

Planarizing Spalled GaAs(100) Surfaces by MOVPE Growth

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ABSTRACT: III-V photovoltaic devices have demonstrated exceptional performance across various applications, with controlled crystal fracturing, known as controlled spalling, emerging as a promising method to reduce costs by enabling substrate reuse. Spalling GaAs(100) substrates, a commonly used substrate in III-V photovoltaics, results in faceted ridges that must be planarized to grow high-quality photovoltaic devices. Here we demonstrate that a GaAs(100) wafer offcut towards $[0\bar{1}1]$ and spalled towards $[011]$ can be efficiently planarized by growing C:GaAs by metal-organic vapor phase epitaxy (MOVPE) on the surface, with up to 95% of the nominally deposited material used to fill the valleys between ridges. We find that reducing the offcut to 2° enhances the planarizing capability of C:GaAs. A surface morphology model indicates that the density of surface dangling bonds significantly influences the growth evolution of undoped GaAs surfaces. In contrast, the model suggests that the effectiveness of C:GaAs as a smoothing layer stems from modifying the atomic surface structure and, consequently, the associated sticking coefficients of the facets, which can alter the evolution of surface morphology. Our findings provide guidelines for the epitaxial planarization of semiconductor surfaces and improve the understanding of MOVPE growth on non-planar surfaces.

KEYWORDS: MOVPE, MOCVD, substrate reuse, spalling, III-V, GaAs, Carbon tetrachloride, surface planarization, patterned substrate

1. INTRODUCTION

III-V photovoltaics have the highest optical-to-electrical conversion efficiency of any material class, making them an attractive option for applications such as solar photovoltaics,^{1,2} waste-heat recovery³, thermal energy grid storage,^{4,5} and power-by-light.⁶ III-V photovoltaics dominate space deployments⁷ but require cost reductions to penetrate terrestrial markets.⁸ Substrate reuse has an enormous potential to reduce III-V photovoltaic costs because substrates account for about a quarter of the cost of high-efficiency solar cells.⁸ High-quality substrates are required for device growth¹ but are not generally part of the final device structure, making substrate reuse a cost-saving possibility.

Controlled spalling has the greatest potential for photovoltaic substrate reuse (see Figure 1(a-d) for the reuse process) among the methods proposed so far,⁹ because of its high-speed throughput, low capital expenses, minimal chemical hazards, and negligible impact on photovoltaic performance.¹⁰ Controlled spalling consists of mechanically fracturing off the epilayers from the substrate with the help of a stressor layer to control the fracture depth (Figure 1(a)).⁹ Ideally, the spalled surfaces of GaAs(100), a common substrate for photovoltaic devices, would be smooth to facilitate the growth of the next photovoltaic devices.¹ Instead, the

spalled surfaces consist of a periodic array of ridges with facets oriented on or near natural cleavage directions.⁹ These ridges form around the depth directed by the applied stress field as these crystal facets have lower surface energy than the (100) facet. To grow high-quality photovoltaics, the surface needs to be planarized to avoid problems such as parasitic shunts as demonstrated in several references.^{1,11,12} This could be done *ex situ* with chemical-mechanical polishing but that proves costly,⁹ or by wet chemical etching but there has yet to be a solution that fully planarizes the surface.^{11,13} Also, both tend to exacerbate substrate thinning. An alternative approach we investigate here is *in situ* surface smoothing by growing specialized III-V epilayers before cell-layer growth. This method can replenish spalled substrate material but should be done with minimal material and growth times to minimize costs.⁸

There have been promising results for *in situ* smoothing of GaAs surfaces.^{1,14-16} Braun et al.¹⁵ planarized 6 μm tall faceted ridges from a GaAs(100) wafer, exfoliated by controlled spalling, by depositing undoped GaAs via hydride vapor phase epitaxy. Although hydride vapor phase epitaxy promises cost reductions for solar photovoltaic growth, most commercial III-V photovoltaics are grown by metal-organic vapor phase epitaxy (MOVPE). Thus, we require

a MOVPE planarization solution to achieve substrate reuse in the short term. Schulte et al.¹ grew 2 μm of Zn:GaInP by MOVPE to partially planarize an acoustically spalled GaAs substrate with initial ridge heights of less than 1 μm . However, growing ternary materials on a patterned surface can spatially vary the composition, causing lattice mismatching¹⁷⁻¹⁹ (see Supporting Information for an example). Kim et al.¹⁴ explored some growth conditions for planarizing 1.5 μm deep valleys, generated by patterned etching, with C:GaAs grown by MOVPE. McMahon et al.¹⁶ planarized 5+ μm tall faceted ridges from a GaAs(100) wafer, exfoliated by controlled spalling, using C:GaAs and Si:GaAs grown by MOVPE and demonstrated that the choice of growth material, surface dopant, along with the offcut and spall directions, have a large impact on surface planarization. Building upon this preliminary work, we find the wafer offcut angle is also crucial for surface planarization.

In this paper, we optimize the planarization process of 5+ μm tall ridges using C:GaAs by MOVPE improving

material use such that the amount of growth to achieve planarization is within 5% of the theoretical minimum, given the growth rate and initial surface geometry. We study the growth evolution for varying carbon gas flow rates and GaAs(100) wafer offcuts and describe the main smoothing mechanisms involved.

