Effect of growth interruption on surface recombination velocity in GaInAsSb/AlGaAsSb heterostructures grown by organometallic vapor-phase epitaxy

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Abstract

The effects of growth interruption on interfacial quality of GaInAsSb/AlGaAsSb heterostructures grown by organometallic vapor-phase epitaxy are reported. In situ reflectance monitoring and ex situ characterization by high-resolution X-ray diffraction, 4K photoluminescence (PL), and time-resolved PL indicate that GaInAsSb is extremely sensitive to growth interruption time as well as the ambient atmosphere during interruption. By optimizing the growth switching sequence, surface recombination velocity as low as 30 cm/s was achieved for GaInAsSb/AlGaAsSb double heterostructures.

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1. Introduction

The performance of minority carrier devices such as light-emitting diodes, photovoltaics, and heterojunction bipolar transistors is sensitive to non-radiative recombination at heterointerfaces, and numerous studies aimed at minimizing surface recombination velocity have been reported for heterostructures comprised of GaAs- and InP-based III–V alloys [1]. More recently, III–V materials based on GaSb are being developed for optoelectronic devices operating in the mid-infrared wavelength range [2]. For example, GaInAsSb/GaSb and GaInAsSb/AlGaAsSb heterostructures are of particular interest since these alloys show great potential for thermophotovoltaic (TPV) devices used to generate power from a thermal source [3]. It was reported that both GaSb and
AlGaAsSb window layers are effective in reducing GaInAsSb surface recombination [4,5]. Either of these layers was shown to improve the external quantum efficiency and open-circuit voltage $V_{oc}$ of GaInAsSb TPV cells compared to cells without the window layer.

From both band-structure considerations and experimental results, however, there appears to be an advantage of AlGaAsSb over GaSb as the window layer. Surface recombination velocity of p-GaInAsSb doubly capped with p-AlGaAsSb layers, which were grown by organometallic vapor-phase epitaxy (OMVPE), was reported to be 720 cm/s compared to 1140 cm/s for GaSb [6]. This lower value was attributed to a more advantageous band alignment between GaInAsSb and AlGaAsSb. The valence-band offset between 0.53-eV Ga$_{0.84}$In$_{0.16}$As$_{0.14}$Sb$_{0.86}$ and 1-eV Al$_{0.25}$Ga$_{0.75}$As$_{0.02}$Sb$_{0.98}$ is almost zero, while the GaInAsSb/GaSb interface is a staggered type-II band alignment. The former alignment minimizes carrier trapping at the heterointerface, and consequently, these heterostructures should have a comparatively lower surface recombination velocity, as was observed [6].

Furthermore, device performance of TPV structures with an AlGaAsSb window layer is slightly higher compared to those with a GaSb window. GaInAsSb/AlGaAsSb/GaSb TPV cells exhibit peak internal quantum efficiency and fill factor values exceeding 94% and 70%, respectively [7,8]. These values, which are approaching theoretical limits, are achieved for structures grown with either type of window layer. The highest reported value of $V_{oc}$, however, is 0.33 V and was measured for devices with an AlGaAsSb window [7]. This value is about 85% of the theoretical limit, and therefore, further increases in $V_{oc}$ should be possible. The quality of heterointerfaces in Sb-containing alloys is extremely sensitive to growth switching sequences, and interruptions during OMVPE growth were reported to alter the interface chemistry, degrade the interface structure, and affect device performance [9–13]. In principle, improvements in interfacial quality between GaInAsSb and AlGaAsSb should lead to a lower surface recombination velocity, and consequently lower dark currents and higher values of $V_{oc}$.

This paper reports the effects of interruption on interfacial quality of GaInAsSb/(Al)Ga(As)Sb double-heterostructures (DHs) grown by OMVPE, and the achievement of extremely low surface recombination velocity ($S$) in GaInAsSb/AlGaAsSb DHs. Both the interruption time and ambient exposure significantly impact the stability of the GaInAsSb interface. The switching sequence was optimized and $S$ as low as 30 cm/s was achieved for p-GaInAsSb/p-AlGaAsSb DHs.

