Novel Wide Bandgap Crystals: Low Temperature Growth of 2H-SiC and β-Gallium Oxide

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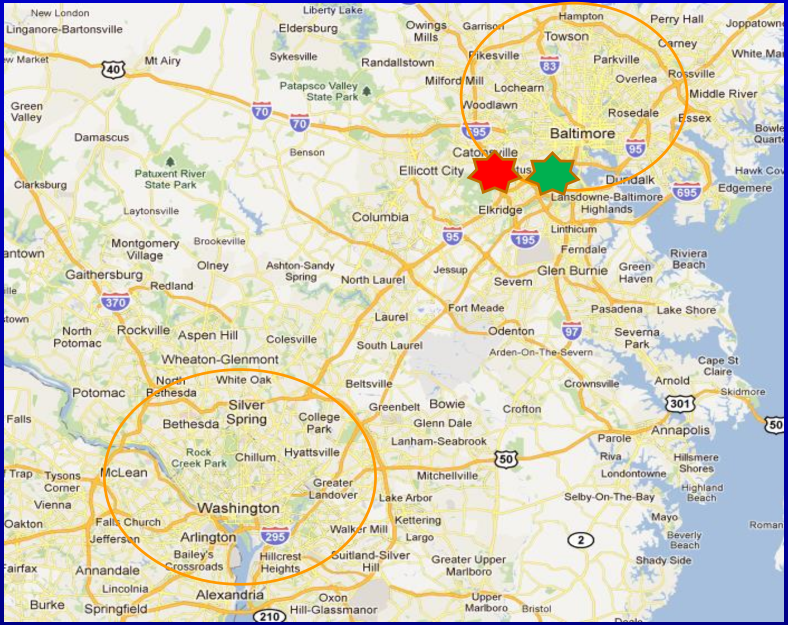
Tahira Raja, Vishnu Razdan, Emily Schultheis

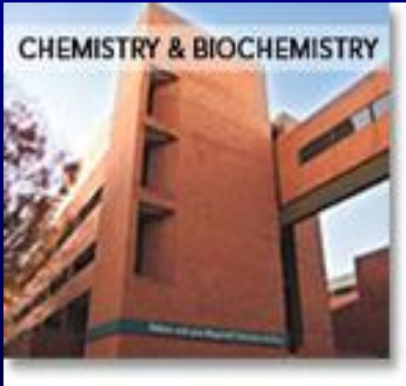
Materials are chosen to meet the strategic needs of DoD, DOE and DHS

Low temperature approach of reactive flux growth (LTRFG) of β-gallium oxide

Outlines

- Background and Objectives
    - Need for lattice/chemistry matched substrates for GaN
    - Problems of SiC were motivation for β-Ga_2O_3
- β-Ga_2O_3 Comparable to 2H-SiC
    - Low temperature reactive flux growth
    - Characteristics of 2H-SiC
- β-Ga_2O_3 Crystals
    - Growth approach: Co-crystallization and growth from melt
    - Solution growth
    - Characterization of grown β-Ga_2O_3 Crystals





We have an excellent team and facilities to execute semiconductor, EOIR and Laser materials and device programs at UMBC

Low temperature growth of β-Ga_2O_3

Objective:

The objective is to investigate scientific parameters for growing cm size of an exciting novel large bandgap material β-Ga_2O_3 crystals by low temperature innovative approach of reactive solution growth (LTRSG) method.

Benefits:

- **The bandgap of β- Ga_2O_3 is >4. 5 eV, which corresponds to the second largest bandgap after that of diamond among semiconductors, good thermal conductivity and mobility and excellent substrate for GaN.**

- **This will enable to develop optical devices, β- Ga_2O_3 deep ultraviolet photo detectors and high power amplifiers for variety of commercial and DOD applications.**

We had used a similar approach of reactive growth for 2H-SiC (β-Ga_2O_3)

We have excellent growth and characterization facilities at UMBC

Solution crystallizer

High temperature annealing furnace

Blue M furnace for high temp synthesis

Flux growth furnace

Custom CZ growth furnace

Bulk synthesis and crystal growth

Bridgman growth gold furnace

Three zone CVD growth furnace

Low temperature Bridgman furnace

Multizone vertical furnace

Wire Saw

Wire Bonder

Thin Film, nano crystal growth and fabrication

Nanoline

Optical and nanoSEM microscopes

Realtime X-ray Laue

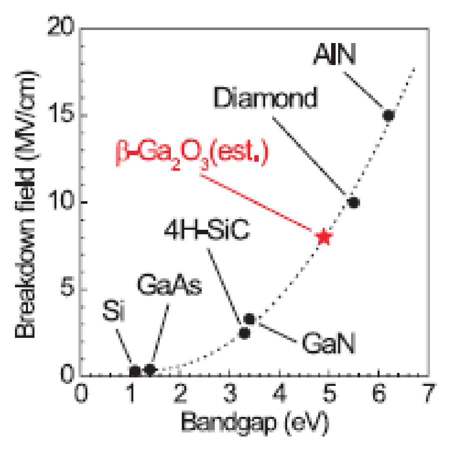
Probe facilities for materials and device characterization

Crystal and device characterization

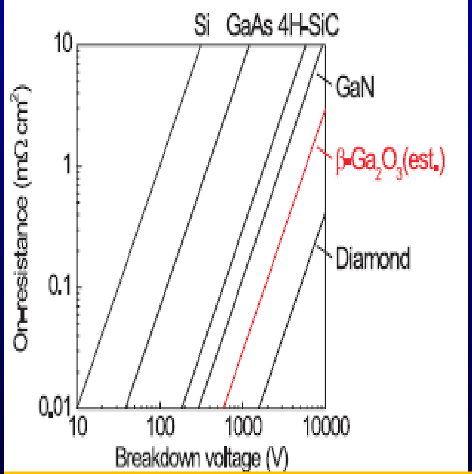
β-Ga_2O_3: A comparison of the merit of several semiconductors

Figure of merit for carious semiconductor materials

	Si	**4H-SiC**	**GaN**	**Diamond**	**β-Ga_2O_3**
Bandgap (eV)	1.1	3.18	3.3	5.5	**4.85**
Electron Mobility (cm^2/Vs.)	1400	700	1200	2000	**400**
Breakdown Field E_b (MV/cm)	0.3	2.5	3.3	10	**8**
Dielectric Constant	11.8	9.7	9.0	5.5	**9.5**
Baliga's Figure of Merit	1	340	870	24664	**3444**



Bandgap and breakdown field for semiconductor materials



Theoretical limit of on-resistance as the function of breakdown voltage

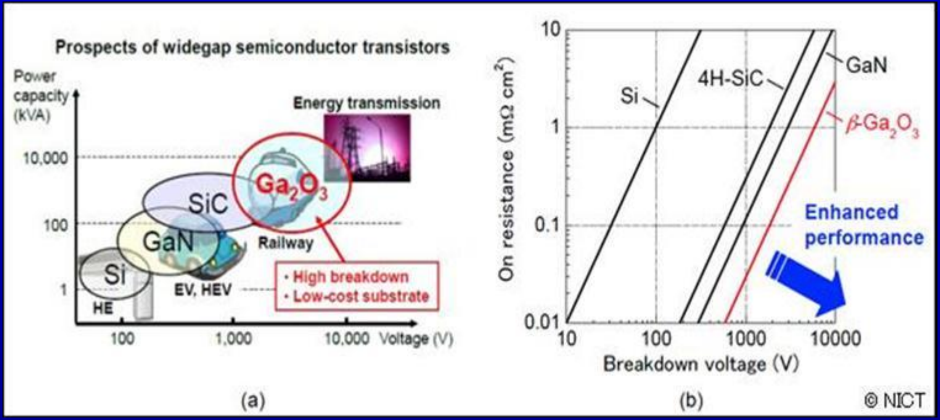
Bandgap and breakdown voltage of β-Ga_2O_3 of semiconductr materials

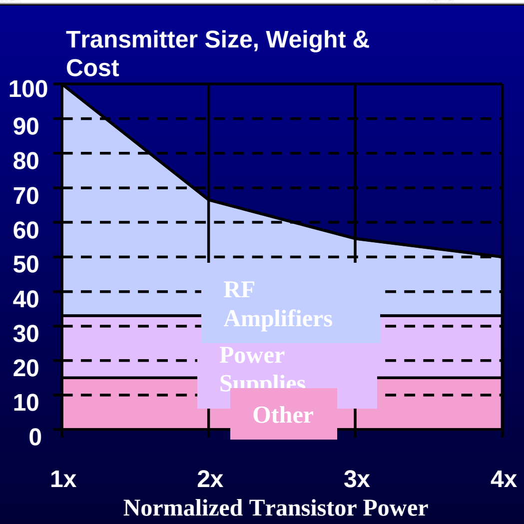
β-Ga_2O_3 has very good properties compared to developed wide bandgap materials

System Advantages of β-Ga_2O_3 Material

Higher Power Transistors Can Lead to 50% Reduction in Transmitter Size, Weight, Cost

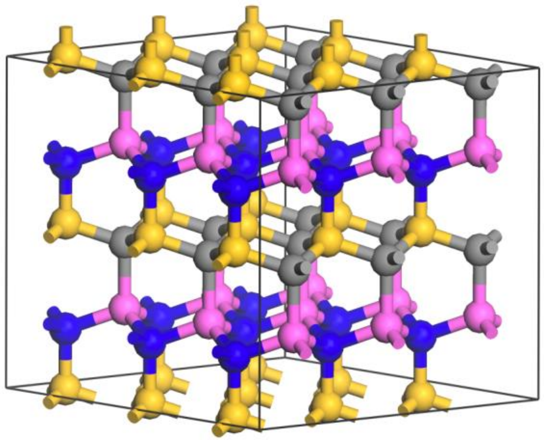
- Higher Power Transistors
  - Fewer Circuits
  - Smaller, Lower Cost Systems
- Improved Thermal Conductivity (>GaN) & Higher Temperature Capability with GaN
  - More Cooling Options
- Higher Voltage Operation
  - Higher Device Impedance
- Reduced Parasitics per Watt
  - Higher Efficiency & Wider Bandwidth
- Pure Heterostructure Possible (GaON)
  - Reduced thermal and mismatch problems

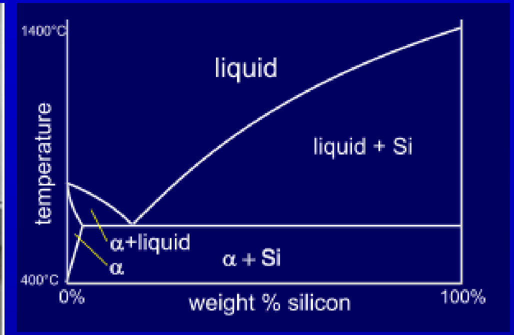




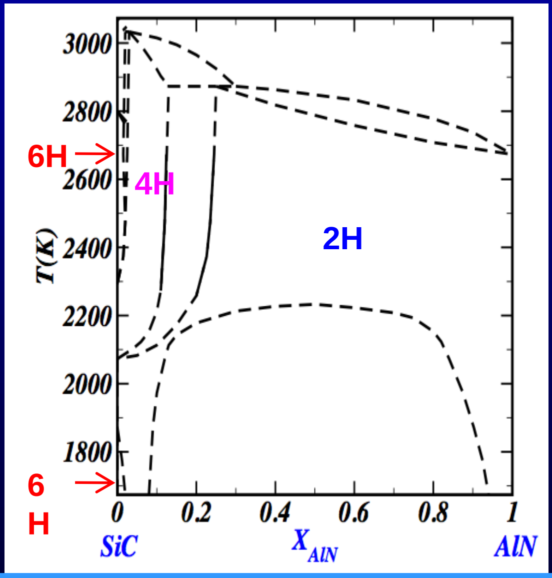
Potentially 10X lower surface traps as compared to AlGaN

2H-SiC: Synthesis by Reactive Liquid-Solid Incorporation (RLSI) Growth is a novel concept to produce large volume



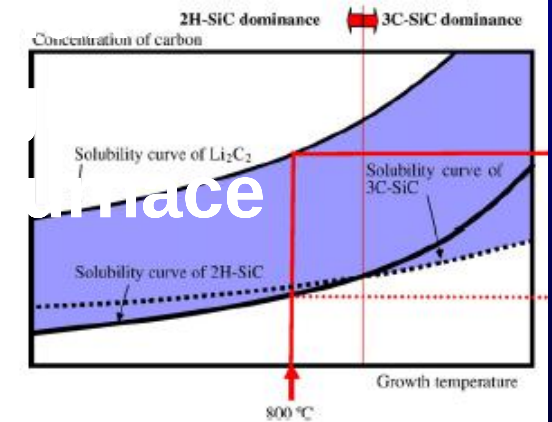


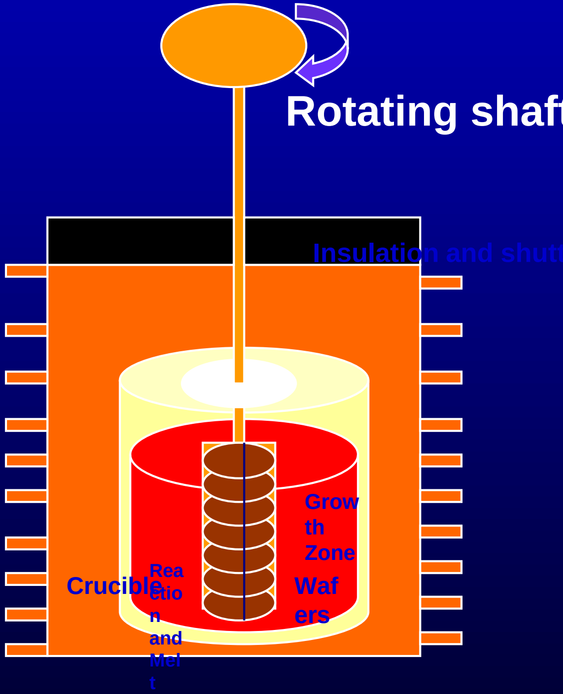
Al-Si liquid melt is suitable for incorporation of carbon and SiC both



