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# **The epitaxy of Alkaline Earth Fluorides on Semiconductors**

S. Heun, M. Sugiyama, S. Maeyama,  
Y. Watanabe, and M. Oshima

Synchrotron Radiation Research Group  
Advanced Materials & Characterization Laboratory  
NTT Interdisciplinary Research Laboratories

# 放射光応用研究グループ (機放G) Synchrotron Radiation Research Group

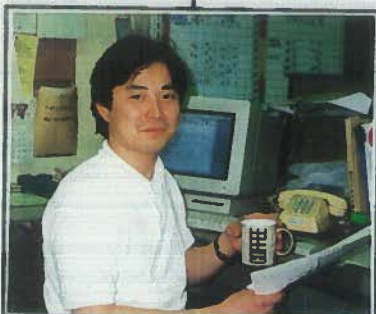


Dr. M. Oshima

## 軟X線サブG (EXAFS, XSW)



Mr. S. Maeyama



Mr. M. Sugiyama



Dr. S. Heun



## VUVサブG (SRPES)



Dr. Y. Watanabe



Mr. F. Maeda



Mr. T. Kiyokura

# NTT R&D, WHICH LEAD UP TO THE BEST SERVICE

## Research and Development Headquarters

### ■ Engineering Planning Department

### ■ Research and Development Management Department

### Network Systems Development Department

Development of access and network systems

### Telecommunication Network Laboratory Group

Planning for research and development of access and network systems

### ■ Telecommunication Networks Laboratories

Planning for basic telecommunications network architecture, and research and development of systems related to the telecommunications network innovation

### ■ Access Network Systems Laboratories

Research and development of optical access facilities and their construction and maintenance technologies

### ■ Network Service Systems Laboratories

Research and development of switching functions and systems to enhance the sophistication and economical features of telecommunications networks

### ■ Optical Network Systems Laboratories

Research and development of functions and systems to implement sophisticated and economical cable transmission systems for telecommunications networks

### ■ Wireless Systems Laboratories

Research and development of functions and systems to implement sophisticated and economic wireless transmission systems for telecommunications networks

### Multimedia System Laboratory Group

Planning for research and development of multimedia and other user systems

### ■ Information and Communication Systems Laboratories

Research and development of databases, protocol processing, and services and operations based on AI technology

### ■ Human Interface Laboratories

Research and development for economical implementation of natural and efficient user-friendly technologies and related systems

### ■ Software Laboratories

Research of software's substance, and efficiency enhancement and systematization of software development

### Science and Core Technology Laboratory Group

Planning for basic technological research and development of parts and materials relating to telecommunications

### ■ LSI Laboratories

Research and development of technologies that integrates element functions into custom LSIs for telecommunications systems

### ■ Opto-electronics Laboratories

Research and development of optical IC and part technologies to implement optical telecommunications systems

### ■ Interdisciplinary Research Laboratories

Research and development of innovative equipment and the related part and material technologies in the telecommunications field

### ■ Communication Science Laboratories

Basic research in information science

### ■ Basic Research Laboratories

Creation of new knowledge and concepts in the telecommunications field



Musashino R&D Center



Shinjyawa Twins



Yokosuka R&D Center



Kyoto (in ATR)



Atsugi R&D Center



Tsukuba R&D Center



Ibaragi R&D Center



Makuhari Bldg

### Service Marketing and Support Headquarters

■ Maintenance Service Planning Department  
**Technical Assistance and Support Center**  
 Development of maintenance and support tools for technicians on the front lines

■ Customer Equipment Department  
 Development of ISDN-related communication equipment, business phones, and phones for home use

### Business Communications Headquarters

■ Network Services Department  
 Development relating to telephone network services, leased line services and ISDN services

■ System Services Department  
 Development of large-scale integrated telecommunications systems

### Service Engineering Headquarters

■ Customer Systems Development Department  
 Development of user systems to provide diversified services including multimedia, high-speed computer and personal communications

■ Telecommunications Software Headquarters  
 Development of switching software to implement new services and operation systems to enhance maintenance and operational efficiency of telecommunications facilities

■ Information Systems Headquarters  
 Development of information systems, primarily software used in NTT

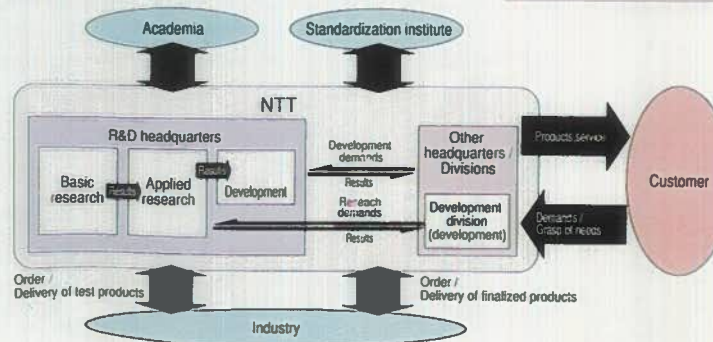
### Packet Network Sector

Development of packet switching services for data transmission and total operation systems for packet networks

### Visual Communications Sector

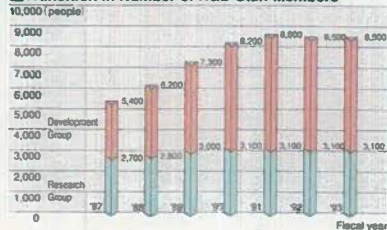
Development of facsimile and video communication services, including videotex and teleconferencing

### ■ Flow from R&D to Service Operation

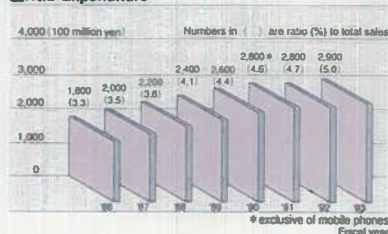


## R&D DATA

### ■ Transition in Number of R&D Staff Members



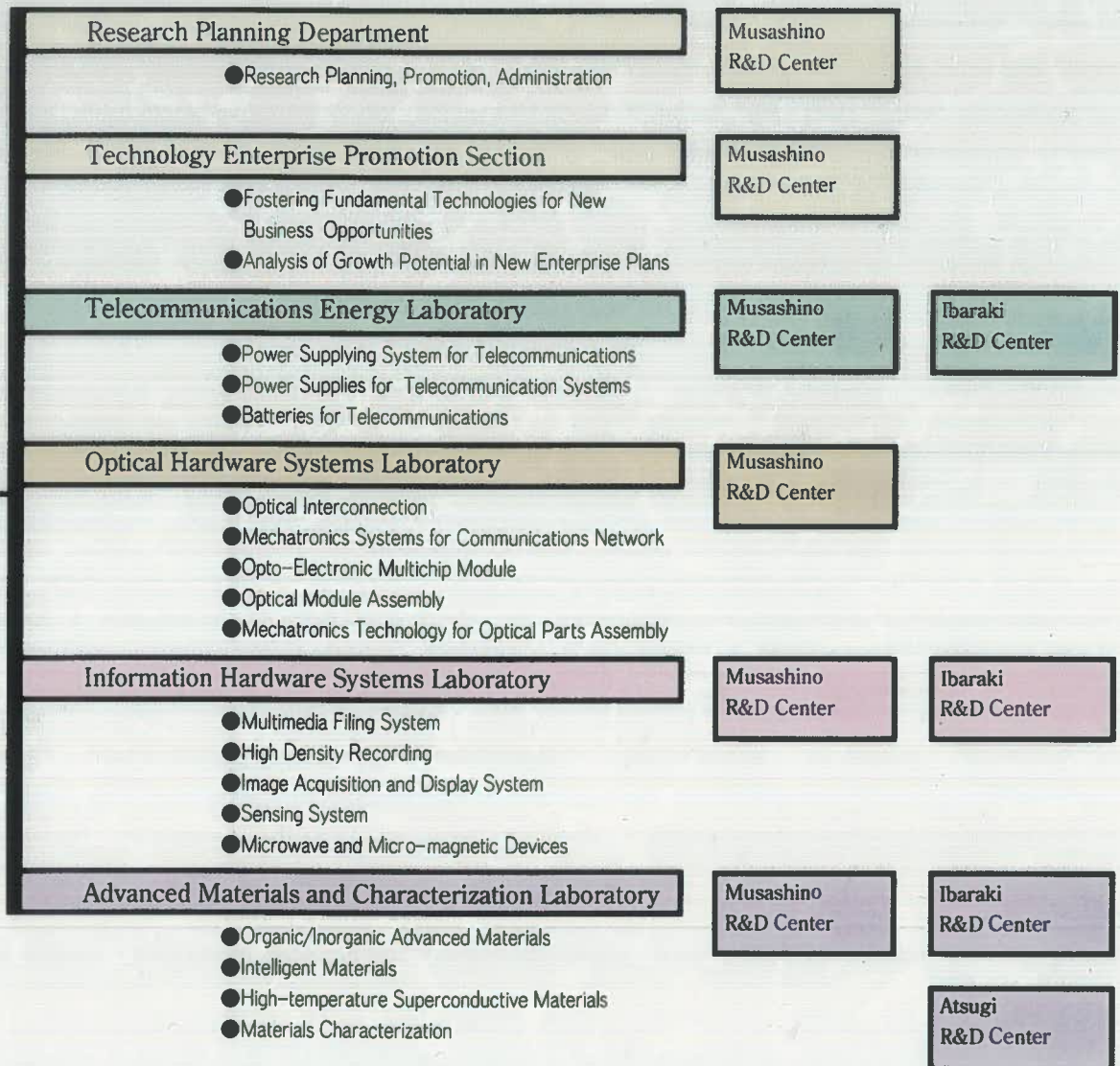
### ■ R&D Expenditure



## NTT Interdisciplinary Research Laboratories

The goals of NTT Interdisciplinary Research Laboratories are not only to contribute to NTT's telecommunications business but also to create new enterprises, advance academic fundamental research, and find solutions for environmental problems. To accomplish the above, we are carrying out research and development in a wide yet consistent spectrum, ranging from materials and equipment to systems development. The foundation of our work consists of three major research and development areas: (1) Optical interconnections, (2) Advanced multimedia hardware, and (3) Telecommunication energy/Innovative new materials.

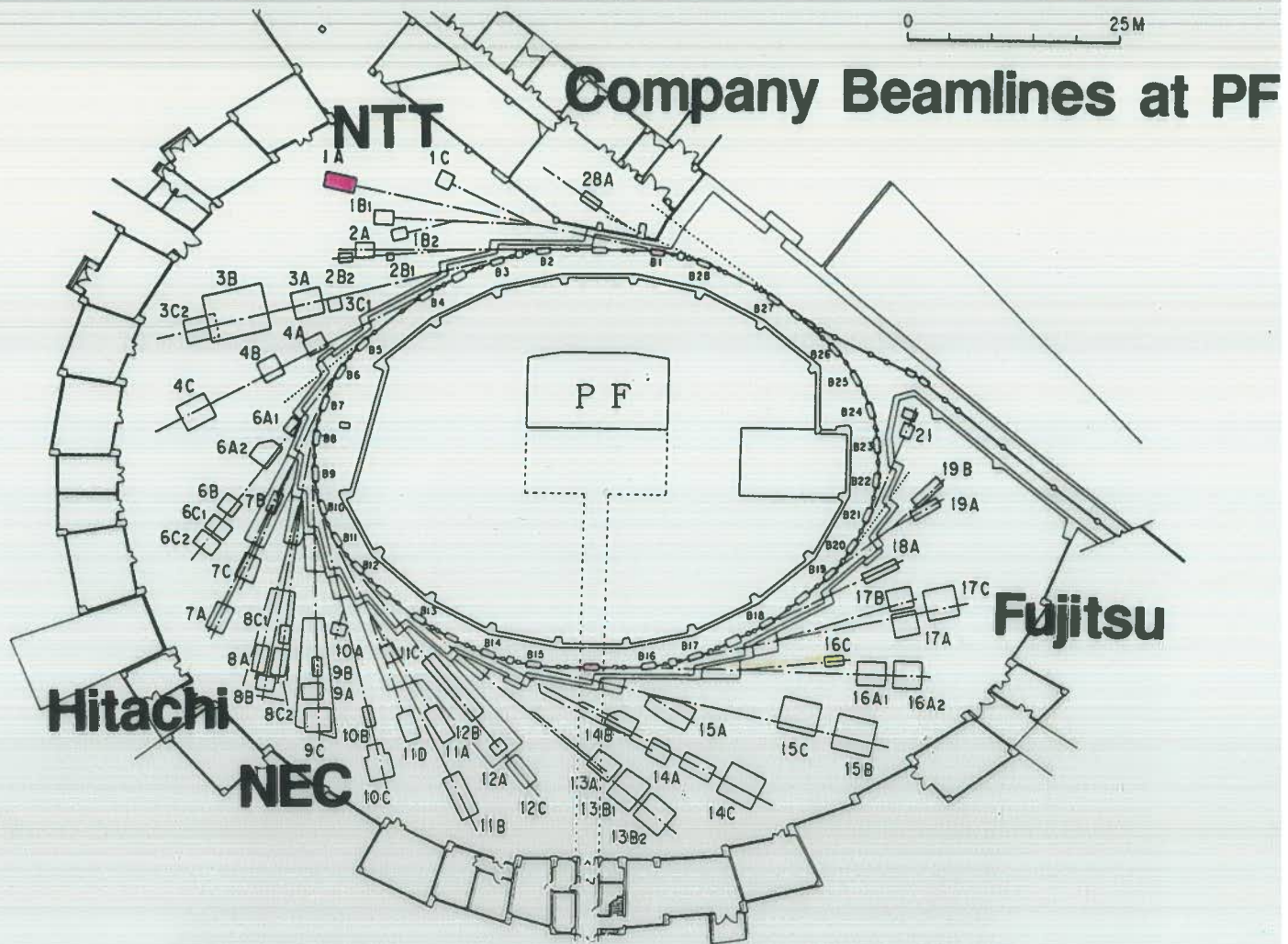
Interdisciplinary Research Laboratories  
Executive Manager



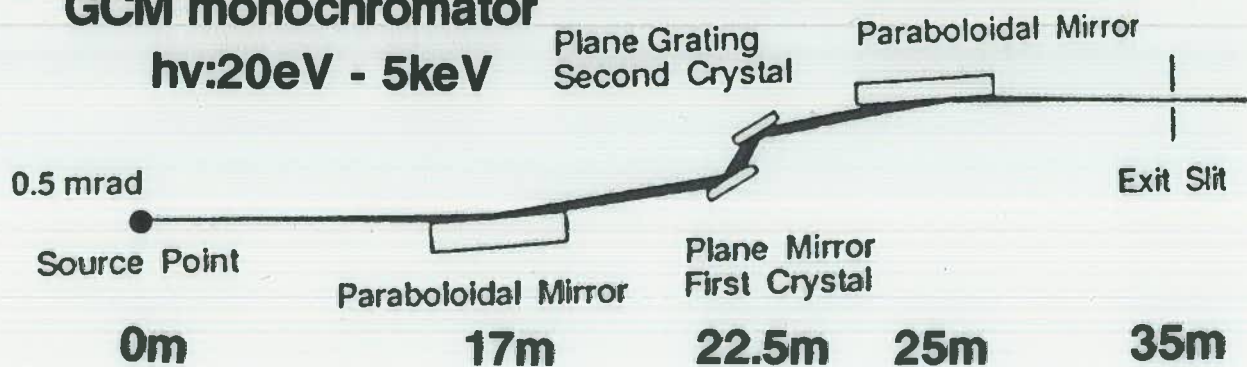


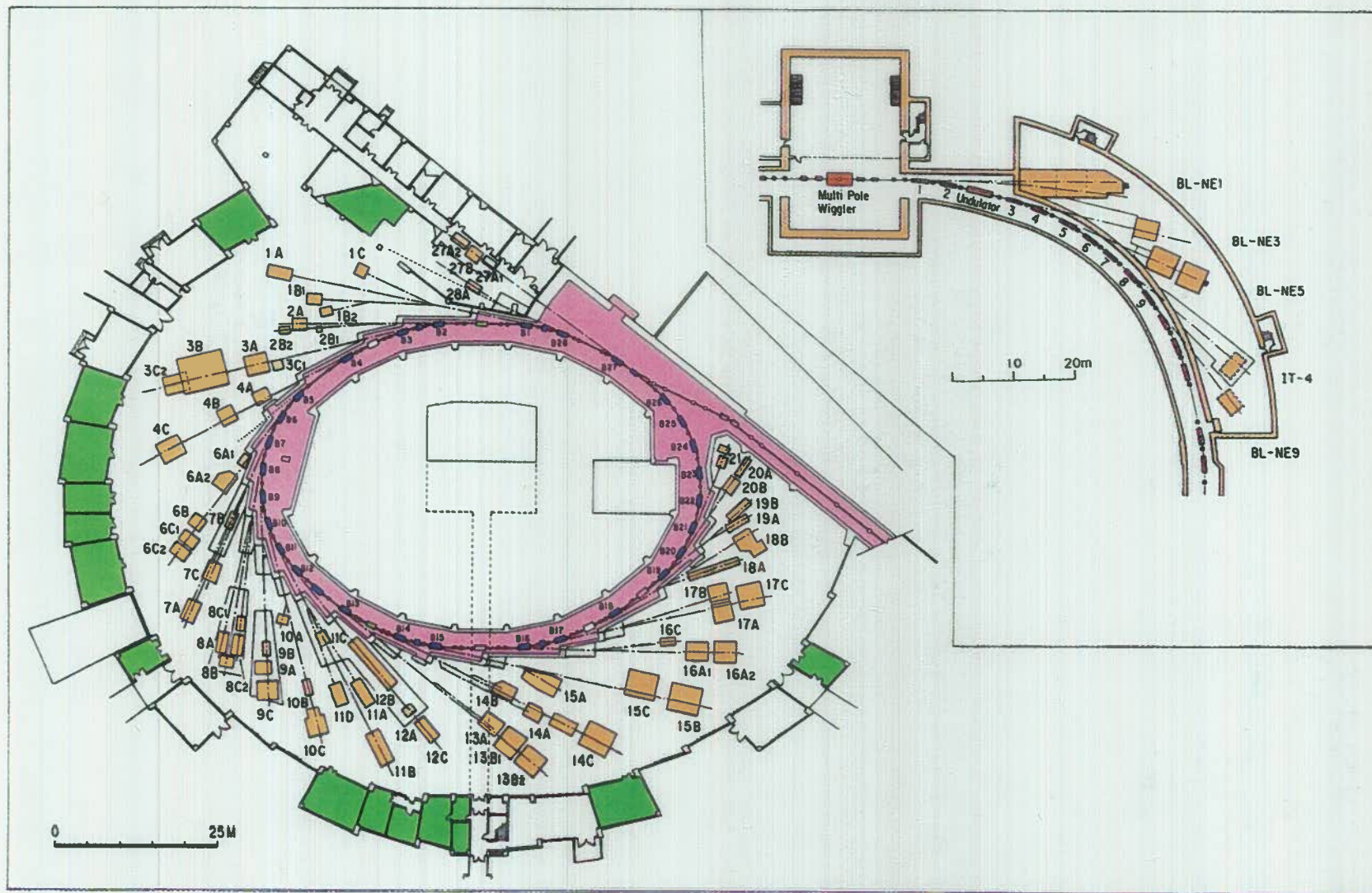


*Bird's-eye view of the 2.5 GeV Linac, the 2.5 GeV PF Ring, the 6.5 GeV AR and the 30 GeV Main Ring.*



