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High rate epitaxial lift-off of InGaP films from GaAs substrates

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Centimeter sized, crack-free single crystal InGaP films of 1 μm thickness were released from GaAs substrates by a weight-induced epitaxial lift-off process. At room temperature, the lateral etch rate of the process as a function of the applied \( \text{Al}_{0.85} \text{Ga}_{0.15} \text{As} \) release layer thickness was found to have a maximum of 3 mm/h at 3 nm. Using 5-nm-thick AlAs release layers, the etch rate increased exponentially with temperature up to 11.2 mm/h at 80 °C. Correlation of the experimental data with the established theoretical description of the process indicate that the model is qualitatively correct but fails to predict the etch rates quantitatively by orders of magnitude. © 2000 American Institute of Physics.

The epitaxial lift-off (ELO) technique in which a III/V device structure is separated from its GaAs substrate using selective wet etching of a thin \( \text{Al}_{x} \text{Ga}_{1-x} \text{As} \) \((x > 0.6)\) release layer, has a large potential for optoelectronic applications. The technique results in a significant cost reduction of III/V devices since theGaAs substrate can be reused after the lift-off process. This is of particular importance for intrinsically large area devices like high efficiency III/V solar cells and the integration of high quality optoelectronic III/V structures on silicon large scale integrated circuits. 5, 6

In 1978 Konagai et al., 7 described the separation of devices from a GaAs substrate using the extreme selectivity of HF acid for AlGaAs with a high Al fraction. A wax layer was applied to support the circa 30-μm-thick fragile films during the process. Yablonovitch et al., 1 noted that the tension induced by the wax caused thinner films, of micrometer thickness, to curl up with a radius of curvature \( R \) as they became undercut. This was concluded to be beneficial for removal of the etch products, leading to an increased lateral etch rate \( V_e \) of the AlAs release layer. By assuming that three moles of \( \text{H}_2 \) gas are produced for every mole of AlAs and that the ability to diffuse away the dissolved hydrogen, which has a low solubility limits the etch rate during the ELO process, they derived an expression for \( V_e \):  

\[
V_e = \frac{1}{\pi \sqrt{Rh/2}} \frac{Dn}{3N},
\]

where \( n \) and \( N \) are the molar concentrations of dissolved \( \text{H}_2 \) and AlAs, respectively, \( D \) the diffusion coefficient of \( \text{H}_2 \) in the solution and \( h \) the thickness of the release layer which generally is 10 nm. 2-6 Based on Eq. (1) Maeda et al., 5 argued that \( V_e \) increases exponentially with temperature like \( D \):  

\[
D = D_0 e^{-E_a/kT},
\]

where \( D_0 \) is the diffusion coefficient at infinite temperature, \( E_a \) is the activation energy, and \( k \) is the Boltzmann constant. Both relations (1) and (2) hold irrespectively of the III/V device that is to be separated from the substrate, provided that the gap between them is opened with a certain curvature \( R \) and out diffusion of \( \text{H}_2 \) is limiting the etch rate.

In the present work the lateral etch rate of the release layers as a function of their thickness and the temperature applied during the ELO process is determined experimentally and compared with theory. For this purpose the application of the ELO method for InGaP layers is examined instead of the generally used \( \text{Al}_{x} \text{Ga}_{1-x} \text{As} \) \((x \leq 0.4)\) based devices. 1-8 Simultaneous etching of InGaP and GaAs layers in a 10% HF solution in water performed in our laboratory showed that InGaP etches about two times faster than GaAs. This difference between InGaP and GaAs is insignificant since the etch rate for GaAs is about \( 10^7 \) smaller than for \( \text{Al}_{x} \text{Ga}_{1-x} \text{As} \). 9 Therefore it is possible to separate thin-film InGaP layers from the GaAs substrate by the use of an Al(Ga)As release layer. The thickness of the released InGaP layers was 1 μm in all experiments and either \( \text{Al}_{0.85} \text{Ga}_{0.15} \text{As} \) or AlAs release layers were used. These III/V structures were grown on 2-in.-diam (100) GaAs wafers by low pressure metal organic vapor phase epitaxy.

A weight-induced ELO (WI-ELO) procedure able to free large area thin films has been developed in our laboratory. The procedure which has been described in detail in previous work 2,3 utilizes a copper support layer and a HF resistant plastic foil mounted with black wax on top of the InGaP structures. The samples are connected to supports at the lid of a HF resistant container and a weight is fitted in the excess foil at one side of the sample (see Fig. 1). One droplet of 10% HF solution, positioned on the plastic foil against the edge of the sample at the side of the weight, is sufficient to perform the ELO process under conditions usually applied. Elevated temperatures in the range between 50 and 80 °C at the position of the samples were obtained by the application of a HF resistant rubber heater element at the bottom of the container. Using this approach, crack-free InGaP films could be obtained with a size up to \( 34 \times 32 \text{ mm}^2 \), which is the entire 2 in. wafer minus cleavage losses. For the other experiments the wafers were cleft in pieces of \( 15 \times 15 \text{ mm}^2 \) and three identical samples were placed in the container simultaneously to determine the reproducibility of the process. \( V_e \) is
given by averaging the lateral etch rates over these samples while a spread in etch rate as large as 30% between the fastest and slowest sample released was observed under all conditions examined.

\[ V_e = \frac{1}{\sqrt{V/h}} \]

where \( h \) is the Al\(_{0.85}\)Ga\(_{0.15}\)As release layer thickness. The results reveal a linear relation between \( h^{-1/2} \) and \( V_e \) for \( h \) in the range from 3 to 40 nm. Samples with thinner release layers did not show any under etching while most samples with \( h > 40 \) nm revealed only partial under etching.

