# Novel Polishing Process to Fabricate Ultra Low Thickness Variation Diamond Substrates For Next Generation Beam Tracking Detectors

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Gaithersburg, MD

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Innovative CMP Solutions

# Outline

- Introduction- Sinmat
  - Sinmat-overview
  - Sinmat Technology & Products
- SBIR Project
  - Objectives
  - Proposed Work
  - Results
- Commercialization
  - Customized solutions for broader acceptable markets
- Accomplishments

# Introduction -Sinmat

# Overview: Sinmat Inc.

- University of Florida Spin-off. Founded: 2000 & Operational: 2002
- Global market leader in polishing of ultra hard materials (e.g Silicon Carbide, GaN, Diamond, Sapphire)
- 80% of SiC global polishing market; (All Major Substrate Manufacturing Companies)
- > 1000 MT/month slurry manufacturing capability.
- Winner of four R&D 100 Awards 2004  2005, 2008 & 2009
- Employees and consultants: 30 (6 PhDs,  5 Masters)
- 20,000 sq.ft R&D and manufacturing space
- Approx 75% revenue from commercial products : Growth rate > 50%/year.
- Developing CMP centric technologies: 30 patents

2004, 2005, 2008, 2009

# Sinmat's Core Competency

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**Develop A High Quality, Affordable Supply Of Innovative Surface Preparation-Promoting Products To Serve A Variety Of Markets**

*Chip Mfg Markets*
- Intel
- Samsung

*Power Device Markets (SiC)*
- Cree
- RF Micro
- Raytheon
- Rohm

High Quality, Affordable Supply of Innovative Engineered Surface Promoting Products

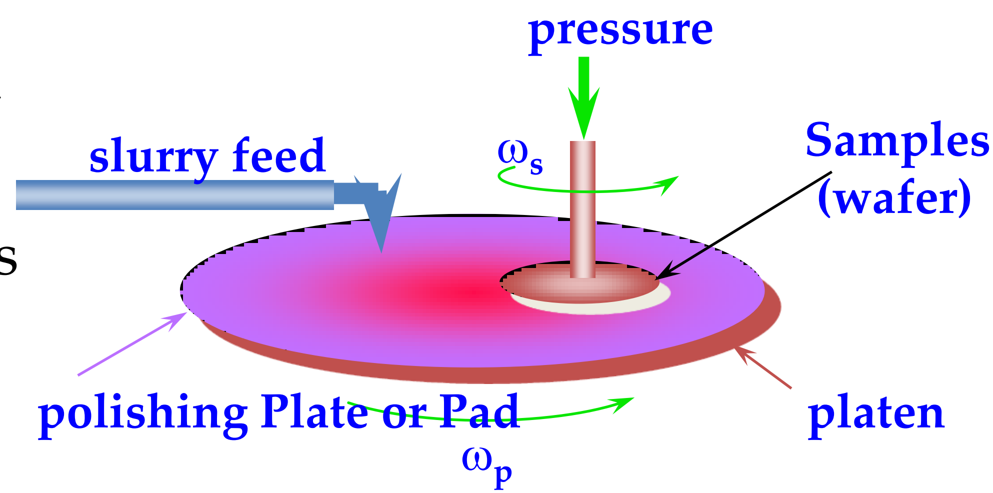
*LED Market*
- Sapphire
- AlN, GaN

*Emerging Markets (Polishing of Hard Materials)*
- Smart Phones
- Wearable Electronics
- PCD tools for Drilling
- Diamond/SiC seals ( automobiles etc)
- DOE & DoD Applications

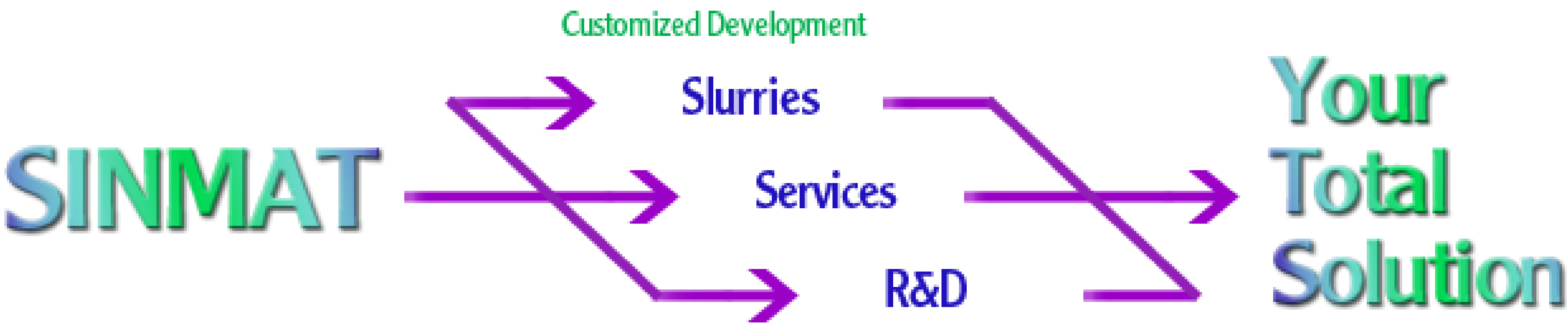
# Chemical Mechanical Polishing (CMP) Process

## Key Characteristics:

- Slurry consisting of chemicals and abrasive particles
- Platen with a plate or pad and a wafer head holding the wafer
- Planarization with simultaneous application of Chemistry (Chemical) and Force/ Friction (Mechanical).
- **Key Differences with Diamond Lapping**
  - **Use of Plate/Pad**
  - **Chemical & Mechanical Action in Polishing Process**



# Sinmat Inc




Sinmat develops products via planarization-enabled technologies for semiconductor manufacturing for computer chips, solid state lighting, power devices, and wearable electronics

Please visit www.sinmat.com

# Slurry Products & Polishing Services

## POLISHING SLURRIES & SERVICES:

- Diamond
- Silicon Carbide
- Nitrides
- Sapphire
- Patterned Sapphire Substrates
- Metals and Dielectrics & Device
- Other Customized Slurries


Atomically terraced surface
After SC final CMP (AFM)

*Epiready Polish & Improving Flatness*
*Thinning& Specific Device Polish*
*Regular wafer  Polish and reclaim*

*Sinmat has over 20 different slurry products*
*For more info please visit www.sinmat.com*

# Phase II Project

# Diamond Applications in Nuclear Physics

- High Thermal Conductivity
- Extreme Radiation Stability
- High Transparency (Optical/High Freq.)
- Excellent Electronics Properties

*Ideal material of choice for wide range of applications in nuclear Physics!!!*

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# Timeline of Diamond Growth & Polishing

**1952**
First Synthetic Diamond methods (Eversole, Union Carbide)

**1954**
High pressure, high temperature diamond growth demonstration (GE)

**1968**
Low pressure vapor solid liquid technology for diamond growth (Derjayuin, Russia)

**1981**
Consistent demonstration of low pressure CVD growth of diamond (1μm/hr) Setaka NRIM, Japan)

**1989**
Large area CVD growth of diamond company established (Diamonix)

**2002**
Ultra Nano Crystalline Diamond (UNCD) low-roughness diamond (~100 Å roughness (Krauss Argonne Lab

**2005**
High rate single crystal diamond growth ability (Carnegie Institute, Washington)

**2007**
Sales of CVD diamond plate products (Element 6, a De Beers Company)

**2009**
Super-smooth 1Å finished 100mm diamond substrates commercialized Sinmat

1950 1960 1970 1980 1990 2000 2010

# Diamond For DOE Facilities

- Beam tracking detectors
  - National Superconducting Cyclotron Lab, Michigan State (US), GSI Darmstadt Germany
- Coherent bremsstrahlung radiators for high energy polarized photon beams
  - Nuclear experiments at JLAB and elsewhere
- Neutron detectors
  - Nuclear Power Industry, Homeland Security
- Dosimetry for protons, electrons and neutrons
- Detectors for high luminosity experiments –CERN
- X-ray monochromators , Optics and X-FEL-ANL,PETRA

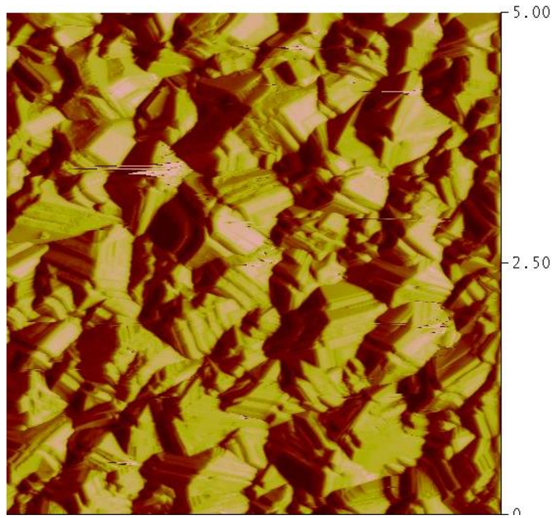
# Sinmat's Diamond Strategy

- Leverage novel diamond polishing technology to fabricate high performance diamond based devices for NP and HEP Applications
  - Diamond Detectors **(NSCL)**
  - Ultra-Thin (< 50 microns) Diamond radiator crystals
  - Diamond X-ray Optics
  - High thermal conductivity substrates

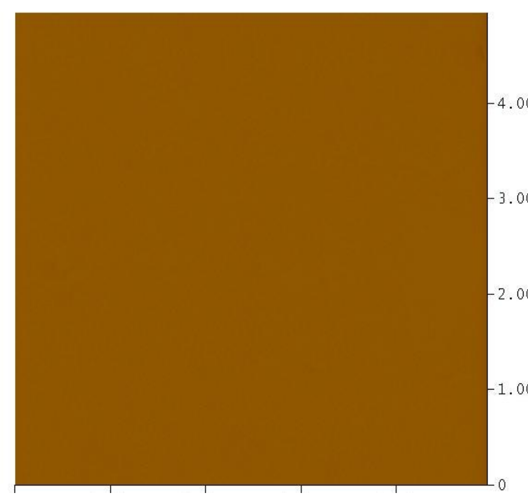
- Work collaboratively with diamond technology providers *( e.g Element Six) and National facilities* to integrate diamond based products

# Roughness Reduction of Micro Crystalline samples with RCMP

- Before Polishing
- After Polishing




Img. Rms (Rq) 81.127 nm
Img. Ra 64.822 nm



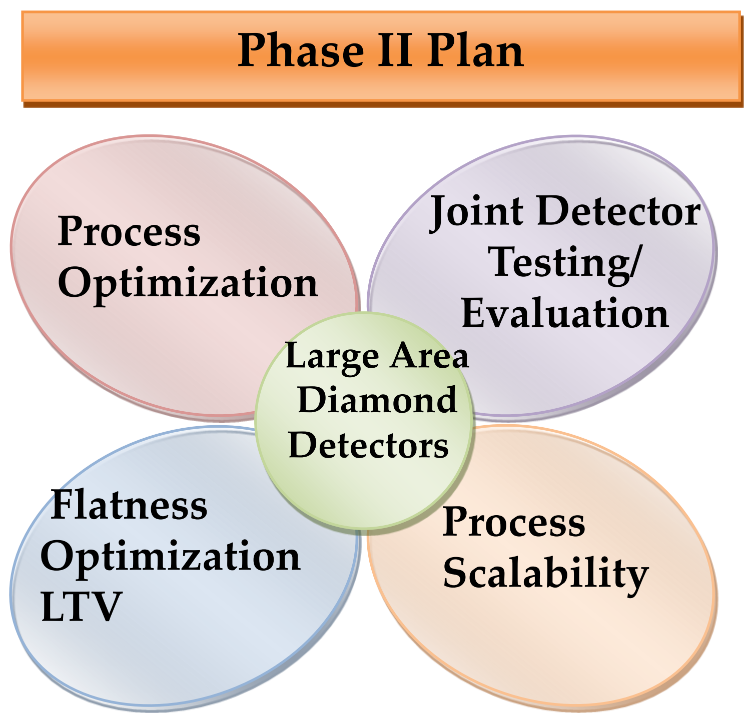

Img. Rms (Rq) 0.335 nm
Img. Ra 0.222 nm

***Prior to Project***

# SBIR Phase II Project Objective

Use RCMP process to fabricate and evaluate diamond based detectors for high energy beam tracking applications

- Optimize RCMP process
- Test & evaluate RCMP process for Detector fabrication



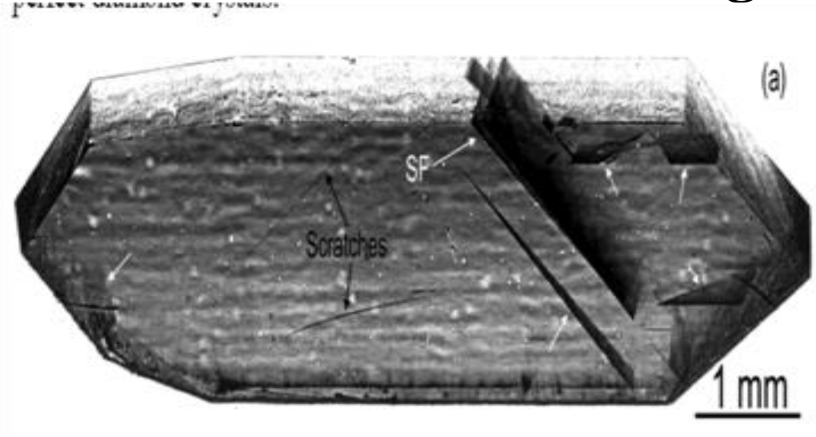
# Ultra-Hard Materials: Polishing Challenges

| Materials | Hardness Knoop ($Kg/mm^2$) | Chemical Action |
|---|---|---|
| **Silicon Carbide** | **2150 - 2900** | **Inert** |
| **Gallium Nitride** | **1580 - 1640** | **Inert** |
| **Sapphire ($Al_2O_3$)** | **2000-2050** | **Inert** |
| **Diamond** | **8000 - 10000** | **Inert** |

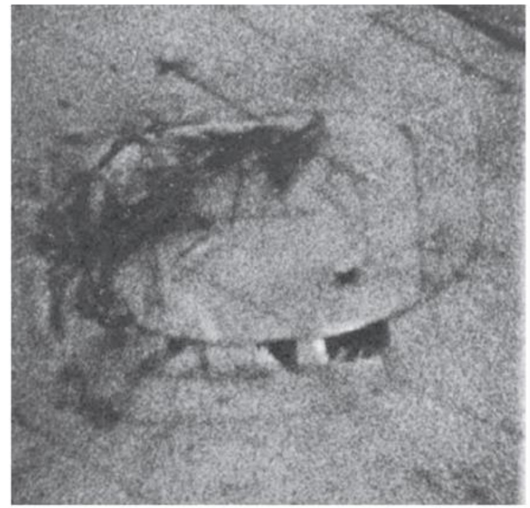
- **Polishing rate is slow**
- **Surface/Sub-surface Damage**

# Problem

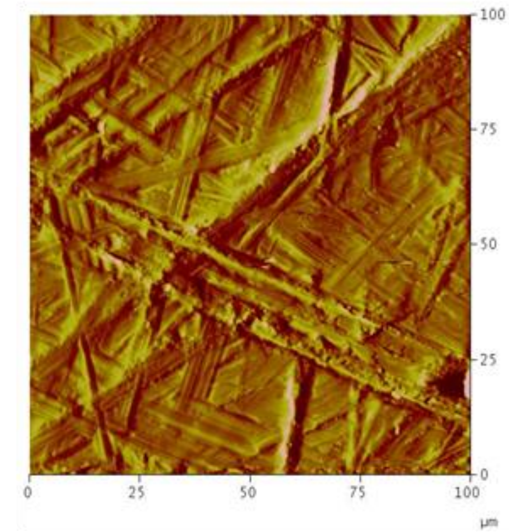
## Surface Polishing




X-ray topograph of single crystal diamond showing scratches



Cathodoluminescence image of subsurface damage caused due to diamond based polishing

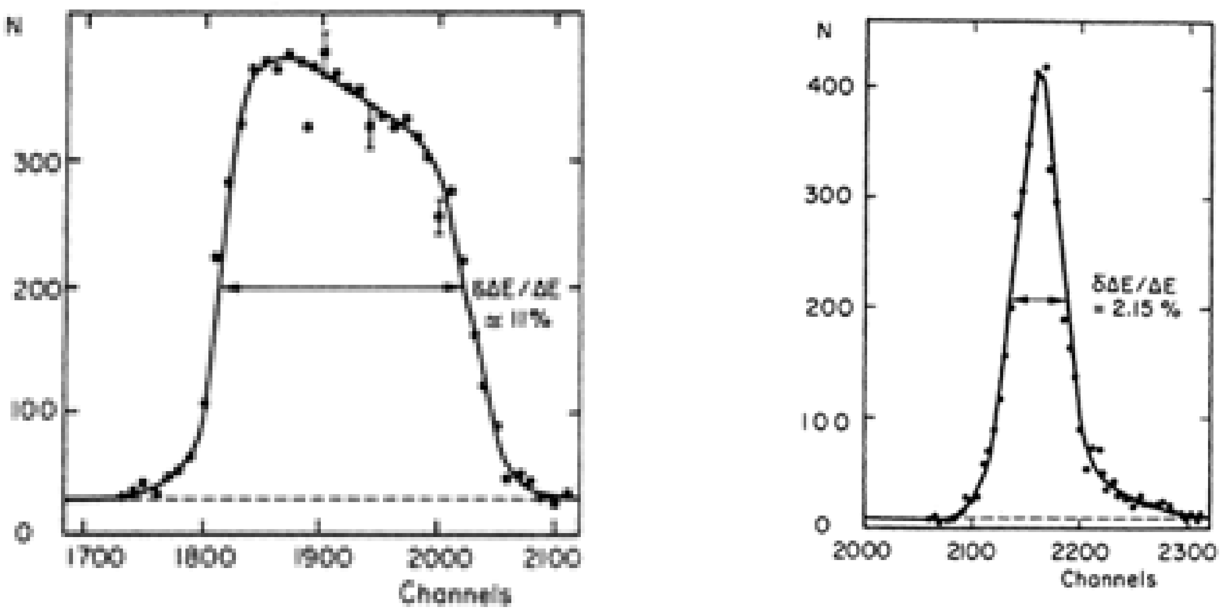



AFM Picture shows surfaces scratch on diamond

a) Xiang Rong Huang, Albert T. Macrander, 10 International Conferences on Synchrotron Radiation Instrumentation
b) Nature Letters M.Casy, Wilks 1973 vol.239 Page 394

