Isolating GaSb membranes grown metamorphically on GaAs substrates using highly selective substrate removal etch processes.

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ABSTRACT

The etch rates of $NH_4OH{:}H_2O_2$ and $C_6H_8O_7{:}H_2O_2$ for GaAs and GaSb have been investigated to develop a selective etch for GaAs substrates and to isolate GaSb epi-layers grown on GaAs. The $NH_4OH{:}H_2O_2$ solution has a greater etch rate differential for the GaSb/GaAs material system than $C_6H_8O_7{:}H_2O_2$ solution. The selectivity of $NH_4OH{:}H_2O_2$ for GaAs/GaSb under optimized etch conditions has been observed to be as high as 11471 ± 1691 whereas that of $C_6H_8O_7{:}H_2O_2$ has been measured up to 143 ± 2. The etch contrast has been verified by isolating 2 µm thick GaSb epi-layers that were grown on GaAs substrates. GaSb membranes were tested and characterized with high-resolution X-Ray diffraction (HR-XRD) and atomic force microscopy (AFM).

I. INTRODUCTION

The ability to isolate thin membranes of narrow gap antimonide semiconductor layers could have significance in the areas of mid to long wave infrared detectors, lasers, and thermophotovoltaics [1-2]. For instance, in the case of Infra-red (IR) focal-plane array (FPA) detectors the removal of the GaSb substrate is crucial as GaSb has a high optical absorption coefficient and a large thermal mismatch in comparison to the Si based read-out integrated circuit [1]. However, the isolation of III-Sb epi-layers from GaSb substrates is not a trivial process since the existing wet etchant solutions for III-Sb based materials have very low selectivities [3]. The GaSb substrate is typically mechanically polished and then etched with a $CrO_3{:}HF{:}H_2O$ solution that has selectivity of 100:1 between GaSb and an InAs etch stop layer [2]. The etch stop layer can be removed with a $C_6H_8O_7{:}H_2O_2$ solution with maximum selectivity of 127 [4]. More recently, selectivities of up to 475 were reported by dry plasma etching of GaSb over InAs/GaSb superlattice etch stop layers [5]. Nonetheless, these selectivites for III-Sb compound semiconductors are still low when compared to the very high selectivity of hydrofluoric acid for AlAs over GaAs [6].

There has recently been a significant interest in growing III-Sb devices on GaAs substrates [7-10]. The GaAs substrates are an attractive alternative to GaSb substrates on account of their semi-insulating nature, lower optical absorption coefficient, relatively lower cost, and ability to scale up to large wafer sizes [10]. The mismatched growth of GaSb epi-layers on GaAs substrates results in a significant threading dislocation density in the GaSb epitaxial layer along with very high interfacial strain due to the 7.78% ($\Delta a/a_{sub}$) lattice mismatch between the two binary semiconductors. However, the growth of GaSb epi-layers with 100 % relaxation and reduced threading dislocation density has been demonstrated by inducing arrays of 90° interfacial misfit dislocations (IMF) at the GaSb/GaAs interface [11]. The residual threading dislocation density in the GaSb epi-layer is in the range of 10^7 (at 2 µm thickness) to mid 10^8 defects/cm^2 (immediately at the interface), which is sufficient for the demonstration of a wide range of devices. While growing on GaAs substrates can solve many of the problems with GaSb substrates, removing the GaAs substrate could possibly improve the performance of some devices. Thus, finding an etchant with a significant contrast between GaSb and GaAs could allow for the realization of several novel thin film antimonide devices.

The most common etchants applicable for GaAs substrate removal are ammonium hydroxide and hydrogen peroxide ($NH_4OH:H_2O_2$) and citric acid and hydrogen peroxide ($C_6H_8O_7:H_2O_2$) solutions [12]. DeSalvo et al. have shown that a citric acid solution etches GaAs more rapidly than it etches GaSb, with the selectivity at 349 [4]. To our knowledge, this is the only publication reporting on the selectivity of an etchant for GaAs compared to GaSb and there are no published results reporting on the etch rates for GaSb using $NH_4OH:H_2O_2$. Furthermore, the quality of the etched GaSb surface has not been investigated in these prior publications.

