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Abstract

This technical report details the processing schedule used to fabricate Inverted Metamorphic Multijunction (IMM) concentrator solar cells at The National Renewable Energy Laboratory (NREL). These devices are used as experimental test structures to support the research at NREL that is focused on increasing the efficiency of photovoltaic power conversion. They are not intended to be devices suitable for deployment in working concentrator systems primarily because of heat sinking issues. This process was developed to be compatible with small sample sizes and to afford rapid turn-around times, providing timely feedback to the research effort.

The report describes the use of electro-deposition of gold for both the back and front contacts. Electro-deposition is used because of its rapid turn around time, economical material usage, and it is a benign metallization technique that is seldom responsible for damage to the semiconductors. The layer transfer technique is detailed including the use of a commercially available adhesive and the etching away of the parent gallium arsenide substrate. Photolithography is used to define front contact grids as well as the mesa area of the cell. Finally, the selective wet chemical etchant system is introduced and its use to reveal the back contact is described.

Introduction

The IMM Solar Cell [1] is grown inverted relative to more conventional multijunction devices. Therefore the top cell (GaInP), is grown first, lattice matched to the substrate, followed by the middle cell that is either GaAs or minimally mismatched GaInAs. The bottom (most highly lattice mismatched) cell is grown last. This direction of growth helps prevent threading dislocations from degrading the higher band gap cells where most of the power is generated. The inverted device structure and the processed device are shown schematically in figure 1. [Note that none of the figures are to scale.]

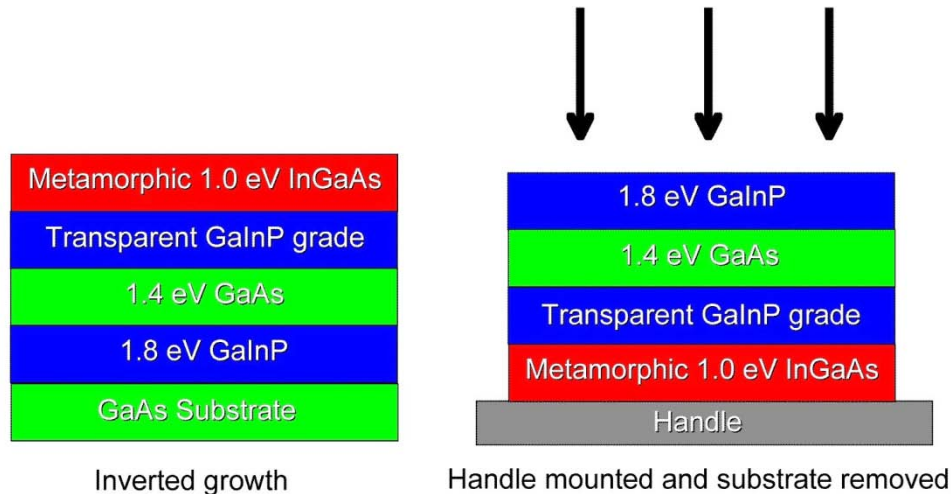


Figure 1: The Inverted Metamorphic Solar Cell Concept

General Process and Product Information

- Photoresist used for this process is **Shipley 1818**. Spin @ 4000rpm for 30 sec. to get $\sim 1.8\mu\text{m}$ thick. The **softbake** step for this photoresist is carried out on a hotplate at 100°C for 5 minutes.
- Exposure dose is $\sim 210\text{mJ}/\text{cm}^2$ (30 sec @ $7\text{mW}/\text{cm}^2$).
- Develop in **MF-319** for ~ 1 min. The pattern should appear after ~ 30 sec. Rinse in DI water and blow dry with nitrogen.
- A **hardbake**, of $100\text{-}110^\circ\text{C}$ for 10 min., can be done before etching to improve the integrity of the photoresist. Do not exceed 110°C or the 1818 will be difficult to remove. The hardbake can be done on a hot plate or in an oven.
- **Tra-bond 931-1 Low viscosity Epoxy**, from Henkel, is used to bond to the secondary substrate. This product is refrigerated. Allow the epoxy to come to room temp before it is mixed. Once mixed and before opening let rest for ~ 1 hr to allow bubbles to settle out and for the viscosity to increase. Avoid bubbles, in the epoxy, when making the bond. Make several test bonds between slides to see how the epoxy flows and how to eliminate bubbles.
- Plating solution is Auroval AU24 Gold cyanide solution @ 60°C but any gold plating solution should work.

- Metal deposition is performed by electroplating Au at a rate of $5\text{mA}/\text{cm}^2$.
- Selective etchants for III-As and III-P layers.
 - Arsenides: 3:4:1 $\text{H}_3\text{PO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$, $\sim 5\mu\text{m}/\text{min}$
or 2:1:10 $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O} \sim 1\mu\text{m}/\text{min}$.
 - Phosphides: Concentrated HCl, $\sim 6\mu\text{m}/\text{min}$
or 4:1 HCl: H_3PO_4
 - GaAs substrate removal: 1:1 $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2$, $\sim 5\text{-}10\mu\text{m}/\text{min}$
For best results use $\sim 15\text{ml}:17\text{ml}$ for a 4 cm^2 sample under white light.

