Passivation of W-structured type-II superlattice long-wave infrared photodiodes.

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Abstract

A critical step in developing type-II superlattice (T2SL) based LWIR focal plane array (FPA) technology is to achieve high performance levels in FPA pixel-sized devices having 20-40 µm pitch. At this scale, device performance tends to be limited by surface effects along mesa sidewalls which are etched to provide pixel isolation. While control of surface leakage has been achieved for MWIR T2SLs, as evidenced by the availability of commercially produced FPAs, the same cannot be said for LWIR T2SLs. Several groups have approached this problem as strictly a matter of surface treatment, including cleaning, chemical treatment, and dielectric coating or epitaxial overgrowth, but with limited success. Here we describe an approach based on shallow-etch mesa isolation (SEMI), which takes advantage of bandgap grading to isolate devices without exposing narrow-gap LWIR regions on diode mesas sidewalls. The SEMI process consists of defining mesa diodes with a shallow etch that passes only 20-100 nm past the junction of a graded-gap “W”-structured type-II superlattice p-i-n structure, where the bandgap remains large (>200 meV). A second, deeper etch is then used to define a trench along the chip border for access to the p-contact. As a result, SEMI diodes have only MWIR layers exposed along sidewalls, while the LWIR regions remain buried and unexposed. We also discuss an investigation of surface passivation of GaSb with sulfur using thioacetamide.

KEYWORDS: type-II superlattice, strained layer superlattice, III-V, IR detector, passivation, ammonium sulfide, thioacetamide

1. INTRODUCTION

As performance of type-II superlattice (T2SL) based detectors have improved, expectations for high performance infrared focal plane arrays (FPAs) using this material system have also been driven up. Some success has already been achieved, with the availability of commercial MWIR units from AIM INFRAROT-MODULE GmbH [1]. It is a different story in the LWIR however, where developing commercially viable T2SL technology has been elusive. The main issue has been controlling dark current, which is dominated by surface effects in pixel sized devices. As the bandgap decreases, devices become more prone to surface leakage, and thus the delay in bringing LWIR technology to market. The typical approach to this problem has been to investigate various surface treatments, dielectric coatings, and overgrowths, and to demonstrate effectiveness on increasingly longer wavelength devices. Unfortunately so far, passivation methods have not been amenable to “scaling-up” in wavelength. Methods that have succeeded on MWIR devices: including recipes for etching and cleaning, and low temperature plasma enhanced chemical vapor deposition (PECVD) of dielectric coatings, have resulted in shorted LWIR devices. Here we describe a different approach, shallow etch mesa isolation (SEMI), that makes use of band-gap engineering to help control surface leakage. We also discuss a related effort using thioacetamide (TAM) to passivate GaSb surfaces with sulfur.
2.1 BAND GAP GRADING

In the W-structured type-II superlattice (WSL), the basic InAs/InGaSb superlattice structure is augmented by using dual InAs electron wells on either side of the InGaSb hole-well, bounded on the outside by AlSb barrier layers [2]. Use of the WSL in infrared photodiodes [3,4] was originally motivated by a desire to improve the quantum efficiency of type-II superlattice (T2SL) photodiodes near the band edge, owing to the quasi-2D density of states for electrons and holes in this heterostructure. It became apparent however that the WSL might offer more of an advantage with regard to dark current suppression, as the increased localization of electron wavefunctions along the growth direction strongly reduced tunneling current.

Another benefit soon emerged, and that was the enormous design flexibility afforded by the additional layers. With the WSL it was possible to independently control the bandgap, the valence and conduction band offsets and the strain over a wide range of values, so that nearly arbitrary band structure profiles could be realized. This led to the development of the graded-gap WSL (GGW) photodiode [5], which has resulted in significant improvement in the dark current performance of T2SL photodiodes.

![Figure 1](image.png)

Figure 1. (a) Simulation of 11 µm cutoff, graded (solid) and an ungraded (dash-dotted) WSL photodiodes with identical doping profiles at equilibrium. (b) GGW diode under flat band conditions highlighting the grading profile.

In the GGW photodiode (Fig. 1), an LWIR absorbing region is connected to an MWIR top contact via a series of 8-10 transition WSLs. In the first transition layers from the absorber, the band gap is increased rapidly using large steps in the valence band offsets, producing a much larger band-to-band tunneling barrier in the GGW device. At the other end of the graded region, the conduction band of the transition WSLs is finely, but steeply graded to oppose the field induced band bending near the junction. As a result, the conduction band is nearly flat in this region at equilibrium (Fig. 1 (a)), and the high field region of the device is moved into the wider gap portion of the diode. This should result in a sharp decrease in generation and recombination processes that predominate in the depletion regions, since they scale exponentially with band gap.