Custom flux

urnace

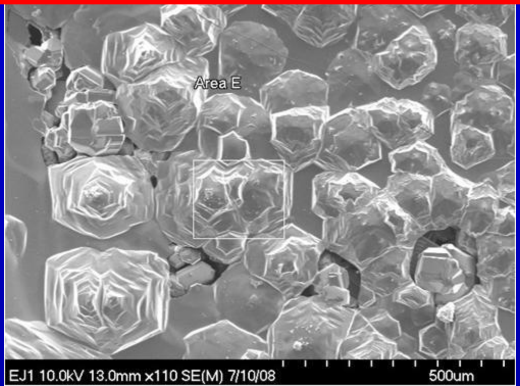


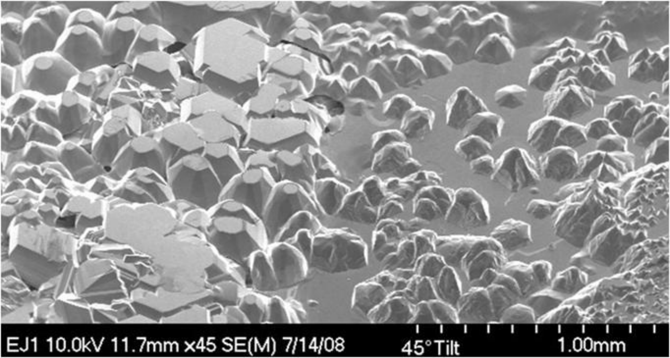


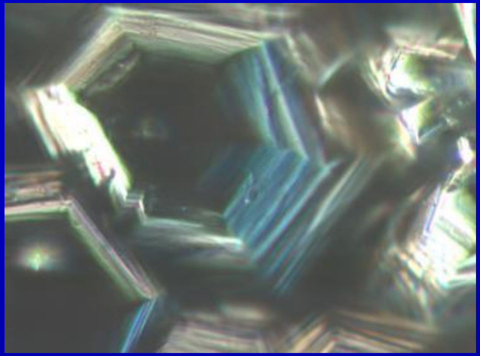
Addition of AlN stabilizes SiC into hexagonal 2H-SiC polytype

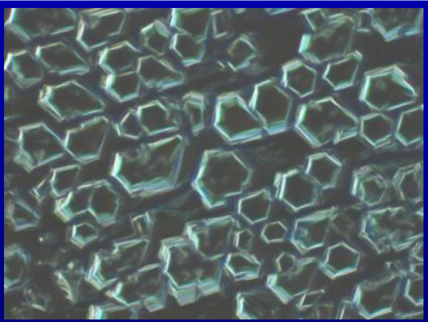
***J. Cryst. Growth Des.*, 2010, *10* (8), pp 3508–3514**

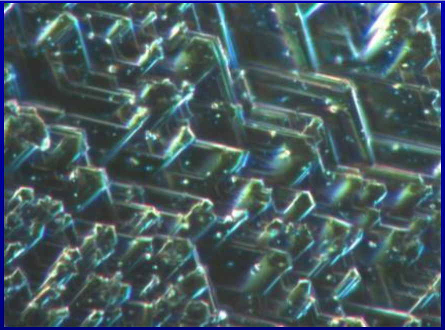
Material nucleated as a disc, developed into hexagons and then in film

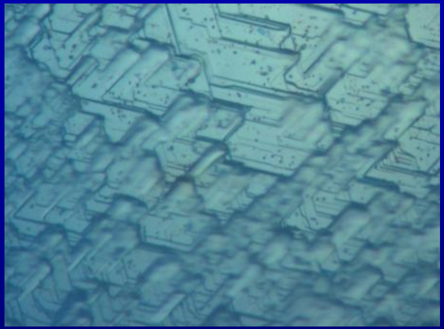




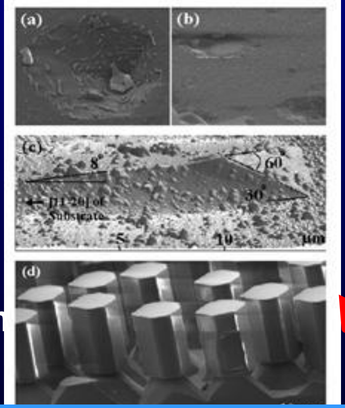








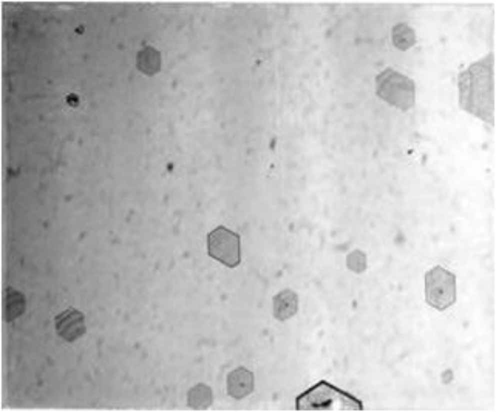
- The SiC deposits begin as discs and grow to become pyramids, before finally coalescing to become a continuous layer.
- 2H is the natural crystal orientation of AlN. AlN rods can be grown on 2H-SiC. The rods coalesce and form a continuous, low-stress layer.
- The rods are typically 12 μm in diameter and 17 μm in length, and exhibit flat (0001) surfaces.

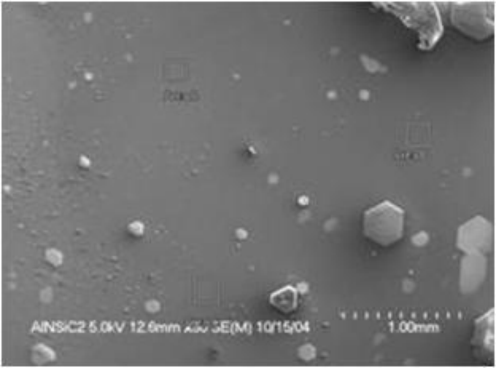


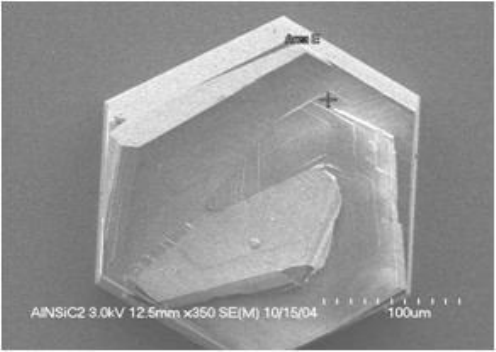
- Nucleation occurred like a disc.
- SiC grew by layer-by-layer growth mechanism.
- We did not observe micropipes in the grains (Yakimova, Yazdi and Syväjärvi – Linköping University, Sweden)

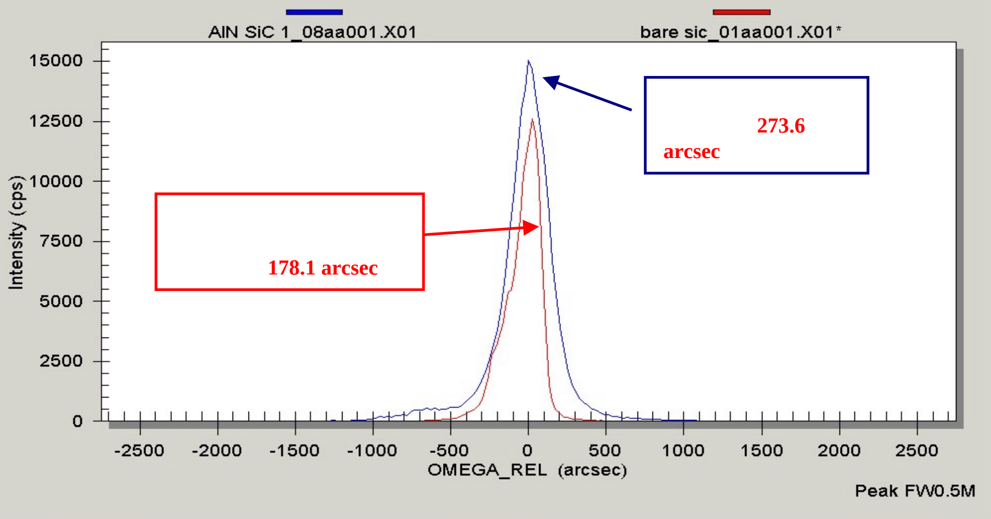
http://images.iop.org/dl/compsemi/magazine/CSJun09p24.pdf

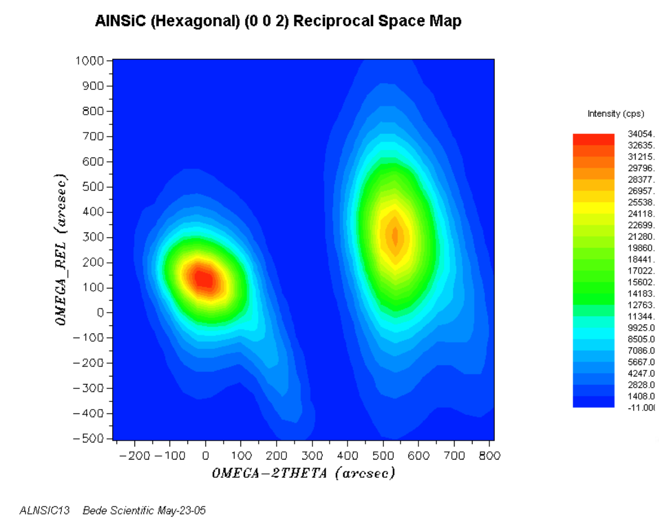
AlN-SiC alloys have structure of AlN (2H) which indicates that SiC changes to Wurtzite