2. Experimental approach

GaInAsSb/AlGaAsSb/GaSb epitaxial layers were grown by OMVPE with trimethylindium, triethylgallium, tritertiarybutylaluminum, tertiarybutylarsine (TBAs), and trimethylantimony (TMSb) as organometallic precursors, and dimethylzinc as the p-type doping source [14–16]. The layers were nominally lattice matched to (001) GaSb miscut $6^{\circ} \rightarrow (1 \bar{1} 1)B$. GaInAsSb was grown at 525 $^\circ$C and $V/III = 1.8$, since this temperature yields excellent optical and structural properties [14]. The alloy composition of GaInAsSb corresponds to a 300 K photoluminescence (PL) peak emission at about 2.3 µm (0.53 eV).

AlGa(As)Sb was grown at 525 $^\circ$C, even though the morphology of AlGa(As)Sb was reported to be better when grown at 550 $^\circ$C [16]. This lower temperature allows the interruption time between GaInAsSb and AlGaAsSb layers to be minimal compared to that when GaInAsSb and AlGaAsSb layers are grown at 525 and 550 $^\circ$C, respectively, since temperature changes cannot be made instantaneously. The $V/III$ was 4.4, which is greater than $V/III = 3.2–3.4$ for AlGaAsSb grown at 550 $^\circ$C [16]. The higher $V/III$ ratio at 525 $^\circ$C was necessary to obtain a defect-free surface morphology, but resulted in less efficient Al incorporation, as shown in Fig. 1. The Al content of AlGa(As)Sb was determined by 4 K PL and Rutherford back-scattering spectroscopy. The negligible Al incorporation for gas phase concentration less than 40% is similar to results reported for AlGaSb grown with dimethylamine alane [17], and is attributed to pre-reactions between the Al...
precursor and TEGa and TMSb. The oxygen impurity level in Al0.25Ga0.75As0.02Sb0.98, as measured by secondary ion mass spectroscopy (SIMS), is about 8 \times 10^{18} \text{cm}^{-3}, which is about two times higher than that measured for layers grown at 550 °C. It is possible that even if AlGaAsSb is of lower quality, GaInAsSb/AlGaAsSb interfacial quality may be better with shorter growth interruptions afforded by constant temperature growth. The C level for this same alloy is \approx 4 \times 10^{17} \text{cm}^{-3}.

In situ spectral reflectance [18] was used to monitor growth interruption of GaSb, GaInAsSb, and AlGaAsSb layers. Growth was paused for several minutes by switching the precursors out of the reactor and exposing the layer to various ambient atmospheres of H2; H2 and TMSb; or H2, TMSb, and TBAs. The TMSb flow was varied from 5 to 30 \times 10^{-6} \text{mol fraction}, and TBAs from 6 to 20 \times 10^{-6} \text{mol fraction}. Epitaxial layers were characterized ex situ by Nomarski contrast microscopy to examine surface morphology. High-resolution X-ray diffraction (HRXRD) and 4K PL were used to qualitatively evaluate interface quality of GaInAsSb/(Al)Ga(As)Sb heterostructures. Quantitative characterization of interfacial quality of GaInAsSb/(Al)Ga(As)Sb DHs was performed by time-resolved PL (TRPL), as previously described [6].

3. Results and discussion

3.1. Effect of growth interruption on in situ reflectance

In situ reflectance is a sensitive monitor for studying growth interruption. Fig. 2 shows reflectance measured at 633 nm as a function of growth time for a layer sequence consisting of GaInAsSb growth for 350 s; growth interruption of 300 s; and GaSb growth for 400 s. This sequence was repeated several times. Although 300 s is a longer time than necessary for making temperature changes during growth, this longer interruption can elucidate the stability of the growth surface during interruption. GaSb was grown after interruption to recover the GaSb reference surface, and re-establish a baseline reflectance. The modulations in reflectance at the onset of GaInAsSb and GaSb growth result from the interference of light from the surface and the epilayer-substrate interface. Whereas a wavelength of 1000 nm has been used to monitor growth oscillations for these mid-infrared alloys [18], 633 nm is used here for monitoring interruptions since initial growth oscillations can still be clearly observed, and the reflectance quickly reaches a steady-state value because the layer is more absorbing at this shorter wavelength.

