Unusual Bi-induced surfaces of III-V semiconductors

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OUTLINE:

1. Motivation for III-V surface studies: ”Surface engineering” to improve device materials:
   - Epitaxial growth of interfaces
   - Development of III-V channel MOSFETs
   - Bi-surfactant growth

2. Experiments
   - Preparation of Bi-induced surface reconstructions
   - Scanning tunneling microscopy (STM)
   - Core-level photoelectron spectroscopy

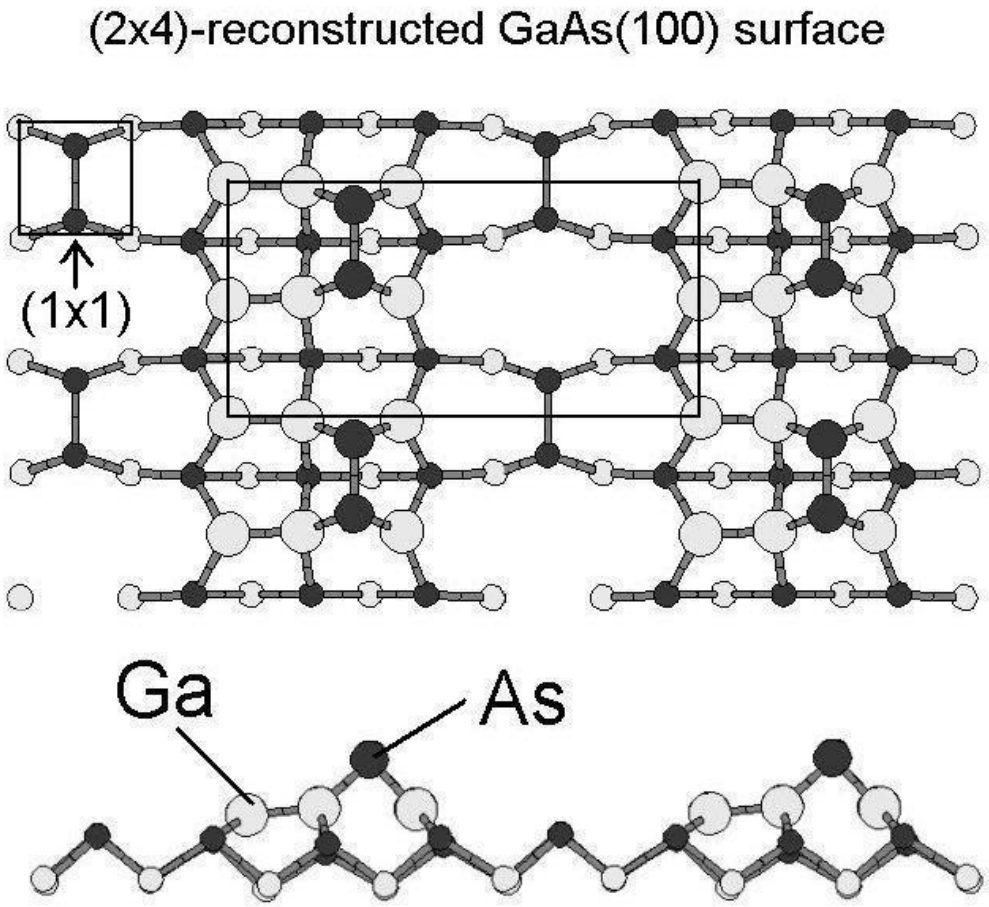
3. Results
   - Phase diagram for Bi-induced GaAs(100) surface
   - Unusual metallic Bi-induced (2x1) reconstructions
   - Bi-induced change in the (2x4) reconstruction of III-V’s
   - Self-assembly of Bi nanowires on InAs

4. Summary

BACKGROUND: Strong atomic rearrangement (reconstruction) occurs naturally on many III-V substrate surfaces to minimize surface energy.

→ Resulted surface atomic structure, that appears on clean III-V substrates in experiments, is often much more complex than that of the corresponding bulk "(1x1)" plane.

It can be rough in atomic scale (corrugated) and have different chemical composition with new atomic bonds as compared to the bulk.

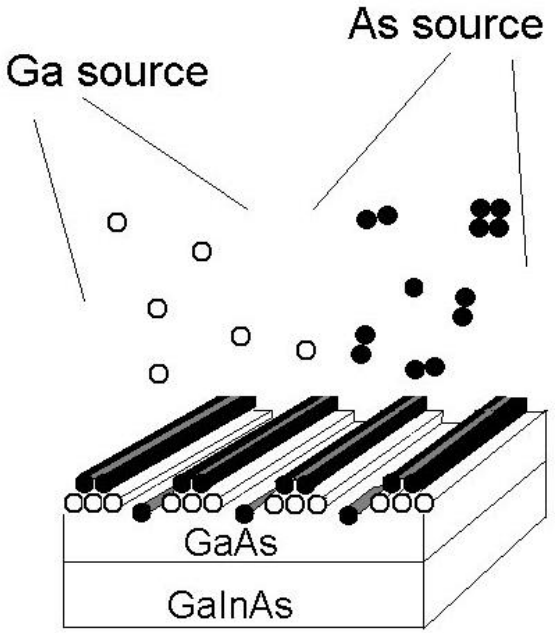


MOTIVATION FOR III-V SURFACE STUDIES: Processing of III-V surface properties to improve device materials

Epitaxial growth of device materials is a surface process which proceeds via reconstructed III-V growth fronts (e.g. via 2x4 for GaAs layers).