In this paper, we investigate the possibility of using the most common GaAs etchants for the isolation of III-Sb epi-layers grown directly on GaAs substrates without an etch stop layer. First, we studied the etch rates of $NH_4OH:H_2O_2$ and $C_6H_8O_7:H_2O_2$ for GaAs and GaSb to determine the etch contrast between GaAs and GaSb for each solution. Once the selectivity of the two etchants is established, their effectiveness in removing the substrate and isolating the GaSb membranes were tested and characterized with high-resolution X-Ray diffraction (HR-XRD) and atomic force microscopy (AFM).

II. EXPERIMENT

To establish etch rates of GaAs and GaSb using $C_6H_8O_7:H_2O_2$ and $NH_4OH:H_2O_2$ solutions, (100) oriented GaAs and GaSb substrates were used. Prior to the etching experiments, the substrates were patterned using AZ4330 photoresist, cleaved into 5 mm x 7 mm rectangles, and mounted on a glass slide. The etchant solution of $C_6H_8O_7:H_2O_2$ was prepared with a volume ratio of 10:1 according to the recipe in DeSalvo's publication [4]. The etch solution of $NH_4OH:H_2O_2$ was prepared with a volume ratio of 1:33 [13]. The GaAs substrates were etched for 1, 5, 10, 15 and 30 minutes while GaSb substrates were etched for 1, 15, 30, 60, and 120 minutes on account of slower anticipated etch rates of GaSb compared to GaAs. The etches were initially performed with both a stirring magnet and a jet etcher. The stirring magnet approach resulted in a residual capping layer, while the jet etching process gave clean, residue free surface and edges. Thus all etches in this study were performed using a jet etcher. It must be noted the use of a stirring magnet vs jet etcher under very similar etch conditions could result in very different etch rates. Upon performing the etch for a specific duration, the samples were thoroughly rinsed with DI water and dried with N_2.

The remaining photoresist was then removed with acetone. A stylus profilometer with an uncertainty of 1nm was used to measure the etch depths of the samples. Finally, scanning electron microscope (SEM) was used to characterize the etch profiles.

To investigate the effectiveness of the two etchants in the isolation of GaSb membranes, 2µm GaSb layers were metamorphically grown on GaAs substrates using the previously described technique of forming interfacial misfit dislocation arrays [11]. The grown samples were cleaved into 1 cm x 1 cm squares, chemically cleaned, and bonded to a glass slide with the epitaxial side down. The GaAs substrates were etched with NH_4OH:H_2O_2 and $C_6H_8O_7$:H_2O_2 using a jet etcher. The crystal quality and surface morphology of the GaSb membranes before and after the substrate removal process was characterized with high-resolution X-Ray diffraction (HR-XRD) and atomic force microscopy (AFM). Root mean square (RMS) surface roughness of the samples was estimated on areas of 3 µm x 3 µm. Eight AFM scans were done for each sample.

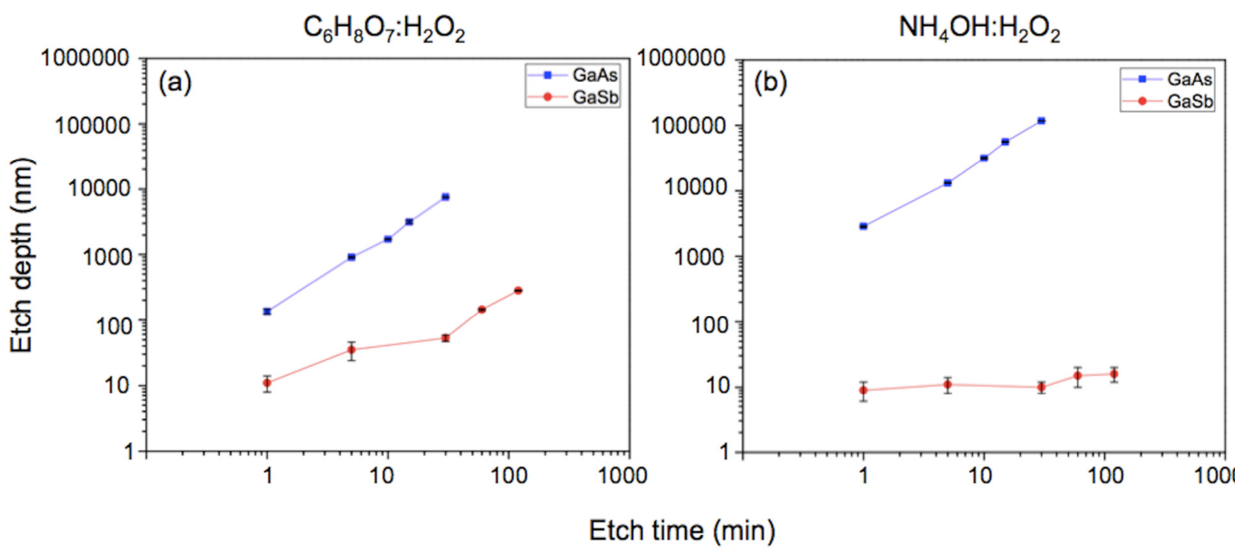

Fig. 1 Etch depth measurements for GaAs and GaSb substrates as a function of etch time