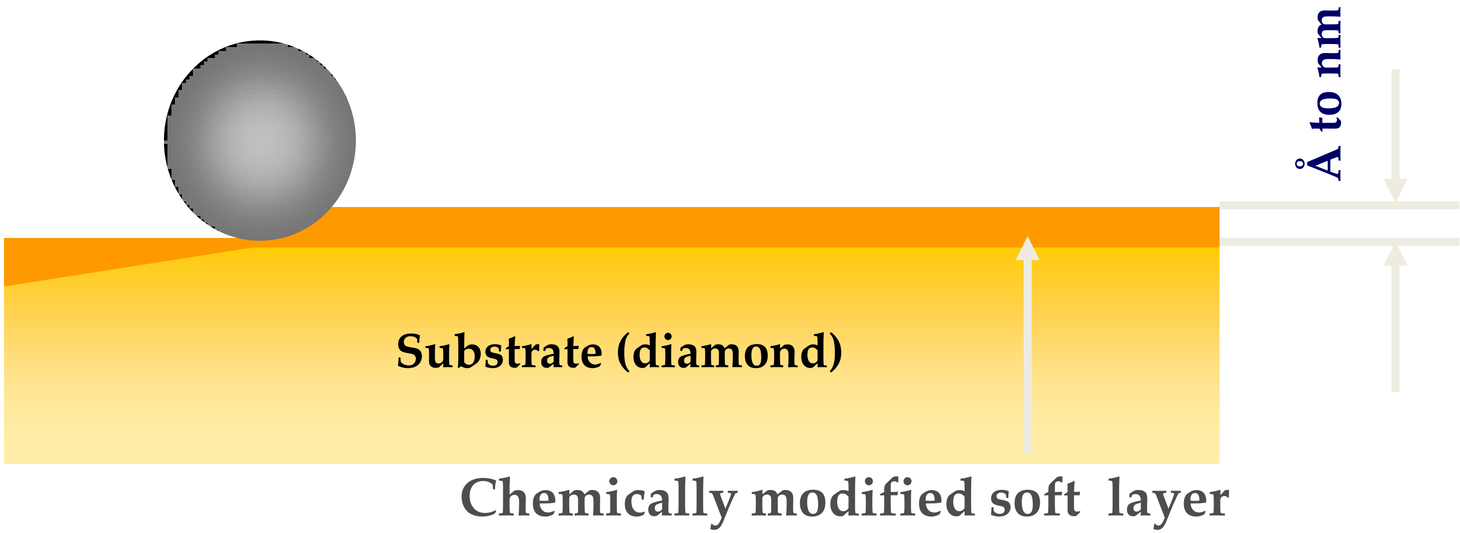
# Problem

## Flatness and Thickness Tolerance Variation




Example of energy straggling in detectors (a) showing poor energy resolution due to energy straggling in the detector and (b) Showing better energy resolution with lesser energy straggling [Muller]

# Reactive CMP (RCMP): Soft layer Polish




- Chemically convert hard Diamond into a soft-layer
- Use nanoparticles
- Remove Soft layer
  - Achieve High Removal Rate
  - No Scratches
- Single Component Slurry

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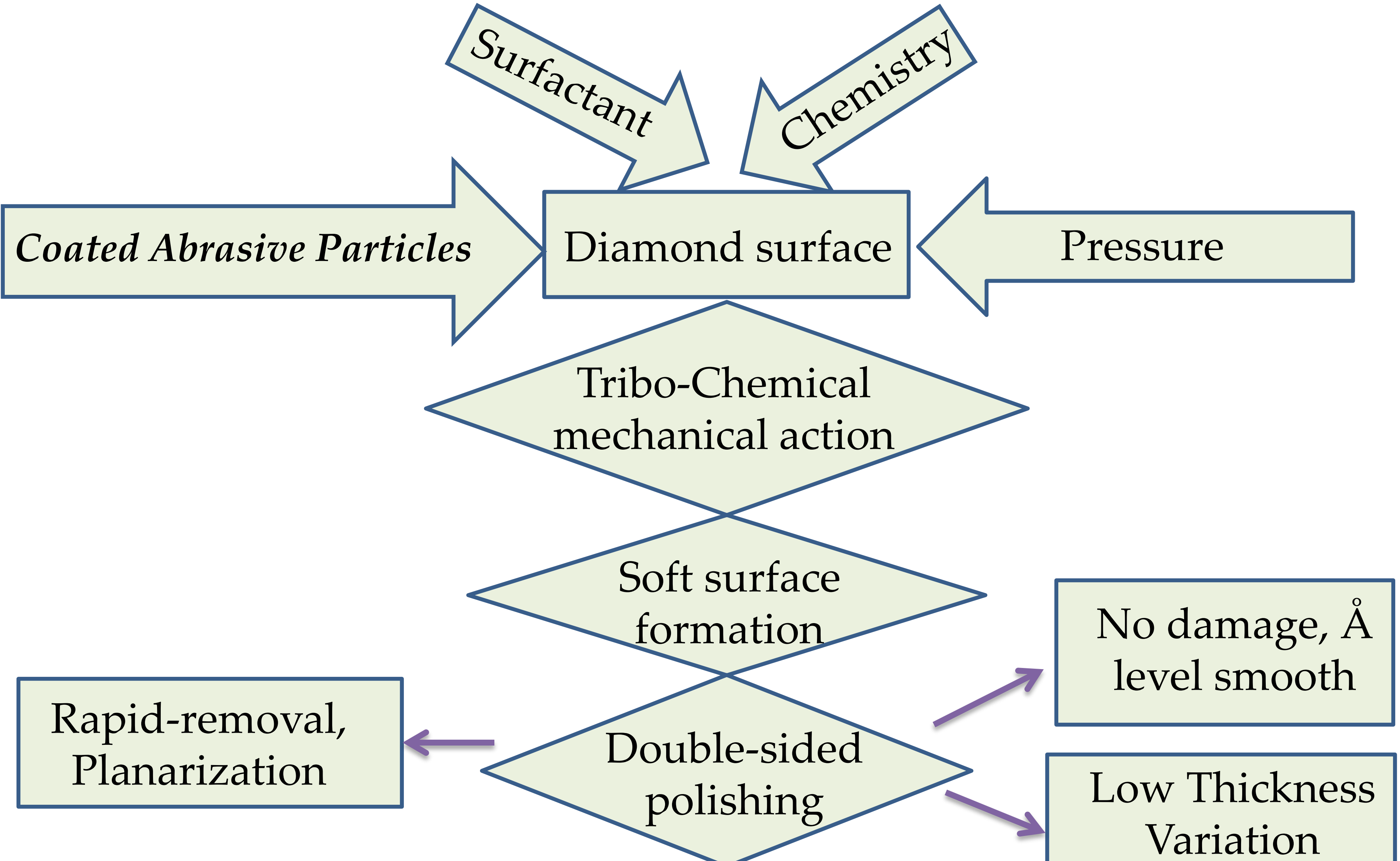
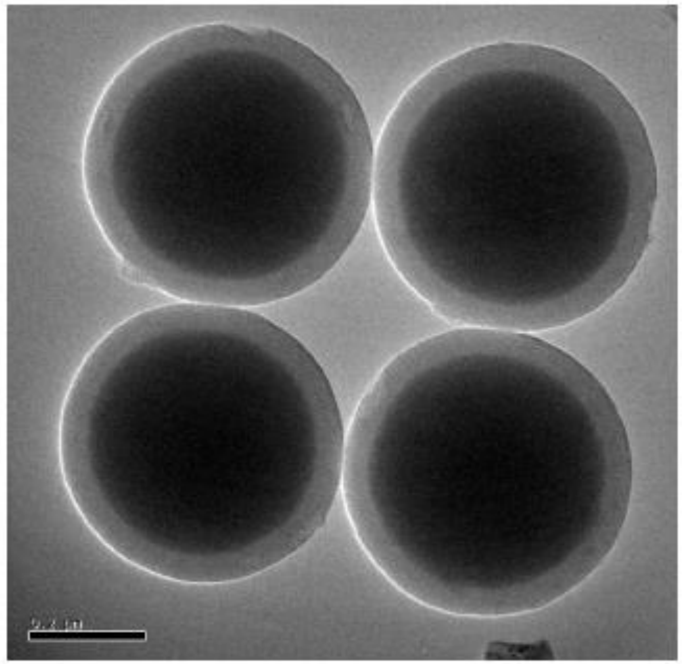
# Reactive CMP (RCMP)



# RCMP slurry - Coated Particles



- TEM pictures of ceria coated hard base particles
- Coated Particle Enhances Chemical Reaction Under Pressure Locally for achieving higher material cut rate
- Low Surface Damage

# Material Removal Rate with three different RCMP Process

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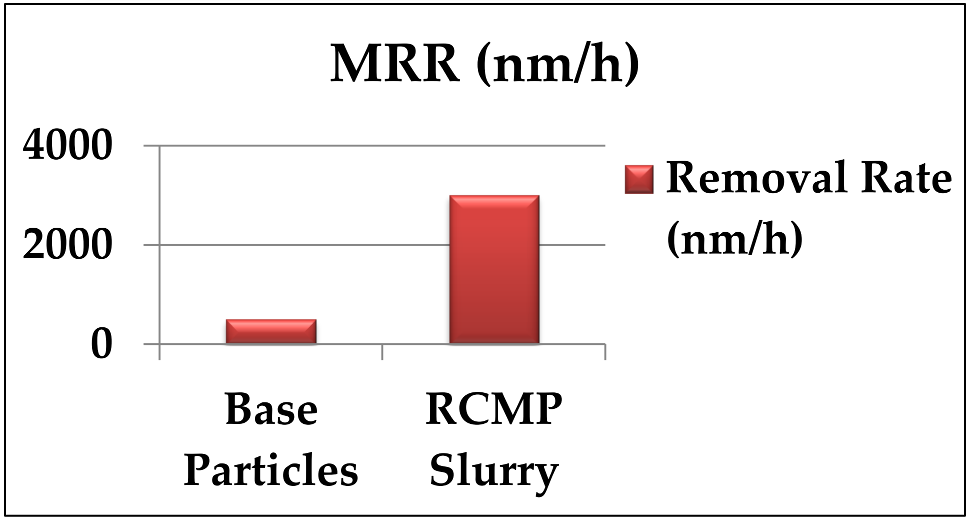
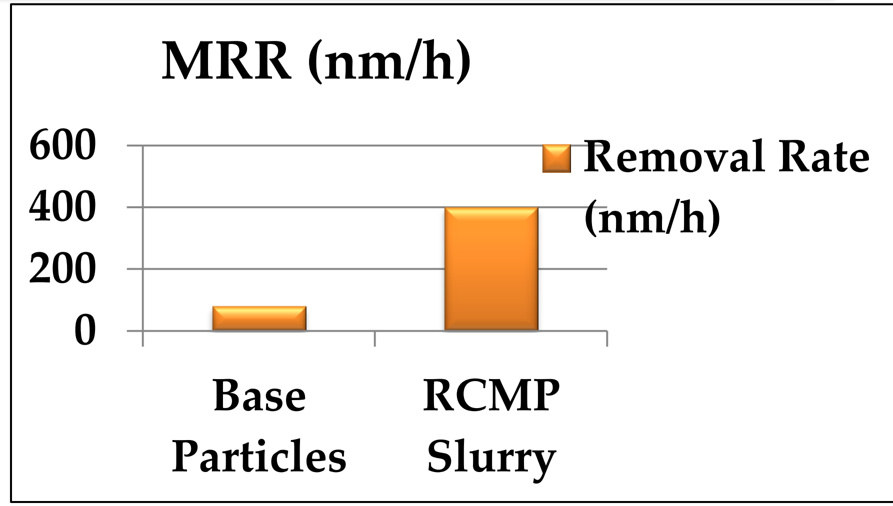
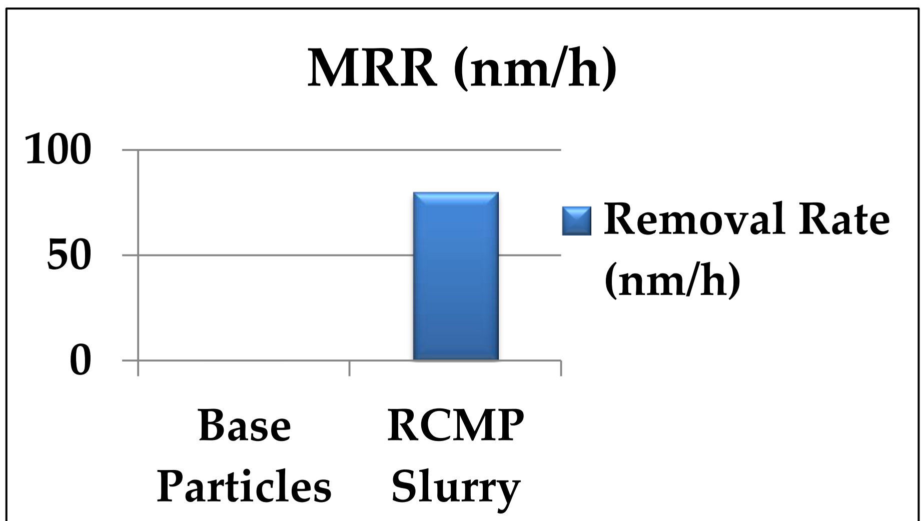



**High Removal Rate RCMP Slurry**



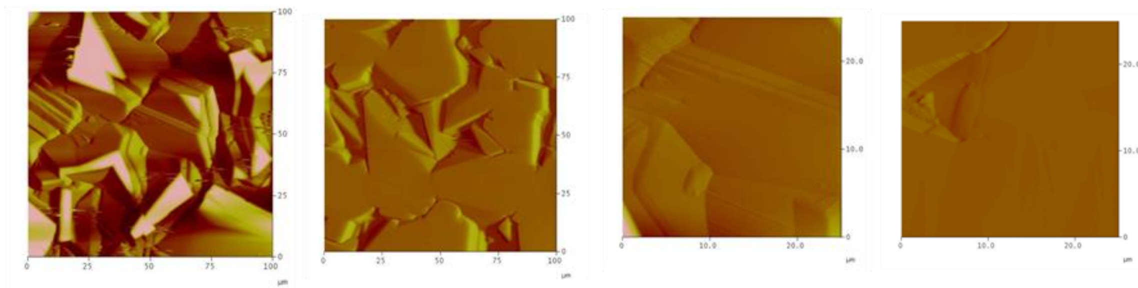

**Medium Removal Rate RCMP Slurry**




**High Finish RCMP Slurry**

# p-Crystalline Diamond Grain Flattening using RCMP





RMS 1.2 micron

RMS 0.6 micron

Thickness variation on PV 5 micron

Thickness variation on PV 1.5 micron

(a) AFM of as received samples (RMS 1.2 micron) (b) After Polish RMS 0.6 micron (c) Peak to valley roughness before polish 5 micron (d) Peak to valley roughness 1.6 micron (e) As received sample showing sharp grains (f) Polished sample showing flattened grains (note porous structure between grains prevented achieving low RMS or PV).