→ Properties of III-V surfaces (e.g., corrugation and composition) affect the properties of epitaxially grown heterointerfaces
(e.g., compositional sharpness).

Interfaces affect strongly the device operation, e.g., power consumption and light output power.



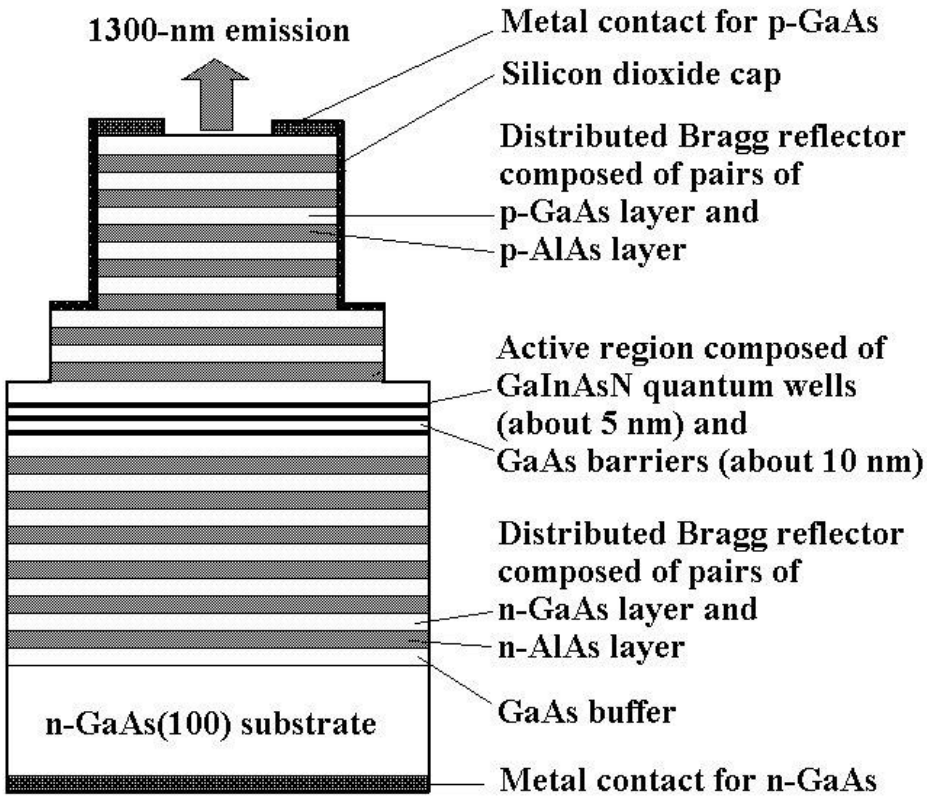
Properties of device interfaces can be affected by “surface or interface engineering” during epitaxy.

It is possible, e.g., to make a short growth break and tailor the growth front structure and composition controllably with RHEED.

Knowledge of III-V surface reconstructions is helpful.

Please find good examples:

- T.Anan, et al., APL 63,1047 (1993).
- B.Z.Nosho, et al., APL 74, 1704 (1999).
- A.S.Bracker, et al., APL 78, 2440 (2001).



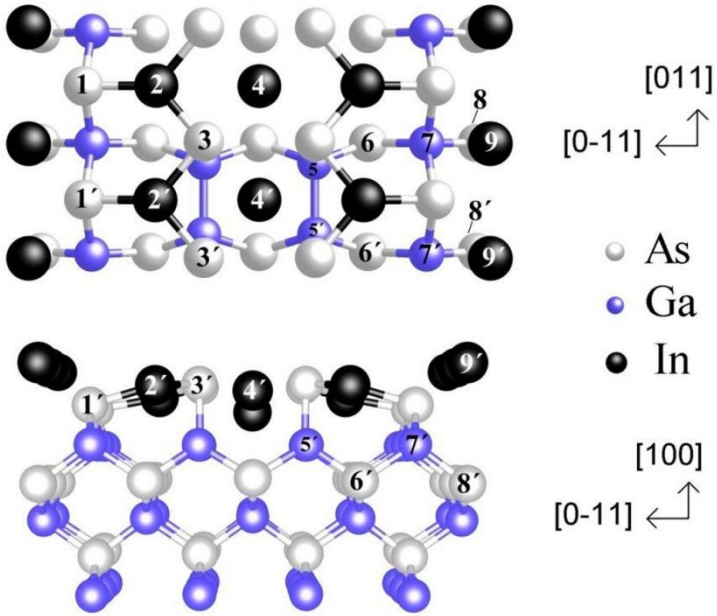
T. Anan, et al. Appl. Phys. Lett. 63, 1047 (1993):

Adding only one atomic layer of indium on GaAs, which causes a substrate reconstruction change to the In-stabilized *c*(8x2) starting growth front on the heteroepitaxy of GaInP/GaAs and InP/InGaAs, improves the properties of the grown heterostructure:

100-fold increase in the photoluminescence (PL) intensity.

