Wet etching for InAs-based InAs/Ga(As)Sb superlattice long wavelength infrared detectors

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Abstract: Wet chemical etching of InAs-based InAs/Ga(As)Sb superlattice long wavelength infrared photodiodes was studied in this paper. The etching experiments using citric acid, orthophosphoric acid and hydrogen peroxide were carried out on InAs, GaSb bulk materials and InAs/Ga(As)Sb superlattices with different solution ratios. An optimized etching solution for the InAs-based superlattices has been obtained. The etched surface roughness is only 1 nm. InAs-based superlattice LWIR detectors with 50 % cut-off wavelength of 12 μm were fabricated. The photodetectors etched with optimized solution ratio show low surface leakage characteristic. At 81 K temperature, the surface resistivity $\rho_{\text{surf}}$ of the detector is $4.4 \times 10^2 \text{Ωcm}$.

Key words: InAs/Ga(As)Sb, type-II superlattice, wet chemical etching, surface morphology

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Introduction

Long wavelength infrared (LWIR) photo-detectors have important applications in the fields of geospatial exploration, marine and environmental monitoring, meteorological forecast, etc. InAs/GaSb Type-II superlattices (SLs) have showed excellent opto-electrical properties for infrared detection and high performance focal plane arrays based on this novel material have been demonstrated [1-5,20-22]. Up to now, InAs/GaSb superlattice materials are mainly grown on GaSb substrates. There exists strain in the GaSb-based InAs/GaSb superlattice since the lat-
The detectors are designed to receive the irradiance from the front sides. The architecture of the single-pixel detectors can be found in our previous paper.

![Fig. 1](image)

Fig. 1 The layered structure of the InAs-based T2SLs long wavelength infrared detector.

**2 Result and discussion**

### 2.1 Etching of InAs and GaSb bulk materials

The chemical reactions of InAs and GaSb etching with citric acid (C\(_6\)H\(_{9}\)O\(_7\)), orthophosphoric acid (H\(_3\)PO\(_4\)) and hydrogen peroxide (H\(_2\)O\(_2\)) are as follows;

\[
\begin{align*}
2\text{GaSb} + 6\text{H}_2\text{O}_2 & \rightarrow \text{Ga}_2\text{O}_3 + \text{Sb}_2\text{O}_3 + 6\text{H}_2\text{O} \quad (1) \\
2\text{InAs} + 6\text{H}_2\text{O}_2 & \rightarrow \text{In}_2\text{O}_3 + \text{As}_2\text{O}_3 + 6\text{H}_2\text{O} \quad (2) \\
\text{InAs} + 4\text{H}_2\text{O}_2 & \rightarrow \text{In}_2\text{O}_3 + 4\text{H}_2\text{O} \quad (3) \\
2\text{M}_2\text{O}_3 + 7\text{H}_2\text{O}_2 & \rightarrow 2\text{M(HPO}_4\text{)}_2 + 3\text{H}_2\text{O} + 6\text{H}_2\text{O} \quad (4) \\
(\text{M = Ga or As or Sb or In}) \\
\text{Sb}_2\text{O}_3 + 2\text{C}_6\text{H}_9\text{O}_7 & \rightarrow 2(\text{Sb(C}_6\text{H}_9\text{O}_7)(\text{H}_2\text{O})) + \text{H}_2\text{O} + 2\text{H}^+ \quad (5)
\end{align*}
\]

Among the above chemical reactions, H\(_2\)O\(_2\) is the oxidizing agent. InAs and GaSb oxidized with H\(_2\)O\(_2\) firstly, then the products are dissolved in water or reacted with H\(_2\)PO\(_4\). Sb\(_2\)O\(_3\) is poorly soluble in water or H\(_2\)PO\(_4\), while it can react with C\(_6\)H\(_9\)O\(_7\), to form a water-soluble complex. Therefore etchants containing C\(_6\)H\(_9\)O\(_7\) is necessary for GaSb, while etchants without C\(_6\)H\(_9\)O\(_7\) is feasible for InAs.