## GCM monochromator hv:20eV - 5keV





*The PF and the AR experimental areas*



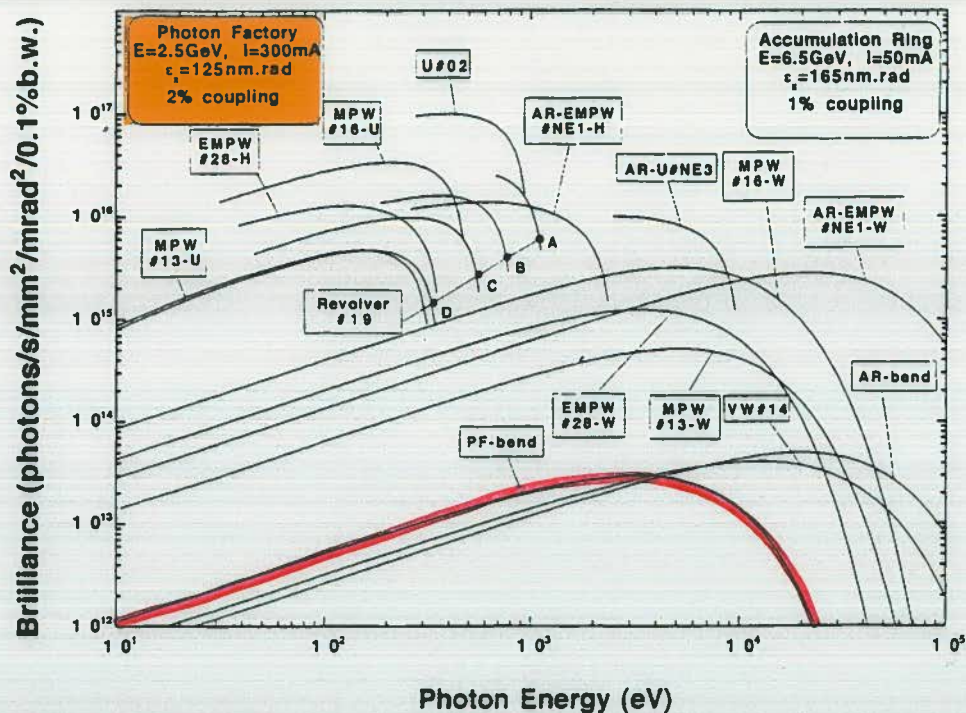
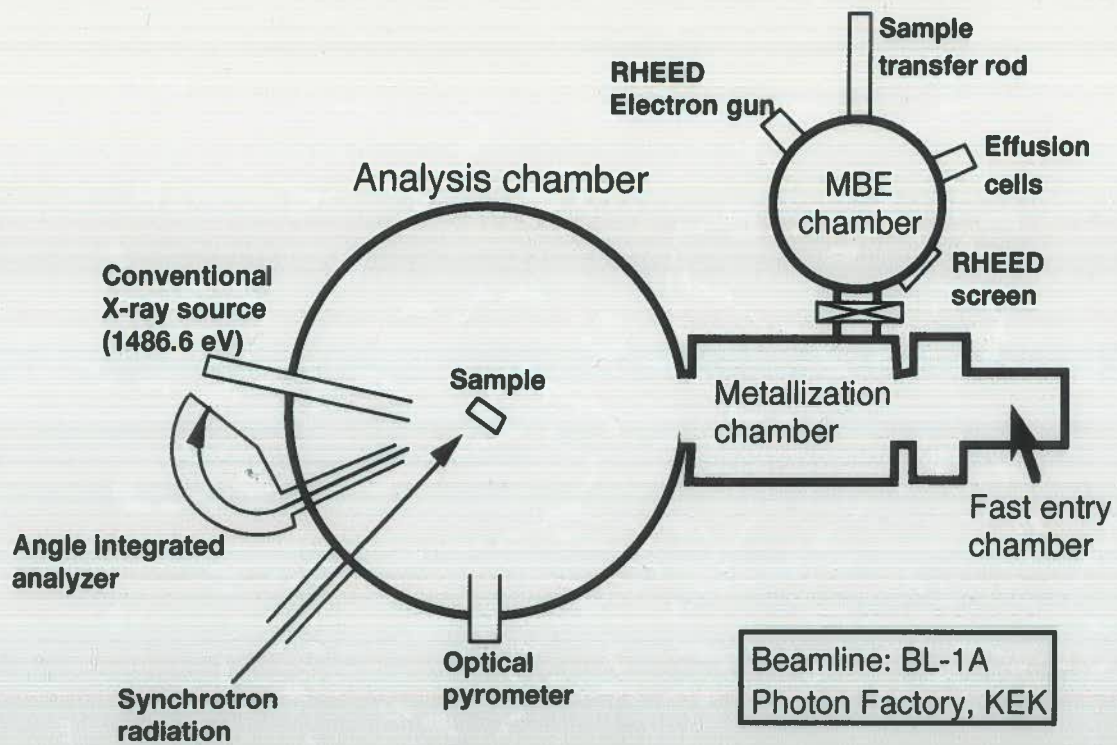


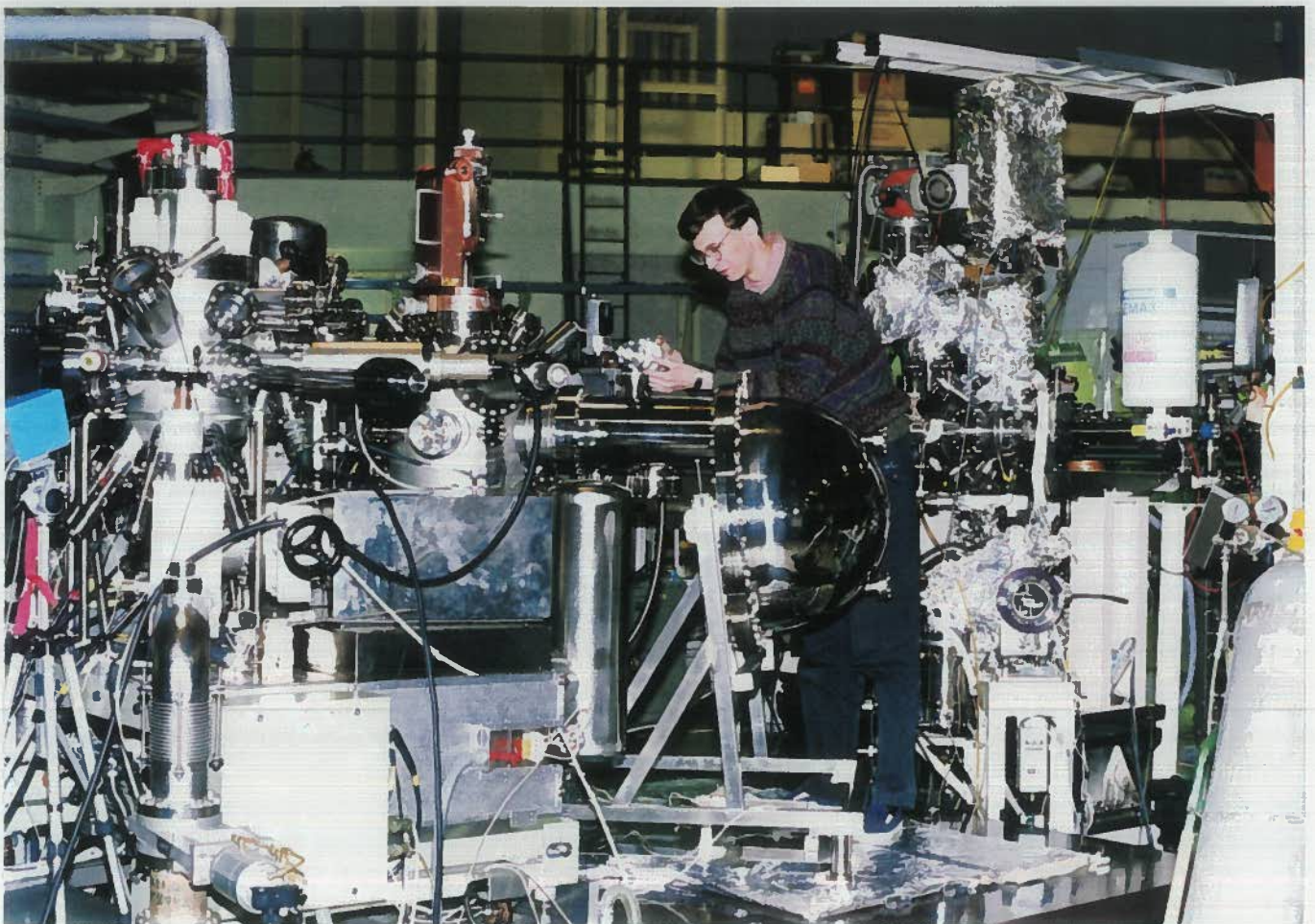
Fig. 12 Synchrotron radiation spectra. Brilliance of radiation vs. photon energy for the insertion devices (U#02, MPW#13, VW#14, MPW#16, Revolver#19 and EMPW#28) and the bending magnet (Bend) of the PF, and for the insertion device (EMPW#NE1) of the AR. The name of each source is assigned in Table C-4. Several insertion devices have both undulator and wiggler modes, which are denoted by U or W, respectively. The spectral curve of each undulator (or undulator mode of multipole wiggler) is a locus of the peak of the first harmonic within the allowable range of K-parameter. Spectra of Revolver#19 are shown for four kinds of period lengths.

Table 9 General parameters of the storage ring.

Energy	2.5 GeV	(0.75 GeV to 3 GeV)
Initial stored current	(multi-bunch)	350 mA (max 500 mA)
	(single bunch)	60 mA (max 104 mA)
Emittance	130nm-rad(horizontal)	
	~2nm-rad(vertical)	
Circumference	187m	(bending radius=8.66m)
RF frequency	500MHz	(harmonic number=312)
Injection	2.5GeV Linac	(positron/electron)
Beam lifetime	60 h (at 300 mA)	$I \cdot \tau \geq 18 \text{ A} \cdot \text{h}$ (at ~250 mA ~ 350 mA)
Vacuum pressure	$\geq 3 \times 10^{-10}$ Torr (at 300mA)	
	$P/I \sim 8 \times 10^{-10}$ Torr/A (at ~250 mA ~ 350 mA)	
	$\sim 3 \times 10^{-11}$ Torr (at 0 mA)	
Insertion devices	Superconducting vertical wiggler 5T 60 period undulator $K=1.78 \sim 0.1$ 26 period multipole wiggler/undulator 1.5T-0.04T Four way revolver type undulator 14 period multipole wiggler Elliptically polarized multipole wiggler	
SR channels	SR experiment 22 Beam diagnosis 3	



## In situ surface analysis system



# Alkaline Earth Fluorides on Semiconductors

New possibilities for dielectric  
insulation and passivation (FET)  
(Farrow / Ishiwara)

- + lattice matching to semiconductors  
( $\text{SrF}_2$  on InP: -1.2%)  $\text{CaF}_2$ : 5.5 Å to  
 $\text{BaF}_2$ : 6.2 Å
- + good insulators  
(band gap: 10 -12 eV)
- + fluorite structure similar to diamond  
or zinc blende structure of  
semiconductors
- + sublime as molecules  
(stoichiometry OK)

perfectly ordered heteroepitaxial  
crystalline insulator -  
semiconductor interface  
(superior transport properties)

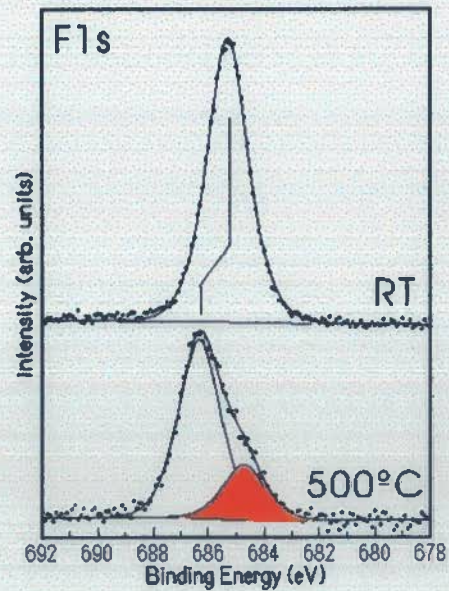
**NTT**



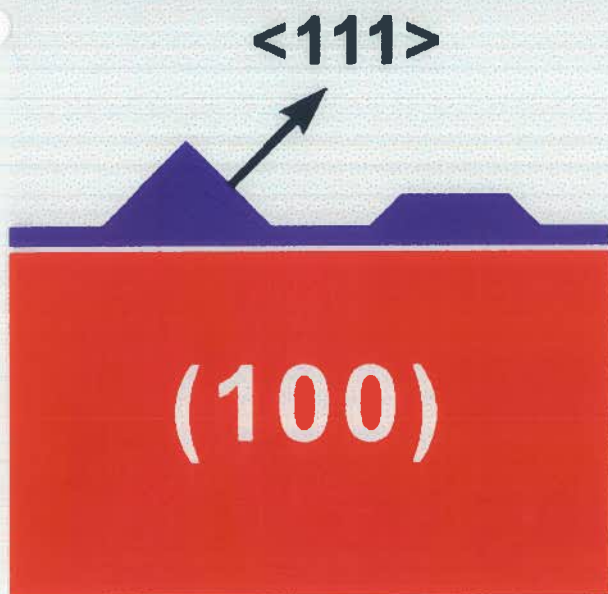
# Interfacial Reaction

e.g.  $\text{SrF}_2$  on  $\text{InP}(111)$

Heun et al,  
PRB 52 (1995) 14917



## Facets



## Layer



Hannover  
(Germany)  
Prof. Henzler  
Dr. Wollschläger

11/93



NTT  
(Japan)

06/95

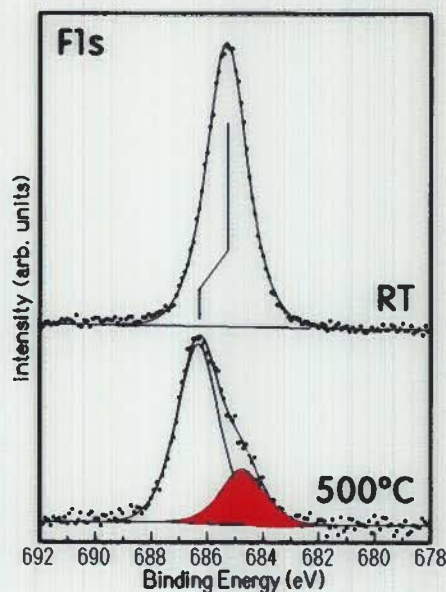


Trieste  
(Italy)  
Dr. Sorba



### SrF<sub>2</sub> on InP

4 int. conf.  
(ALE, MBE,  
ICG, IPRM)  
4 paper  
(ASS, JCG,  
2 x PRB)

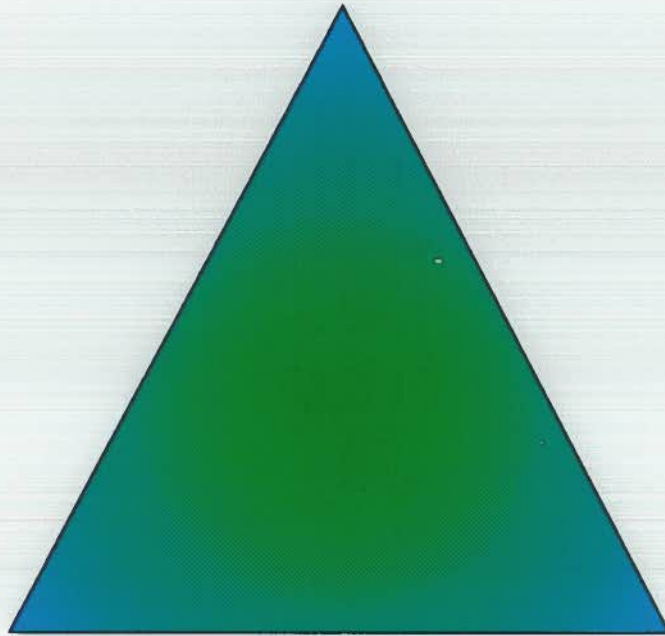


### CaF<sub>2</sub>/Si/GaAs

collaboration with  
Dr. Wada,  
NTT LSI Labs.  
Quantum Dev. Lab.