III. RESULTS AND DISCUSSION

Figure 1 shows the plots of average etch depth versus etch time for both etchant solutions. The error bars in the graphs represent the standard deviation from the mean etch depth. The calculated etch rates from these measurements are summarized in table 1. The etch rates of the GaAs substrates increase with time. The etch rates were expected to be constant specially for the $C_6H_8O_7$:H_2O_2 solution. Nonetheless, it is clear that the etch rate of GaAs with NH_4OH:H_2O_2 is considerably faster than with $C_6H_8O_7$:H_2O_2. For GaSb substrates, the etch rates decreases drastically after the 1 min etch time. We believe this may be due to initial faster etching of the native oxide on the surface of the GaSb. After 1 min etch time, the etch rate of GaSb using $C_6H_8O_7$:H_2O_2 stays almost constant but the etch rate of GaSb using NH_4OH:H_2O_2 keeps decreasing with increased etch time. The variation in etch rates with etch times may be due to degradation of the etchant solutions. The selectivity of each etchant was calculated by dividing the etch rate of GaAs by the etch rate of GaSb at the common etch times of 1, 15, and 30 minutes. The resulting selectivities for $C_6H_8O_7$:H_2O_2 range from 12 ± 5 to 143 ± 2 and the ones for NH_4OH:H_2O_2 range from 320 ± 166 to 11471 ± 1691. Despite the fluctuations in etch rates and selectivities, the NH_4OH:H_2O_2 solution shows a greater etch rate differential between GaAs and GaSb than the $C_6H_8O_7$:H_2O_2 solution.

TABLE I. Etch rate summary

Etch Time (min)	**Mean etch rate ± standard deviation (nm/min)**				**Selectivity**	
	GaAs substrate		GaSb substrate			
	$C_6H_8O_7$:H_2O_2	NH_4OH:H_2O_2	$C_6H_8O_7$:H_2O_2	NH_4OH:H_2O_2	$C_6H_8O_7$:H_2O_2	NH_4OH:H_2O_2
1	135 ± 30	2880 ± 582	11.10 ± 3.58	9.00 ± 3.22	12 ± 5	320 ± 166
5	181 ± 9	2636 ± 109				
10	171 ± 5	3167 ± 111				
15	211 ± 11	3723 ± 75	2.33 ± 0.76	0.71 ± 0.23	91 ± 30	5244 ± 1702
30	253 ± 3	3900 ± 39	1.77 ± 0.01	0.34 ± 0.05	143 ± 2	11471 ± 1691
60			2.40 ± 0.09	0.25 ± 0.08		
120			2.33 ± 0.03	0.13 ± 0.04		

Figure 2 shows SEM images comparing the etch profiles of GaAs and GaSb. Figures 2a and 2b show GaAs substrates after being etched for 15 minutes with NH_4OH:H_2O_2 and $C_6H_8O_7$:H_2O_2 respectively. Figure 2c and 2d show GaSb substrates after being etched for 2 hours with NH_4OH:H_2O_2 and $C_6H_8O_7$:H_2O_2 respectively. From the scale on the SEM images, it is evident that the deepest etch profile is for GaAs etched with NH_4OH:H_2O_2. In addition, Figures 1c and 1d show that the etchants have a minimal effect on GaSb substrates. However, $C_6H_8O_7$:H_2O_2 does result in a slightly more pronounced etch profile and a rougher surface than NH_4OH:H_2O_2.

The above results provide an excellent estimate for the behavior of the etchants in substrate removal and isolation of GaSb grown on GaAs. Both etchant solutions have successfully achieved the removal of the GaAs substrate and subsequent isolation of the GaSb membranes with out the need of an etch stop layer as the significant difference in the etch rate of GaSb and GaAs is sufficient to etch the substrate with minimal damage to the GaSb epitaxial layer.

