

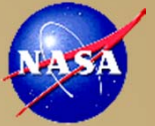
Semi-metallic Materials and Rare-Earth Doped Ferroelectric Materials for Spectral Variation

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Areas of talk to be covered

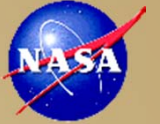
Semi-metallic materials for spectral Shift Control

- Fundamental Concept
- RF-Plasma Sputtering Growth in the Ultra High Vacuum (UHV) chamber
- Microscopic characterization: AFM
- Optical characterization: Variable Angle Ellipsometry
- Electric characterization: Hall Effect Measurement
- Prototype device: Programmable smart grating device

Rare-Earth Doped Ferroelectric Materials

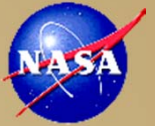
- Fundamental Concept
- Growth of $\text{BaTiO}_3:\text{Eu}$
- Material characterization

Conclusions

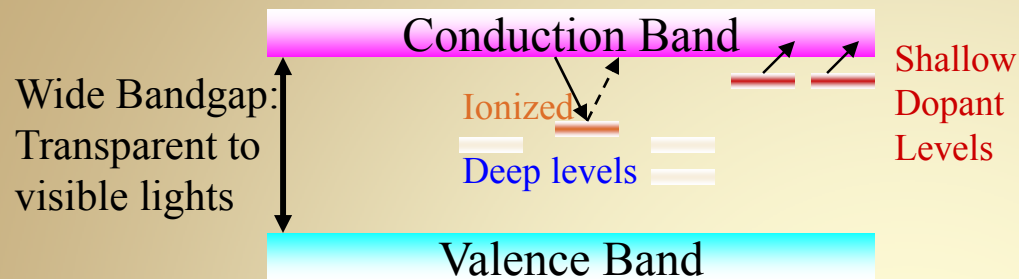


Introduction to Smart Optics

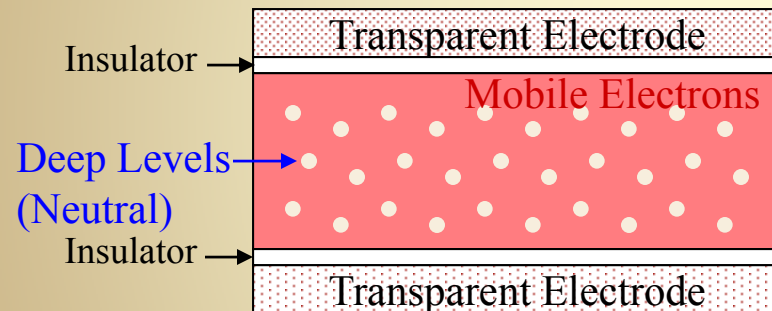
- With electric and magnetic field, the atomic levels in the material shows the energy shift due to the **Stark** effect and **Zeeman** effect.
- In the wideband gap semiconductors,
 - Visible lights can penetrate the layers.
 - Dopant states and mid-bandgap states determine the energy state of **space charge region**.
 - There is a finite number of carriers, electrons or holes, that are mobile according to the applied electric field.
 - Redistribution of the these carriers influence the degree of light into the layer.
 - The change in media absorption coefficient determines the index of refraction as calculated by the Kramers-Kronig relation.
- **Definition of Smart Optics Media** – Media where index of refraction changes and/or spectral shift occurs in response to an applied electric/magnetic field



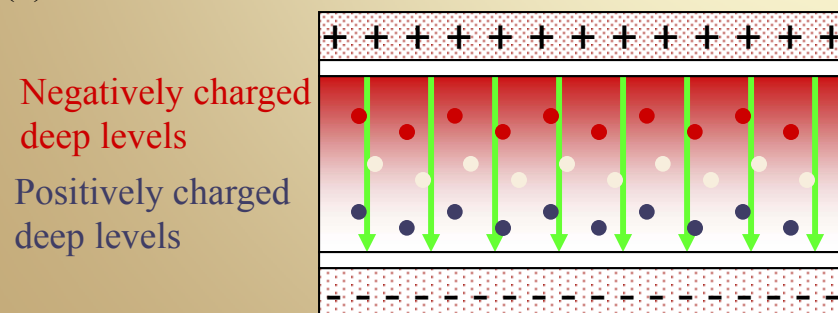
Distribution of Carriers and Ionization of Deep Levels



(1) Without Electric Field



(2) With Electric Field: **Redistribution of Mobile Electrons**



For wide band-gap materials:

- Transparent to visible lights
- Carriers in **shallow dopant levels** are mobile to conduction or valence band.
- Deep levels in crystal imperfection capture or emit mobile charges.
- Bandgap structure is ionized with the loss or capture of carriers.

For $|\vec{E}| = 0$,

- Mobile electrons distributed **uniformly** in media layer.
- Most of the deep levels are **neutral** in this state.

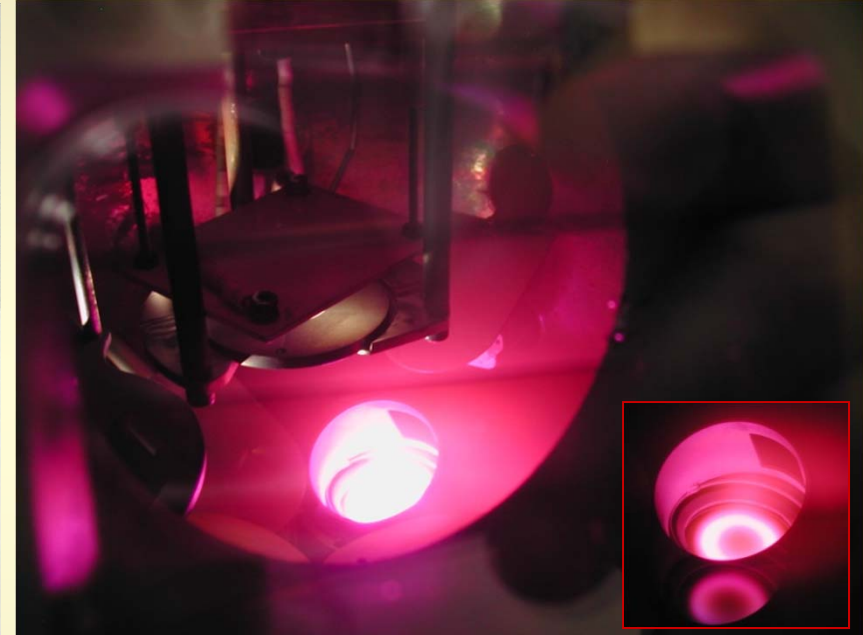
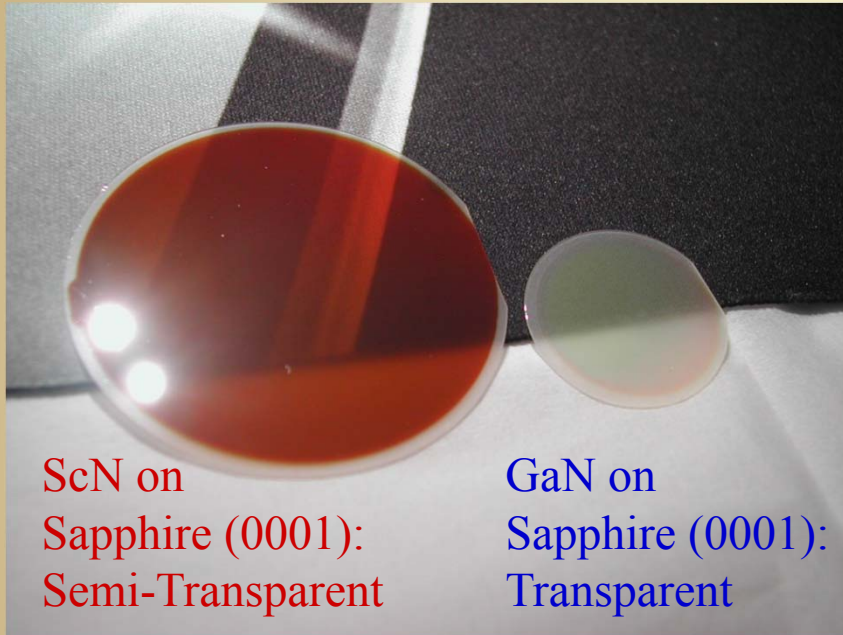
For $|\vec{E}| \gg 0$,

- Mobile carriers (electrons in the picture) are **re-distributed**
- Deep levels are **ionized** and form **new color centers**.
- Absorption coefficient and index of refraction are changed



Growth of ScN & GaN

Epitaxial Growth with Magnetron Sputtering



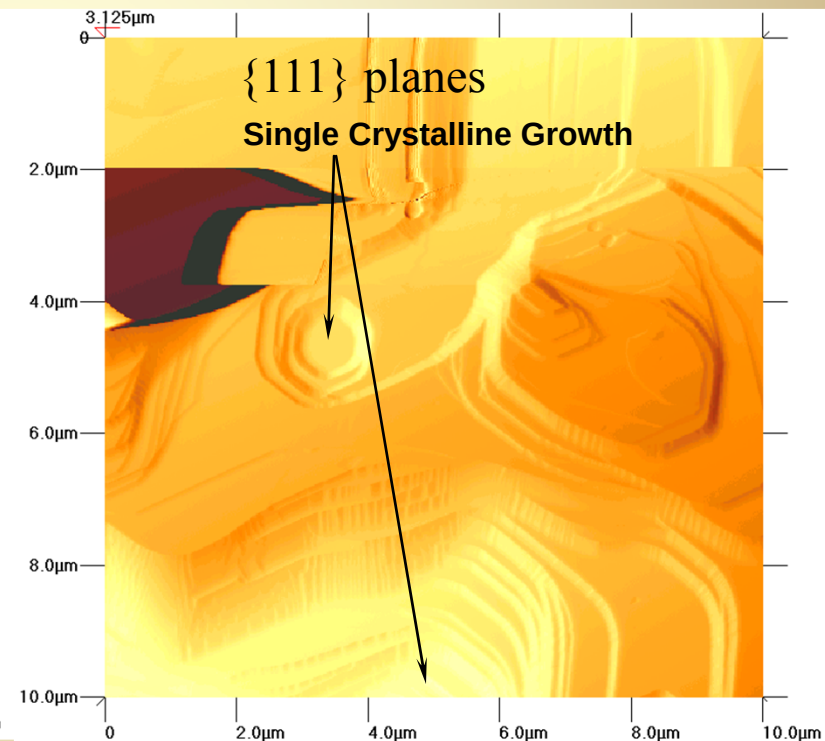
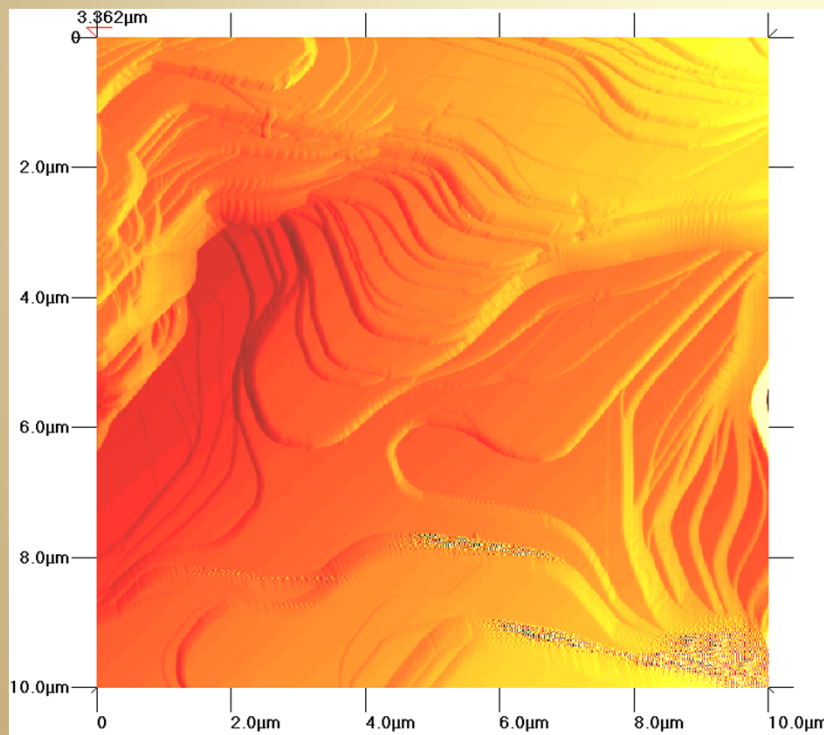
As-grown 2" ScN and intrinsic 1" GaN films on Sapphire Al_2O_3 (0001) substrate under the low pressure N_2 and Ar environment.