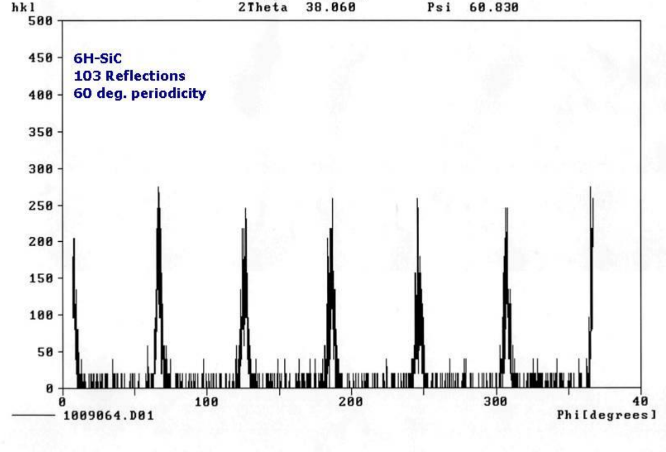








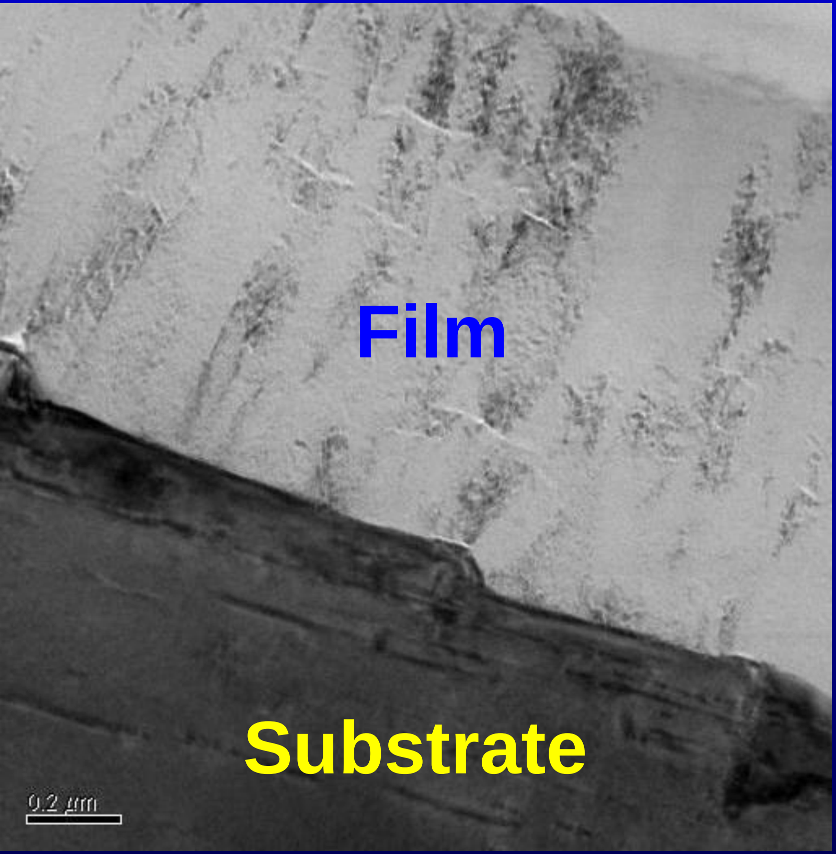




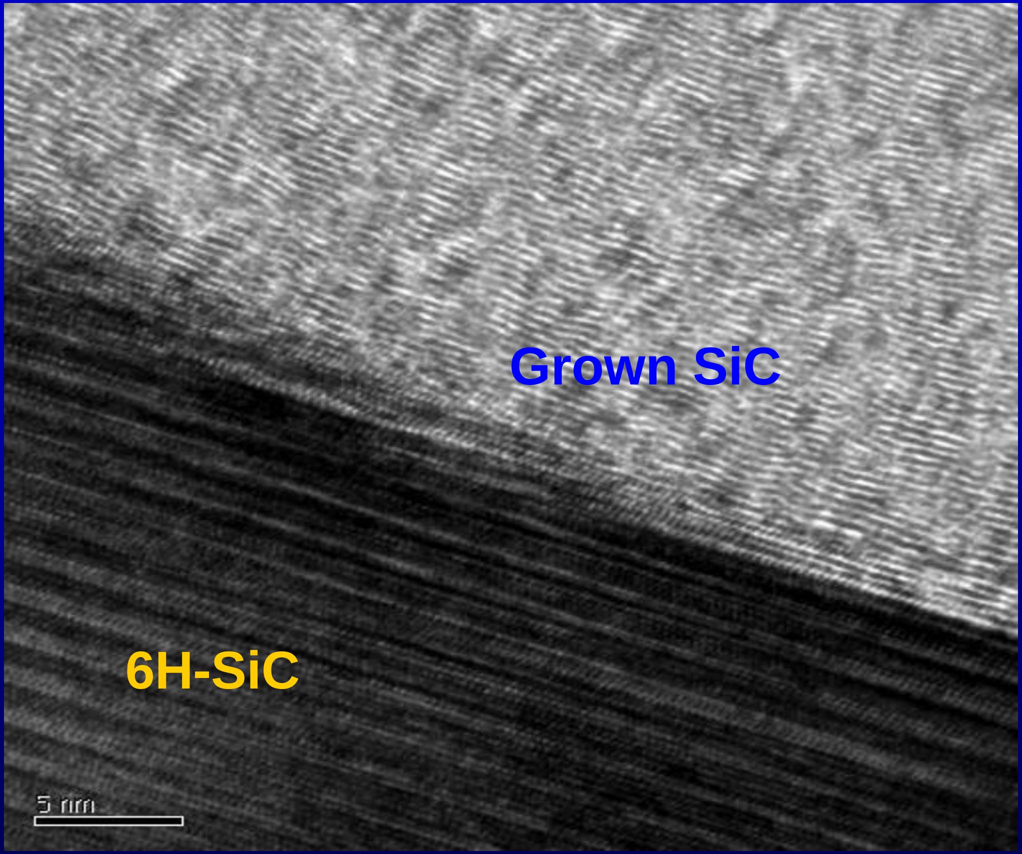
Data shows both substrate and alloy peaks

Hexagonal morphology was observed

HRTEM clearly shows formation of Wurtzite structure on 6H-SiC substrate



TEM image showing film and substrate. Film/substrate interface is not flat and film morphology is columnar.

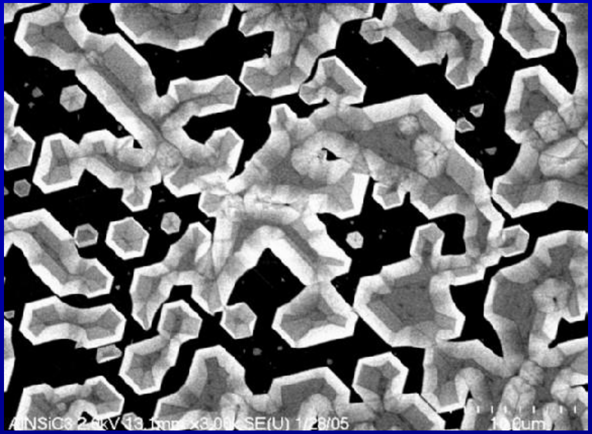


High resolution TEM image showing part of the film and 6H-SiC substrate

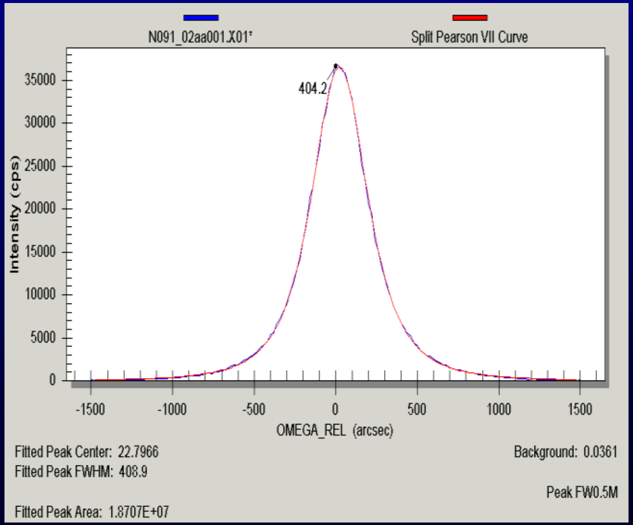
TEM morphology at the interface is very different for the substrate and new material

SiC grown on thick film of AlN was used for GaN growth.

- Growth morphology of GaN and formation of small angle boundaries
- One can design experiments to reduce the defect density



Growth morphology of GaN



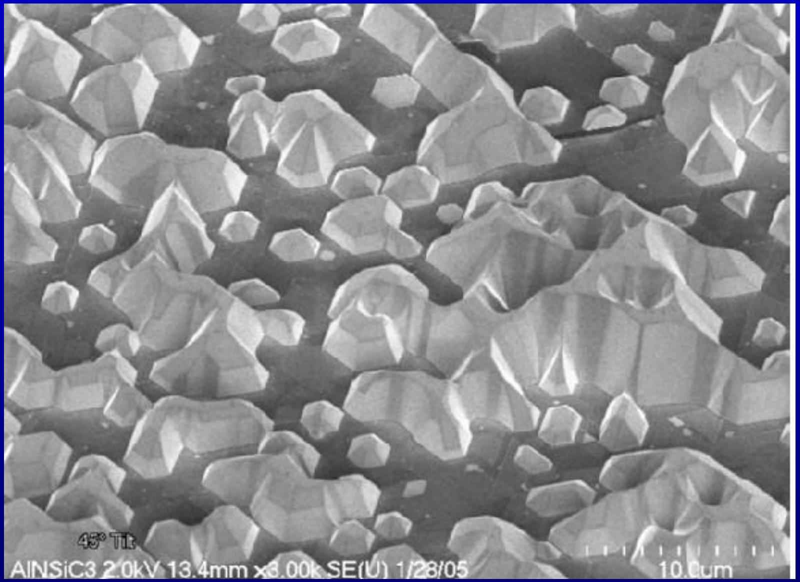
Fitted Peak Center: 22.7966

Fitted Peak FWHM: 408.9

Fitted Peak Area: 1.8707E+07

Background: 0.0361

Peak FW0.5M



- FWHM is 404.2 arcsec
- GaN peak is located at expected location for epitaxial (0001) GaN
- Important to note that the orientation was maintained from substrate, to alloy material, to GaN, thus the GaN is in fact epitaxial

Summary for 2H-SiC

- 2H-SiC with pure hexagonal symmetry is stable in presence of AlN
- 2H-SiC has higher electron velocity and larger bandgap which translates into better devices.
- SiC can be grown at temperature below 1200C and hence Si wafers with AlN seed can be used to nucleate SiC.
- Low temperature reactive growth is good process for SiC growth
- Low temperature SiC growth opens possibility of large area SiC growth at low cost
- Low cost large area SiC with superior properties and low defects will be possible

Low temperature process provides a pathway for growth of large crystals

Low temperature growth of β-Ga_2O_3

Objective:

The objective is to investigate scientific parameters for growing cm size of an exciting novel large bandgap material β-Ga_2O_3 crystals by low temperature innovative approach of reactive solution growth (LTRSG) method.

Background

- **Commercially available Ga_2O_3 often consists of a mixture of the α- and β-phases.**
- **The β-phase is the thermodynamically stable modification, with a formation Gibbs energy that surpasses that of corundum.**
- **Additionally the γ–, δ–, and ε-Ga_2O_3 phases are known in literature.**

We used a similar approach of reactive growth process for β-Ga_2O_3 crystal

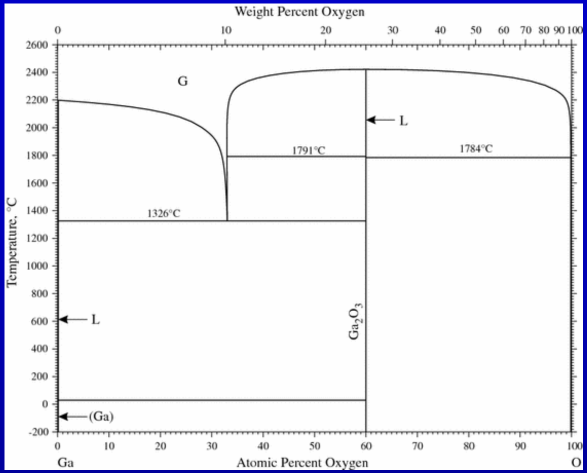
Chemistry and Solid-liquid equilibrium data

Background on Crystal Chemistry

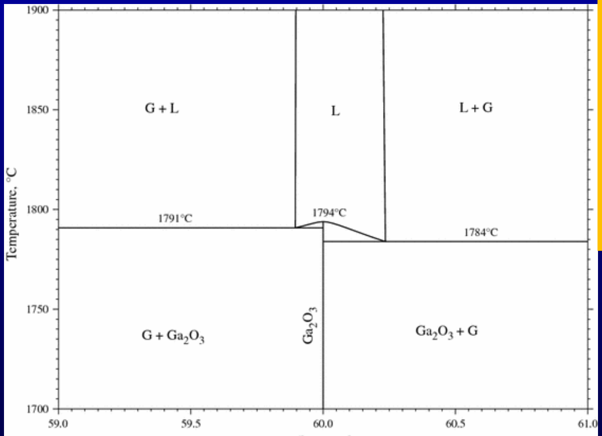
Gallium oxide is precipitated in hydrated form upon neutralization of acidic or basic solution of gallium salt. It can occur in five different modifications, α,β,δ,γ and ε.

β-Ga_2O_3 is the most stable form

- **β-Ga_2O_3 can be prepared by heating nitrate, acetate, oxalate or other organic derivatives above 1000˚C.**
- **α-Ga_2O_3 can be obtained by heating β-Ga_2O_3 at 65kbars and 1100˚C for 1 hour giving a crystalline structure. The hydrated form can be prepared by decomposing precipitated and "aged" gallium hydroxide at 500˚C.**
- **γ-Ga_2O_3 is prepared by rapidly heating the hydroxide gel at 400˚C-500˚C.**
- **δ-Ga_2O_3 is obtained by heating $Ga(NO_3)_3$ at 250˚C.**
- **ε-Ga_2O_3 is prepared by briefly heating δ-Ga_2O_3 at 550˚C for 30 minutes**



H. Okamoto, J Phase Equilibrium and Diffusion, December 2008, Volume 29,6, pp 550-551



M. Zinkevich and F. Aldinger, Thermodynamic Assessment of the Gallium-Oxygen System. *J. Am. Ceram. Soc.*, 2004, 87(4), p 683-691

A very tight control of composition and temperature and high gradient will be required to grow from melt

Approach for the low temperature growth

There are two approaches:

(α)β-Ga_2O_3 single crystals using tin and tin-gallium solution method (problem of Sn)

(b) $GaCl_3$ nitration followed by treatment with hydroxide

(c) Growth by hydrolysis of gallium(III)-isopropoxide and from aqueous $GaCl_3$ solution by addition of aqueous tetramethylammonium hydroxide (TMAH)

- **Controlling the growth rate: We will control the growth rate and hence the quality by cooling rate**
- **Nucleation rate: We propose to use nucleus grown by urea method**
- **Characterization:**
  - **Bandgap**
  - **Lattice parameters:**
  - **Quality by X-ray rocking curve**
  - **Morphology by SEM**
  - **Resistivity and Mobility**
  - **Impurities by PL**
  - **Fabrication by cutting and polishing (AFM)**

Phase	**β-Ga2O3**
Crystal system	**Monoclinic**
Space group	**C2/m**
a [˚ A]	**12.214 (3)**
b [˚ A]	**3.0371 (9)**
c [˚ A]	**5.7981 (9)**
Beta	**103.83 (2)**
Cell volume[˚A3]	**208.8**

This low cost approach has potential for producing large and high quality crystals

There are pathway to move ahead where we can avoid use of Sn

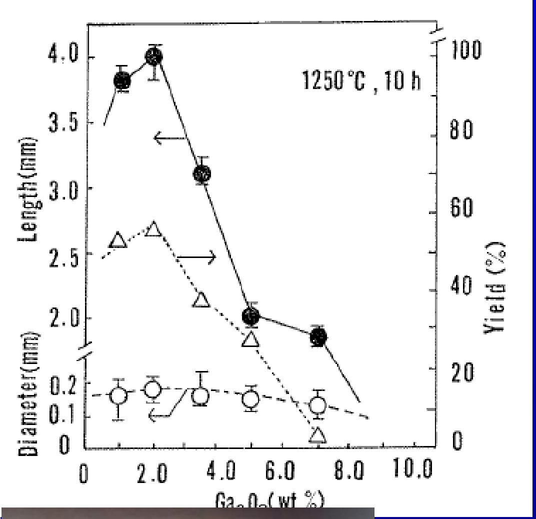
- **Cocrystallization in catalyzed environment:** In this biomimetic approach, the hydrolytic enzyme motif from the silicateins, consisting of nucleophilic hydroxyl of serine and amine of histidine, catalyzes the hydrolysis of the gallium precursors and results in both GaOOH and -Ga$_2$O$_3$ nanocrystal formation with a wide size range.
  - Urea melt