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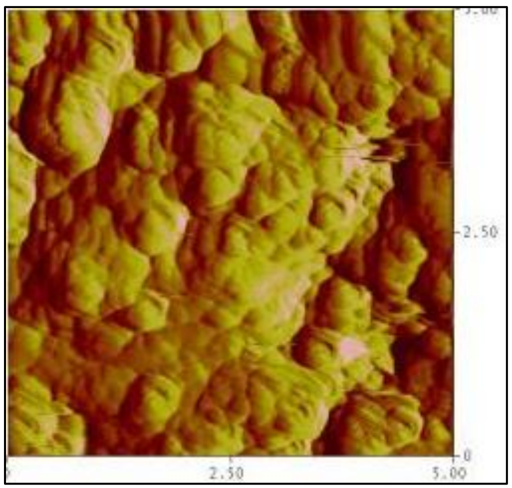
# p-Crystalline Diamond Polishing

## <25 micron grains

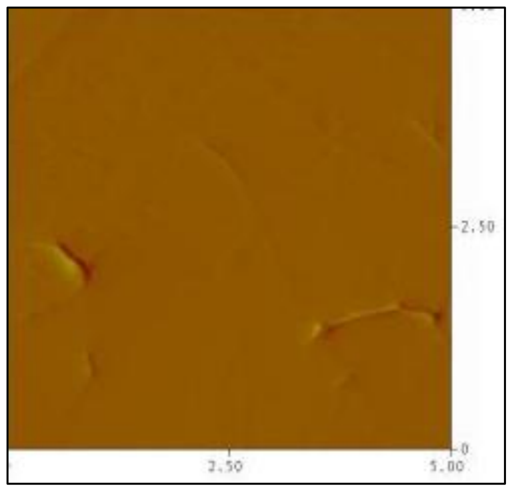
As-received
Lapped Sample




RMS ~ 59.4 nm

**(5x5 sq.μm)**

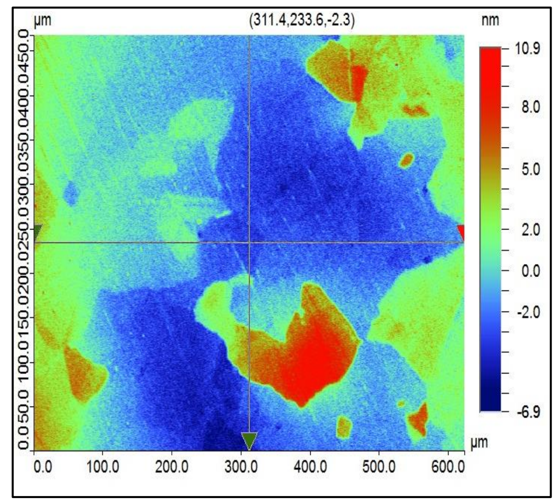
AFM Image




RMS ~ 4.6 nm

**(5x5 sq.μm)**

Wyko Image



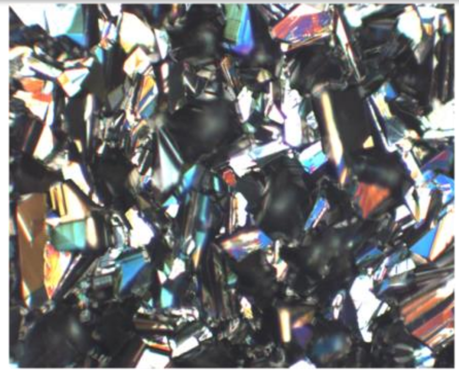

| Label | Value | Units |
|---|---|---|
| Average | 0 | nm |
| Ra | 2.263 | nm |
| Rp | 10.889 | nm |
| Rq | 2.837 | nm |
| Rt | 17.745 | nm |
| Rv | -6.856 | nm |

Ra ~ 2.2 nm

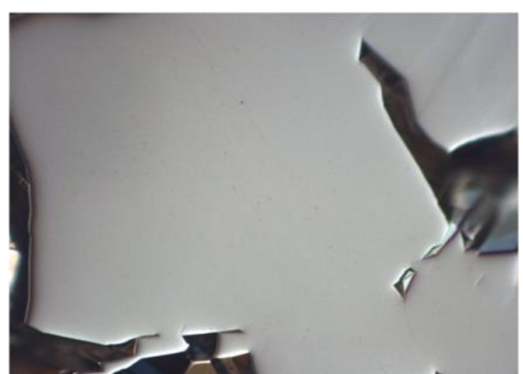
**(600 μm x 450 μm)**

# Large Grain Flattened by RCMP

> 100 micron grains



**The initial surface and progressive changes over time during polishing**



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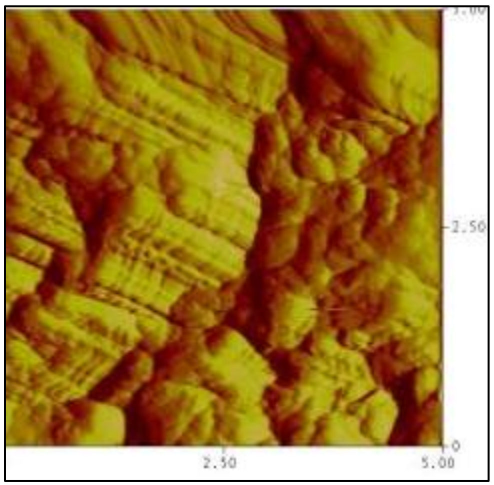
# Single Crystalline Diamond Polishing

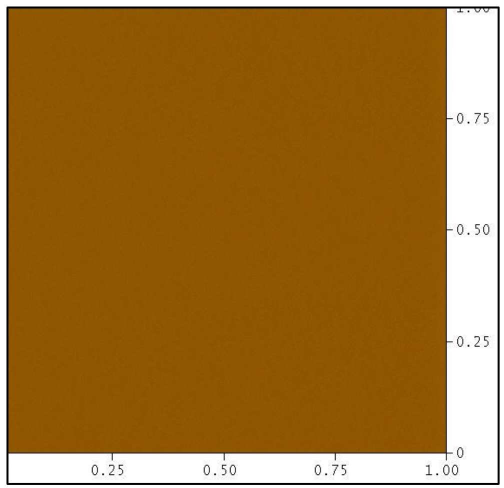
As-received
Lapped Sample




RMS 119.6 nm

**(5x5 sq.µm)**

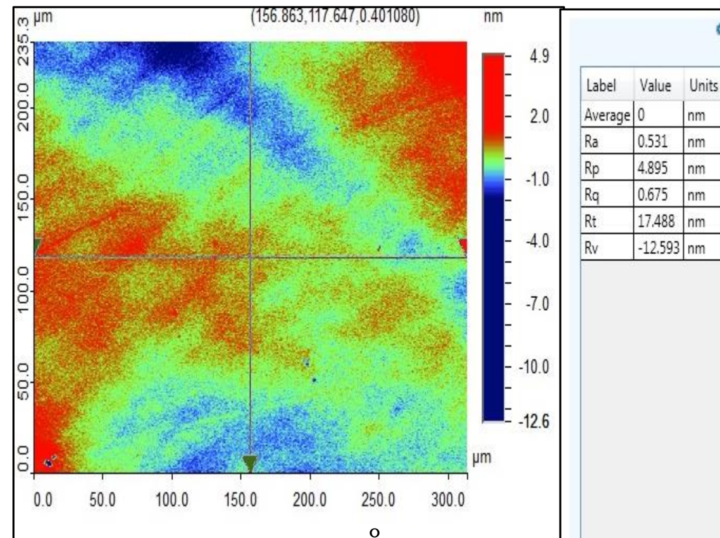
AFM Image




RMS ~ 1.5 Å

**(1x1 sq.µm)**

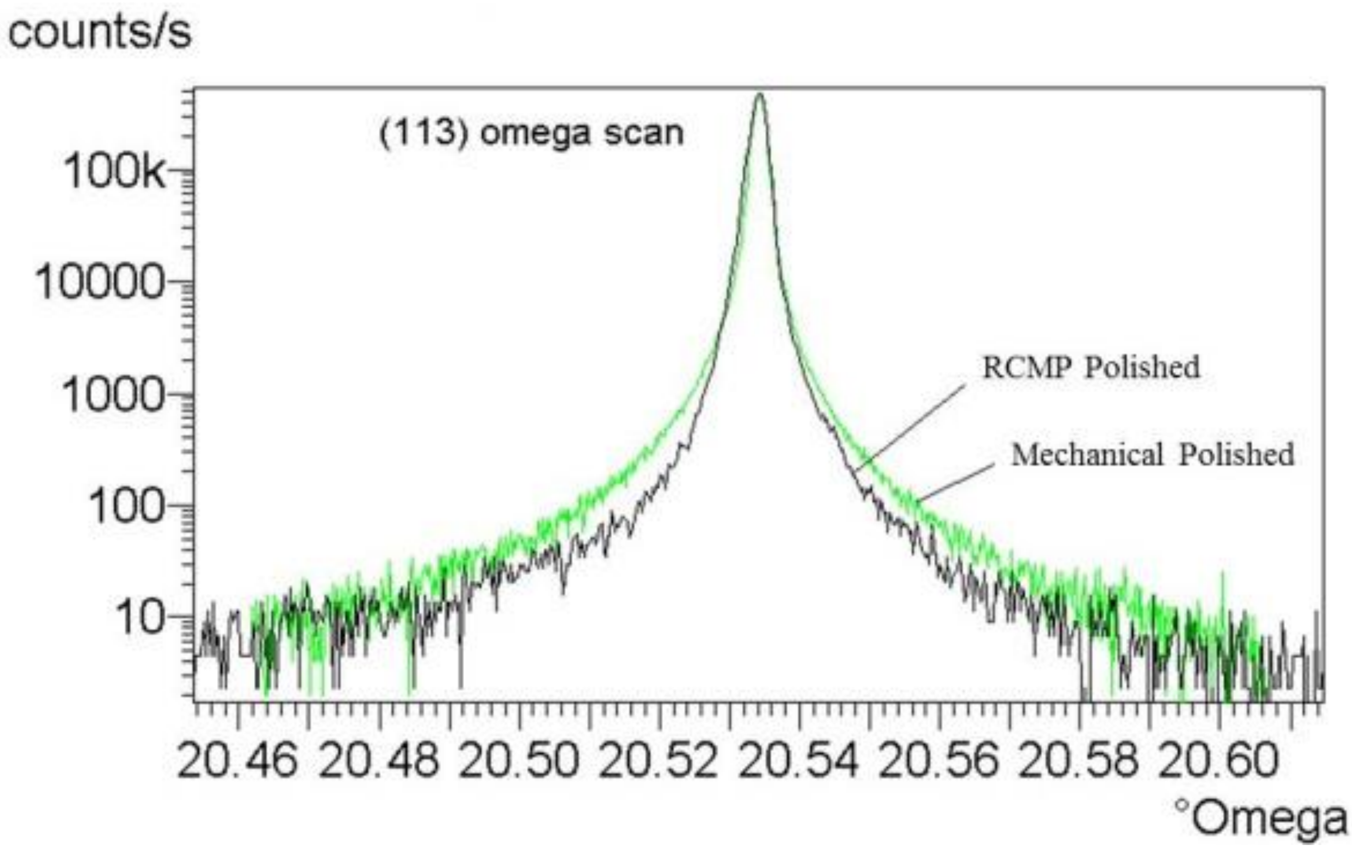
Wyko Image




Ra ~ 5.3 Å

**(300 µm x 235 µm)**

# X-ray Rocking Curve Studies

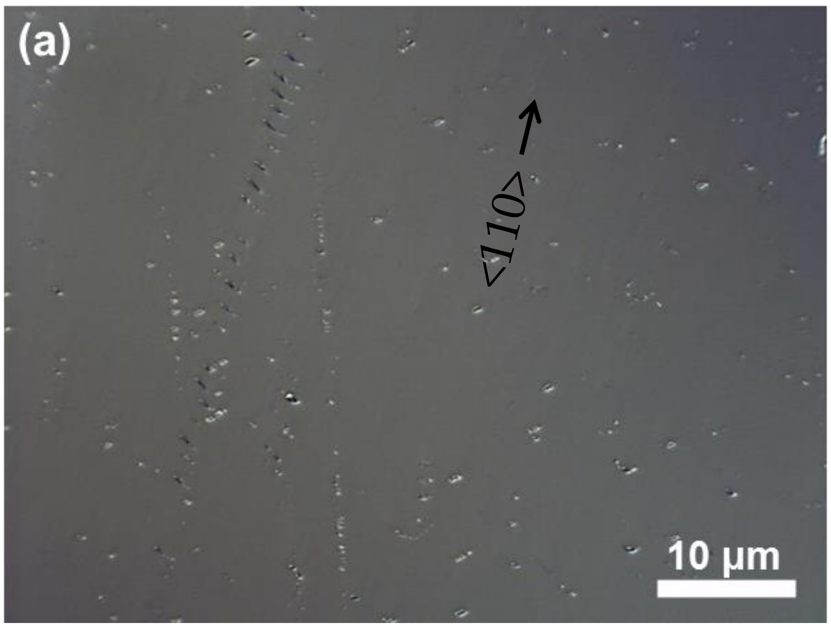



**RCMP Process –reduced X-ray rocking curve width**

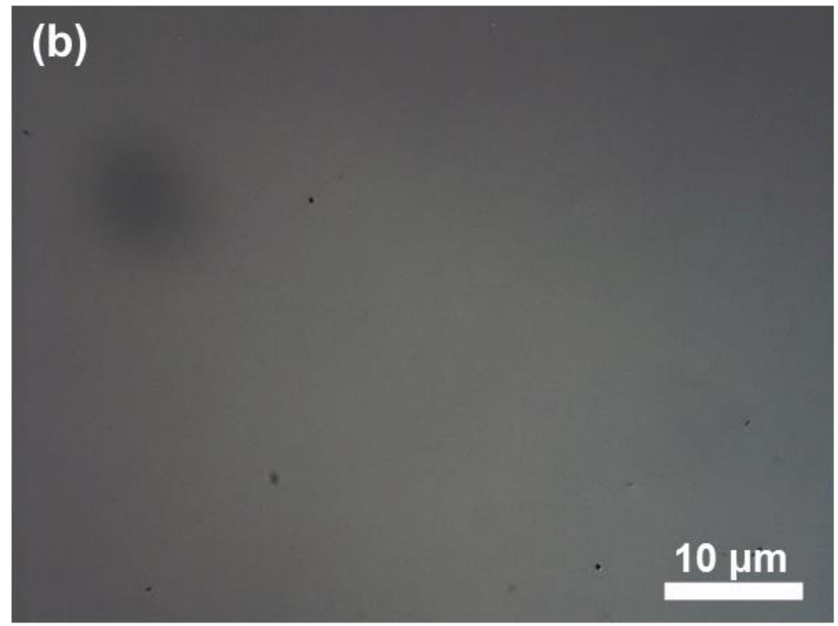
# Optical Microscope Images

- Surface morphology of HPHT diamond before and after RCMP

Mechanical polishing




Reactive CMP

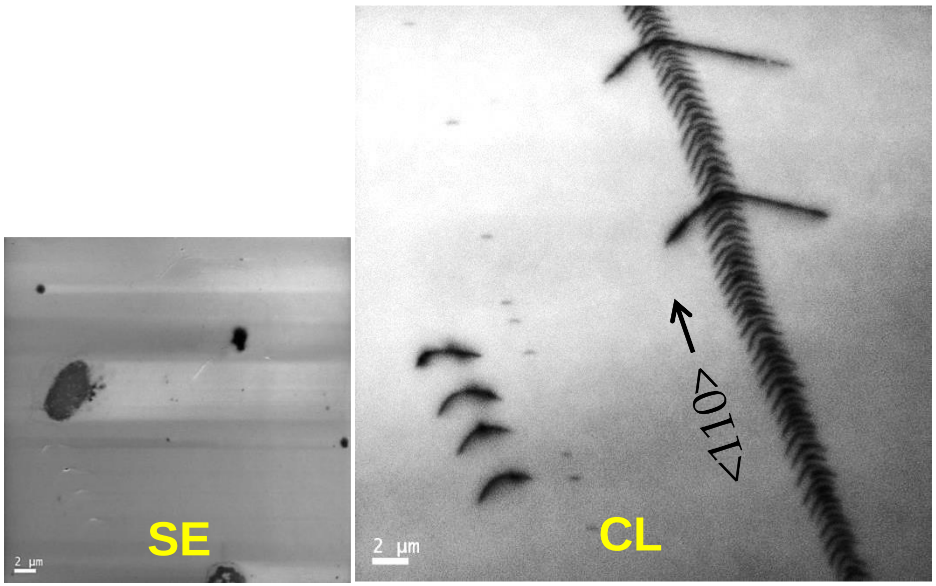



- Scratch lines
- Fracture points
- Striations aligning to <110> direction

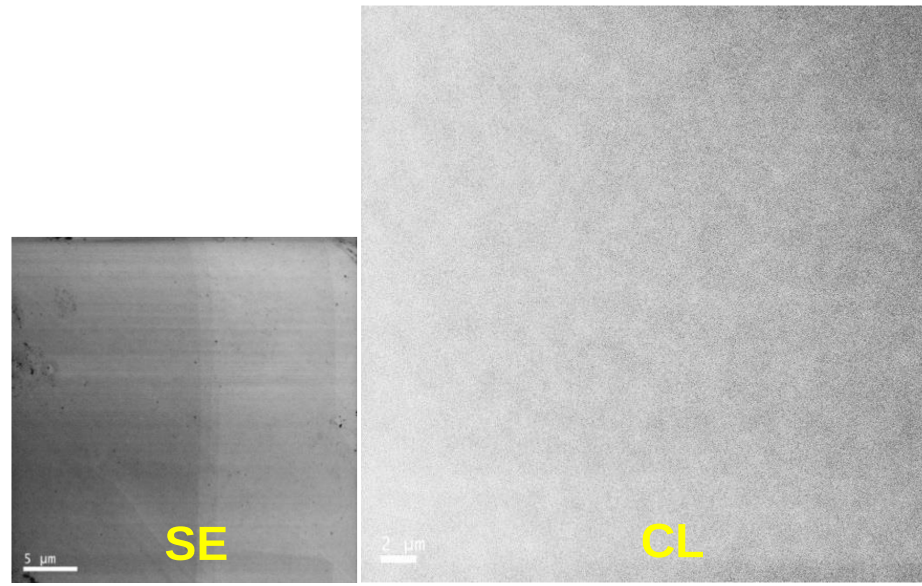
- Scratch lines absent
- Traces of fracture points
- Completely devoid of striation marks

# SEM & Panchromatic CL (HPHT)

**Mechanical polishing**




**Reactive CMP**




- Dark spots indicating the fracture defects as non-emission points
- Multiple V-fracture