**The role of an  
Si ICL  
between  
GaAs and  $\text{CaF}_2$**

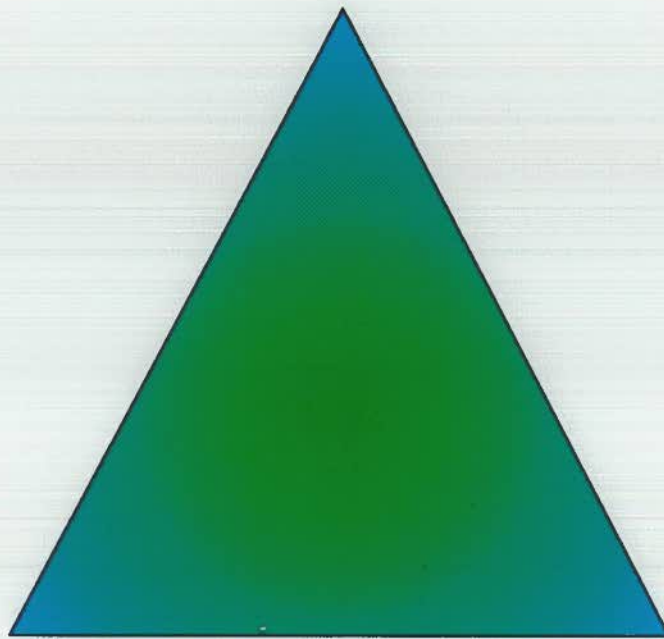
Film  
morphology  
(XRD, RHEED,  
SEM, AFM)



Electrical  
properties  
(C-V-curves)

Chemical  
bonding  
(SRPES,  
XPS)

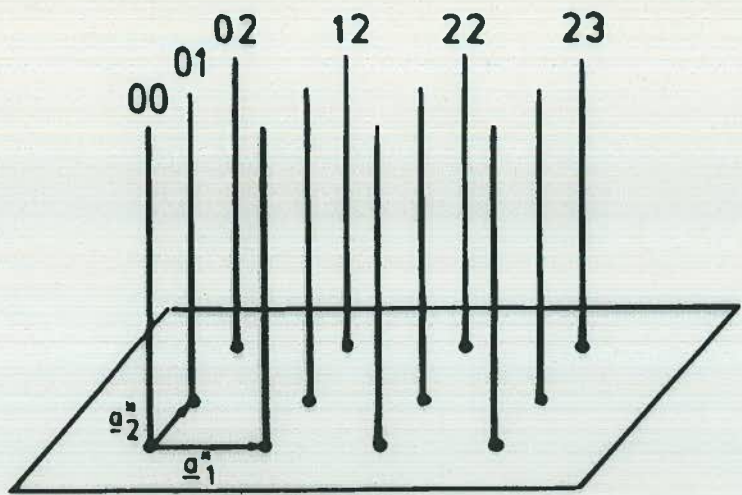
Film  
morphology  
(XRD, RHEED,  
SEM, AFM)



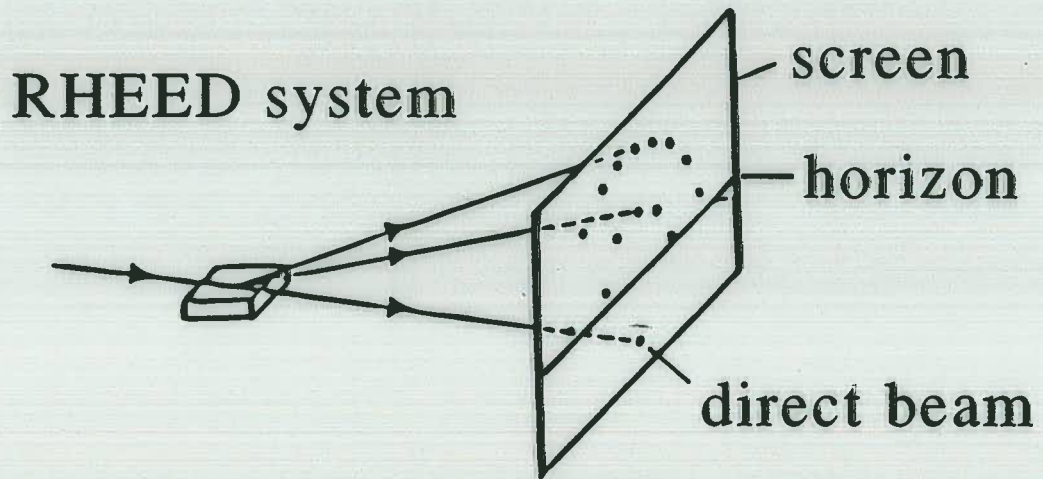
Electrical  
properties  
(C-V-curves)

Chemical  
bonding  
(SRPES,  
XPS)

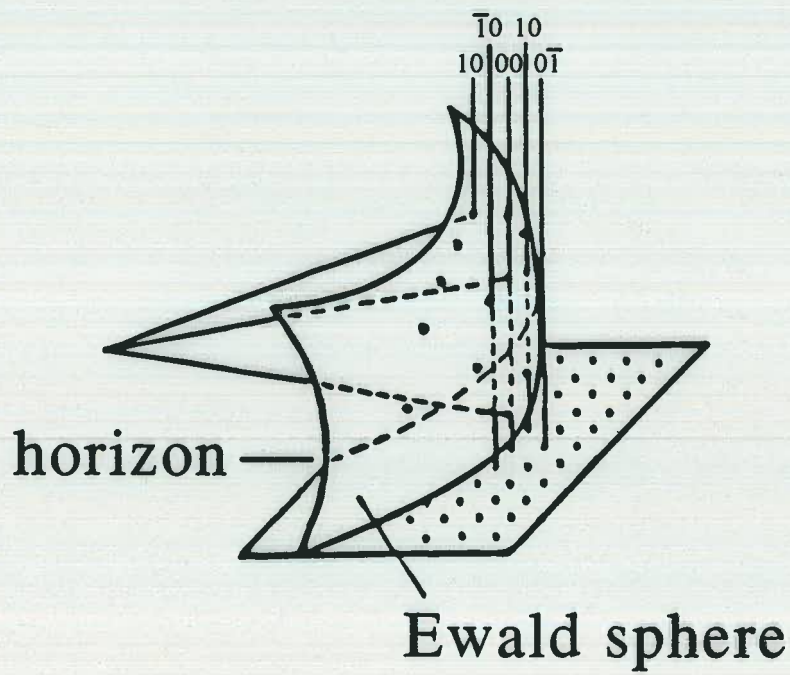




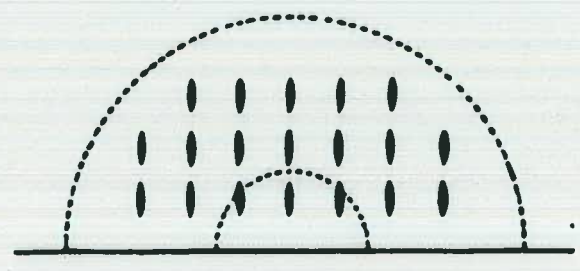
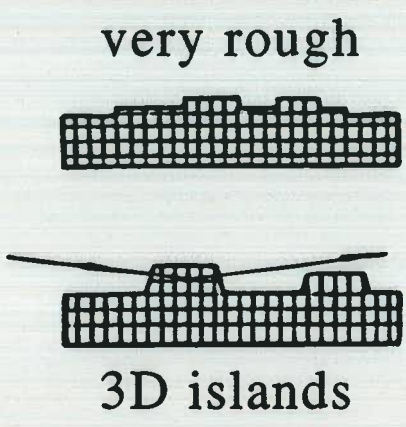
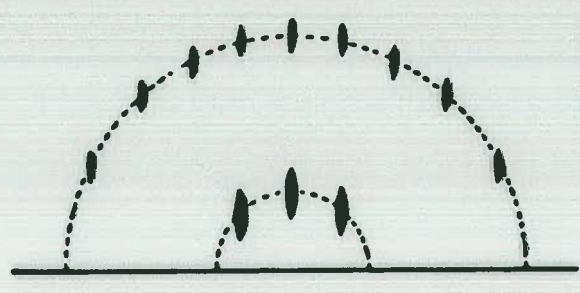
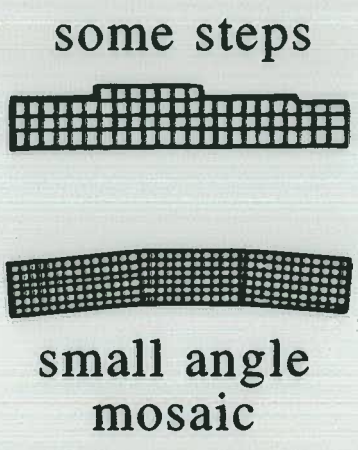
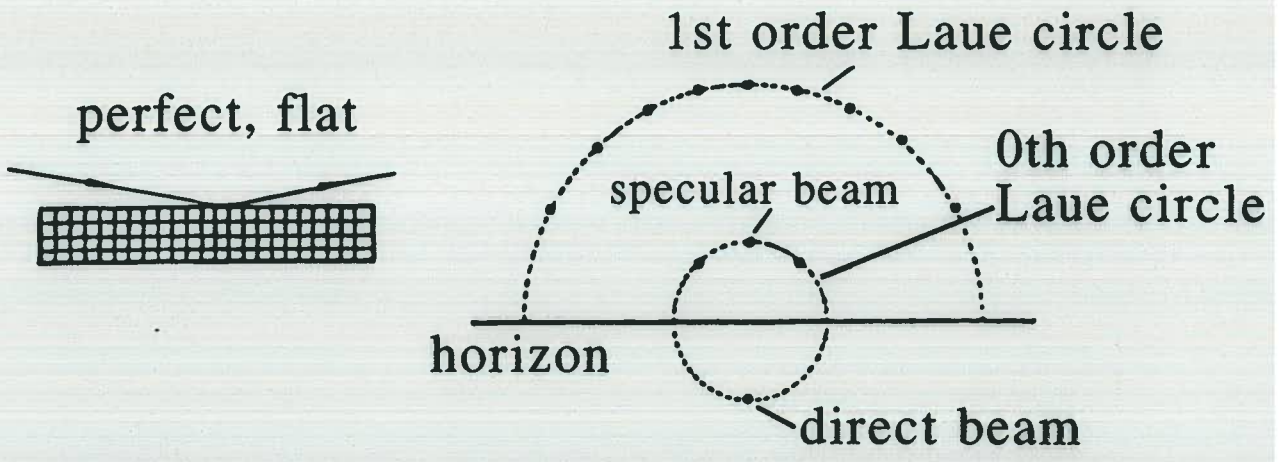
reciprocal space (CTRs)



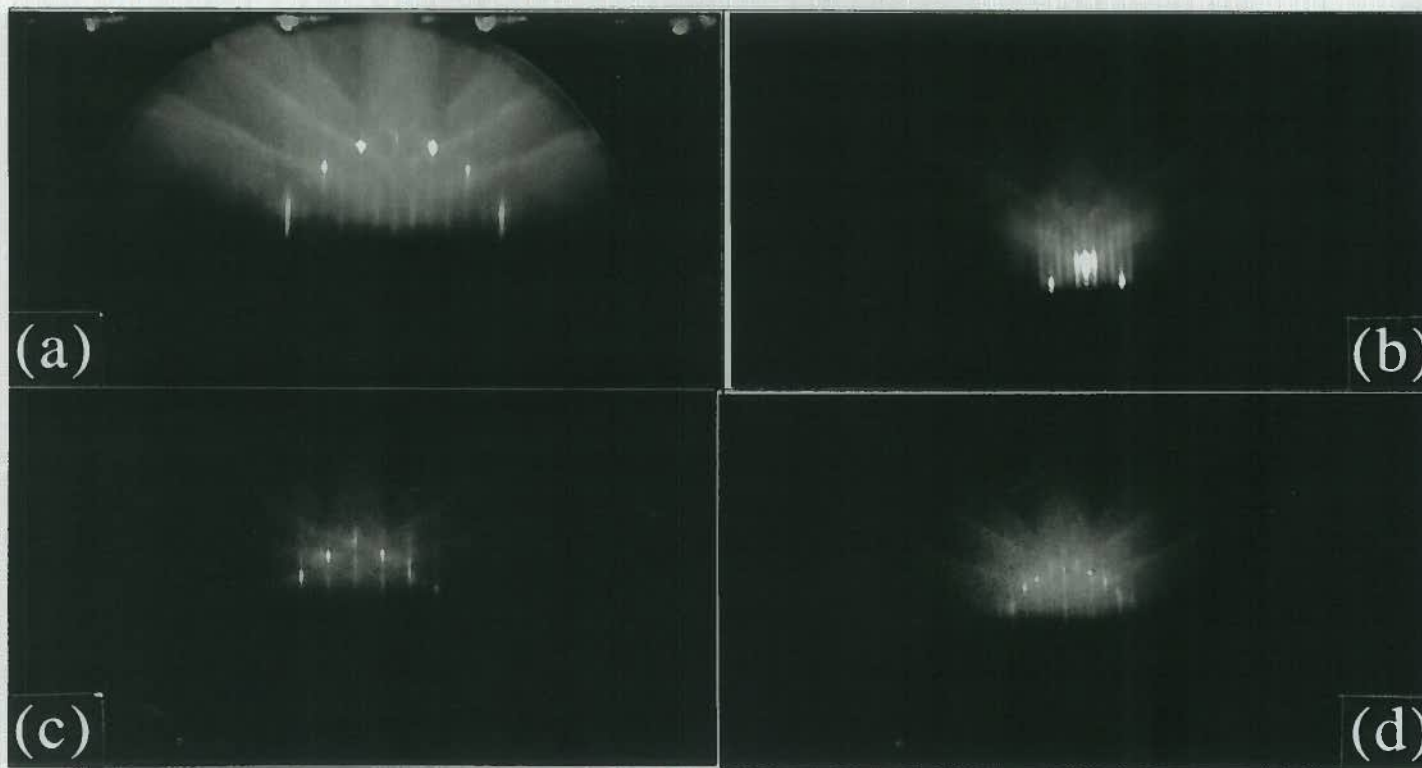
RHEED system



Ewald sphere



# Si on GaAs (100) - (2x4)



clean  
GaAs  
2x4

2 ML Si  
at 500°C

1x2

[011]

[0 $\bar{1}$ 1]

# GaAs (100) - (2x4)

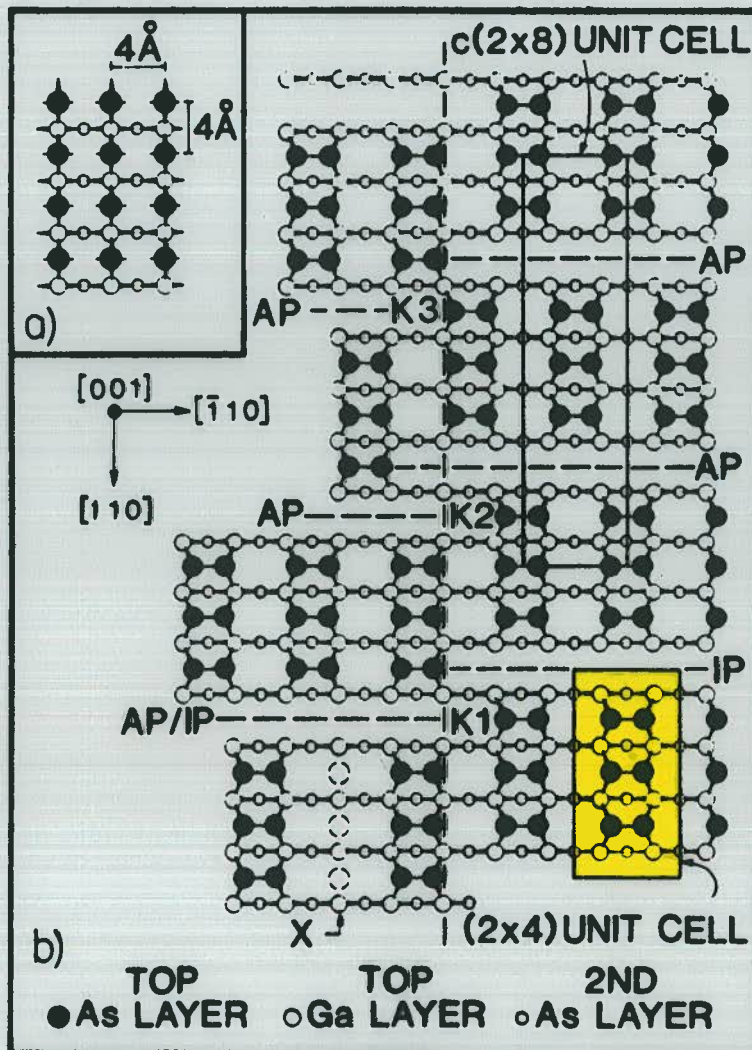
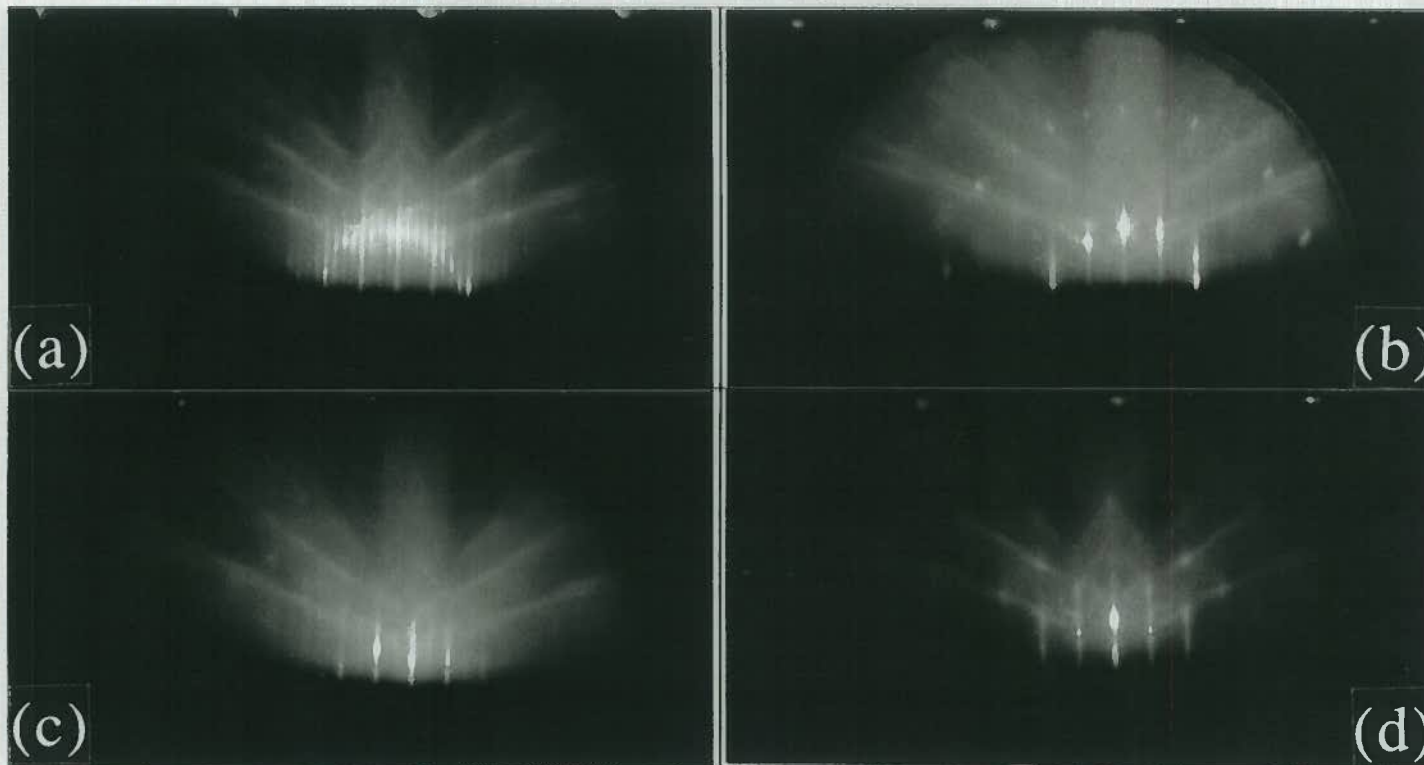


FIG. 1. (a) The structure of the unreconstructed GaAs(001) arsenic-rich surface. (b) The missing-dimer model for the GaAs(001) (2x4) surface. The two types of missing-dimer boundary, in-phase (IP) and antiphase (AP), are shown giving rise to (2x4) and c(2x8) structures. The intersection of a domain boundary along the [110] direction with the IP and AP boundaries is shown giving rise to three types of boundary kinks:  $K_1$ ,  $K_2$ , and  $K_3$ . Disorder in the arsenic pairing (X) with three missing arsenic atoms (dashed circles) is also shown.

