SPALLING FRACTURE BEHAVIOR IN (100) GALLIUM ARSENIDE

by

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ABSTRACT

Record-high conversion efficiencies inherent in III-V solar cells make them ideal for one-sun photovoltaic applications. However, material costs associated with implementation prevent competitive standing with other solar technologies. This dissertation explores controlled exfoliation of III-V single junction photovoltaic devices from (100) GaAs substrates by spalling to enable wafer reuse for material cost reductions. Spalling is a type of fracture that occurs within the substrate of a bilayer under sufficient misfit stress. A spalling crack propagates parallel to the film/substrate interface at a steady-state spalling depth within the substrate. Spalling in (100) GaAs, a semiconductor with anisotropic fracture properties, presents unique challenges. Orientation of the cleavage plane is not parallel to the steady-state spalling depth which results in a faceted fracture surface. A model is developed by modifying Suo and Hutchinson’s spalling mechanics to approximate quantitatively the spalling process parameter window and the thickness of the exfoliated film, i.e. spalling depth, for use with (100) GaAs and other semiconductor materials. Experimental data for faceted (100)-GaAs spalling is shown to be in agreement with this model. A faceted surface leads to undesirable waste material for low cost application to the solar industry. Therefore, methods to mitigate the facet size are explored. Trends in facet size and distribution are linked with both the stressor film deposition parameters and the spalling pull velocity. A spalling fracture is a high energy process where damage to the exfoliated material is a concern. Spalled material quality is assessed directly by dislocation density analysis and indirectly by characterization of electrical performance of high quality spalled photovoltaic devices sensitive to material damage such as dislocation and microcrack occurrence. Controlled application of spalling in (100) GaAs is achieved by exfoliation of a high performance single junction solar cell resulting in 18.2% conversion efficiency without the use of an anti-reflective coating. It is shown that spalling in (100) GaAs is a successful device exfoliation
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CHAPTER 1
INTRODUCTION

Record-high conversion efficiencies inherent in high-quality III-V solar cells make them an ideal choice for one-sun photovoltaic applications.\cite{1}\cite{2} However, high costs of both the epitaxial growth techniques and substrates used for the production of III-Vs will limit expansion into this area unless both costs are significantly lowered.

Traditionally, III-V devices are grown epitaxially by metal-organic vapor phase epitaxy (MOVPE) or molecular beam epitaxy (MBE). These processes are time consuming with low growth rates and involve costly precursors. A less developed technique for III-V epitaxial growth is hydride vapor phase epitaxy (HVPE). HVPE can produce high material quality at much lower costs by utilizing high growth rates of up to 1.5 $\mu$m/min (90 $\mu$m/h), which is 1-2 orders of magnitude higher than traditional growth methods, and elemental metals rather than expensive metal organic precursors. \cite{3}\cite{4}\cite{5}\cite{6}\cite{7}

Because III-V devices are grown epitaxially, it is optimal to use a growth substrate with a lattice parameter and orientation that matches the device layer materials. Gallium arsenide is ideal as a growth substrate with low defect densities. However, other substrate materials such as germanium are utilized due to high costs associated with GaAs, which is further increased for growth of a single junction PV device as opposed to multifunction devices. Substrates are only necessary in the epitaxial growth process and do not contribute to device performance in the field. Exfoliation of the device material after growth can enable subsequent growth and exfoliation cycles on a single wafer, significantly reducing the costs associated with the substrate. The motivation for this dissertation study is to find an exfoliation method that can be used to enable wafer reuse for GaAs, which is one part of a larger study that includes III-V growth by HVPE to lead to low-cost high-performance solar devices.
GaAs wafers for growth of epitaxial device material are traditionally oriented in (100). III-V epitaxial growth on varied crystallographic orientations such as (110) has not been explored thoroughly with only sub-micron growth achieved. This study focuses on the exfoliation of (100) oriented GaAs material. In addition to the cost saving advantage of removing the substrate from thin film devices, some devices show significant performance enhancement when removed from the parent substrate. GaAs solar cells, for instance, benefit from the use of a back reflector and decreasing the thickness of the base layer, increasing the probability for self-adsorption of radiated photons known as photon recycling. Photon recycling leads to an increase in open-circuit voltage and conversion efficiency. Thin devices removed from their substrate can be bonded to other junctions to create high efficiency multijunction PV cells or bonded to a flexible substrate to utilize the pliable nature inherent when solid-state devices are thinned.

One method in use for device exfoliation is called Smart Cut. Ion implantation of helium or hydrogen induces platelet formation creating a weakened layer within the substrate and is subsequently used in conjunction with wafer bonding. This was first developed as a method to produce Si on insulator materials (SOI). Smart Cut exfoliation techniques have been applied to various semiconductors such as SiC, GaAs, InP, and LiNbO$_3$. However, extensive damage can occur to the near-surface region due to the high level of proton bombardment, referred to as blistering or bubbling and surface roughness needs to be mitigated after exfoliation. Additionally, implantation equipment and techniques are costly especially when attempting to exceed depths of a few micrometers.

Others have successfully exfoliated III-V epitaxial layers from parent wafers by using selective chemical etchants. Lee et al., Adams et al., and Bauhuis et al. utilized a sacrificial epitaxial layer of AlAs which is grown between the substrate and device material and removed by selective chemical etchant hydrofluoric (HF) acid. Slow lateral etch rates of 6 – 30 $mm/h$ make this an inherently low-throughput process, and post-etchant residues can also inhibit substrate reuse. Alternatively, Cheng et al. developed a process that utilizes
InAlP sacrificial layers that are removed by HCl acid, avoiding the use of hazardous HF acid. [25] However, HCl can attack other active device layers, and lateral etch rates are still low, taking about 8 hours at 60°C to fully remove a layer from a 2” substrate. [28]

A more recent development that has the promise of much higher throughput and does not involve the use of hazardous HF acid is the process of utilizing a spalling type of fracture in a controlled manner to propagate a crack at a desired depth in substrate material. Spalling is a type of fracture that occurs spontaneously beneath an adherent thin film containing sufficiently large residual tensile stress. In 1989, Suo and Hutchinson published quantitative spalling mechanics theory to be utilized in thin film applications as a means to avoid occurrence of spalling type cracking. [29][30] According to Suo and Hutchinson’s developed mechanics, a critical crack parallel to the film/substrate interface propagates spontaneously by a sufficiently high misfit tensile stress, with the $K_I$ ‘opening mode’ and the $K_{II}$ ‘shear mode’ stress intensity factors determining the conditions under which fracture occurs and its behavior during crack propagation. It is presented that a spalling fracture occurs when the $K_I$ stress intensity factor in the bilayer system exceeds the fracture toughness, $K_{IC}$, i.e. the critical $K_I$ stress intensity factor of the substrate material. An appropriate combination of the strain mismatch and thickness of the adherent film creates the strain energy needed to overcome a threshold energy value determined by the fracture toughness of the substrate. Once this energy threshold is reached, fracture occurs at a depth where the $K_{II}$ is minimized (i.e. zero), referred to as the steady-state spalling depth, schematically shown in Figure 1.1.

![Figure 1.1: Sufficient misfit stress in a film/substrate system enables a spall fracture parallel to the interface at a specific steady-state depth in the substrate material.](image)
Counter to avoidance of this type of fracture, in 2007, Dross et al. realized the idea of intentional spalling for eventual application to device exfoliation by creating a sufficiently high stress mismatch in a bilayer. [31] There are various ways of creating the necessary stress mismatch in a bilayer to induce spalling. Dross et al. deposit layers of Al and Ag paste on a Si wafer. [31] These layers have a thermal expansion coefficient that is higher than the substrate material. Through a steps of annealing at high temperature $900^\circ C$ and subsequent cooling to room temperature, they were able to create the stress mismatch needed to induce a spontaneous spalling fracture and successfully exfoliate films $30 - 50 \mu m$-thick over a $25 cm^2$ area. [30] This method requires high temperature anneals which cannot be used on most epitaxial device materials and relies on spontaneous fracture occurrence which is not easily controlled. A variation of this technique was used by a group at Astrowatt Inc. through a process of electroplating a metal film to the surface, annealing in hydrogen atmosphere to move hydrogen into the substrate and then cooling for a thermally induced stress increase and using a wedge to separate thin foils from the substrate for device processing. [32] This technique has led to fabrication of single heterojunction solar cells using $25 \mu m$ c-Si foils exfoliated from (100) and (111) Si wafers [33] and the exfoliation of Ge based single junction solar cells from Ge wafers [14][34]. A group at the IBM T. J. Watson Research Center has achieved exfoliation by deposition of a metal layer with the residual tensile stress contained in the film creating the stress mismatch needed for spalling. [17][35][30][36][37] Films are deposited by sputtering or electroplating. Silicon films exfoliated by spalling are used for CMOS device fabrication. [17][35] Deposition of a stressor film is also used by Bedell et al. to remove thin film device material grown on (100) Ge by MOVPE, producing single junction III-V solar cells at 17% conversion efficiency [30] and InGaP/(In)GaAs/Ge tandem at 28.7% efficiency [36]. In some cases, the inherent flexibility of the removed thin material is utilized by bonding a tandem III-V cell and CMOS circuits to a flexible plastic handle. [17][35][37] All published information containing devices exfoliated or processed on exfoliated films show no significant degradation due to the spalling techniques used for exfoliation.
Figure 1.2: Due to cleavage plane orientation in GaAs, attempted spalling in (100) GaAs substrates results in faceting along \{110\} planes.

Many thin devices have been created utilizing spalling in Si and Ge substrates. Little has been explored on spalling in GaAs. Thin GaAs films were successfully removed by Bedell et al. from a (110) orientated GaAs ingot by direct electroplating of a stressor film on the boule. [30] Spalling of (100) oriented GaAs is reported to exhibit facet features on the fracture surface. [30] One particular issue in spalling is that cleavage planes in brittle crystalline materials govern the crack propagation path, with the fracture traveling preferentially along the weak planes of the crystal. If a cleavage plane is oriented parallel to the steady-state spalling depth, the crack tip will propagate along that plane creating a flat, planar surface. In this way, a flat surface results for layers removed from (100) Ge, (111) Si, (100) Si, and (110) GaAs [30][35][36] because the cleavage planes are oriented parallel to the steady-state spalling depth. However, if the cleavage planes are not parallel to the steady-state spalling depth, the resulting surface will be a non-planar surface. For the zinc blende crystal structure in materials such as GaAs, \{110\} planes are the only favorable cleavage planes due to their charge neutrality and low surface energy. [38] When fracture is restricted to \{110\} planes, a (100)-targeted spall fracture will occur on the two equally stressed weak (110) and (\overline{1}10) planes for crack propagation in the [010] direction as shown by the diagram in Figure 1.2. For this reason, a planar fracture along \{100\} planes in (100)-GaAs spalling has not been achieved and faceting of the fracture onto a set of complementary \{110\} planes is observed. [30] No previous work has been done to study the factors that influence facet propagation,
controlling facets, or the effects that a faceted (100)-GaAs spall has on device performance.

Waste minimization is the main benefit for wafer reuse. As depicted in Figure 1.3, there are two sources for material waste in (100) GaAs spalling, which are (1) the deviation away from planar crack propagation or facets that occur and (2) the level of precision of where the depth at which spalling occurs in relation to the device material. In other spalling studies, spall depth is not considered an important factor as in the case of Si, the wasted material due to deep spalls is of little concern due to its lower cost. For GaAs-based devices, however, controlling the spall depth and hence minimizing waste of the expensive material, is significant.

![Figure 1.3: Material waste in spalling occurs from non-optimization of the spalling depth and excess that occurs due to non-planar, faceted, crack propagation.](image)

1.1 Thesis Layout

The main focus of this dissertation is to exfoliate thin films from (100) GaAs substrates enabling wafer reuse while maintaining that material waste minimization is a key component. This is explored by; (1) understanding the principles and theoretical concepts in applied spalling technology, (2) developing methods for spalling to be successfully applied to (100) GaAs, (3) investigating faceted crack propagation and the spalling parameters that may influence facet size, (4) analysis of the material quality after spalling, and (5) applying spalling to PV device exfoliation.

Chapter 2 outlines the methods developed to achieve a controlled spalling lift-off for (100) GaAs. This chapter answers the questions of how to create sufficient strain energy in the
bilayer to induce and control a spalling fracture in (100) GaAs. Observations of the resulting fracture surface morphology are examined and conditions to produce an optimized spalling fracture surface is defined.

Chapter 3 assesses what theoretical models exist and which are appropriate to apply to a spalling fracture in (100) GaAs, specifically exploring the critical parameters of stress and film thickness and their correlation to predicting spall depth for controlled spalling.