Usually the threshold current of a laser diode is inversely proportional to the PL intensity.

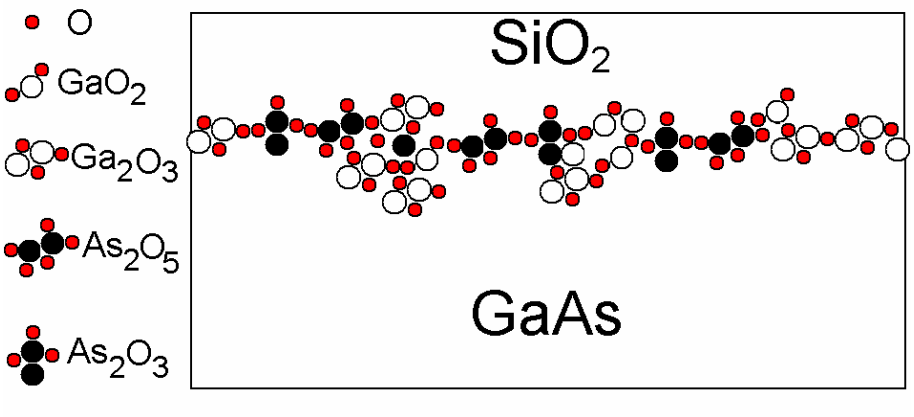
GaAs(100)*c*(8x2)-In



J. Lång, et al., PRB 81, 245305 (2010).

Development of III-V channel MOSFETs: Role of III-V surface properties and their processing

Long-standing but good problem also for surface-science people



Atomic-scale knowledge and processing of III-V starting surfaces become more and more important in the development of III-V MOSFETs.

Presence or formation of amorphous (or polycrystalline) natural III-V oxides in the interface between a III-V channel layer and an insulator film has hindered the development of III-V MOSFETs that meet commercial criteria.

Bi-surfactant effects

Surfactant floats on the growth front but does not incorporate into a crystal.

Bi surfactant has been found, for example :

- **to smooth the grown III-V materials** [JVST 18, 1232; JCG 251, 449; JCG 304, 402]
- **to increase the PL intensity of GaInAsN QW** [JCG 251, 449]
- **to enhance the nitrogen incorporation into GaAsN** [JCG 251, 449; JCG 279, 316; JCG 304, 402]
- **to remove the CuPt-like crystal order of GaInP** [APL 76, 2716]

Concomitant with the above useful Bi-surfactant effects, the surface structure of the growth front has been often found to change due to presence of Bi atoms on the surface.

- Normal As-induced or P-induced (2x4) or c(4x4) growth front has been found to change, at least, to Bi-induced (1x3), (2x1), and (2x4) reconstructions in experiments (RHEED).

- (2x1) reconstruction has been observed also during the growth of GaAsBi / GaAs quantum wells (APL 93, 131915, 2008)

- Little is known about the Bi-induced surface structures, as compared to As-induced (2x4) and c(4x4) surfaces, appearing normally on the III-V growth fronts.

EXPERIMENTS: Preparation of Bi-induced surfaces

We have utilized two separate ultrahigh vacuum (UHV) systems:

(1) Surface-science one contains (i) analysis chamber with low-energy-electron-diffraction (LEED), scanning-tunneling-microscopy/spectroscopy (STM/STS), x-ray photoelectron-spectroscopy equipments, and (ii) preparation chamber in which Bi was deposited on substrates using a home-made W-wire or Ta-envelope evaporator. The substrate was at room temperature during the deposition.

(2) GaAs-MBE connected to photoemission chamber. In MBE, Bi was deposited from Knudsen cell. Reflection high energy electron diffraction (RHEED) was used to monitor in situ Bi-induced surface changes as a function of the substrate temperature and As amount.