Processing Instructions: Read completely before beginning process.

I. Back contact deposition

1. Paint 1818 photoresist on back of the GaAs substrate to maintain a Au free surface for the substrate removal etch. Paint in one direction to avoid causing bubbles.
2. Bake in oven for 10 min. at 110°C . Cool to room temperature.
3. Dip in 5% HCl for 1 min. rinse in DI H_2O (oxide removal step) and blow dry with nitrogen.
4. Deposit $\sim 1\mu\text{m}$ of Au on the GaInAs back contact layer. Plate at $2.5\text{ mA}/\text{cm}^2$ for 2 min. then ramp up to $\sim 5\text{mA}/\text{cm}^2$ and plate for 8min. Figure 2 shows the device at the end of this step.
5. Remove photoresist with Acetone, rinse in IPA and blow dry with nitrogen.

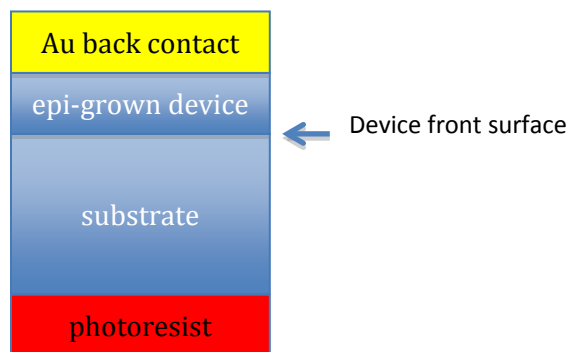


Figure 2: Device at end of step I.1.

II. Mounting to secondary handle and GaAs substrate removal

1. Pour a small drop of low viscosity epoxy (Tra-Bond 931-1 Bipax) in the center of handle (typically Si wafer or glass slide). Be careful not to use too much epoxy (a small drop is fine) or the epoxy will wick up over the sides and top of the sample. This will cause a problem when performing the substrate removal and when doing the contact photolithography.
2. Place sample onto epoxy (Au side down). Figure 3 shows the device at the end of this step.
3. Place a small weight, $\sim 30\text{gms}$. in the center of the sample and let sit for 20 min. at 125°C . Be sure that the sample does not slide around on top of the secondary substrate and that the weight does not stick to the sample. If epoxy creeps on top of the GaAs substrate try

to remove it before starting the etch. Epoxy on this surface will cause highly non-uniform etching of the substrate.

4. Etch off GaAs substrate with 1:1 $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2$. This reaction is slightly exothermic depending on the GaAs surface area exposed to the etchant. For the best result use ~15ml:17ml for a 2cm x 2cm sample. Substrate removal is best under white light. Place the sample vertically in the etchant and rotate every 10 min. The sample surface will repeatedly oxidize and flake off. The oxidized film will pool at the bottom of the beaker. Good success has been achieved by removing the very first “orange-looking” oxidized layer with a q-tip then letting the other layers flake off on their own. Etch usually takes 30-60 minutes. The GaInP stop-etch layer should look shiny. Rinse in DI water and blow dry with nitrogen. Figure 4 shows the device at the end of this step.
5. Peel the excess epoxy from the edges of the sample with a razor blade so that it does not rise above the new surface of the sample. This is necessary to facilitate contact lithography.

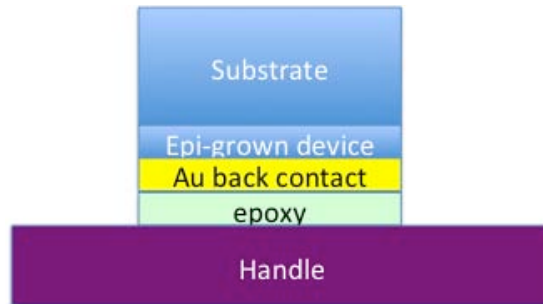


Figure 3: Device at end of step II.2.

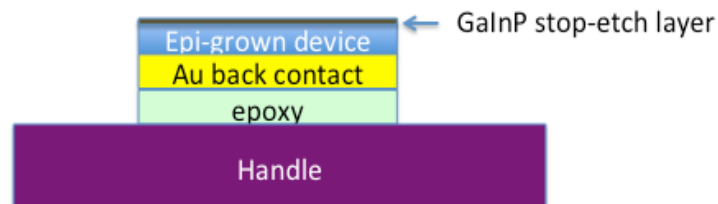


Figure 4: Device at end of step II.5.

III. Front contact deposition

1. Remove GaInP etch stop layer with concentrated HCl.
2. Spin 1818 photoresist onto the front (GaInAs contact layer) surface and softbake on a hotplate at 100°C for 5 minutes.
3. Expose front contact pattern 30 sec @ $7\text{mW}/\text{cm}^2$ ($\sim 210\text{mJ}/\text{cm}^2$) and develop (1min.)
4. Inspect the sample surface. If there are any flaws around the perimeter, fill them in (paint brush) with 1818 so that there is no undercutting at the sample edge during the isolation etches. If there is a problem with the pattern, rinse in acetone, IPA, blow dry with nitrogen and repeat step 2.