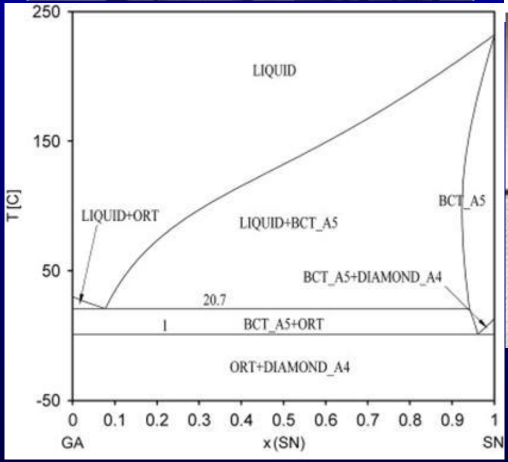
- **Growth from Melt**
- Ga-Sn Experiment: Experiments were performed using several Ga:Sn ratio in the range (1:1 to 3:1 ratio)
- Effect of temperature: High temperature required (1100 to 1300C)
  - Sn-Ga Eutectic melt
- Solution growth experiments with and without urea: Dissolve 5 gram urea and 1-2 gm gallium salt in HNO3+H2O (10%HNO3) in a test tube
  - Dissolved and cooled for recrystallization
  - Got gallium oxide co-crystallize with urea

Co-crystallization and flux growth are two promising approach

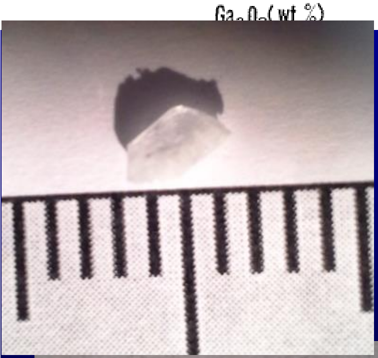
Synthesis by Reactive Liquid-Solid Incorporation (RLSI) Growth is a novel concept to produce large volume

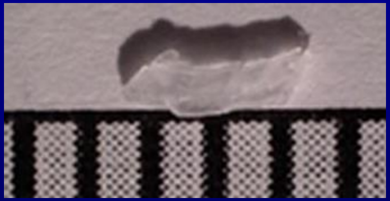
RLSI Furnace, Alumina crucible and substrate

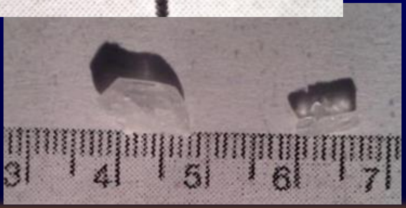


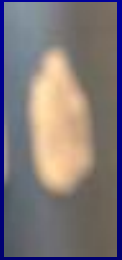


Ga-Tin Eutectic melt was used









Different morphologies were observed in Alumina crucible

Effect of composition of Ga/Tin has been reported in Japan

Ratio of flux and position controls morphology. However, by stirrin one can alter the morphology and hence the crystal size

Synthesis from gallium chloride and hydroxide material

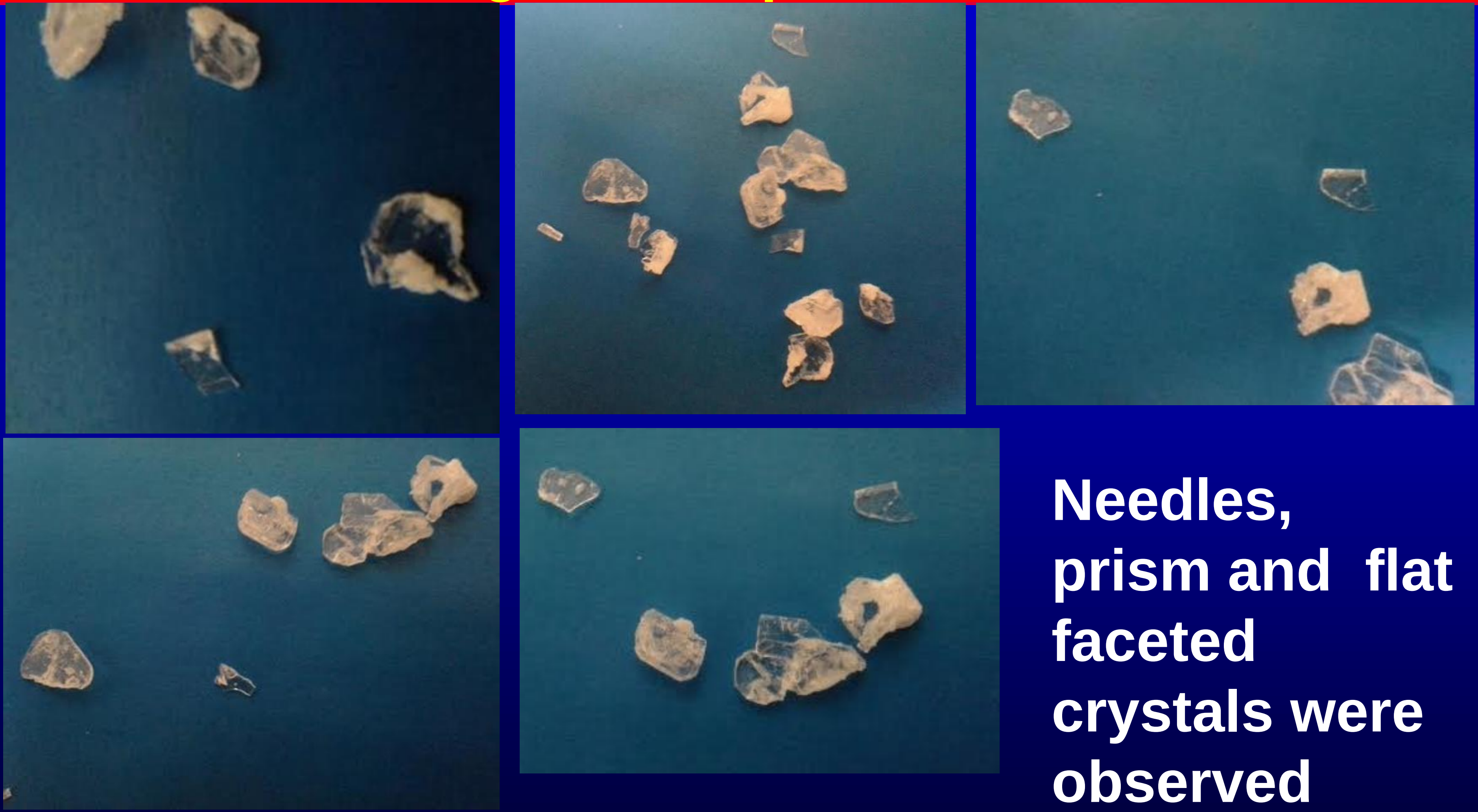
There traces of gallium chloride in presence of traces of HCl. Excess HNO_3 is added to avoid chloride

Dissolution and nitraion and neutralization has to be optimized

Morphology of crystals

Uncontrolled crystallization was slow and produced mm to cm size crysta

Morphology of crystals harvested from the second growth experiment



Needles, prism and flat faceted crystals were observed

Hrrvested crystals had different morphologies

Four major morphologies of crystals were observed in the second growth experiment

- **Different morphology of as grown 2mm to 7mm size virgin crystals**
- **Very important clues about effect of**
    - **pH**
    - **Concentration and gradient**
    - **Nucleation**
    - **Stirring**
    - **Cooling rate**

Crystals had four morphologies indicating effect of pH, concentration and rotationstirring

Preliminary characterization of grown crystals

- Characterization:
  - Bandgap
    - Measured optically: 4.7eV
  - Lattice parameters:
    - a = 5.797^{0}A
    - b = 3.04
    - c= 12.198
    - Angle β = 103.68
  - Morphology by SEM
  - Quality by X-ray rocking curve
  - Resistivity and Mobility
  - Impurities by PL
  - Fabrication by cutting and polishing (AFM)

Phase	β-Ga2O3
Crystal system	Monoclinic
Space group	C2/m
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c [˚ A]	5.7981 (9)
Beta	103.83 (2)
Cell volume[˚A3]	208.8

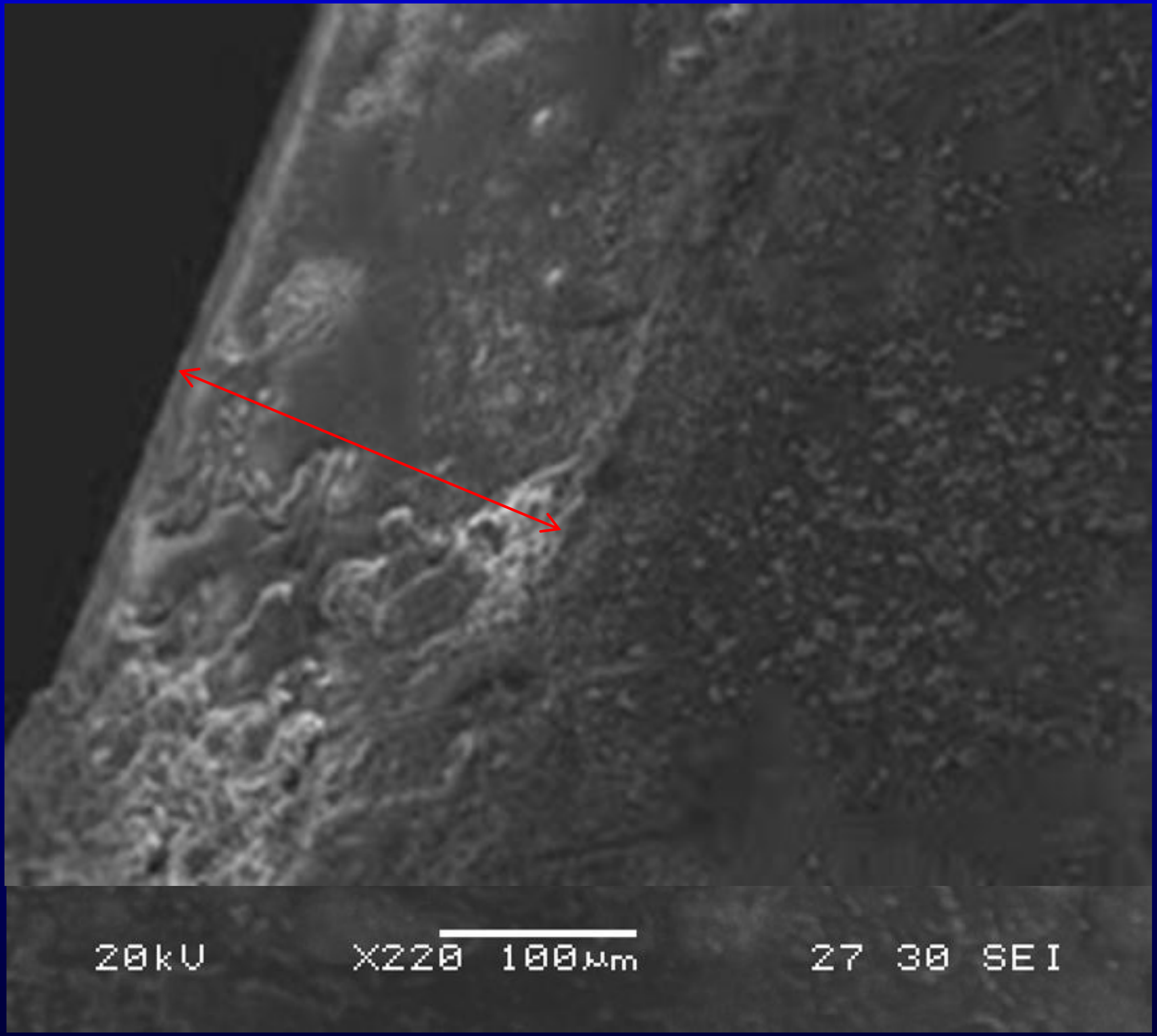
X-ray produced the lattice parameters very closed to literature value

JEOL SEM system was used for morphology

- System used : JEOL 560
- Voltage: 20KV
- No sputtering
- We studied morphology to determine layering
- Composition
- Growth steps
- Surface structures
- Major point defects
  - Precipitates
  - Voids
  - Cracks
  - bubbles