The GaInAsSb/interrupt/GaSb sequence was repeated with a different flow of TMSb switched into the reactor during the growth interruption. For the first interruption, GaInAsSb was exposed only to the H2 carrier gas, while for the second, third, and fourth interruptions, 1, 2, and 3 sccm (1, 2, and 3 \times 10^{-4} \text{mol fraction}) TMSb was introduced in the H2 carrier, respectively. With the H2 interruption, an initial increase in reflectance, followed by a slight decrease is observed. Subsequent interruptions with TMSb indicate that GaInAsSb is sensitive to TMSb partial pressure (pTMSb). At a low flow rate of 1 sccm, the GaInAsSb reflectance is stable. At 2 sccm, the reflectance is initially stable. However, after about
250 s (near the end of the third interruption), a slight decrease in the reflectance is observed. At 3 sccm TMSb, the reflectance decreases after about 50 s. The decrease in reflectance can be attributed to either increased light scattering, or from changes in surface stoichiometry, which would alter the optical constants of the surface layer, and thus the reflectance. Examination of the layer after growth by Nomarski optical microscopy revealed surface defects. Therefore, it is possible that both of these effects are responsible.

A similar experiment was performed with either TMSb or a mixture of TBAs and TMSb introduced during interruption, and the reflectance data are shown in Fig. 3. The ratio of \( p_{\text{TBAs}} / (p_{\text{TMSb}} + p_{\text{TBAs}}) \) during the interrupt was the same as that used for growth of the GaInAsSb layer [14], and the total TMSb flow varied from 0.5 to 1.7 sccm. Fig. 3 shows that the reflectance decreases during the interruption whenever TBAs is introduced. As the total group \( V \) mole fraction increased, the magnitude of the reflectance change increased. Although the reflectance does not completely recover after a large decrease in reflectance during interruption, in situ reflectance monitoring is nevertheless indicative of the GaInAsSb stability. Thus, the mixture of TBAs and TMSb is more destabilizing than TMSb. The morphology of this sample exhibited no growth defects, and only a very slight increase in surface roughness. This decrease in reflectance is more likely due to modification of surface stoichiometry, since As/Sb exchange at the epilayer surface is commonly observed [19,20].

In another set of experiments, GaInAsSb was grown at 525 \( ^\circ \)C, growth was interrupted and the epilayer was heated to 550 \( ^\circ \)C in order to accommodate growth interruption for deposition of AlGaAsSb at 550 \( ^\circ \)C. In numerous tests, in situ reflectance decreased even with a low flow of TMSb during the interruption. Therefore, immediately after GaInAsSb growth, GaSb was grown to protect the GaInAsSb interface, and then the sample was heated to 550 \( ^\circ \)C. The thickness of the GaSb interfacial layer was varied from 1 to 5 nm. Based on the criteria of stable in situ reflectance during heating and temperature stabilization, a 2.5 nm-thick GaSb layer was found to be sufficient. Thus, a minimal thickness of GaSb can be used to protect the GaInAsSb surface during temperature changes.

Similar interruption experiments were performed for GaSb and AlGaAsSb, with \( \text{H}_2 \) or TMSb exposure. The GaSb reflectance was more
stable with an overpressure of TMSb during interruption compared to H₂. Furthermore, the reflectance was insensitive to the mole fraction of TMSb. However, previously reported studies of GaSb surfaces that were annealed under various TMSb concentrations indicated a smoother surface morphology at the lowest TMSb concentrations [21]. Therefore, 5 × 10⁻⁵ mol fraction TMSb was used for GaSb growth interruptions. The reflectance of AlGaAsSb was insensitive to ambient exposure during interruption.

