

antimony source thermal treatment method.

Surface morphology and roughness of the epitaxial layer are key factors to both homo-epitaxial and hetero-epitaxial growths as they will directly affect the quality of the consecutively grown layers as well as the quality of the interface between different layers. Especially, the modern semiconductor based photoelectronic devices are usually composed of a dozen or even dozens of epitaxial layers, of which the performance relies greatly on not only the individual grown layer but also the interface quality between the different layers. Therefore, good surface morphology and small roughness are highly desired during the growth of semiconductor films. To this end, lots of efforts have been devoted to study material surface and various kinds of techniques have been developed accordingly.[30-32] In this work, as shown in Fig. 1, the GaSb films grown by the antimony source thermal treatment method have a very smooth and mirror-like surface. The root mean square (RMS) roughness of these as-grown GaSb films is as small as 0.777 nm.

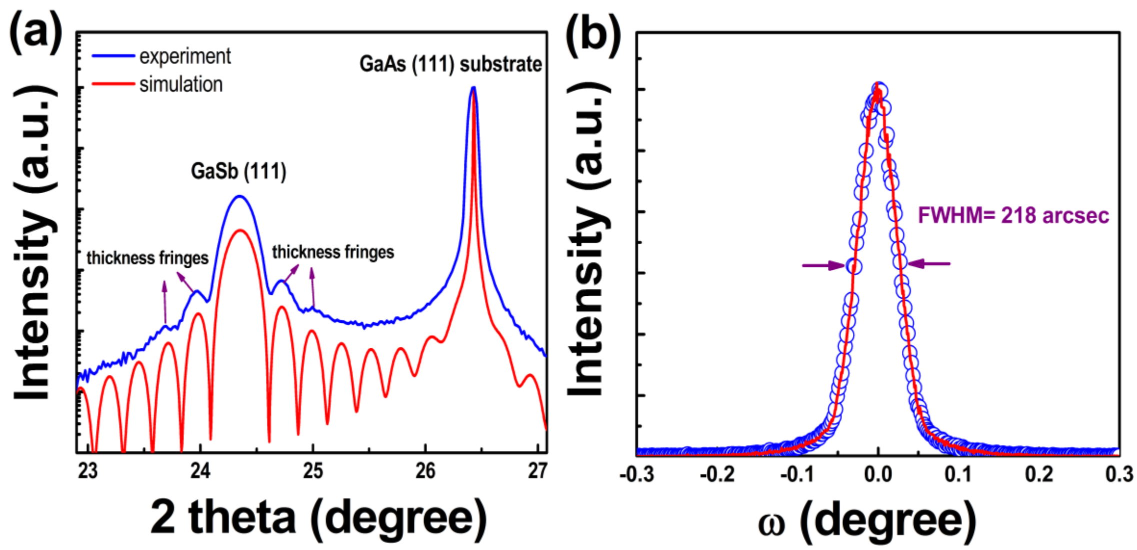

Fig. 2 XRD *w*-2*θ* scan (a) and high-resolution X-ray rocking curve (b) of the GaSb film grown on the GaAs (111) substrates by the antimony source thermal treatment method.

The good surface morphology of these as-grown GaSb films can be further confirmed by the XRD w-2θ scan as shown in Fig. 2(a). Obvious thickness fringes can be observed from the XRD scan, which reveals that the GaSb films grown by the antimony source thermal treatment method have a very flat surface. Moreover, it is found that the thickness of the as-grown GaSb film is only as small as about 35 nm estimated by fitting the XRD w-2θ scan. Due to the large mismatch (~7.8%) between GaSb and GaAs, the critical thickness is expected to be within the range of a few monolayers (MLs).[30-32] Therefore, the 35 nm GaSb layer should be fully relaxed. It has been widely reported that the large lattice constant mismatch (~7.8%) between the GaSb and the GaAs will significantly precludes layer-by-layer growth of GaSb on GaAs substrate.[10] So the initial growth of GaSb on GaAs substrate was found to be highly three dimensional, which made it very difficult to obtain a thin GaSb film with very good surface morphology on the highly mismatched GaAs substrate. According to the work of Qian *et al* that as the epilayer grows thicker, a substantial coalescence occurs among these grown GaSb neighboring islands and the GaSb surface coverage reaches only to about 87% at the thickness of 50 nm in their work.[15] Considering that the grown GaSb films in this work is only as small as 35 nm and its surface is very smooth without any grain boundaries, one can see that the antimony source thermal treatment method is able to facilitate the two dimensional growth of the GaSb films during the initial growth stage.