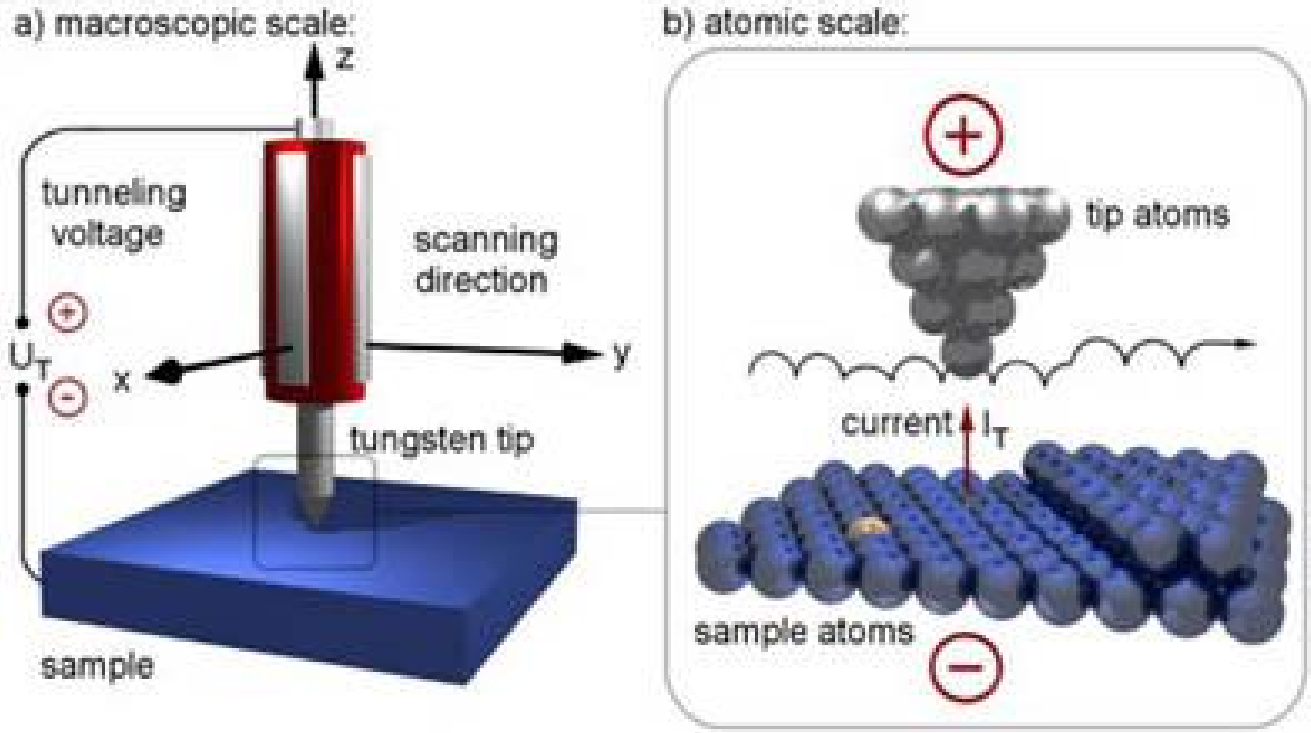
Scanning tunneling microscopy/spectroscopy (STM/STS)

- STM gives the image of the charge distribution of the surface.

- Combined with ab-initio calculated images, STM is a powerful tool to elucidate the surface atomic structure.

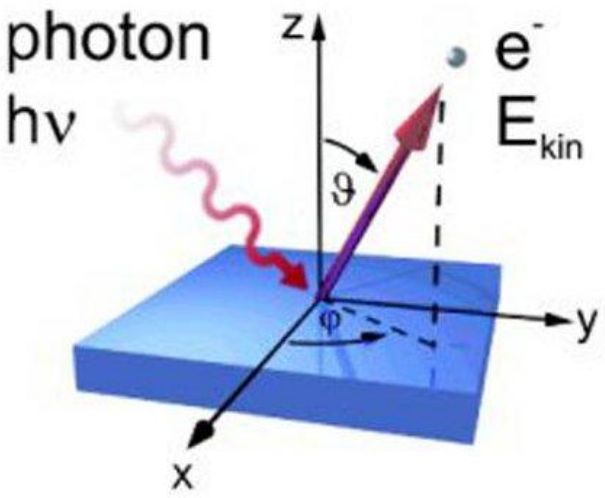
- Large-scale images are useful to conclude two-dimensional character (smoothness) and terrace size of the sample.