# Si on GaAs (100)-c (8x2)



clean  
GaAs  
c 8x2

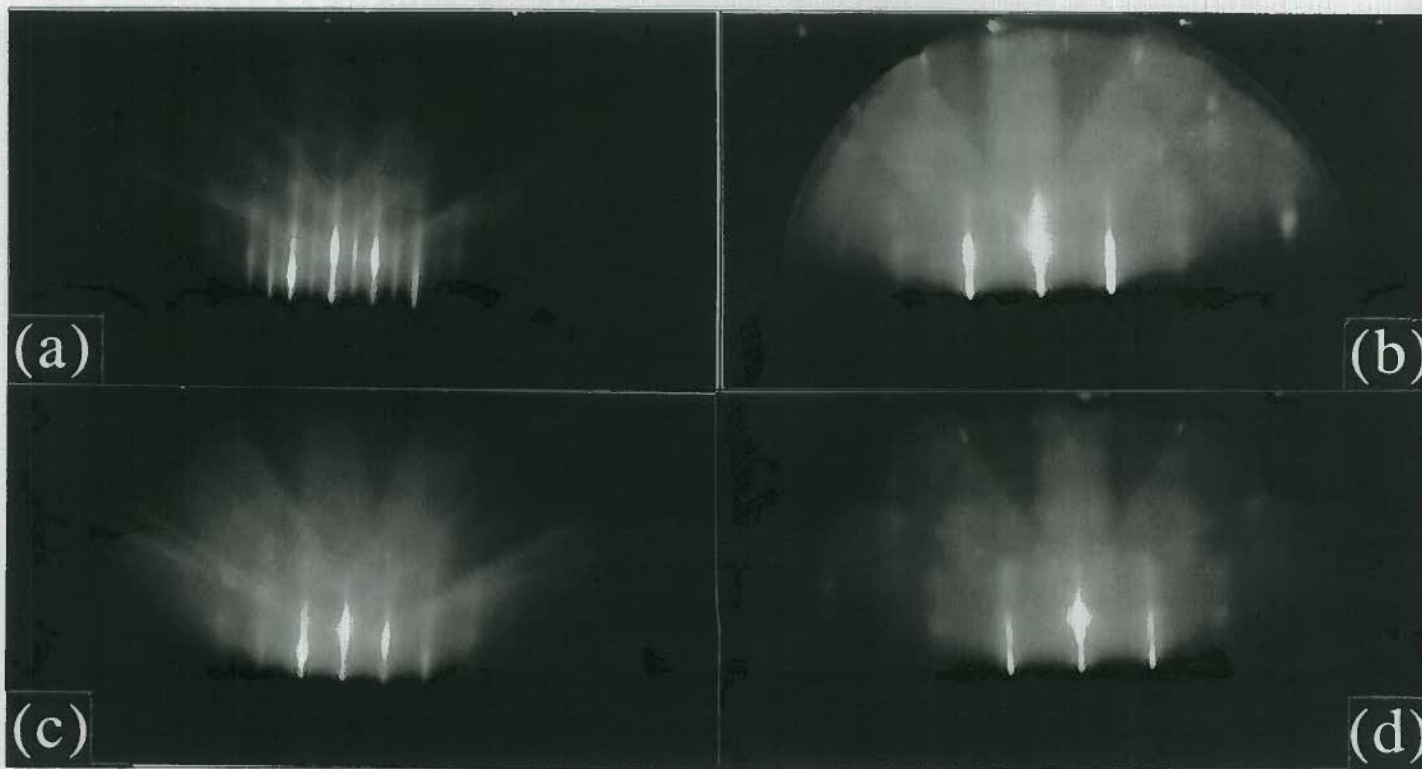
0.5 ML Si  
at 450°C

2x1

[011]

[0 $\bar{1}$ 1]

# Si on GaAs (111) A - (2x2)



clean  
GaAs

2x2

0.5 DL Si  
at 450°C

1x1

$[01\bar{1}]$

$[\bar{2}11]$

# GaAs (111)A - (2x2)

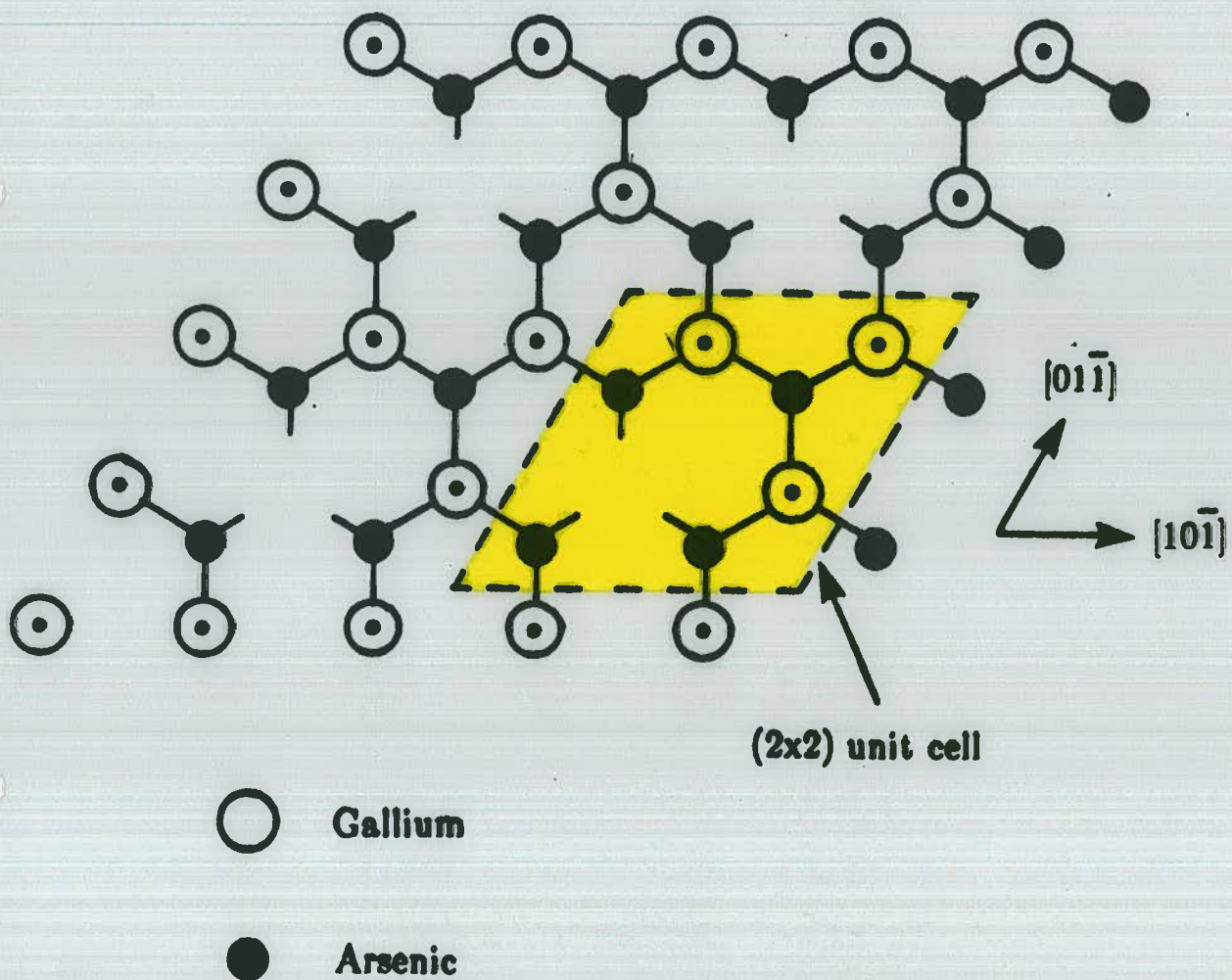
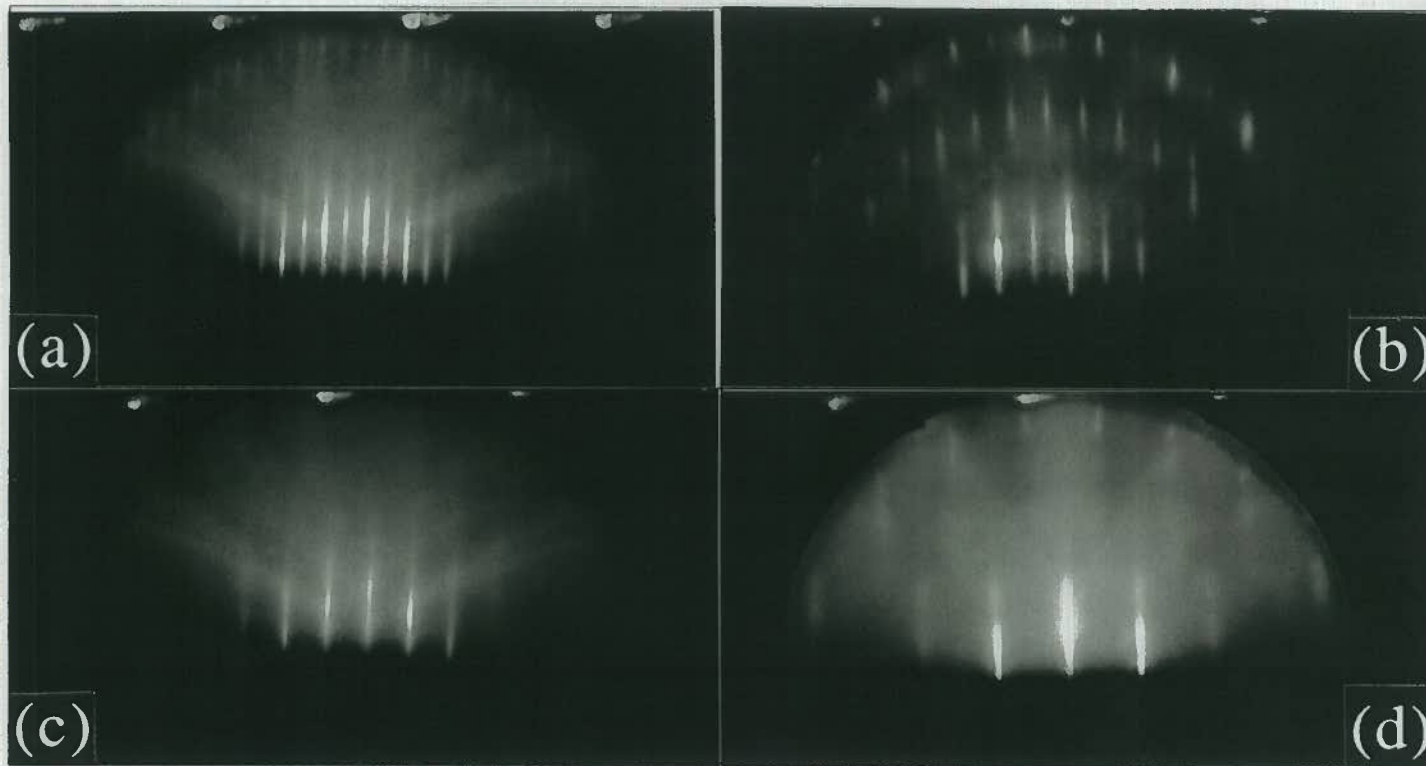


FIG. 1. Top view of the single-gallium-vacancy model of the GaAs(111)A-(2x2) reconstruction proposed by Tong *et al.* (Ref. 4) showing the surface gallium atoms and the arsenic atoms immediately below. The (2x2) unit cell is 8 Å on the side. Dangling bonds on the arsenic atoms resulting from the gallium vacancy are shown. The gallium dangling bonds out of the surface are shown as dots on each gallium atom.

# Si on GaAs (111)B - (2x2)



clean  
GaAs

2x2

0.5 DL Si  
at 450°C

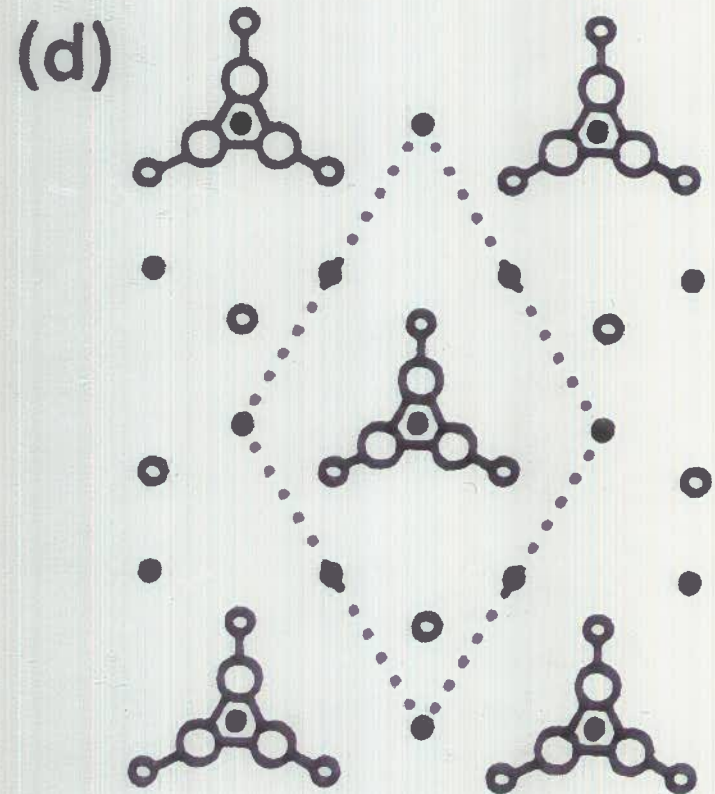
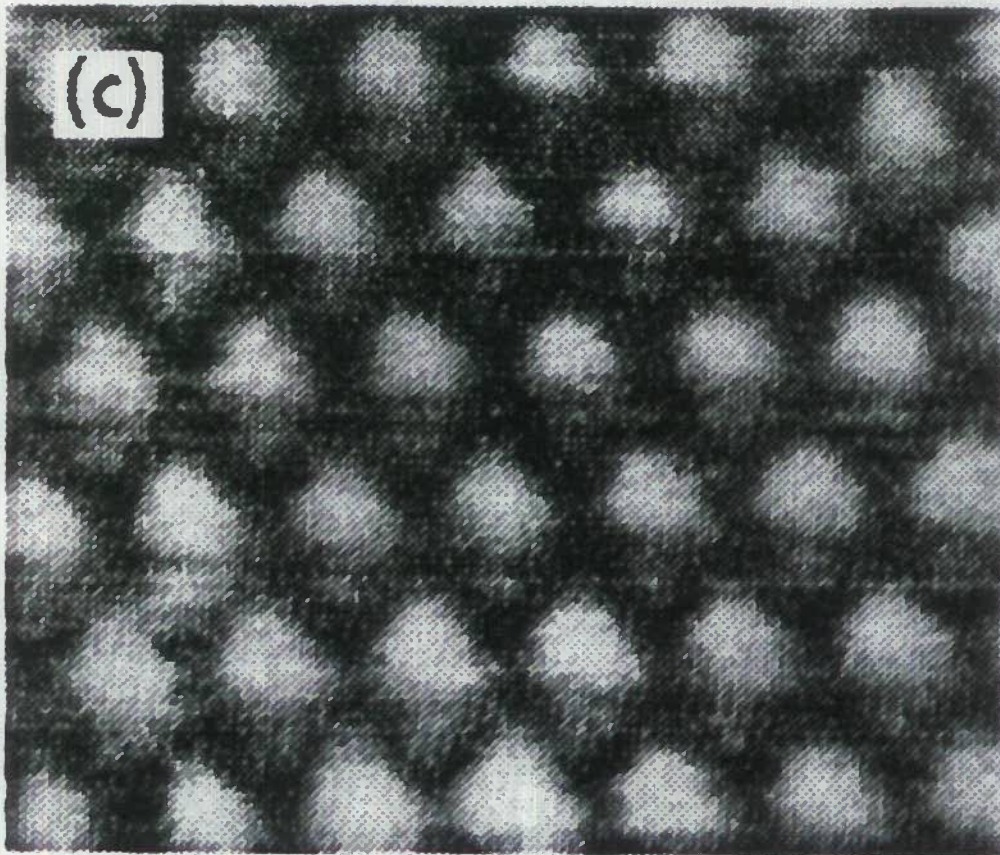
1x1