As can be seen in Figure 2, these innovations have led to dark current performance of GGW photodiodes approaching that of MCT. Since GGW devices often need to operate under a small reverse bias (~40-400 mV), the comparison in Figure 2(a) is made between the effective dynamic resistance–area product (\(RA_{eff}\)) of GGW photodiodes vs. the zero-bias \(R_0 A\) values of MCT. \(RA_{eff}\) is defined as the Johnson noise resistance–area product equivalent to twice the shot noise produced by the current density \(J_b\), at operating bias \(V_b\) and temperature \(T\). \(B\) is the noise bandwidth.
In Fig. 2 (b), the $R_{A_{eff}}$ values are replaced with $R_{A_{bulk}}$, which is the value of $R_{A_{eff}}$ in the limit of infinite diode radius (no sidewall surface leakage) obtained from 1/intercept of the line fitting $1/R_{A_{eff}}$ vs. perimeter-to-area ratio. Comparing the plots, it is evident that most of the difference in performance can be eliminated with effective sidewall passivation.

\[
\frac{4kTB}{R_{A_{eff}}} \equiv 2qBJ_b \quad \Rightarrow \quad R_{A_{eff}} = kT/qJ_b
\]  

(1)

Given the difficulty in achieving adequate surface passivation of LWIR T2SL photodiodes using chemical treatments and the deposition of insulating layers, we wished to explore how passivation might be addressed through structural means. The result was shallow etch mesa isolation (SEMI), a technique that we hope will lead to improved passivation and simplified fabrication of LWIR T2SL photodiodes by eliminating sidewall exposure of narrow gap active regions. It works in conjunction with bandgap grading by limiting the mesa isolation etch depth to 20-100 nm past the doping-defined junction, well short of the narrow gap absorber, as illustrated in Figure 3. A second etch is then performed to define a deep trench along the periphery of the array to allow access to the $p$-contact of the diodes. The advantage is that the shallow etch is sufficient to isolate pixels, while leaving only a short MWIR region exposed along the mesa sidewall, making surface passivation more tractable.
In the SEMI process, the etch that defines pixels in the array is typically only 200-400 nm in total depth, rather than the deep trenches normally used to pass through the active region between pixels. With high-quantum efficiency structures already over 6-µm in thickness, this greatly simplifies processing. Another advantage is that SEMI structures can be defined so that the area of the electrical junction is much smaller than the optical area, with dark current scaling accordingly as shown in the illustration of Figure 4(a). Provided photo excited carriers are within a lateral diffusion length $L_x$ from the edge of the shallow mesa, they can be collected. Finally, as shown in Figure 4(b), the elimination of trenches between pixels allows for 100% fill factor.

Figure 4. (a) illustration of SEMI defined to minimize the electrical junction area while maintaining full optical area. (b) Elimination of inter-pixel trenches allows for 100% fill factor.

2. SEMI VS. DEEP ETCH RESULTS

A study of the effectiveness of the SEMI process was performed using five LWIR GGW photodiode wafers. Two dies were fabricated from each wafer using the same maskset to define a series of mesa isolated photodiodes of varying diameters (100-400 µm). One die of each pair was processed using full mesa isolation (FMI), with mesa isolation and p-contact access defined by a single 3-4 µm deep etch that penetrated at least 85% of the way through the absorber (except for the 13.4 µm cutoff sample where the etch was only 2 µm deep and went only half way through the absorber). The SEMI process was used to fabricate the second die in each pair, with the shallow mesa-defining etch stopping 20-100 nm past the junction, well short of the absorber. Access to the $p$-contact on the SEMI
processed die was made by etching a deep trench along the outer border of the sample. All etching was done using a wet etch composed of a mixture of citric-acid, hydrogen peroxide, phosphoric acid and de-ionized (DI) water, and no additional chemical treatments or insulating overlayers were applied.

The results are shown in Figures 5 (a-e), in which J-V data for the deep etch (solid) and SEMI (dashed) processed dies are plotted for each wafer. It is evident that most of the difference in the samples occurs near zero bias. To quantify the change, the dynamic resistance parameters were evaluated at V=0 and listed in the table in the figure. sidewall resistivity \( \rho_{SW} (\Omega\cdot cm) \), was determined from the slope of \( 1/R_0A \) vs. Perimeter/Area of circular diodes with varying radii, while \( R_0A_{BULK} (\Omega\cdot cm^2) \) was obtained from the intercept.

\[
\frac{1}{A} \frac{\partial I}{\partial V_0} = R_0A^{-1} = R_0A_{BULK}^{-1} + \rho_{SW}^{-1} \frac{P}{A}
\]

(2)

There is a strong trend in the data of Fig. 5 in which it can be seen that the relative increase in \( R_0A, R_0A_{BULK} \) and sidewall resistivity in going from a deep to a SEMI process follows the increase in the magnitude of the operating bias. The operating bias refers to the small reverse bias (40-400 mV) required for each GGW photodiode to reach about 95% of maximum quantum efficiency (QE). This results from excess background doping that induces more band-bending than the grading profile is designed to overcome, producing a small potential barrier in the conduction band (Fig. 6).