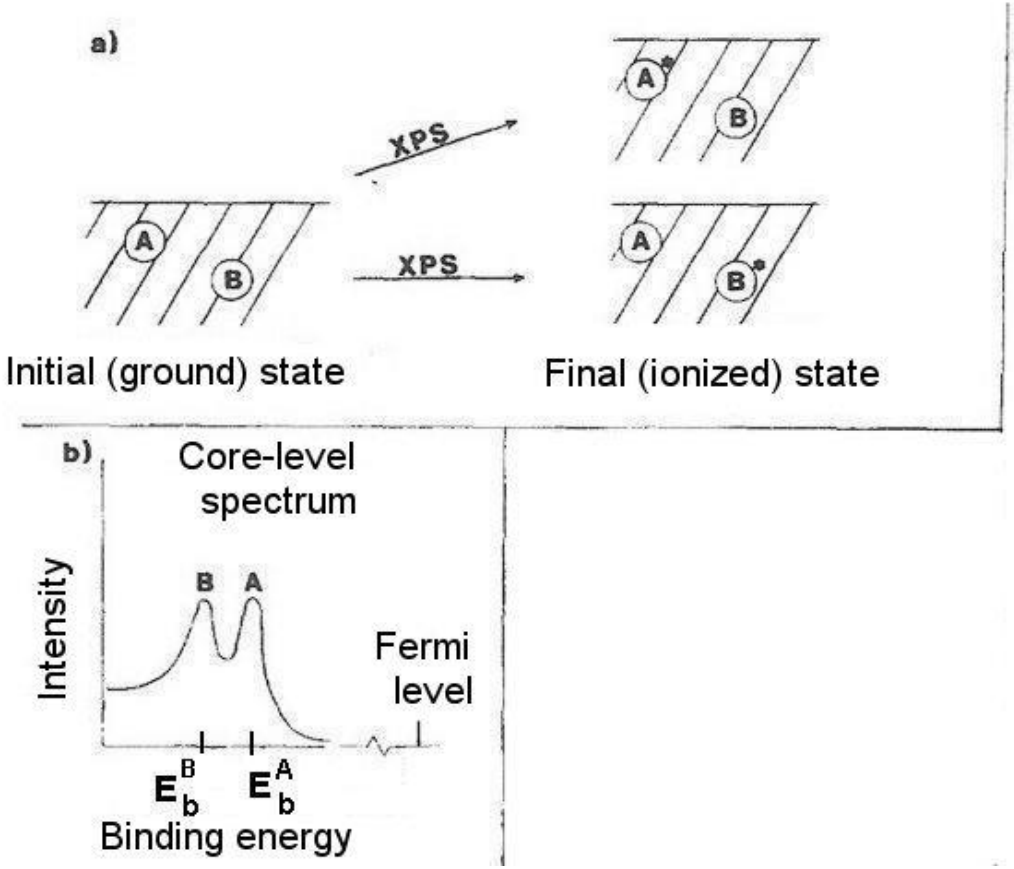
- From STS I-V curve, it is easy to conclude if the surface structure is metallic or semiconducting.



Photoelectron spectroscopy yields information about chemical composition and atomic geometry of surfaces via the core-level electron binding energies and shifts in them. These energy shifts arise from changes in valence charge distribution and reflect changes in atomic bonding geometry. Again the comparison of the measured and calculated core-level shifts is a powerful method to elucidate atomic structure of the surface.

X-ray photoelectron spectroscopy (XPS)





Combining measurements: LEED, RHEED, STM/STS, photoemission, as well as calculations: energetics, surface core-level shifts, and simulated STM images, we have studied the atomic structures and formation mechanisms of following Bi-induced surfaces:

- GaAs(100)(2x1)-Bi: PRL 100, 086101. PRB 78,195304.
- GaAs(100)(2x4)-Bi: Surf. Sci. 600, 2349. PRB 78,195304.
- GaAsN(100)(2x1)-Bi: PRB 74,155302.
- GaInAs(100)(2x1)-Bi: APL 90, 082101.
- InAs(100)(2x4)/(2x8)-Bi: Surf. Sci. Lett. 598, L361.
- InAs(100)(2x10)-Bi (nanolines): APL 92, 011926. +one submitted
- InP(100)(2x4)-Bi: Surf. Sci. 60, 3395.
- InSb(100)*c*(2x6)-Bi: PRB 81,035310.
- GaAs(100)c(4x4)-Bi and –(1x3)-Bi (not published yet)

Results for the following four issues are presented next:

(1) GaAs substrate conditions for different Bi-induced surface structures: RHEED can be used to control Bi-induced surface changes.