2. EXPERIMENTAL SECTION

Standard single-junction GaAs solar cells were grown on epi-ready 2" (100)GaAs wafers with 6°A, 6°B, 4°B, and 2°B offcuts. These substrates were spalled towards [011] forming A-faceted ridges, defined here as an A spall, and then growth conditions were varied to determine their impact on planarizing the spalled surface. The A spalls formed ridges that ran parallel to the (111)A "Ga-terminated" atomic steps from an A offcut as depicted in Figure 1(e,f). For the spalling conditions used in this study, these spalls formed approximately 5 μm tall {h11}A faceted ridges. When a B offcut wafer was A spalled, the "As terminated" (111)B atomic steps from the offcut ran perpendicular

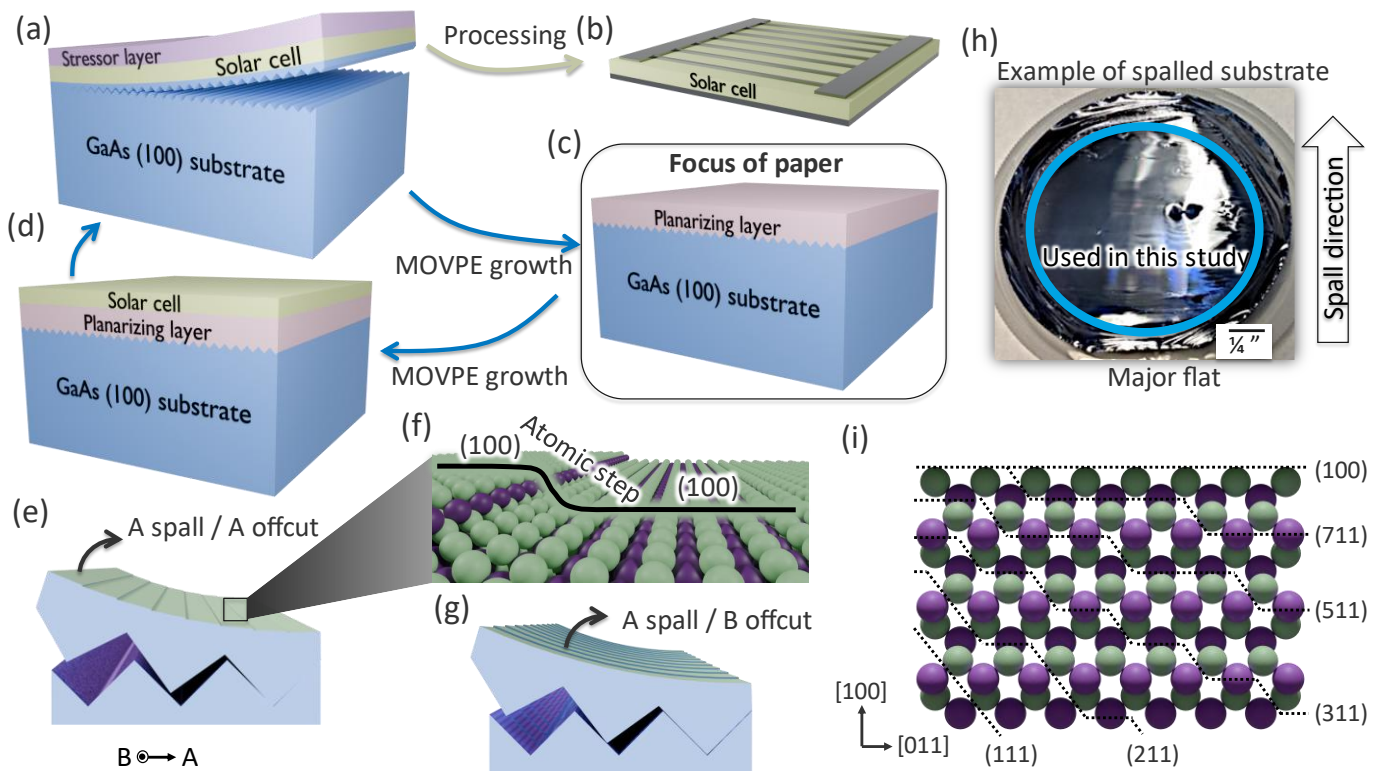


Figure 1. GaAs(100) substrate reuse process via controlled spalling. (a) Schematic diagram of the controlled spalling technique with the crack propagating near the GaAs (100) substrate surface causing a faceted surface. (b) The solar cell can be processed into devices. The spalled substrate can be reused by first (c) planarizing the surface, then (d) growing another high-quality solar cell and (a) re-spalling. (e) Schematic diagram of an A spall on an A offcut wafer. The lines on the light green surface represent (111)A atomic steps between two (100) terraces, as depicted in (f), with the purple spheres representing Ga atoms. The spalled purple surface is a facet comprising dense atomic steps. (g) Schematic diagram of an A spall on a B offcut wafer with atomic steps perpendicular to the ones in (e). These atomic steps can be represented by (f) but with the purple atoms being As. (h) Top view photograph of a spalled 2" GaAs(100) wafer, spalled starting at the major flat. (i) Illustration of the atomic arrangements between the (100) and (111) surfaces. For A-type facets, purple and green spheres in (i) represent Ga and As atoms, respectively, and vice-versa for B-type facets.

to the (111)A facets forming the sides of the ridges, as shown in Figure 1(g).

All spalled wafers were processed using the controlled spalling technique with a stressor layer made of Ni alloyed with P and a roller to peel off the top surface,⁹ as illustrated in Figure 1(a). The stressor layer was deposited by electrodeposition in a bath composed of 0.6 M nickel(II) chloride hexahydrate and 5 mM phosphoric acid. The deposition was done at a fixed current density of 15.6 mA/cm² for 18 to 30 minutes to tune the spall depth. After electrodeposition, the wafer was laminated with tape, and an external force was applied to the wafer surface using a linearly actuated motor to initiate and propagate the spalling fracture. Other relevant procedures followed that of ref.⁹ A top-view photograph of a GaAs(100) offcut wafer, exfoliated by controlled spalling is shown in Figure 1(h). The interior part of the spalled wafer, demarcated by the thick blue line, was used to investigate planarizing growth, ensuring a consistent baseline for each experiment. Most samples were loaded directly into the reactor without preparation, except for one sample etched with H₂SO₄:H₂O:H₂O₂ at a bottle strength volumetric ratio of 8:1:1 for 13.5 minutes at 30°C which followed the procedure of ref.¹³ to reduce the ridge height.