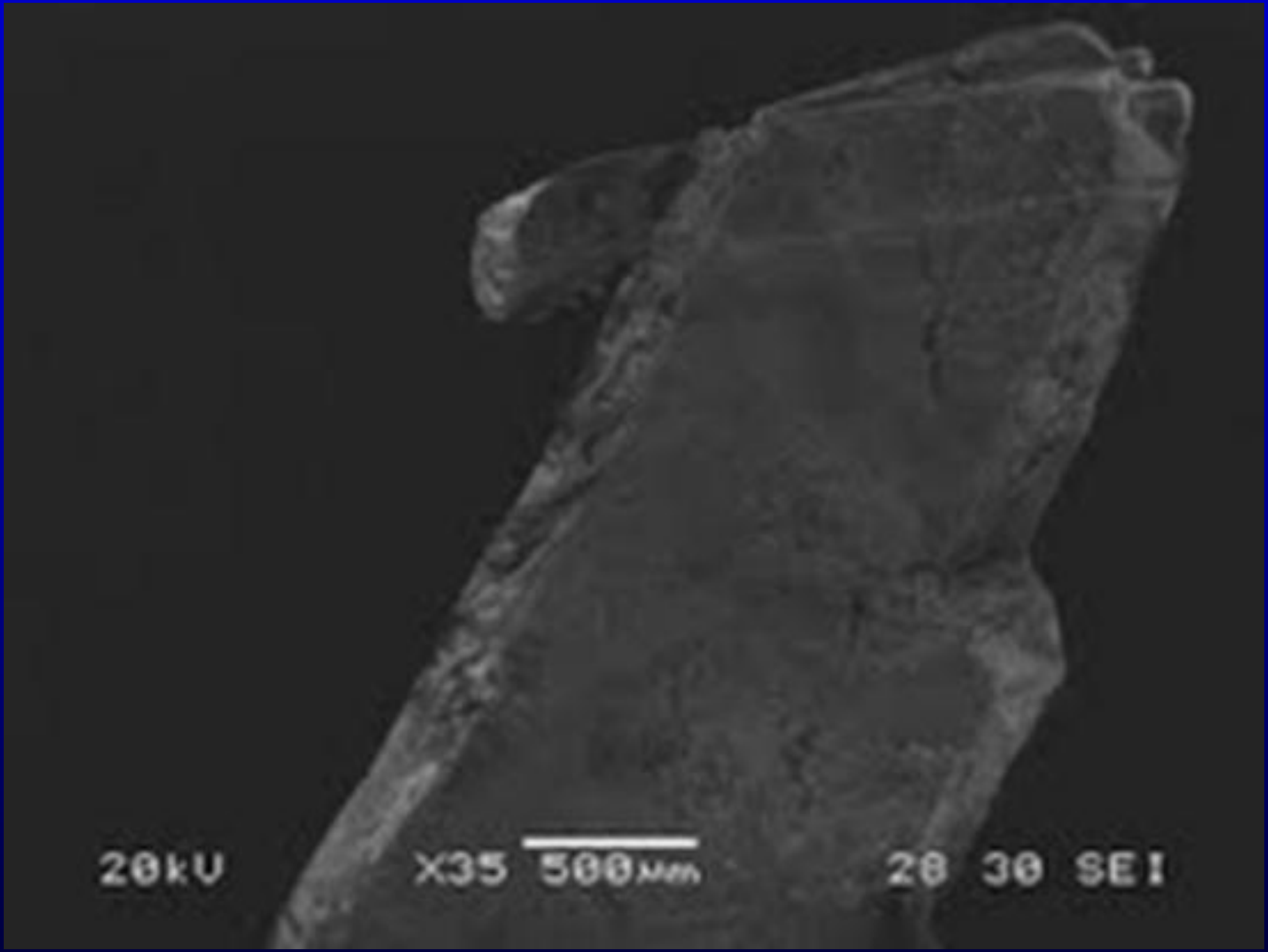
Morphology and composition (EDS) was studie

As grown needles shape crystals



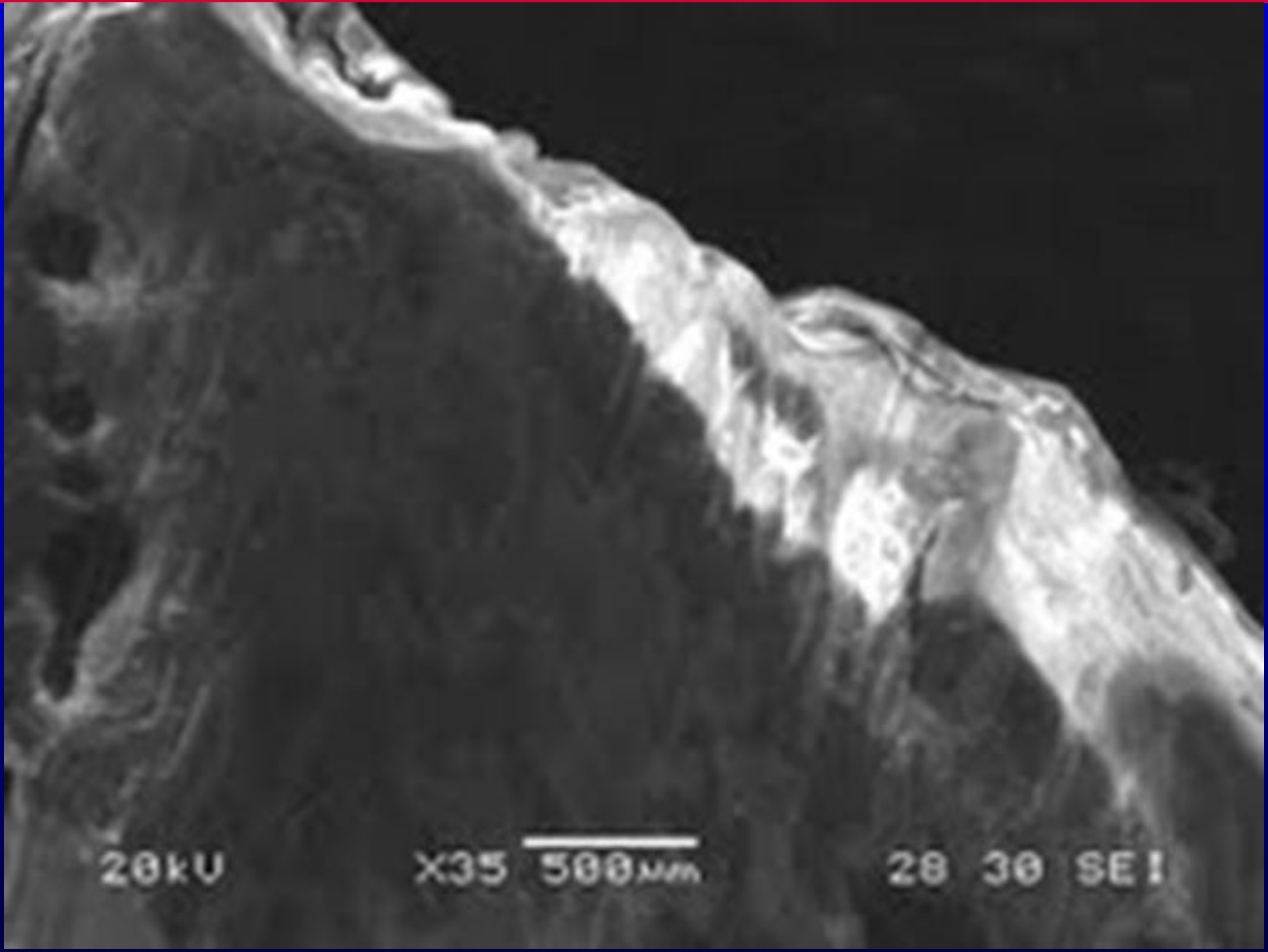
Large needles (100μm diameter) of β-Ga_2O_3 were observed

As grown prism shape crystals



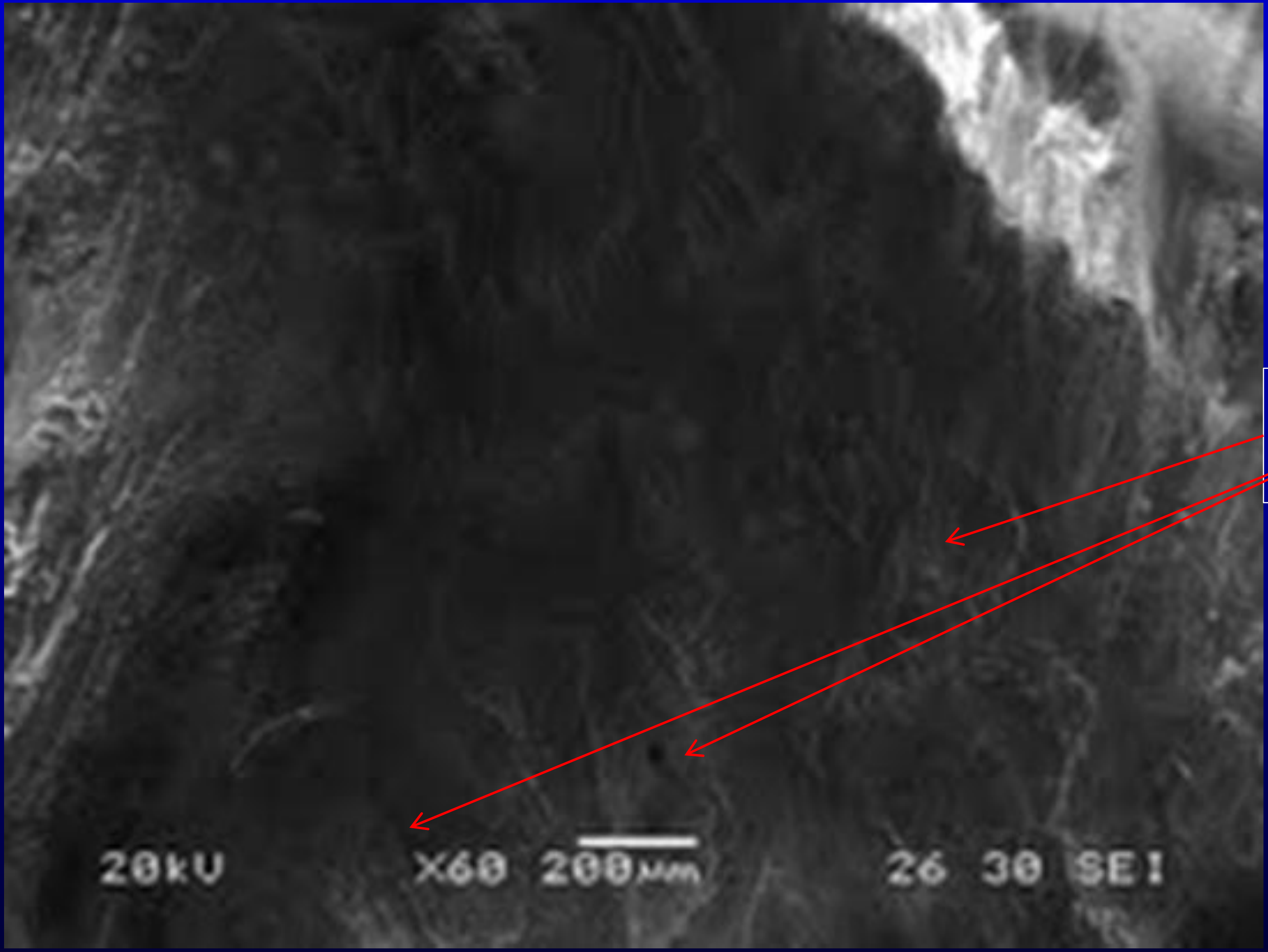
Large prism shape crystals of β-Ga_2O_3 were observed in the crucible

Morphology of Gallium Oxide



We did not observe soft layering and hence no sign of clevage was observed

Morphology of β-Ga_2O_3 crystal



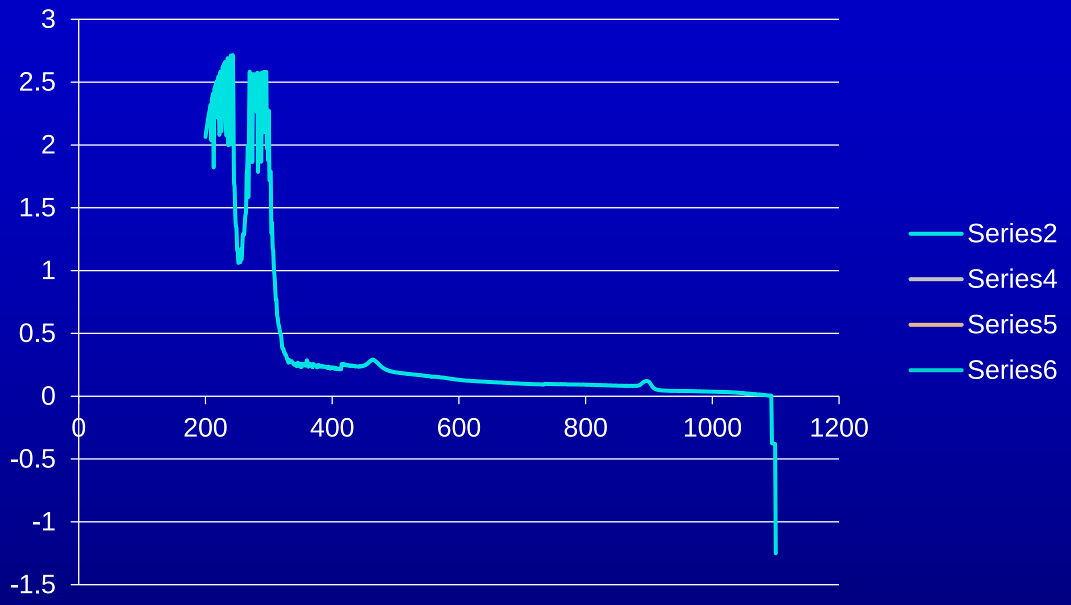
Growth steps

Growth steps (needles and prism)were observed in virgin crystals

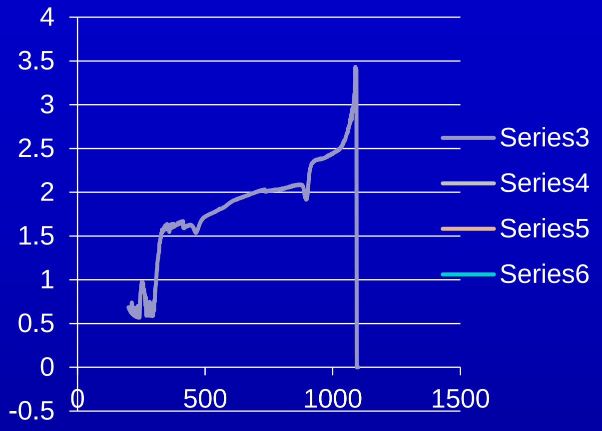
Optical absorbance and transparency was measured for the β-Ga_2O_3 as grown crystal