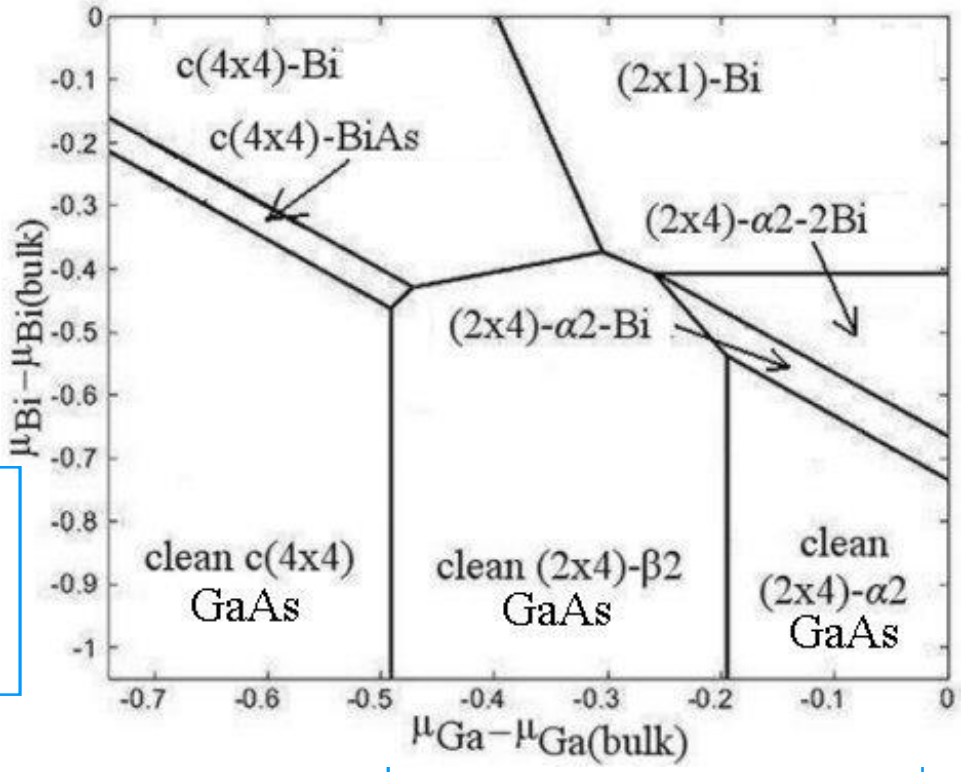
(2) Unusual metallic Bi-induced reconstructions of III-V's: Metallic nature of some Bi-induced reconstructions might be useful for device material growth.

(3) Bi-induced change in (2x4) reconstruction of III-V's: Bismuth stabilizes different (2x4) structure, so called alfa phase, as compared to normal As-stabilized "beta" (2x4) structure.

(4) Self-assembly of Bi nanowires on InAs: This uniformly patterned nanoline surface provides an interesting template to study various phenomena.

Calculated ab initio phase diagram (DFT VASP code), which shows energetically favored surface structures, describes well the Bi-induced reconstructions observed in experiments on GaAs.

→ Amounts of Bi (coverages) in the different reconstructions are obtained from the energetically stable models.



Amount of Bi increases in experimental conditions

(2x1):
1 monolayer (ML) of Bi

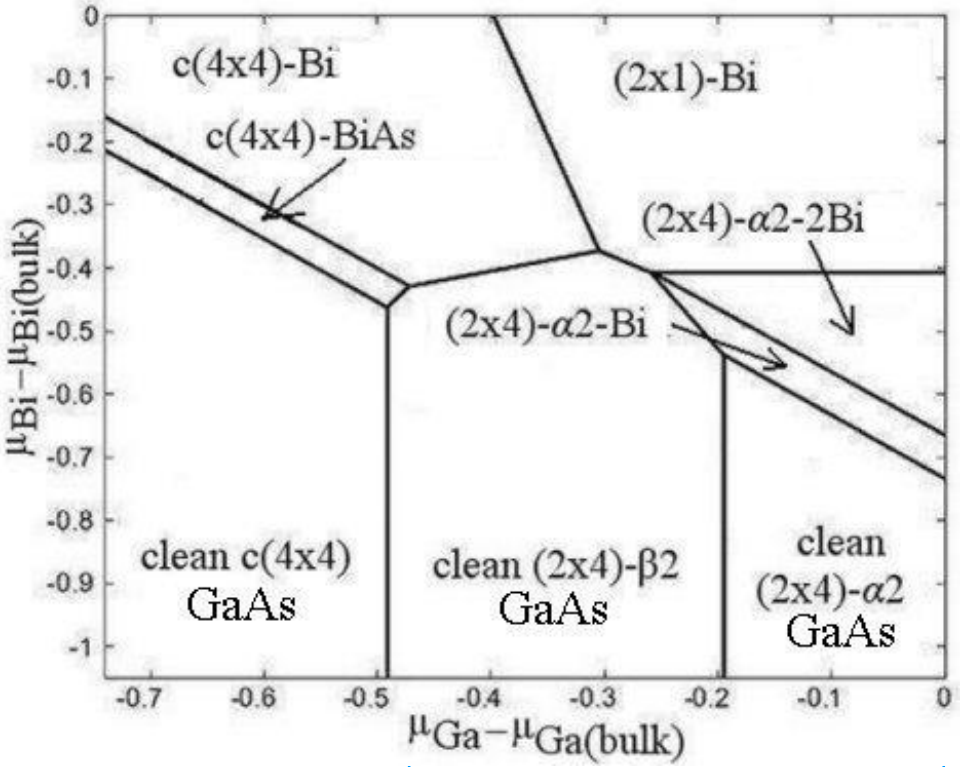
c(4x4):
0.75 - 0.375 ML of Bi

(2x4):
0.5 – 0.25 ML of Bi

Amount of As increases in experimental conditions

Bi deposition on GaAs-(2x4) at room temperature + heating at 300 - 400°C → Bi-induced (2x1) → further heating 400 - 450 °C → Bi-induced (2x4)

Bi deposition on heated GaAs-c(4x4) or heated GaAs-(2x4) in MBE-RHEED → Bi-induced (1x3) at 300 °C → decreasing further the substrate temperature to 200 °C caused Bi-induced c(4x4)



Amount of Bi increases in experimental conditions

Amount of As increases in experimental conditions

Temperatures at which Bi strongly evaporates from the substrates:

GaAs:	450 °C
InP:	400 °C
GaInAs:	350 °C
InAs:	350 °C
InSb:	300 °C

If the substrate surface includes Bi more than 1 ML (e.g. 3D islands), even 100 °C higher temperature is needed to remove Bi from the surface.