1. Growth Details.

III-V epi-layers were grown in a custom-built atmospheric-pressure MOVPE reactor, using trimethylgallium, triethylgallium, trimethylaluminum, trimethylindium, AsH₃, PH₃, CCl₄, Si₂H₆, H₂Se, and diethylzinc as sources. The CCl₄ was mixed with purified hydrogen in a dilution line. Although CBr₄ could have allowed for faster planarization,²⁰ CCl₄ was used as it was already installed on our reactor. Each planarization growth included spalled and as-received wafer samples with identical offcuts and were cleaved to be no less than 1 cm × 1 cm. The planarizing growth consisted of an initial 0.1 μm undoped GaAs layer with a subsequent 10-layer superlattice composed of 1 μm C:GaAs planarizing layers and 0.2 μm C:Al_{0.43}Ga_{0.57}As marker layers. All stated layer thicknesses correspond to the nominal values expected for undoped GaAs grown on a planar GaAs(100) offcut wafer. Cross-sectional scanning electron microscopy images were acquired to characterize the growth evolution with a Hitachi S-4800 operating at 3 kV and a 7 μA beam current. The cross-sections were prepared by cleaving along {110} planes, perpendicular to the spalled ridges.

The CCl₄ gas flow rate was varied from 0.0 to 0.1 sccm. At the highest rate of 0.1 sccm, C:GaAs can be doped at 10¹⁹ cm⁻³ (p-type) in this MOVPE reactor under typical growth conditions. This doping level is

commonly used in tunnel junctions and has not been observed to adversely affect the morphology of subsequent layers. Four recipes were investigated: the recipe from McMahon et al.¹⁶ (M), the best planarizing recipe from Kim et al.²⁰ (K), and two variations (K_{slow} & K_{fast}) around recipe K. Growth parameters for the recipes are provided in Table 1. They include nominal growth rates for the corresponding material grown undoped on a planar GaAs(100) offcut substrate. The AlGaAs layers were grown at a V/III ratio of 80 with CCl₄ flow rates and growth temperatures identical to the GaAs layers.

Table 1. Growth conditions for planarizing epi-layers. *T* is the growth temperature. Recipe M comes from McMahon et al. ¹⁶. Recipe K is the best planarizing recipe extracted from the results given by Kim et al. ²⁰.

Recipe	<i>T</i> (°C)	GaAs growth rate (μm/h)	GaAs V/III	AlGaAs growth rate (μm/h)
M	650	6	17	4
K _{slow}	680	3.5	17	4
K	680	6	60	4
K _{fast}	680	7	60	12

3. RESULTS AND DISCUSSION

1. Impact of CCl₄ Flow Rate on Planarization.

Increasing the CCl₄ gas flow improved the planarization capability of C:GaAs material. Cross-sectional scanning electron microscope images of four A spall/A offcut samples with CCl₄ flow rates varying from 0.0-0.1 sccm are shown in Figure 2. Including CCl₄ gas improved the valley filling rate of the ~5 μm ridges, reducing the nominal growth needed to fill the valley trench from 9 μm (no gas flow) to 4 μm (0.1 sccm). The mechanisms that influenced these growths will be discussed in Section 3.4.

In Figure 2, we identify the observable crystal facets formed after the valley trenches were filled. Facet emergence depends on the surface morphology, with the fastest-growing facets forming at concave areas and the slowest-growing at convex areas during growth.²¹ The (100) crystal plane had the slowest growth rate among the available facets and was further inhibited by CCl₄ or its by-products. At large CCl₄ flow rates, the highest growth rate facets shifted towards shallower facet angles, from (311)A to (711)A (see Figure 1(i) for a cross-sectional illustration of these atomic surfaces). However, the final surface remained non-planar with remnant facets (Figure 2(b)), which are unfavorable for subsequent solar cell growth.¹ These facets can form when one side of a valley trench is taller than the other; once the trench fills, the extra height of the taller side remains as a remnant facet. Subsequent examples will

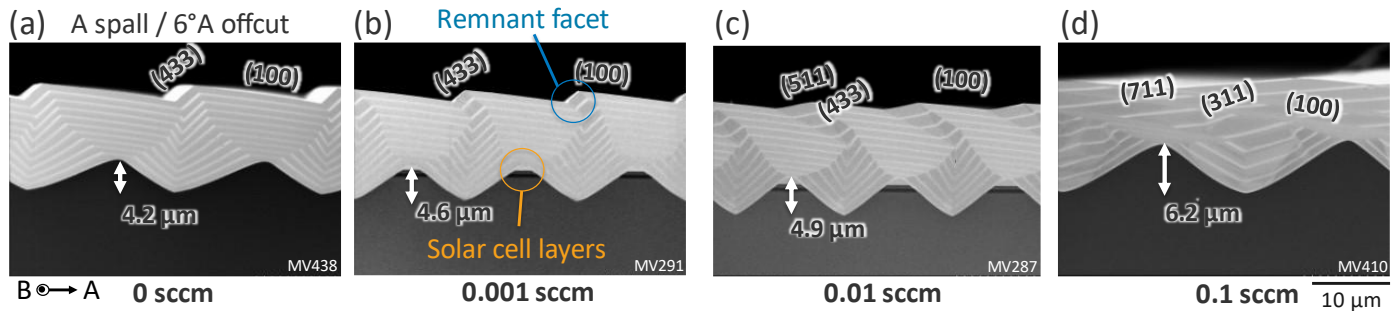


Figure 2. C:GaAs grown on A spall/ 6° A offcut samples. Cross-sectional scanning electron microscope images of spalled substrates with C:GaAs planarizing epi-growth at CCl_4 gas flow rates of (a) 0.0 sccm, (b) 0.001 sccm, (c) 0.01 sccm, and (d) 0.1 sccm. These growths utilize the recipe M. The horizontal epilayers at the ridge peaks in (b,c) are solar cell layers pierced by the spalling process. Note: The spall that gave the samples for (b,c) was a preliminary depth-calibration controlled spall, subsequent spalls did not pierce epilayers as shown in (a,d).

show that these remnant facets can be avoided with an A spall on a B offcut wafer configuration.

The epi-layer stack at the ridge tips in Figure 2(b,c) was not part of our planarization recipe, and their origins are summarized in the figure caption. These epi-stacks should not affect our planarization growth as the initial 0.1 μm undoped GaAs layer provides a constant starting point before growing our planarizing layers.

