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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 the 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 interruption sequence, surface recombination velocity as low as 20 cm/s was achieved for GaInAsSb/AlGaAsSb double heterostructures.

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, which were grown by organometallic vapor phase epitaxy (OMVPE).

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

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of p-GaInAsSb doubly capped with p-AlGaAsSb layers 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 \( \sim 0.53 \text{-eV} \) Ga\(_{0.84}\)In\(_{0.16}\)As\(_{0.14}\)Sb\(_{0.86}\) and 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 is anticipated to be better compared to that 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]. Since this value is only about 85% of the theoretical limit, further increases in \( V_{oc} \) should be possible. In principle, if the interface between GaInAsSb and AlGaAsSb can be improved to lower surface recombination velocity, then \( V_{oc} \) should increase, and thus improve overall TPV cell performance.

The quality of heterointerfaces in Sb-containing alloys is extremely sensitive to growth sequences, and interruptions during OMVPE growth were reported to alter the interface chemistry, degrade the interface structure, and affect device performance [9-13]. This paper reports the effects of interruption on the quality of GaInAsSb/(Al)Ga(As)Sb double-heterostructures (DHs) grown by OMVPE, and the achievement of extremely low surface recombination velocity in GaInAsSb/AlGaAsSb DHs. Both the interruption time and ambient atmosphere significantly impact the stability of the GaInAsSb surface. Surface recombination velocity below 50 cm/s is reported for three different sets of p-GaInAsSb/p-AlGaAsSb DHs, and one with surface recombination velocity as low as 20 cm/s.

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° toward (1-11)B. GaInAsSb
was grown at 525 °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 °C, even though the morphology of AlGa(As)Sb was reported to be better when grown at 550 °C [16]. The lower temperature of 525 °C 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 °C, respectively, since temperature changes can not be made instantaneously. The V/III was 4.4, which is greater than V/III = 3.2-3.4 for AlGaAsSb grown at 550 °C [16]. The higher V/III ratio at 525 °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 backscattering spectroscopy. 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 oxygen impurity level in AlGaAsSb, as measured by secondary ion mass spectroscopy (SIMS), is about 8 x 10 cm⁻³, which is about two times higher than that measured for layers grown at 550 °C.

In-situ spectral reflectance [17] 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 1 to 3 x 10⁻⁴ mole fraction, and TBAs from 6 to 20 x 10⁻⁶ mole fraction. Epitaxial layers were characterized ex-situ by Nomarski contrast microscopy to examine surface morphology, high-resolution x-ray diffraction (HRXRD) and 4 K PL to evaluate the structural and interface quality of GaInAsSb/(Al)Ga(As)Sb heterostructures. Further characterization of interfacial quality of (Al)Ga(As)Sb/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

It was found that in-situ reflectance is sensitive to changes in the reflectance of epitaxial layers during growth interruption. Figure 2 shows the reflectance 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. Although 300 s is a longer time than necessary for making temperature changes during growth, this longer interruption can elucidate the stability of the reflectance signal 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 [17], 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 four times with a different flow of TMSb into the reactor during the growth interruption. During the first interruption, GaInAsSb was exposed only to H₂, while during the second, third, and fourth interruptions, 1, 2, and 3 sccm (1, 2, and 3 x 10⁻⁴ mole fraction) TMSb was introduced in the H₂ carrier, respectively. An increase in reflectance is observed with the H₂ anneal. Subsequent anneals with TMSb indicate that the GaInAsSb surface is sensitive to TMSb flow rate. For a low flow rate of 1 sccm, the GaInAsSb reflectance is stable. For 2 sccm, the reflectance is initially stable. However, after about 250 s (near the end of the anneal cycle), a slight decrease in the reflectance is observed. For 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 present. Thus, the mixture of TBAs and TMSb is more destabilizing than TMSb. As the total group V mole fraction increased, the magnitude of the reflectance change increased. The morphology of this sample exhibited no growth defects, and only a very slight increase in surface roughness. The decrease
in reflectance might result from modification of surface stoichiometry, since As/Sb exchange at
the epilayer surface is difficult to prevent [18-19].

In another set of experiments, GaInAsSb growth at 525 °C was interrupted and the epilayer
was heated to 550 °C in order to accommodate growth interruption for deposition of AlGaAsSb
at 550 °C. In numerous tests, the reflectance decreased even with a low flow of TMSb during
the interruption. Therefore, the GaInAsSb was capped with a thin layer of GaSb, also grown at
525 °C, before heating the sample. This GaSb interfacial layer was varied from 1 to 5 nm.
Based on the criteria of stable in-situ reflectance during heating from 525 to 550 °C, 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 layers, with H2 or
TMSb ambients. 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 [20]. Therefore, the lowest flow of TMSb was used for any GaSb growth
interruptions. The reflectance of AlGaAsSb appeared insensitive to the ambient atmosphere
during interruption.

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

The effect of interruption at the GaInAsSb surface was also studied by growth and
characterization of MQW structures consisting of five-periods of 10 nm GaInAsSb wells and 40
nm 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 4b show HRXRD and 4 K 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.