RHEED can be used to monitor Bi-induced reconstructions in situ. In some cases, care is needed in RHEED analysis since:

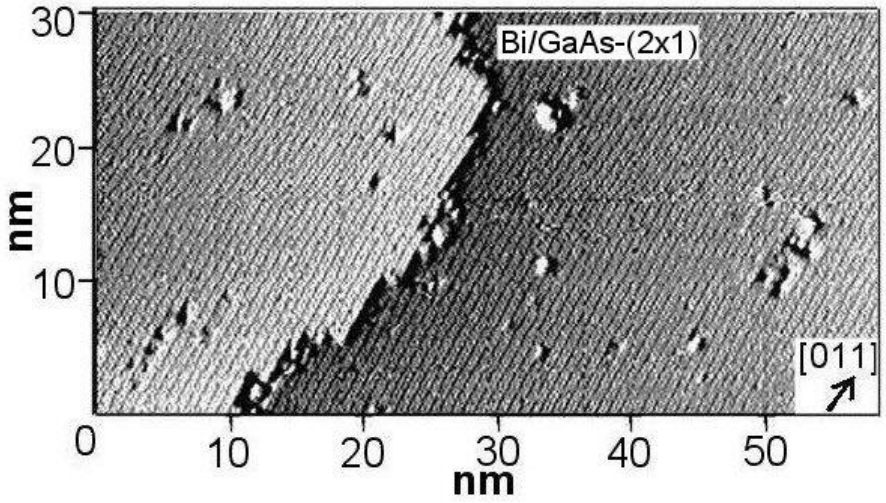
- Bi induces the same (2x4) and c(4x4) periodicities as As and P atoms do. The Bi- and As-induced (2x4) reconstructions can be distinguished from each other by means of intensities of the x4 half order spots (please see JVST B8, 903 and PRL 73, 2208).

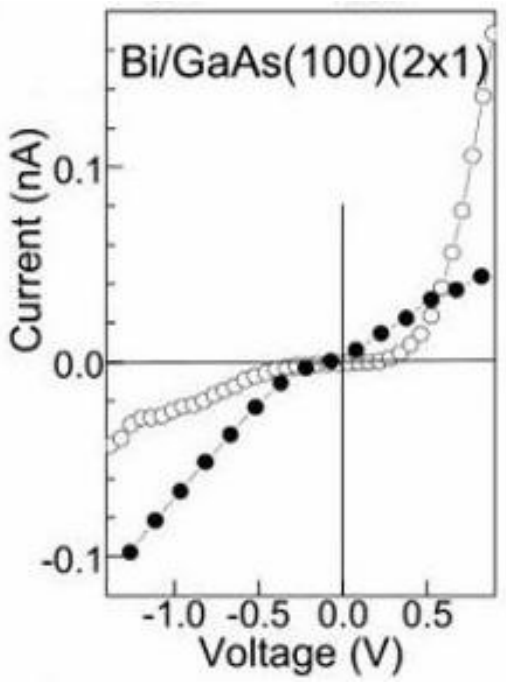
- Along the 2x direction, all (2x1), (2x4), and c(4x4) look similar.

Unusual metallic Bi-induced (2x1) reconstructions

Normally group-V induced III-V reconstructions obey the famous electron counting model (or rule), and tend to be non-metallic to decrease the surface energy.

Bi induces a metallic (2x1) reconstruction at least on GaAs(100), GaInAs(100), InAs(100), and InP(100) substrates.





To elucidate the atomic structure of the unusual Bi-induced (2x1) reconstructions, we have:

1) studied total energies of different atomic models of the (2x1)-Bi layer to find an energetically favored structure and to study the stability of (2x1) in relation to other reconstructions

2) compared measured and calculated STM images for different models

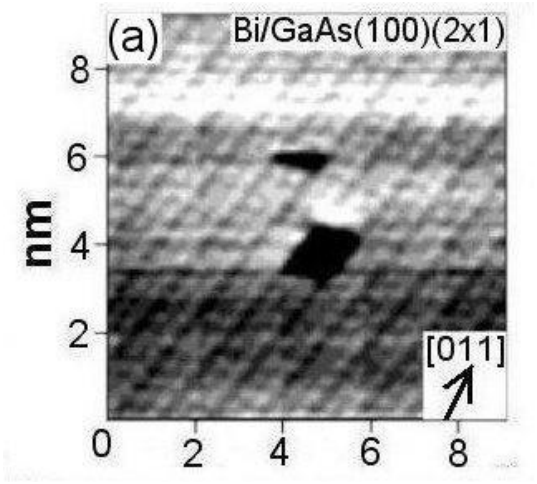
3) compared measured and calculated core-level photoemission shifts

4) compared measured and calculated conductivity (metallic vs insulator) properties and valence-band dispersions.