2. Material Flow Analysis During C:GaAs Epitaxy.

Despite the challenges posed by remnant facets imaged in Figure 2 and illustrated in Figure 3(a), these growths enabled us to evaluate material flow during epitaxy before filling the valley trenches. A consistent material transfer from (100) plateaus to valley regions was observed and is depicted in Figure 3(b). This transfer was evident during at least a portion of each growth cycle, with all instances exhibiting positive valley growth gains relative to conformal growth. We calculated this gain by comparing the measured cross-sectional valley growth area to the nominal cross-sectional growth area, considering the valley width of a planarizing layer as the average between the cladding marker layer corner edges, as shown in Figure 3(c). We calculated the valley growth gain for each planarizing layer up to the layer that filled the valley trench and plotted the results in Figure 3(d). Comparing the four red curves (recipe M) shows that the valley growth gain increases with CCl_4 flow rate.

We find that growth conditions impact the valley growth gain. By comparing the green (recipe K_{slow}) and blue (recipe K) triangles in Figure 3(d), we demonstrate 71%_{rel} higher average valley growth gain for slower growth rates. We also investigated the optimal growth conditions for C:GaAs as suggested by reference¹⁴ (recipe K), which involves a 30°C higher growth temperature and a V/III ratio that is 3.5 times higher than our standard recipe M. Additional research is required to conclusively determine the impact of these

modified growth conditions on planarizing spalled GaAs(100) surfaces.

When employing the highest CCl_4 flow rate of 0.1 sccm, we achieved the maximum valley filling gain, marked by the thick green curve in Figure 3(d), for smaller (100) plateau areas. Here, the entirety of the nominally grown material contributed to filling valleys. However, for larger (100) plateaus, we observed a departure from the maximum valley filling, indicating a finite diffusion length of Ga-adatoms across these plateaus.

The diffusion length of Ga-adatoms on (100) surfaces was found to increase with the CCl_4 flow rate. This diffusion length was quantified by comparing measured and calculated [100] growth as a function of the (100) plateau width. The data are plotted in color in Figure 3(e), along with modeled black/grey background curves calculated assuming diffusion lengths from 1-11 μm . The measured data come from taking the ratio between the [100] growth on (100) plateaus against flat 6° A offcut witness samples. The calculated values assume a simple Ga-adatom diffusion model based on geometrical considerations (see “Adatom diffusion model” section in Supporting Information for model details). The Ga-adatom diffusion length on (100) surfaces increased with carbon flow, ranging from 3 μm to 8 μm for 0.0 to 0.1 sccm CCl_4 flow rates, respectively. These values are about 100 times larger than the Ga-adatom diffusion lengths on crystal facets perpendicular to (111)B during MOVPE growth of undoped GaAs nanowires for growth temperatures less than 470°C .²² However, they are of the same order of magnitude as Ga-adatom diffusion lengths on (100) crystal facets during molecular beam epitaxy of undoped GaAs,^{23,24} ranging over 0.4-8.0 μm depending on the growth conditions and movement direction. Our values may be underestimated as the model does not consider the Ehrlich-Schwoebel barrier,²⁵ which acts as an obstacle