- No dark spots
- Completely free of fracture defects

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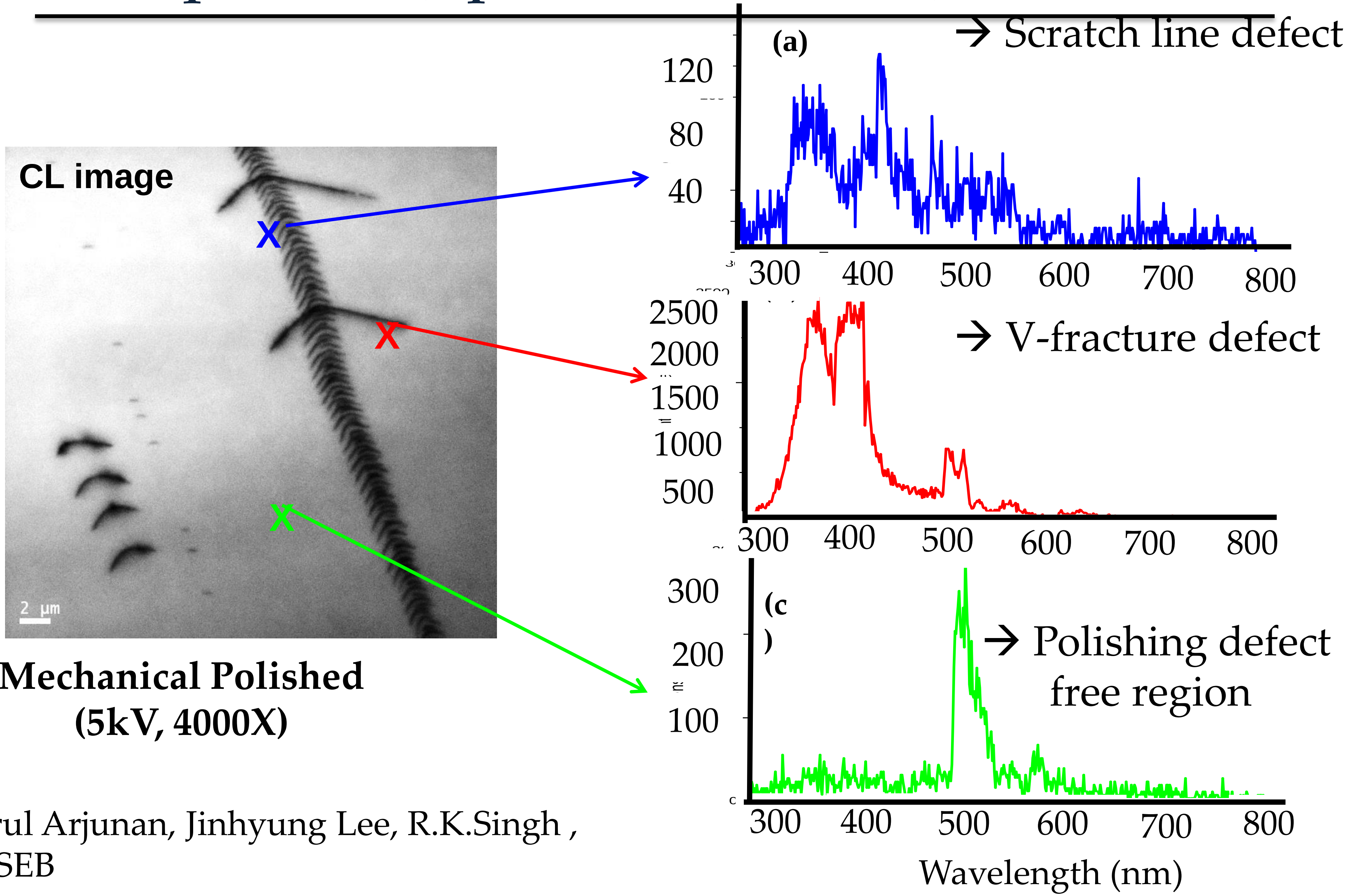
MSEB

# CL Spectra (Spot Area Mode)




**Mechanical Polished (5kV, 4000X)**

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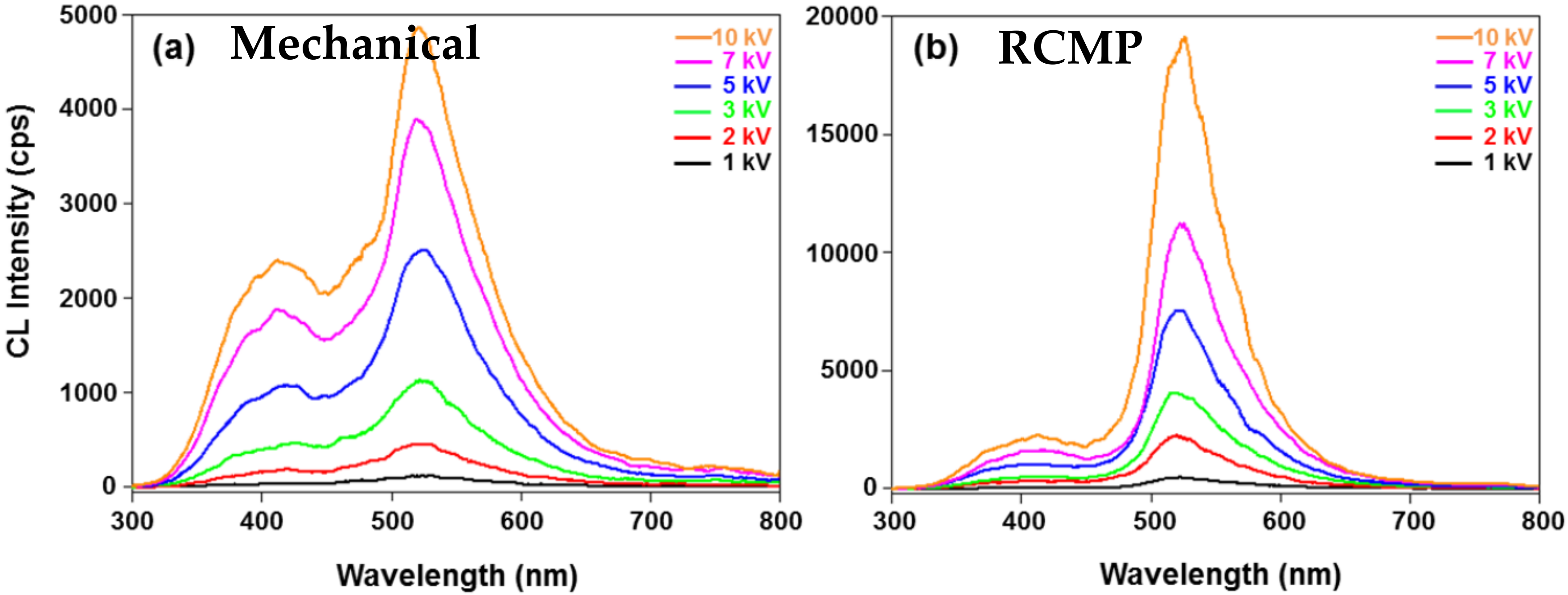
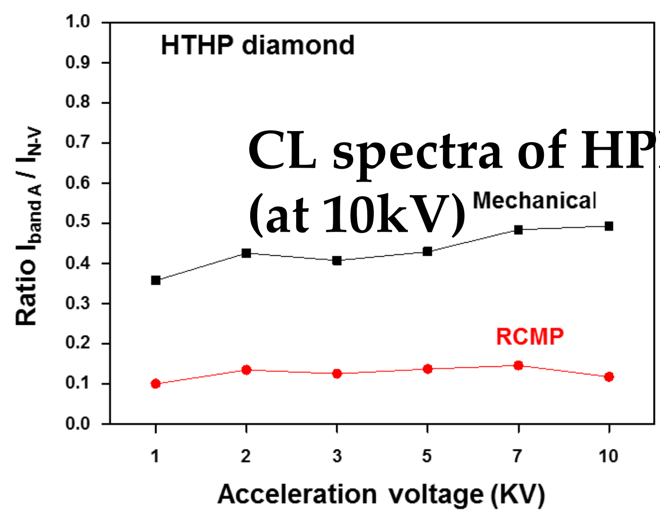
# CL spectra (Mechanical vs. RCMP)




**CL spectra of HPHT diamond (at 5kV)**




**CL spectra of HPHT diamond (at 10kV)**

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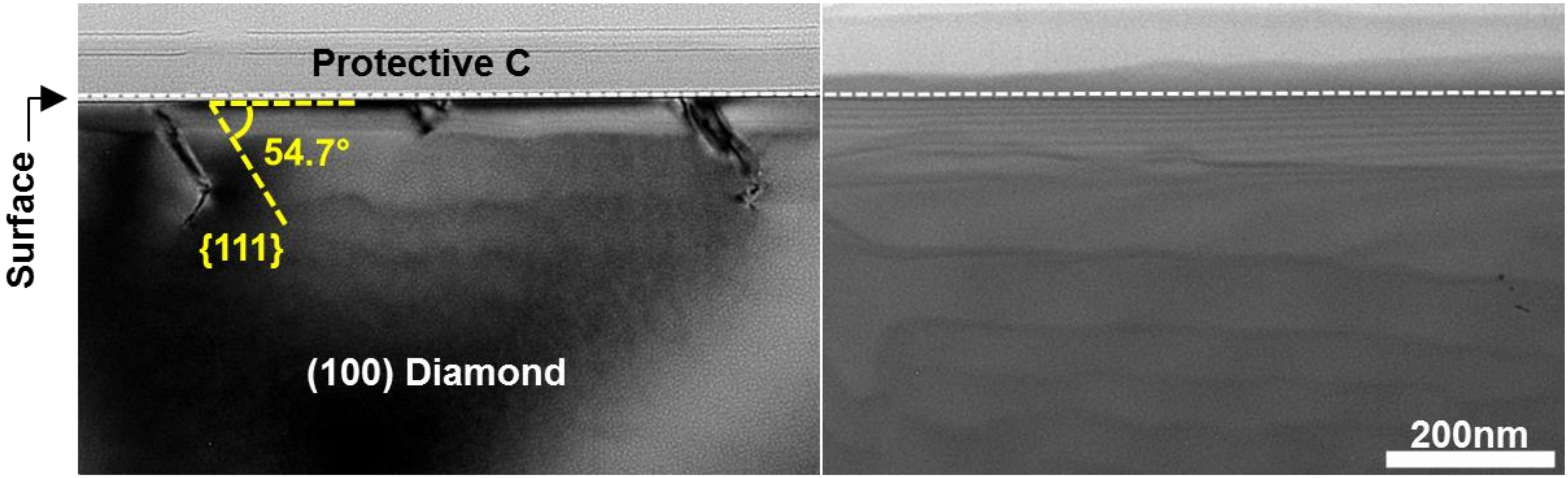
# Cross-sectional TEM

**Mechanical polishing** **Reactive CMP**




- Depth of polishing damage ~ 150nm
- Fractures penetrated with 54.7° direction of polished plane
  - Lower strength and energy for fracture on {111} planes

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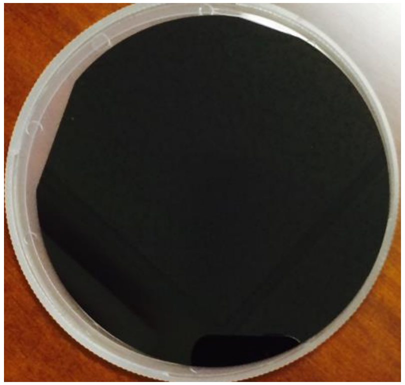
# RCMP Scale-up

## Large Area Substrate Polishing



4 inch sample polishing

## Multiple Sample Polishing

Five 3″ inch samples polishing

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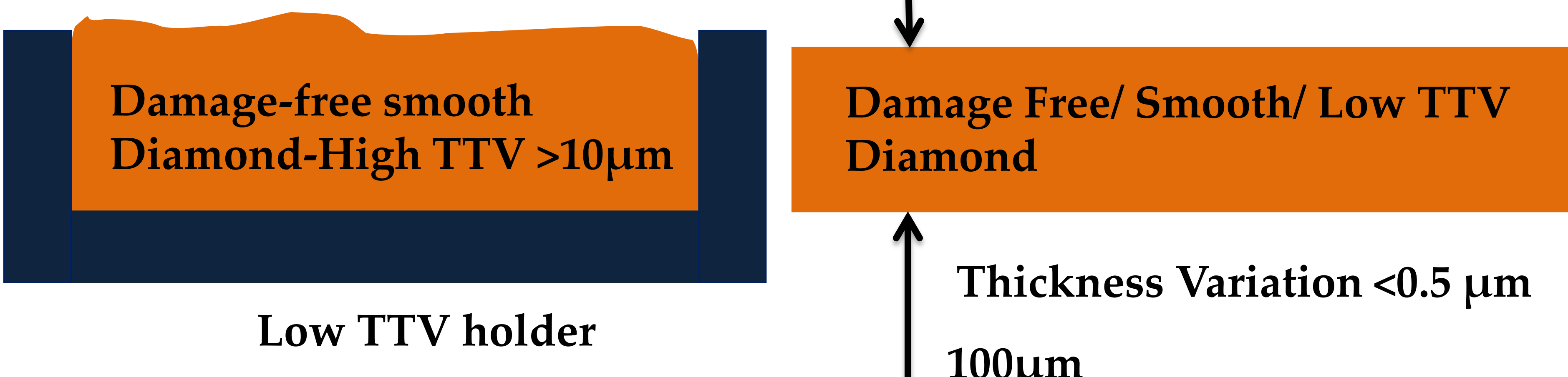
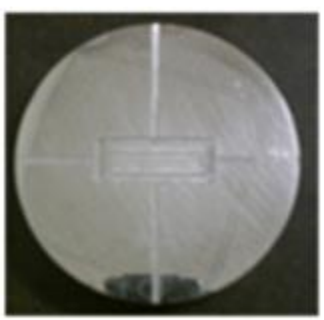
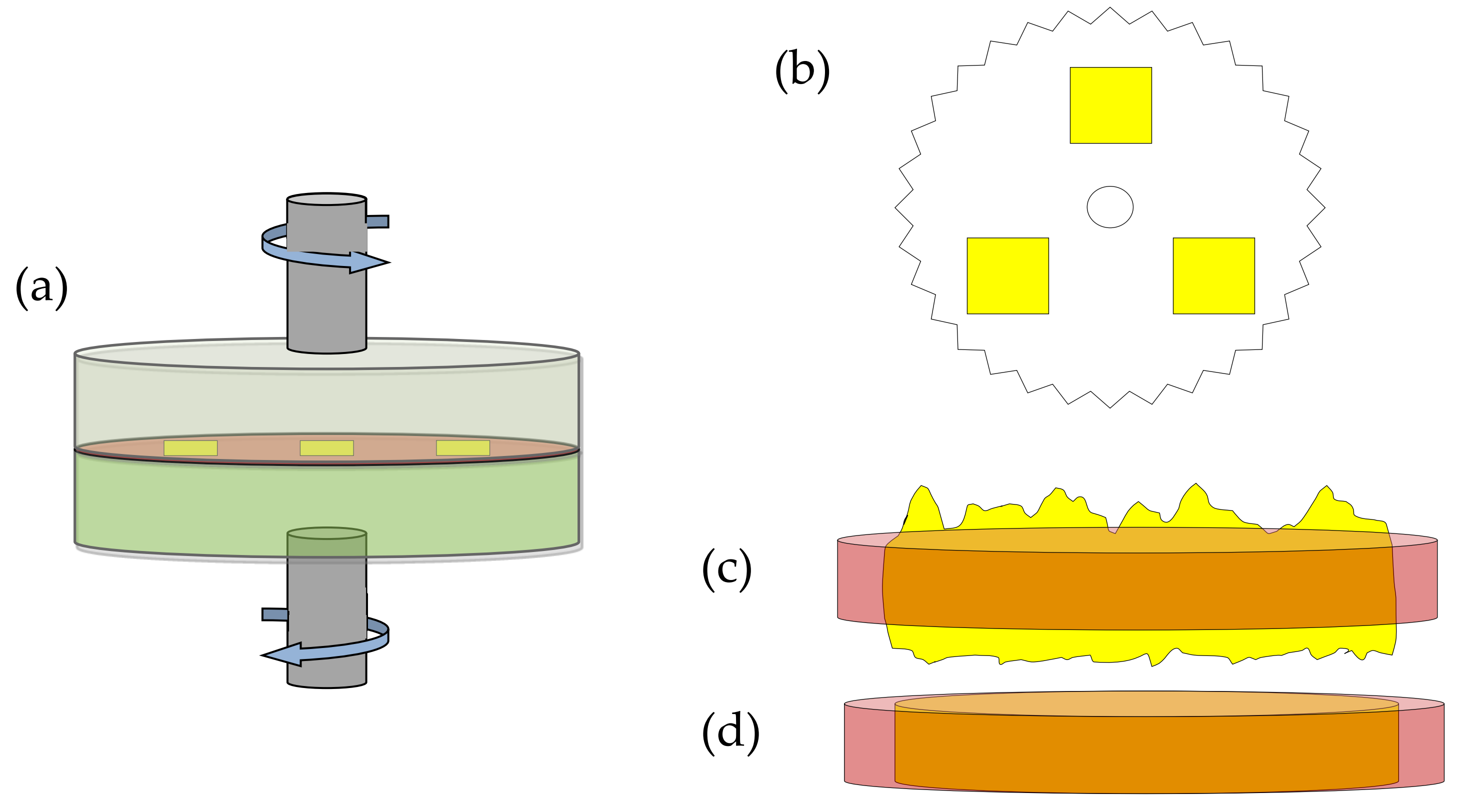
# Solution 1: Ultra Flat Holder (Phase I)

**Proposed RCMP Processes using specialized holder**



# Solution 2: Double-sided polishing Phase II




Schematic of (a) double sided polishing (b) Gear sample fixture (c) unpolished samples (d) double sided polished sample with ultra low TTV