3.2. Effect of growth interruption on GaInAsSb/GaSb multiple-quantum-well structures

The effect of interruption at the GaInAsSb interface was further studied by growth and characterization of MQW structures consisting of five-periods of 10-nm thick GaInAsSb wells and 40-nm thick GaSb barriers. An interruption was introduced after growth of each GaInAsSb well, and the interruption time was either 0.2 or 60 s and the ambient was either H₂ or 1 sccm TMSb in the H₂ carrier. Figs. 4a and b show HRXRD and 4K PL, respectively, of the three structures. The inset in Fig. 4a shows details of the structure and growth interruption. Overall, the HRXRD curves of all samples exhibit a number of intense and sharp satellite peaks, which is indicative of high structural quality and compositionally abrupt interfaces throughout the structure. The resolution of the peaks, however, is better for samples with TMSb introduced during the interrupt compared to the H₂ ambient.

The optical quality as measured by 4K PL is significantly more sensitive to interruption, as shown in Fig. 4b. The highest PL intensity is observed for the sample with the shortest interruption time of 0.2 s with TMSb. Increasing the TMSb interruption time to 60 s reduces the PL intensity by about 25%, and H₂ interruption for 60 s results reduces it by almost 60%. All samples have similar full-width at half-maximum values of about 9 meV. However, the PL peak position shifts to shorter wavelengths with the decrease in PL intensity. Since a lower As or In content would decrease the PL wavelength, this shift may be related to a loss of As or In at the surface. Alternatively, differences in band alignments due to interfacial layers could also affect the optical transition energy. It is likely that interface states, which are non-radiative recombination centers, result from growth interruption and are responsible for this decrease in optical efficiency.
3.3. Surface recombination velocity of GaInAsSb/(Al)Ga(As)Sb double heterostructures

Quantitative determination of interfacial quality can be determined by analysis of minority carrier lifetime measurements to extract surface recombination velocity [1,6]. The effective lifetime was experimentally measured using TRPL. This lifetime is dependent on bulk and interfacial recombination processes, and can be separated according to the equation

$$\frac{1}{\tau_{PL}} = \frac{1}{\tau_{BLK}} + 2S/W,$$

where $\tau_{PL}$ is the lifetime measured by PL decay, $\tau_{BLK}$ is the bulk lifetime, $S$ is the surface recombination velocity, which is assumed to be equal at the front and back heterointerfaces, and $W$ is the active layer thickness. This approximation assumes that photon recycling effects are negligible and that $S$ is relatively small compared to the ratio of minority carrier diffusion constant $D$ to $W$ ($S < D/W$). These approximations are reasonable when $W < \sim 0.5 \mu m$ [22]. Thus, $S$ can be determined from measurements of $\tau_{PL}$ for samples with various thicknesses.

AlGaAsSb/GaInAsSb/AlGaAsSb DHs with varying GaInAsSb thicknesses were grown at 525 °C. The layer structure, schematically shown in Fig. 5a consists of a 0.1 μm p-GaSb buffer, 0.02 μm p-AlGaAsSb, p-GaInAsSb (thickness varied), 0.02 μm p-AlGaAsSb, and 0.025 μm p-GaSb. Short interruption times of 4 s or less were introduced between successive layers. The p-GaInAsSb active layer was doped at $2\times10^{17}$ cm$^{-3}$, and GaInAsSb thickness was varied from 0.15 to 0.4 μm. Nominally undoped AlGaAsSb is p-type with hole concentration dependent on Al content [16]. For the samples in this study, two sets of DHs were grown with different AlGaAsSb concentrations. The Al content in these samples was estimated from the data in Fig. 1, and is about 0.2 and 0.25. This range of Al yields a hole concentration in the range 1 to $2\times10^{17}$ cm$^{-3}$.