Moreover, high-resolution X-ray rocking curve from the (111) Bragg reflection of the as-grown GaSb film has been measured to evaluate its crystalline quality as shown in Fig. 2 (b). The full width at half maximum (FWHM) of the rocking-curve is as small as 218 arcsec, which directly demonstrates the high crystalline quality of the as-grown GaSb films. Table 1 shows a comparison of the GaSb films grown on GaAs substrates in this work with other reported works, where different growth methods have been employed to improve the crystalline quality of the grown GaSb film on GaAs substrates. It can be seen that both the FWHM value and the roughness of our grown GaSb films is comparable to other reported results, meanwhile it is worth noticing that the thickness of our grown GaSb film is extremely small compared with other works.[8,17,22,23,33,34] Therefore, our proposed growth method has the capability of growing high quality ultra-thin GaSb films on the highly mismatched substrate. Moreover, this method also has advantages of simple process and low cost. Furthermore, a rough estimate of the dislocation density of the epilayers can be derived from the rocking curve width. This is because the existence of dislocations will cause the broadening of the rocking curve. Typically, there is a high density of threading dislocations in the GaSb epilayers grown on the GaAs substrates due to the lager lattice mismatch.[19] Therefore, the small FWHM value reveals that the antimony source thermal treatment method helps to reduce the dislocation density of the GaSb films grown on the GaAs substrates. The mechanism can be understood as follow: The antimony source thermal treatment will initiate two important processes. One is that lots of the arsenic atoms will escape from the GaAs substrate surface during the thermal treatment due to the high vapor pressure of the arsenic, leaving behind a large amount of group V atom vacancies on the GaAs substrate surface. The other one is that plenty of antimony atoms will occupy the group V atom vacancies on the GaAs substrate surface during the antimony source treatment process. As a result, the above two processes will give rise to a thin quasi-GaSb layer onto the surface of GaAs substrate before starting the growth of GaSb epitaxial layer. Since there is no external Ga atom injected into the reactor during the antimony source thermal treatment, this thin quasi-GaSb layer is forced to grow two dimensionally. Meanwhile, the small FWHM value (218 arcsec) of the grown GaSb films indicates that the large amount of dislocations generated at the interface between the GaAs and GaSb could be confined within a small region in the quasi-GaSb layer instead of penetrating into the upper epitaxial layer. That is why the following grown GaSb has very smooth surface and high crystalline quality with a very small dislocation density even thought its thickness is just as small as 35 nm.

Table 1. Summary of reported FWHM values for the GaSb films on GaAs substrates.

Sample	Our work	Ref. 22	Ref. 33	Ref. 23	Ref. 34	Ref. 3	Ref. 17
Growth technique	MOCVD	MBE	MBE	MBE	MBE	MOCVD	MOCVD
Growth method	by the Sb-source thermal treatment	using three-step ZnTe buffer layers	using GaSb buffer layers	interfacial misfit (IMF) array	with AlSb buffer layers	with epitaxial lateral over growth	interfacial misfit dislocations (IMF) growth
Thickness (nm)	35	-	500	1000	500	2500	300
RMS (nm)	0.777	3.3	0.93	-	0.67	-	2.7
FWHM (arcsec)	218	606	468	240	348	189	229

Figure 3 shows the temperature dependence of the carrier concentration and Hall mobility for the grown GaSb films. It is worth noticing that our MOCVD grown undoped GaSb films show high *p*-type conductivity with the hole concentration of 5.29 $\times 10^{17}$ cm^{-3}, and the mobility of 337 $cm^2V^{-1}s^{-1}$ at room temperature, even though no acceptor dopant is employed during the growth. The hole concentration of the undoped GaSb films increases with increasing the temperature, which is the typical semiconductor behaviors. The inset of Fig. 3(a) shows the Arrhenius plot of the measured free hole concentration. The acceptor energy level of the grown GaSb films can be determined using the Arrhenius plot according to the following equation:

$$p = p_0 e^{-E_A/k_B T}, \qquad (1)$$

where E_A is the activation energy, k_B is the Boltzmann constant. As shown, two straight lines with different slope can be seen by the linear fits of the experimental data, which correspond to a deep acceptor level and a shallow acceptor level, respectively. It has been widely observed that the undoped GaSb films usually exhibits *p*-type concentration, owing to native lattice defects including Sb vacancies and antisite defects, *i.e.*, Ga atoms in Sb sites, and complex defects ($V_{Ga}Ga_{Sb}$). The high *p*-type conductivity of our grown GaSb films can be ascribed to the antimony source thermal treatment process. This is because plenty of group V atom vacancies as well as some antisite defects will form onto the GaAs substrate during this stage, and consequently give rise to complicate acceptor levels including the deep levels and shallow levels. It can be seen from the Fig. 3(b) that the hole mobility will first increase when the temperature is decreased from the room temperature. This region is the typical lattice scattering dominated regime, where the mobility of the carriers is mainly limited by the phonon scattering. At lower temperature, the lattice vibrations are getting smaller, thus the mobility will increase with decreasing the temperature. Furthermore, the mobility is peaked at 535 $cm^2V^{-1}s^{-1}$ when the temperature is decreased to about 170 K, and it is decreased with further decreasing the temperature. This phenomenon is usually observed in highly doped materials, where the ion impurity scattering becomes the dominant limit to the mobility at low temperature. This is because decrease of the temperature will extend the amount of time carriers spent passing the impurity ions, which will in turn decrease the carrier mobility. According to the above discussion, one can see that the high *p*-type concentration is caused during the antimony source thermal treatment and thus should be mainly located in the thin quasi-GaSb layer, that is, the free holes coming from the thin quasi-GaSb layer mainly contribute to the high *p*-type conductivity.