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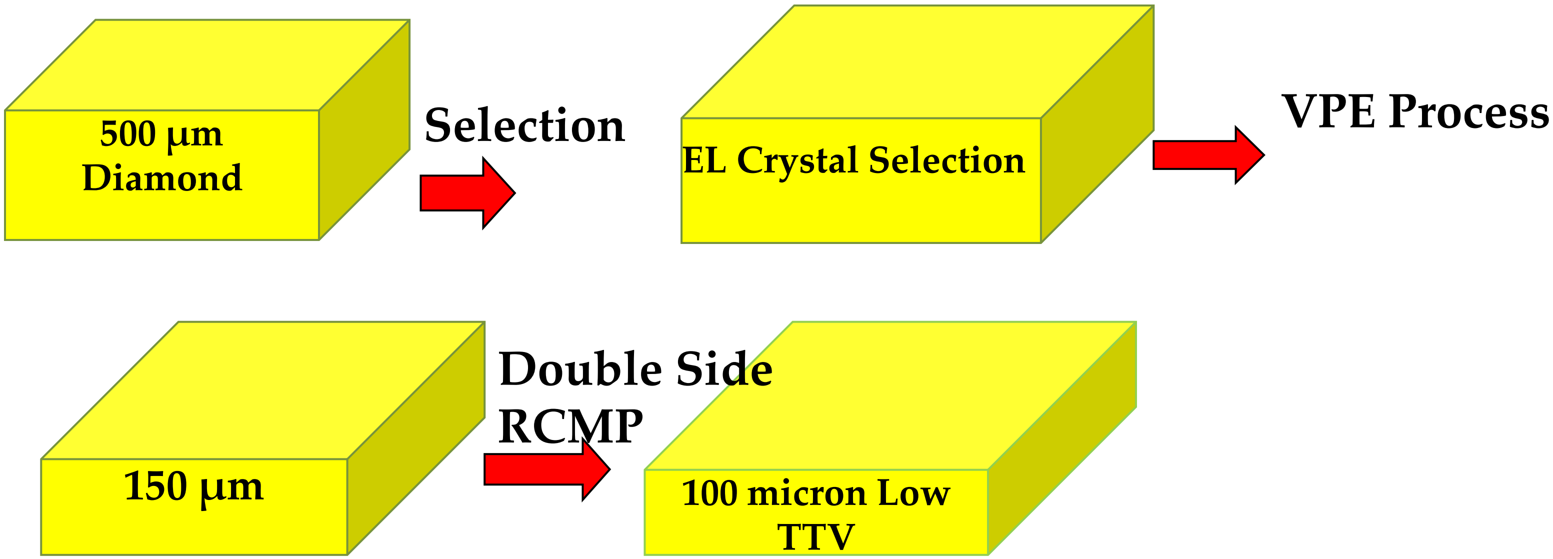
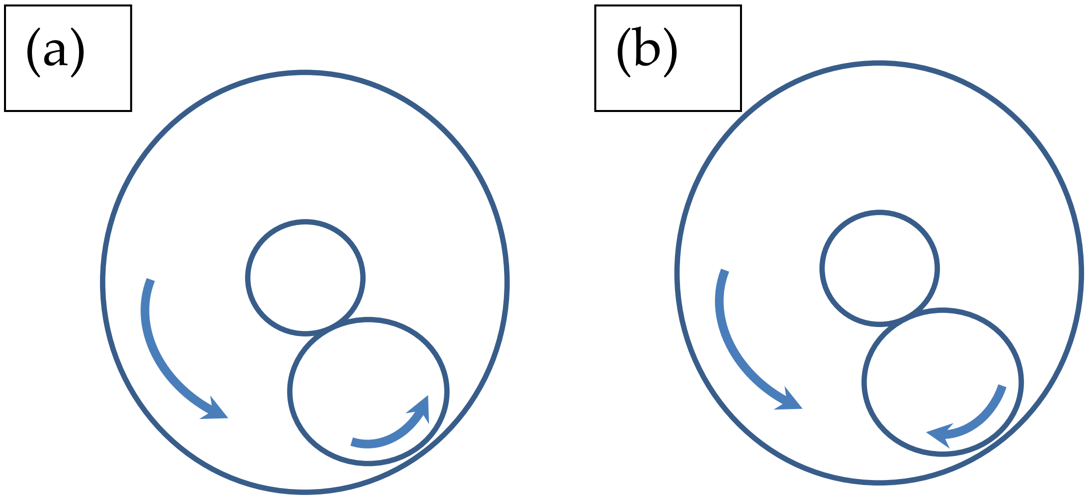
# Solution 3: Dry Etch + DS-RCMP Phase II Extension

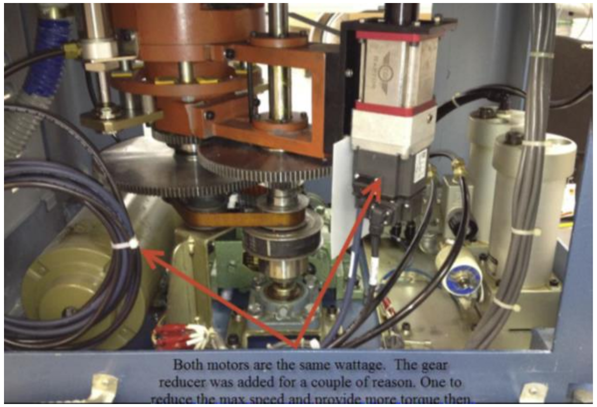



Process flow schematic to show fabrication of ultra-low TTV electronic -grade diamond crystals for detectors using (1) Electronic grade selection (2) vapor phase etching followed by (3) Double side RCMP process

# Custom Double-sided polishing




(a) Rotation of carrier and plate in the same direction & Plate will wear concave (b) Carrier and plate rotation in opposite direction & Plate will wear convex

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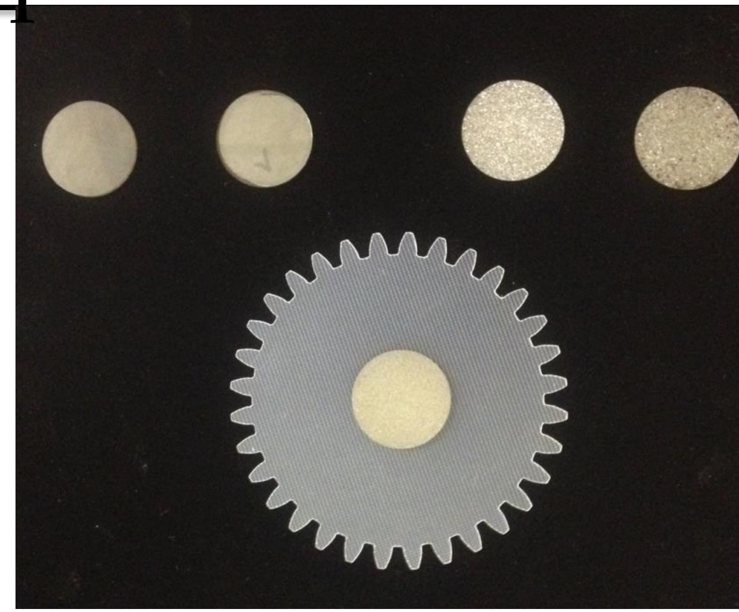
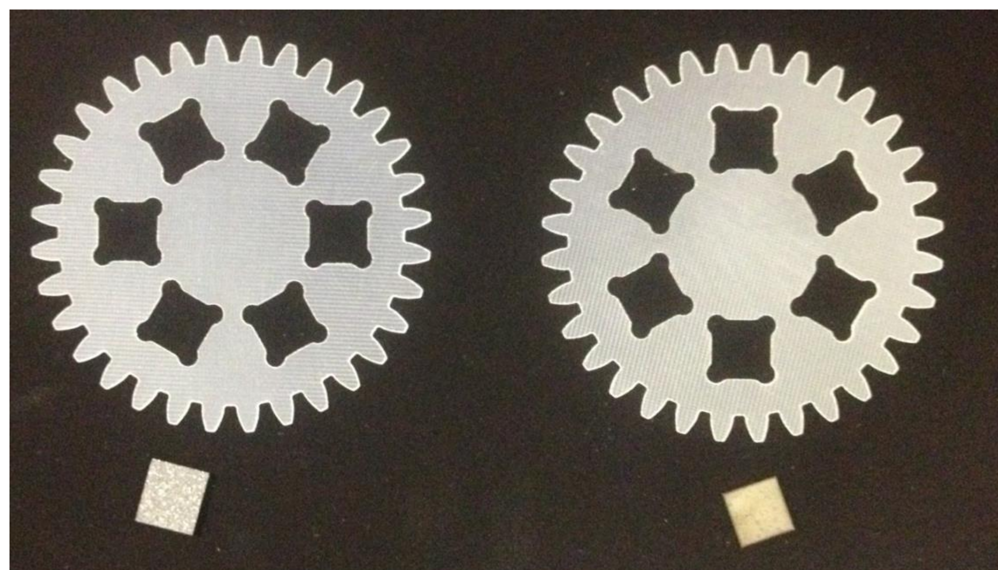
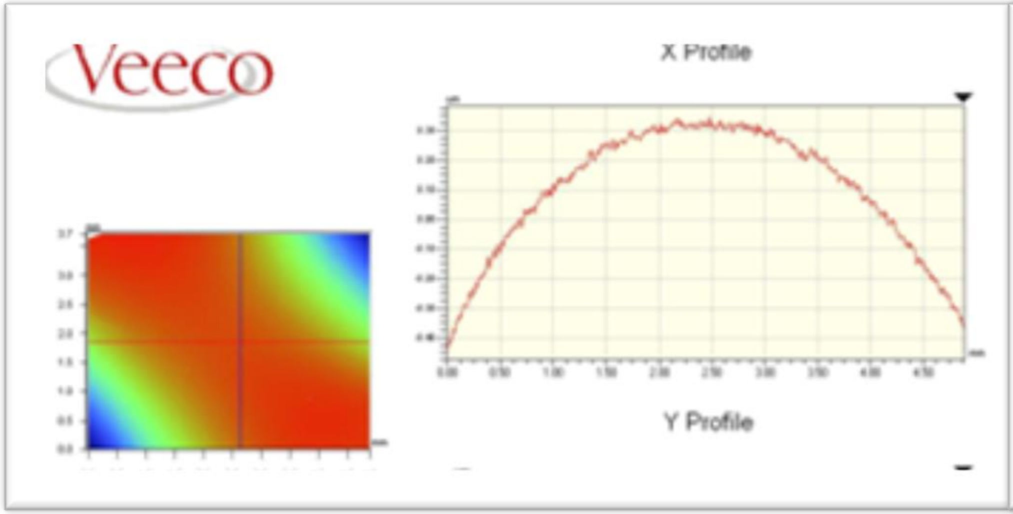
# Custom Double-sided polisher

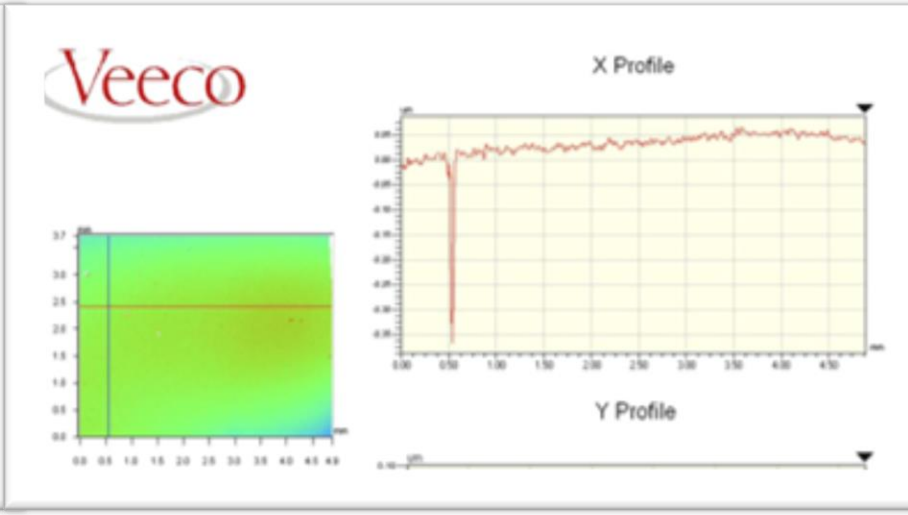

Samples Polished





# Ultra Flat Polishing



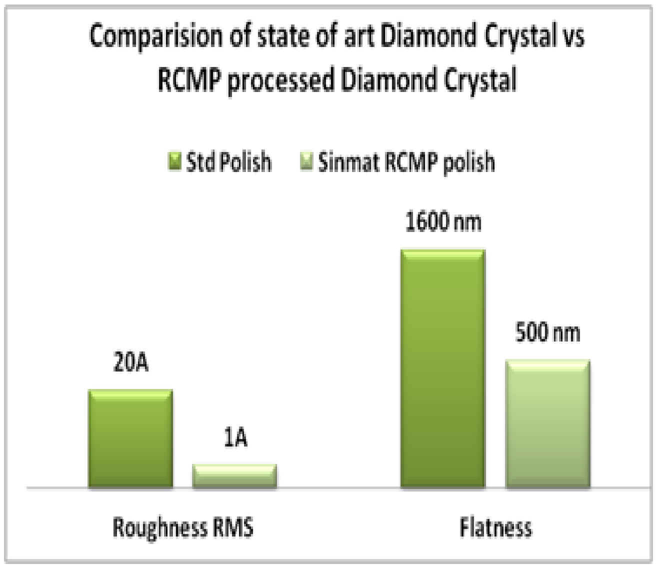



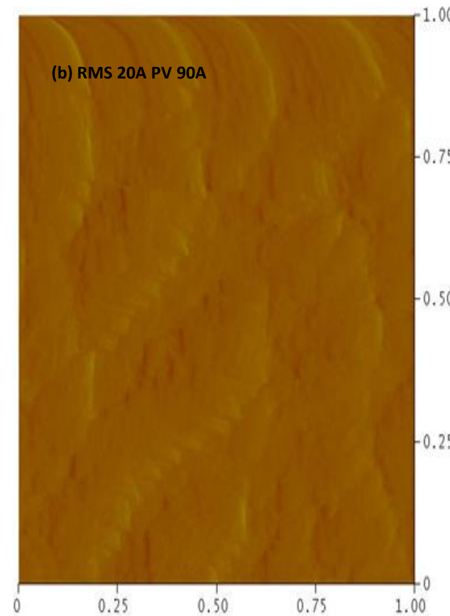

Peak to Valley Roughness
2.9 micron

Peak to Valley Roughness
0.55 micron

Single crystalline sample (a) before polishing showing non-flat surface (PV~2.9) (b) flat surface after polishing (PV~ 0.55)

# Ultra smooth Surface Finish





RMS roughness reduction by 1 order and optical flatness reduction from 1.6 micron to 0.5 micron with Sinmat's Reactive CMP (RCMP) polishing, (b) AFM picture of standard polish showing fractured surface (RMS 20A, (Peak to Valley) PV 90A) and (c) AFM picture of RCMP surface shows atomic smooth surface (RMS 1A, PV 10A).

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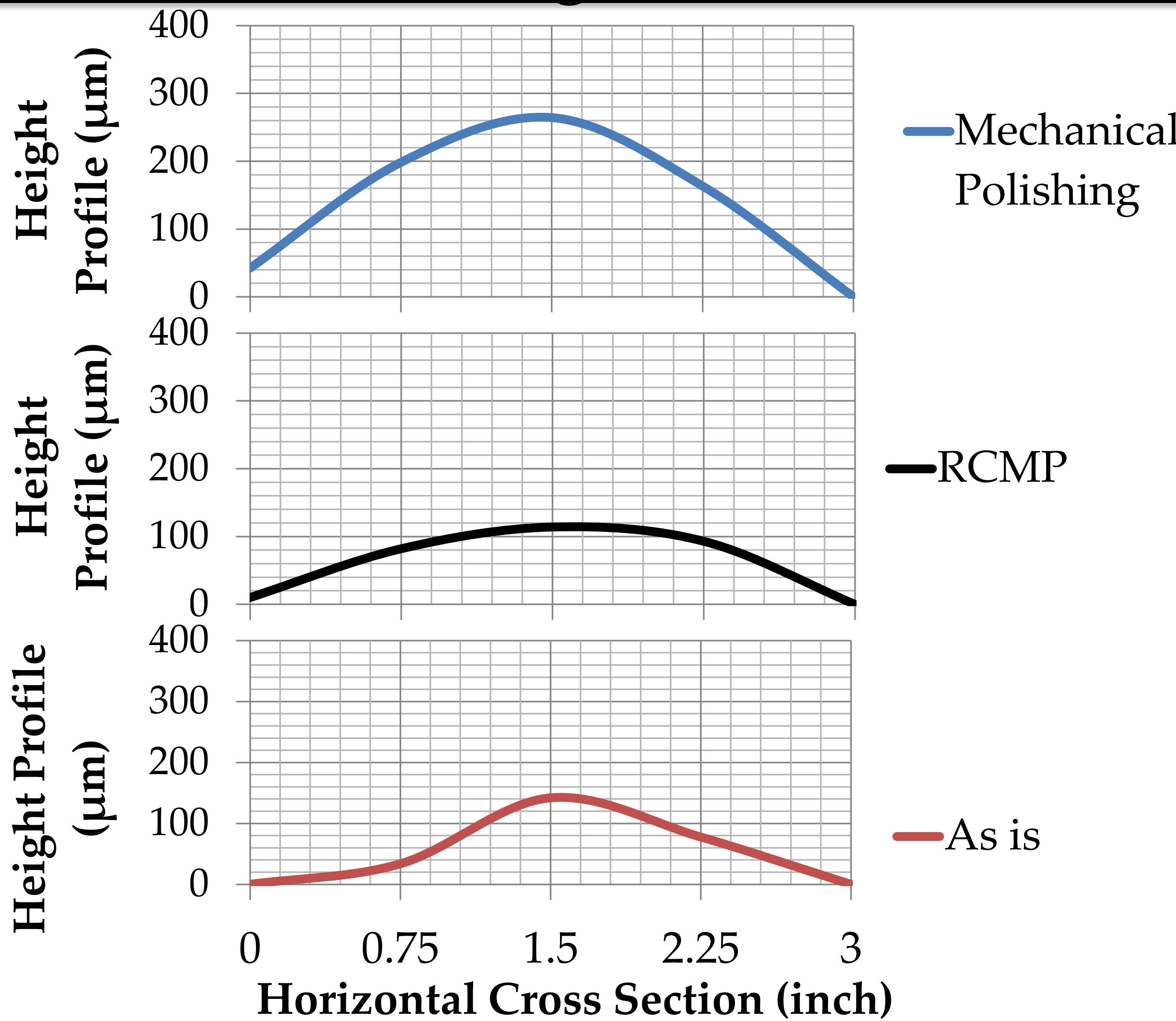
# Stress Free Polishing- Reduced Bow