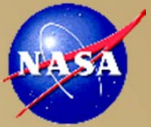
The films were grown at 400°C with 2 sccm of N_2 gas flow and the chamber pressure was 20 mtorr with N_2 .



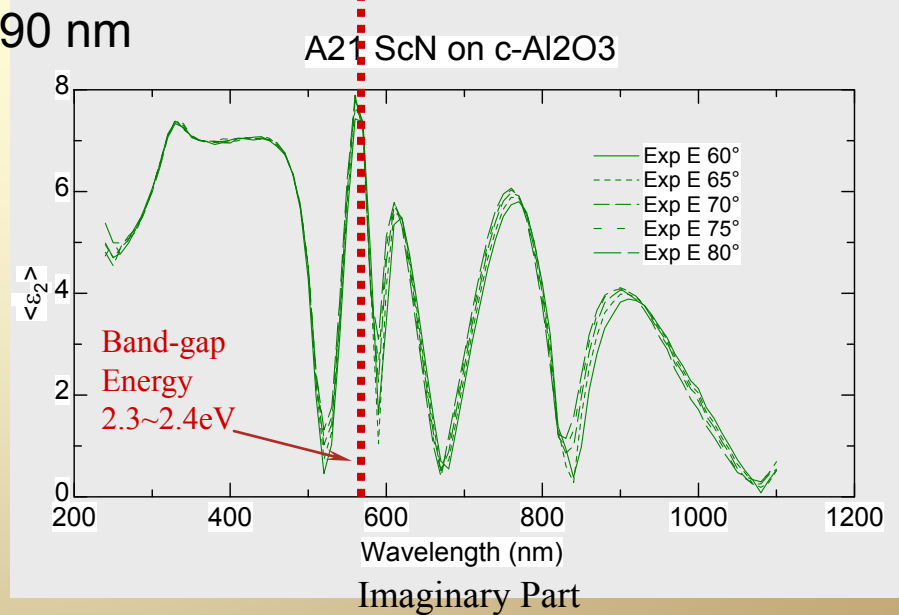
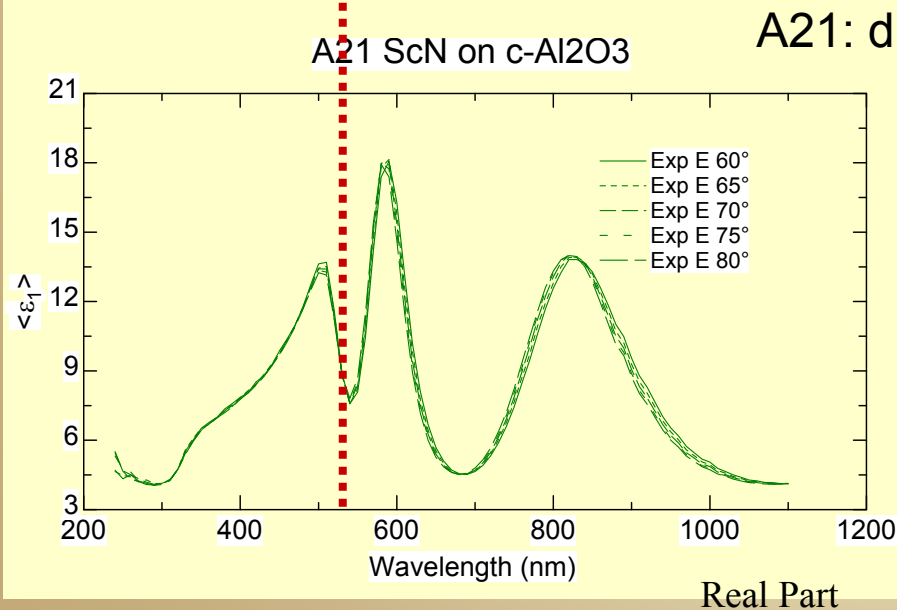
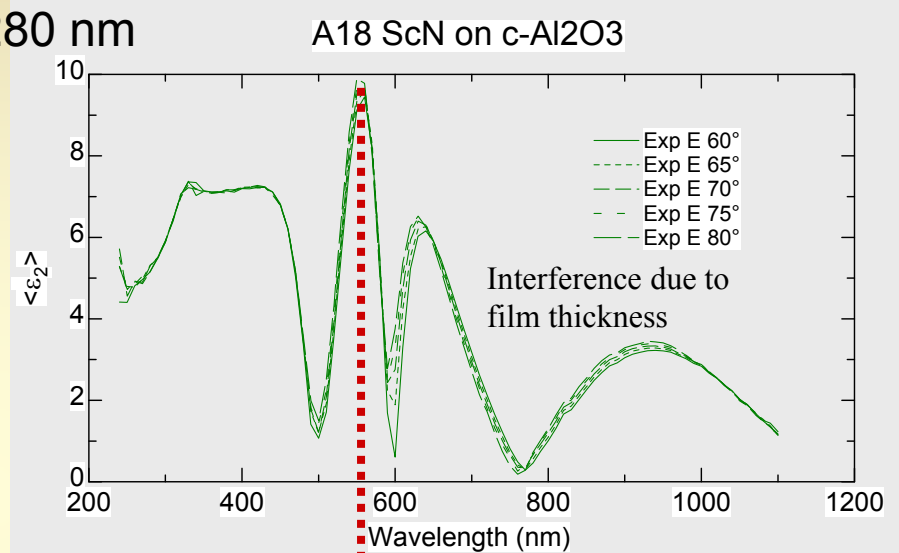
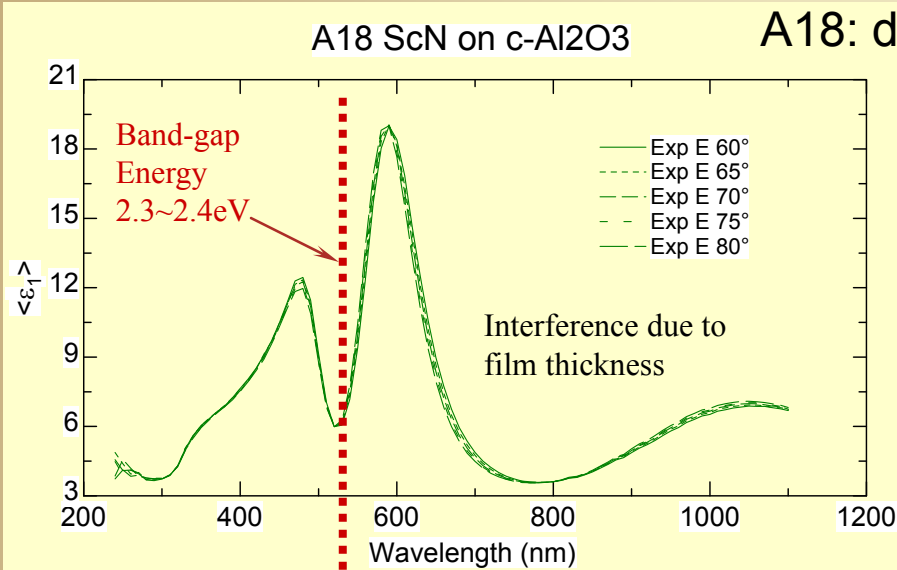
Epitaxial Growth of ScN on Sapphire

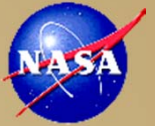
- ScN grows with (111) interface upon Sapphire Al_2O_3 (0001) surface.
- ScN is a **semiconductor with the rock-salt crystal structure**.





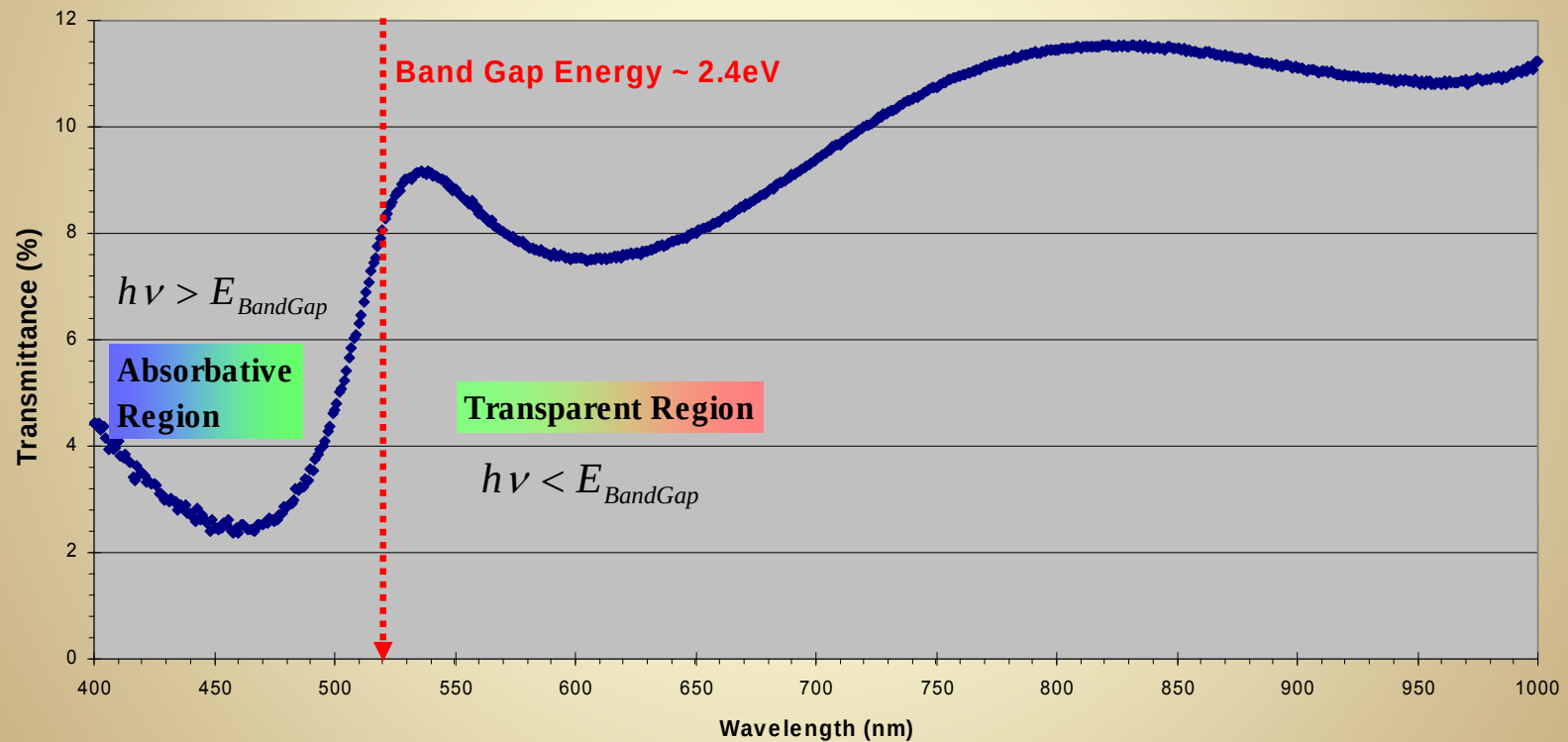
Measurement by Variable Angle Ellipsometry