Chapter 4 looks at the faceting behavior that occurs during (100)-GaAs spalling. This chapter examines feasibility of inhibiting or reducing facet size by various methods. Additionally, the relationships between facet size and spall depth, stressor film parameters and spalling process parameters are presented.

In chapter 5, the quality of the spalled material is examined. This is explored through dislocation density analysis and the electrical performance of sensitive photovoltaic devices after exfoliation by spalling in (100) GaAs.

Chapter 6 evaluates contributions to the field of controlled spalling achieved in this thesis and the technological implications of these advances.
Several groups have applied spalling to exfoliate devices from Si and Ge substrates. However, very little detail is shared on the process steps used or how the film deposition process parameters may be tuned to influence the thickness and quality of the resulting spalled film. Spalling is a spontaneous fracture event. In order to apply this fracture mode as an exfoliation technique, a controllable process is needed. Bedell et al. deposits internally stressed Ni by magnetron sputtering as the stressor film and initiates exfoliation by applying a manual force to initiate the fracture avoiding spontaneous self-initiated spalling. This is referred to as controlled spalling. Data on the manually initiated process window for spalling (100) Ge is shown in Figure 2.1 [35]. This shows the stressor film thickness and residual stress used to experimentally define controlled spalling based on their definition and spalling techniques. Similar information is not available for spalling in other semiconductors.

Figure 2.1: Process window for initiated spalling of (100) Ge substrate using sputtered Ni stressor film [35]
Spalling in GaAs has not been investigated in the same manner for device application nor has the spalling process window been defined. In this dissertation, spalling in GaAs is achieved by reproducing selected methods used by others to spall Ge and Si. [30] Deposition of a highly stressed film allows for room temperature spalling. Deposition by electroplating offers flexibility in residual stress control [39], and the ability to easily achieve thick films and high stress levels quickly at low costs. Various bath chemistries provide varied levels of stress. For a current density range of 3-11 mA/cm², a Ni sulfamate, basic semi bright, and Watts Ni bath can produce stress levels in the Ni electrodeposit of 0-55 MPa, 35-150 MPa, and 125-185 MPa, respectively. [40] Film stresses above ~300 MPa are needed to exfoliate (100)-GaAs material less than ~20µm, found by calculated approximation using theories developed in Chapter 3.

An additive-free Watts nickel chemistry composition is a well-established Ni electroplating system that can achieve high stress levels with ranges that vary by chloride composition changes. Raising the chloride content in a Watts nickel bath increases the amount of residual stress that can be obtained with an all-chloride composition achieving tensile stress levels of 275-340 MPa for current densities ranging 25-100 mA/cm². [40] Additionally, stress is proportional to electroplating current density, where increasing current density may further increase residual stress. [40]

Electroplated Ni film thickness in micrometers,

\[ s = \frac{100 m}{dA} = \frac{12.294 aIt}{A} \]  
(2.1)

is found from the mass of Ni deposited at the cathode, \( m \), the electroplating current density, \( I/A \), the Ni density, \( d \), time, \( t \), and current efficiency ratio, \( a \). [40] This relation is derived using the atomic weight, Faraday’s constant, and the number of electrons, found in the anode reaction, \( \text{Ni}(s) \rightarrow \text{Ni}^{+2} \text{[aq]} + 2e^- \). During electroplating, a small percentage of the current is consumed in the discharge of hydrogen ions from water and this loss is represented in the efficiency variable.
This chapter discusses the experimental spalling methods used throughout the thesis. Additionally, the electroplating process window is defined for spalling (100) GaAs and the definition of controlled spalling is refined to consider fracture surface morphology leading to a more narrow and precise process window for optimal results.

2.1 Experimental Methods

The stressor film is deposited by electroplating a Ni film in tensile stress. An all-chloride Watts bath chemistry is established that has the ability to achieve a range of stress levels, while keeping the spalled film thin enough to maintain waste reduction and thick enough to contain a photovoltaic device of 2-4 µm-thick. Immediately prior to electrodeposition, the exposed GaAs surface is prepared by 1 min of etching, removing ∼ 1µm in a 2:1:10 solution (by volume) of \( \text{NH}_4\text{OH} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} \). Backside and edges of GaAs wafer samples are masked for electrodeposition by a jig designed in Solidworks and produced by a 3D extrusion printer in acrylonitrile butadiene styrene (ABS) material, Figure 2.2. SolidWorks drawings of the electroplating jig detailing size specifications are presented in Appendix A. This consists of an inset area sized 18 x 18 mm to accommodate a quarter of a 2” wafer and a gasket for sealing the back of the wafer samples. A front cover frames the area for deposition. A chemical-resistant rubber gasket lies between the sample and window to seal sample edges from the chemical bath. A copper tape strip on the window gasket makes contact with both the front of the sample and the contact pin in the jig. Front contact is chosen to avoid applying a bias across devices during electroplating. The window is fastened to the jig by vinyl screws exposing a 16 x 16 mm sample area for electroplating. The jig is designed to attach to a 99.9% pure Ni plate that serves as the anode. Nickel with a high internal tensile stress is electroplated onto the GaAs surface exposed in the electroplating jig at 58°C. The electrochemical bath has a composition consisting of of 300g \( \text{NiCl}_2 : 6\text{H}_2\text{O} \) and 35g of boric acid per liter of deionized water. Electroplating is performed in a constant current mode. Various residual stress values are produced in the nickel film by utilizing a range of current densities (20-160 mA/cm²).
After Ni deposition, samples are etched by $NH_4OH:H_2O_2$ (unless otherwise noted as in device spalling preparation, detailed in Chapter 5) to remove the GaAs around the edges of the nickel to a depth of 15µm. Residual stress level in the Ni is measured to understand the relation between stress and film thickness. X-ray diffraction (XRD) is used on the backside of wafer samples to track peak shift associated with substrate curvature as depicted in Figure 2.3. XRD scans of (400) GaAs reflections are collected at 2mm translation intervals across the substrate. Knowing translational displacement and the peak shift, $\Delta \theta$, associated (as in the sample of data collected shown in Figure 2.4), curvature, $\kappa$, can be calculated using trigonometric principles,

$$\kappa = \frac{1}{(2mm) \tan \Delta \theta}.$$  \hfill (2.2)

From curvature calculations, stress, $\sigma_f$ is calculated using the Stoney formula [41],

$$\sigma_f = \frac{E_s h_s^2 \kappa}{6 h_f (1 - v_s)},$$  \hfill (2.3)

where $h_s$ and $h_f$ is the thickness of the substrate and the film, respectively, and $E_s$ and $v_s$ is the Young’s modulus and Possion’s ratio of the substrate. The error in stress is determined by propagating variations in stressor thickness and measured curvature through the Stoney equation.
Figure 2.3: Displacement of an X-Ray diffraction beam is used to calculate curvature of GaAs to calculate the stress in the Ni film.

Figure 2.4: Three X-Ray diffraction scans taken 2mm translation intervals on GaAs substrate. The peak shift ($\Delta \theta$) is due to GaAs curvature.
Spalling is initiated by an automated jig comprised of an adhesive coated cylinder that rolls by gravitational acceleration down an incline and over the sample that is held onto the jig by vacuum. The adhesive adheres to a tape strip pre-adhered to the nickel surface and an upward force is applied to the nickel from the rolling cylinder to initiate spalling fracture and propagate the crack across the wafer. The spalling event occurs in less than 0.1s. Pull force can be varied by varying spalling jig parameters of ramp length and ramp angle. The pull force and jig design details are discussed in Chapter 4. An additional element known to affect subcritical crack growth is environmentally dependent. Many glasses and various ceramics experience crack growth due to moisture in the ambient environment. For GaAs, liquid water at the crack tip is very effective in assisting crack propagation. However, crack growth will not occur in GaAs due to water contained in inert gases or liquids. [42][43] Samples are dried before spalling initiation by pressurized N₂ gas. Environmental humidity level is not a concern and no additional attempts are made to control the environmental humidity present during the spalling fracture. To establish the electroplating process window for spalling (100) GaAs, current density and deposition time are varied and the spalling results are recorded noting whether a spall occurs spontaneously, by initiation, or not at all. A spontaneous spall is established by visual inspection as any amount of film peeling before spall initiation, as seen at the edges in the example in Figure 2.5. All data presented in chapters 3-5 are results from samples spalled using optimized electroplating conditions as defined later in this chapter, where, generally, samples are removed from the electroplating bath before the stressor layer reaches the critical thickness for spontaneous spalling at a given current density.

Spalled GaAs film and nickel thicknesses are examined by cross-sectional SEM imaging. For cross-sectional preparation, a lateral pull to tear the thin nickel film and cleave the GaAs along a (110) plane is utilized. Average spall depth is defined here as the average depth between the maximum and minimum facet heights, as measured from the Ni/GaAs interface, shown in Figure 2.6. Error in spall depth and film thickness per sample is calculated as the
standard deviation in average spall depth measurements from cross-sectional SEM images at various locations across the center cross-section on the sample.

Figure 2.6: Spalling depth defined as the average between the maximum and minimum depth from the Ni/GaAs interface.

2.2 Results and Discussion

It is found that an all-chloride Watts Ni bath chemistry provides adequate stress levels to spall GaAs films in the desired range of thickness (3-15µm). Spalled film thicknesses achieved are discussed further in Chapter 3. In Figure 2.7, the experimental average Ni thickness is shown against the Ni thickness calculated using eq. 2.1. The measured Ni thickness is consistently higher than the estimated values. Electroplating Ni at high current densities leads to relatively high microporosity levels that in turn creates the high internal stresses and results in a deposited layer thicker than theoretical Ni layer thickness containing the same quantity of Ni. The uniformity of the electroplated Ni is inconsistent due to edge
Figure 2.7: Estimated Ni thickness and experimental Ni thickness as measured by cross-sectional SEM imaging.

Effects. The Ni thickness in this case for a square area increases radially out from the center. Analysis of the cross-section through the center shows up to 11% difference from the center to 25% distance from the edge and the largest percent change of up to 160% of center thickness occurring within 100µm from the edge. In a spalling system, having thicker areas of stressor film at the edges may lead to both a larger energy for ease of spalling initiation and a deeper spalling fracture in this region due to the spall depth/stressor thickness relationship described in Chapter 3. Three current densities were chosen for Ni stress measurements (30, 50, and 110mA/cm²) with electroplating times that correspond to the initiated spall point in the process window just before the occurrence of a spontaneous spall at 13, 7, and 2 minutes, respectively. Data showing the correlation between electroplating parameters and measured stress is shown in Figure 2.8.

Increasing the current density raises the internal tensile stress in the Ni. For current densities ranging 30-110mA/cm², resulting tensile stress is 296 ± 11MPa to 494 ± 33MPa. Electroplating process parameters for (100)-GaAs spalling are shown in Figure 2.9(a). This details the conditions at which a spall will occur spontaneously (green), by external force application (blue), or not at all (red). The available spalling process window for electro-
Figure 2.8: Film stress verses current density for Ni electroplated onto (100)-GaAs samples using an all-chloride Watts bath chemistry.

Electroplating time widens for samples prepared at lower current densities due to a decrease in the deposition rate. For example, the initiated spalling process window occurs at electroplating times of approximately 4.5 to 6.5 min at 50 mA/cm$^2$ and widens to a range of 10 to 14 min at 30 mA/cm$^2$, a difference of 2 min widening to 4 min window for electroplating time adjustments. This allows for higher resolution in deposition parameters at lower current densities, increasing the ability to achieve more precise Ni thicknesses.

Within the range of Ni thicknesses electroplated at a specific current density, differences in the fracture surface morphology are observed. A schematic representing three distinctly different fracture surface morphologies is shown in Figure 2.9(b). Each feature type (1-3) corresponds to a spalling region in the electroplating process window, Figure 2.9(a). Location within the process window for each feature type is approximated based on observation. The electroplating time within the process window where type (3) will occur over the entire surface of a sample is unknown for a current density of 30 mA/cm$^2$ and is therefore represented in the plot as a dashed circle. Samples spalled at conditions between (1) and (2) and between (2) and (3) contain elements of each of the surrounding surface morphology types. For a given current density, fracture surfaces resulting from initiated spalling (blue,
Figure 2.9: Electroplating process window (a) for spalling of (100)-GaAs substrate where spalling occurs spontaneously (green), by initiation from an external peeling force (blue), or no spall occurs (red). At each specific current density level, three distinct fracture surface features evolve from 1-3 with increased electroplating time. (b) A schematic representation of visually observed fracture surface morphologies is shown.
Figure 2.9(a)) have surfaces that contain one or a combination of features (1) and (2) depicted in Figure 2.9(b). At low electroplating times, the fracture surface of initiated spalling exhibits discontinuous faceting, where the crack tip can propagate through the GaAs to meet the Ni film and in some cases (initiated spalling with the lowest electroplating time) partial delimitation occurs between regions of spalled GaAs as in Figure 2.10. Pyramid-like GaAs features are formed on the surface of the spalled film creating a surface that visually appears hazy as represented in Figure 2.9(b), (1). Initiated spalls (blue, Figure 2.9(a)) with the longest electroplating time result in the removal of a continuous symmetrically faceted GaAs film as shown in Figure 2.11 and Figure 2.12.