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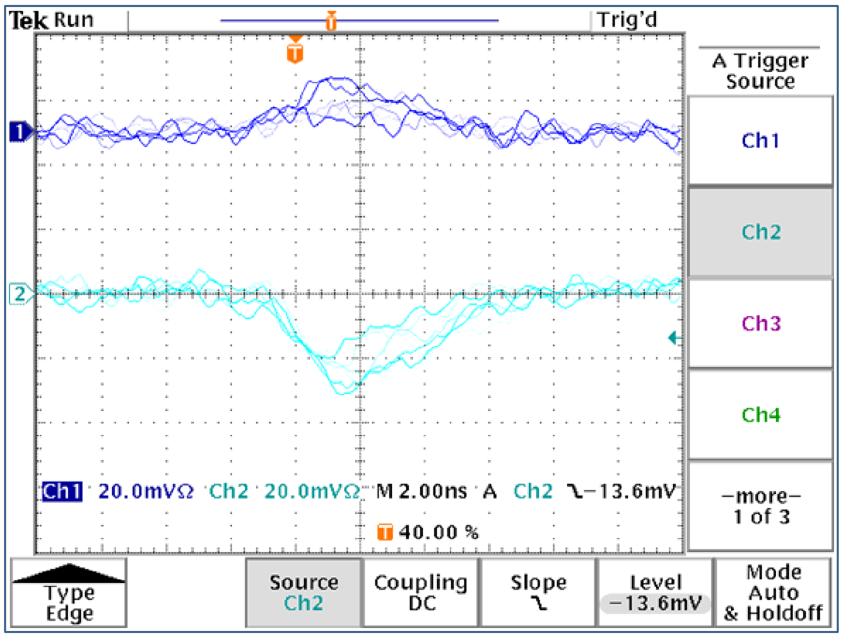
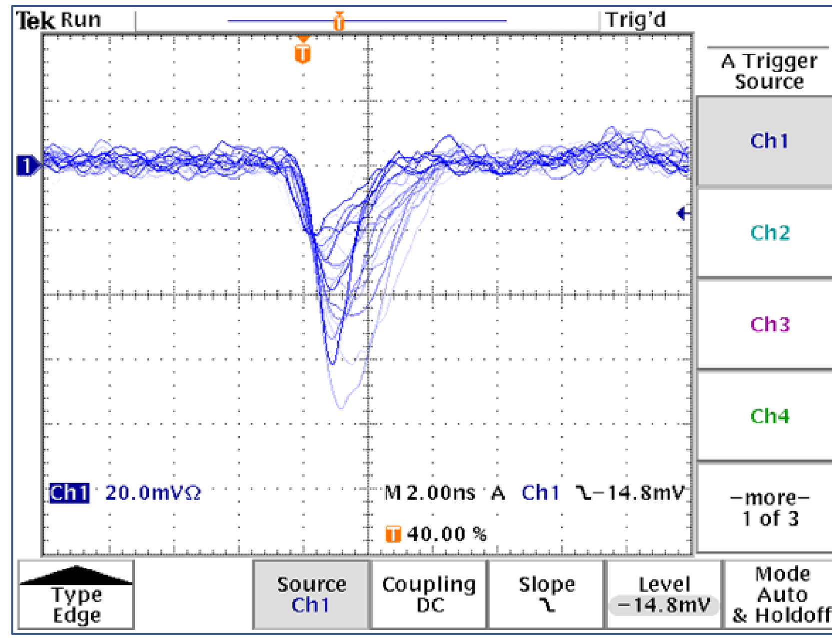
# Detector Testing-NSCL ( Solution 1)

**Standard diamond**




**Sinmat finish diamond**

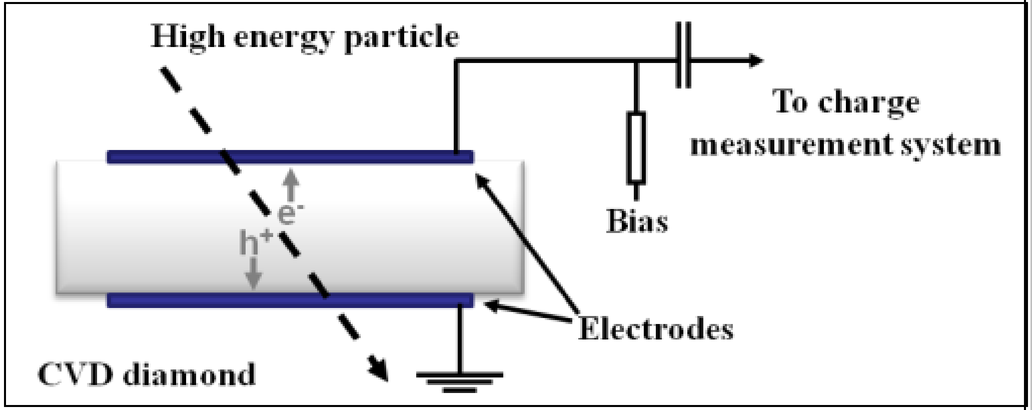



Detector response for U232 Alpha source at 100V bias (a) vendor polished sample – showing pulse height of 20-30 mV (b) RCMP polished diamond sample showing pulse height of 80mV. Both the plates were approximately 100μm thick **(Courtesy: Dr.Stolz , at NSCL)**

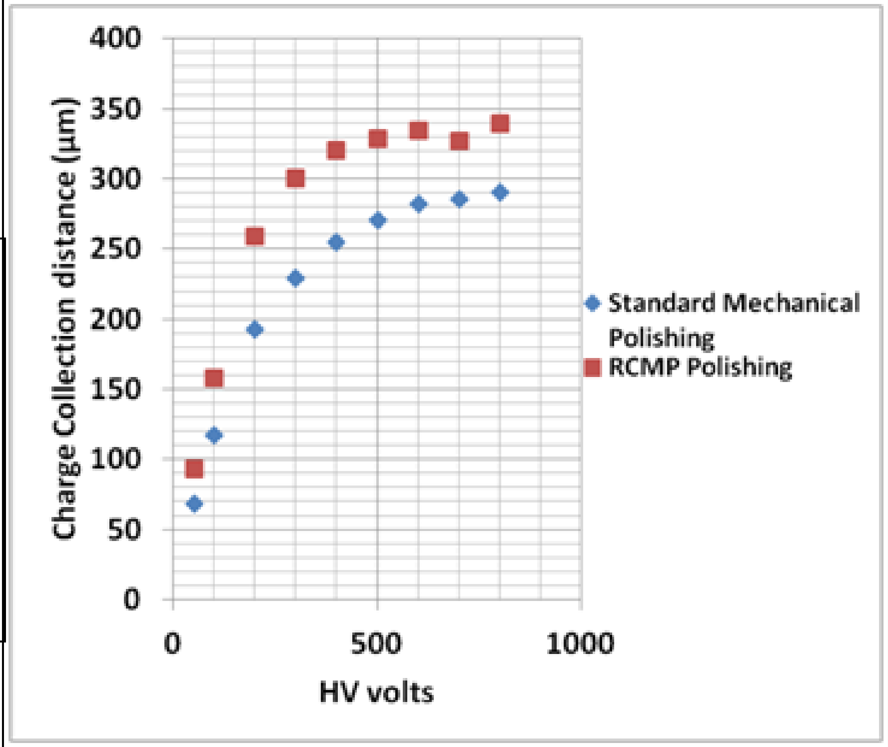
Polishing did not degrade the detector performance

# Detector Testing-OSU( Solution 2)

## $^{90}$Sr source

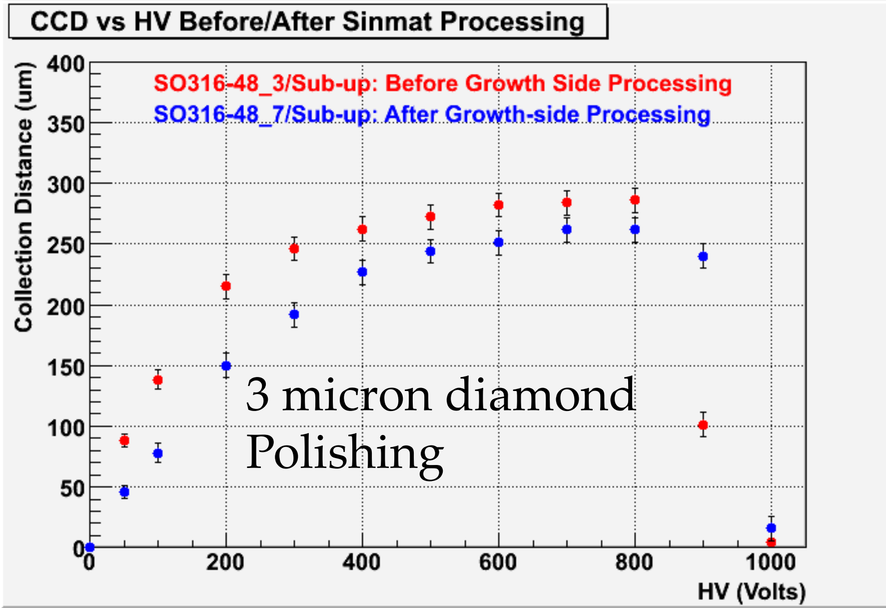


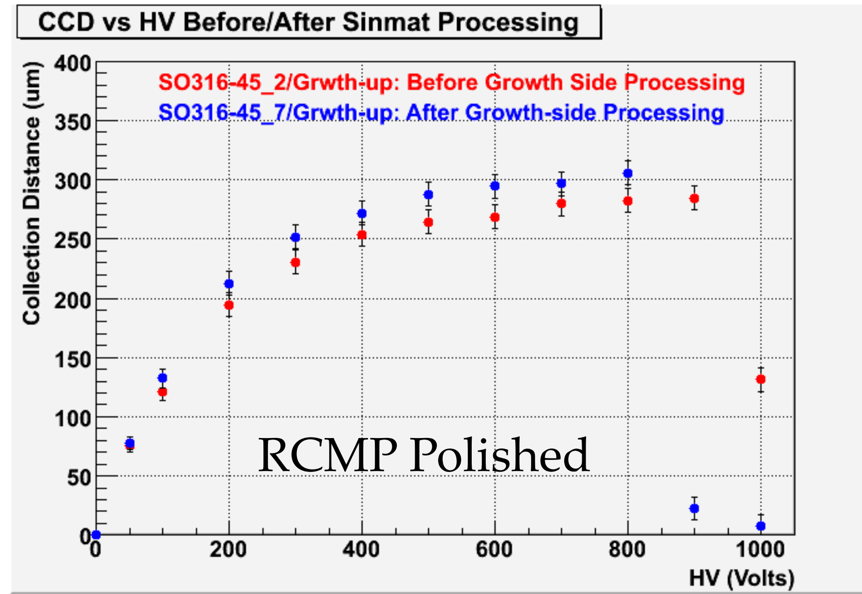

Set-up to Measure Charge Collection Distance

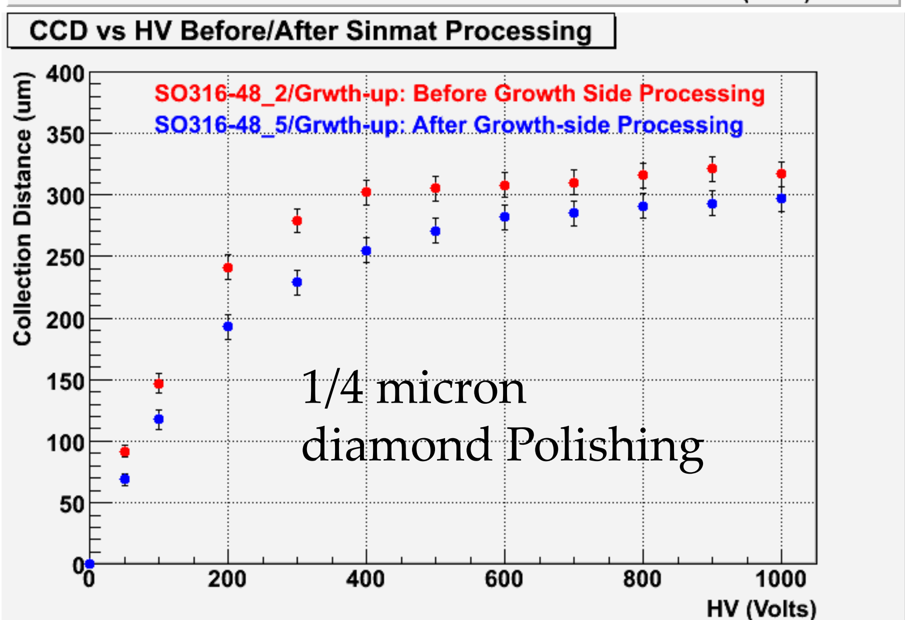



RCMP Polished Sample showing Higher Charge Collection Distance: Courtesy: Dr.Harris Kagan OSU

# Detector Testing-OSU ( Solution 2)



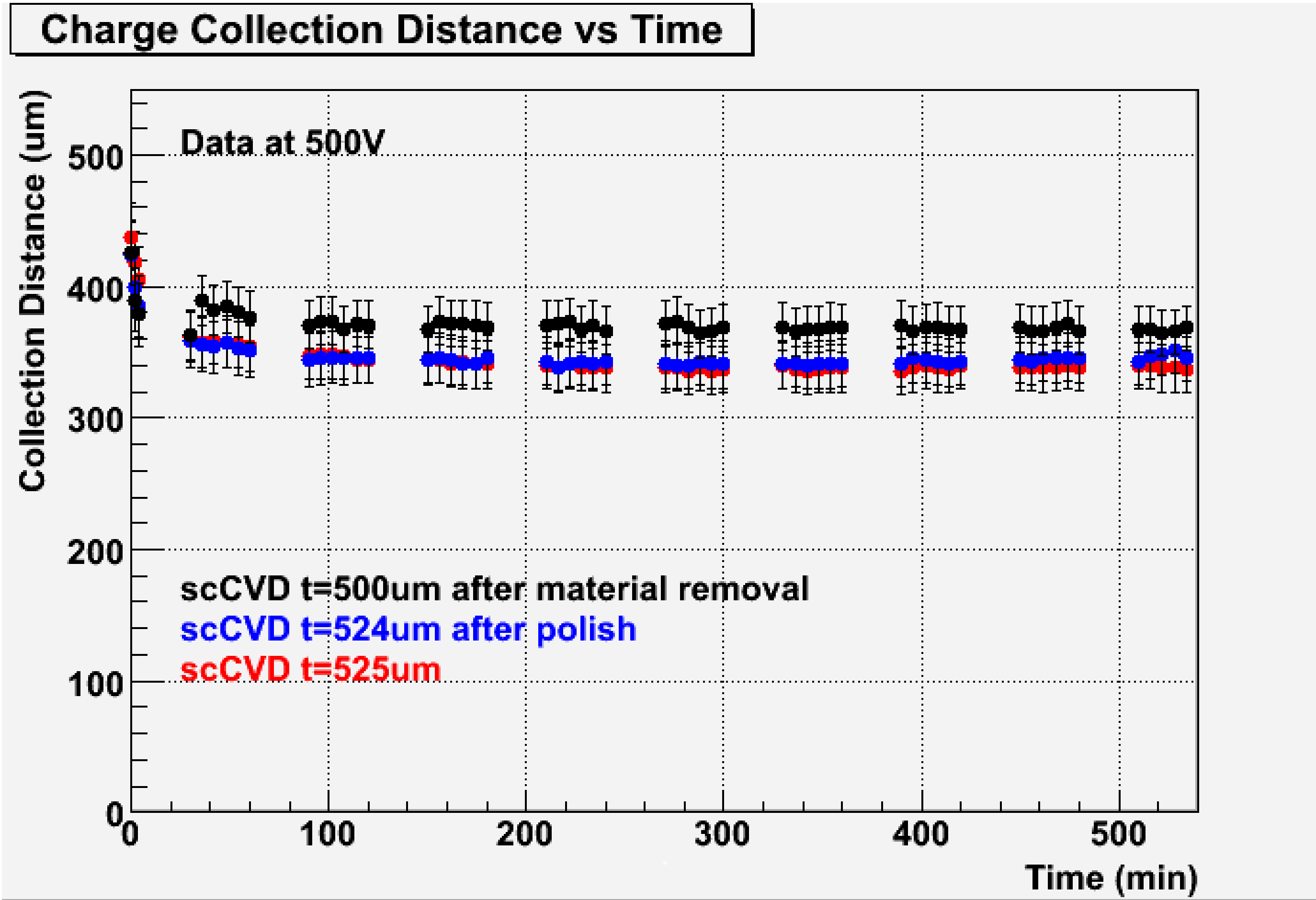




- RCMP Improves Detector Performance Significantly
- Mechanical Polishing Degrades Detector Performance