Figure 4b shows that the 4K PL peak intensity is extremely sensitive to interruption time and
ambient. 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 reduces the PL intensity. The lowest PL efficiency is observed for the sample with 60 s H₂ interruption. 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. These results are consistent with the reflectance data, which show significant changes during interruption of GaInAsSb growth. 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 ultimately be performed by analysis of minority carrier lifetime measurements to extract surface recombination velocity [1,6]. The effective lifetime was experimentally measured using time-resolved PL. This lifetime is dependent on bulk and interfacial recombination processes, and can be separated according to the equation

\[ \frac{1}{\tau_{PL}} = \frac{1}{\tau_{BLK}} + \frac{2S}{W}; \]

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 [21]. 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\( \mu \)m p-GaSb buffer, 0.02 \( \mu \)m p-AlGaAsSb, p-GaInAsSb (thickness varied), 0.02 \( \mu \)m p-AlGaAsSb, and 0.025 \( \mu \)m p-GaSb. Short interruption times of 4 s or less were introduced between successive layers. The p-GaInAsSb active layer was doped at 2 x 10⁷ cm⁻³, and GaInAsSb thickness was varied from 0.15 to 0.4 \( \mu \)m. Nominally undoped AlGaAsSb is p-type with hole concentration dependent on Al content [16]. For the samples in this study, three 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, 0.25, and 0.3. This range of Al yields a hole concentration in the range 1 to $5 \times 10^{17}$ cm$^{-3}$.

The structure of lifetime samples grown at 525 °C in the present study is contrasted with that grown in previous studies [6,21], and the structure 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 above, 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, a 2.5-nm-thick GaSb layer was grown at this same temperature. The growth was interrupted for 100s 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 measured by TRPL are shown in Fig. 6 where $1/\tau_{\text{PL}}$ is plotted as a function of $1/W$. The data for the three sets of samples with different Al content demonstrate a linear dependence, and $S$ is determined to be 46, 27, and 20 cm/s for Al content in AlGaAsSb of 0.2, 0.25, and 0.3, respectively. These low values are significantly smaller than the value of 720 cm/s that was previously reported for samples grown with interruption times on the order of minutes, shown in Fig. 5b [6]. 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 only reduced by about 200 cm/s. Therefore, the benefits of minimizing growth interruption are apparent. The three sets of data yield an average $\tau_{\text{BLK}}$ value of 48 ns. Overall, $\tau_{\text{PL}}$ values are slightly lower for the samples with Al content of 0.3. SIMS analysis of bulk AlGaAsSb layers indicated that samples with higher Al content are associated with higher levels of O impurity, which creates nonradiative recombination centers in Al-based III-V alloys and can degrade minority carrier lifetime [22].

Also shown in Fig. 6 for comparison is $\tau_{\text{PL}}$ for a DH sample with p-GaSb capping layers. Assuming that GaSb capped DHs would have the same $\tau_{\text{BLK}}$ value as AlGaAsSb capped samples, an estimate of $S$ with GaSb capping layers yields a significantly higher value of $S$.
~400 cm/s. The higher S is consistent with previous observations, and is attributed to accumulation of electrons at the GaInAsSb/GaSb type-II interface [6] and thermionic emission resulting from lower electron confinement of GaSb confining layers [23]. It is likely that both the thin interfacial GaSb layers as well as growth interruptions are responsible for the higher S values obtained 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 surfaces was monitored by in-situ reflectance. These studies indicate that the GaInAsSb epilayer surface is extremely sensitive to the ambient atmosphere 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 interfacial quality of GaInAsSb/AlGaAsSb double heterostructures, which were grown under optimized conditions, was characterized by minority carrier lifetime measurements by PL decay. Surface recombination velocity is as low as 20 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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References

Figures

Fig. 1. Incorporation of Al in AlGa(As)Sb as a function of TTBAI gas phase concentration: growth at 550 °C (▲) [ref. 16]; and at 525 °C (○, ●). Al content was determined by 4 K photoluminescence (○) and by Rutherford backscattering spectroscopy (●).

Fig. 2. In-situ reflectance of growth sequence consisting of GaInAsSb growth; growth interruption with H₂ or TMSb, which is highlighted; and GaSb growth.
Fig. 3. In-situ reflectance of growth sequence consisting of GaInAsSb growth; growth interruption with TMSb or (TBAs + TMSb); and GaSb growth.

Fig. 4. (a) High-resolution x-ray diffraction and (b) 4K photoluminescence of 5-period GaInAsSb/GaSb MQW structures grown with various interruptions. The inset in Fig. 4a shows details of the structure and growth interruption.
Fig. 5. Schematic AlGaAsSb/GaInAsSb/AlGaAsSb double heterostructures for measurement of minority carrier lifetime: (a) structure grown at 525 °C and (b) GaInAsSb and AlGaAsSb grown at 525 and 550°C, respectively.

Fig. 6. Inverse PL lifetime versus inverse GaInAsSb thickness of GaInAsSb/AlGaAsSb double heterostructures: (■) GaSb capping layers; (▲) Al content of AlGaAsSb is 0.2; (○) Al content of AlGaAsSb is 0.25; and (●) Al content of AlGaAsSb is 0.3.