Figure 5. J-V data for five wafers comparing deep etched (solid) and SEMI processed (dashed) die results. Zero bias parameters for the five samples extracted from the J-V plot are given in the table.
Figure 6. Barrier formation in GGW diodes due to excess background doping.

If one plots the ratio of SEMI to deep-etch IV parameters as a function of operating bias, the parameters evaluated at zero-bias \((R_{0A}, R_{0A_{\text{bulk}}}, \rho_{sw})\) can be seen to increase exponentially with the operating point (Fig 7 (a) half-filled symbols). On the other hand, a plot of the same parameters evaluated at the bias point \((R_{\text{eff}}, R_{\text{eff}_{\text{bulk}}}, \rho_{\text{eff}_{sw}})\), shows that the SEMI processed devices perform about the same as the normally etched diodes, independently of operating bias (Fig. 7 (a) unfilled symbols). The interplay between the barrier and surface leakage current indicated by the data is suggestive. In the SEMI diodes, with the barrier lying buried below the surface, both bulk and surface currents are effectively suppressed until the bias is sufficient for carriers to surmount the potential hill. In the deep etched samples however, with the barrier region exposed along the sidewalls, surface leakage currents appear to simply by-pass the barrier.

Recasting the data as a function of cutoff wavelength (Fig. 7(b)) shows that the dark current performance of the SEMI processed dies is independent of bandgap. For low bias levels then, the SEMI process does help to decouple LWIR optical performance from the electrical characteristics.

Figure 7. (a) Ratio of SEMI to deep-etch IV parameters vs. GGW diode operating bias. Parameters evaluated at zero bias have half-filled symbols and those extracted at the operating point are unfilled. (b) Same data as in (a) but plotted as a function of cutoff wavelength.
Another way in which the SEMI processed dies differed markedly from the deep-etched samples was in the stability of the IV characteristics. Typically variations in IV data are seen over the course of days or weeks in unpassivated samples. The highest performance is measured on the first cool-down with subsequent performance degraded, with some random variation over time, as illustrated in Figure 8(a). Unpassivated SEMI processed devices however, yielded much more repeatable results with no degradation or fluctuations evident in either the raw IV data or extracted parameters such as $R_0A=(dJ/dV)^{-1}$ (Fig 8(b)). We attribute this difference to a much lower sensitivity to surface adsorbents in the SEMI structure, with the narrow-gap layer shielded from direct exposure.

Figure 8. (a) IV data from normally etched mesa devices showing fluctuations over time. (b) Data from the same wafer with diodes fabricated using SEMI exhibiting stable IV characteristics.

The SEMI structure has another important effect on device operation, particularly for closely spaced pixels. In SEMI photodiodes, there is strong lateral collection of photoexcited electrons within the un-etched active region adjacent to the mesa. The apparent quantum efficiency (QE) is thus enhanced by the additional lateral area ($A_{lat}$) accessible by electron diffusion (illustrated in Fig. 9).

If the lateral collection length ($L_{lat}$) is small relative to the diode radius, one can fit the measured QE of a series of diodes of varying radii as function of the ratio of mesa diameter to area, $L_{mesa}/A_0$ with
\[ QE = QE_{\infty} \left( \frac{A_0 + A_{\text{lat}}}{A_0} \right) \approx QE_{\infty} \left( 1 + \pi L_{\text{lat}} \frac{L_{\text{mesa}}}{A_0} \right) \] (3)

One can then extract both the quantum efficiency in the limit of a diode of infinite radius \( QE_{\infty} \), and the lateral collection length, \( L_{\text{lat}} \). \( L_{\text{lat}} \) can then be used to determine the minimum junction area of diode-pixels as in Figure 5, while maintaining 100% fill factor for optical collection.

Crosstalk between adjacent pixels is a potential downside of the lateral collection in SEMI diodes, although it is likely to be no more of an issue than in planar MCT diode technology, where lateral diffusion lengths are expected to be much larger. Unfortunately, reliably predicting this effect is complicated by the anisotropic bandstructure and transport in the superlattice, and we expect that it will be more practical to directly measure cross talk in arrays than to simulate.