5. Remove a small corner of photoresist, with acetone on a q-tip, to facilitate contact for electroplating. Paint photoresist on the handle, if conductive, and backside (anywhere Au should not plate) and bake in the oven at 110°C for 10 min. Paint in one direction to avoid causing bubbles in the photoresist.
6. Dip sample in 5% HCl for 30 sec., rinse in DI water and blow off with N₂ immediately prior to electroplating.
7. Deposit 1 μm of Au. Figure 5 shows the device at the end of this step. Rinse in Di water and blow dry with nitrogen.
8. Remove photoresist with Acetone, rinse in IPA and blow dry with nitrogen.

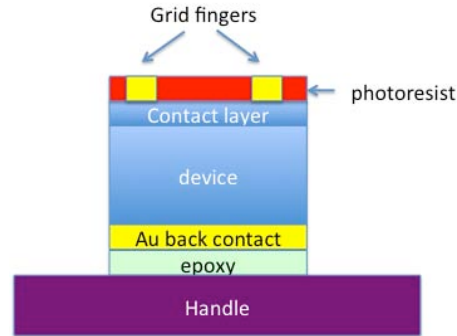


Figure 5: Device at end of step III.7.

IV. Cell isolation

1. Spin photoresist and softbake.
2. Expose with mesa isolation mask (~210mJ/cm²) and develop (1min.)
3. A hardbake can be used to help the photoresist hold up to the multiple etches. 100-110°C for 10 min. on hotplate or in an oven.
4. Etch through the phosphide and arsenide layers sequentially with HCl and 3:4:1 etchants until the Au back contact is exposed, with a DI H₂O rinse and N₂ blow-off in between etches. Make sure that there is no water on the sample before etching in HCl (otherwise etch will be ineffective). A short bake at 100°C on the hotplate (~ 1 min or so) prior to etching can be used to ensure no water is present. Going back and forth between the etchants can degrade the photoresist. If this happens stop etching and re-pattern for the mesa isolation.
5. Remove photoresist with Acetone, rinse with IPA and blow off with N₂.
6. Etch away the GaAs front contact layer using 2:1:10 NH₄OH:H₂O₂:H₂O to minimize damage to the aluminum bearing window layer. Figure 6 shows the device at the end of this step. Minimize the etch time of this step to prevent undercutting of the grid fingers. Transmission line measurements (TLM) can be taken before this step to characterize the gold/GaAs contact resistance.

Notes: Processing problems in this structure normally manifest in the isolation step. It is a complicated structure with many alternating layers that uses selective wet chemical etchants. Care must be taken to be sure that you are completely through each layer before proceeding to the next layer. Getting out of sequence with the etchants will usually lead to a poor result. It is a good practice to make a diagram of the structure and check off each layer as it is etched through. Etching GaAs and GaInAs can be done with

both the $\text{H}_3\text{PO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ etch or the $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2$ etch but the contact layer should never be removed with the phosphoric etch because it causes damage to the aluminum bearing window layer resulting in a degradation of the open circuit voltage of the device. GaInP can be etched with either concentrated HCl or a mixture of HCl and H_3PO_4 . Various ratios may be used. We have found 4 parts HCl to 1 part H_3PO_4 to be useful when pure HCl is problematic. Finally, the selective etchants depend on abrupt interfaces and occasionally structures are grown where there is inadvertent mixing at the interface between two alloys resulting in thin layers of indeterminate composition. In these cases a non-selective etchant may be resorted to such as $\text{HCl}:\text{KIO}_3$ although we have had mixed success with this.

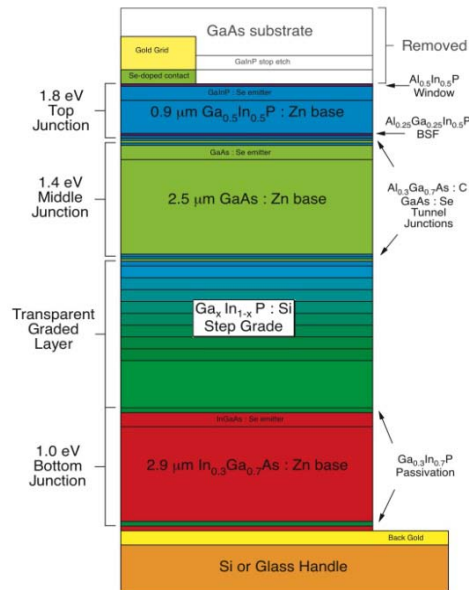


Figure 6: Cross-sectional schematic of completed IMM cell.

References

[1] “40.8% efficient inverted triple-junction solar cell with two independently metamorphic junctions,” J. F. Geisz, D. J. Friedman, et al., *Appl. Phys. Lett* 93, p. 123505, Sept. 2008.