The etching rate and surface roughness with different etchants for InAs bulk materials were shown in Table 1. When H\(_2\)PO\(_4\) : H\(_2\)O\(_2\) = 1:1 and without C\(_6\)H\(_9\)O\(_7\), the surface is the smoothest and the roughness is only 0.4 nm, which was shown in Figure 2 (a). While maintaining the ratio of H\(_2\)PO\(_4\) : H\(_2\)O\(_2\) = 1:1, the surface roughness is increased with increasing the proportion of C\(_6\)H\(_9\)O\(_7\). The presence of C\(_6\)H\(_9\)O\(_7\) does not improve the InAs mesa sidewalls morphology, similar to reports in the literature\(^{18}\).

When the proportion of H\(_2\)O\(_2\) is slightly more than that of H\(_2\)PO\(_4\), it has little effect on the surface roughness, while the surface roughness is increased with increasing H\(_2\)PO\(_4\) content. That is because if H\(_2\)PO\(_4\) content is increased, the dihydrogen phosphate will further react with H\(_2\)PO\(_4\), which lead to form a poorly soluble salt (monohydrogen...
Table 1 Etching rate and surface roughness with different etchants for InAs bulk materials.

<table>
<thead>
<tr>
<th>C₆H₅O₇·H₂PO₄·H₂O₂</th>
<th>Etching rate (μm/min)</th>
<th>Surface roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0:0:1:1</td>
<td>0.26</td>
<td>1.4</td>
</tr>
<tr>
<td>0:0:5:1</td>
<td>0.35</td>
<td>0.5</td>
</tr>
<tr>
<td>0:1:1</td>
<td>0.45</td>
<td>0.4</td>
</tr>
<tr>
<td>0:5:1</td>
<td>0.35</td>
<td>10.9</td>
</tr>
<tr>
<td>0:10:1</td>
<td>0.25</td>
<td>15.6</td>
</tr>
<tr>
<td>0.2:1:1</td>
<td>0.33</td>
<td>1.1</td>
</tr>
<tr>
<td>1:1:1</td>
<td>0.32</td>
<td>2.7</td>
</tr>
</tbody>
</table>

The presence of these complexes will adsorb on the mesa sidewalls to form a dense film and prevent the etching reaction to continue and strongly deteriorate the mesa surface sidewalls morphology. Keeping H₃O₇ as a complexing agent to react with Sb₂O₃, the etching rate and surface roughness with different etchants for InAs-based superlattices were investigated, as shown in Table 3. When C₆H₅O₇·H₂PO₄·H₂O₂ = 3:1:1, the surface roughness is the smallest, only 1 nm. The AFM picture was shown in Figure 2 (c).

Table 2 Etching rate and surface roughness with different etchants for GaSb bulk materials.

<table>
<thead>
<tr>
<th>C₆H₅O₇·H₂PO₄·H₂O₂</th>
<th>Etching rate (μm/min)</th>
<th>Surface roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:1:1</td>
<td>0.32</td>
<td>0.7</td>
</tr>
<tr>
<td>3:1:1</td>
<td>0.45</td>
<td>1.5</td>
</tr>
<tr>
<td>1:1:1</td>
<td>0.86</td>
<td>2.4</td>
</tr>
<tr>
<td>10:1:5:1</td>
<td>1.2</td>
<td>6.8</td>
</tr>
<tr>
<td>10:1:3</td>
<td>0.26</td>
<td>1.1</td>
</tr>
</tbody>
</table>

The InAs-based superlattice LWIR detector was fabricated by the optimized etchants of C₆H₅O₇·H₂PO₄·H₂O₂ = 3:1:1 (Sample 311). At the same time, another sample was used for comparison that etched by the etchants of C₆H₅O₇·H₂PO₄·H₂O₂ = 10:1:1 (Sample 1011). The SEM pictures of the InAs-based superlattice mesa sidewalls of (a) sample 1011 and (b) sample 311 were shown in Fig. 3. The etching surface of sample 311 is smoother than that of sample 1011.

The InAs-based superlattice LWIR detector was fabricated by the optimized etchants of C₆H₅O₇·H₂PO₄·H₂O₂ = 3:1:1 (Sample 311). At the same time, another sample was used for comparison that etched by the etchants of C₆H₅O₇·H₂PO₄·H₂O₂ = 10:1:1 (Sample 1011). The SEM pictures of the InAs-based superlattice mesa sidewalls of (a) sample 1011 and (b) sample 311 were shown in Fig. 3. The etching surface of sample 311 is smoother than that of sample 1011.