$[01\bar{1}]$

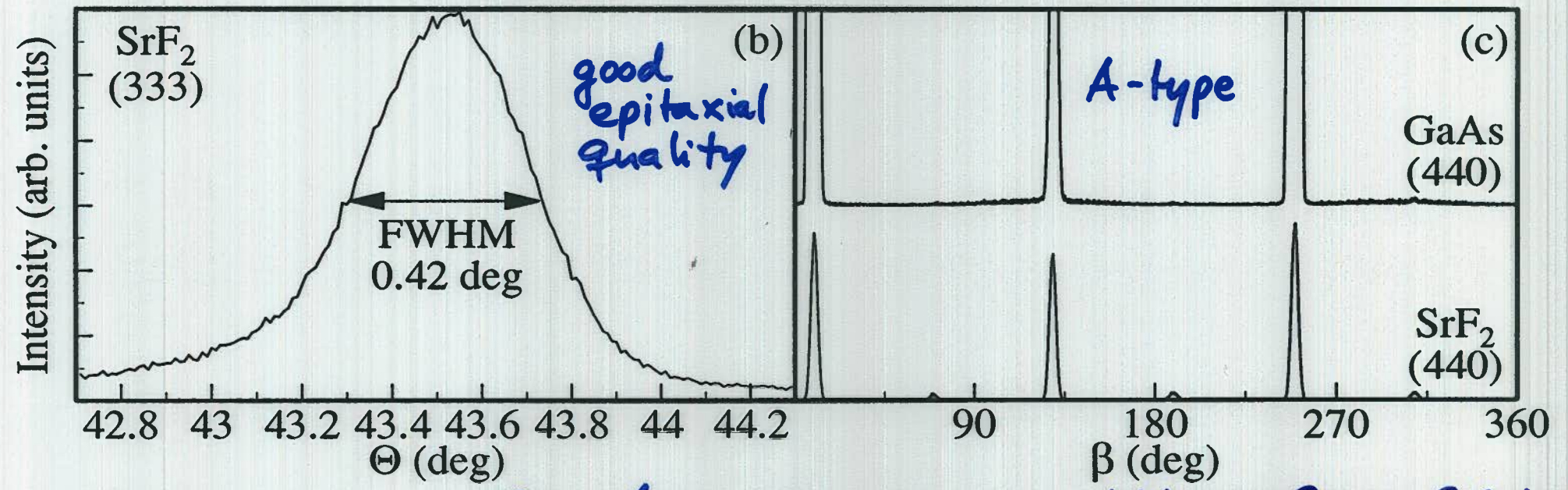
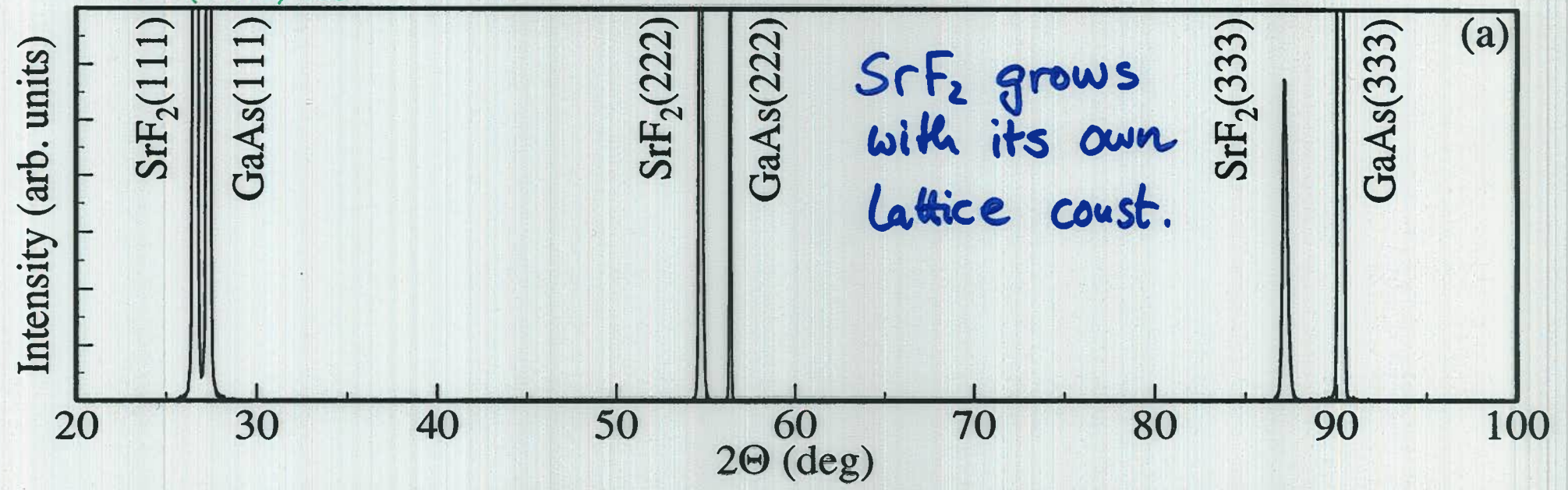
$[\bar{2}11]$



# GaAs (111)B - (2x2)



Biegelson et al.: PRL 65(1990)452



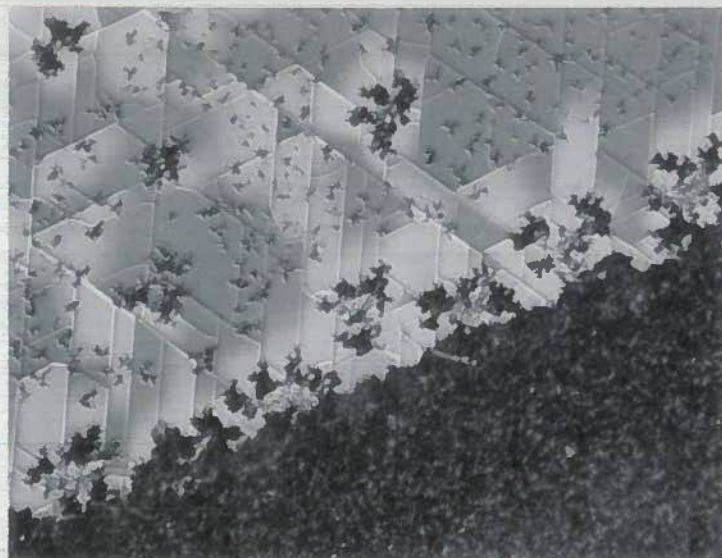
SrF<sub>2</sub> on Si / GaAs (111)

Ishiwara: SrF<sub>2</sub> on Si (111) : B  
SrF<sub>2</sub> on GaAs (111) : A

## Relaxation of lattice mismatch by dislocations



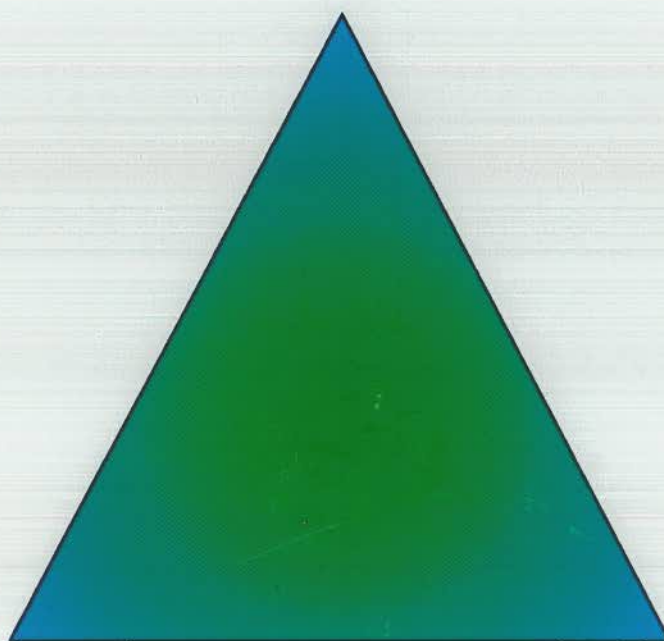
1000Å SrF<sub>2</sub> on 8ML Si on  
GaAs(100)-(2x4) at 500°C,  
x1000



3000Å SrF<sub>2</sub> on 1.5ML Si on  
GaAs(111)A at 530°C,  
x500

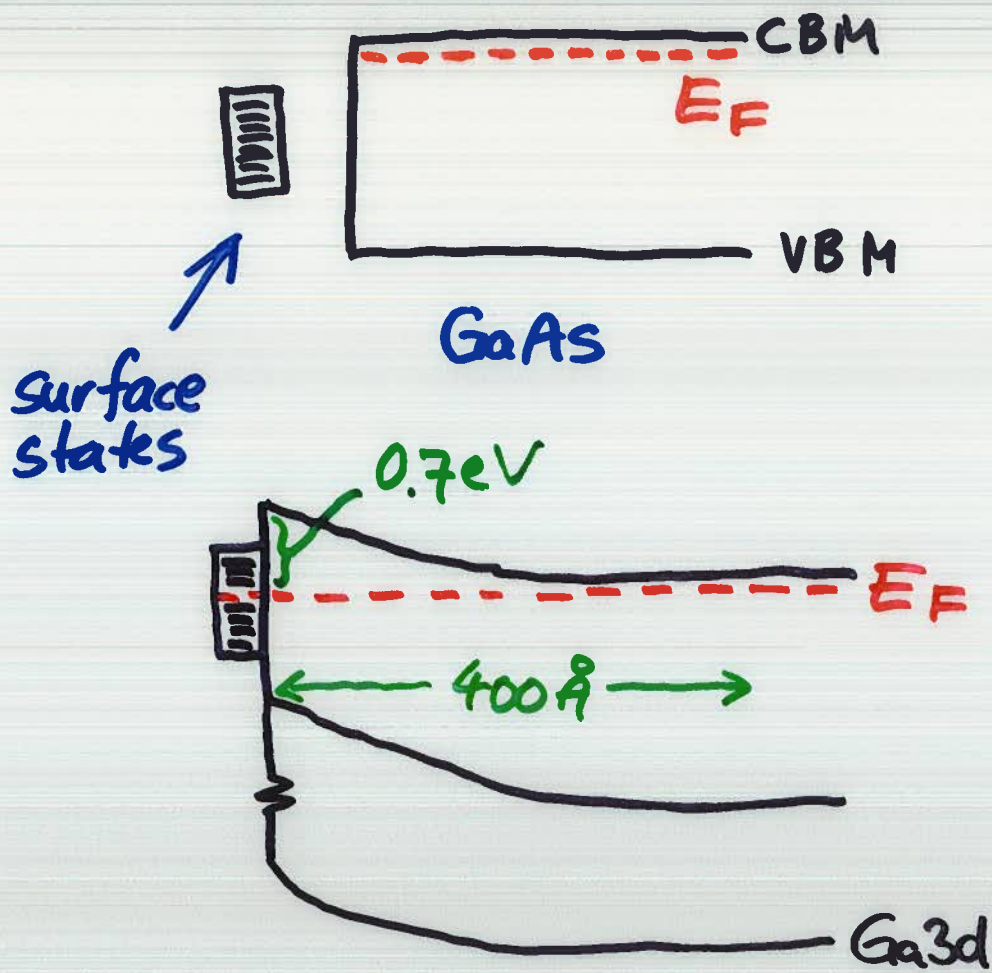


Film  
morphology  
(XRD, RHEED,  
SEM, AFM)

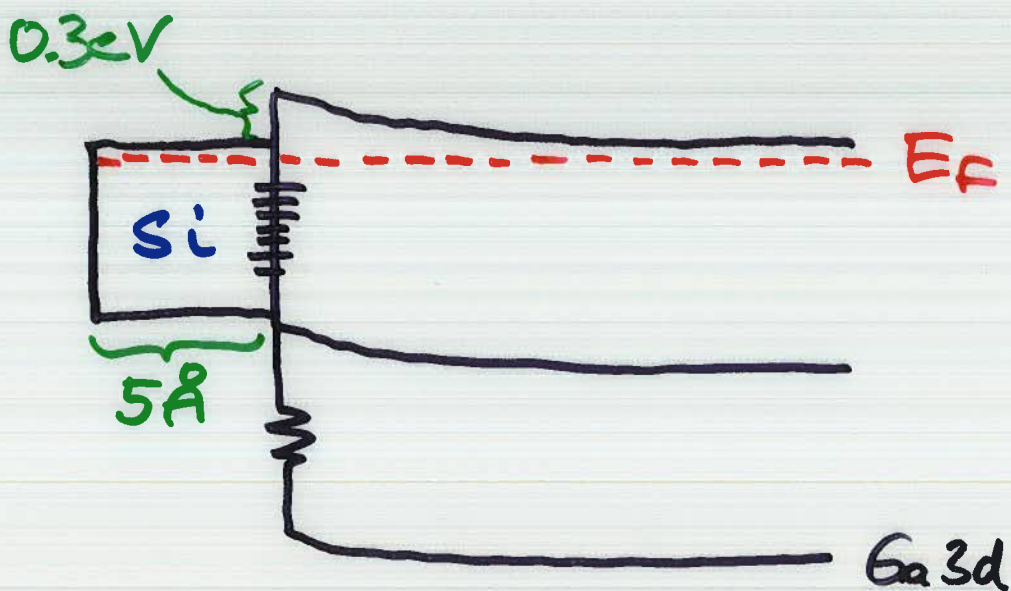


Electrical  
properties  
(C-V-curves)

Chemical  
bonding  
(SRPES,  
XPS)

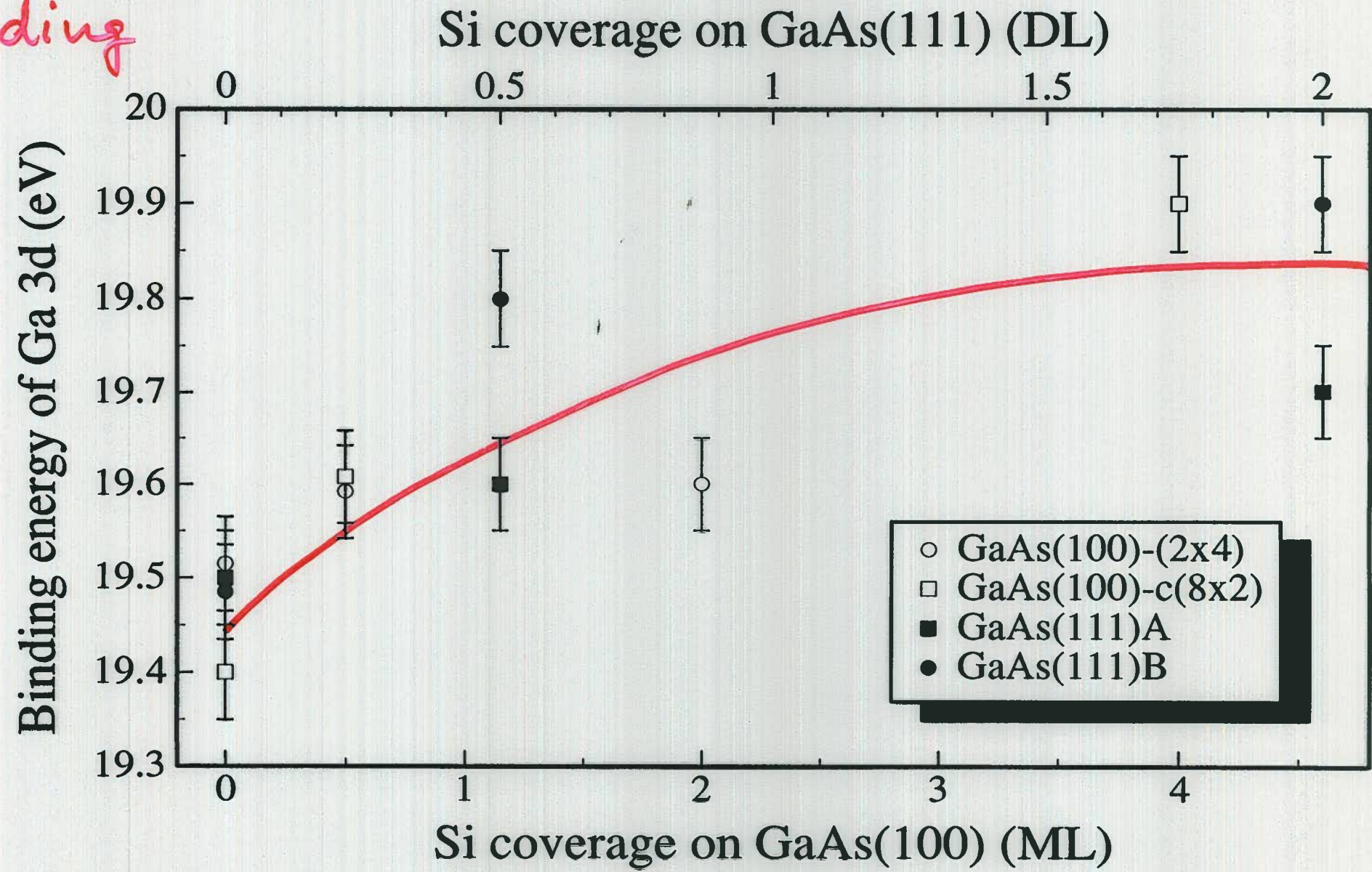


band bending

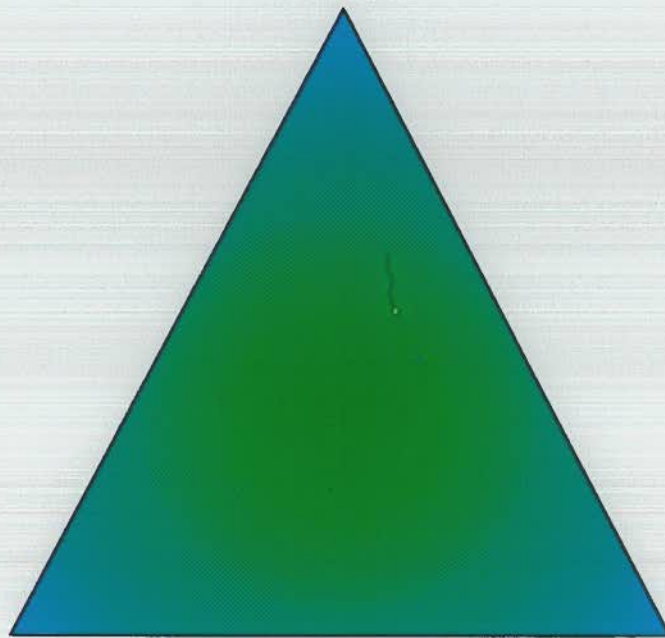


relaxation of band bending  
after deposition of Si

Relaxation of band bending



Film  
morphology  
(XRD, RHEED,  
SEM, AFM)