Courtesy: Dr. Harris Kagan OSU

# Detector Testing-OSU ( Solution 2)




Enhanced Charge Collection Distance after removing surface defects

Courtesy: Dr. Harris Kagan OSU

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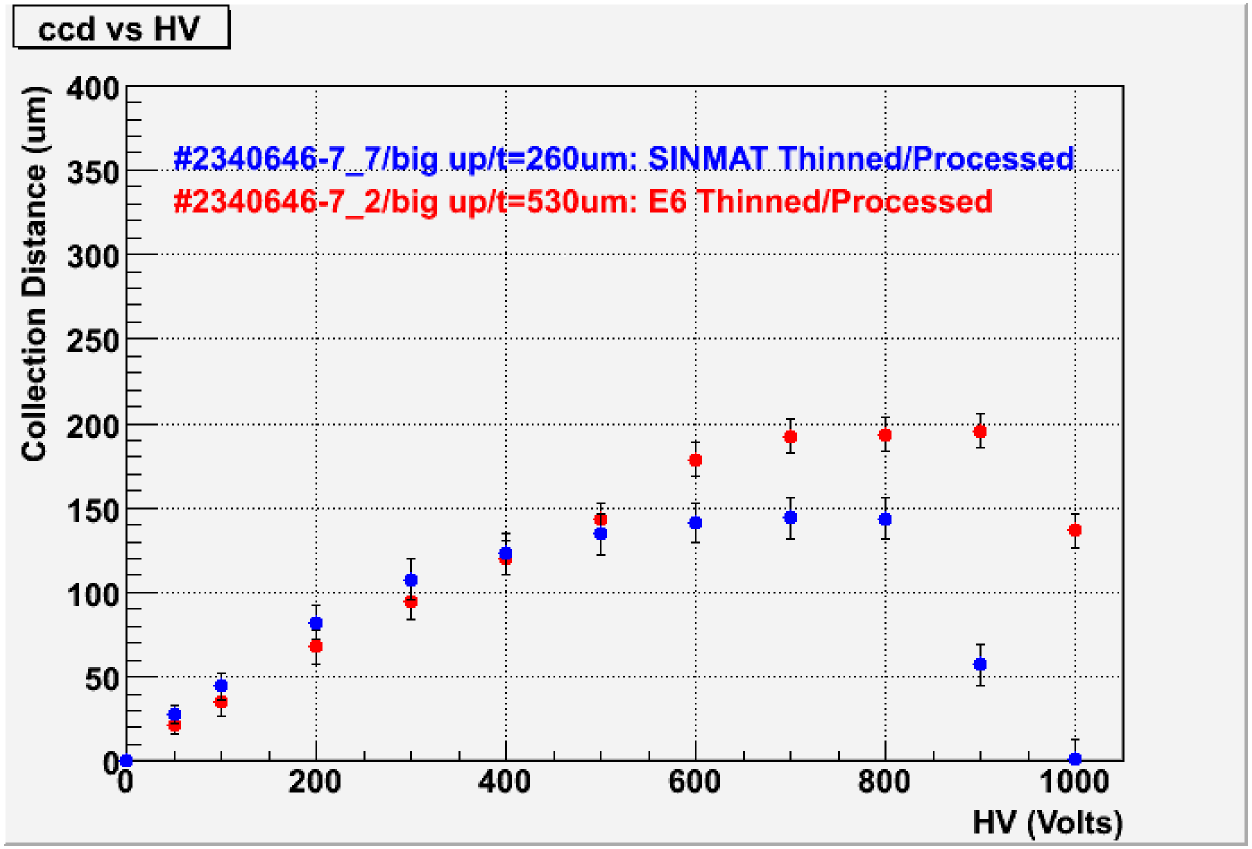
# VPE +RCMP Thinned Samples ( Solution 3)




**Charge Collection Distance vs High Voltage**
**As received 530 um sample shows 200 um ccd**
**Processed sample thickness 230um shows ccd 150um**

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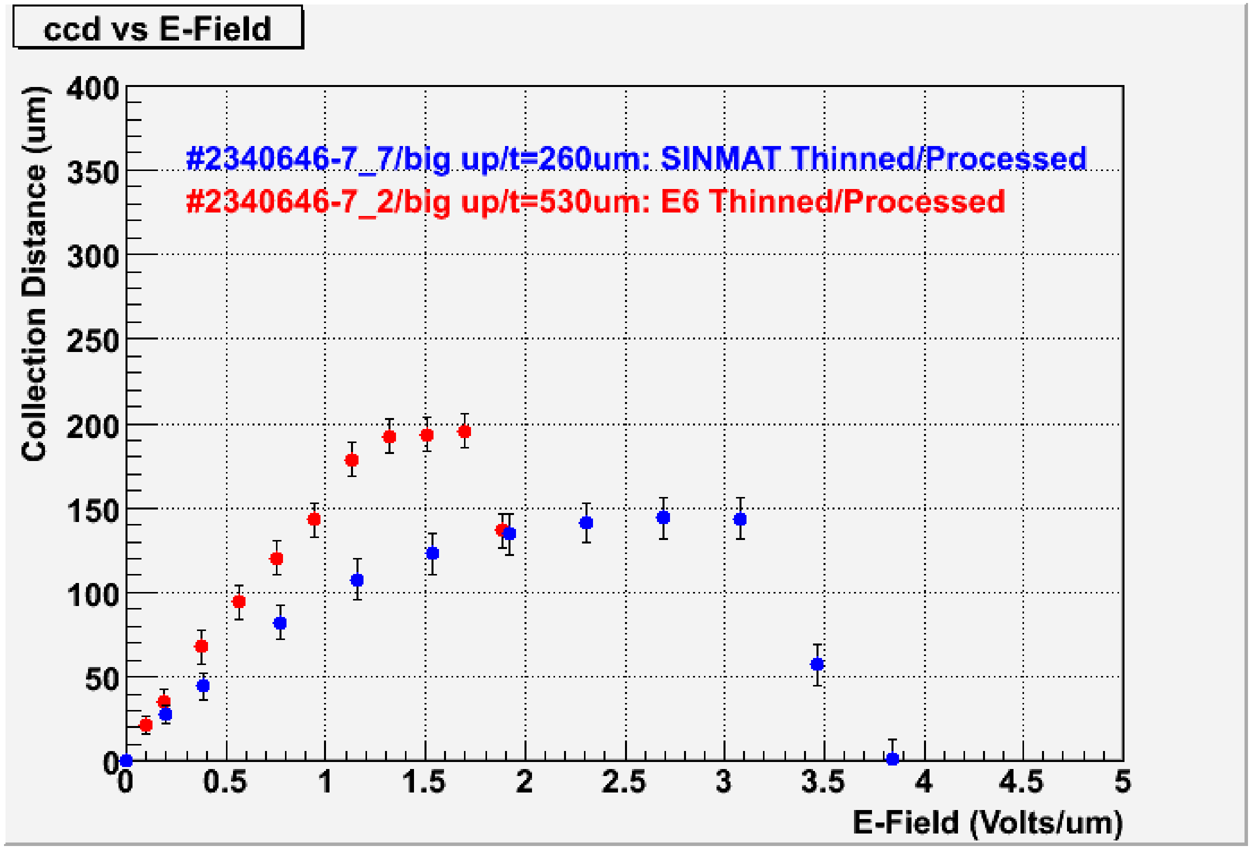
# VPE +RCMP Thinned Samples ( Solution 3)




## Charge Collection Distance vs E-field

- **As received 530 um sample shows breakdown at 1.75 Volts/um**
- **Processed sample thickness 230um shows breakdown at 3.1 Volts/um**

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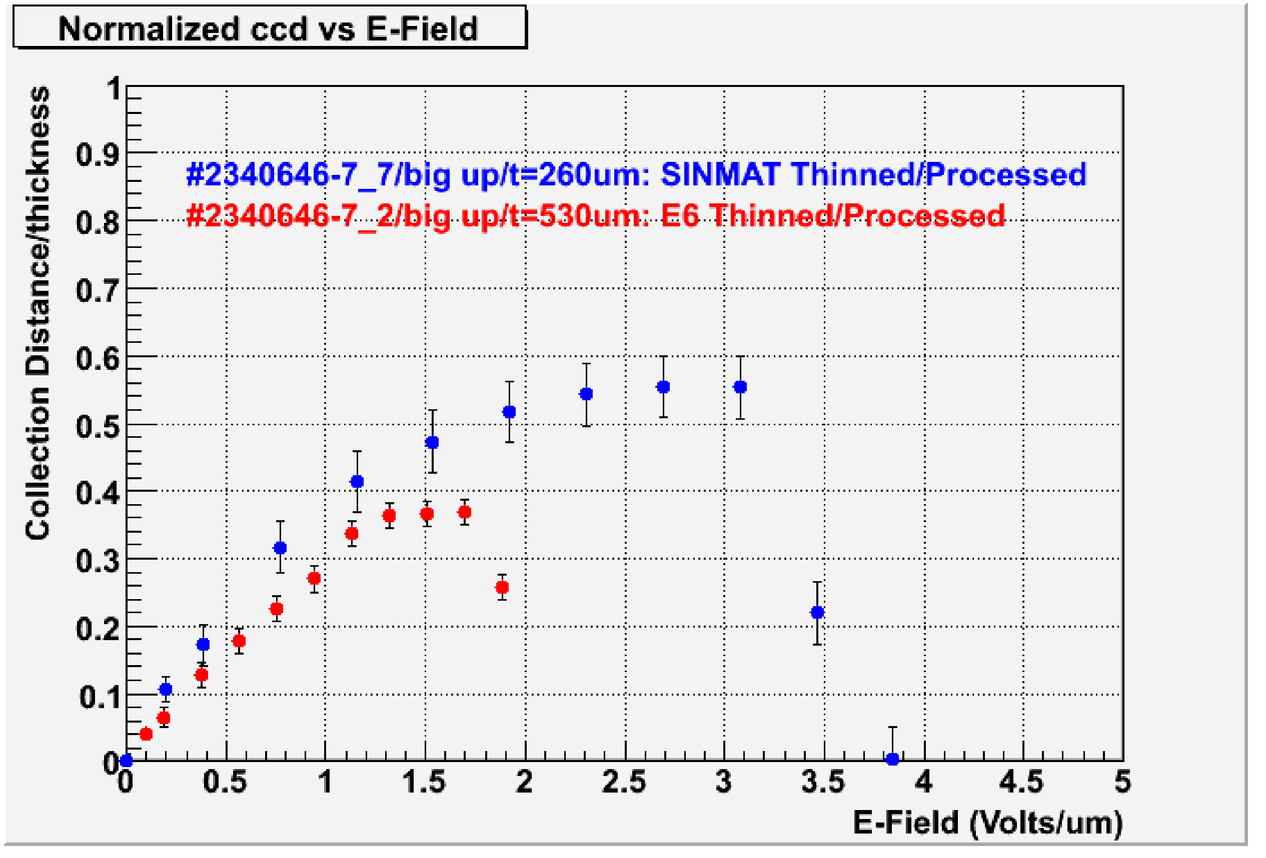
# Detector Testing-OSU ( Solution 3)




**Charge Collection Distance/thickness vs E-Field (Volts/um)**

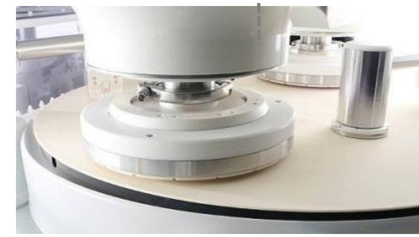
- **Shows > 50% more charge collection and break down**

*Dr.Kagan OSU*

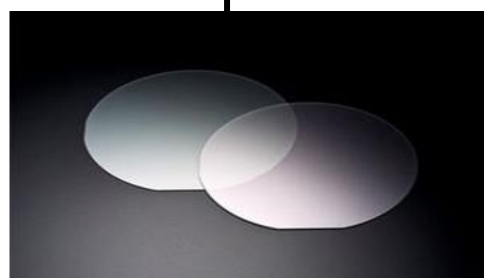
# Commercialization Plan

# Custom Solution 1: Optical Sapphire/SiC Finishing Technologies

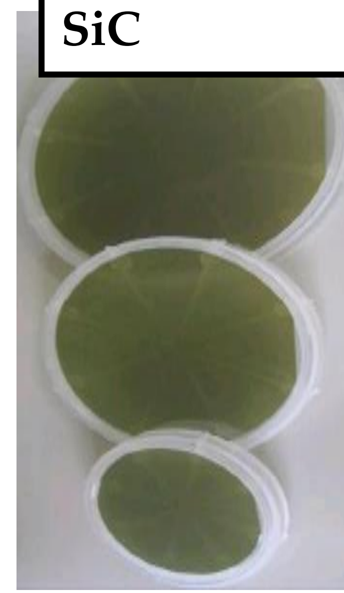
**Slicing** → **Grinding** → **Lapping** → **Polishing**



**Sapphire**



**SiC**



I. Grinding 30 -40 micron hard carbide

II. Lapping – 3-5 microns diamond slurries

III. Final Polishing – Silica based slurries

- Finishing more intensive operation
    - Both side polishing
    - 3 dimensional surfaces/multiple edges for wearable electronics

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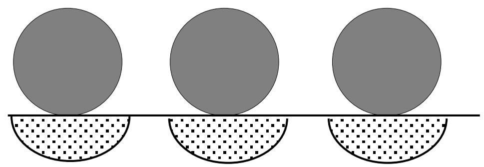
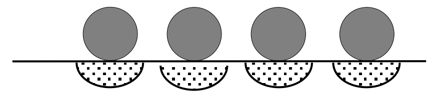
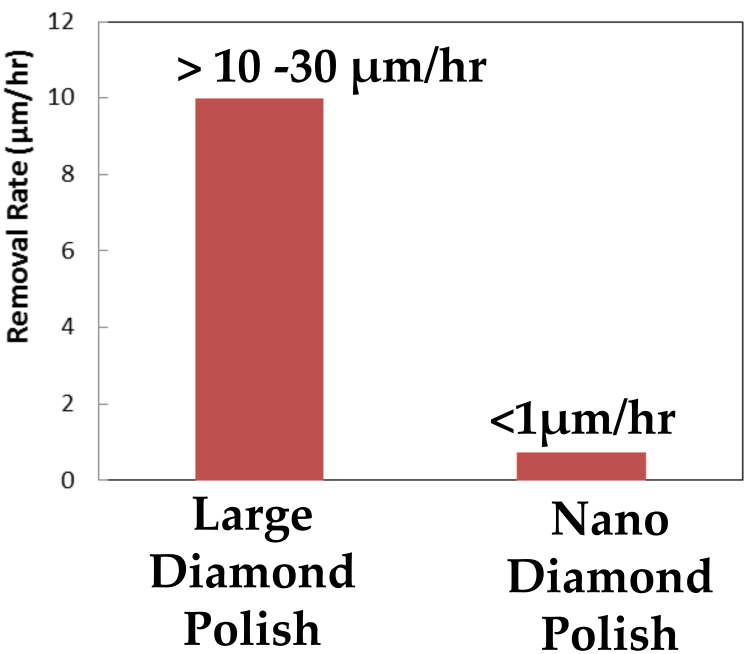
# Nano-Diamond Lapping Dilemma

| Issues | Mechanical Polishing (MP) | Nano diamond Polishing |
|---|---|---|
| Core particle Size | 3 -5 μm diamond  High sub-surface damage | Nano diamond 5 to 500 nm particles  Reduced sub-surface damage |




- Small diamond polishing significantly reduces size of defects
- Low polishing rates observed

# Comparison Removal Rates: Diamond Lapping and Nanodiamond CMP

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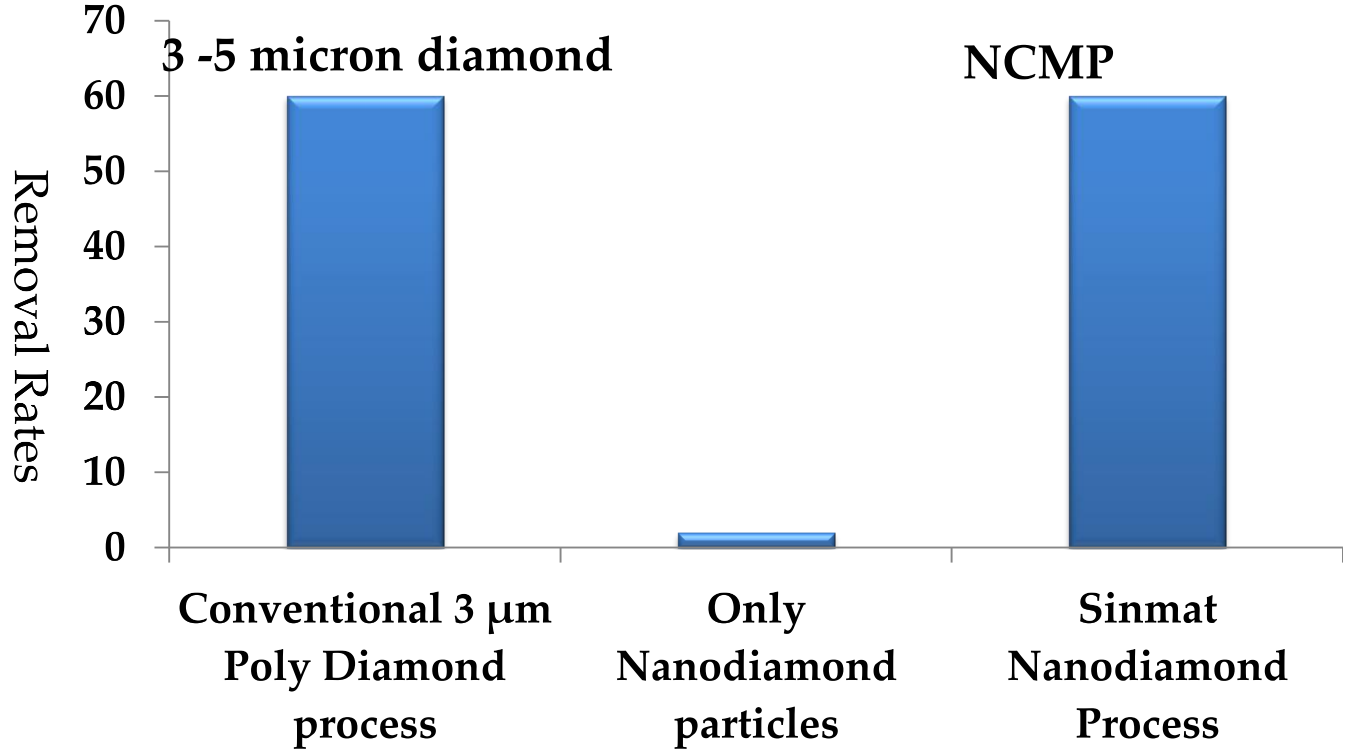
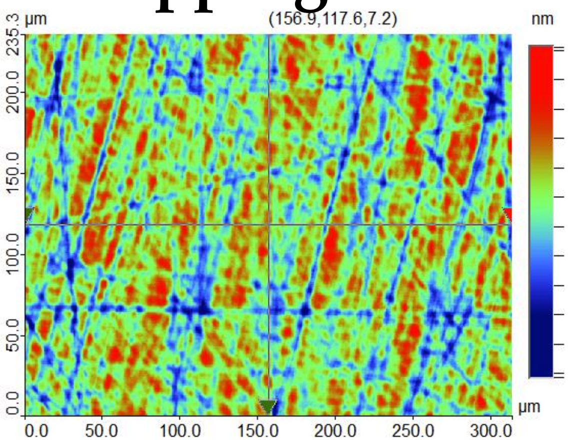