The InAs-based superlattice LWIR detector was fabricated by the optimized etchants of C₆H₅O₇·H₂PO₄·H₂O₂ = 3:1:1 (Sample 311). At the same time, another sample was used for comparison that etched by the etchants of C₆H₅O₇·H₂PO₄·H₂O₂ = 10:1:1 (Sample 1011). The SEM pictures of the InAs-based superlattice mesa sidewalls of (a) sample 1011 and (b) sample 311 were shown in Fig. 3. The etching surface of sample 311 is smoother than that of sample 1011.

The InAs-based superlattice LWIR detector was fabricated by the optimized etchants of C₆H₅O₇·H₂PO₄·H₂O₂ = 3:1:1 (Sample 311). At the same time, another sample was used for comparison that etched by the etchants of C₆H₅O₇·H₂PO₄·H₂O₂ = 10:1:1 (Sample 1011). The SEM pictures of the InAs-based superlattice mesa sidewalls of (a) sample 1011 and (b) sample 311 were shown in Fig. 3. The etching surface of sample 311 is smoother than that of sample 1011.
Figure 4 (a) shows the current responsivity spectrum of the InAs-based SL detector measured at 81 K. The 50% cut-off wavelength of the detectors reaches 12 μm. The fabricated photodiodes have a similar peak responsivity of 1.6 A/W at 81 K, corresponding to quantum efficiency (QE) of 38%. Figure 4 (b) shows the dark current density and dynamic differential resistance-area product values (RA) of sample 311 (red dots) and sample 1011 (black dots) with mesa area of 200 × 200 μm². The dark current density of sample 311 and sample 1011 are 5.7 × 10⁻⁷ A/cm² and 9.2 × 10⁻⁷ A/cm², respectively, under a bias of -20 mV at 81 K. The surface resistivity $\rho_{\text{surface}}$ of two samples were calculated by a linear least squares fitting (see Figure 4 c) between the $R_A$ (RA denotes the differential-resistance-area product at zero bias) of diodes and P/A ratio based on the following equation:

$$
\frac{1}{R_A} = \frac{1}{R_{A_{\text{bulk}}}} + \frac{1}{\rho_{\text{surface}}} \frac{P}{A}
$$

Where $R_{A_{\text{bulk}}}$ is the bulk differential-resistance-area-product, P is the perimeter of the diode mesa, and A is the cross-sectional area of the detector. $\rho_{\text{surface}}$ of sample 311 is 4.4 × 10⁵ Ωcm, which is almost eight times larger than that (5.1 × 10⁵ Ωcm) of sample 1011, indicating a good surface quality obtained by the optimized etchants and an InAs-based SL LWIR detector with enough low surface leakage currents has been fabricated.

3 Conclusion

Wet chemical etching of InAs-based InAs/Ga (As) Sb superlattice long wavelength infrared photodiodes was studied in this paper. The etching experiments using citric acid, orthophosphoric acid and hydrogen peroxide were carried out on InAs, GaSb bulk materials and InAs-based superlattices with different solution ratios. H$_2$O$_2$ was used as an oxidant, H$_3$PO$_4$ was used to react with the oxide products and C$_6$H$_5$OH was used as a complexing agent. The optimized proportion of H$_2$O$_2$ and H$_3$PO$_4$ is around 1:1 and the proportion of H$_2$O$_2$O$_2$ can be slightly more than that of H$_3$PO$_4$. The C$_6$H$_5$OH content in the etching etchants is related to the Ga(As)Sb thickness ratio in InAs-based superlattice. An optimized etching solution for the InAs-based superlattices has been obtained. The etched surface roughness is only 1 nm. The InAs-based LWIR detectors with 50% cut-off wavelength of 12 μm were fabricated. The photodetectors etched with optimized solution ratio show low surface leakage characteristic. At 81 K, the surface resistivity $\rho_{\text{surface}}$ of the detector is 4.4 × 10⁵ Ωcm.

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