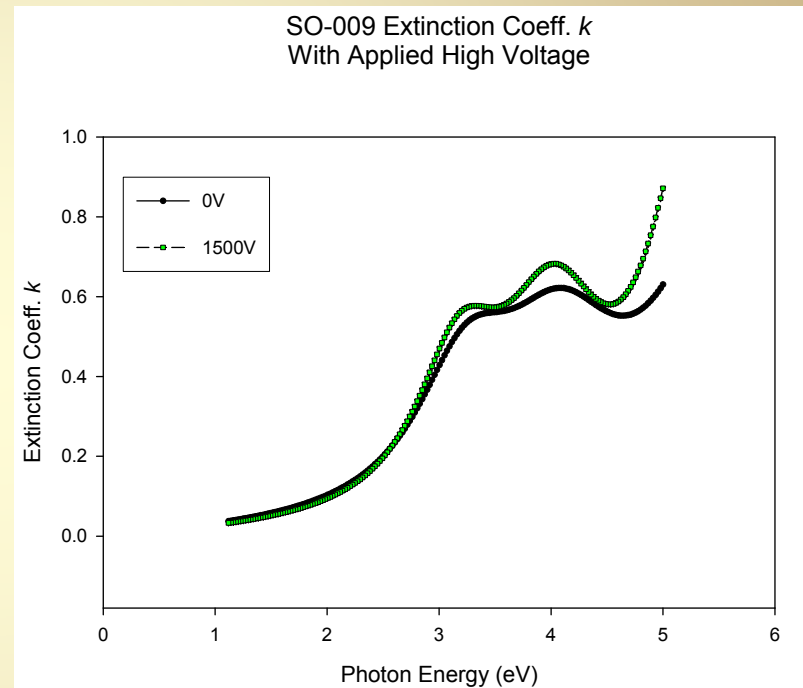
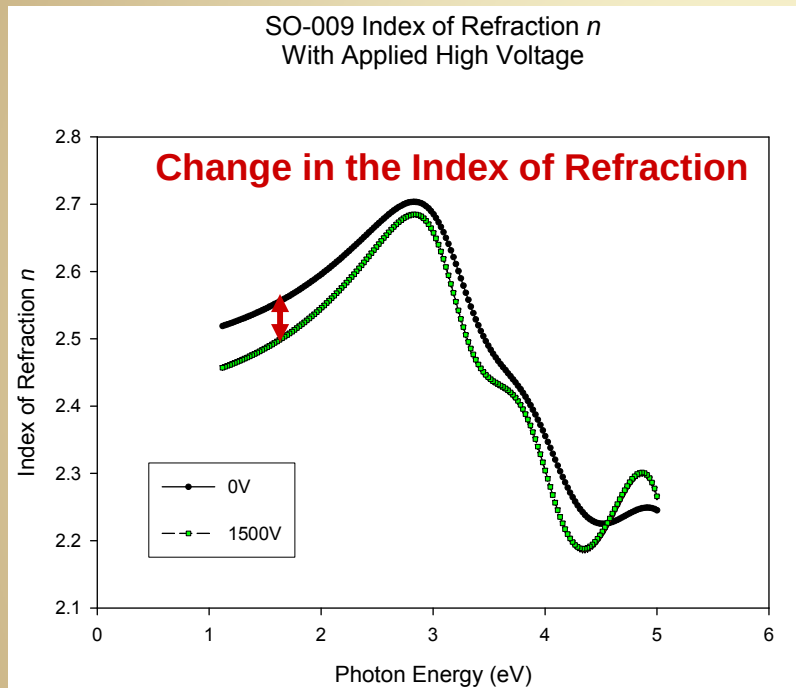
Band-Gap Identification with Spectrometer

Transmittance of ScN on Single-Side-Polished Sapphire
with white light source

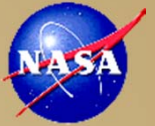




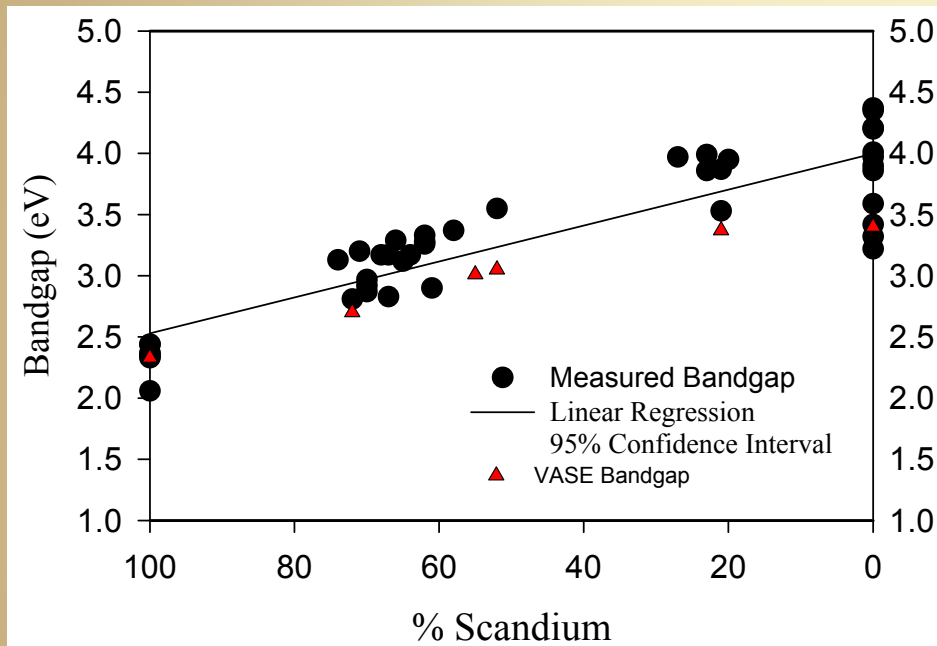
Change of the Index of Refraction in ScN



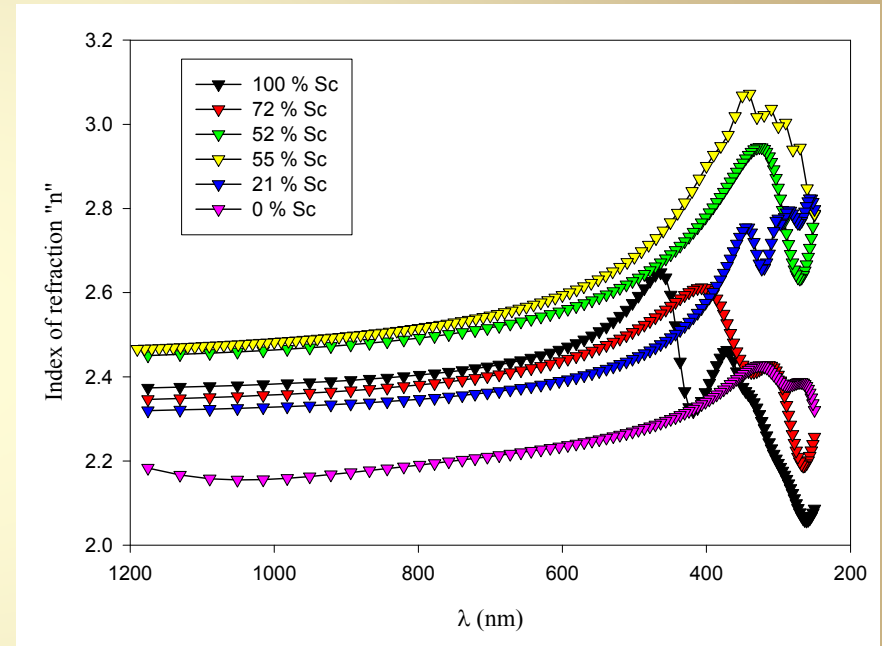
Note that the electric field was applied with a few mm gap.



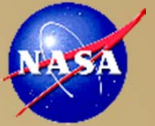
$\text{Ga}_x\text{Sc}_{1-x}\text{N}$ Alloy System



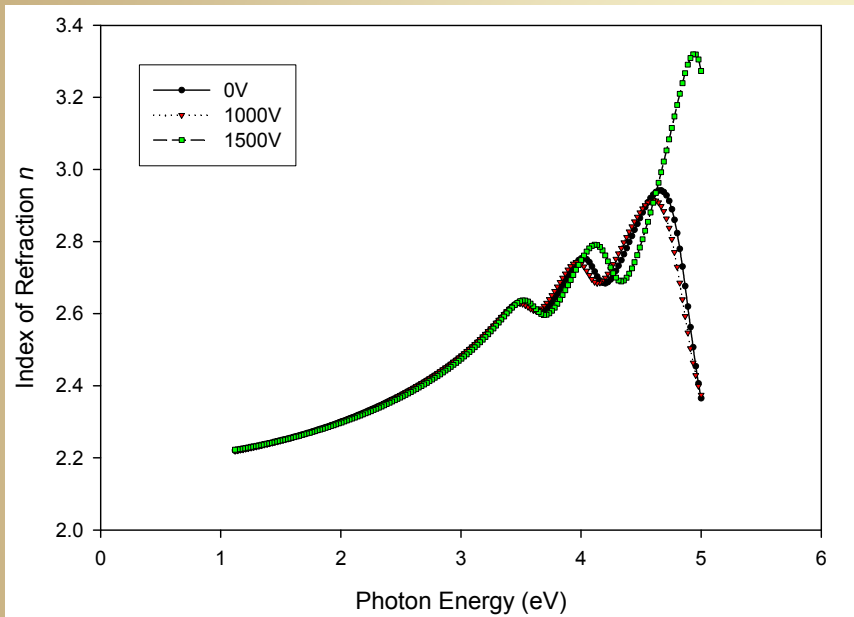
Bandgap Energy versus Scandium Concentration in $\text{Ga}_x\text{Sc}_{1-x}\text{N}$ alloy system.



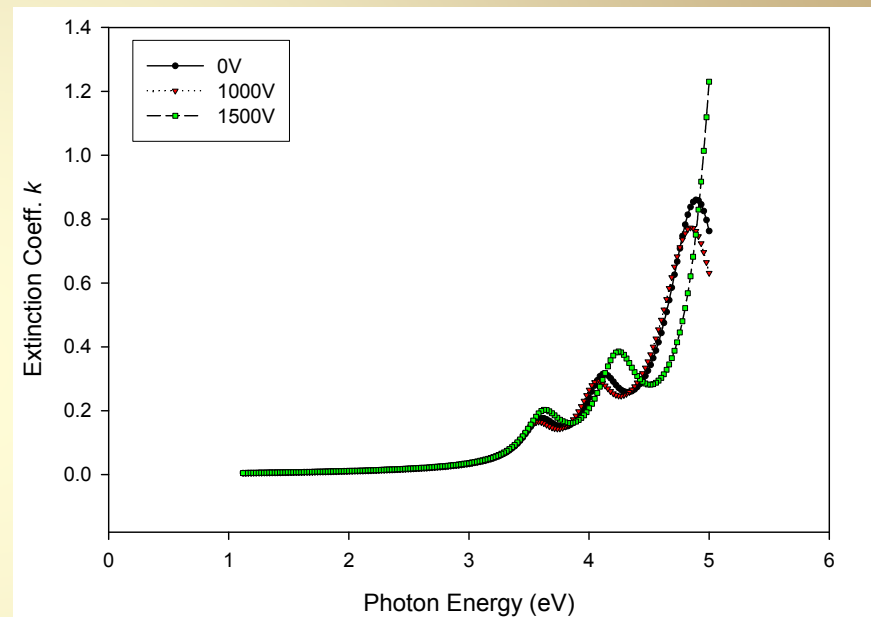
Index of refraction in the region below optical absorption



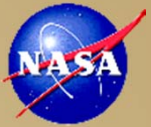
Spectral Shifts of $\text{Ga}_x\text{Sc}_{1-x}\text{N}$ Alloy System



A thin-film of scandium-alloyed gallium nitride ($\text{Ga}_x\text{Sc}_{1-x}\text{N}$, $x=0.47$) developed on a quartz substrate shows both the spectral and refractive index shifts very clearly from 3.5 eV to higher photon energy.



Extinction coefficient data shows a similar response as refractive index in the left, very clearly from 3.5 eV to higher photon energy.