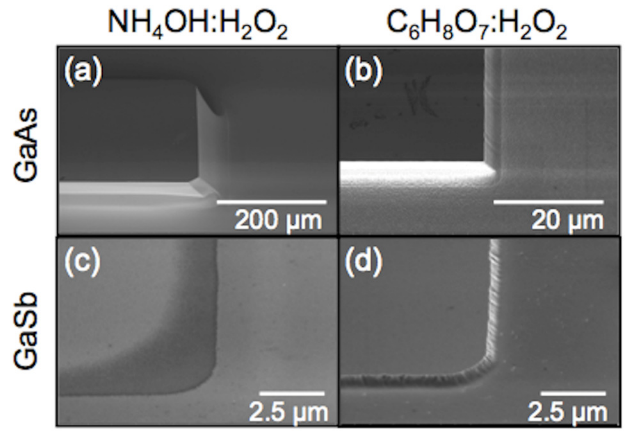

Fig. 2 SEM images comparing the etch profiles of GaAs and GaSb, (a) and (b) show GaAs substrate after been etched for 15 minutes in $NH_4OH:H_2O_2$ and $C_6H_8O_7:H_2O_2N$, respectively, (c) and (d) show GaSb substrate after been etched for 2 hours in in the mentioned solutions

Figure 3 shows results from an ω - 2θ HR-XRD spectra from a symmetric scan. Figure 3a is the diffraction spectra before the etch process. This shows the GaSb epi-layer peak and the GaAs substrate peak. The presence of two distinct peaks with the absence of a pseudomorphic growth region is very typical of metamorphic layers grown using interfacial misfit dislocation arrays [14]. The full width at half maximum (FWHM) of the GaSb peak is 250 ± 8 arcsec indicating good crystal quality. After symmetric and asymmetric XRD scans, calculations show that the GaSb epi-layer is almost 100% relax. After the etch process, the substrate peaks no longer appear in the diffraction spectrum. This indicates the successful removal of the substrates. The remaining GaSb epi-layer peak after removing the GaAs substrate with $C_6H_8O_7:H_2O_2$ has a FWHM of 270 ± 11 arcsec and the one remaining after using $NH_4OH:H_2O_2$ has a FWHM of 290 ± 13 arcsec.

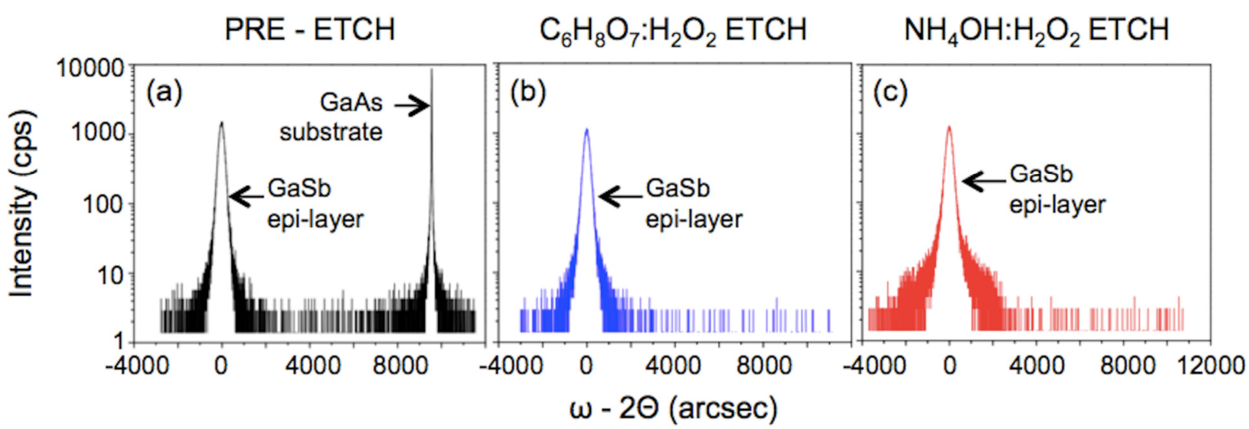

Fig. 3 Pre and post etch ω - 2θ (004) high-resolution X-Ray diffraction spectra of GaSb/GaAs samples. (a) is the diffraction spectrum before the etch process and (b) and (c) are the diffraction spectra after etching away the substrate with $C_6H_8O_7:H_2O_2$ and $NH_4OH:H_2O_2$ respectively

Figure 4 shows AFM micrographs of GaSb membranes before and after isolation. The GaSb epitaxial layer metamorphically grown on GaAs exhibits a RMS surface roughness value of 1.5 ± 0.4 nm. The surface roughness of the GaSb film isolated by etching the substrate with $C_6H_8O_7$:H_2O_2 results in a RMS value of 2.6 ± 0.8 nm and the one isolated by using NH_4OH:H_2O_2 results in 0.9 ± 0.2 nm.