![Image](image1.png)

Figure 2.10: Spalling surface obtained under undesirable initiated spalling conditions as type (1) morphology in Figure 2.9(b). Areas of discontinuous GaAs film reveals the Ni stressor layer show between the pyramid-like GaAs structures.

Facet peaks and valleys (as depicted in Figure 2.9(b) (2)) occur perpendicular to the spall direction as shown in Figure 2.13. Facet direction depends only on spalling direction and is not influenced by the orientation of the wafer in 4-6° off-cut (100) GaAs. Trials conducted for spalling propagation in crystallographic directions of [001], [00\bar{1}], [010], and [0\bar{1}0] result in similar faceted fracture surfaces with facet trenches and peaks oriented perpendicular to the crack propagation direction. The majority of samples prepared in the range of initiated spalling (blue, Figure 2.9(a)) are dominated by type (1) morphology (Figure 2.9(b)) with only the samples at the longest electroplating times in the initiated range showing type
Figure 2.11: Spalling fracture surface morphology example created using optimized initiated spalling conditions as in schematic (2) in Figure 2.9(b)

Figure 2.12: Exfoliated GaAs thin films created using optimized initiated spalling conditions as in schematic (2) in Figure 2.9(b)
(2) dominant fracture surface. Areas of spontaneous spalling exhibit type (3) (green, Figure 2.9(a)). The facet peaks and valleys emanate from one or all corner or edge regions in a curved manner as approximated in diagram (3) of Figure 2.9(a). Films removed are continuous with great variations in the facet heights. Examples are shown in Figure 2.14 where the orientation of the facets reveal the propagation direction of the spontaneous spalling where spalling fracture emanates from edges and corners. Samples that are processed under conditions between morphology types labeled in Figure 2.9(a) can have fracture surfaces that contain elements of both features that occur under surrounding conditions.

Figure 2.13: Spalling crack propagation direction is perpendicular to resulting peaks and valleys

Figure 2.14: Spalling surface examples for spontaneous spalling as schematic type (3) morphology in Figure 2.9(b) obtained at varied process conditions that result in varied average facet height of relatively large (left, center) and small (right).
In order to achieve controlled spalling, an initiated spall is desirable, avoiding a spontaneous spalling event. Within the region of initiated spalling (blue region figure Figure 2.9(a)), there is potential for the exfoliation of a continuous or discontinuous films. In this thesis, optimized spalling conditions for (100) GaAs are defined as those creating a fracture surface that contains only type (2) morphology (Figure 2.9(b)). This occurs at conditions just below the spontaneous spalling point resulting in exfoliation of a continuous film. At initiated spalling conditions below optimized conditions, the surface becomes discontinuous as if the energy requirement for spalling was only reached in some small areas, allowing the crack to propagate to the Ni/GaAs interface in other areas. An initiated spalling fracture only propagates as long as an additional pull force is applied, i.e. if pulling is discontinued after propagating a fracture half-way across the substrate, the fracture will not continue across to completion and the substrate will have only spalled half way. This indicates that a non-spontaneous spalling fracture does not contain enough energy to continue fracture propagation without an external force. It is assumed that conditions for an ideal spall are available at every stress level (current density) by varying the stressor film thickness. However, the ability to deposit Ni to a precise depth decreases at greater current densities which narrows the process window. From this chapter, empirical conditions under which (100) GaAs can be spalled are established, setting the groundwork for understanding control of spalled GaAs thickness, faceting, and defect formation.
CHAPTER 3
MODELING SPALLING FRACTURE FOR SEMICONDUCTORS

In order to effectively apply spalling mechanics as a wafer exfoliation tool, an ability is needed to predict and control the thickness of the removed film while understanding the limitations of the materials and conditions necessary to spall. Modeling the mechanics of (100)-GaAs spalling presents three challenges; (1) GaAs is a weakly anisotropic material, (2) due to the crystallography, cleavage planes are not aligned parallel to the surface inhibiting flat crack propagation, resulting in a faceted fracture surface, and (3) controlled initiation force is not included in spalling fracture mechanics. These challenges are described and a set of assumptions are made to allow an approximation of the critical stressor film properties for optimized spalling and the resulting spalling depth.

Currently, Suo and Hutchinson’s mathematical analysis of spalling mechanics, discussed in Chapter 1, is the most relevant theory to this work. They established the use of edge loading to model the stresses in the adherent film and present the stress intensity factors and the energy release rate in a spalling system. However, this model is based on linear elastic fracture mechanics and assumes isotropic mechanical material properties. Gallium arsenide and other single crystalline materials that may be of interest for semiconductor device lift-off applications are at least weakly anisotropic linearly elastic materials. Gallium arsenide is linearly elastic with cubic symmetries at room temperature. Sih, Paris, and Irwin developed general equations for crack-tip stress fields in rectilinearly anisotropic bodies. [44] The relationships describing deformation in anisotropic bodies are the same as isotropic relations with the addition of Hooke’s law, the principle that the force needed to extend or compress a spring by some distance is proportional to that distance. Hoenig continued this work by treating a three-dimensional problem of a through crack in anistropic material. [45] A number of numerical studies followed from Atluri et al.[46], Boone et al. [47], and Tohgo
et al. [48] to refine mathematical models. However, there is no adaptation of anisotropic fracture modeling that can be applied to spalling because of the complexity in loading.

The crystallographic structure in GaAs leads to a spalling fracture that oscillates during propagation for a (100) oriented wafer, as discussed in Chapter 1. Established spalling mechanics theory [29] applies to relatively flat crack propagation and does not account for crack-tip kinking. Spalling is considered a mode I fracture with the criterion that fracture occurs parallel to the bilayer surface in the substrate at a depth where the mode II component is minimized to zero. Spalling fracture propagation in (100) GaAs becomes mixed mode as the crack tip kinks away from the steady state spalling depth onto a complementary \{110\} plane. Sih defines an application of a strain-energy-density factor as a critical value that governs a mixed propagation of mode I and mode II fracture, where a crack can grow in an arbitrary direction from its original position. [49]. Hussain et al.[50] and Erdogen and Sih [51] also provide models for mixed-mode fracturing but none have been applied to an edge loaded bilayer system geometry as defined in a spalling fracture, especially since spalling has only been defined as occurring on a flat planar trajectory.

Implications of misorientation between the mode I plane and crystallographic cleavage plane have not been explored in the literature. One of the inherent difficulties facing treatment of mixed-mode effects is the difference between global (apparent) mode-mixity and local (crack tip) mode-mixity. Locally, in (100)-GaAs spalling, the crack tip trajectory has two components: the forward trajectory parallel to the film/substrate interface and the component of travel perpendicular that moves toward and away from the interface. Faceting occurs in a symmetric fashion with consistent kink angles, where the path toward the interface is mirrored during travel away from the interface. During optimized spalling, the crack does not travel outside a localized region and is contained at a specific depth in the substrate parallel to the bilayer interface. Results produced in Chapter 2 show the ability to remove continuous films with faceting occurring in a wide region localized at a specific depth within the substrate. On a global scale, it would appear that the established spalling
mechanics may have some application to this system. No previous work has explored this
application nor additional theoretical models to include a mixed-mode nature into the estab-
lished spalling model. This chapter evaluates the fracture system from a global perspective,
negating the fluctuation of the crack tip during spalling. This allows for the application of
Suo and Hutchinson spalling model with minor adjustments to account for the increased
surface area that results in faceted crack propagation. This model is used to predict the con-
ditions needed to initiate and propagate a spalling fracture and to determine at what depth
the fracture occurs in various semiconductors. Experimental spalling results for (100)-GaAs
are generated and compared to theoretical relationships.

3.1 Mathematical Methods

The elastic properties of GaAs and Ni are treated as isotropic, even though it is acknowl-
egedged that GaAs is weakly elastically anisotropic. The universal anisotropy index [52],

\[ A^U = \frac{6}{5} \left( \sqrt{A} - \frac{1}{\sqrt{A}} \right)^2, \]  

(3.1)
is a variation on the Zenar anisotropy index,

\[ A = \frac{2C_{44}}{C_{11} - C_{12}}, \]  

(3.2)
that accounts for both the shear and bulk contributions, where \( C_{44}, C_{11}, \) and \( C_{12} \) are elastic
constants of the material. GaAs has a universal elastic anisotropy index of 0.74 compared to
silicon and germanium of 0.563 and 0.308, respectively, as calculated by the elastic constants
[53][54] where deviation from zero defines the extent of crystal anisotropy. An example of a
material with relatively high anisotropy is bulk Ni with a universal anisotropy index of 1.47.
[55] Comparitivy, electroplated Ni is polycrystalline having a small consistent grain size and
therefore is assumed isotropic in this thesis.

Suo and Hutchinson’s model is used to approximate the behavior in (100)-GaAs spalling.
[29] Conventions and geometry for this model are defined in Figure 3.1.
The stress intensity factors are related to the external loads, $P$ and $M$, film thickness, $h$, and dimensionless parameters relative cracking depth $\lambda$, substrate/film thickness ratio $\lambda_o$, and the relative elastic moduli mismatch of the two materials. The stress intensity factors, $K_I$ and $K_{II}$, are defined as

$$K_I = \frac{P}{\sqrt{2Uh}} \cos \omega + \frac{M}{\sqrt{2Vh^3}} \sin(\omega + \gamma)$$

$$K_{II} = \frac{P}{\sqrt{2Uh}} \sin \omega - \frac{M}{\sqrt{2Vh^3}} \cos(\omega + \gamma).$$

Dimensionless positive numbers $U$ and $V$ and $\gamma$ are defined for calculation of the critical spalling parameters,

$$U = \left( \frac{1}{A} + \frac{12 \left( \Delta + \frac{\lambda_o - \lambda}{2} \right)^2}{(\lambda_o - \lambda)^3} + \frac{1}{\lambda_o - \lambda} \right)^{-1},$$

$$V = \left( \frac{1}{i} + \frac{12}{(\lambda_o - \lambda)^3} \right)^{-1},$$

$$\gamma = \sin^{-1} \left( \frac{12\sqrt{U}V \left( \Delta + \frac{\lambda_o - \lambda}{2} \right)}{(\lambda_o - \lambda)^3} \right),$$

where $\gamma$ is restricted to $|\gamma| < \pi/2$. External loads $P$ and $M$ are
\[ P = h\sigma \left( 1 - C_1 - C_2 \left( -\Delta_o + \lambda_o + \frac{1}{2} \right) \right) \]  
\[ M = h^2\sigma \left( \frac{1}{2} - C_3 \left( -\Delta_o + \lambda_o + \frac{1}{2} \right) - \Delta + \lambda \right), \]  

where \( \sigma \) is the residual stress in the film. Nondimensional numbers, \( C_1, C_2, \) and \( C_3, \) are defined,

\[ C_1 = \frac{A}{A_o} \]  
\[ C_2 = \frac{A(\Delta - \Delta_o - \lambda + \lambda_o)}{j_o} \]  
\[ C_3 = \frac{j}{j_o}. \]  

Parameters, \( \Delta \) and \( \Delta_o, \) measuring the levels of the neutral axes depend on \( \lambda, \lambda_o, \) and elastic properties,

\[ \Delta = \frac{2e\lambda + e + \lambda^2}{2(e + \lambda)} \]  
\[ \Delta_o = \frac{2e\lambda_o + e + \lambda_o^2}{2(e + \lambda_o)}. \]  

Additional nondimensional relations are included in the above parameters for calculations,

\[ A = e + \lambda \]  
\[ A_o = e + \lambda_o, \]  

and

\[ j = \frac{1}{3} \left( 3\Delta\lambda(\Delta - \lambda) + e \left( 3(\Delta - \lambda)^2 - 3(\Delta - \lambda) + 1 \right) + \lambda^3 \right) \]  
\[ j_o = \frac{1}{3} \left( 3\Delta_o\lambda_o(\Delta_o - \lambda_o) + e \left( 3(\Delta_o - \lambda_o)^2 - 3(\Delta_o - \lambda_o) + 1 \right) + \lambda_o^3 \right). \]
Across the interface between the substrate and the stressor film, the Dundurs’ elastic mismatch parameter, \(\alpha\), is defined as,

\[
\alpha = \frac{(\bar{E}_f - \bar{E}_s)}{(\bar{E}_f + \bar{E}_s)},
\]