Meanwhile, we have made measurements on diodes of varying size to extract the lateral collection length and \( QE_{\infty} \) using Eqn. 3. The results are shown in Figure 10, where the QE spectra are plotted for a set of diodes of varying diameter processed with shallow (a), and deep etching (b). While the 300-nm shallow etch stopped 350 nm above the absorber, the deep etch went 2-µm into the wafer, leaving 1.65 µm of the absorber layer intact. Thus the incomplete removal of the absorber results in some spread in the deep-etched QE spectra, but much less so than for the SEMI sample, where the influence of lateral collection is much stronger. The lateral collection radius for both dies is obtained from a fit of Eqn. 3, shown in Fig. 10 (c). \( QE_{\infty} \) for both samples is about 21%, but the lateral collection length of the SEMI sample is 17 µm, is about four times larger than that of the deep-etched die.

### 3. THIOACETAMIDE (TAM) SURFACE PASSIVATION

While the results of the previous section show promise for SEMI as a way of reducing surface currents, it should also be clear that the remaining exposed MWIR surface still needs to be treated and encapsulated. One method that has been used successfully over the last 20 years to reduce the density of surface states in GaAs has been to terminate dangling bonds at the surface with sulfur [6, 7, 8]. The usual method is immersion in an aqueous solution of ammonium sulfide \((\text{NH}_4)_2\text{S}\) or \((\text{NH}_4)_2\text{S}_x\) (with additional sulfur), and results for this technique have been reported in the treatment of T2SL photodiodes [9]. While the data showed improvement in dark current performance, with a large apparent reduction in trap-assisted tunneling, ammonium sulfide also produced significant etching of the T2SL material. Another drawback of ammonium sulfide is the deposition of excess sulfur on the surface, evident in a “yellow” hue to the sample that further interferes with subsequent processing.
Thioacetamide (TAM) is an alternative vehicle to passivate T2SL materials with sulfur. TAM (CH$_3$CSNH$_2$) is an organic molecule consisting of a methyl and amine group tied to a common carbon atom double bonded to sulfur.

Figure 11. TAM molecule CH$_3$CSNH$_2$

The reaction of ammonium sulfide and water produces HS$^{-1}$, which in the presence of dissolved oxygen, tends to combine to form longer anions HSS$^{-1}$, HSSS$^{-1}$, etc. These can then deposit in varying lengths on the semiconductor surface (Fig. 12 (a)). TAM molecules on the other hand, hydrolyze in solution, and present lone, singly bonded hydrogen sulfides to the surface (Fig 12(b)).

Figure 12. Schematic of sulfur deposition by (a) ammonium sulfide (b) TAM

In the TAM reaction, sulfur atoms are brought to the semiconductor surface in a controlled manner, rather than raining down on the surface in clusters of arbitrary size. Furthermore, since TAM can be activated in either a basic or acidic solution, etching of the semiconductor surface can be minimized.

Earlier work at NRL focused on TAM treatment of InAs [10], and found that surfaces passivated in TAM solutions were more stable against reoxidation in ambient air than surfaces passivated in ammonium sulfide solutions. In this work we focused on the passivation of GaSb. A 1 µm-thick GaSb buffer layer was grown by molecular beam epitaxy to provide an undamaged GaSb surface with a native oxide overgrowth. Samples were treated with either an acidic TAM (“A-TAM”), or a basic TAM (“B-TAM”) solution. For A-TAM, the procedure was to immerse the sample in a 0.18 M TAM solution with acetic acid/DI-H$_2$O (1:10) for 40 minutes at 70°C, while for B-TAM, the sample was immersed in a 0.18 M TAM solution with NH$_4$OH(30% aq.)/DI-H$_2$O (1:10) for 40 minutes at 70°C. Simple optical inspection indicated that no changes in the samples occurred during treatment. Epi-ready GaSb substrates were used for the untreated XPS samples. These were etched in AZ400K developer, rinsed in DI-H$_2$O, and dried in nitrogen.

The samples were then loaded into a Thermo VG Scientific Escalab 220i-XL x-ray photoelectron spectroscopy (XPS) system equipped with a mono-chromatic Al Kα source [11], and brought to high vacuum within 5-10 minutes of chemical treatment. After the initial XPS measurement, the samples were left in room air between subsequent XPS measurements taken over a 14 day period.
The initial Sb 3d and Ga 2p XPS core level spectra for the A-TAM treated and untreated samples are shown in Figure 13. The A-TAM spectra (upper curves) show only the presence of Sb and Ga sulfides (in addition to bulk Sb and Ga). The XPS spectra for the untreated material (lower curves), exhibits significant amounts of Sb and Ga oxides. The absence of oxide peaks in the upper traces show that the oxidized layers have been effectively removed by the A-TAM treatment. Analysis [11] of the attenuation of the bulk signals and peak compositions indicates a 4.5 monolayer (ML) thick sulfidized overlayer.