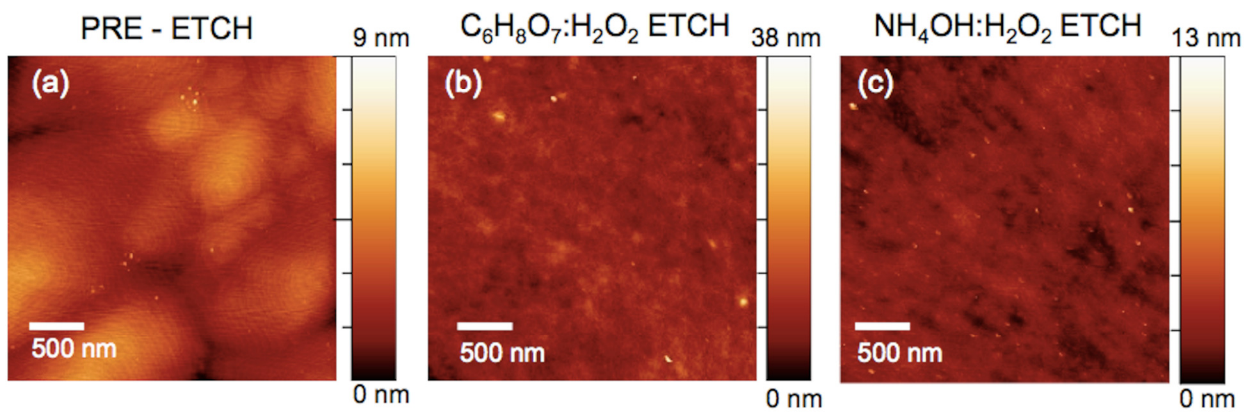

Fig. 4 AFM micrographs of GaSb surface roughness after (a) growth, (b) $C_6H_8O_7$:H_2O_2 etch and (c) NH_4OH:H_2O_2 etch

V. Diode fabrication

The p-i-n GaSb diodes were grown on semi-insulating (100) GaAs substrates by means of molecular beam epitaxy (MBE). After thermal oxide desorption at 630℃, the substrate is cool down to 580℃ to deposit a 200 nm GaAs buffer layer.

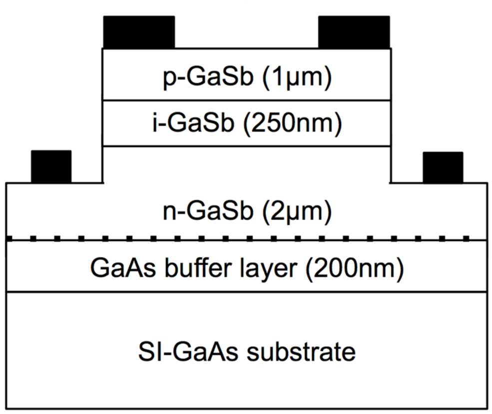

Fig. 5 GaSb diode structure.