Hall Effect Measurement

● RESULTS	B = 0.51 [T]	D = 0.28 [um]
	Carrier Density: $\times 10^4$	
Nb =	-5.7963E+20 [/cm ³]	Ns = -1.6230E+16 [/cm ²]
μ =	11.50203 [cm ² /V·s]	Rh = -1.0769E-02 [m ² /C]
ρ =	9.3631E-04 [Ω ·cm]	Conductivity: $\times 10^5$
		σ = 1.0680E+03 [1/ Ω ·cm]
delta_R =	1.9616E-02 [Ω]	alpha = 0.12167
Nb : Bulk concentration		
μ : Mobility		
ρ : Bulk resistivity		
delta_R : magnetoresistance		
Ns : Sheet concentration		
Rh : Hall coefficient		
σ : Conductivity		
alpha : V/H Ratio of Resistance		

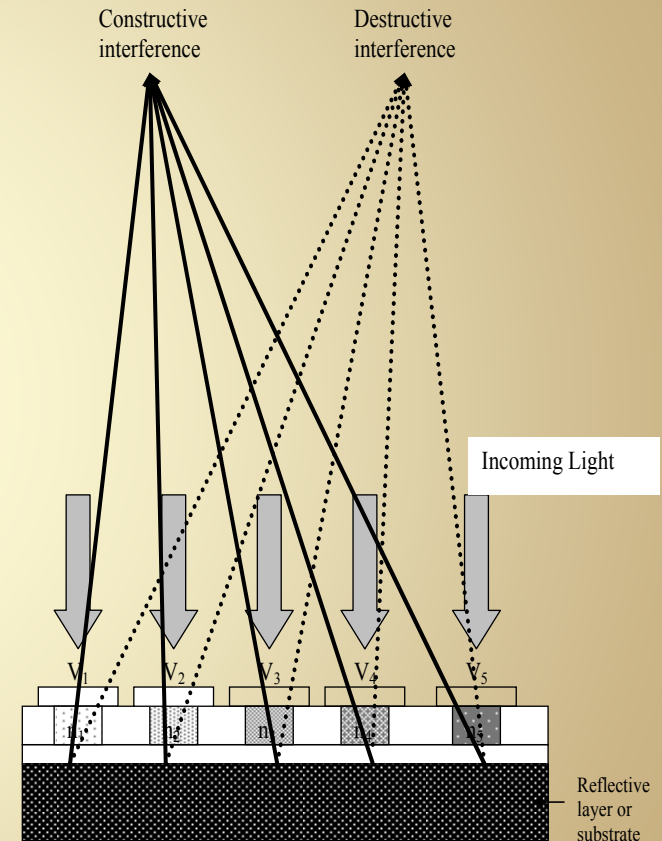
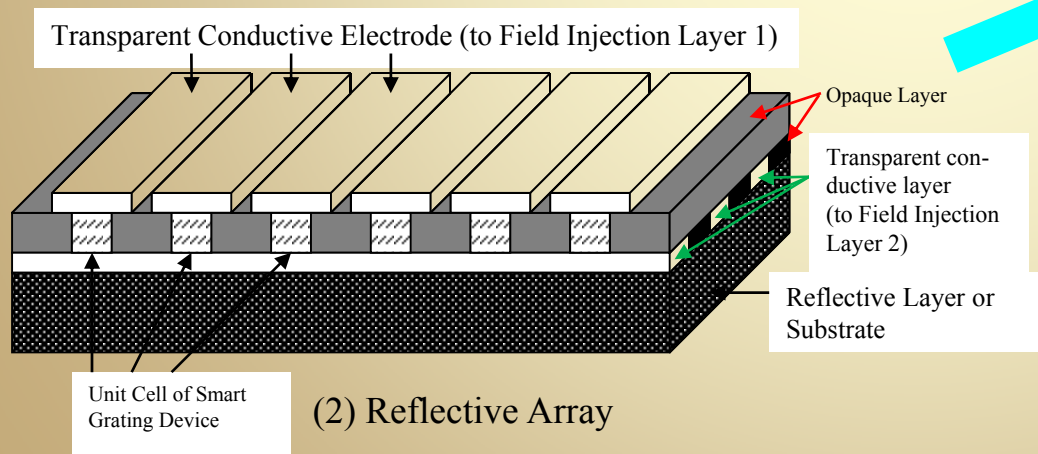
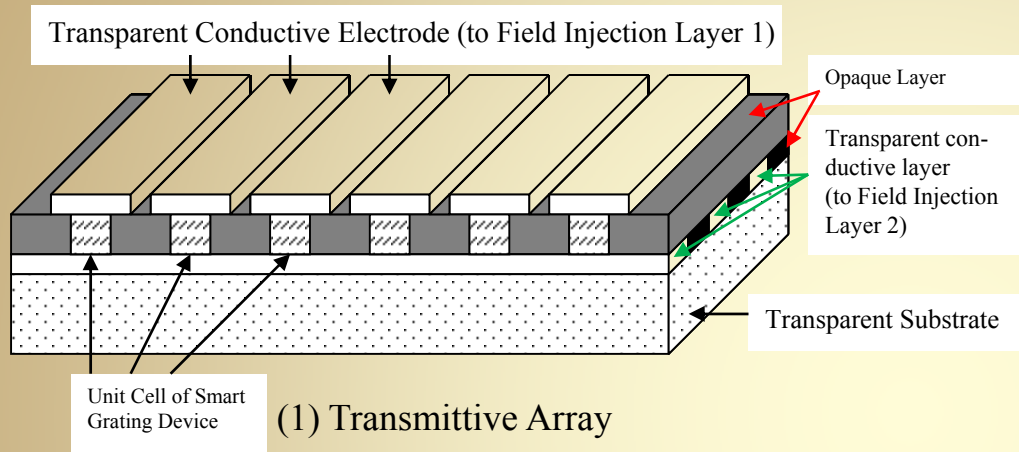
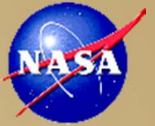
As Grown ScN on Al₂O₃

● RESULTS	B = 0.51 [T]	D = 0.397 [um]
Nb =	-6.6835E+16 [/cm ³]	Ns = -2.6534E+12 [/cm ²]
μ =	2.22096 [cm ² /V·s]	Rh = -93.39652 [m ² /C]
ρ =	52.87408 [Ω ·cm]	Conductivity: $\times 10^5$
		σ = 1.8913E-02 [1/ Ω ·cm]
delta_R =	1.5208E+04 [Ω]	alpha = 0.16824
Nb : Bulk concentration		
μ : Mobility		
ρ : Bulk resistivity		
delta_R : magnetoresistance		
Ns : Sheet concentration		
Rh : Hall coefficient		
σ : Conductivity		
alpha : V/H Ratio of Resistance		

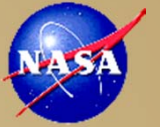
Intrinsic GaN on Al₂O₃

Application:

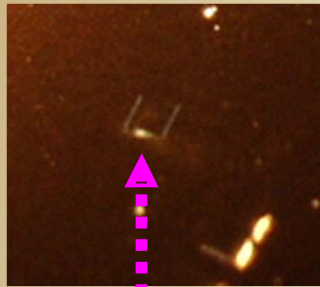
Programmable Smart Grating Device



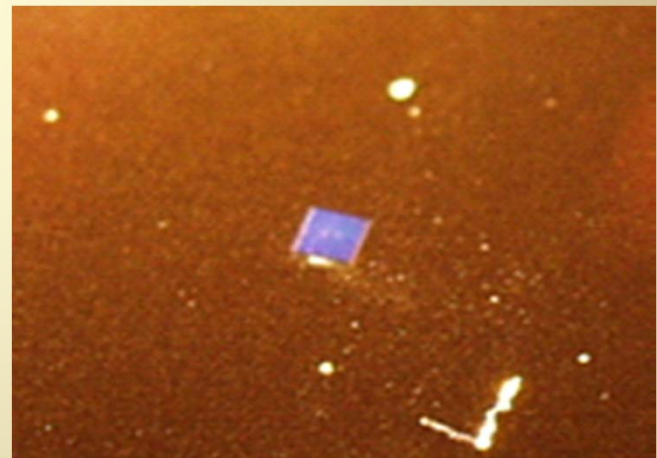
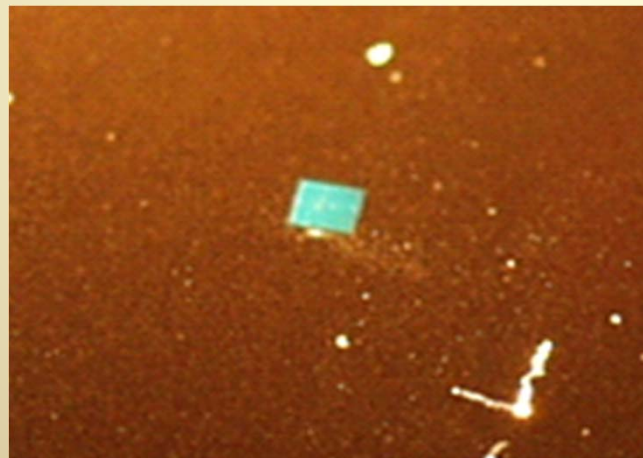
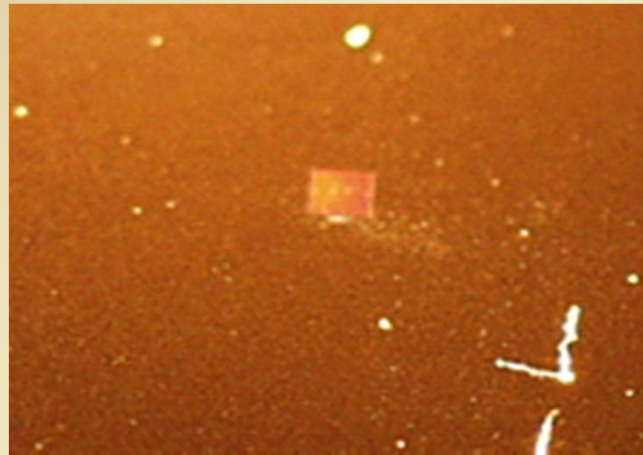
The index of refraction of each cell is determined by the applied voltage.



Spectral Response of Device Area

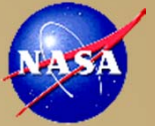


Device Area

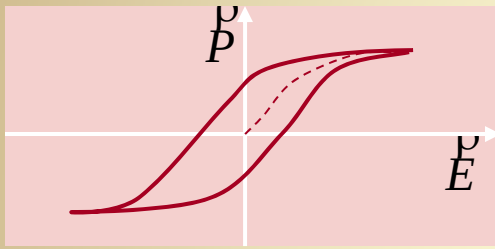


Geometric Grating Effect from the Reflective Array

Ferroelectric BaTiO₃



- Ferroelectric materials have the hysteresis of electric polarization due to the reorientation of permanent electric dipole moment. They are now widely used in high capacity non-volatile memories.



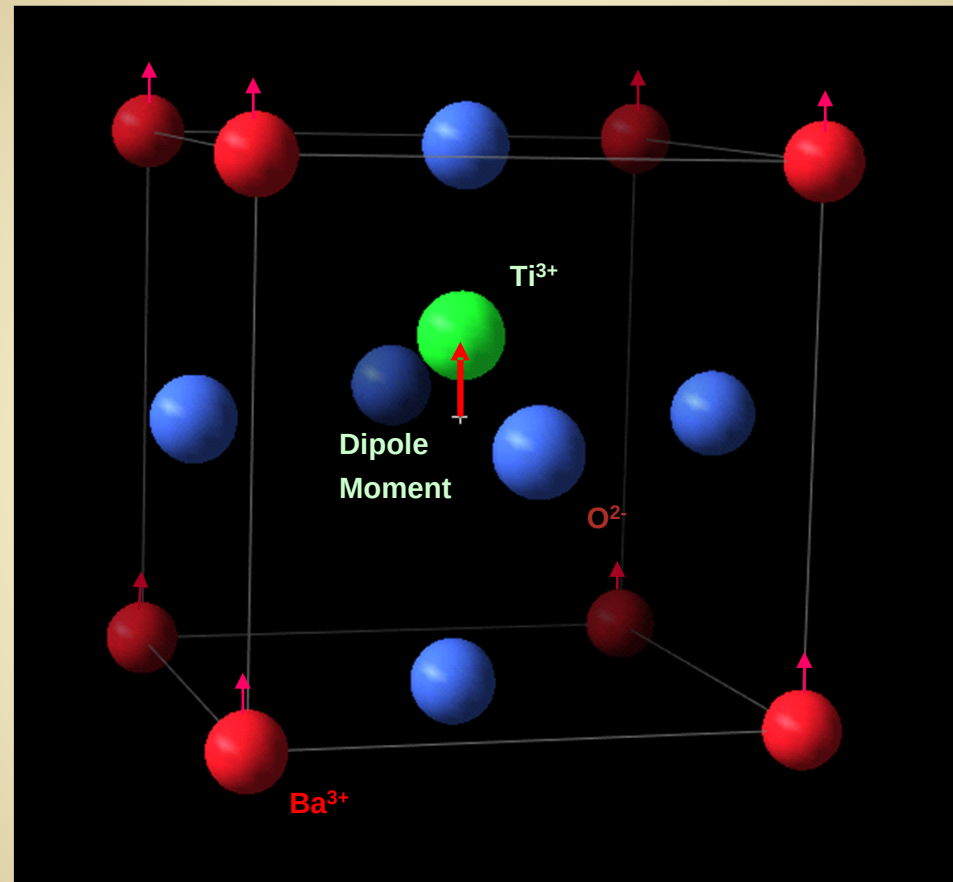
Barium Titanate (BaTiO₃) has important optical properties:

- Strong ferroelectricity with domain structure
- Piezoelectricity
- Strong electro-optic coefficient
- Photorefractance for wave-mixing
- High dielectric constant
- Birefringence in tetragonal structure ($n_o=2.4727$ and $n_e=2.4115$ at 532nm)

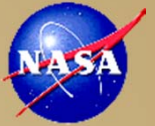
- Previously Reported Ferroelectric Semiconductors

- $\text{Sn}_2\text{P}_2\text{S}_6$, $\text{Sn}_2\text{P}_2\text{Se}_6$ and CuInP_2S_6
Y. Samulionis, J. Banys, Y. Vysochanskii, Physica status solidi A - Applied research 201 (9): 2143-2147 Jul 2004
- TlGaSe_2
V. P. Aliyeva, S. S. Babayeva, T. G. Mammadov, Mir-Hasan Yu Seyidov, and R. A. Suleymanov, Solid State Communications (128) 1, p.25-28 (2003)
- SbSBr
T. Inushima, K. Uchinokura, Ferroelectrics 286, p.841-851 (2003)
- $\text{Zn}_{1-x}\text{Li}_x\text{O}$
E. Islam, A. Sakai, A. Onodera, Ferroelectrics 261 (1-4), p.915-920 (2001)

Ferroelectric BaTiO_3



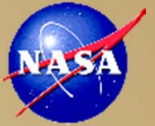
Perovskite BaTiO_3 : Rattling Ti^{3+} atoms (green) make an electric dipole moment.



Electrical and Optical Property of $\text{BaTiO}_3:\text{Eu}$

Rare Earth Lanthanoids	57	58	59	60	61	62	63	64	65	66	67	68	69	70
	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb

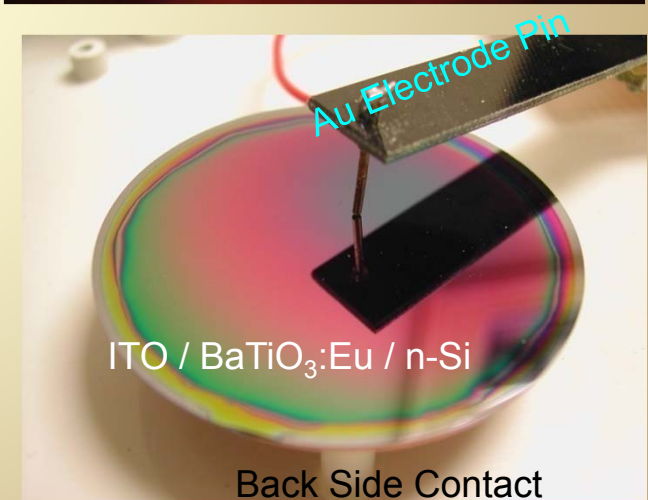
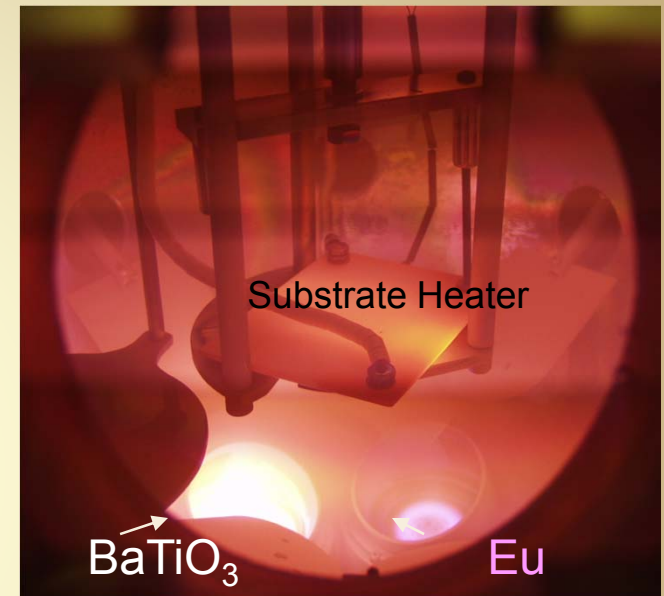
- Rare-Earth (RE) elements have ultra sharp spectral lines and long life times because their optical transitions occur in the inner shell due to the inverted electron shell structure.
- The spectral lines of RE elements are not easily affected by the neighbor atoms because the optical transition occurs in the inner electron shell.
- Europium is the most reactive RE element which easily make Europium Oxide (Eu_2O_3). It is widely used for phosphor materials due to their strong red light (~620nm) emission. (Low threshold impact ionization energy of $^5\text{D}_0$, 2.1eV)
- Very recently, strong room temperature photoluminescence signals (617, 667, 695 nm) were obtained from 0.1% Eu doped BaTiO_3 by C.B. Samantaraya, M.L. Nanda Goswami, D. Bhattacharyya, S.K. Ray, and H.N. Acharya, Materials Letters 58 p.2299–2301 (2004)
- However, the electrical properties of Eu doped BaTiO_3 epitaxial layer are not yet reported. This is the motivation for our study.



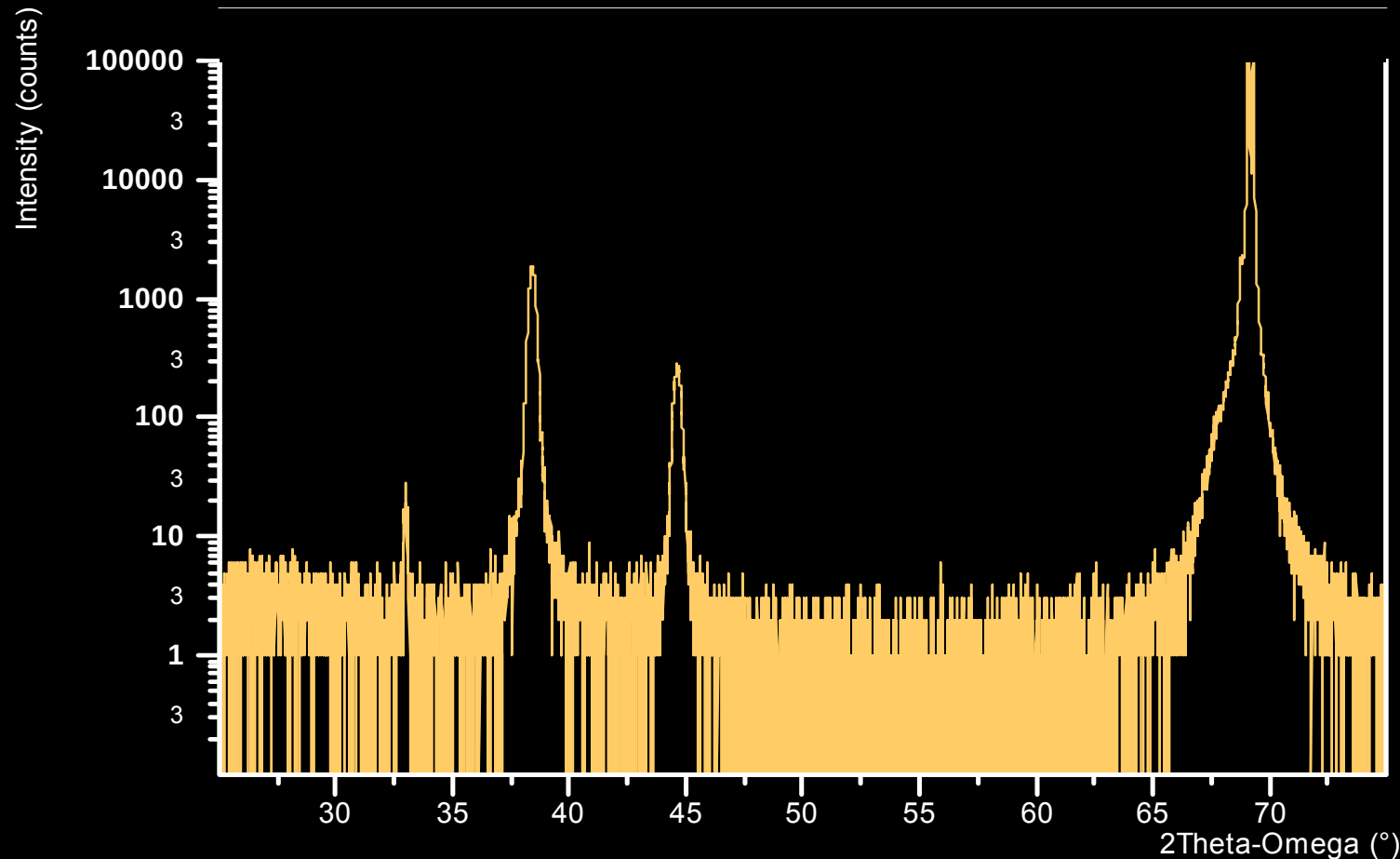
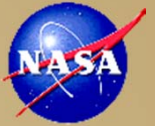
Dual Source Plasma Sputtering

Growth Condition

- Substrate: 2" n-Si (100) Wafer, $n_e = 5 \times 10^{14} \text{ cm}^{-3}$, $\rho = 7 \text{ } \Omega \cdot \text{cm}$
- Substrate Temperature: 400°C
- RF Sputtering of BaTiO_3
- DC Sputtering of Eu
- Sputtering Gas: Ar at 24 mtorr
- Oxygen was generated from BaTiO_3 target material during sputtering.
- Film thickness and Eu alloy concentration was monitored by crystal thickness monitor.
- 200nm of the transparent conductor, Indium Tin Oxide (ITO) film was deposited after the growth of $\text{BaTiO}_3\text{:Eu}$ on n-Si wafer



X-ray Diffraction Measurement



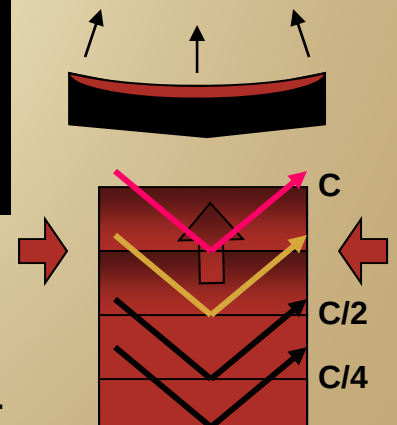
$$a_{\text{Si}} = 5.431 \text{ \AA}$$

Measured Value

$$a_{\text{BaTiO}_3} = 4.056 \text{ \AA}$$

$$c_{\text{BaTiO}_3} = 4.056 \text{ \AA}$$

Poly-crystalline
Cubic BaTiO_3
was obtained.



X-ray source: Cu K_{α} line. Ni filter was used.

The forbidden Si (002) peak (its structure factor=0) shows up due to the bending of Si wafer by the epitaxial stress of BaTiO_3 layer.