- Nanodiamond CMP can have similar polishing rates as 3- 5 micron poly diamond (40-50 microns/hr)
- 20 to 40 times higher than particles alone

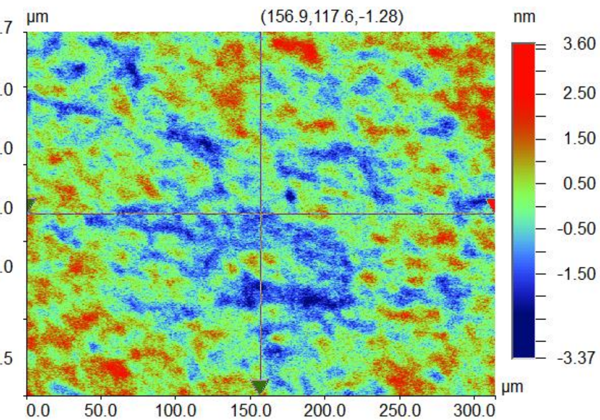
# Comparison Surface Finish: Diamond Lapping and Nanodiamond CMP

**Diamond Lapping**



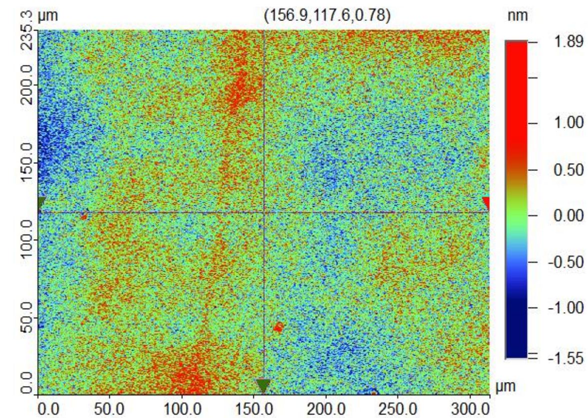

**Ra ~ 8-10 nm**
**Damage 10um+**

**Nanodiamond CMP**




**Ra ~ 0.7 nm**
**Damage0.25um**

**Silica CMP**

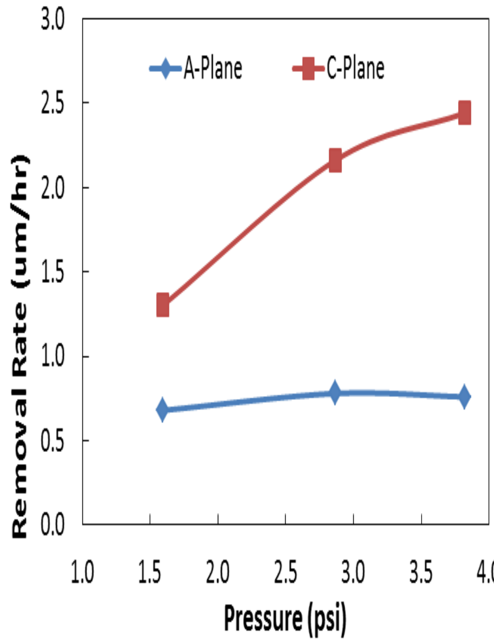


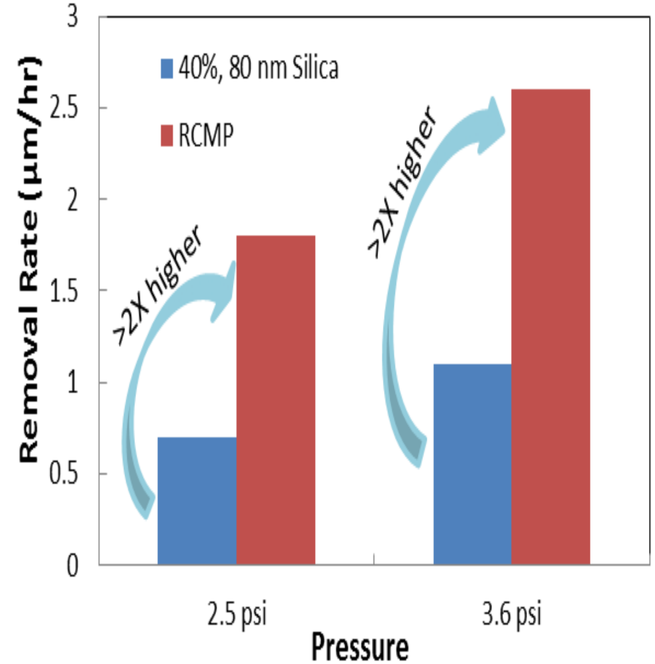

**Ra ~ 0.4 nm**
**No Damage**

- **Nanodiamond CMP has surface quality close of standard CMP process but with 10-15 X higher rates**
  - **Significantly smaller flaw size (25X low subsurface damage**
  - **Reduce Polish Times by 5X**

# Customized Solution 2: A-Face Sapphire Polishing for Wearable Electronics Applications

Reactive Chemical Mechanical Polishing (RCMP) of Sapphire




- High Polishing Rate, High Surface Finish Process
- Working together with end users
- Process Qualified For Wearable electronics with fortune 100 companies
- Expected High ROI

# Customized Solution #2: Ultra-Rapid Polishing of SiC & GaN

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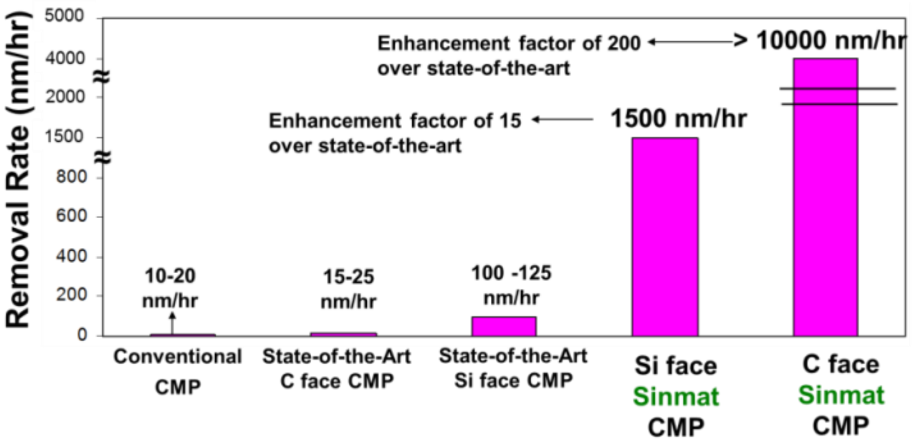
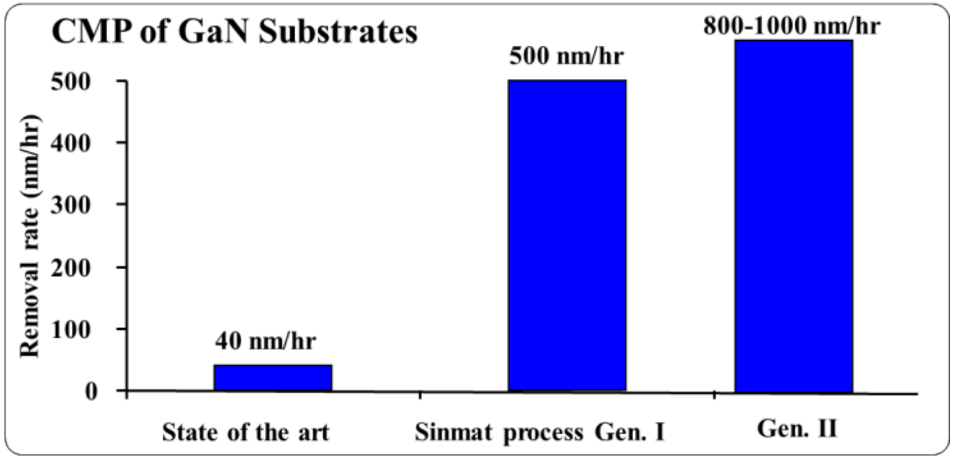
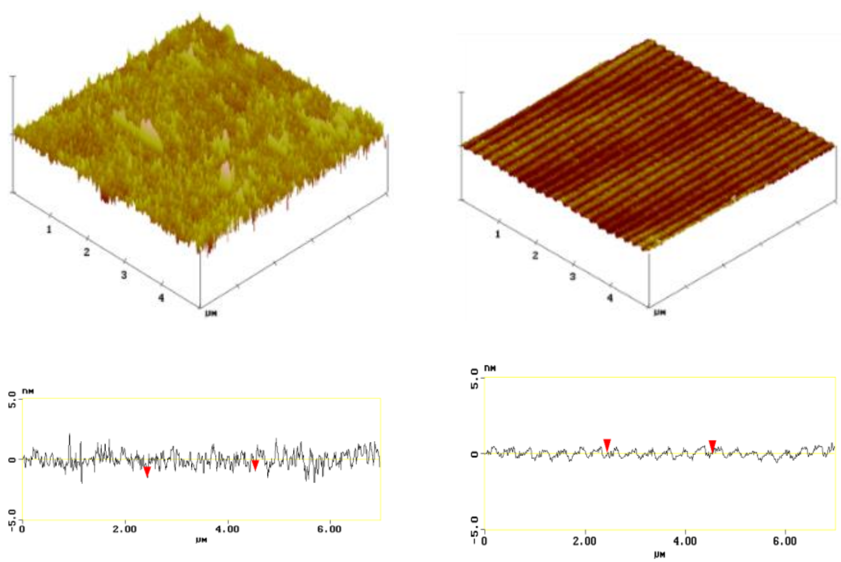


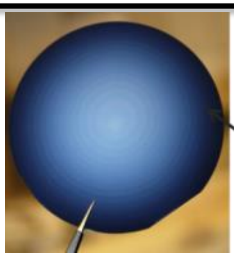



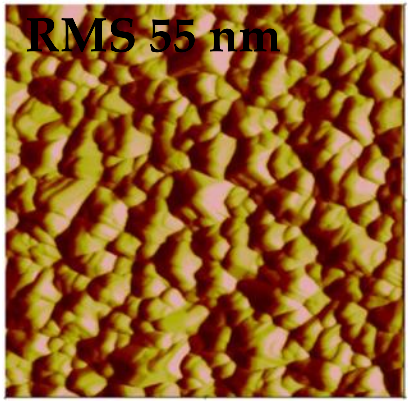
- Ultra–Rapid Polishing Rates (SiC, GaN)
- Ultra–smooth Flawless Surfaces (SiC and GaN)
- Low stress/ Robust Polishing Process
- >80% of worldwide CMP market (~1 million wafers/year)

# **Customized Solution # 3**: Polishing of Diamond Films for Thermal Conductivity Applications

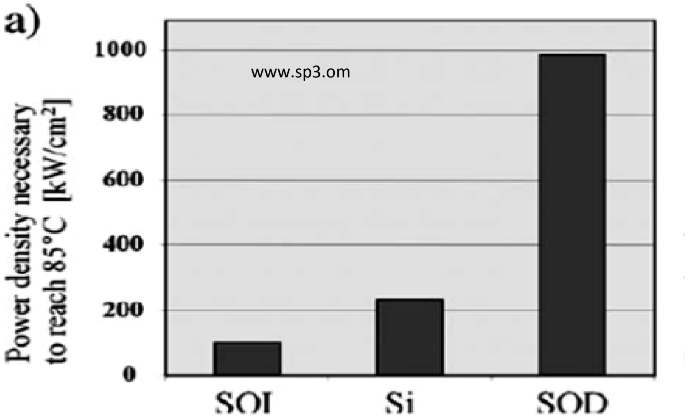
**Reactive chemical mechanical polishing (RCMP) process**

- ❑ **Ultra Smooth Diamond films (<0.3 nm rms roughness)**
- ❑ **Rapid, damage-free, scalable polishing technology**

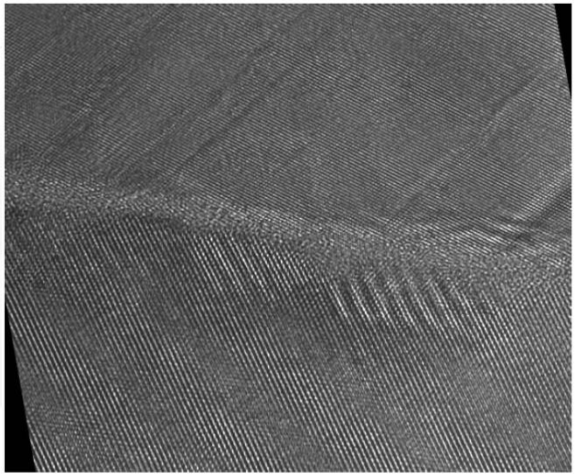


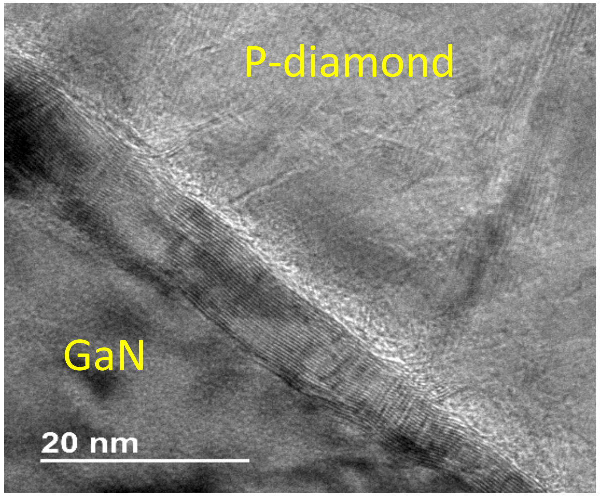





HRTEM

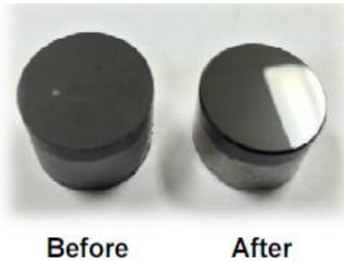


TEM of Fabricated Si on Diamond




TEM of Fabricated GaN on Diamond

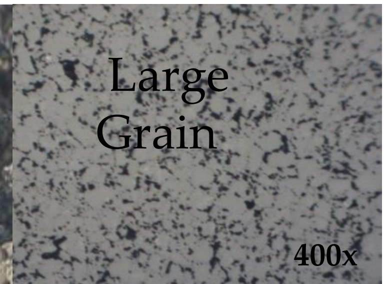
# Customized Solution Example # 4: Scalable CMP Polishing Poly diamond Composite & Seals

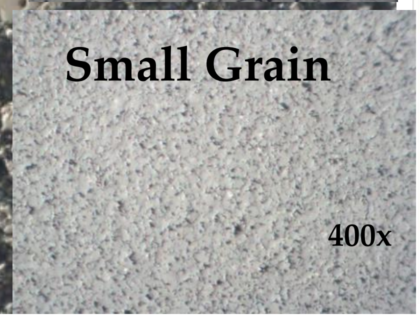




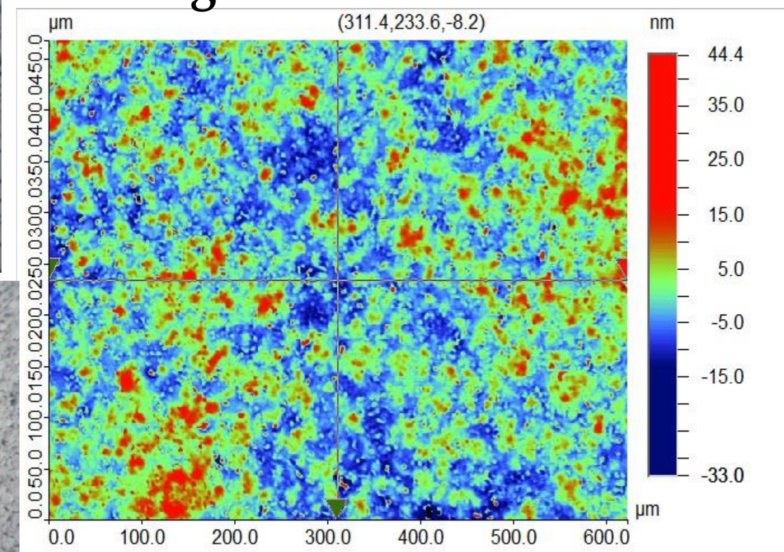
**Before**

**After**




**Roughness Ra = 5 nm**




- **First time demonstration of smooth (Ra =4-5 nm) PCD materials using CMP**
- **Scalable, Low pressure , short time, low velocity, low temperature process**
- **Can be adapted to non-flat 3D surfaces, nitride materials**
- **Low consumable cost**
- **Process qualified with leading manufacturers of PDC**

# Summary Of Accomplishments:

**Developed RCMP Process help to achieve** :

- Faster removal rate 10X
- Ultra smooth (~ 1-2 A) & Damage Free surface on diamond
- Ultra Flat and Low TTV (Peak valley roughness <0.5 micron) diamond
- Scalable to large size and multiple crystal polishing
- 30 - 50% higher charge collection distance
- Patent filed for the technology

**Commercialization:**

- DOE & DOD Applications
- Wearable and other electronic applications: Nano diamond reactive mechanical polishing for Sapphire, SiC and other hard materials
- Poly diamond compacts for Oil and Gas drilling applications & cutting polishing
- Silicon on diamond and GaN on diamond for thermal management in high power and future Integrated circuits

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# Thank you for Collaboration

Harris Kagan Ohio State University

Andreas Stolz NSCL Michigan State University