(3.19)

where \(\bar{E}_f\) and \(\bar{E}_s\) are the elastic modulus for the film and substrate, respectively, for a plane stress or plane strain system. The Dundurs’ parameter is simplified into parameter \(e\) to include the elastic mismatch character of the two materials into the above equations,

\[
e = \frac{\alpha + 1}{1 - \alpha}.
\]

(3.20)

To solve for the critical film parameters, stress \((\sigma)\) and thickness \((h)\), mode mixity \([56]\),

\[
\Phi = \tan^{-1}(K_{II}/K_I)
\]

(3.21)

is set equal to be zero based on the criterion that \(K_{II}\) is zero at the steady-state spalling depth. Relative spalling depth parameter, \(\lambda\), is extracted by defining stressor film thickness, \(h\), values. Spalling depth i.e. the thickness of exfoliated substrate material, \(\lambda h\), is found for each thickness value, \(h\). To find the critical stress values associated with this set of film thickness values, the mode I stress intensity factor, equation 3.3, is set equal to the critical stress intensity i.e. fracture toughness, \(K_{IC}\), of the substrate material and solved for the residual stress, \(\sigma\). A value of 52\(^{\circ}\) for \(\omega\) is used, which is identified as a reasonable approximation for most material systems. [29]

For application to the Ni/GaAs bilayer examined here, the following properties are utilized in calculations of the critical spalling parameters. A Young’s modulus of 85\(GPa\) and a Poisson’s ratio of 0.32 are used for GaAs. [57] Nickel electroplated at high current densities is known to have relatively lower Young’s modulus values due to increased micro-porosity. [58] The Young’s modulus of Ni electrodeposited onto GaAs is measured by nanoindentation on sample cross-sections that are prepared by metallographic techniques. [59] The averaged Young’s modulus obtained of 121 ± 11\(GPa\) is used for all calculations. A Poisson’s ratio of 0.31 [60] is used for Ni. For all computations, plane strain is assumed producing a modulus
value, $\bar{E}$, of

$$\bar{E}_{f,s} = \frac{E_{f,s}}{1 - v_{f,s}^2}$$

(3.22)

where $E_{f,s}$ and $v_{f,s}$ is the Young’s Modulus and Poisson’s ratio, respectively, for the stressor film, $f$, or substrate, $s$. As GaAs fractures only on $\{110\}$ planes, an experimentally determined fracture toughness for $(100)$ is not available, thus we begin by using the value for fracture along the $(110)$ plane in GaAs of $0.44 \text{MPa}\sqrt{m}$ [57]. Experimental results are discussed in the following sections of this chapter to estimate an “effective fracture toughness” for $(100)$-GaAs fracture for use in this model.

The critical stress parameters and spall depth are calculated for bilayer systems with elastic mismatch values of -0.4, 0, and 0.4 as a function of stressor thickness according to the mathematical steps outlined above. The fracture toughness of the substrate is not needed for spall depth calculations. The elastic mismatch values for various stressor film/substrate combinations, some of which have been used previously in the literature, are displayed in Table 3.2 which are calculated using the mechanical properties listed in Table 3.1. Young’s modulus values for metals may be much lower if the film has a high level of residual stress as is the case for electroplated Ni used in this study. Spall depth calculations are conducted assuming an infinite wafer thickness, as is the case of spalling from a crystal boule, and repeated for a finite wafer thickness of $350 \mu m$, a typical commercially available semiconductor wafer thickness.

### 3.2 Critical Stressor Film Conditions and Spalling Depth

In this section the mathematical processes discussed above are used to generate a graphical representation of the critical stressor film parameters needed to reach the spalling fracture energy threshold and predict the spalling depth. Parametric relationships are examined for a range of elastic mismatch values, enabling estimation of these critical parameters for a bilayer of known substrate fracture toughness and elastic properties.
Table 3.1: Mechanical properties for photovoltaic single crystal substrates and a range of stressor materials

<table>
<thead>
<tr>
<th></th>
<th>Young’s modulus (GPa)</th>
<th>Poisson’s ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Substrate Materials</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>on (100) in [001] dir.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silicon [61]</td>
<td>130</td>
<td>0.28</td>
</tr>
<tr>
<td>Gallium arsenide [57]</td>
<td>85</td>
<td>0.32</td>
</tr>
<tr>
<td>Germanium [62]</td>
<td>103</td>
<td>0.26</td>
</tr>
<tr>
<td><strong>Stressor Materials</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gold [60]</td>
<td>83</td>
<td>0.37</td>
</tr>
<tr>
<td>Silver [63]</td>
<td>69</td>
<td>0.33</td>
</tr>
<tr>
<td>Nickel [60]</td>
<td>200</td>
<td>0.31</td>
</tr>
<tr>
<td>Ni (electrodeposit)</td>
<td>121 ± 11</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Table 3.2: Summary of elastic dissimilarity for spalling photovoltaic materials

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>GaAs</th>
<th>Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>-0.18</td>
<td>0.01</td>
<td>-0.07</td>
</tr>
<tr>
<td>Silver</td>
<td>-0.29</td>
<td>-0.1</td>
<td>-0.17</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.22</td>
<td>0.40</td>
<td>0.33</td>
</tr>
<tr>
<td>Ni (electrodeposit)</td>
<td>0.03</td>
<td>0.17</td>
<td>0.10</td>
</tr>
</tbody>
</table>
Critical stressor film parameters of residual stress and thickness are plotted for varied material systems in Figure 3.2 for elastic mismatch values of -0.4, 0, and 0.4. For reference, elastic mismatch values of example stressor film and semiconductor materials are presented in Table 3.2. This serves as a starting approximation for brittle substrate spalling. Calculated stress values $\sigma$ are normalized by $K_{IC}$ in the graphic. With knowledge of the fracture toughness, $K_{IC}$, of the substrate material and the elastic mismatch in the bilayer, critical stress can be calculated for a given stressor film thickness value. All curves are calculated using a substrate thickness of $350 \mu m$. Critical stress parameters are impacted mainly by the stressor film thickness and the elastic properties of the system. A system with a comparatively stiff film to the substrate, i.e. positive elastic mismatch, requires a greater residual stress to reach the same energy levels at a given stressor thickness than that of a system with a negative elastic mismatch.

![Figure 3.2: Critical spalling parameters for bilayer systems with an elastic mismatch of -0.4, 0, and 0.4 and a substrate thickness of 350$\mu m$.](image)

The influence of the elastic mismatch and substrate thickness on spalling depth is illustrated in Figure 3.3. Spalling depth is plotted against stressor thickness for elastic mismatch values, $\alpha$, of -0.4, 0, and 0.4 for an infinitely-thick and $350 \pm 50 \mu m$-thick substrate. The width of the region represents the uncertainty in the substrate thickness of $\pm 50 \mu m$. An infinite substrate assumption, commonly used in applied spalling literature, [31],[35] produces
Figure 3.3: Spalling depth (i.e. exfoliated film thickness) for material systems with an elastic mismatch of -0.4, 0, and 0.4 and a substrate 350±50μm-thick (solid) and an infinite substrate thickness (dashed).

a linear relationship between stressor thickness and steady-state spall depth. However, for finite substrate thickness values, a nonlinear relation between stressor thickness and spalling depth emerges and differences become more prominent as stressor thickness increases. During spalling in a system with a substrate of finite thickness, bending of the bilayer occurs, relieving some of the film’s internal stress, lowering the stress field intensity in the substrate. The amount of this influence increases as stressor thickness increases, resulting in a more shallow spall depth. A larger stressor thickness is required to produce an equivalent spall depth in a relatively thinner substrate, for each elastic mismatch value. The spalling depth variation between a system of finite and infinite substrate thickness is most pronounced for $\alpha = 0.4$ over the range of elastic mismatch values evaluated here, and becomes more severe for all stressor film/substrate combinations as stressor thickness is increased.

For a given film thickness, spalling depth is positively correlated to the elastic mismatch of the bilayer. If the stressor film has a higher stiffness than the substrate, i.e. positive elastic mismatch value, the stress field will reach far into the substrate material resulting in a relatively deep spall depth compared to a negative elastic mismatch value, where the
substrate stiffness restricts the extent of the stress field for a shallow spall. Both the elastic mismatch of the chosen materials and the substrate thickness significantly influence the spalling depth. A wide range of exfoliated film thicknesses can be produced depending on the materials used and the substrate thickness, for a given stressor film thickness. When used in conjunction with Table 3.2, the stressor thickness required to obtain the desired spall depth can be determined for various semiconductor materials. For example, if attempting to remove a 10µm-thin film from a 350µm-thick silicon wafer by electroplating stressed Ni, the elastic mismatch in the system is -0.2. This is between the black region in Figure 3.3 corresponding to \( \alpha = 0 \) and the gray region corresponding to \( \alpha = -0.4 \); thus, the stressed Ni film needs to be about 8µm thick. From this value, the approximate stress value needed to initiate a spalling fracture is then determined by Figure 3.2

### 3.3 Spalling Parameters for (100) GaAs

In this section, the calculations of the critical spalling parameters and the spalling depth presented in the previous section are compared to experimental results for spalling in (100) GaAs using an electroplated Ni stressor film.

#### 3.3.1 Critical Stressor Film Conditions

Experiments are conducted to identify the relationship between the film stress and the thickness required for controlled spalling of (100) GaAs, under conditions defined in Chapter 2 to produce an optimized controlled spalling fracture. The stress measurements reported in Chapter 2, Figure 2.8, are used in this Chapter to illustrate the critical process window for comparison to theoretical approximations. The process window for (100)-GaAs spalling is defined in Figure 3.4. Samples not shown with greater stressor film thicknesses at a given stress begin to exhibit undesirable spontaneous spalling at the sample edges or corners. Thinner stressor thickness results in undesirable surface morphologies or do not spall under external force provided by the spalling jig. Critical stress values trend inversely with changes in the critical thickness for controlled spalling in (100) GaAs. The Ge spalling process window
[35] exhibits a similar curve shape to what is found here.

Figure 3.4: Experimental process window for controlled spalling in (100) GaAs (violet) compared to theoretical approximation for spontaneous spalling using (110) GaAs fracture toughness ($K_{IC} = 0.44\, MPa\sqrt{m}$, solid) and the empirical effective (100)-GaAs fracture toughness implied by data collection ($K_{IC} = 0.55\, MPa\sqrt{m}$ dashed).

The spalling fracture mechanics model is developed for a system with a pre-existing critical crack [29]. A system with a critical length pre-crack should propagate if the conditions are energetically favorable. Observation in this thesis finds that the initiation during a controlled spall is added to a system that is not able to initiate and propagate a spalling fracture spontaneously. In order for a spontaneous spalling fracture to occur, sufficient energy and a critical crack must be present. It is assumed that one or both of these elements are not present in the case of a spalling fracture not occurring with additional pull force. If one element is present, such as the critical crack, but the energy is below threshold, the system is subcritical. It is found that in a subcritical spalling crack growth can occur with the addition of a pull force. Samples prepared with subcritical energy (i.e. optimized spalling conditions as defined in Chapter 2) will only experience crack growth during the addition of a pull force. A partially spalled sample has a critical crack but does not continue to spall spontaneously. The spalling fracture does not continue to propagate without continued additional pull force. Suo and Hutchinson’s spalling fracture theory states that once a critical
crack exists, a spalling fracture will continue spontaneously if the bilayer contains a sufficient strain energy mismatch. In this thesis, it is asserted that the conditions predicted by spalling mechanics theory serve as the upper boundary for controlled spalling conditions, below which an initiated spalling fracture can occur and above which a spalling fracture occurs spontaneously. The boundary between the spontaneous spalling region and the initiated spalling region is depicted in Figure 3.2 for varied material systems and Figure 3.4 for (100)-GaAs specifically. This is in contrast to what is put forth in the spalling application literature [35]. Bedell et al. proposes the theory by Suo and Hutchinson to serve as the lower boundary in their experimental process window for Ge, i.e. the boundary line between the regions of no spalling and controlled spalling Figure 2.1. Here their placement of this boundary appears misplaced because once pulling begins, the presence of a critical length crack would continue to propagate spontaneously under the critical stresses defined by Suo and Hutchinson.