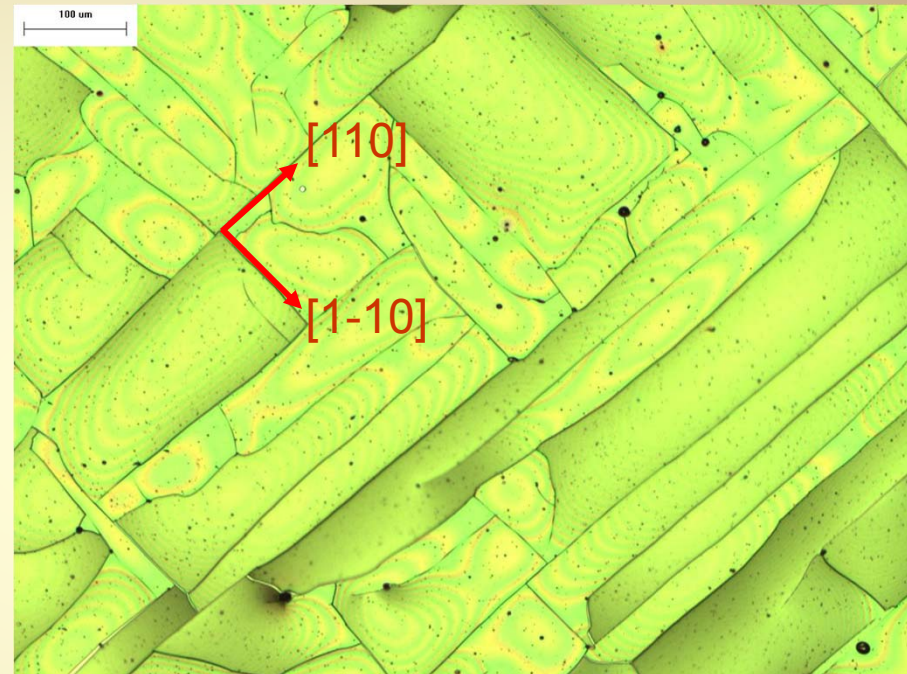
Microscopic Images



BaTiO₃ (200nm) on n-Si (100)



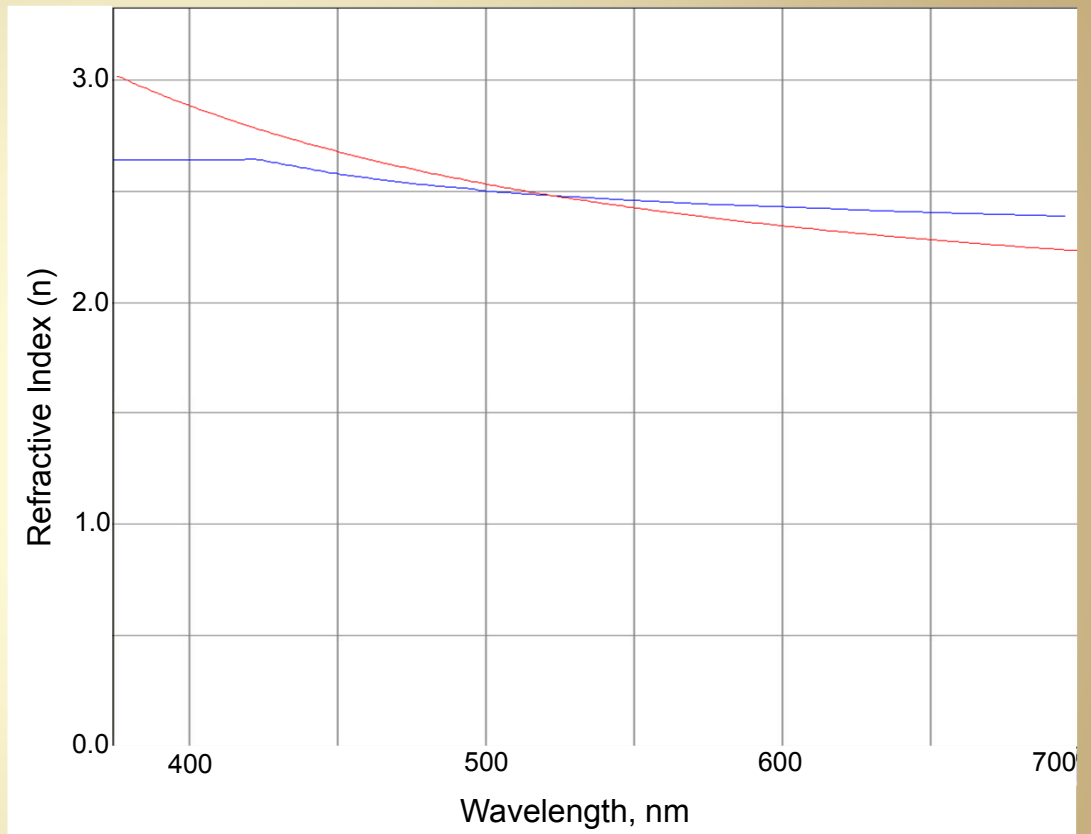
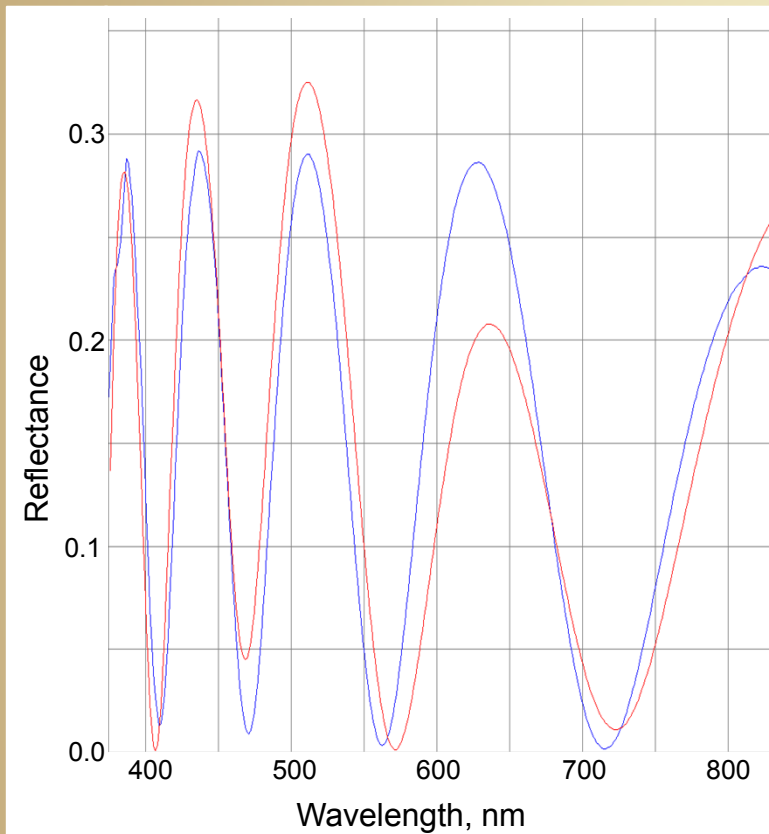
BaTiO₃:Eu (220nm) on n-Si (100)



Thick (>500nm) BaEuTiO₃ with Eu>5%
on n-Si (100) beyond the critical thickness

- Different color is a result of interference due to the different film thicknesses.

Refractive Index of BaTiO₃:Eu

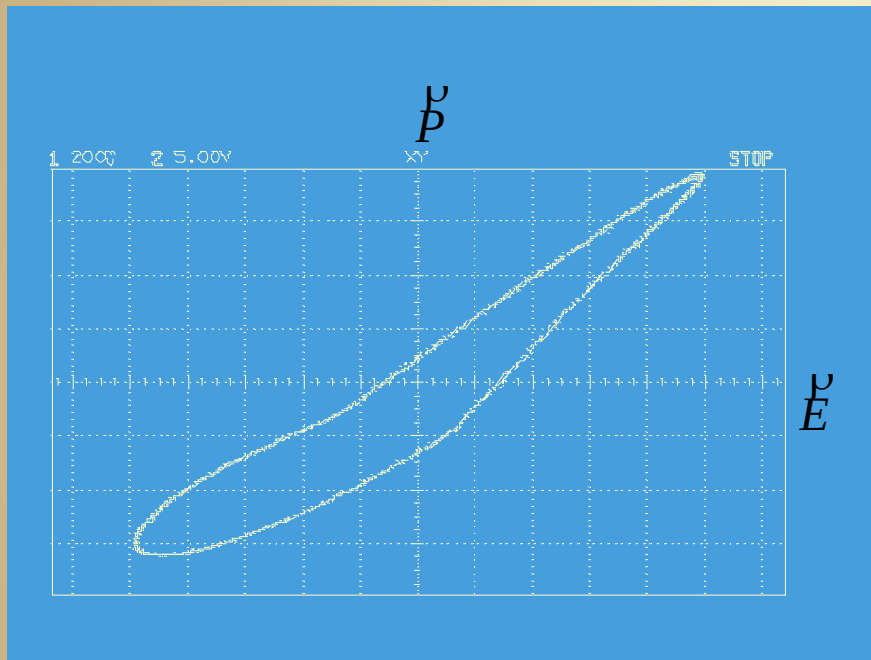


Measured (-) and Simulated (-)
Reflectance with the estimated film
thicknesses of ITO and BaTiO₃:Eu
layers

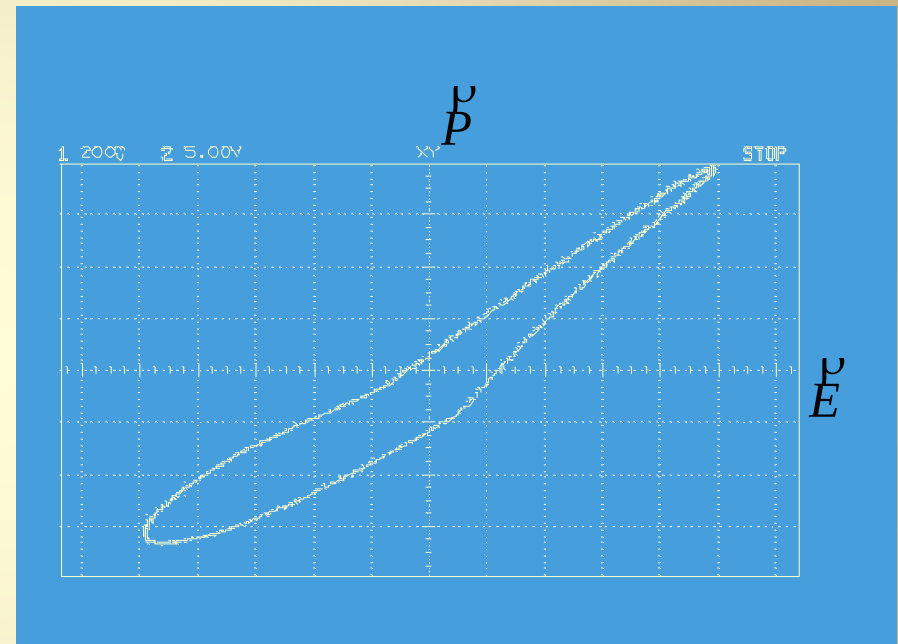
— Refractive Index of BaTiO₃ (Library Reference)
— Measured Refractive Index of BaTiO₃:Eu