Based on these results a 5 nm release layer thickness was chosen as a standard for the experiments at elevated temperatures and the WI-ELO container was modified to facilitate access with a pipette in order to apply a new droplet of HF whenever the previous would be nearly evaporated. In practice it turned out difficult to refresh the HF droplet during the experiments and in several occasions the droplet adhered not only to the front edge but also to the side rims of the sample. Since such a sample is simultaneously etched from more than one side, this results in a significant faster release of the InGaP layer from its substrate. On one such occasion, a 15 \( \times \) 15 mm\(^2\) film processed at 80 °C was released within less than an hour. For the final analysis, however, the results from these incidents were rejected and the experiments (in three-fold) were repeated to obtain sufficient data points to determine the average lateral etch rate of the here applied AlAs release layers as a function of temperature (see Fig. 3). The results confirm the predicted exponential behavior with temperature following from Eq. (2) and an activation energy, \( E_a = 0.22 \) eV is deduced from the best linear fit through the data points in Fig. 3. Note that extrapolation of this linear relation also agrees well with the etch rate of a 5 nm Al\(_{0.85}\)Ga\(_{0.15}\)As layer at room temperature as deduced from Fig. 2.

As indicated by Figs. 2 and 3, both series of experiments show qualitative agreement with theory. Quantitative agreement is verified by replacement of \( n \) by \( n_{\text{max}} \) which is the solubility of H\(_2\) in Eq. (1) and substitution of the constants by the appropriate values. Generally \( R \) is in the order of 5 cm and \( h \) was about 5 nm in most of the here described experiments. At room temperature \( n_{\text{max}} / N \) and \( D \) were determined to be \( \sim 2 \times 10^{-5} \) and \( \sim 5 \times 10^{-5} \) cm\(^2\)/s, respectively, so that a maximum etch rate is derived of about 3 \( \mu \)m/h. This value is several orders of magnitude less than the 3 mm/h experimentally found in the present work and the recently reported values in literature (see Table I). Consequently, H\(_2\) gas cannot be a major reaction product if it is assumed that its transport from the etch front is correctly described by diffusion with a constant \( D \) as stated above. Although etching of AlGaAs in HF has been reported to be a reaction-rate limited process, the value of \( E_a = 0.22 \) eV as obtained in the present work is a strong indication that the process is diffusion rate limited as was also assumed by Yablonovitch et al. in order to derive Eq. (1). Based on the qualitative agreement
but quantitative discrepancy between the here determined results and established theory, we propose that $V_e$ is limited by out diffusion of a reaction product different from $\text{H}_2$, e.g., a fluorine ligand with Al or As.

A high $V_e$ is considered essential for industrial applications.\textsuperscript{5,6} Therefore, recently $V_e$ as obtained by different approaches of the ELO method has been elaborated in literature (see Table I). From Table I it becomes clear that the WI-ELO technique at elevated temperatures has large potential provided that the released thin-film structures are of sufficient quality. In this respect it should be mentioned that, analogue to our previously reported GaAs thin films,\textsuperscript{2} none of the InGaP films reveal cracks. Hence, it was also possible to release and process several square centimeter sized InGaP thin-film structures to solar cells. The cell design was adapted from the structure reported by Takamoto et al.\textsuperscript{12} using a base thickness of 0.95 $\mu$m and a back surface field doping level of $7 \times 10^{17}$ cm$^{-3}$. Under standard solar illumination (AM1.5) we generally obtain efficiencies ($\eta$) between 15% and 16% for such cells on GaAs substrates while a maximum of $\eta=18.5\%$ has been reported in literature.\textsuperscript{12}

Processing of thin-film InGaP cells took place by the so-called reversed sequence which is described in detail in previous work of our group on thin-film GaAs cells.\textsuperscript{2,3} The $J/V$ curve of the best cell obtained is characterized by a short circuit current density $J_{sc}=11.0$ mA/cm$^2$, an open circuit voltage $V_{oc}=1.32$ V, and a fill factor $FF=0.79$ at a maximum power point of 9.97 mA/cm$^2$ and 1.15 V. The resulting AM1.5 efficiency of 11.5% for this cell can be considered fair in comparison with the performance of its counterparts on a GaAs substrate for which we typically obtain $\eta=15.5\%$ ($J_{sc}=14.0$ mA/cm$^2$, $V_{oc}=1.35$ V, and $FF=0.82$).

The lower efficiency of the thin-film cells is probably a result of the additional difficulties encountered during handling and contacting these fragile structures.

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\begin{table}
\caption{Overview of applied curvature inducing mechanisms, typical process conditions, and resulting maximal lateral etch rates. RT stands for room temperature, S10 indicates addition of a surfactant and antifoaming agent to the 10% HF etch solution, and $p$ represents the pressure above the solution.}
\label{tab:1}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Curvature & $h$ [nm] & $T$ [°C] & Other conditions & $V_e$ [mm/h] & Reference \\
\hline
wax & 2–100 & RT & standard configuration & 0.3 & 1, 8 \\
\hline
wax & 50 & RT & 49% HF vapor phase & 0.125 & 8 \\
\hline
screw & 10 & 40 & S10 & $-1$ & 5 \\
\hline
weight & 10 & 50 & S10, $p=5$ atm. & $-2$ & 6 \\
\hline
weight & 3 & RT & & 3.0 & present work \\
\hline
weight & 5 & 80 & & 11.2 & present work \\
\hline
\end{tabular}
\end{table}