Optical method showed bandgap >4.7eV for as grown crystal

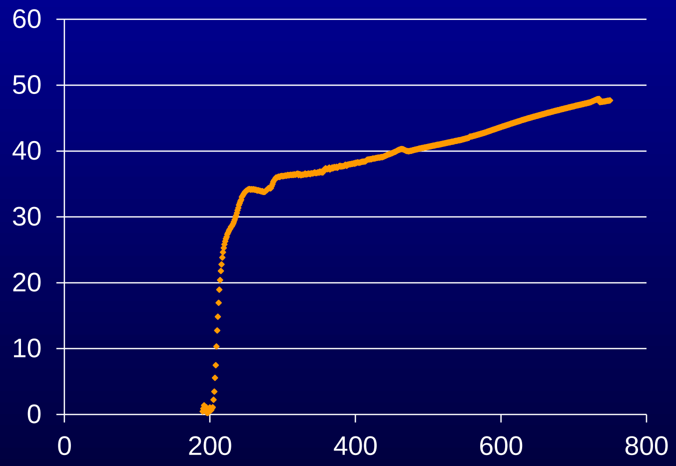
Optical characteristics of the material



Absorbance with as grown crystal



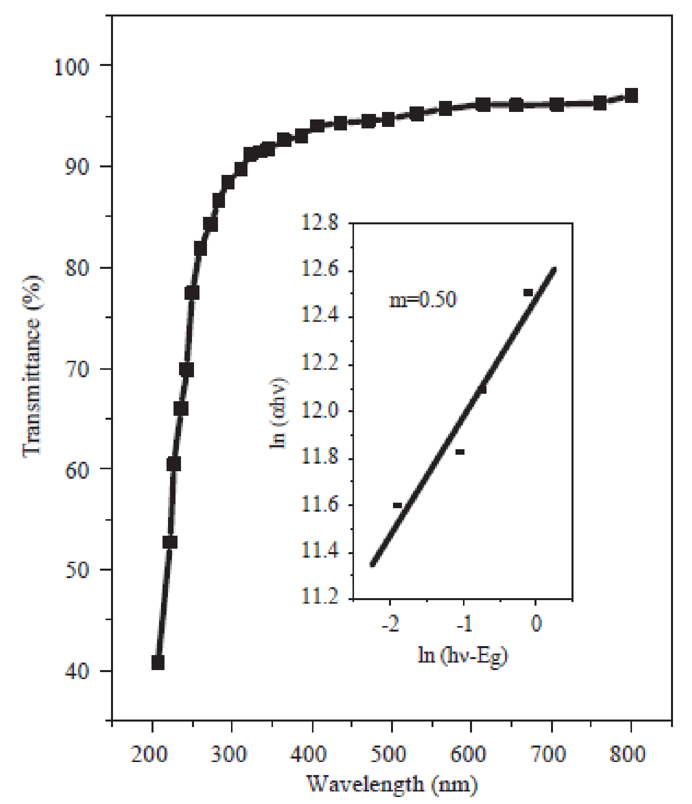
Cutoff wavelength for crystal in tin flux

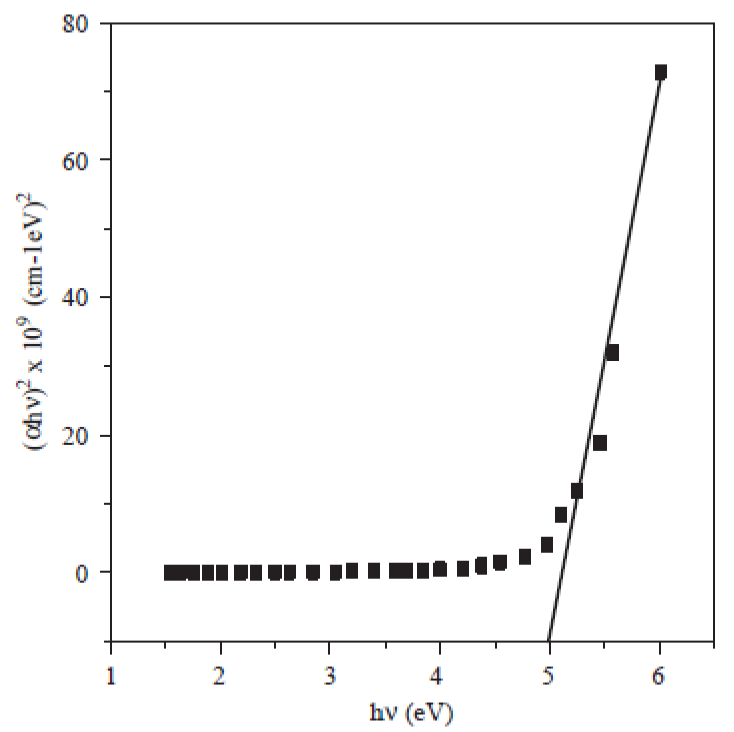


Transmission of as grown new crystal crystal

Both absorbance and transmission indicated the bandgap of 4.7eV
New crystals indicated bandgap of 5.90eV

Optical characteristics of film grown by dip coating (JCG 276 (2005) 204-207



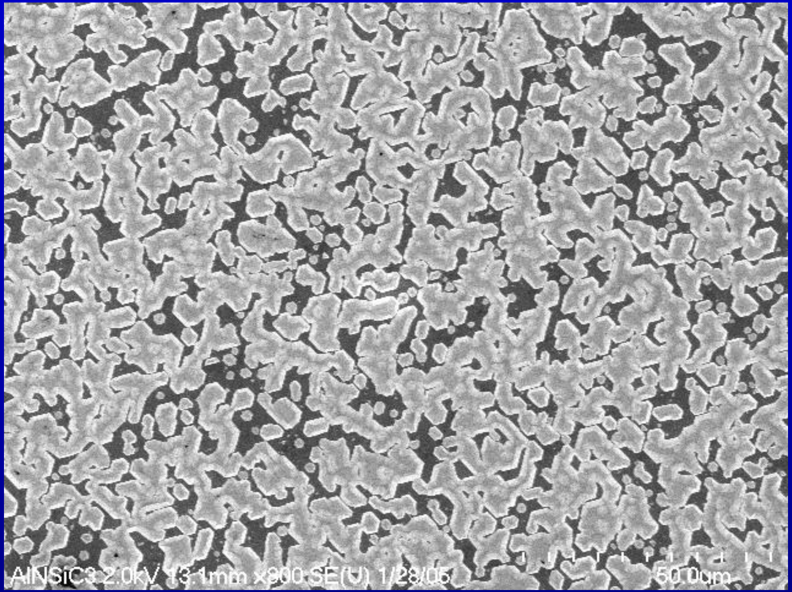


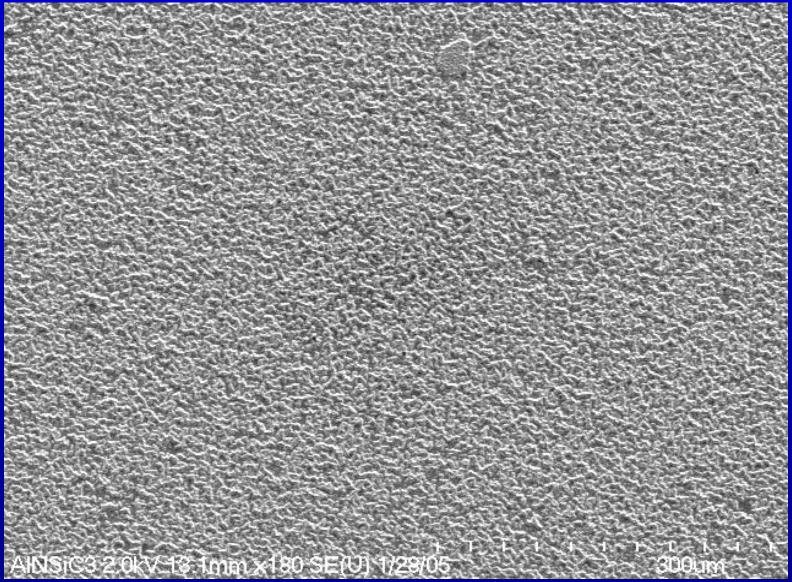
Transmittance Vs wavelength trace for pure a-Ga$_2$O$_3$ thin film. Inset shows ln (αhν) vs. ln (hνEg) plot.

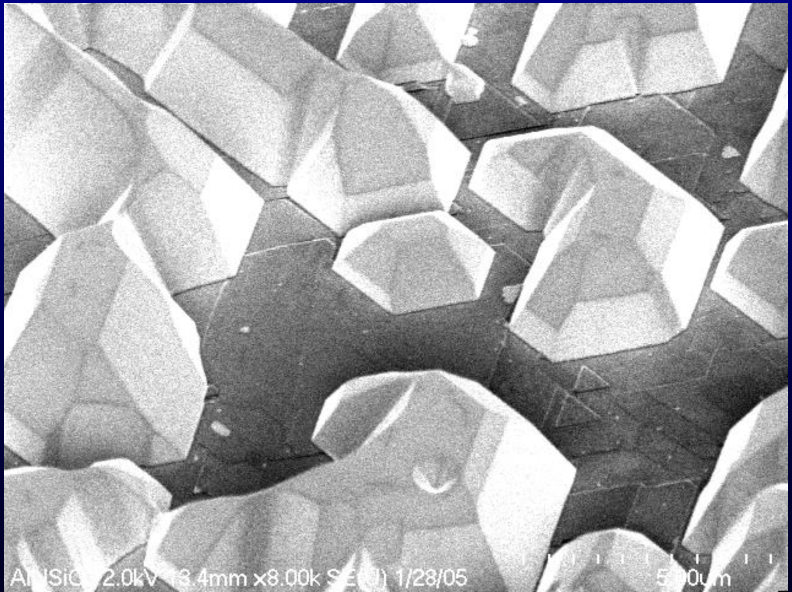
(hαν)2 vs. hν trace for pure a-Ga$_2$O$_3$ thin film indicates Eg = 4.98 eV.

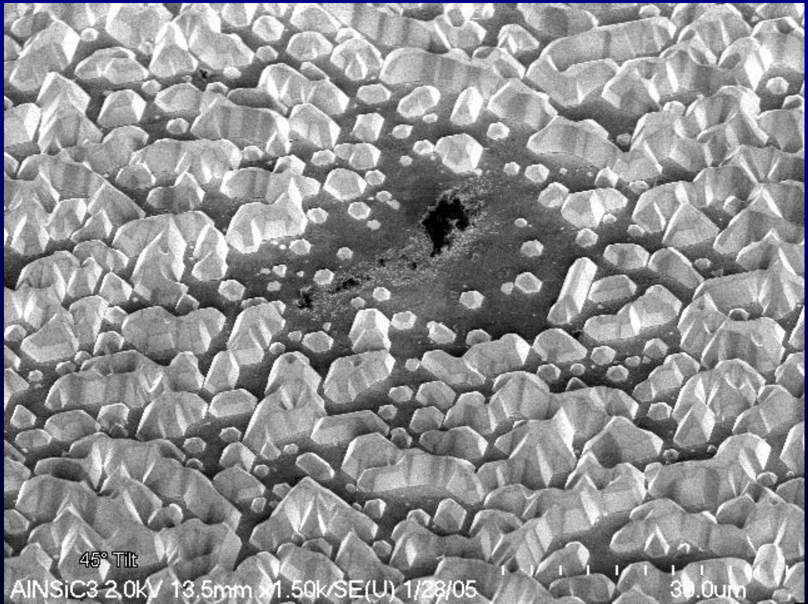
Both absorbance and transmission indicated the bandgap > 4.7eV