Electrical  
properties  
(C-V-curves)

Chemical  
bonding  
(SRPES,  
XPS)



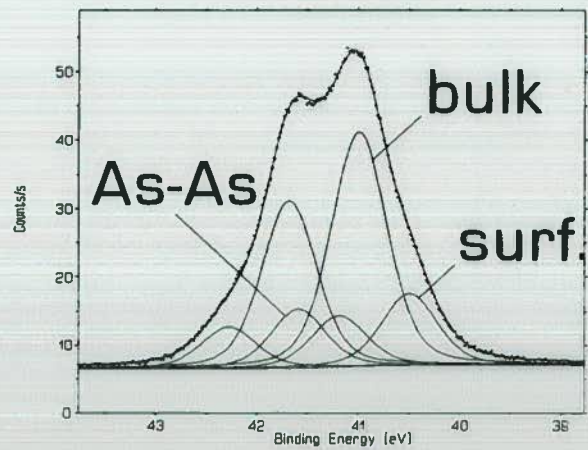
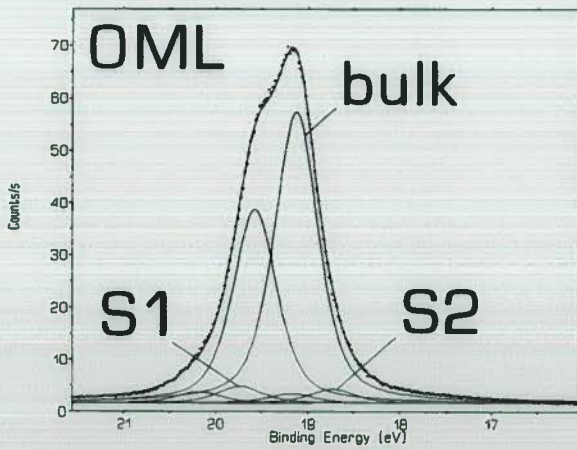
# Results

- distance between As 3d and Ga 3d bulk components is constant  
→ assignment OK
- binding energy of the peaks in SRPES 0.1 ~ 0.2 eV smaller than in XPS → band bending model OK
- All doublets fitted with a fixed parameter set:
  - Ga 3d: Voigt, FWHM = 0.55 eV, mix = 0.45  
 $\Delta_{s_0} = 0.45 \text{ eV}$ , BR = 1.5 [Le Lay]
  - As 3d: Voigt, FWHM = 0.65 eV, mix = 0.75  
 $\Delta_{s_0} = 0.69 \text{ eV}$ , BR = 1.4 [Le Lay]
- peak positions, chemical shifts agree with literature values (if available)

# Si on As-rich GaAs(100)

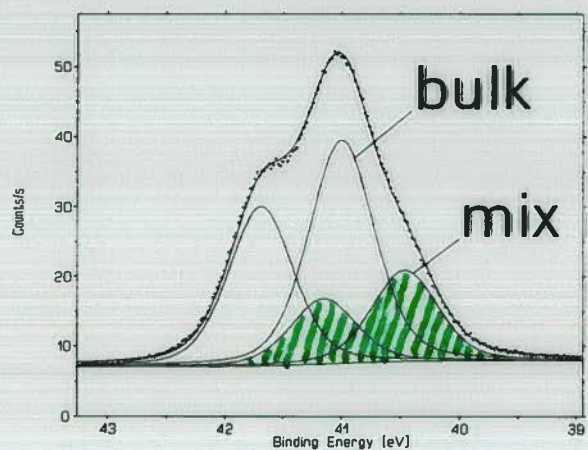
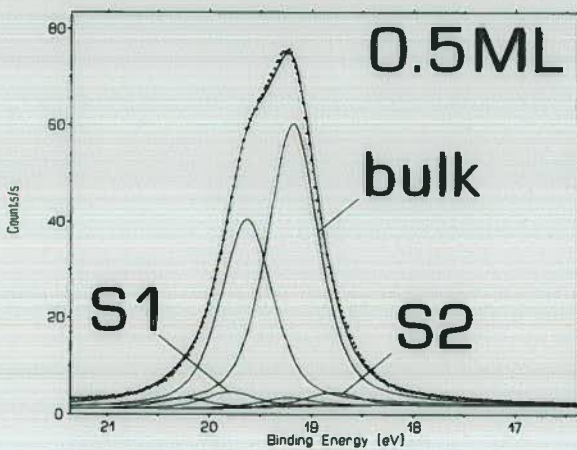
## Ga 3d

## As 3d

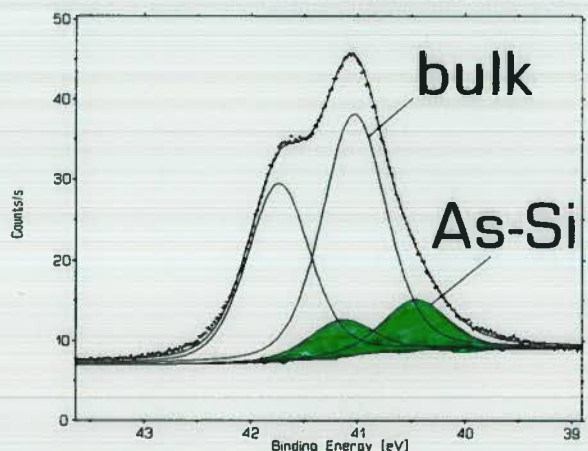
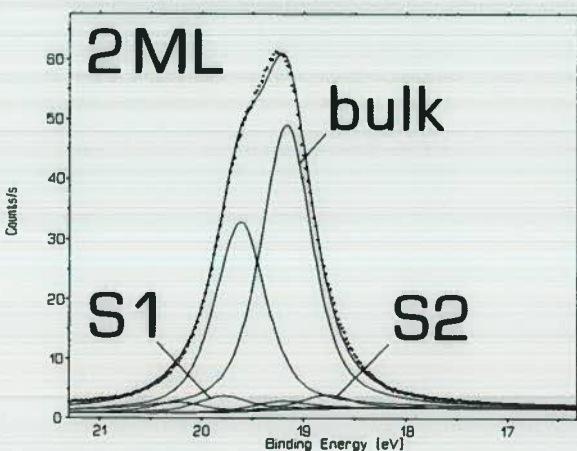


$$r = \frac{\text{As}}{\text{Ga}}$$

$$r = 0.3$$



$$r = 0.6$$



$$r = 0.1$$

No As-segregation

? Why As-Si peak at lower binding energy?

Electronegativities:

Ga 1.6

Si 1.8

As 2.0

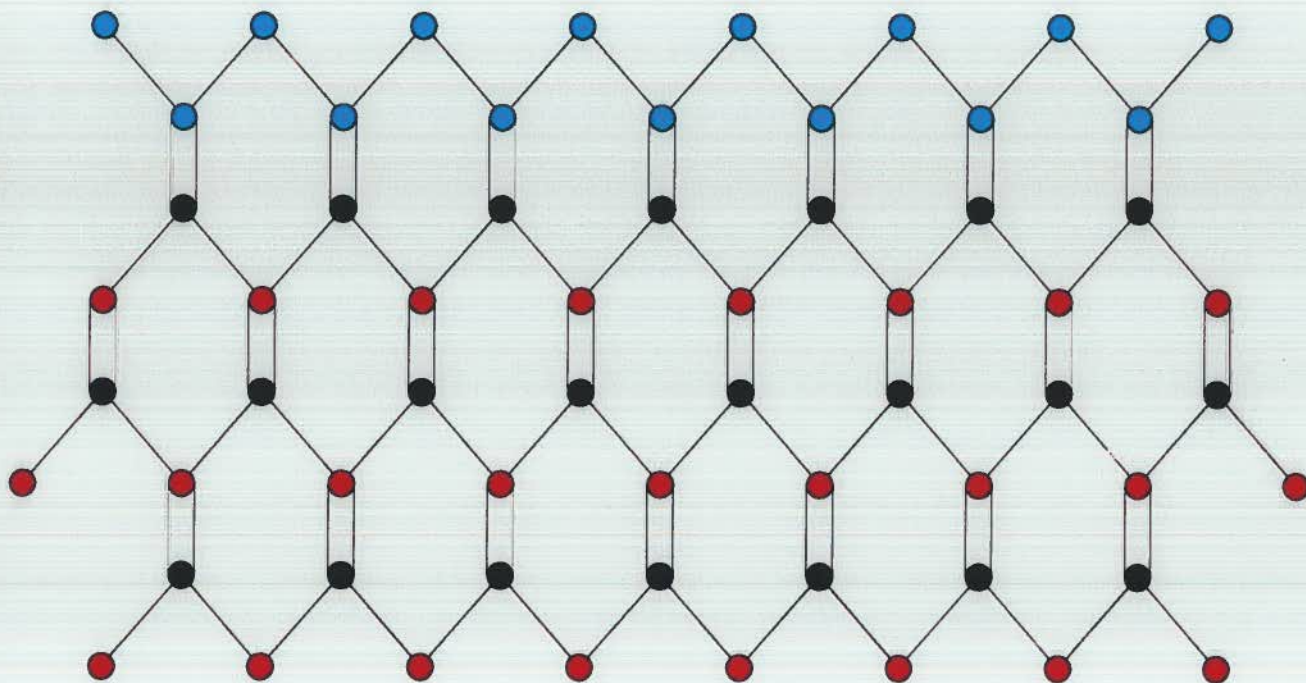
Bachrach et al. (J. Vac. Sci. Technol.  
B5 (1987) 1135)  
found the same

→ Madelung energy must be taken into account

(cf. Gatz (10), Davernport et al.

Solid State Comm. 40 (1981) 999)

# Si on As-rich GaAs(100)



• Ga

• As

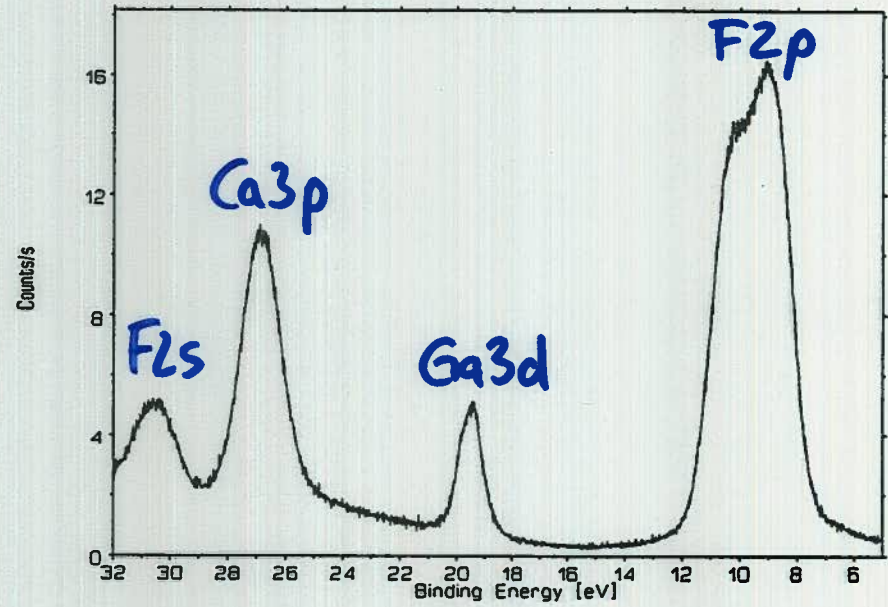
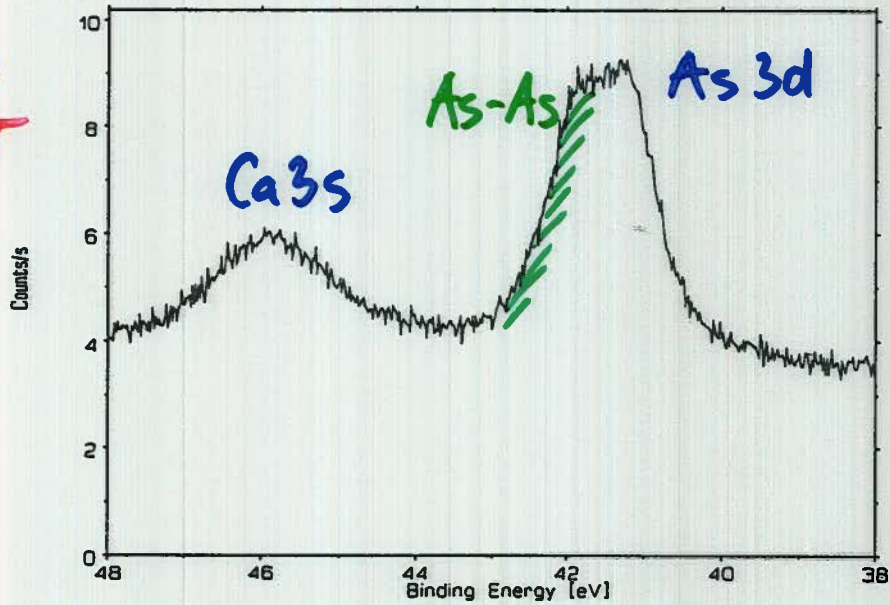
• Si

12Å CaF<sub>2</sub> / 2ML Si /

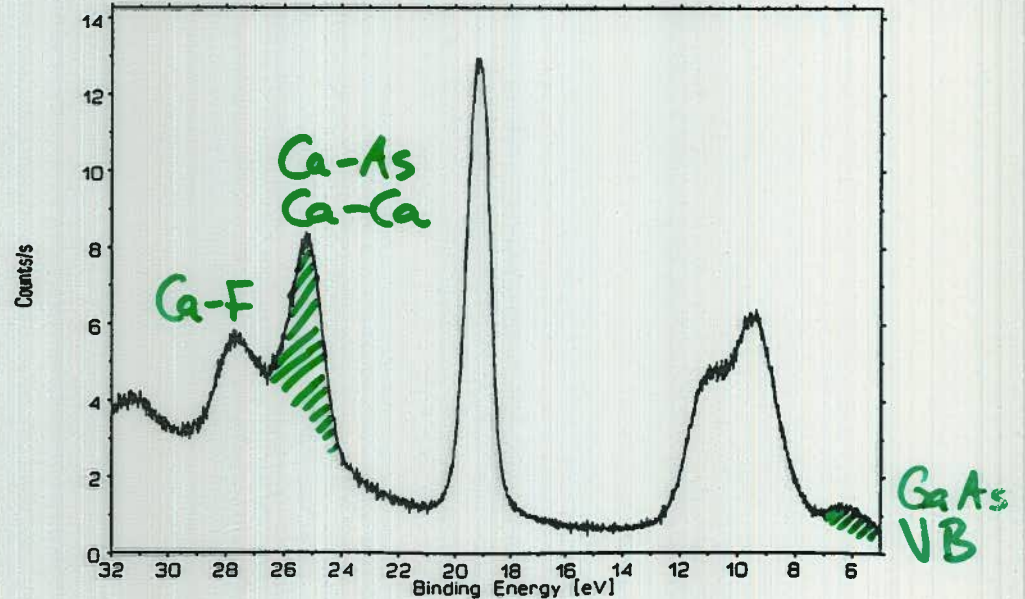
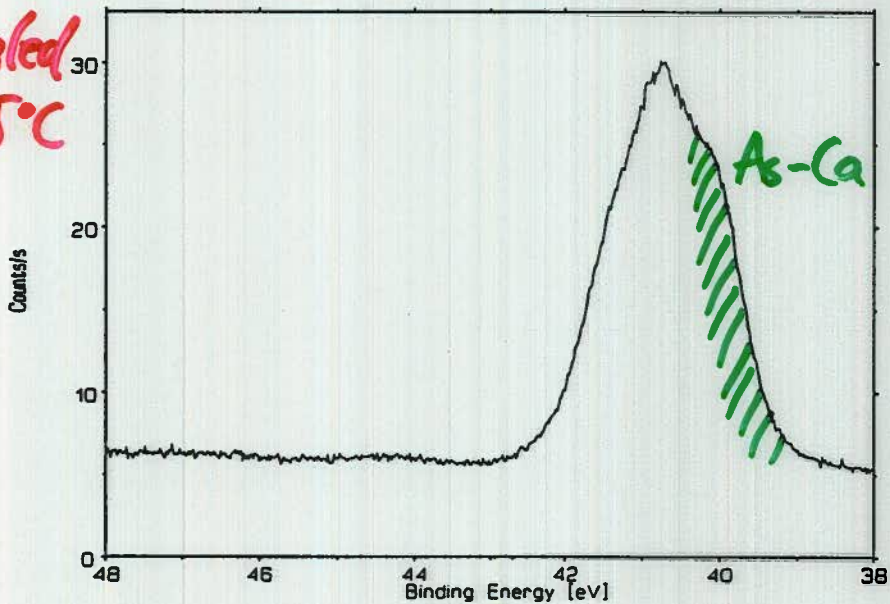
As-rich GaAs(100)