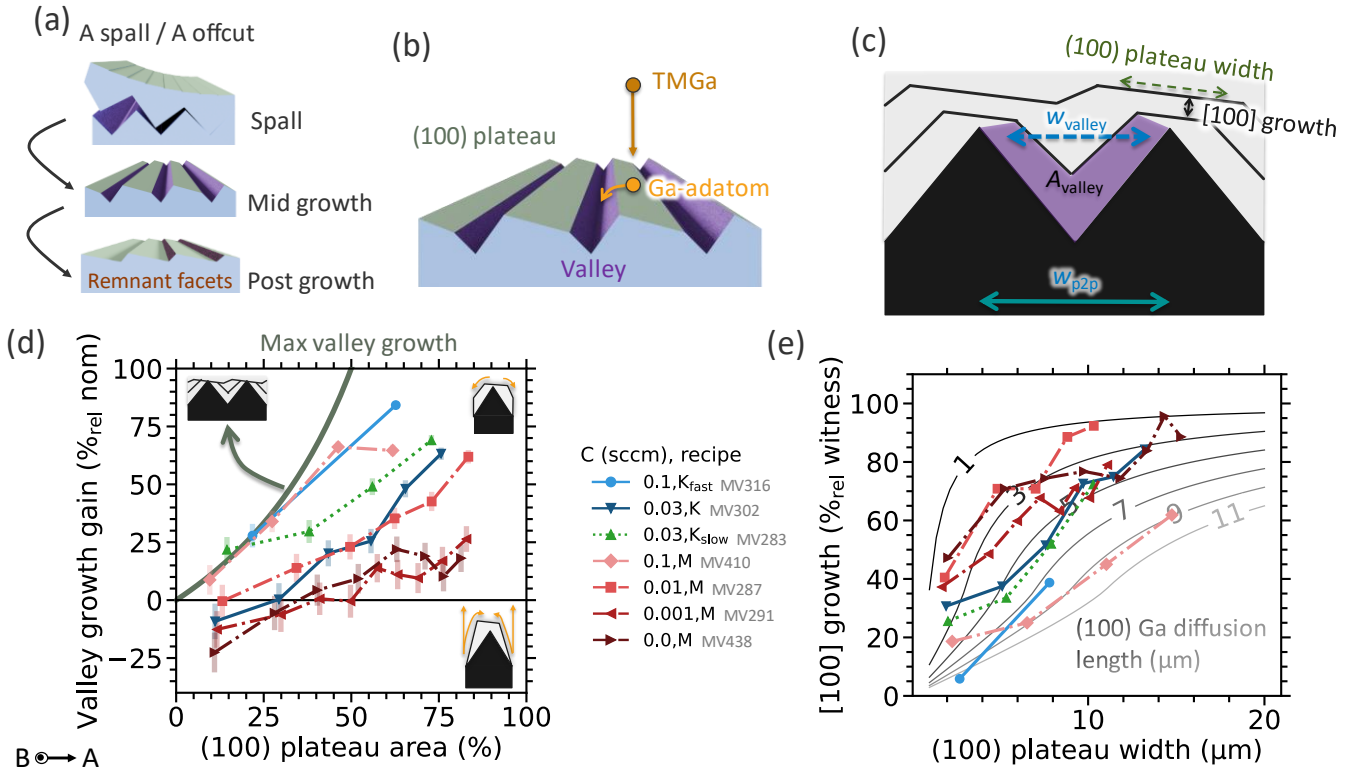


Figure 3. Ga-adatom diffusion on (100) surfaces. (a) Schematic diagram showing the growth evolution of the A spall/A offcut samples with the slowest growing crystal facet not perpendicular to the surface normal, causing remnant facets. (b) Schematic illustration of the growth process with diffusion across the (100) plateaus, starting with TMGa precursors that deposit Ga-adatoms on the (100) surface which then diffuses to the valleys. (c) Schematic diagram of C:GaAs grown on A spall/A offcut samples used to define the axis in (d,e). (d) The gain in valley growth relative to the nominal growth on a flat surface $\{(1 - A_{valley}/[w_{valley} \times \text{Nominal growth}]) \times 100\}$ as a function of the (100) plateau horizontal width relative to the periodic structure width $\{(1 - w_{valley}/w_{p2p}) \times 100\}$. The thick green curve represents the maximum valley growth gain. (e) Plotting measured [100] growth on the (100) plateaus relative to the growth on 6°A offcut witness samples as a function of the (100) plateau width. Comparing to simulated curves with the “Adatom diffusion model” detailed in Supporting Information. The error bars in (d) indicate a 50 nm uncertainty in the position of the layer interfaces. Assuming the same uncertainty, error bars for (e) are approximately $\pm 10\%$ absolute but are not shown, to improve the plot’s clarity.

to adatoms descending an atomic step (hinders adatom movement to the right in Figure 1f).

3. Impact of B Offcut on Planarization.

Unlike A spall/A offcut samples, the A spall/B offcut configuration suppresses remnant facet formation, thereby facilitating surface planarization. This outcome is visible in the scanning electron microscope images shown in Figure 4(a-d). The growth experiments with C:GaAs, conducted at the highest CCl_4 flow rate of 0.1 sccm, demonstrate that smaller B offcuts improve planarization performance. We highlight the effectiveness of the best planarizing growth with the top-view photographs in Figure 4(e), where we compare an as-spalled sample to a planarized sample (same sample as Figure 4(d)) and its corresponding witness sample. In the A spall/B offcut configuration, the two-dimensional surface plateaus that developed at the ridge tops maintained the wafer’s original B offcut orientation, as depicted in Figure 5(a). These plateau

surfaces were composed of (100) terraces interspersed with (111)B atomic steps.

Smaller B offcuts reduce parasitic deposition on the plateaus. Reducing the density of (111)B atomic steps decreases the nominal growth of C:GaAs needed to fill the valley trenches, defined as nominal growth to planarize. The $(100)2^\circ\text{B}$ surface, with nominally threefold fewer (111)B steps than the $(100)6^\circ\text{B}$ surface, required at least two times less nominal growth to fill the valleys for a given ridge height, as illustrated in Figure 5(b). This observation suggests that the (111)B steps have a higher sticking coefficient than the (100) terraces for our growth conditions. Notice that the required growth to planarize samples with 2°B offcuts stays within 30% of the minimum growth to planarize (thick green line).

Incorporating an etching step to partially planarize the spalled surface before the growth phase can reduce the amount of material required to achieve a planar surface by decreasing the initial ridge height. Lowering the initial ridge height reduces the theoretical limit of

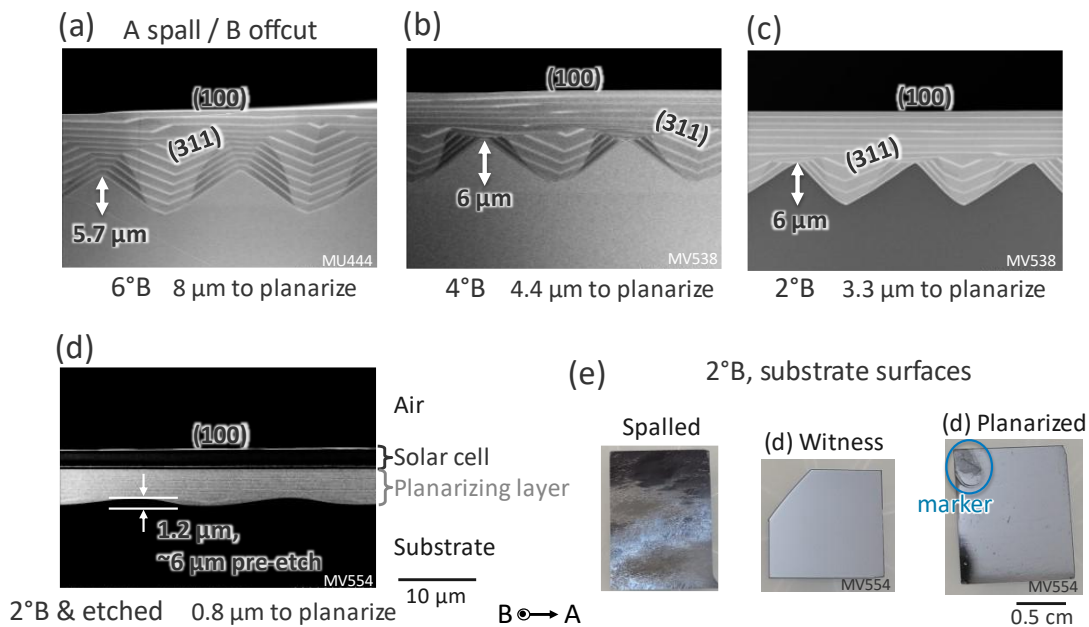


Figure 4. C:GaAs grown on A spall/B offcut substrates. Cross-sectional scanning electron microscope images of spalled substrates with C:GaAs planarizing epi-growth for GaAs substrates offcut from (100) towards (a) 6°B, (b) 4°B, and (c,d) 2°B. (d) Using an etching step before planarizing growth, with halved planarizing layer nominal thicknesses. The dark layers above the planarizing layers in (d) comprise a single-junction GaAs solar cell. (e) Top-view photographs of 2°B wafers in their A spalled state, alongside the planarized sample shown in (d) and its corresponding witness sample. All growths use recipe M and are at a CCl_4 flow rate of 0.1 sccm.

material needed to fill in the valleys, which can be calculated geometrically. For example, Figure 4(c) and Figure 4(d) depict identical growth conditions and sample offcuts, but the sample in Figure 4(d) which included a planarizing etching step required four times less C:GaAs to achieve a planar surface. In addition to requiring less growth material, adding the etching step

reduced the planarization growth time from approximately 33 minutes to 8 minutes.