Morphology of GaN shows excellent morphology and Ostwald ripening

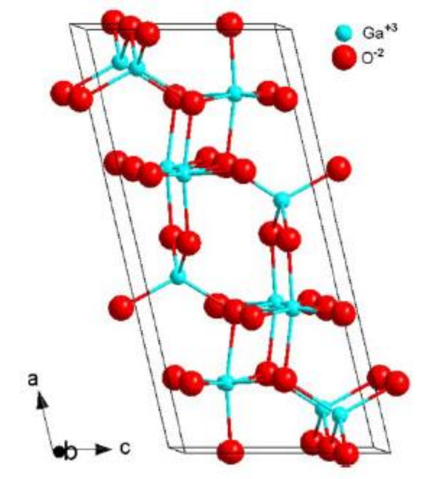




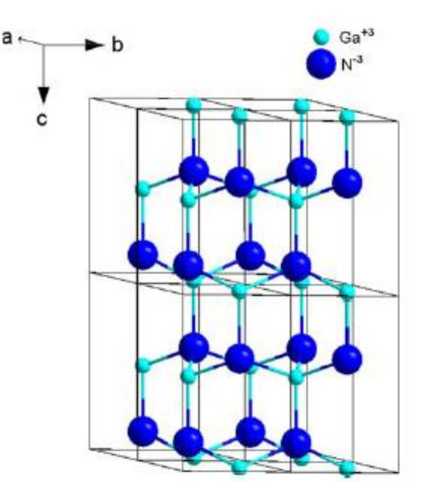




Suitability β-Ga_2O_3 for for GaN Devices

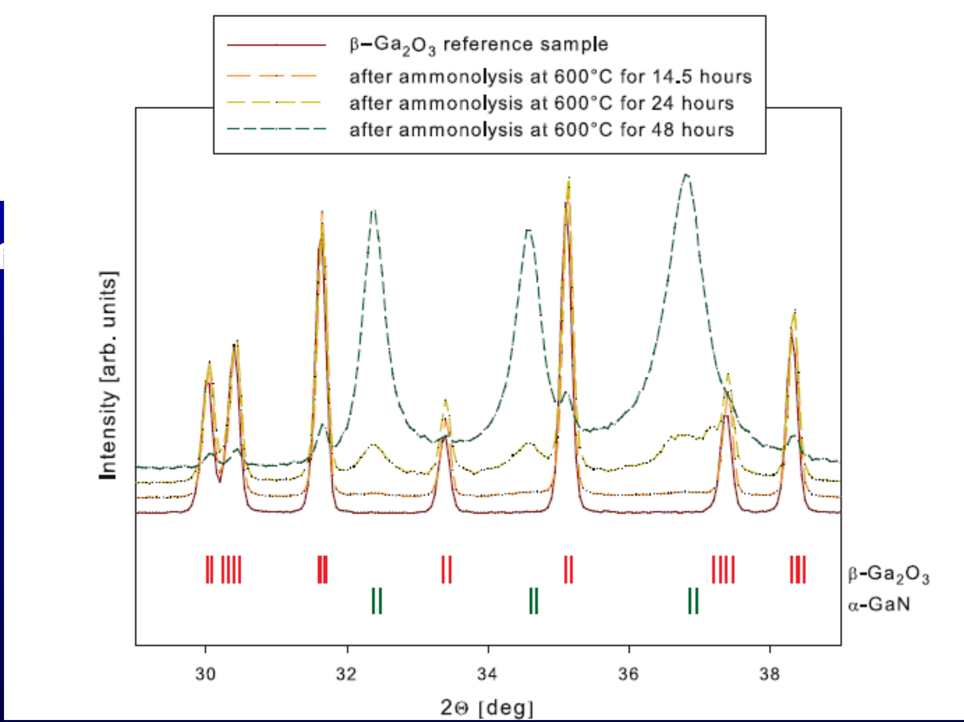


Crystal structure of β–Ga_2O_3



Hexagonal structure of GaN

X-Ray Diffraction pattern for amonolyzed at 600C for extended time duration



Literature indicates that a buffer layer can be grown for deposition of GaN growt

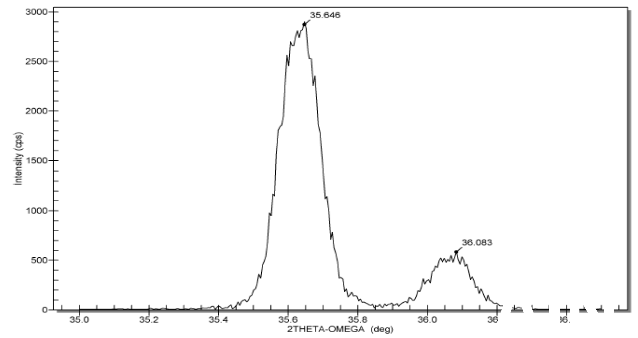
Summary

- A low temperature growth method for the growth of a novel wide bandgap materials β-Ga_2O_3
- The approach involves low temperature reactive flux growth of crystals
- Preliminary studies indicated that co-crystallization and Sn-based flux can be used for the growth of large crystals
- Small crystals grown in Sn showed a bandgap of 4.7eV, while crystals with nitrate showed as high as bandgap of 5.90 eV.
- The proposed method is suitable for scaling the growth without large equipment investments
- Lattice parameters, bandgap, thermal conductivity and mobility are main parameters for investigation
- The β-Ga_2O_3 is an excellent substrate for GaN growth

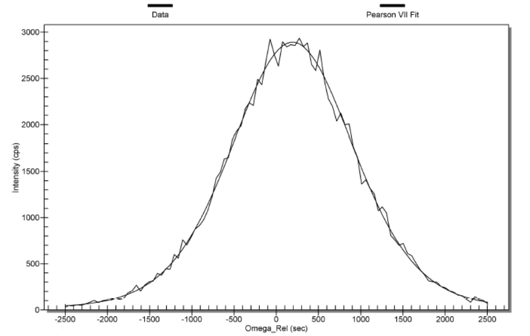
Preliminary results based on small crystals are very exciting

Thank you very much

XRD Survey Indicates Crystalline SiC Deposited on AlN/Si <111> Substrate.

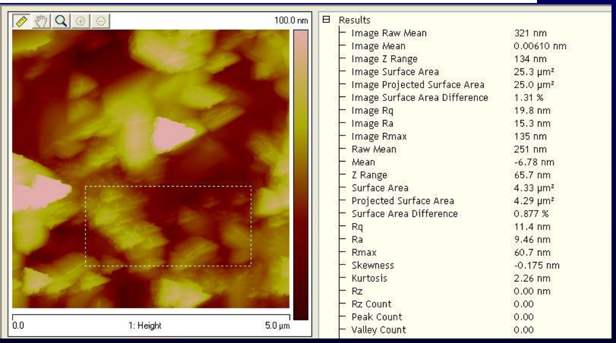


DCC SCAN DATA: Control2 version 2.6.02
File: D:\Data\Brian Wagner\HMDS SiC on AlN-Si L02-1\L02-1 AlN04_03aa001.X01
Scan Source: Run from User Interface
User: bede
Specimen: L02-1 AlN04 Crystal: Si Reflection: 1 1 1
Wavelength: 1.54056 Å Bragg Angle: 14.2206 kV: 40.00 mA: 40.00
HMDS SiC on AlN on Si 111 Count Time: 0.2 Datapoints: 304



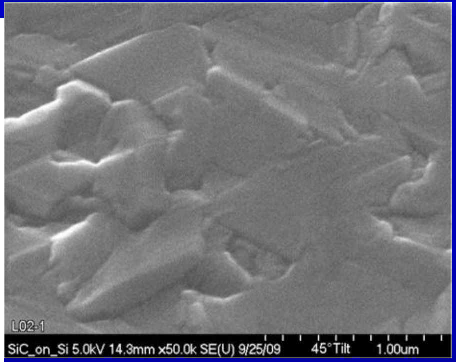
Fitted Peak Center: 191.573
Fitted Peak FWHM: 1706
Background: 20.8947
Goodness of Fit: 41.4983

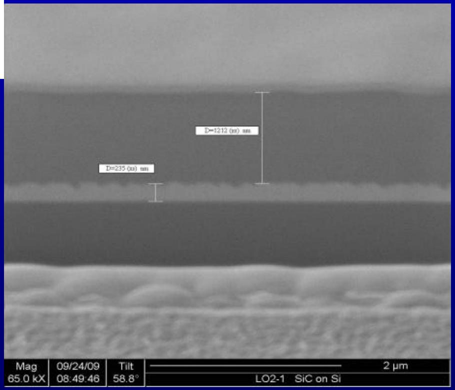
Fitted Peak Area: 5.4160E+06

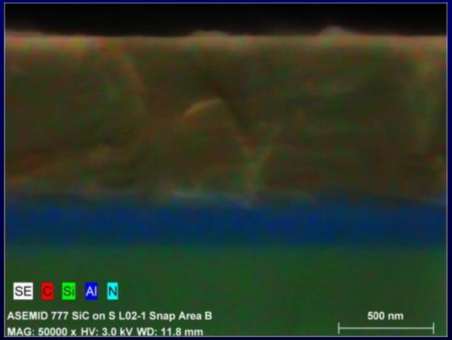


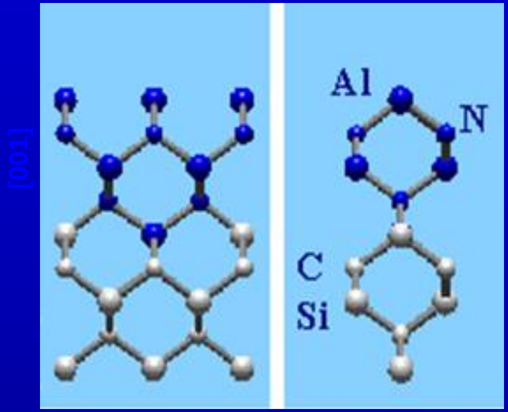
Results

Image Raw Mean	321 nm
Image Mean	0.00610 nm
Image Z Range	134 nm
Image Surface Area	25.3 µm²
Image Projected Surface Area	25.0 µm²
Image Surface Area Difference	1.31 %
Image Rq	19.8 nm
Image Ra	15.3 nm
Image Rmax	135 nm
Raw Mean	251 nm
Mean	-6.78 nm
Z Range	65.7 nm
Surface Area	4.33 µm²
Projected Surface Area	4.29 µm²
Surface Area Difference	0.877 %
Rq	11.4 nm
Ra	9.46 nm
Rmax	60.7 nm
Skewness	-0.175 nm
Kurtosis	2.26 nm
Rz	0.00 nm
Rz Count	0.00
Peak Count	0.00
Valley Count	0.00





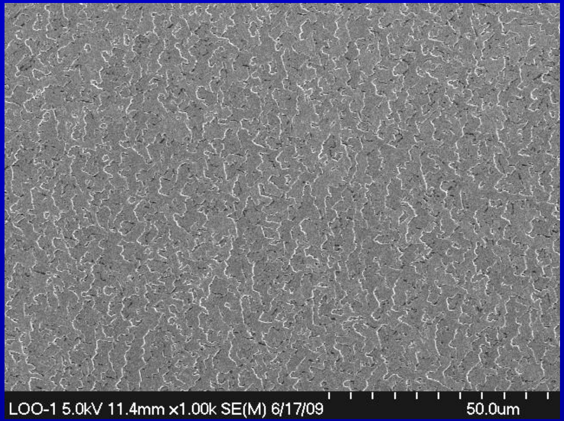


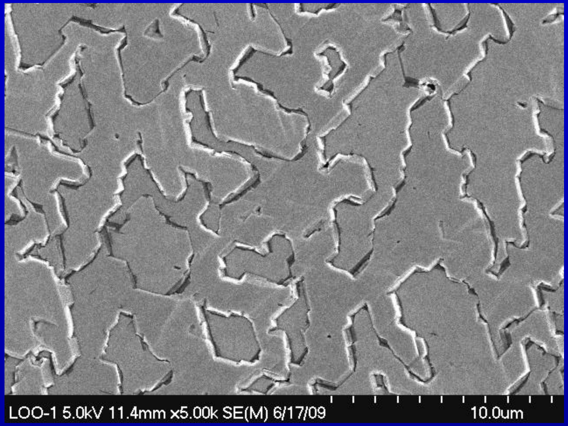


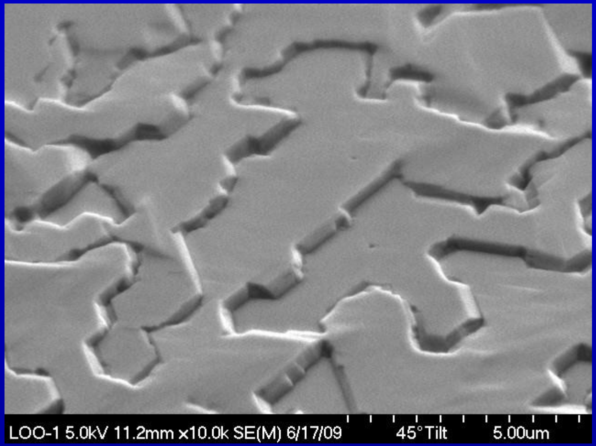
- For coverages <1/2 Monolayer (ML), nitridated Si-pairs are formed
- At 1ML zincblend sites are metastable: Hydrazine like Si_4N_2 complexes are formed coating the surfaces
- Nitridation is favored, and growth is inhibited
- Interface mixing occurs as a stable configuration and reconstruction occurs by deposition of Si^{+4} ions.
- There is a possibility of amorphisation of the interface during above process.