BB = 0.5eV

depo.  
at RT



annealed  
at 645°C

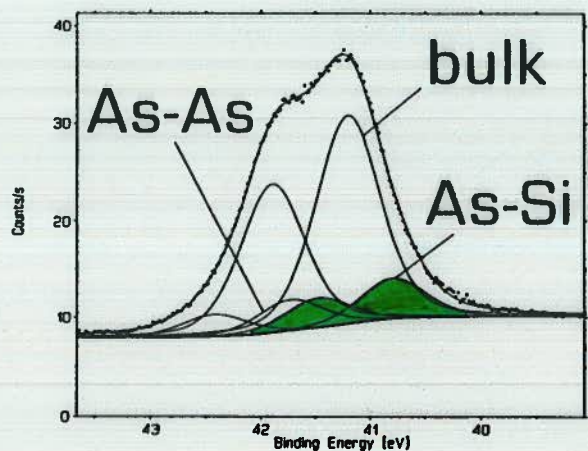
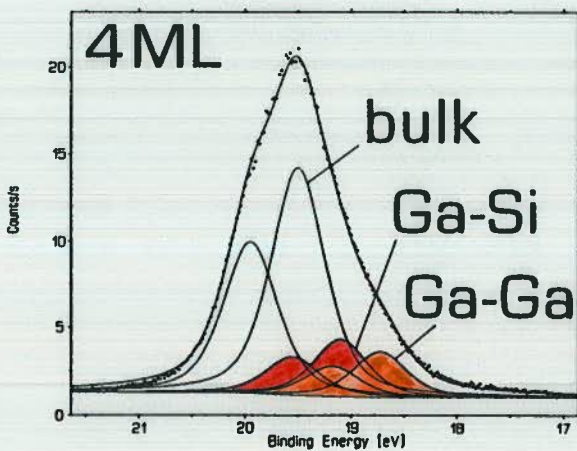
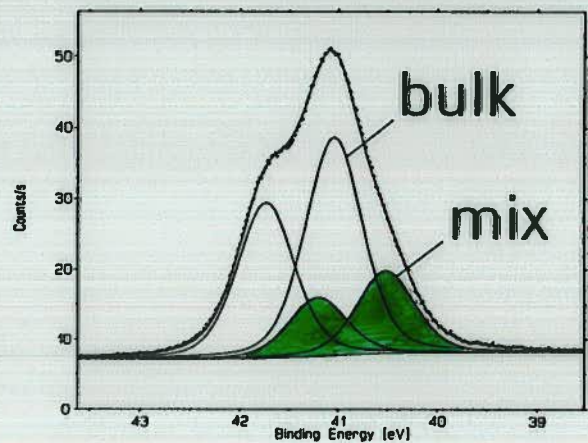
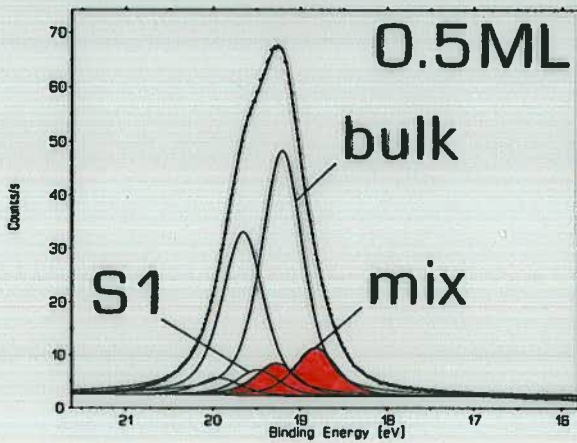
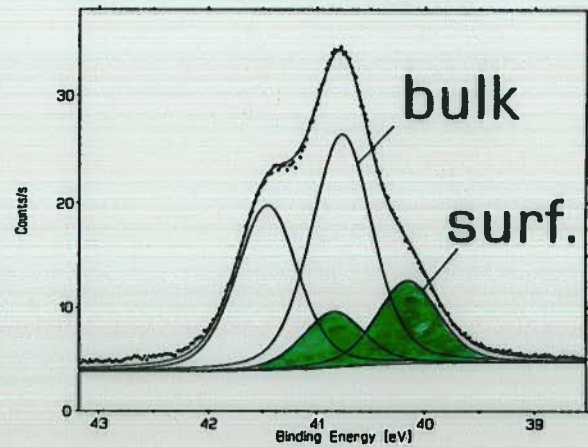
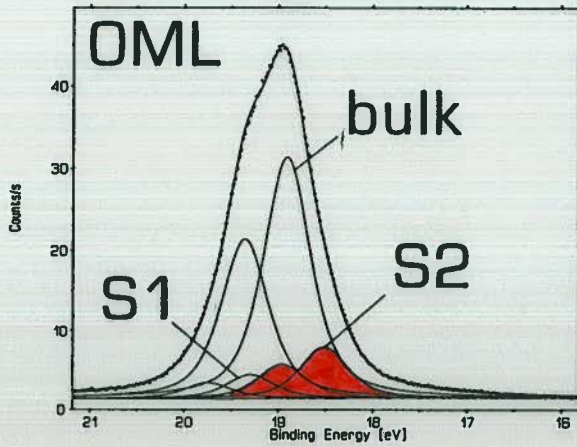


-c(8x2)

# Si on GaAs(100)-(4x2)

## Ga3d

## As3d

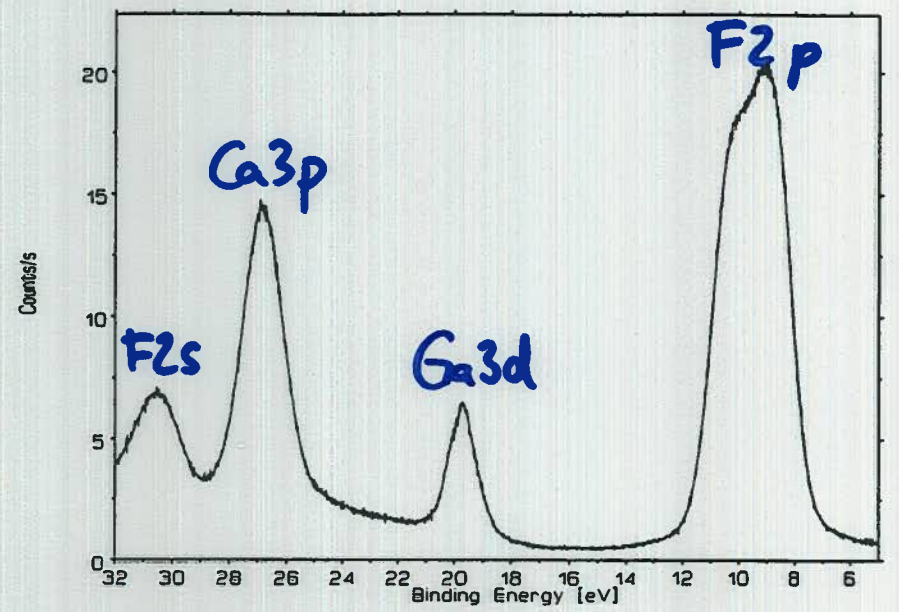
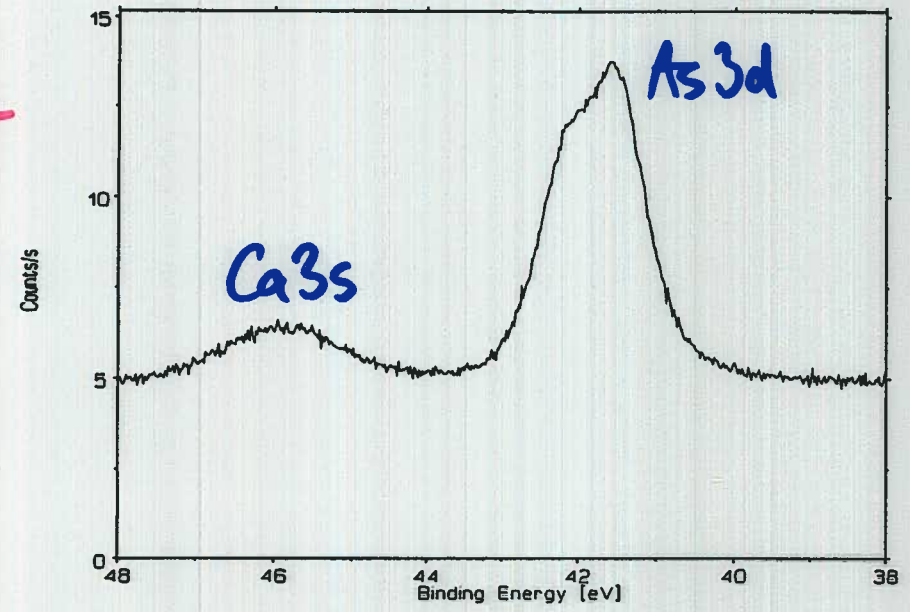


As segregates to the surface !

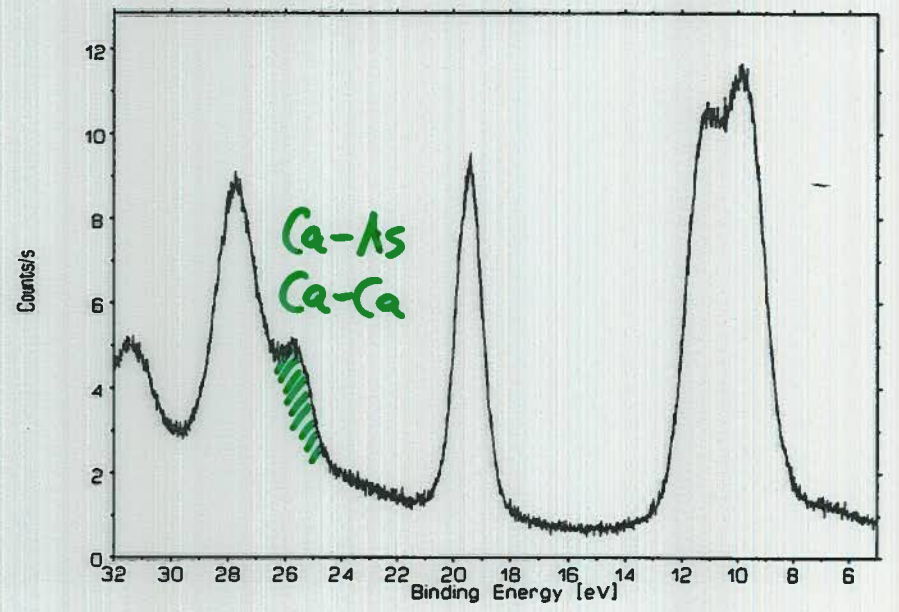
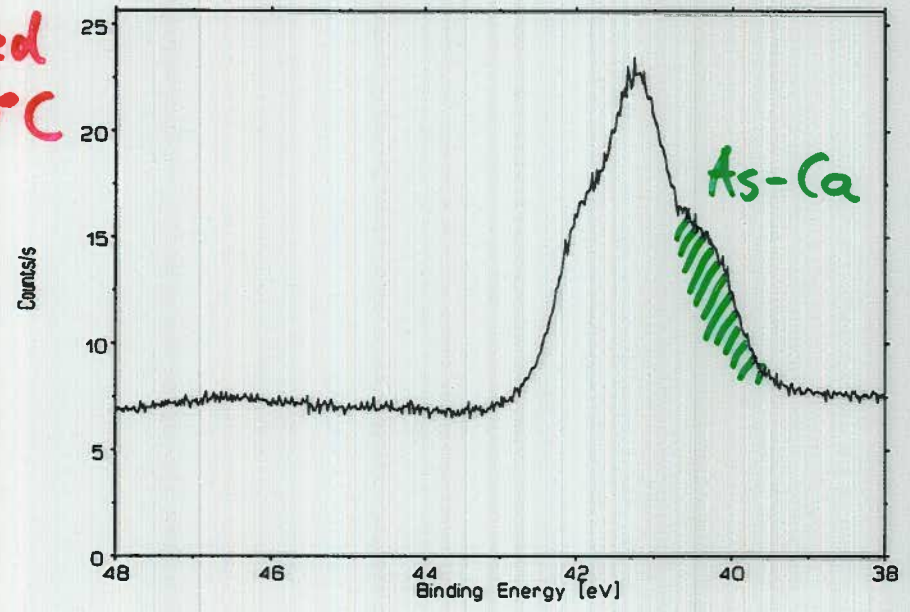
12 Å CaF<sub>2</sub> / 4 ML Si / GaAs(100) - c(8x7)

BB = 0.35 eV

depo.  
at RT



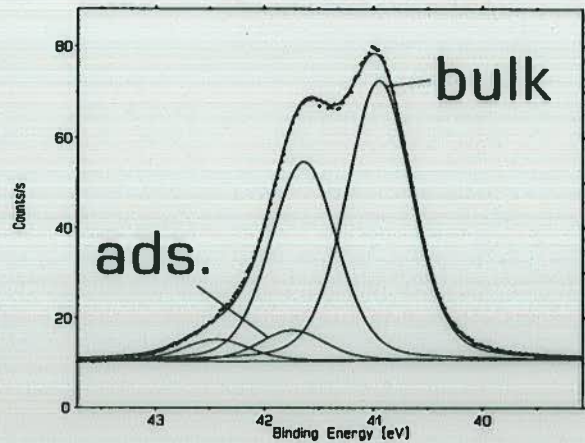
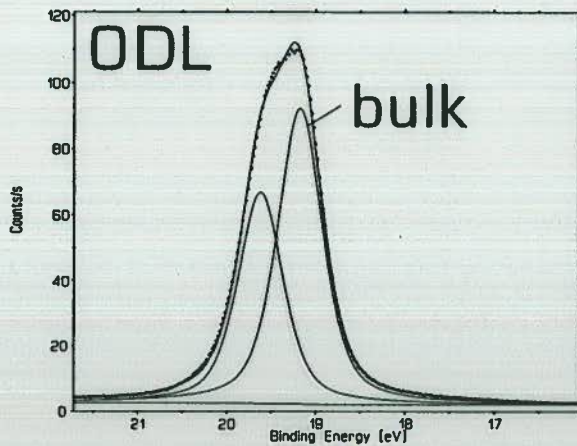
annealed  
at 620°C



# Si on GaAs(111)A-(2x2)

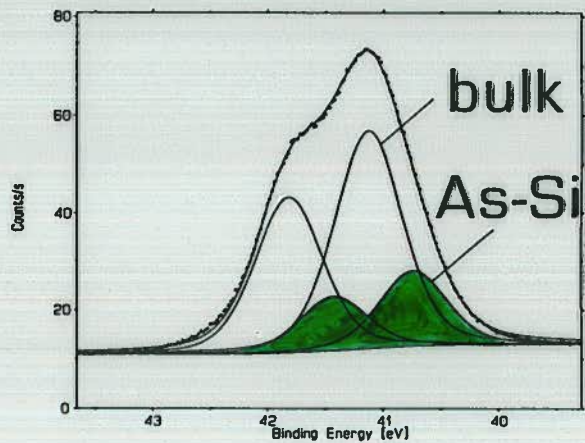
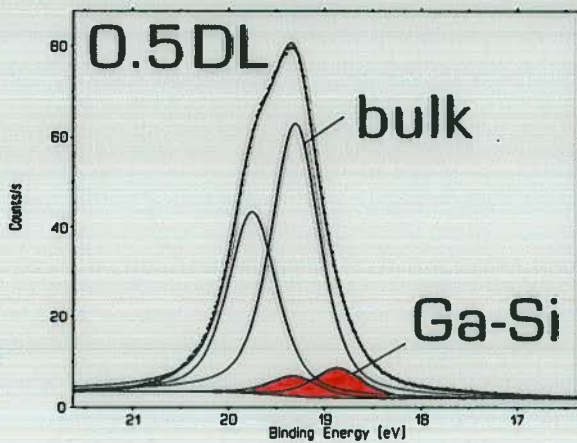
## Ga3d

## As3d

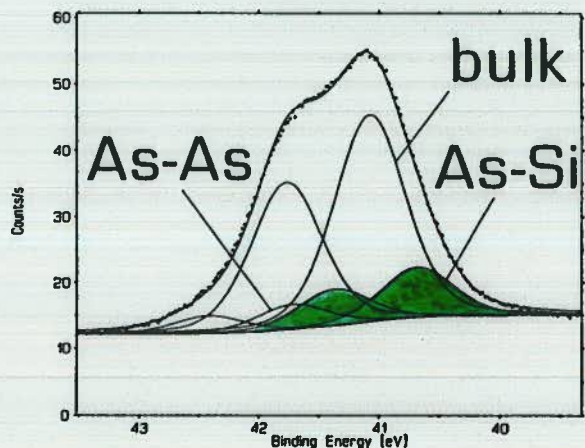
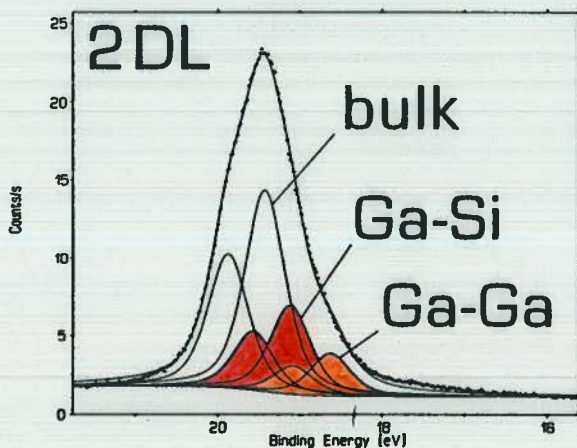


$$r = \frac{As}{Ga}$$

$$r = 0.6$$



$$r = 0.8$$



$$r = 1.9$$

As segregates to the surface!