![Figure 13. XPS spectra just after A-TAM treatment vs. untreated samples in the vicinity of the (a) Sb 3d and (b) Ga 2p core level peaks. Each spectrum has been fit to two components, as indicated.](image)

XPS spectra taken three days later (Fig. 14) show that significant re-oxidation had occurred, particularly of antimony (Fig. 14(a)). Analysis of the spectra indicates that 3 ML of oxide had grown on the overlayer, composed of 3 parts Sb-O and 1 part Ga-O.

![Figure 14. XPS spectra three days after A-TAM treatment vs. untreated sample in the vicinity of the (a) Sb 3d and (b) Ga 2p peaks.](image)

The compositions and thicknesses of the overlayers were determined from quantitative analysis of the XPS spectra using the methods described in reference 11, and are plotted in figures 15 (a, b, c). The thickness of the overlayer as a function of time is shown in 15(a) for the A-TAM (■), B-TAM (□), and untreated samples (△). On the latter sample, a 5 ML-thick native oxide forms within 5-10 minutes (t = 0) after etching the GaSb surface, then slowly grows by only 0.5 ML over the next 3 days. The A-TAM treated sample appears to start out with a similar overlayer of 4.5 ML thickness (15(a) ■’s), but the film is composed entirely of sulfides (Figs. 15(b,c) ■, ●’s) as the native
oxides have been stripped and replaced. For the case of the B-TAM sample, the initial film is only 1.5 MLs thick, and consists of about 1/3 oxide and 2/3 sulfide (Figs. 15(a,b,c) □,○’s). This suggests a low rate of sulfide formation relative to oxidation in B-TAM, and may also indicate incomplete removal of the native oxide. The ensuing oxidation of the overlayer is also more rapid for the B-TAM samples, and is nearly complete within 3 days. For A-TAM, the process is more gradual and linear, especially for Ga. It remains to be seen if, left in room air, the overlayer will eventually be entirely oxidized.

After 3 days, the overlayer growth rate slows for the treated samples and becomes comparable to that of the native oxide, perhaps a result of self-limiting due to the complete oxidation of the top layers. By the end of two weeks, the overlayer thickness on the A-TAM sample is about double that of the initial native oxide. The composition of the 10 ML thick film is 56% oxide and 44% sulfide, with 81% of the Sb and 32% of the Ga oxidized. The growth of the overlayer on the B-TAM sample appears to follow a similar trend, but is much more heavily oxidized. After 7 days, the overlayer is 8 MLs thick and composed of 94% oxide, and 6% sulfide, with 100% of the Sb oxidized and 87% of the Ga.

Looking at the early stages of growth by expanding the time scale (Fig. 16 (a,b)), it can be seen that the A-TAM sample remains oxide free for at least 4 hours, long enough to encapsulate the surface and prevent it from oxidizing further. This is not the case for the B-TAM treatment, as oxide grows on the surface immediately after treatment. Based on the foregoing results, A-TAM followed by suitable encapsulation, can provide an oxide-free, sulfur-passivated GaSb surface.

Figure 16. Same data as figure 15 (b, c) but on an expanded time scale.

4. SUMMARY

Shallow etch mesa isolation (SEMI), is a new technique to improve passivation, simplify fabrication, and increase fill-factor in LWIR focal plane arrays made using type-II superlattice photodiodes. Results for this method, which
works in conjunction with bandgap grading using W-structured type-II superlattices, were presented for 5 LWIR photodiode wafers, showing strong suppression of dark current near zero bias, independent of the energy gap. At operating biases however, dark current performance was similar to that of normally processed devices. The IV characteristics of SEMI processed devices also showed much greater stability over time. Lateral collection measurements indicated collection lengths of 10-20 µm, enabling the reduction of the junction area in SEMI processed devices, so that a substantial reduction in dark current may be obtained even where IV performance levels are similar.

Results were also presented for a study of surface passivation of GaSb using thioacetamide (TAM). Acid- and base-activated TAM solutions were used to process an MBE grown GaSb buffer layer, which was then probed using x-ray photoelectron spectroscopy at different times over a two-week period. The results show that the acid activated treatment was much more effective in removing native oxides and preventing reoxidation.

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