The initial ridge width influences the quantity of growth required to achieve a planar surface. The material use, defined as the ratio between the minimum and nominal growth needed to planarize a surface with a given initial geometry, as a function of initial ridge width (w) is shown in Figure 5(c) for the 2°B

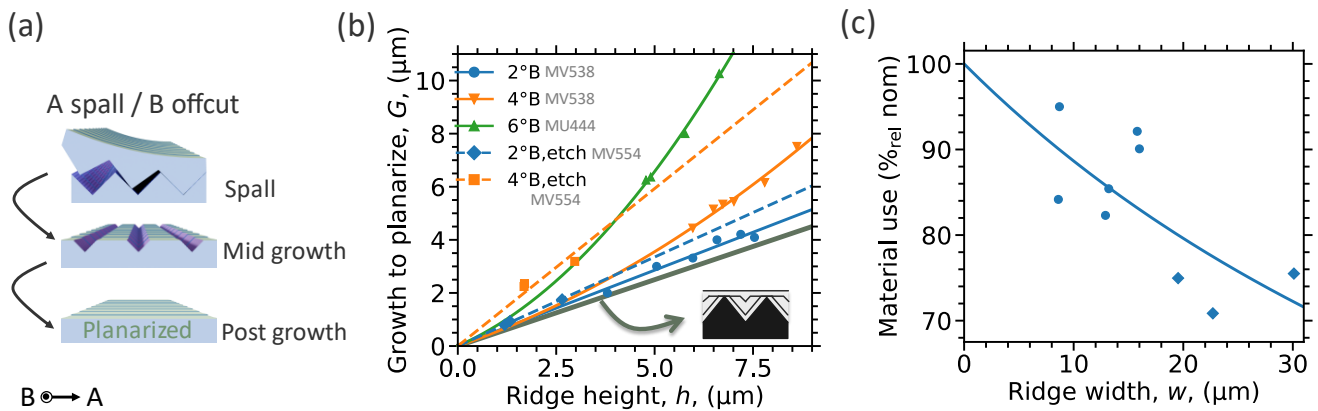


Figure 5. Quantifying C:GaAs planarizing capability on A spall/B offcut samples. (a) Schematic diagram of the growth evolution for A spall/B offcut samples where the slowest growing crystal plane is perpendicular to the surface normal. The lines on the planar surface represent atomic steps. (b) Nominal growth required to planarize the spalled surface for a given ridge height. We acquired data over multiple locations on the samples to get a range of ridge heights. The thick green curve represents the best-case scenario where all nominal material is used to planarize the surface. The other curves are quadratic fits to the data to guide the eye. (c) The material used to planarize, defined as the ratio between the minimum and nominal growth to planarize the surface for a given initial surface geometry $\{(0.5/[G/h]) \times 100\}$, as a function of the ridge width for 2°B etched and unetched samples. The solid curve in (c) is to guide the eye. The data in (b) and (c) were collected at the same locations. All the growths use recipe M with a 0.1 sccm CCl_4 flow rate.

experiments. Up to 95% of the nominal material was used to fill the valleys (highest data point in Figure 5(c)), with the remainder either desorbed or deposited on the plateaus. The curve in Figure 5(c) serves as a visual guide and follows the functional form, $0.5/(0.5 + 0.0064w)$. This equation is based on the physical principle that the minimum growth to planarize an initial triangular surface geometry, is 0.5 (slope of the thick green curve in Figure 5(b)). The actual required growth (denominator) can be represented by the sum of the ideal case (0.5) and a perturbation ($0.0064w$) resulting from the finite diffusion length of Ga adatoms. Using values from this curve, a spalled sample with a ridge width of 30 μm would require 36% more nominal growth to achieve a planar surface compared to a sample with a 10 μm ridge width, assuming identical ridge heights.

4. Modeling Surface Morphology Evolution.

To begin to understand the physical mechanisms that cause our observed growth modes, we simulated the surface morphology evolution during growth with the model from ref.²¹ that considers the facet growth rate (R) and the diffusion length (L), and compared those results to cross-sectional scanning electron microscope images in Figure 6. We used different sets of parameters, R and L , for each simulated surface morphology evolution, ensuring they remained constant within each simulation. The model assumes the time (t) dependent vertical (z) growth is given by:²¹

$$\begin{aligned} \frac{\partial z}{\partial t} &= \sqrt{1 + p^2} R(\phi) \\ &- \frac{\sqrt{1 + p^2} L^2}{2} \left(\frac{\partial^2 R(\phi)}{\partial s^2} - R(0) \frac{d^3 x}{ds^3} \right) \\ ds &= \sqrt{1 + p^2} dx, \quad p = \frac{\partial z}{\partial x} \end{aligned} \quad (1)$$

where x is perpendicular to the wafer's surface normal and ϕ is the angle deviated from the wafer's surface normal (as defined in Figure 6(a)). Although an atomic model combining fluid dynamics with kinetic Monte-Carlo simulations can be more robust,^{25,26} we chose the analytical model from ref.²¹ due to its simplicity, since it only has two free parameters, L and $R(\phi)$. Though it cannot be used to accurately extract physical parameters, the model reproduces surface morphology evolution allowing us to postulate dominating growth mechanisms on the faceted surfaces. The modeled results in Figures 6(d-f) show equally time-spaced snapshots of the surface morphology with the colored curves. Note that the model disregards growth extending into the third dimension (into the page). A detailed description of the model is given in the

Supporting Information; here we summarize the main physical inputs.