Small Signal P-E Measurement

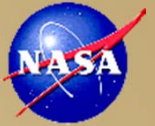


BaTiO₃ / n-Si

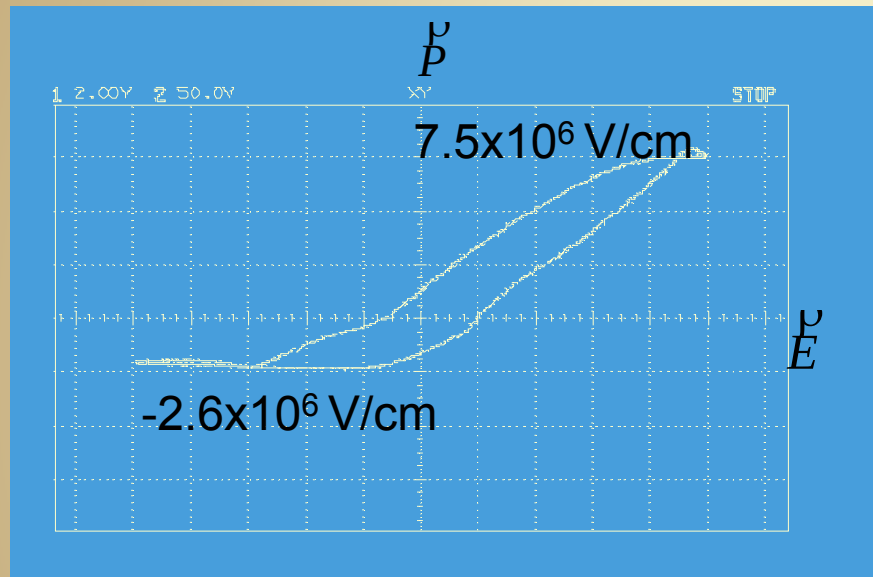


BaTiO₃:Eu / n-Si

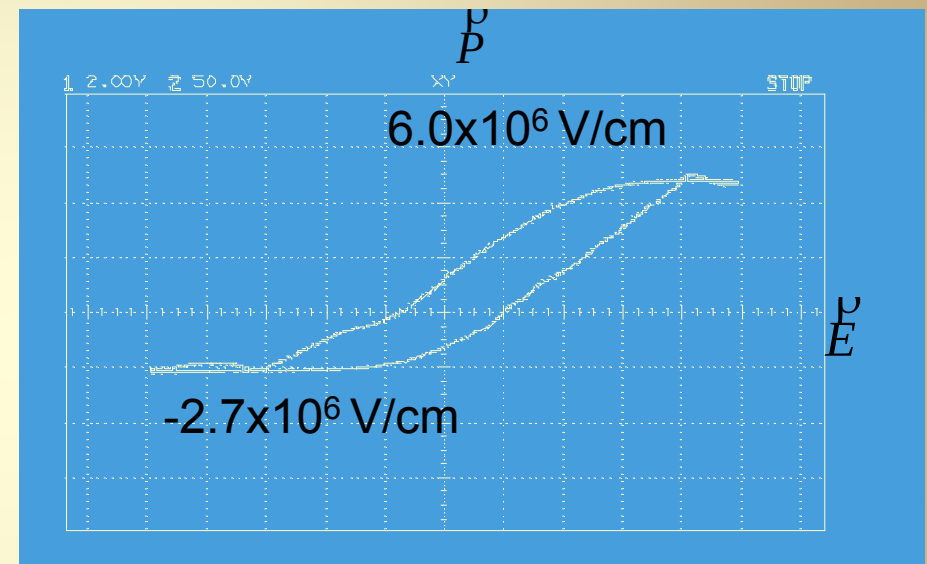
Excitation = 20V (10^6 V/cm), 1kHz, Sawyer-Tower $C_{\text{ref}}=150\text{pF}$



Full Hysteresis Measurement

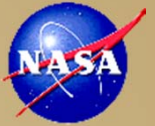


BaTiO₃ / n-Si



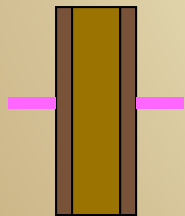
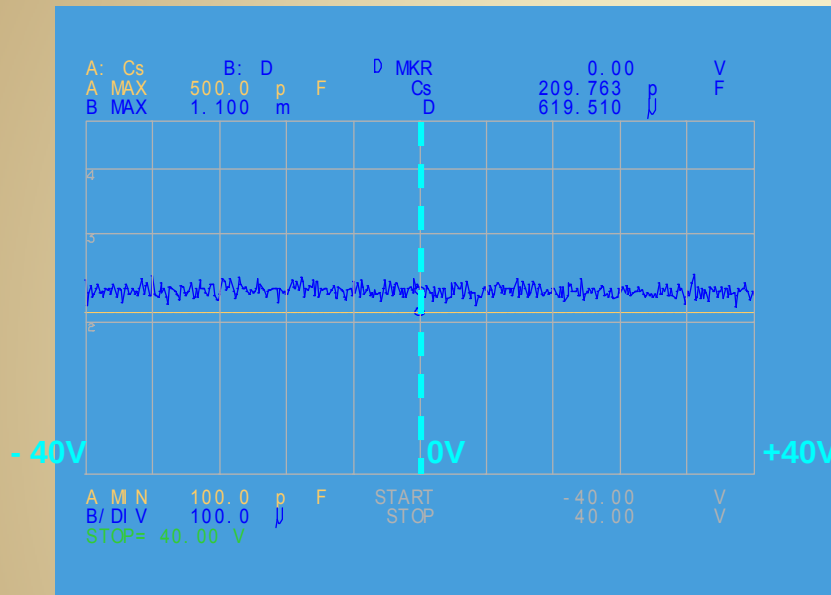
BaTiO₃:Eu / n-Si

Excitation = 200V (10^7 V/cm), 1kHz, $C_{\text{ref}}=150\text{pF}$



Standard C-V Measurement

Normal Capacitor (Commercial)

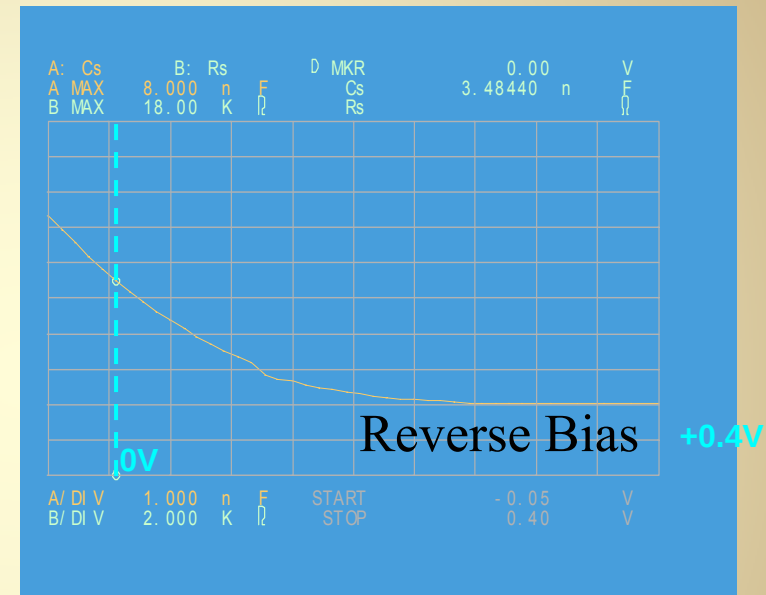


$$C = \frac{A}{\epsilon \cdot d}$$

— Series Capacitance, Cs

— Dissipation Factor, R/|X|

Normal Diode (Commercial)

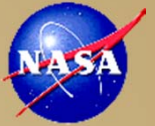


Weak Reverse Bias



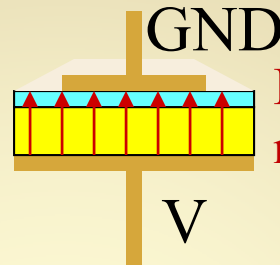
Strong Reverse Bias

Depletion width
~ capacitance gap distance



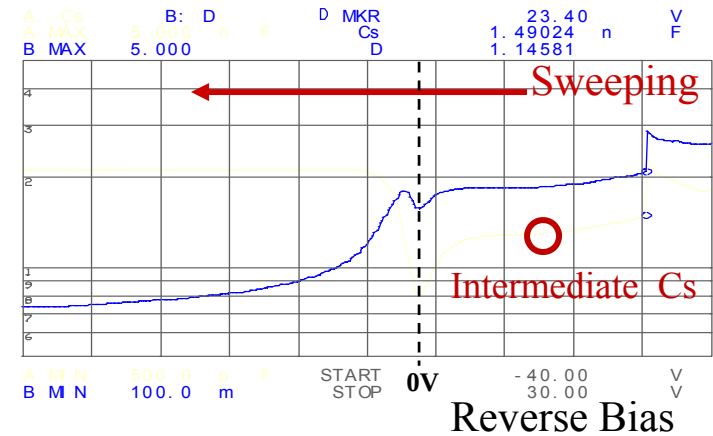
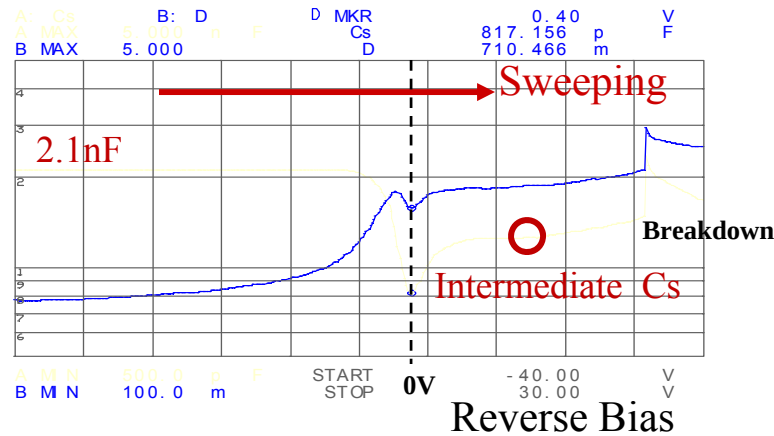
Capacitance-Voltage Measurement

- Series Capacitance, C_s
- Dissipation Factor, $R/|X|$

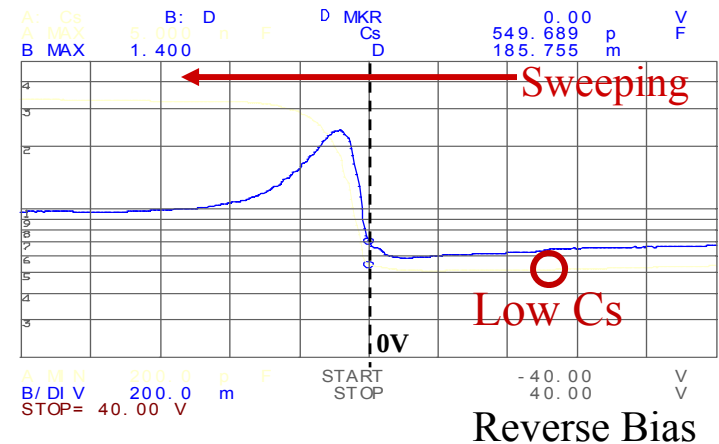
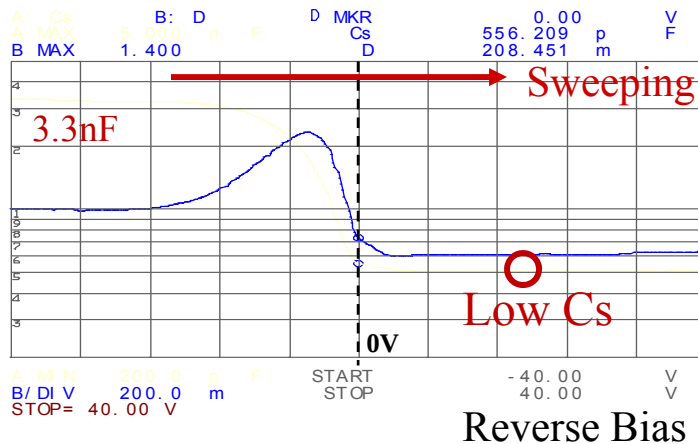


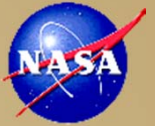
BaTiO_3 , $\text{BaTiO}_3:\text{Eu}$
 n-Si , $n_e = 5 \times 10^{14} \text{ cm}^{-3}$, $\rho = 7 \Omega \cdot \text{cm}$

BaTiO_3
on $\text{n-Si}(100)$



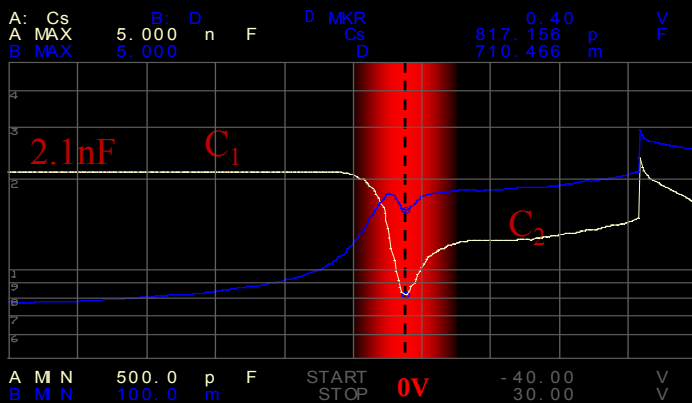
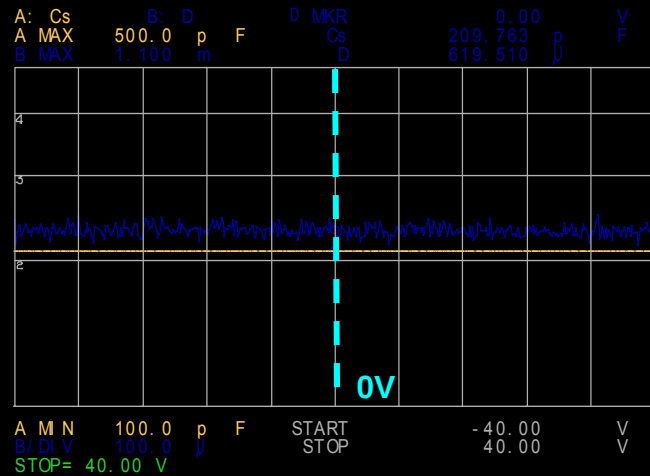
$\text{BaTiO}_3:\text{Eu}$
on $\text{n-Si}(100)$