A (100)-GaAs spalling fracture propagates in a faceted manner, creating a larger surface area than a flat planar surface which would result in a (110) oriented spalling fracture. A greater strain energy is required to create two new surfaces with a larger surface area. The data in Figure 3.4 fall along and below the spontaneous boundary calculated using the fracture toughness of (110) GaAs (represented by solid line); however, a number of data points fall above and to the right of the theoretical curve. Positions above the curve should show signs of spontaneous spalling such as edge peeling before spalling initiation as defined in Chapter 2. This discrepancy indicates that the (110) fracture toughness underestimates the position of the spontaneous spalling envelope for (100) GaAs. The increase in fracture surface area can be accounted for by effectively increasing the substrate toughness and thus the additional energy required to propagate the spalling fracture. If the curve for spontaneous spalling is shifted to exclude the experimental data from the spontaneous spalling region, as approximated by the dashed line in Figure 3.4, the resulting apparent fracture toughness is at least $0.55 MPa\sqrt{m}$. The faceted (100)-GaAs spall involves a mixed-mode fracture that is not accounted for in Suo and Hutchinson’s theory. An increase in the surface area
created during a faceted crack propagation when compared to flat crack propagation is an increase in the critical energy release rate. The critical energy release rate is proportional to the critical stress intensity factor. An increase in the critical energy release rate effectively increases the critical stress intensity required to release additional bonds to form the faceted surface. Even though this is not a pure mode I fracture, effectively increasing the critical stress intensity allows for quantitative critical stress parameter estimations using Suo and Hutchinson’s spalling mechanics. The validity of applying aspects to Suo and Hutchinson’s to faceted (100)-GaAs spalling is further examined by comparison of experimental spalling depth to predicted values.

3.3.2 Spalling Depth

Exfoliated film thickness (or spalling depth) is recorded from a set of spalled GaAs samples created by optimized controlled spalling under similar electroplating parameter ranges to that of samples prepared and measured non-destructively in the previous section for the definition of the spalling process window. The relationship between spalling depth and film thickness is shown in Figure 3.5 for spalling in (100) GaAs. Both regions are calculated using an electroplated nickel Young’s modulus range of $121 \pm 11 GPa$ represented by the width of the region. The thinnest spall layer, $8.1 \mu m$, is produced from a nickel stressor film thickness of $4.4 \mu m$. The thickest spalled material presented here is a $21.5 \mu m$ produced from a deposited stressor layer of $9.3 \mu m$. For the purposes of device exfoliation, an appropriate spalling depth includes room for device material, faceted fracture propagation, and error in spalling depth accuracy.

Data obtained for thin layers spalled from $350 \mu m$ (100)-GaAs substrates follows this trend of increasing spall depth with increasing stressor thickness shown in Figure 3.5. Nearly all data collected at various stressor thickness values lie below the infinite approximation and more closely follow the curve calculated using a finite substrate. Previous device spalling work employing a vacuum substrate chuck and rigid frame for film peeling assumes an infinite substrate thickness, [35] but the spall depth data reported are not consistent with theoretical
Figure 3.5: Steady-state spall depth for GaAs/electroplated Ni system plotted against stressor thickness for an infinite thickness substrate (gray region) and 350 µm-thick substrate (black region). The regions are shown for a range of electroplated Ni Young’s modulus range determined by nanoindentation (121 ± 11 GPa). Experimental spalling data for layers exfoliated from 350 µm-thick (100) GaAs substrates (blue) correlate well to the theoretical relation.

Spall depth calculations. Based on computations in this thesis, an infinite substrate would result in a linear relationship between the spall depth and stressor film thickness that passes through zero. Data presented by Bedell et al. follows a general linear trend that would intersect between 3 and 4 µm as reproduced in Figure 3.6 where spalling theory spalling depth trends extrapolate to zero; it is unclear where the inconsistency in that work originates. From experimental spall depth data obtained in this study, spalling fracture mechanics predicts spall depth for a bilayer that is free to naturally flex during the spalling process when finite substrate thickness is taken into account. Further research may be needed to assess the degree to which anisotropic material properties and mixed mode fracturing influence predictions to obtain a target spall depth. Isotropic property assumptions result in theoretical spall depths and spalling parameters that are consistent with experimental results for the case of a GaAs/stressed electroplated Ni bilayer for the purposes of providing a first approximation for device fabrication.
Figure 3.6: Experimental spall depth per stressor film thickness for (100)-Ge spalling obtained by Bedell et al. This plot is reprinted from [35]
CHAPTER 4
ON FACETING IN (100) GALLIUM ARSENIDE SPALLING

The last chapter presented methods to predict the conditions needed to exfoliate films of a desired thickness. Faceted crack propagation due to the crystallographic orientation of the cleavage plane is an additional challenge for spalling (100) GaAs. For application to device exfoliation, the size and distribution of the facets affects the determination of how deep into the material one must initiate a fracture while avoiding crack penetration into undesirable regions, such as the epitaxial device materials. Additionally, if the region containing the faceted crack propagation is large, it can be a disadvantage in wafer reuse applications due to the high cost associated to material waste. Understanding faceted crack propagation may lead to further control over the process to enable controlled reduction of the facet height. Additionally, controlled faceted spalling can lead to engineered surface textures that are beneficial to device performance. Textured surfaces have been shown to improve Si-based photovoltaic device efficiency by light trapping. [64][65][66] Understanding the faceted crack propagation is the first step to controlling the facet morphology in a spalling fracture process. This chapter explores the extent to which facets can be understood and influenced.

This chapter first looks at the feasibility of using epitaxial materials to inhibit crack tip propagation as a means to inhibit faceting during spalling. Results show that a better understanding of the faceting behavior is needed before efforts to control and influence propagation can be employed. Average trends in facet size are presented. Relationships between facet size and stressor film deposition parameters of thickness and current density are found experimentally. The driving force for faceting is discussed in order to further explore the origins of facet size dependence. Specific features of fracture in controlled spalling of (100) GaAs are found to violate key assumptions made in existing fracture mechanics models, making direct modeling of the crack tip behavior difficult. Thus, attention is turned to the
far-field behavior, away from the crack tip, to provide a potential explanation for the faceting behavior. In the absence of a comprehensive framework for the theoretical underpinnings of faceted behavior in controlled spalling, the issue of engineering facet size is approached empirically. The influence of the spalling initiation processes is examined experimentally, as is the influence of pull velocity on the resulting facet size.

4.1 Inhibiting Facet Propagation

Crack propagation in the substrate occurs when the threshold energy to overcome the substrate’s resistance to crack growth is reached. For this system, the Ni stressor film properties of thickness and residual stress must be sufficiently large to enable spalling fracture initiation in (100) GaAs. Early in the project, it was theorized that the inclusion of an epitaxial material with a significantly higher fracture toughness than GaAs could be used to deflect or inhibit crack propagation. This would serve as a relatively simple option to contain the large facets to a smaller region. Choosing an appropriate III-V material for the epitaxial layer requires consideration of both a lattice constant near that of GaAs for maintenance of epitaxial growth and a significantly higher fracture toughness than GaAs. Select III-V materials with a lattice constant between 5 and 6.5 Å. Materials shown have a fracture toughness between 0.3 and 0.7 MPa $\sqrt{m}$ with inverse proportionality between fracture toughness and the lattice parameter. An exception to this trend is AlAs with a fracture toughness of 1.7, significantly higher than GaAs. A trial sample is prepared by metal-organic vapor deposition consisting of two AlAs layers buried beneath a GaAs layer to represent epitaxial device placement, Figure 4.2(a), at a depth defined by experimental trials for specific spalling conditions. After spalling, analysis by SEM of a cross section along the crack path shows no effect on crack propagation from the epitaxial inclusion of the AlAs layers, Figure 4.2(b). This implies that crack deflection is not easily contained by the use of a material layer with a higher fracture toughness. Macroscopic stress fields generated by the stressor layer and crystallography dominate the fracture behavior. Thus, in order to influence or control the faceting, further understanding
of crack propagation trends in (100)-GaAs spalling is needed.

Figure 4.1: Fracture toughness and lattice constant relation for various III-V materials

Figure 4.2: (a) Epitaxial structure (b) SEM cross-section of fracture surface showing crack propagating through AlAs layers.

4.2 Understanding Facet Behavior

Faceted crack-tip propagation results in a patterned fracture surface in (100)-GaAs spalling. Large facets remaining after exfoliation have a negative effect on waste minimization. The obtainable facet size range for spalling is not previously reported in literature. To examine faceting that occurs under the range of spalling conditions applied in this thesis, fracture surface scans are conducted using a profilometer with a 2µm-radius tip for samples presented in the spalling depth results in Chapter 3. An example of the profilometry data collected is presented for a small region in Figure 4.3 showing the periodic nature of faceting.
Facet height statistics are extracted first by recording the height difference of each nearest peak and valley across the fracture surface. Methods to extract these values are detailed in Appendix B.

![Surface Topography](image)

Figure 4.3: Selected sample area of spalling fracture surface profile

The ratio of facet size to spalling depth ranges from 0.3 to 1.0 with an average of 0.8 for the evaluated range of conditions in this thesis, showing that faceting is a significant portion of the average spall depth in Figure 4.4. Facet size corresponds to spall depth within this range, where an increase in depth leads to an increase in facet size. The stressor film deposition parameter, electroplating current density, is compared to the facet size in Figure 4.5. Facet size may be weakly correlated to the current density where the maximum facet size increases with decreased current densities. Current density correlates to the stress level in the deposited film as discussed in Chapter 3. This implies lower stress levels may lead to larger facet size maximums. Because stress was not specifically measured in this data set, variations in film properties may not be accounted for when looking at the applied current density. The measured electroplated film thickness is compared to the facet size in Figure 4.6. A general increase in facet size is seen for a thicker stressor film.

Experimental data suggests a weak correlation between stressor film deposition conditions and facet size within the small range tested. Unfortunately, because the range of film thickness evaluated is limited to 4-10 \( \mu m \) due to the overarching goal for device application, some facet size trends may not appear unless spalling conditions are tested for a larger
Figure 4.4: Average facet size in relation to spalling depth

Figure 4.5: Average facet size in relation to the current density
range. Overall, trends imply a facet size correlation to the stressor film conditions which are summarized in Figure 4.7, where facet size increases left to right along the spalling condition curves and increases away from zero following the spalling depth curve. The influence on facet size may be more apparent for larger scale processing variation outside of the range examined in this thesis.

Figure 4.6: Average facet size in relation to the average stressor film thickness

Figure 4.7: Facet size increases (in direction of arrows) from left to right with film thickness for parametric relationships defined in Chapter 3

Spalling mechanics defines that fracture occurs at a depth where the shear stress component is minimized i.e. $K_{II} = 0$ referred to as the steady-state spalling depth ($d_{ss}$). A spalling fracture in (100) GaAs propagates along $\{110\}$ planes which are oriented 45° from $d_{ss}$. Dur-

43
ing spalling propagation, the crack travels away from $d_{ss}$ until reaching a certain distance at which the crack tip changes direction by transferring onto another complementary \{110\} plane and propagates back toward this depth. This oscillating behavior remains confined to a region at a specific depth, resulting in consistently sized facets across the fracture surface. A driving force or resistive element must exist to redirect the crack growth direction, ultimately inhibiting propagation through to the film/substrate interface. The origin of this driving force is explored.

Suo and Hutchinson’s spalling model includes defined stress intensity factors for an edge loaded adherent film/substrate system simulating the stress field geometry present in spalling. In absence of theory to describe mixed-mode behavior in spalling, this theory is applied to a (100)-GaAs spalling system with necessary assumptions made. As discussed in Chapter 3, use of this theory is made by the assumption that deviations from flat crack propagation are relatively small by taking a far-field approach. It is assumed that the crack tip experiences symmetric oscillation about the steady-state spalling depth, $d_{ss}$, as shown in Figure 4.8 (a). The resistive element builds during crack growth away from $d_{ss}$ and is maximized at crack turnaround locations. This resistant element maintains crack propagation within a finite region at a specific depth. $d_{ss}$ occurs at the depth where $K_{II} = 0$, deviation away from this depth implies variation of $K_{II}$ during crack propagation. For simplicity, $K_{II}$ is viewed as a dominant resistive contribution due to the increase in the shear stress intensity as the crack is located further from $d_{ss}$. As the crack intersects $d_{ss}$, crack growth is driven by $K_I$ and $K_{II} = 0$ and it is energetically favorable to propagate without deflection. This leads to shear resistance increasing as the crack travels further from this depth and decreasing as it travels toward this depth. A schematic for the envisioned relation between $K_{II}$ and facet propagation is shown in Figure 4.8. Symmetry accounts for a repeated finite increase in $K_{II}$ away from $d_{ss}$ in both directions (toward and away from the film/substrate interface).

To look further into what happens to $K_{II}$ as the crack travels in an area of increased $K_{II}$ surrounding the steady-state spalling depth, $d_{ss}$, $K_{II}$ curves are plotted from equation 3.4
Figure 4.8: Symmetric crack-tip oscillation around the steady-state spalling depth, $d_{ss}$ (where $K_{II} = 0$) (a) with the shear stress intensity factor ($K_{II}$) increasing as the crack tip propagates away from $d_{ss}$.

for varied stressor film conditions in terms of the depth into the substrate Figure 4.9. $K_{II}$ is calculated for $3\mu m$, $10\mu m$, and $20\mu m$ stressor thicknesses which corresponds to critical residual stresses of $523 \text{ MPa}$, $289 \text{ MPa}$, and $215 \text{ MPa}$, respectively, by using the quantitative model discussed in Chapter 3. A fracture toughness, $K_{IC}$, of $0.44 MPa\sqrt{m}$ and substrate thickness of $350\mu m$ is assumed.