The structure of lifetime samples grown at 525 °C in the present study is contrasted with that grown in previous studies [6], which is schematically shown in Fig. 5b. Previously, GaInAsSb was grown at 525 °C, while AlGaAsSb was grown at 550 °C. Thus, interruption times on the order of minutes were required for temperature changes. As discussed in the Section 3.1, a thin interfacial layer of GaSb can be deposited on GaInAsSb to protect its surface during heating. For symmetry, GaInAsSb is capped on both sides with GaSb. The growth sequence was as follows. After the lower AlGaAsSb layer was grown at 550 °C,
thick GaSb layer was grown at this same temperature. The growth was interrupted for 100 s and the temperature was reduced to 525 °C. GaInAsSb was grown at this lower temperature, capped with a 2.5-nm-thick GaSb layer, and then growth was interrupted for 60 s to increase the temperature to 550 °C for deposition of the AlGaAsSb and GaSb cap layers.

Minority carrier lifetime data for DHs grown at 525 °C are shown in Fig. 6 where $1/\tau_{\text{PL}}$ is plotted as a function of $1/W$. The data for the two sets of samples with different Al content demonstrate a linear dependence, and $S$ is determined to be $\sim 50$ and $\sim 30$ cm/s for Al content in AlGaAsSb of 0.2 and 0.25, respectively. These low values are significantly smaller than the value of 720 cm/s that was previously reported for samples, shown in Fig. 5b [6], grown with interruption times on the order of minutes. That value of $S$ did not account for photon recycling and was determined from samples with active layer thicknesses greater than 1 μm. Even when photon recycling is factored into estimation of $S$, it is reduced by about 200 cm/s. Therefore, the benefits of minimizing growth interruption to a few seconds are apparent. Furthermore, the low $S$ values for DHs grown at 525 °C are apparently unaffected by the high O levels of $\sim 8 \times 10^{18}$ cm$^{-3}$.

Also shown in Fig. 6 for comparison is $\tau_{\text{PL}}$ for a DH sample with p-GaSb capping layers. This value of $\tau_{\text{PL}}$ is about 40% lower than that measured for the structure with similar thickness and AlGaAsSb capping layers. This reduction is likely related to a higher $S$ value, although it cannot be determined from this single point. The lower lifetime for GaSb capped structures is consistent with previous observations [6], and is attributed to accumulation of electrons at the GaInAsSb/GaSb type-II interface and to thermionic emission resulting from lower electron confinement of GaSb confining layers [22]. It is likely that both the thin interfacial GaSb layers as well as long growth interruptions are responsible for the
higher $S$ values obtained for GaInAsSb/AlGaAsSb DHs in previous reports [6].

Since the highest performing Sb-based TPV cells to date were fabricated from structures in which GaInAsSb and AlGaAsSb layers were grown at 525 and 550 °C, respectively, with the long interruption times [7], it seems reasonable to expect further increases in $V_{oc}$ if TPV structures are grown under the conditions reported in this study, which lead to very low surface recombination velocities of <50 cm/s.

4. Conclusions

In conclusion, growth interruption at GaSb, GaInAsSb, and AlGaAsSb interfaces was studied by in situ reflectance and ex situ HRXRD, PL, and TRPL. The GaInAsSb interface is extremely sensitive to ambient exposure as well as the length of interruption time. Introduction of a low flow of TMSb during the interruption was found to stabilize the surface. GaSb and AlGaAsSb, on the other hand, are only slightly perturbed by growth interruption. The optical properties of GaInAsSb/AlGaAsSb MQWs are more sensitive to growth interruption than structural properties. DHs that are grown under optimized conditions have surface recombination velocity as low as 30 cm/s, which is over an order of magnitude lower than values reported previously. These results suggest that performance of GaInAsSb/AlGaAsSb TPV devices could be further improved if grown under similar conditions reported in this study.

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