Following the approach from reference,²⁷ we assume the facet growth rate (R) at an angle θ from (100) is given by:

$$R(\theta) \propto C_0 D_i(\theta) [1 + C_1 S(\theta) + C_2 W(\theta)] + (1 - C_0) \cos(\phi) \quad (2)$$

where C_j with $j = 0,1,2$ are weighting factors and $D_i(\theta)$ with $i = 0,1$ represents the unreconstructed dangling bond density of As saturated A-facets. However, $D_1(\theta)$ further assumes zero (100) terrace dangling bonds. Additionally, $S(\theta)$ represents a [711]A growth rate spike, while $W(\theta)$ represents a sinusoidal growth rate as a function of θ with maxima at ($n11$)A facets for n -odd. All these functions of θ (excluding $D_0(\theta)$) can serve as proxies for atomic surface reconstructions,^{28,29} impacting facet sticking coefficients. Finally, $\cos(\phi)$ is a proxy for gas- or adatom-phase diffusion anisotropy; gas-phase boundary layers may enhance gas flux at the plateau tops versus the sidewalls, and/or adatoms could preferentially diffuse up the sidewalls.¹⁶ The terms' relation with θ are shown in Figure 6(g) and detailed in the Supporting Information. We determined the average facet growth rates from Figure 6(a-c) following the method described in ref.¹⁵, with the results presented in Figure 6(h). For the undoped growth, the (100) growth rate was averaged across all ten layers shown in Figure 6(a). For C:GaAs growth, the (711)A facet growth rate was measured from Figure 6(b), employing the layers after the valleys were filled. The (100), (211)A, and (311)A facet growth rates were measured from Figure 6(c), using the layers before the valleys were filled.

We find growth for undoped GaAs with recipe M is determined by the surface's unreconstructed dangling bond density and anisotropic Ga diffusion. Qualitatively comparing Figure 6(a) to Figure 6(d), the model matches well with the features observed in the scanning electron microscope cross-section images. Both form (100) plateaus starting at the initial ridge tips and have similar remnant facets. To get this good match, we use the growth rate function shown in Figure 6(h) (dashed line) which assumes the following fitting parameters for Eq. 2: $i=0$, $C_0=0.55$, $C_1=C_2=0$. Based on the values of these fitting parameters, the dangling bond density impacts growth rate by 55% with the remaining attributed to anisotropic diffusion, while surface reconstructions have a negligible impact on growth. We also replicate the measured conformal growth of undoped GaAs on a B-faceted surface from a B spall/A offcut substrate with the model, with results in the Supporting Information, and arrive at a similar