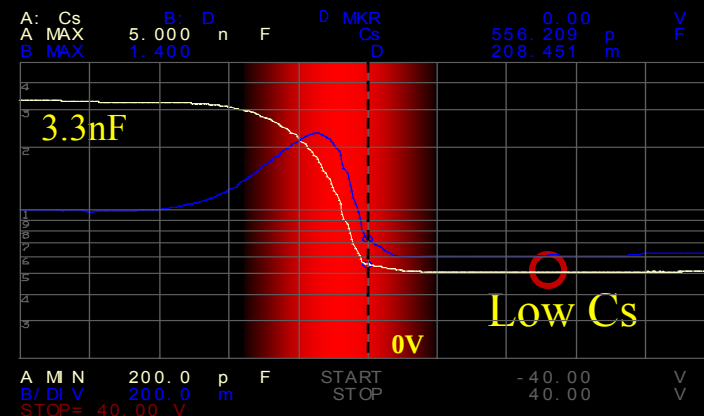
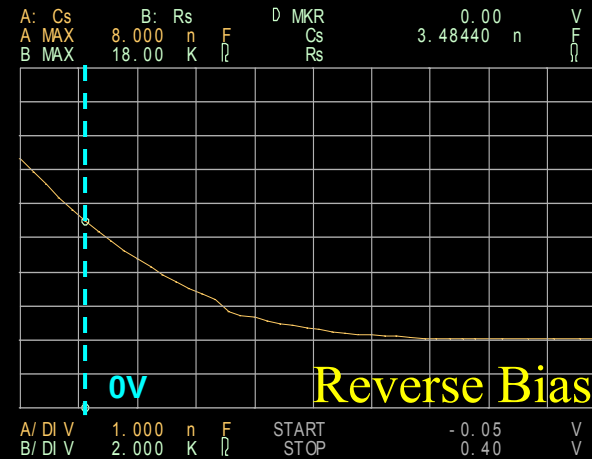
Comparison of C-V Measurement

Ideal Capacitor



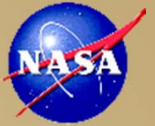
BaTiO₃ on n-Si

Ideal Diode

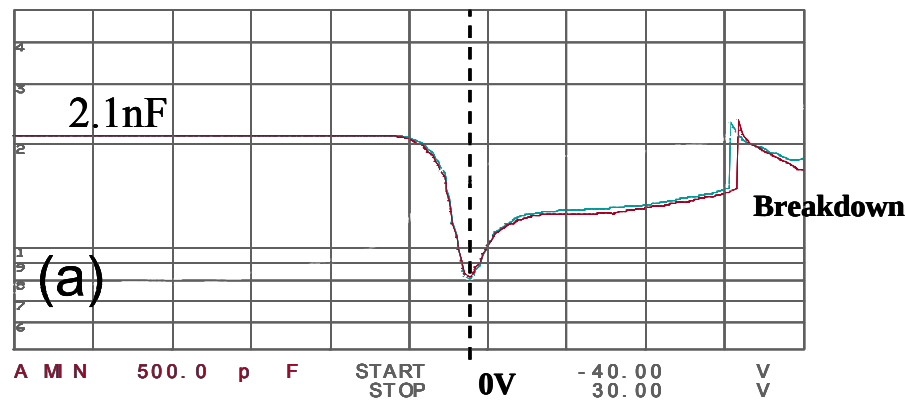


BaTiO₃:Eu on n-Si

Hysteresis on C-V Measurement

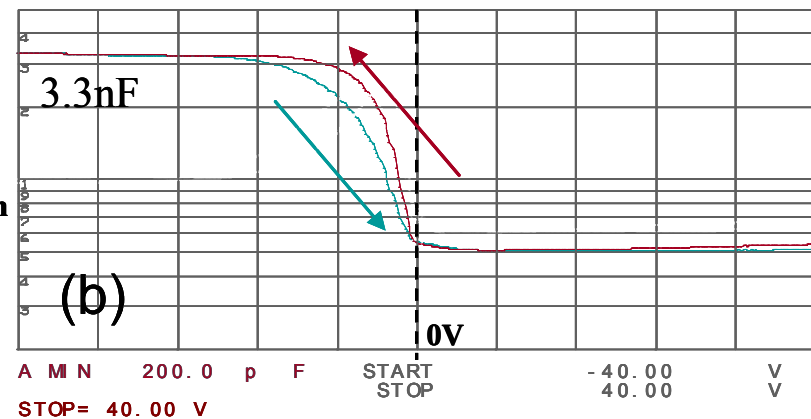


A: Cs
A MAX 5.000 n F

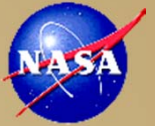


BaTiO₃ on n-Si

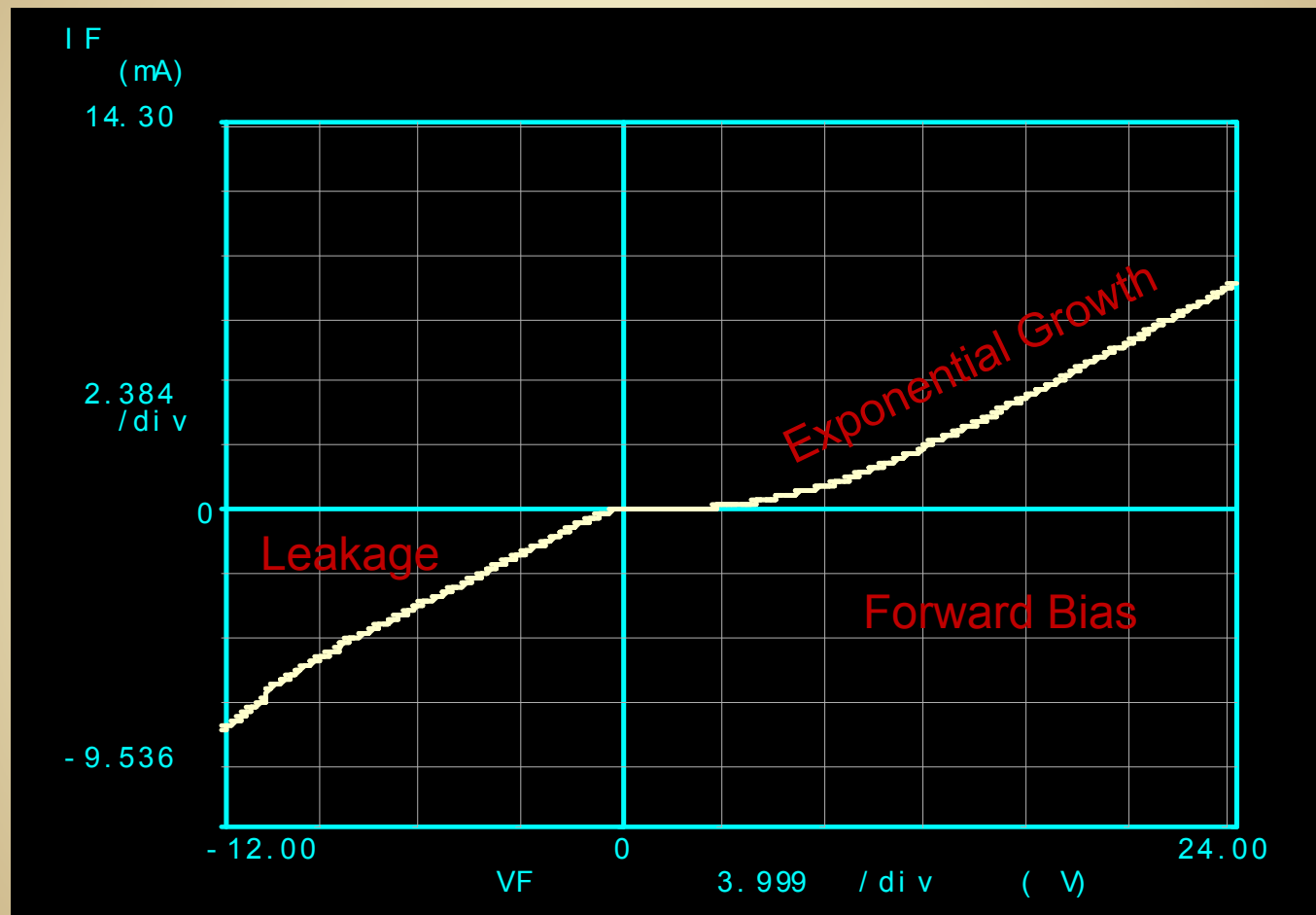
A: Cs
A MAX 5.000 n F



BaTiO₃:Eu on n-Si



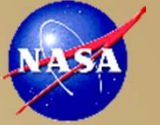
I-V Measurement of $\text{BaTiO}_3\text{:Eu}$ / n-Si



Leaky diode behavior of $\text{BaTiO}_3\text{:Eu}$ / n-Si

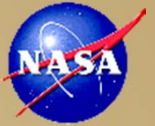
- Forward bias region: exponential growth which is common in diodes
- Reverse bias region: straight line of a leaky resistor.

Conclusions for Semi-metallic ScN

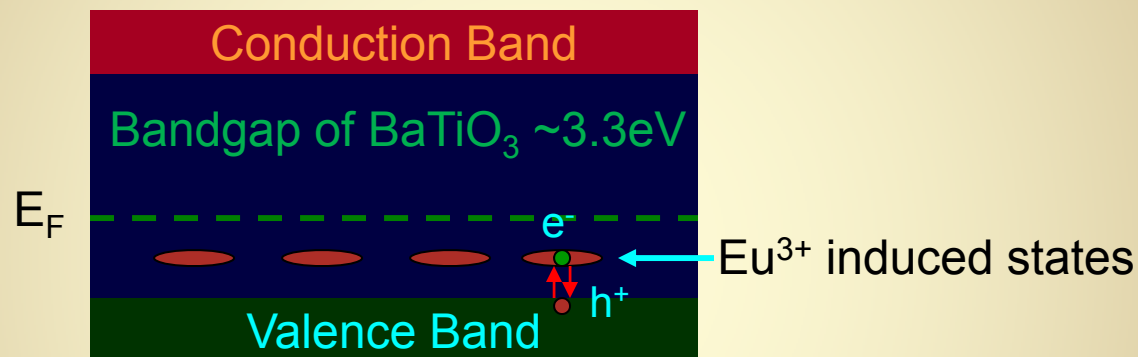


- Hall effect measurement result of ScN shows a high electron density and is regarded as a semi-metallic material which satisfies KKR
- ScN shows spectral shift and refractive index shift beyond its bandgap energy 2.4 eV under the applied electric field
- Ga-doped ScN shows spectral shift and refractive index shift beyond its bandgap energy 3.5 eV under the applied electric field
- Potential application of semi-metallic materials is the programmable smart grating devices

Conclusions for $\text{BaTiO}_3\text{:Eu}$



- Our measurements show that 400°C sputtering grown Eu doped BaTiO_3 is a **p-type ferroelectric wide-bandgap semiconductor** with a close gap states toward the valence band.



- When compared with other wide-bandgap semiconductors, such as GaN, most impurities except Mg dopants in GaN show n-type property. Therefore it is very new and interesting that Eu can give p-type property to wide-bandgap ferroelectric material BaTiO_3 .
- The energy level, capture & emission cross sections and occupied sites of Eu in BaTiO_3 are yet to be determined.