Figure 4.9: Shear stress intensity ($K_{II}$) for various stressor film thicknesses ($3$, $10$, and $20 \mu m$) versus the depth into the substrate from the film/substrate interface in a system undergoing spontaneous spalling. The x-intercept for each curve identifies the steady-state cracking depth, $d_{ss}$. For stressor films that are relatively thinner with higher internal stress (left), the $K_{II}$ slope is larger, indicating a higher resistive element per unit length of crack extension which may contribute to smaller facet size.

The x-intercept of $K_{II}$ defines the steady-state spalling depth, $d_{SS}$. The slope of $K_{II}$ near the $d_{ss}$ represents the gradient in shear stress intensity the crack tip experiences as it prop-
agates away from $d_{ss}$. For decreasing stressor thickness, there is a higher $K_{II}$ value for the same amount of crack propagation away from the steady-state depth, $d_{ss}$. Higher gradients in $K_{II}$ act as an increased resistance that prevent further propagation away from $d_{ss}$ and encourage the return of the propagating crack to $K_{II} \approx 0$ via faceting onto complementary \{110\} planes. Crack kinking occurring closer to $d_{ss}$ result in smaller facet size on the fracture surface. This relationship between facet size and film thickness/stress is consistent with the experimental trends shown in Figure 4.7, where a spalling fracture conducted using a thin highly stressed film comparatively exhibits smaller facet heights than a sample spalled using a thicker Ni film deposited at a lower stress.

This analysis is incomplete, lacking a quantitative relation between stress components and facet size, but represents a starting point for incorporating mixed-mode faceting into the established spalling mechanics. Description of this behavior requires a theoretical approach that considers anisotropic fracture properties and crack propagation in a mixed mode manner. In fracture mechanics, crack kinking is known to potentially be a result of dislocation build up until eventual crack tip redirection occurs at a threshold value, however, it is shown in Chapter 5 that dislocations are not generated during (100)-GaAs spalling. There is varied perception of which stress intensity components dominate during crack propagation under mixed-mode loading. Many theories assert that once a kinked crack is formed, the crack will grow under mode I loading. [51][50][49] Zhang and Wang find that under mixed-mode loading, crack growth direction is dominated by maximum resolved shear stress on favorable slip systems rather than the maximum tangential stress for single crystals. [70] In GaAs, spalling crack growth occurring along \{110\} planes is more favorable than flat crack propagation at a depth of minimal shear component. Applying Suo and Hutchinson spalling mechanics to (100)-GaAs crack kinking behavior implies that crack growth occurs under mode I with mode II acting as a resistive force to contain crack propagation within a region of lowest shear component. The largest discrepancy in applying Suo and Hutchinson mechanical theory is due to the orientation of the crack direction with respect to loading direction. Kinked crack
propagation contained within a region near the steady-state spalling depth is a peculiar result. Crack tip propagation is dominated by crystallographic orientation yet, the stress field created by the adherent film has enough influence to maintain propagation within a region around the steady-state spalling depth, $d_{ss}$, preventing propagation outside this region for sufficiently stressed films.

Further modeling to include mixed-mode propagation for materials of anisotropic fracture properties may lead to a quantitative understanding of the relationship between the facet size (point of crack tip turnaround) and the resistive influence of the stress field imparted into the substrate.

### 4.3 Controlling Facet Size

Controlled spalling of (100) GaAs incorporates several elements that are unique and not addressed by theory. In addition to mixed mode propagation, the pull to initiate the fracture in the spalling process adds additional force elements which are not included in the spontaneous process described by spalling mechanics theory. Without theoretical guidance on how to fine tune and control facet size, engineering the spalling initiation process is investigated.

In single crystalline Si, the fracture surface features resulting from a cleavage fracture can be modified empirically by the bending velocity. [71–73] Single crystal Si fractured under bending prefers to fracture along the (110) cleavage plane when under low strain energy and velocity of up to 1500 m/s. Under the same conditions with increased strain energy and velocity above 2900 m/s, it will fracture along the (111) plane. Under intermediate velocities, crack tip will facet from (110) plane onto (111) plane. This system varies significantly from that presented in this thesis, but may be an indication that influencing the speed or force administered during spalling crack initiation can have an affect on the resulting fracture surface morphology. To test this hypothesis, a jig is devised to easily vary the velocity of fracture initiation. The facet size and distribution is recorded and analyzed.

A basic jig is used to automate the spalling process. Variation in facet size was first noted when comparing a set of GaAs samples prepared by manually initiated spalling to a
set prepared using the spalling jig. Hand-spalling is conducted using minimum force, just enough to propagate the spalling fracture continuously. Spalling by jig occurs at a much faster rate. The average facet heights for hand-spalled GaAs is compared to jig-spalled samples in Figure 4.10. Samples spalled by hand have an average facet height of 5.5 to 9 \( \mu m \) and compared to jig spalled samples with facets 2 to 5.5 \( \mu m \) for similar electroplating conditions. This shows evidence that a change in pull velocity may influence the facet size.

![Figure 4.10: Average facet height for hand-spalled and jig-spalled (100) GaAs.](image)

### 4.3.1 Spalling Jig Physics

The conditions of the spalling initiation process can be controlled by variation to the spalling jig. In order to control the conditions of the pull velocity exerted on the sample during the spalling process, a jig is designed using SolidWorks and printed using a 3D extrusion printer. The jig consists of a incline where the sample (substrate side down) is held by vacuum pressure, Figure 4.11. Tape is pre-adhered to the Ni and a strip of tape with adhesive side up. A cylinder with 3\( in \) diameter and 2.5\( in \) width is rolled down the incline (initiated by gravity) adheres to the tape which applies a force to the Ni film pulling and spalling GaAs along with the Ni film. Figure 4.12 shows an example ramp configuration with spalling jig and attachment of two extension pieces.

Kinematics can be used to estimate the pull force and velocity the jig exerts on the sample during spalling initiation and identify what parameters can be changed to affect the
pull process, Figure 4.11. The total kinetic energy of the ramp system is

\[
\frac{1}{2}mv_0^2 + \frac{1}{2}I\omega^2 = \frac{1}{2}(k + 1)mv_0^2; \quad k = \frac{I}{mR^2}
\]  

(4.1)

where \( I \) is the moment inertia about the center of mass of the cylinder, \( m \) is the mass of the cylinder, \( v_0 \) instantaneous velocity of the center of mass at the bottom of the ramp, \( \omega \) is the rotational velocity, \( R \) is the radius of the cylinder. Energy is conserved when the cylinder does not slip so the total kinetic energy must equal the change in its potential energy,

\[
\frac{1}{2}\left(\frac{I}{mR^2} + 1\right)mv_0^2 = mgy,
\]

(4.2)

where \( y \) is the height of the ramp, and \( g \) is gravity. From this, we can solve for the instantaneous velocity \( v_0 \) at the bottom of the ramp,

\[
v_0 = \sqrt{\frac{4}{3}gy}.
\]

(4.3)
Figure 4.13: A pull force perpendicular to the incline is applied to the sample by cylinder in the spalling jig.

The pull force applied to the sample by the cylinder is perpendicular to the incline plane of the spalling jig as shown in Figure 4.13. Acceleration of the sample is equal to the centripetal acceleration of the cylinder, \( a_c \), which is used to determine the pull force experienced by the sample,

\[
F = ma_c = m \frac{v_0^2}{R} = \frac{4}{3R}mg. \tag{4.4}
\]

where \( m \) is the mass of the sample. Pull force, a function of acceleration, is increased by increasing the tangential velocity of the cylinder. The velocity can be increased by increasing the ramp height.

4.4 Controlled Spalling Velocity

The velocity of the cylinder at the sample is measured experimentally while changing the initial ramp height position and the weight of the cylinder. Cylinders of weight 587g and 285g are recorded by video. Three trials each at starting ramp height of 5mm, 21mm, 37mm, 54mm, and 70mm are recorded. The ramp height is measured as the difference between the initial height of the cylinder/ramp interface and the point of first contact of the cylinder with the sample, \( y \), in Figure 4.11. Video is analyzed by noting the distance traveled by the cylinder in two frames. To approximate the instantaneous velocity of the cylinder at the sample, measurements are recorded from just at and before the sample’s stationary position.
Through use of the spalling jig, the pull velocity can be varied in a consistent repeatable manner by changing the ramp height. The physics of the ramp system used to spall samples shows that the pull force can be influenced by varying the velocity of the roller and that the roller velocity depends on the height of the ramp as in equation 4.4. The theoretical pull velocity is plotted against ramp height and compared to experimental roller velocity measurements in Figure 4.14. Error in the measured velocity is calculated as the standard deviation from three runs at each ramp height. The measured velocity lies just below the theoretical. The loss in velocity can be accounted for by friction and wind resistance.

![Figure 4.14: Spalling jig cylinder velocity versus ramp height](image)

Velocity effects on spalled samples are compared by electroplating three samples each under identical conditions of 160mA/cm² for 78s using the electroplating jig and Ni Watts chemical composition as previously described in Chapter 2. Each sample is spalled using the same cylinder of weight 285g. Cylinder starting points are varied at 5mm, 37mm, and 70mm ramp height. To measure the fracture surface features, a profilometer with 2µm-radius tip performs a line scan across the center of each of the remaining faceted wafers after spalling. Facet information from a length of 8mm in the center of each sample is used for analysis. This excludes areas that may be influenced by edge effects during spalling.

Samples electroplated at consistent conditions were spalled using a roller released from ramp heights of 70mm, 37mm, and 5mm. To examine the roller velocity’s effect on facet
Figure 4.15: Cumulative distribution plot for facet height spalled by roller of varied velocity height and distribution, the cumulative fraction is plotted against facet height in Figure 4.15. The sample pulled at the highest roller velocity, 0.85\(m/s\), shows a facet height distribution from about 3.5\(\mu m\) to 6.5\(\mu m\) compared to the sample spalled at the lower roller velocity, 0.20\(m/s\), with a facet height distribution between 4\(\mu m\) and 8\(\mu m\). It is sensible that the mechanics of the pull during a controlled spalling fracture affect the surface morphology. A controlled spall does not propagate spontaneously and needs a continuous pull force to propagate the crack tip across the sample. In a subcritical spalling system, fracture is initiated at each infinitesimal region across the sample. This leads to the notion that the pull speed may take a role in the crack stability during growth. From the experimental results, the facet size can be affected to a small degree by variation in the spalling pull velocity exerted on the sample. Controllable methods explored in this chapter do not have a significant affect on facet size for the range of process conditions explored. Material waste produced by the thickness of the faceted region is still an issue to be addressed for the application of (100)-GaAs spalling to solar cells or devices where material costs is a primary concern.
CHAPTER 5
SPALLED MATERIAL QUALITY AND DEVICE APPLICATION

In the previous chapter, kinked crack-tip propagation behavior during a (100) GaAs spalling fracture is discussed. Due to the faceting that occurs, there is a concern for possible damage or defect generation to occur especially in areas of abrupt directional changes. Avoidance of damage is important when applying spalling techniques to exfoliate material for use in sensitive devices. Defects such as dislocations introduce non-native recombination centers in layered epitaxial solar devices, which can decrease the open-circuit voltage and reduce the device conversion efficiency. [74][75][76][77]. If dislocations occur at the spalling interface, propagation into the epitaxial device material would degrade the performance of the processed device. Defects that occur and extend toward the substrate can negatively affect the performance of epitaxial device material grown on the remaining wafer after spallation. During epitaxial growth any dislocations in the substrate thread through the newly formed epitaxial layers. Several spall/regrowth cycles would multiply this affect inhibiting device quality control through the accumulation of defects. Microcrack generation in the spalled film is another event that can affect the performance of a processed solar device by directly impacting the solar cell dark current resulting in open-circuit voltage (VOC) degradation. [37]

If extended damage, dislocations, or cracks occur in spalled material, it shows as performance degradation in the spalled device. Spalling has been used to remove devices from Si and Ge substrates at various thicknesses with no significant performance degradation compared to non-spalled devices. [33][31][17][36][34] To date, no work has been done to study the effects that a highly faceted (100)-GaAs spall has on device performance. Unlike previous spalling efforts on other substrates and orientations, this device features faceted crack propagation that has greater potential to generate dislocations and microcracks into
the device. A high performance device sensitive to this would reveal defects by electronic performance degradation. Additionally, minimizing the amount of waste material is key for use with GaAs to lower costs from material consumption. However, spalling while trying to minimize the amount of Si material removed or the distance between the epitaxial device/Ge substrate interface and spalling location has not been a focus in the spalling application literature.