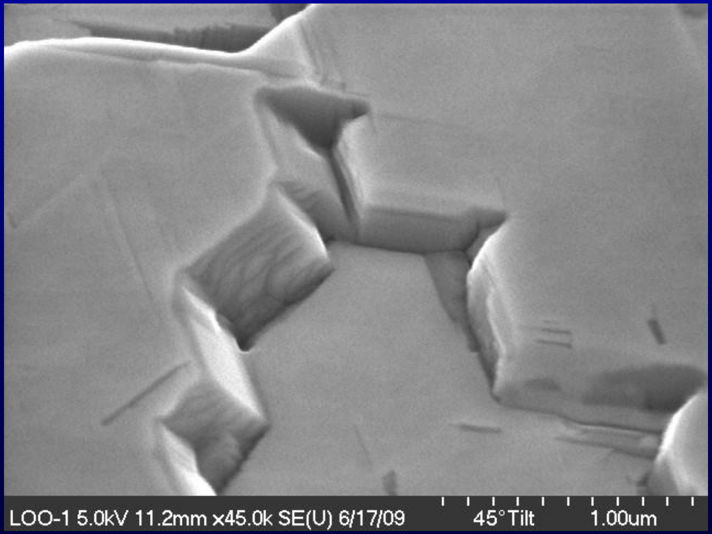
References also support that AlN forces SiC to grow to Wurtzite (2H-) symmetry

We developed low temperature growth of SiC . There was no sign of screw dislocation and micropipe







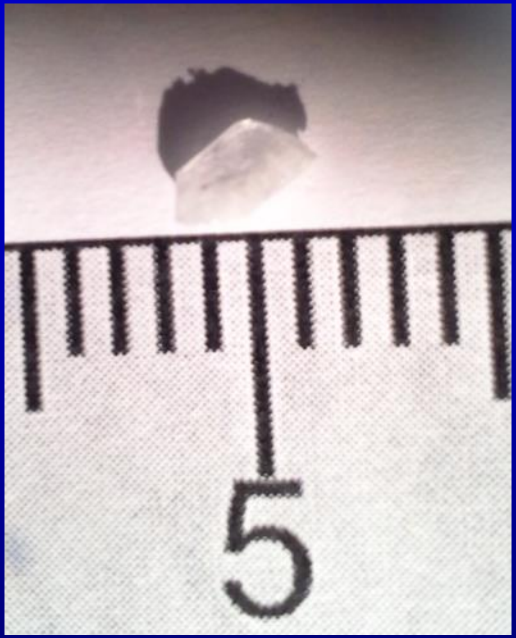


Growth using HMDS shows layer by layer growth

References support 2H- structure in presence of AlN for SiC:

- **J-F, Li and R. Watanabe, J. Materials Science. Vol. 26 (1991) 4813.**
- **Y. Xu, Y; A. Zangvil, A; M. Landon, and F. Thevenot, J. American Ceramic Society, 75 (1992) 325.**
- **G. E. Hilmas and Tseng-Ying Tien, J. Materials Science, 34 (1999) 5613..**
- **Miura, M; Yogo, T; S-I, Hirano, J. Ceramic Society of Japan, 101 (1993) 1281.**
- **Huang, J-L; Jih, J-M, J. American Ceramic Society, 79 (1996), 1262**

Low temperature growth occurs as layer by layer mechanism and does not show micropipe in the bulk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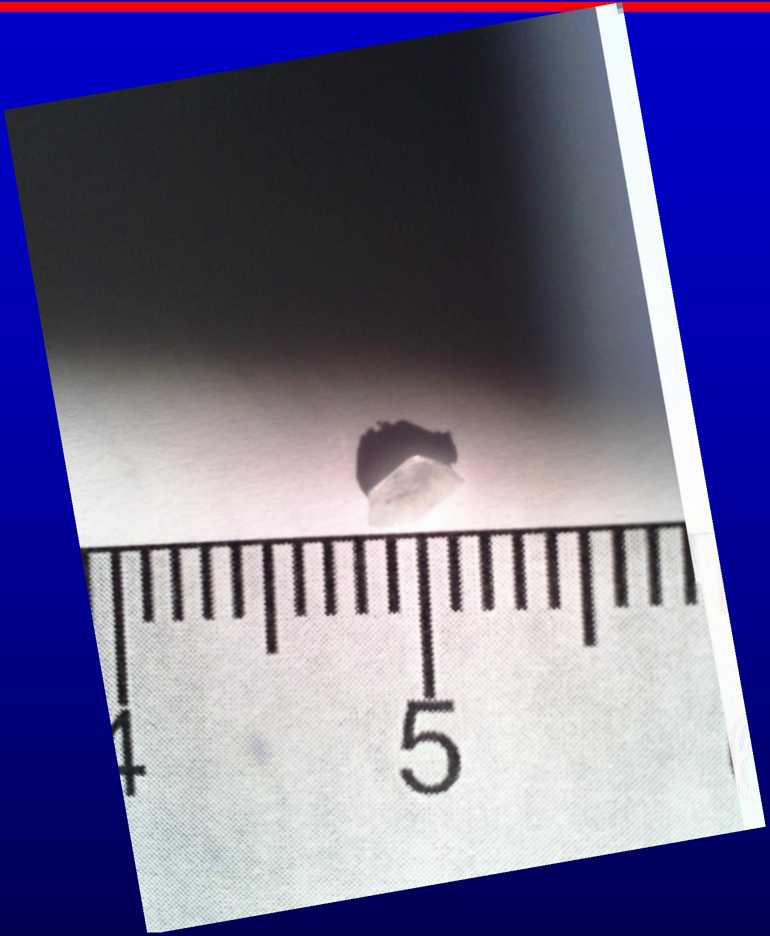
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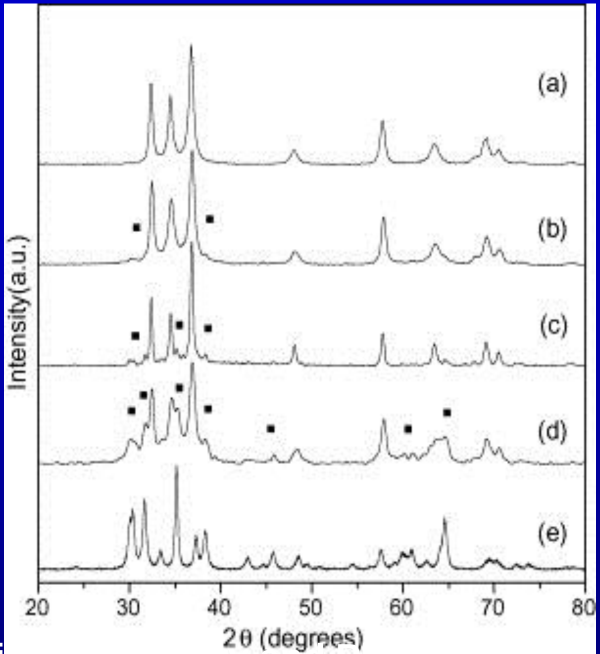
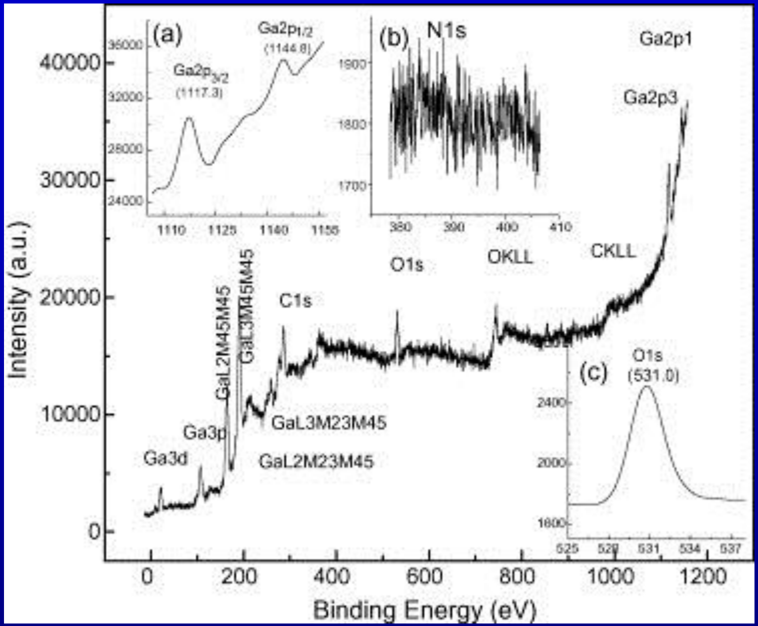
Synthesis and structural properties of beta-gallium oxide particles from gallium nitride powder



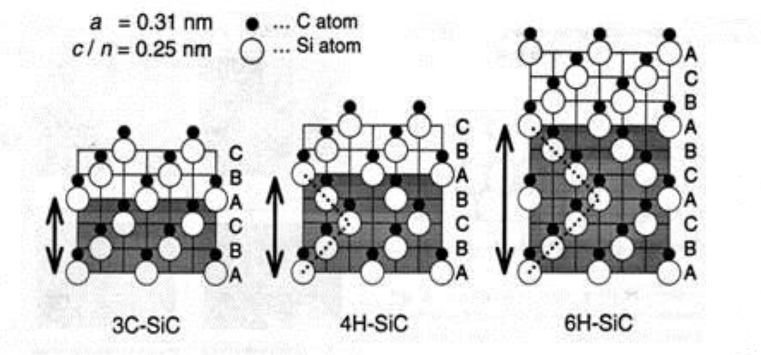


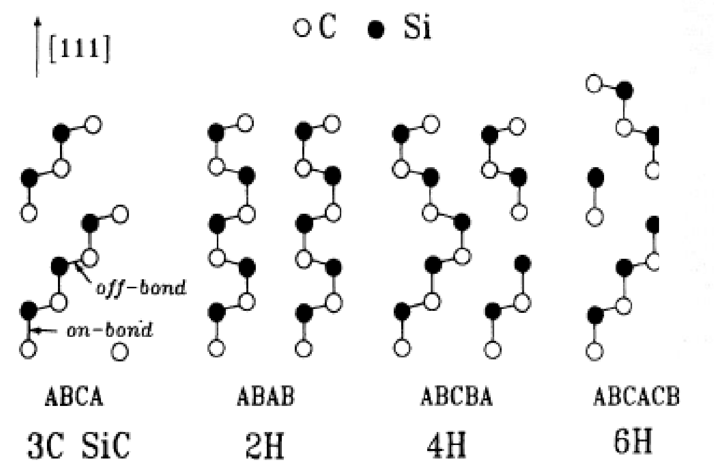
Materials Chemistry and Physics, 101, 1, 15 January 2007, Pages 99–102

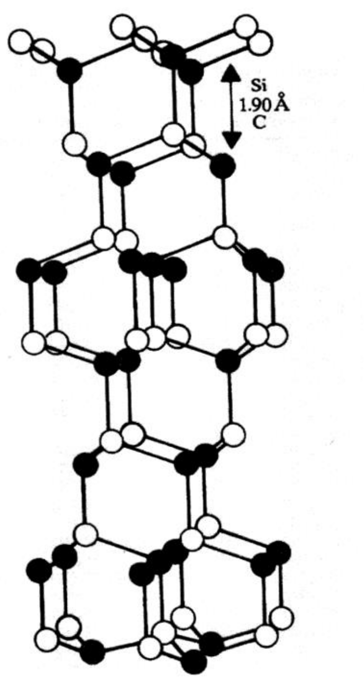
Beta-gallium oxide (β-Ga_2O_3) powders have been synthesized through simple thermal annealing gallium nitride (GaN) powders in the opening air at 900 °C. The observations revealed that Ga_2O_3 on the surface of GaN particles has been formed below 500 °C, the rate of Ga_2O_3's formation under air is slow in the temperature range from 500 to 800 °C and is fast in the temperature range of 800–900 °C. The as-obtained products at 900 °C are pure, single-crystalline monoclinic Ga_2O_3 particles, and the size of β-Ga_2O_3 is about 50–300 nm.

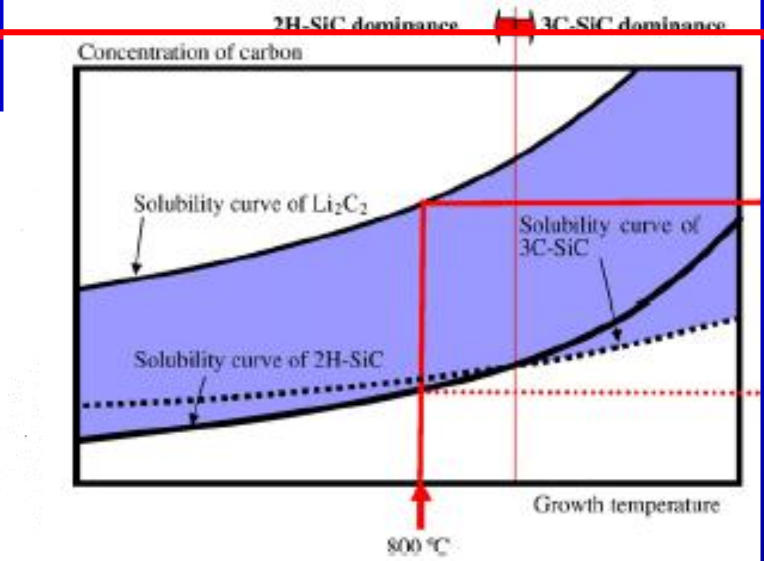
Oxidation process is very difficult to produce gallium oxide

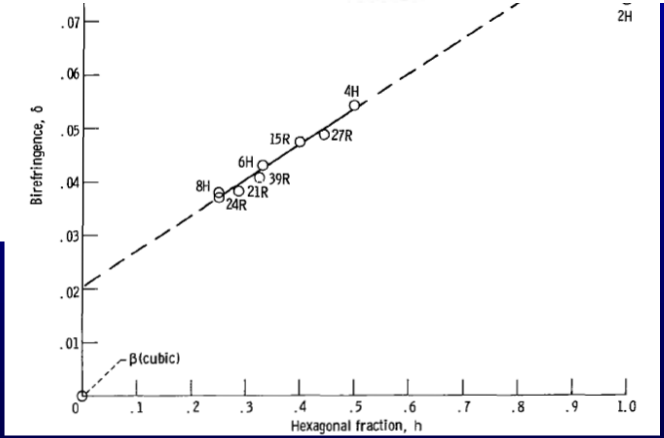
What is 2H-SiC: It is 100% Hexagonal











Low temperature reactive growth facilitates 2H-SiC