Once ensuring a smooth starting surface, the IMF growth technique is used to grow the GaSb epitaxial layers. The Ga shutter and As valves are closed allowing the As surface layer to desorb. When the reflection high electron energy diffraction (RHEED) transitions from a 2 x 4 pattern (As rich) to a 4 x 2 pattern (Ga-rich), the Sb source is opened so that Sb can replace the desorbed As. Then, the temperature is reduced to 510℃ under constant Sb overpressure. The growth of GaSb is intiated as soon as 510℃ is reached. As shown on figure 5, the diode starts with a 2 µm thick n- type GaSb epitaxial layer doped with tellurium. Next, a 250 nm non-intentionally doped intrinsic GaSb is grown followed by a 1 µm thick p-type GaSb epitaxial layer doped with beryllium.
Next, simple circular mesa diodes with diameters of 50 um, 100 um, 150 um, 200 um, 300 um were fabricated using standard photolithography and dry etching. The processing was initiated by etching the mesas 0.5 µm below the i-GaSb epitaxial layer, using an inductively coupled plasma reactor with BCl_3 gas. Next, top and bottom metal contacts were deposited via e-beam evaporator. The contacts for p-GaSb consist of Ti/Pt/Au and the ones for n-GaSb consist of Ni/Ge/Au/Pt/Au. The n-contacts were annealed at 290 ℃ for 45 seconds. Prior to each metal deposition, HCl treatment was done to remove native oxides of the GaSb surface. After processing the diodes, the samples were cleaved into 1 x 1 cm^2 and bonded to a glass slide with the epi-layer side down using a crystal bond adhesive. Then, the GaAs substrate was etched away with a NOH4:H2O2 1:33 solution in a jet etcher. The selectivity of the etchant solution for GaAs compared to GaSb is high enough that no etch stop layer was needed. Once the substrate is removed, the crystal bond adhesive was dissolved in acetone to detach the diode from the glass slide. Then the diode was transfer to a host substrate.
The thin film diodes were tested with by 4-probe measurement before and after substrate removal.

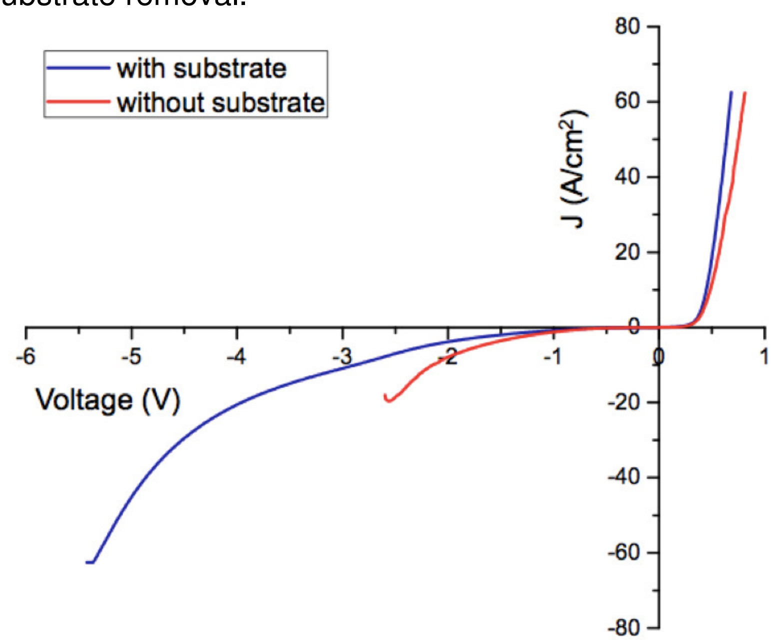

Fig. 6 J-V curves from the GaSb diodes.

A representative plot of the J-V characteristics at ambient light before and after substrate removal is shown in figure **6**. In the forward bias regime, the photodiode shows a turn-on voltage of about 0.3 V when is on the GaAs and also when the substrate is removed. In the reverse bias region, the diode exhibits high leakage current without a defined breakdown voltage. This may be due surface leakage from the mesa walls, to the residual threading dislocations from the lattice mismatch, or to the interfacial states at the GaSb/GaAs interface (Ga dangling bonds due to the IMF growth mode). Hence, a sample was processed with passivated walls and compared to the unpassivated sample. To analyze the effect of the IMF array, a homoepitaxial p-i-n GaSb diode was grown and processed on a GaSb substrate.

V. SUMMARY

It has been shown that the ammonium hydroxide base etchant has a greater etch rate differential for the GaSb/GaAs material system than the citric acid base etchant. The selectivity of $NH_4OH:H_2O_2$ for GaAs/GaSb ranges from 320 ± 166 to 11471 ± 1691 whereas that of $C_6H_8O_7:H_2O_2$ ranges from 12 ± 5 to 143 ± 2. The selectivity of the etchant solutions increased with time as the etch rates seem to be strongly dependent on etch time. Despite the difference in selectivity, in the second part of the experiment, the successful isolation of 2µm thick GaSb epi-layers was demonstrated by etching away the substrate with ether etchant with out the need of an etch stop layer. The combination of this highly selective etch process and the interfacial misfit dislocation growth technique give an alternative to III-Sb base optoelectronic devices that often need the thin down or complete removal of GaSb substrates to improve their performance.

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