It has been observed in Si that crack tips can propagate without dislocation generation as a brittle atomically sharp fracture at low temperatures (below the brittle-ductile transition, BDT, temperatures, 500 to 800°C) [78][79]. Before a development of a more refined definition, the BDT temperature in semiconductors was associated with the initial temperature at which dislocation generation occurred from the front of the crack tip during fracture. [79] For GaAs, the BDT is 300 to 380°C. [80] Therefore, crack propagation at room temperature is likely not to generate dislocations. However, spalling in (100) GaAs creates an atypical crack path compared to a cleavage fracture with the occurrence of significant changes in direction.

In this chapter, the faceted surface is analyzed by transmission electron microscopy (TEM) to assess the integrity of the spalled material specifically looking for dislocations at crack tip pivot regions. Additionally, the electrical performance of III-V single junction solar cells spalled from their (100)-GaAs growth substrate are characterized as an indirect measurement of any physical damage that may have occurred during the spalling process.

5.1 Spalled Material Analysis

For dislocation analysis, two samples are spalled by jig at 15 mm ramp height after electrodeposition of Ni at 30mA/cm² for 13 minutes. Material analysis of the faceted GaAs surface is initiated by the removal of thin sections (35µm in length) from a spalled film and the remaining wafer by focused ion beam (FIB) machining. TEM specimen preparation was achieved by ”lift-out” method using a FEI Helios dual column FIB. The region of interest is located by the FIB imaging capabilities and a protective platinum layer is deposited to
prevent damage to the area that can occur during milling and imaging, Figure 5.1(a). Two trenches are milled on either side of the platinum using a large ion beam current for fast milling, Figure 5.1(b). A smaller beam current is used to further thin the central membrane on either side of the platinum to a thickness of 1-2\(\mu m\), Figure 5.1(c)(d). Three cuts are then made through the sample to frame the area of interest, Figure 5.1(e). A probe arm is attached to the edge of the membrane by deposition of platinum between the probe and sample, Figure 5.1(f). The remaining area attached to the membrane is milled away and the specimen is moved by the probe to a mount for thinning, Figure 5.1(g). The specimen is thinned to be electron transparent, Figure 5.1(h).

Figure 5.1: Example of TEM specimen preparation steps by focused ion beam (FIB) removed from across facets of spalling fracture surface for dislocation analysis.

Three thin specimens are removed from the two spalled samples. One specimen is removed across the facets from the remaining wafer after spallation and two specimens are removed, one from each spalled film in an orientation perpendicular to the facets and in the trench parallel to a facet, as depicted in Figure 5.2. TEM and STEM imaging was carried out at 200 KeV with a Philips/ FEI CM200 transmission electron microscope and FEI Talos, respectively. Dislocation density is calculated by recording the total number of dislocations intersecting the cross-sectional area inspected in the three samples. Specimens are evaluated from multiple angles using bright and dark field imaging in addition to annular dark field (ADF) incoherent imaging which is useful for z-contrast imaging. [81][82][83]
Figure 5.2: Thin samples removed from across the facets (a) and along a facet trench (b) by focused ion beam machining for dislocation analysis.

Figure 5.3: GaAs sample diffraction pattern (upper left) and 4200X magnification TEM all beams (upper right), bright field (lower left), and dark field (lower right) images of a facet region on the spalled film.
Figure 5.4: 32000X TEM image of facet valley GaAs/Pt interface by bright field (upper) and all beams (lower).

Figure 5.5: TEM images of area removed along facet trench removed from a spalled (100) GaAs facet valley at 4200X bright field (upper left), 42000X dark field (upper right), 13000X dark field and 30000X dark field (lower right).
Figure 5.6: STEM images of facet valley cross-section removed bright filed (upper left), dark field (upper right), high angle annular dark field (lower left) and dark field (lower right)
GaAs and other III-V compounds have a zincblende structure which consists of two interpenetrating FCC sublattices with each occupied by a Group III or Group V element. Seen experimentally and theoretically, dislocations move on slip planes (widely spaced planes with a large density of atoms per area). [84] The operative slip system in a diamond cubic is a/2 <110> {111}. [78] It follows that in GaAs the majority of any dislocations generated should lie along <110> directions on {111} planes. [85] Based on the orientation of the lifted out specimens, it is hypothesized that dislocations emanating from the crack tip kink region would show as a series of lines that move along <110> away from the facet and dotted lines that show along {100} propagating in <110>.

Collected STEM images at 4200X magnification are shown of a facet region inspected in the spalled film (Figure 5.3). Bright field and dark field images at 32000X magnification are shown where GaAs is on the left (Figure 5.4). No dislocations or indication of damage or strain is seen. Also in the spalled film, STEM shows no dislocations or interruptions in the sample removed from a facet trench region imaged at 4200-30000X magnification (Figure 5.5). The sample analyzed from a facet region lifted from a traverse cut on the remaining (100) GaAs wafer after spallation has no dislocations as well, (Figure 5.6). Images presented are bright field, dark field and high angle annular dark field which show a range between z-contrast, transmission and topological features. It is apparent in some images that residual strain may have resulted from the spalling event along the facet slope. It appears that this is a low strain energy below the threshold required for dislocation generation. From cumulative examination of these three regions, it is asserted that dislocations are not readily produced by faceted spalling crack propagation in (100) GaAs. Zero dislocations were found in the area examined. An approximate dislocation density value is calculated for the existence of one dislocation in the observed cross-sectional area of $10^5 / cm^2$. This implies that the actual dislocation density does not exceed this value. Yamaguchi and Amano calculated the relation between solar cell performance perimeters and the dislocation density under AM0 for AlGaAs/GaAs heteroface solar cells, as shown in Figure 5.7. They show the onset
of performance degradation in this junction occurs at a dislocation density above $10^5/cm^2$. Additionally, TEM and STEM imaging of the facet shape seen in Figure 5.3, Figure 5.4, and Figure 5.6 reveals a unique feature. The facets do not appear as sharp pivot points where the crack experiences an abrupt change in direction. Instead the crack tip appears to gradually alter its path during propagation creating more of a parabolic-like shape in the area as opposed to a sharp angular feature.

Figure 5.7: Calculated solar cell parameters under AM0 illumination for AlGaAs/GaAs thin-film solar cells as a function of dislocation density in the GaAs layer. [77]

Between the morphology of the facet, the absence of observed dislocations, and the evidence that dislocations can be absent for low temperature fracturing in brittle semiconductor materials, it can be assumed that energy in a (100) GaAs spalling fracture is not sufficient to generate dislocations during crack propagation nor is it necessary for dislocations to be emitted to propagate the crack tip through a crystallographical mis-oriented spalling system.

5.2 Spalling Photovoltaic Devices

The quality of the material after spalling is further tested by exfoliation of a sensitive photovoltaic device using spalling principles. A twofold attempt was made; the first of which served as a proof of concept by performance of a spalling fracture deep into the substrate
before controlled spalling depth was refined. In industrial application, one is interested in spalling primarily for the reduction of waste. A more precise spalling depth is preferred, where fracture occurs deep enough to occur below the device yet shallow enough to conserve material. In the second attempt the spalling fracture is controlled and occurs near the device/wafer interface to demonstrate the feasibility of wafer reuse.

For the initial set of devices tested, inverted single-junction GaAs homojunction solar cell material with InGaP cladding layers is grown on a 350µm-thick p-type (100)-GaAs wafer by metal-organic chemical vapor deposition (MOCVD) and spalled off of the substrate using an electroless Ni deposition process for the stressor film. This allowed for low stress layer deposition in the early stages of this project before reaching the ability to consistently exfoliate thin films from GaAs. As the stress/thickness relationship discussed in Chapter 3 implies, a thick stressor layer is needed to spall material using a very low residual stress which is easily obtainable by electroless Ni deposition. A thick (> 35µm) layer of Ni was deposited for two hours using a commercially available electroless Ni kit. The device and the processing steps are shown schematically in Figure 5.8. A 50nm layer of InGaP is included as a surface etch stop to protect the back contact of the device (Figure 5.8(i)). Immediately before nickel deposition, the protection layer is removed by a chemical etch in a 1:1 solution of \(HCl : H_3PO_4\) (by volume). Nickel is deposited on the device (Figure 5.8(ii)) and fracture is induced in the GaAs substrate at a depth below the etch stop in Figure 5.8(iii). Polymide adhesive film is applied to the Ni surface and used as a handle to manually peel by using a low force pull. In the initial trial, tweezers were used to grip the Ni and peel to spall the sample. After removal, the film is mounted, by use of black wax, to Si as a rigid substrate for handling and processing. It is submerged in a 1:1 solution of \(H_2O_2 : NH_4OH\) (by volume) to remove residual GaAs to the etch stop. The spalled material is then processed with Au front metal contacts, utilizing the remaining nickel layer as a back contact for the completed device (Figure 5.8(iv)). For comparison, a nominally identical epitaxial layered material composition is subsequently grown. This cell is not spalled from the substrate, but rather
the substrate is chemically etched away. Electroplated Au is used for both the front and back contacts. Devices have an area of $0.10cm^2$. Current-voltage characteristics are measured in a calibrated XT-10 solar simulator under AM1.5G conditions [86] to assess the quality of the spalled devices. Processed spalled devices are shown in Figure 5.9. Photovoltaic devices are removed from the GaAs substrate by spalling deeply enough to ensure that no facets reach the level of the devices. Spalling depth is over $50\mu m$ as measured in samples processed under similar conditions. Actual spalling depth for this sample is unknown because depth measurements require destructive cross-sectioning methods.

![Diagram](image)

Figure 5.8: Device and etch stop layers are epitaxially grown on a GaAs substrate (i). Stressed nickel is electroplated onto the epitaxial surface (ii). The device is removed from the substrate by controlled spalling (iii). Excess GaAs is removed and the device is processed with electrical contacts for testing (iv). Direction of illumination is indicated with arrows.

![Image](image)

Figure 5.9: Spalled device material mounted on a Si wafer for stability and processed with metallization with the Ni stressor layer as the back contact and reflector.

Current-voltage characteristics of spalled and traditionally processed devices are compared in Figure 5.10. Values for standard solar cell metrics are listed in Table 5.1. Initial tri-
Figure 5.10: Current-voltage characteristics for devices processed on deep spalled and non-spalled material. No significant degradation outside of run-to-run variation is observed.
Table 5.1: Averaged current-voltage characteristics for spalled deep into the substrate and non-spalled single junction GaAs solar cells

<table>
<thead>
<tr>
<th></th>
<th>Traditional</th>
<th>Spalled</th>
<th>Percent change</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{OC} \ (V)$</td>
<td>0.972</td>
<td>0.940</td>
<td>-3.3</td>
</tr>
<tr>
<td>$J_{SC} \ (mA/cm^2)$</td>
<td>17.64</td>
<td>17.15</td>
<td>-2.8</td>
</tr>
<tr>
<td>Fill factor (%)</td>
<td>76.89</td>
<td>80.49</td>
<td>+4.6</td>
</tr>
<tr>
<td>Efficiency (%)</td>
<td>13.18</td>
<td>12.97</td>
<td>-1.6</td>
</tr>
</tbody>
</table>

als show an average efficiency of 13.0% for spalled devices compared to 13.2% for non-spalled devices. Spalled devices show less than 1.7% efficiency degradation and a 4.7% increase in fill factor compared with non-spalled devices. $V_{OC}$ values are 0.972V and 0.940V for devices on non-spalled and spalled material, respectively. Parameters are within run-to-run device variation, showing no significant degradation in the electrical performance properties ($V_{OC}$, $J_{SC}$, fill factor, efficiency) as compared to devices processed from non-spalled material. Initial devices presented here and devices in the literature with reported spalling depth experience fracture propagation occurring very far from the device/substrate interface. If defects were to occur near the crack-tip, they may not show up in these deep spalling trials. For that reason, additional trials are completed once the film deposition and spalling process is established and repeatable.

In order to produce an exfoliated device, the desired spalling depth needs to be determined while considering the additional depth needed for the size of the facets. If the etch stop layer is penetrated during crack propagation, the GaAs etchant will attack the device layers below, with subsequent processing etchants affecting multiple device layers. Nomarski images are taken of such devices after the excess GaAs is etched away following spalling, Figure 5.11. This example shows rectangular etch pits running in parallel pattern across the surface, resembling the periodicity of facet peaks. This implies the crack penetrated the etch stop. Another possible cause implied by the rectangular shape is microcrack formation at the location of crack-tip kinking. If micro cracks are present in this sample, handling could be a
contributing factor. In a sample with relatively large facet size, there will be a higher stress concentration in the facet trenches on the surface of the spalled film when the sample is flexed. Existence of microcracks near the device material will show as performance degradation. For the second device spalling trial, spalling depth is specifically performed very near to the device material to indirectly test the material quality by electrical performance characterization at a more ideal spalling depth.