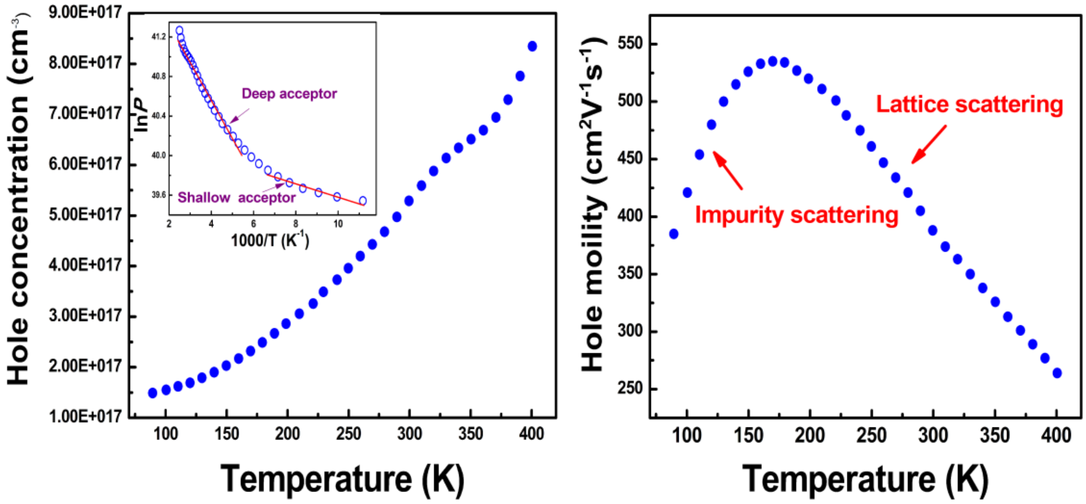

Fig. 3 Temperature dependence of hole concentration (a), and of hole mobility (b), for the GaSb film grown on the GaAs (111) substrates by the antimony source thermal treatment method. The inset in (a) shows the Arrhenius plot of hole concentration.

Low-temperature PL measurements over a wide temperature range have been carried out on the GaSb films grown by the antimony source thermal treatment method to investigate their optical quality. The temperature dependence of the PL spectra of the GaSb films have been summarized and shown in Fig. 4. As shown, obvious PL emissions can be observed from the samples from 50 K to 125 K. Considering that the thickness of the GaSb films is just 35 nm, the obvious PL emissions directly demonstrate the good optical quality of the GaSb films grown by the antimony source thermal treatment method.

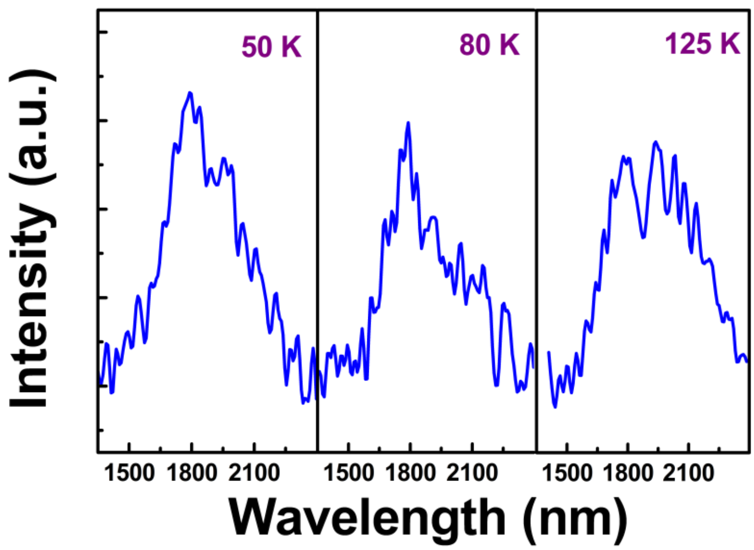

Fig. 4 Low-temperature PL spectra of the GaSb film grown on GaAs (111) substrates by the antimony source thermal treatment method.

Conclusion

High quality GaSb films with mirror-like morphology, very small roughness, good crystalline quality and good optical quality have be grown directly on (111) GaAs substrates via metal-organic chemical vapor deposition by employing a simple antimony source thermal treatment. Moreover, it is found that the thickness of our grown GaSb films can be as small as 35 nm, which demonstrates the capability of this method to grow an ultra-thin GaSb film on a highly mismatched GaAs substrate. This work shows a simple and feasible buffer-free strategy for the growth of high quality GaSb films directly on GaAs substrates and the strategy may also be applicable for hetero-growth of other materials.

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