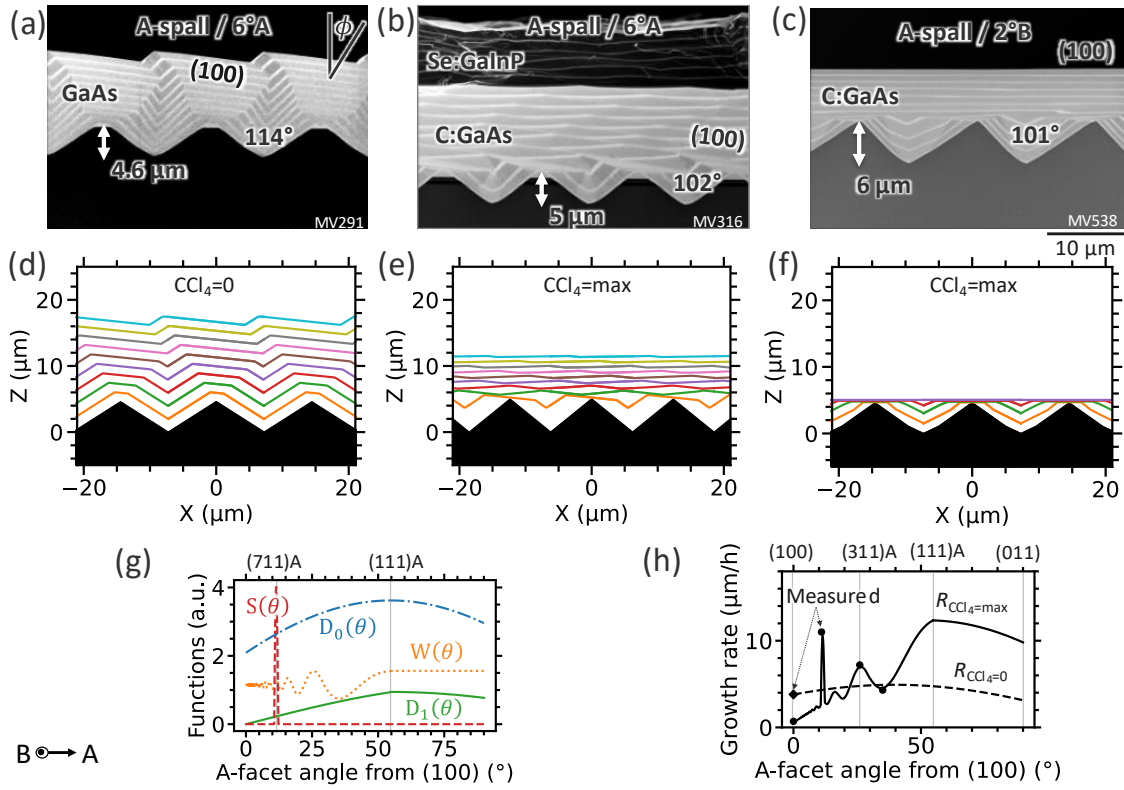


Figure 6. Modeling growth morphology. (a-c) Cross-sectional scanning electron microscope images of planarizing GaAs growth on A spalled wafers with (a) 6°A offcut and no CCl₄ (recipe M), (b) 6°A offcut and 0.1 sccm CCl₄ flow rate (recipe K), and (c) 2°B offcut and 0.1 sccm CCl₄ flow rate (recipe M). (d-f) Modeled growth morphology of the surface for the respective images above their positions. We assumed diffusion lengths (L) of 3 μm for (d) and 8 μm for (e,f), and growth rates (R) according to Eq. 2 with $i = 0$, $C_0 = 0.55$, and $C_1 = C_2 = 0$ for (d) and $i = 1$, $C_0 = 0.95$, $C_1 = 7$, and $C_2 = 0.7$ for (e,f). (g) Functional forms of terms in Eq. 2. (h) Facet growth rate as a function its angle towards [011] relative the (100) facet along the (111)A path, used for the model input parameter (R) for (d) $R_{CCl_4=0}$ and for (e,f) $R_{CCl_4=max}$. Measured growth rates are also included in (h). The darker 6-layer stack grown above the lighter 10-layer stack of C:GaAs in (b) is Se:GaInP with GaAs marker layers.

conclusion. The rising slope versus growth time on the side of the ridge in Figure 6(a), which is not simulated in Figure 6(d), may be attributed to a net adatom flow from the plateaus to the valleys, as indicated in Figure 3(d), combined with a short adatom diffusion length on the ridge's side. This limited diffusion length could result from large facet sticking coefficients and/or Ehrlich-Schwoebel barriers.

We observed that introducing a high flow of CCl₄ during GaAs growth on A-faceted surfaces altered the physical processes dominating growth. The measured growth morphologies are reproduced with the model, as shown in Figure 6(b,e) and Figure 6(c,f), using the growth rate function shown in Figure 6(h) (solid line) which assumes the following fitting parameters for Eq. 2: $i=1$, $C_0=0.95$, $C_1=7$, $C_2=0.7$ for Figure 6(e) and 6(f), respectively. These values suggest that CCl₄ or its by-products may be inducing surface reconstructions which significantly impacts growth. McMahon et al.¹⁶ proposed that C plays a dominant role, noting that Si₂H₆, another group IV element, exhibited similar planarizing capabilities to C. They attributed this dominant role to

the formation of similar surface reconstructions on GaAs(100) facets by both Si and C. However, Kim et al.²⁰ demonstrated poorer planarizing performance with CCl₄ compared to CBr₄ at the same gaseous mole fractions, which could be due to differing surface interactions from Cl compared to Br or a higher C deposition rate with CBr₄. Further research is required to determine the impact of CCl₄ by-products on surface reconstructions.

The surface morphology evolution model works well to simulate growth on structured surfaces with sizes less than the Ga-adatom diffusion length as growth follows the relative probabilities of sticking to the facets. However, when only one facet is available, the growth rate instead follows the probability of adatom desorption. Consequently, after planarizing the A spall/2°B offcut sample (Figure 6(c,f)), the model underestimates growth on the (100)2°B facet due to the change in growth mechanism.

4. CONCLUSIONS

Reusing GaAs(100) substrates via controlled spalling presents a promising approach to reduce III-V photovoltaic costs; however, the spalling process can create faceted ridges that must be planarized to enable the growth of high-quality photovoltaics.

We grew C:GaAs by MOVPE to planarize A-faceted GaAs(100) substrates, achieving up to 95% material utilization relative to nominal deposition for surface planarization by optimizing the wafer offcut. We demonstrated that B offcut wafers produce planar surfaces and that reducing the B offcut enhances planarization performance. Introducing a wet etching step to partially planarize the spalled substrate reduced the planarizing growth time to approximately 8 minutes. This time is negligible compared to the 7.5 hours required for the epitaxial growth of high-efficiency solar cells.³⁰ Additionally, we developed a method to extract adatom diffusion lengths during MOVPE, finding values ranging from 3 to 8 μm for (100) surfaces, depending on the CCl_4 gas flow.

Our modeling efforts provided insights into the growth mechanisms, indicating that optimal planarization is achieved when the sticking coefficient is zero for the crystal facet parallel to the bulk wafer surface while neighboring facets have non-zero coefficients. First-principles calculations, as demonstrated by Batyrev et al.,³¹ could further explain preferential facet growths and the impacts of surface dopants on atomic surface reconstructions. Coupling these calculations with surface morphology evolution models could enhance their predictive capabilities, allowing for a comprehensive investigation of growth conditions that significantly impact planarization.¹⁶

The knowledge gained from this study could guide the planarization efforts of other substrate surfaces via epitaxial growth, potentially expanding beyond GaAs(100) substrates. It could also motivate further study of the atomic structure of crystal surfaces during MOVPE growth, given the strong impact on the growth behavior for non-planar surfaces.

SUPPORTING INFORMATION

Cross-sectional scanning electron microscope images of various growth configurations for planarization not shown in the main article, a detailed description of the adatom diffusion model and the surface morphology evolution model, an expanded derivation of the dangling bond density model to include facets between (111) and (011), and modeling results of the surface morphology evolution of undoped GaAs grown on a B spall / A offcut faceted surface.

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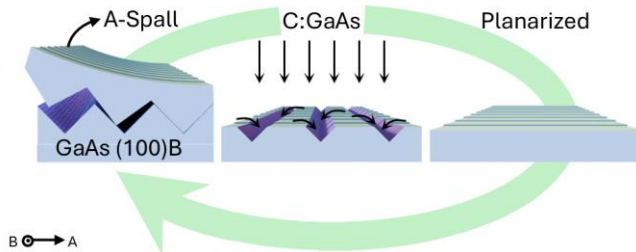
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Planarizing Spalled GaAs(100) Surfaces by MOVPE Growth

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This study offers insights into MOVPE growth on non-planar surfaces and epitaxial planarization techniques, facilitating III-V substrate reuse for cost reductions. Controlled crystal fracturing (spalling), a method of removing the epitaxial structure from GaAs(100) substrates, creates ridges needing planarization. The surface is efficiently planarized by growing C:GaAs via MOVPE on a GaAs(100) substrate offcut towards $[0\bar{1}1]$ and spalled towards $[011]$.