![Nomarski images of processed device surface after spalling at an undesirable shallow depth.](image)

A high performance GaAs rear heterojunction device grown in an inverted manner [9] with InGaP cladding layers and an AlGaAs back contact layer is grown on a 350μm-thick p-type (100)-GaAs wafer by metal-organic vapor phase epitaxy (MOVPE) and spalled off of the substrate. The general growth/spalling processing steps are consistent with previous device trials shown schematically in Figure 5.8. For comparison, a nominally identical cell is subsequently grown and its substrate is chemically etched away as for the control in the first device trials. Current-voltage characteristics are measured in a calibrated class A solar simulator under AM1.5G conditions at 1000W/m² to assess the quality of the devices. The Ni stressor layer is deposited by electrodeposition using bath chemistry and methods as described in Chapter 2 at a current density of 30mA/cm² for 13 minutes. Photoresist S1813 is applied over the Ni just after electroplating while still in the electroplating jig that masks the edges of the sample to protect the Ni during the edge etching procedure. Once dry, the sample is removed and heated on a hot plate at 80°C for 1.5 minutes to further set the photoresist. Approximately 10μm of III-V material is removed around the edge of the Ni
by alternate etching using 3:4:1 composition by volume of $H_3PO_4 : H_2O_2 : H_2O$, 2:1:10 by volume of $NH_4OH : H_2O_2 : H_2O$, and 37% HCl to remove the alternating layers of AlGaAs, InGaP, GaAs, and InGaAs in the epitaxial structure. Spalling is completed using the jig as described in chapter 4 at a ramp height of 70 cm. Actual spall depth is unknown due to destructive nature in spalling depth measurements. However, bare (100) p-type GaAs samples electroplated and spalled under the same conditions have a minimum spalling depth of approximately 10 $\mu$m. Processed devices have an area of 0.25 cm$^2$. The traditionally processed device uses a Ni back contact to mimic the spalled device which utilizes the Ni stressor layer as the back contact and reflector. Devices do not have an anti-reflective coating (ARC) on the surface. Electronic characteristics are compared in Figure 5.12. No difference is seen between the devices. A table of electrical performance properties are summarized in Table 5.2. Devices are high performance with a $V_{OC}$ of 1.070 and 1.072 for traditionally processed and spalled devices, respectively. Samples exhibit conversion efficiencies just over 18%. With an ideal ARC on the surface, devices can reach upwards of 23-25% efficiencies.

[9] High performance devices such as these are very sensitive to defects. It is noted that other devices have been successfully removed from Si and Ge where the cleavage plane was oriented with the steady-state spalling depth. This reported device results from (100) GaAs spalling, non-cleavage plane spalling. Faceting in spalled (100) GaAs could represent an additional degradation mechanism, but our results indicate that spalling is a viable process to remove thin films from (100) GaAs, and that the stress and handling associated with this process does not significantly degrade material properties or device performance.

Table 5.2: Current-voltage characteristics for spalled near device interface and non-spalled single junction GaAs solar cells

<table>
<thead>
<tr>
<th></th>
<th>Traditional</th>
<th>Spalled</th>
<th>Percent change</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{OC}$ (V)</td>
<td>1.070</td>
<td>1.072</td>
<td>+0.19</td>
</tr>
<tr>
<td>$J_{SC}$ (mA/cm$^2$)</td>
<td>20.4</td>
<td>20.2</td>
<td>-0.98</td>
</tr>
<tr>
<td>Fill factor (%)</td>
<td>84.4</td>
<td>84.1</td>
<td>-0.36</td>
</tr>
<tr>
<td>Efficiency (%)</td>
<td>18.4</td>
<td>18.2</td>
<td>-1.09</td>
</tr>
</tbody>
</table>
5.3 Discussion

Dislocations were not observed in the spalled material and the absence of electrical performance degradation of epitaxial device material after spalling exfoliation implies the absence of other material damage. Using a spalling fracture is a viable process for sensitive device exfoliation. Additionally, very low defect generation during a spalling fracture implies that nearly all the plastic strain energy goes into fracture propagation and no loss occurs from defect generation.
Figure 5.12: Current-voltage characteristics for devices processed on material spalled and non-spalled material. No significant degradation is observed.
Spalling fracture was examined for the purpose of understanding the physical influences pertinent to current spalling applications in single-crystal semiconductors. Spalling is intended for incorporation as a processing step in solid state device fabrication to exfoliate epitaxial devices or semiconductor material from the substrate to enable wafer reuse. This has been successfully applied to Ge and Si substrates for device processing. Interest in (100) GaAs exfoliation is due to the high material quality resulting in low-defect epitaxial growth of III-V based devices. This thesis study is focused on using spalling to exfoliate single junction III-V photovoltaic device material from (100) GaAs while maintaining a minimal amount of waste material.

6.1 Modeling Faceted (100) GaAs Spalling

Minor adjustments are made in Suo and Hutchinson’s material spalling mechanics in Chapter 3 to quantitatively determine spalling conditions. In the absence of a spalling theory that accounts for mixed mode fracture propagation, a far-field approach is assumed based on the general forward propagation occurring parallel to the film/substrate interface. Crack tip oscillations are maintained within a region shown by experimental results in Chapter 3 to be located at the steady-state spalling depth predicted by theory. Experimental critical spalling conditions in (100) GaAs define an “effective fracture toughness” value for (100) GaAs of $\geq 0.55 MPa$ for use in spalling mechanics. This artificial adjustment accommodates for the increase in surface energy required to release material bonds in a faceted spalling fracture as opposed to a flat planar fracture. We find in Chapter 5 that faceted spalling crack propagation occurs in a curved non-abrupt manner at the crack tip pivot regions and that a faceted spalling fracture does not lead to emission of dislocations. This implies no plasticity in fracture and no energy loss due to dislocation generation, adding validity to the
estimation derived from spalling fracture mechanics for a faceted fracture. It is asserted in this thesis that theoretical prediction serves as the upper boundary in the spalling process window below which controlled spalling can occur by applying a pull force and above which a spalling fracture occurs spontaneously.

6.2 Controlling the Spalling Process and Influencing Fracture Surface Morphology

Fracture surface morphology can change by variation of stressor film thickness values at a specific residual stress value. In Chapter 2, the process of controlled spalling was optimized to only include initiated samples that have favorable surface morphologies. A optimized result in (100)-GaAs spalling is defined as an initiated spall that results in a continuous film with a consistent faceted surface where facet size variation is minimal. This result occurs at energies just below occurrence of any spontaneous spalling, as defined by the spalling mechanics in Chapter 3. Initiated spalling at conditions too far below the spontaneous spalling threshold result in undesirable surface morphologies and discontinuous films. In addition to the stressor film parameters having some effect on the facet size, it is found that the pull velocity during spalling propagation also influences the facet size. An automated spalling jig was constructed to consistently apply a pull force to peel and initiate a spalling fracture. It is found and discussed in Chapter 4 that facet size can be reduced by increasing the pull velocity.

6.3 Application of Spalling to Thin Film Device Exfoliated

III-V based single junction solar cell material was exfoliated from (100) GaAs substrates without indication of degradation compared to similar traditionally processed devices. These are the first reported devices exfoliated by spalling from a (100) GaAs substrate as well as the first devices to be removed from a substrate with the additional challenge of a mismatch between the cleavage plane in the material and the steady-state spalling plane where the spalling fracture predominately travels along the cleavage planes which are not parallel to
the substrate surface, resulting in faceted crack propagation. Spalling was performed near the device/substrate interface without evidence performance degradation.

6.4 Technological Outlook

Facets cannot be significantly reduced using the methods discussed in Chapter 4 which include the variation of the stressor film deposition conditions or the spalling pull velocity for the range of spalling depths produced in this thesis. Facet size is larger than desired for waste minimization in a wafer reuse procedure, resulting in > 5μm in material consumption per spalling lift-off. To be a viable process for photovoltaic (100)-GaAs substrate reuse, methods outside of this study to mitigate facet size need to be established or the significant reductions in growth costs are needed to make this amount of material waste acceptable. Alternatively, establishing growth methods for epitaxial device structures onto substrates with the cleavage plane oriented parallel to the film/substrate interface, such as (110) GaAs, could reduce material consumption during spalling. Currently, epitaxial growth on (110) oriented GaAs presents new challenges for dopant integration and has not been developed for III-V device structures. Spalling mechanics proves to be accurate in describing conditions needed to exfoliate GaAs. It is likely that these principles can be used to control the spalling depth that occurs in other mildly anisotropic semiconductor materials, as well. Additionally, in Chapter 5, the spalling fracture was found not to produce damage in the semiconductor materials during propagation including during the occurrence of faceted crack growth. Sensitive devices can be removed by spalling without experiencing performance degradation. In alternative applications that do not have the requirement for waste minimization or have cleavage planes that are oriented more favorably, spalling may be a useful method for quick exfoliation of thin flexible films.
APPENDIX A - TECHNICAL DRAWINGS FOR SPALLING AND ELECTROPLATING

JIG CONSTRUCTION

Technical drawings on the following pages outline the electroplating and spalling process jig design constraints. All parts are created in ABS material using 3D extrusion printing.

A.1 Electroplating Jig

Jig assembly used for electroplating samples include a backing plate, a cover, and arms to attach the jig to the anode. Specifications for assembly of the electroplating jig is included in Figure A.1. The backing plate is printed at 100% fill to prevent leaking of the electroplating chemicals into the part while in use. Anode holding arms are affixed to the backing plate by the use of acetone and pressure fitting them together in place until dry. Detailed specifications are shown for the backing plate, anode holding arms, and cover piece in Figure A.2, Figure A.3, and Figure A.4, respectively. Wires are inserted into the three holes to allow for front or back contact electroplating. The front contact electroplating configuration is utilized in this thesis.

A.2 Spalling Jig

The spalling jig assembly consists of a main jig part and an extension piece that can be printed in multiples extending the length of the ramp. Assembly configuration is shown in Figure A.5. Detailed specifications for the main spalling jig part is shown in Figure A.6. This consists of a hole that is tapped after printing for connection to a vacuum pump to hold the wafer sample in place during spalling. Specifications for the extension piece are shown in Figure A.7. The extension is designed to fit in place with the main part and additional extension parts. For this thesis two extensions were used to achieve appropriate ramp length. Vertical through holes in the main spalling jig part and extensions parts are tapped to insert a bolt for height adjustment. This method allows for the desired height to be achieved.
Figure A.1: Electroplating jig assembly.
Figure A.2: Electroplating jig part: backing plate
Figure A.3: Electroplating jig part: anode holding arms
Figure A.4: Electroplating jig part: front window cover
Figure A.5: Spalling jig assembly
Figure A.6: Main spalling jig
Figure A.7: Extension ramp for spalling jig
Fracture surface morphology data are collected by profilometer scans recording 4000 points per 1mm. A range of 8mm length across the surface is selected between position 3 and 11 for the selected sample shown here. Maxima and minima height positions are extracted for this range. Maxima and minima are shown as red and blue point overlays on the collected surface profile. A closer view of the faceted surface with the highlighted

\[
\begin{align*}
3 & / 0.0025 + 1 \\
11 & / 0.0025 + 1 \\
12001 & \\
44001 & \\
\end{align*}
\]

on the collected surface profile. A closer view of the faceted surface with the highlighted

\[
\text{ListLinePlot[dataset,Prolog→PointSize[Large],Red,Point[peaks],Blue,Point[valleys],Frame→True,FrameLabel→"Surface position (mm)","Height (um)"]}
\]
Facet heights are taken as the difference between neighboring maxima and minima.

The resulting facet size array can be seen in relation to the surface position by
For three samples created under varied spalling pull velocity conditions, the cumulative facet height distribution is calculated and plotted by using the cumulative distribution function.

```plaintext
t18 = EmpiricalDistribution[facets18];
t19 = EmpiricalDistribution[facets19];
t21 = EmpiricalDistribution[facets21];

Plot[{CDF[t18, x], CDF[t19, x], CDF[t21, x]}, {x, 0, 10}, PlotRange -> All,
PlotLegends -> "Expressions", Frame -> True, FrameLabel -> Style["Facet height (µm)", 16,
FontFamily -> "Arial"], Style["Cumulative Fraction", 16, FontFamily -> "Arial"],
FrameStyle -> Directive[GrayLevel[0], FontSize -> 14], GridLines -> Automatic,
GridLinesStyle -> {Dotted, Gray}, {Dotted, Gray}], PlotStyle -> Thickness[Large]]
```
REFERENCES CITED