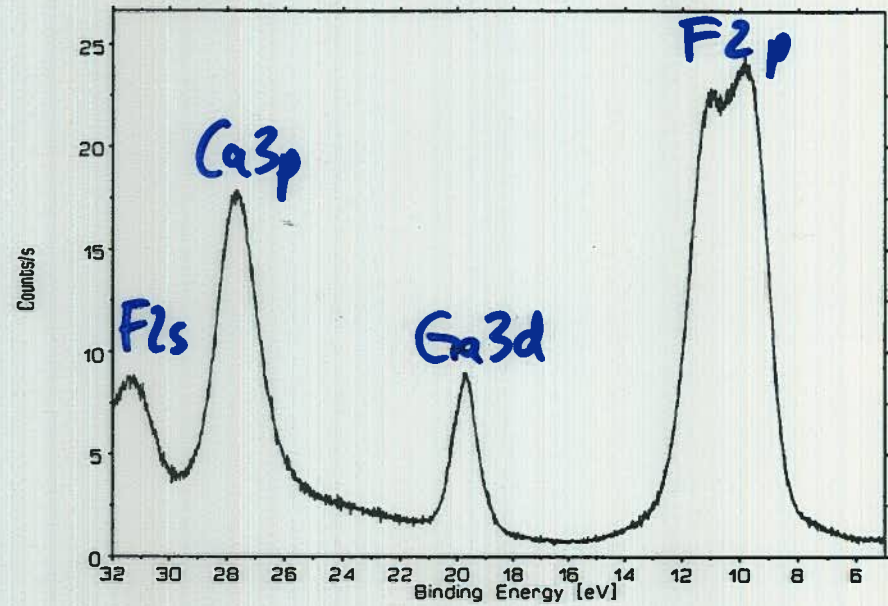
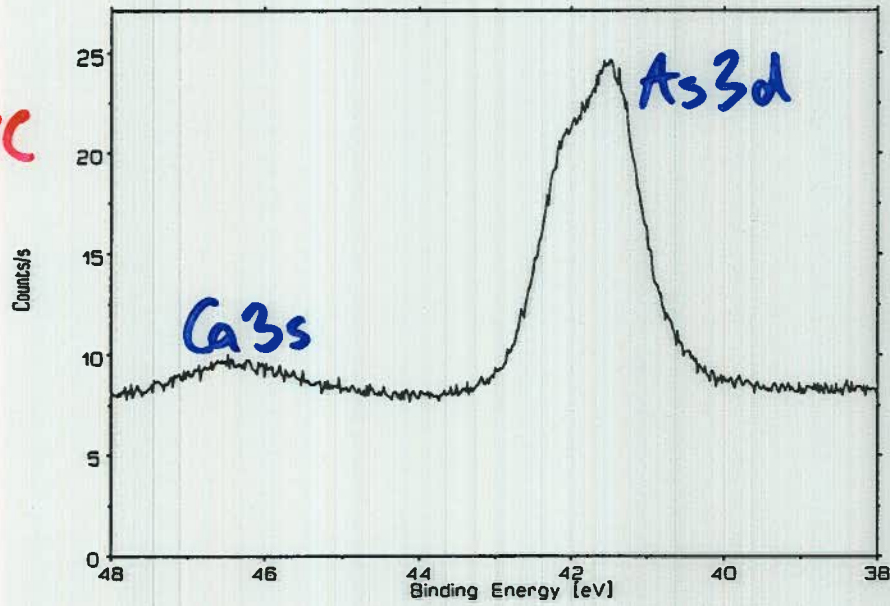




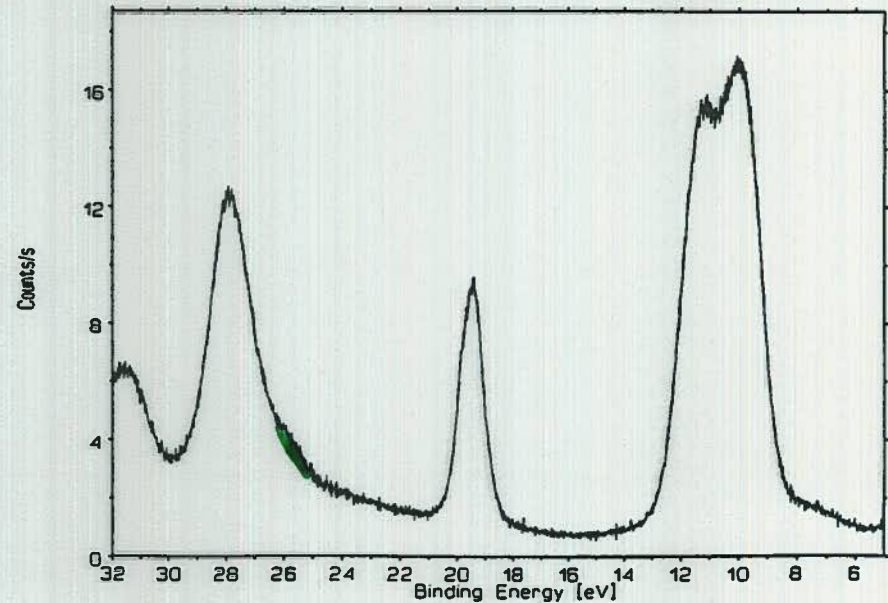
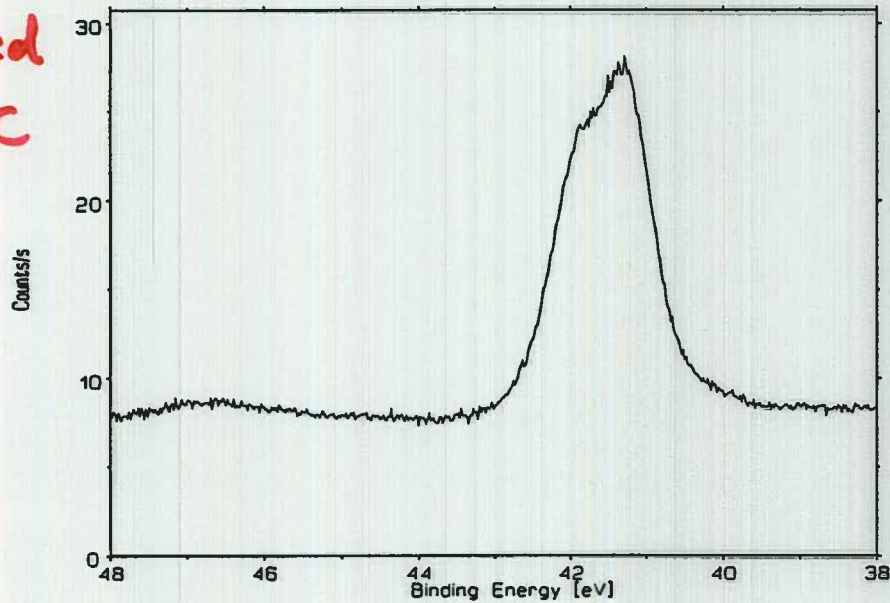
12 Å CaF<sub>2</sub> / 2DL Si / GaAs (III) A

BB = 0.25 eV

depo.  
at 450°C



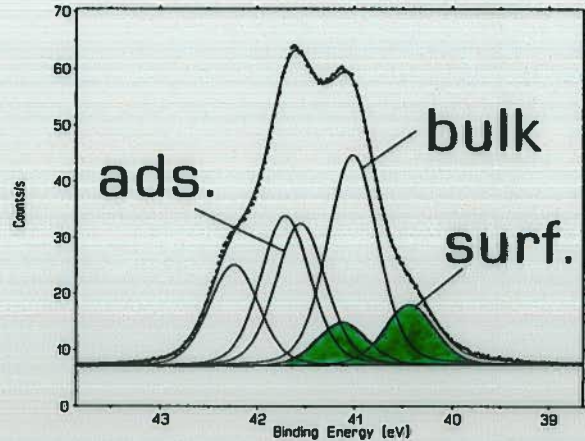
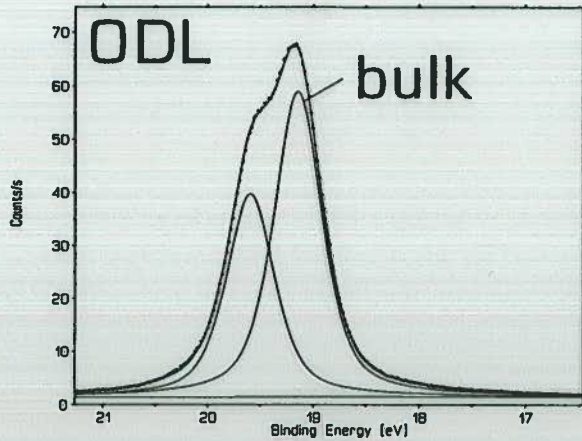
annealed  
at 620°C



# Si on GaAs(111)B-(2x2)

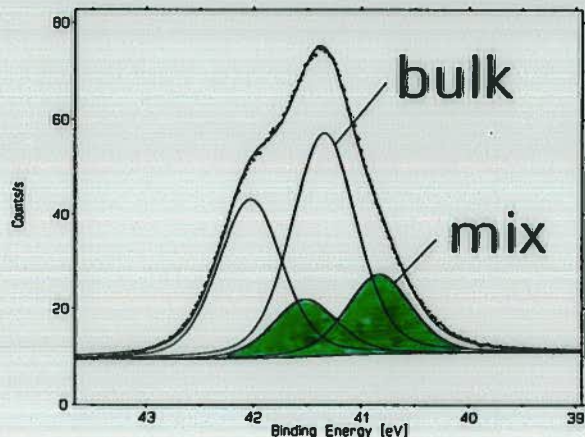
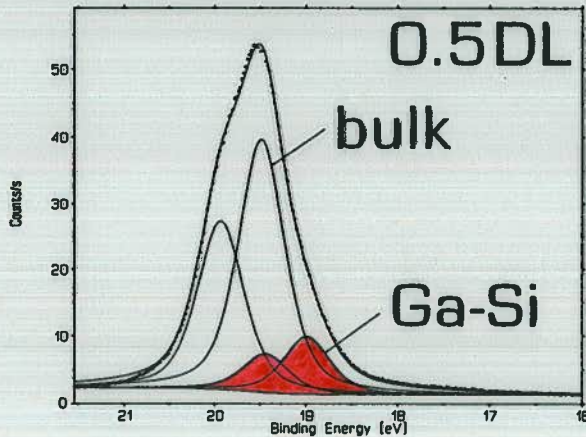
Ga3d

As3d

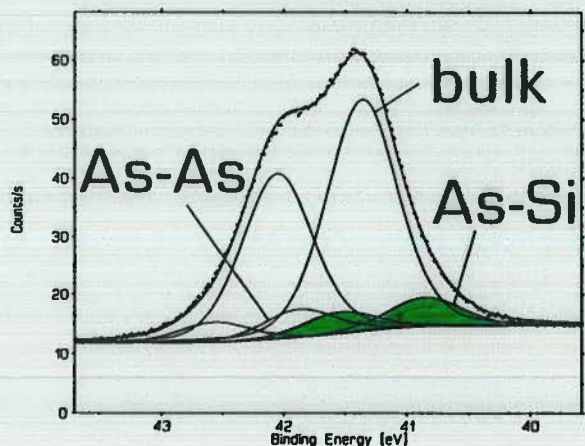
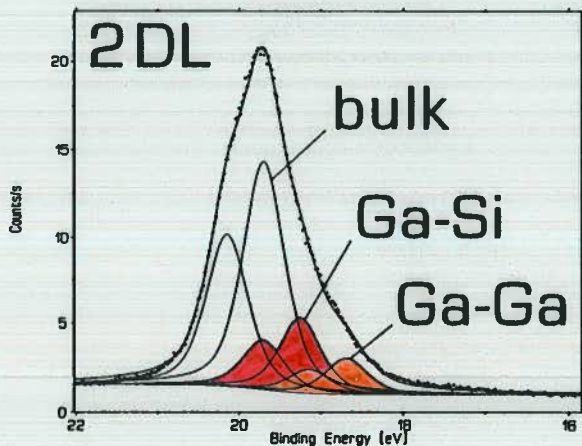


$r=0.9$

$r^*=0.6$



$r=1.3$



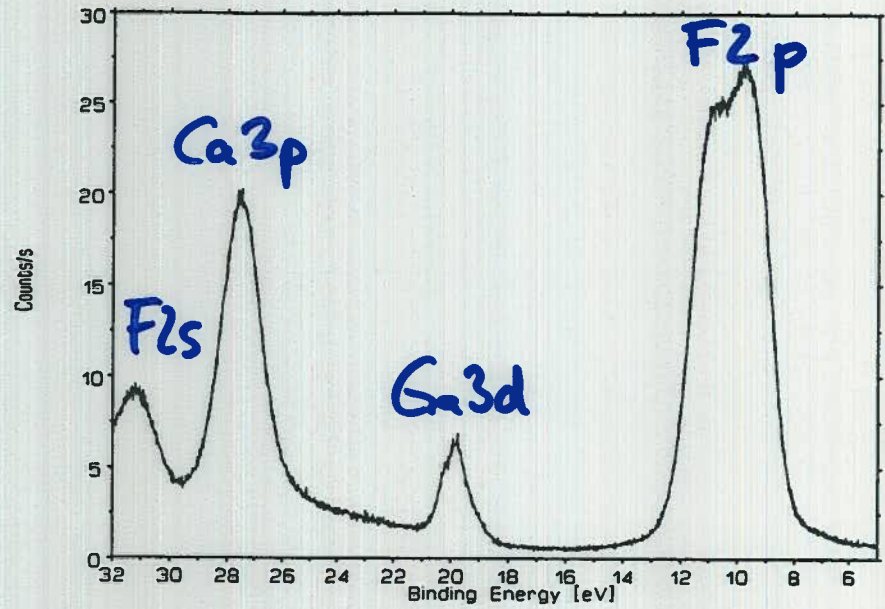
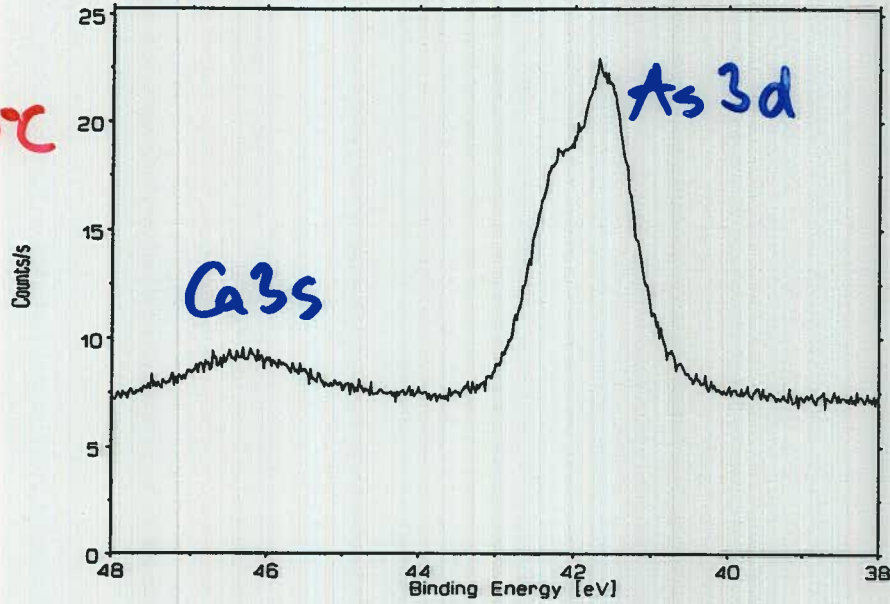
$r=2.7$

$$r = \frac{I_{As}}{I_{Ga}}$$

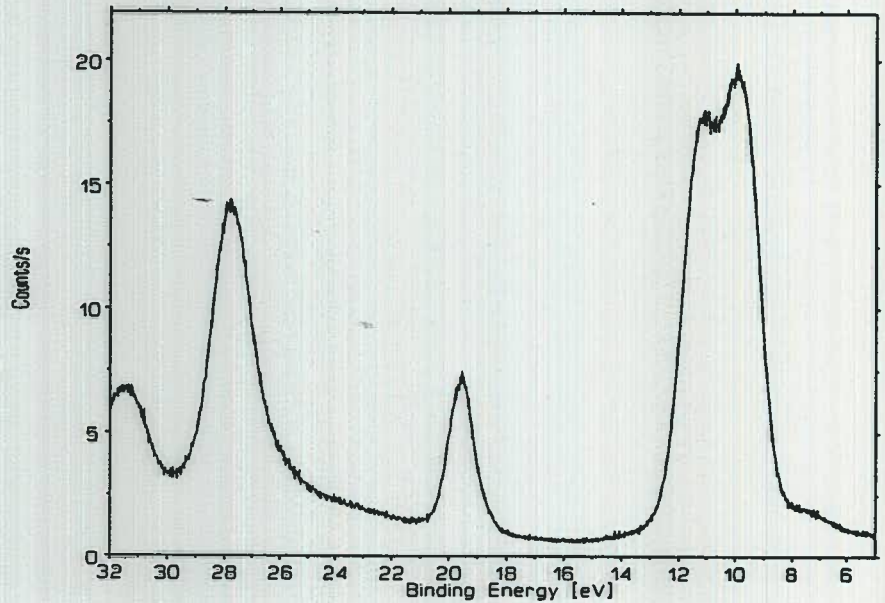
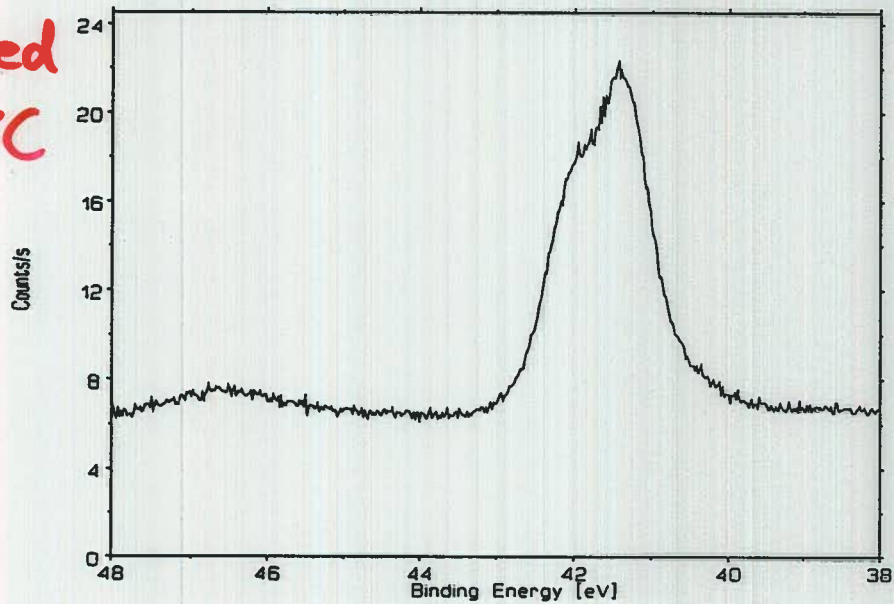
As segregates to the surface!

12Å CaF<sub>2</sub> / 20L Si / GaAs (III) B

depo.  
at 450°C



annealed  
at 620°C



# Conclusions

Good epitaxial quality obtained for

Si on GaAs

CaF<sub>2</sub> on Si / GaAs(111)

Si - ICL is a good passivating layer

No interfacial reaction between

CaF<sub>2</sub> and Si / GaAs(111)

# Outlook



Fisica della Materia

LABORATORIO TASC - INFM

Istituto Nazionale per la Fisica della Materia

Director: Prof. A. Franciosi

III-V-MBE

Si on GaAs

II-VI-MBE

blue laser



💡 measurements in Elettra

💡 collaboration with NTT