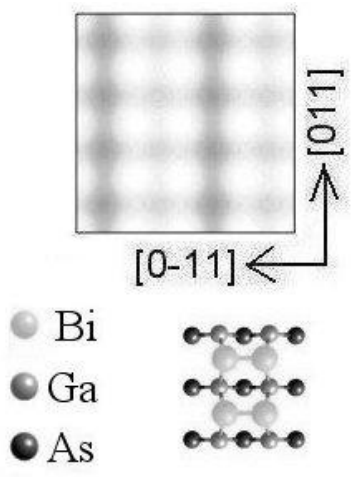
(2x1)-Bi surface is constructed from Bi-Bi or Bi-As (Bi-P) dimers: the Bi coverage is 0.5 – 1 ML

GaAs(100)(2x1)-Bi

measured

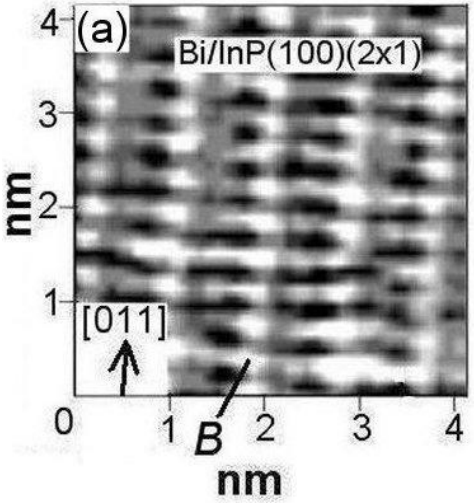


calculated

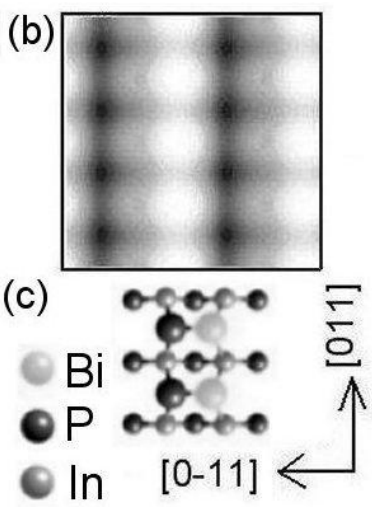


InP(100)(2x1)-Bi

measured



calculated

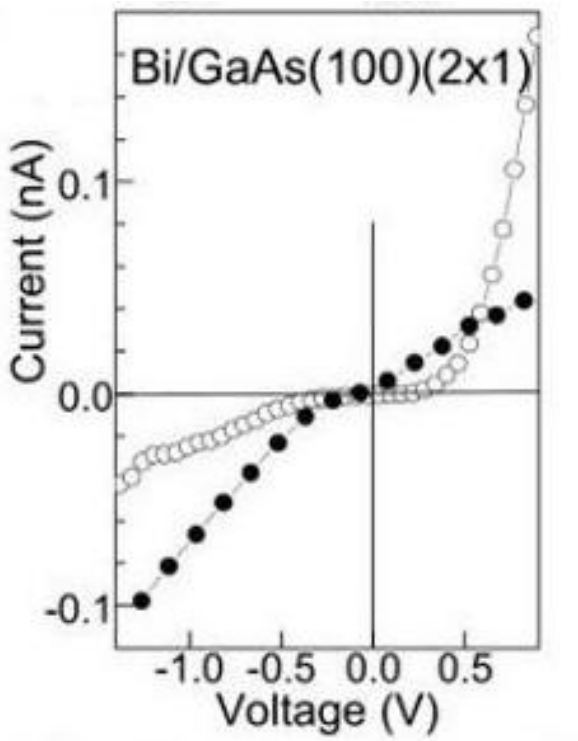


Why does (2x1)-Bi reconstructed surface appear to include also non-metallic areas?

Bi might occupy part of the second-layer group-III sites below the dimers.

Formation of such Bi antisites leads to a non-metallic (2x1)-Bi areas according to the electron counting model and to ab initio DOS.

This is supported by the comparison of the measured and calculated STM images as well as core-level photoemission shifts.



Ab initio calculations reveal two driving forces, which arise from large atom size of Bi, behind the formation of metallic (2x1)-Bi surface structure:

1. Surface-stress relief due to pairing of Bi atoms (i.e., Bi atoms have the largest tendency to dimerize among group-V elements)

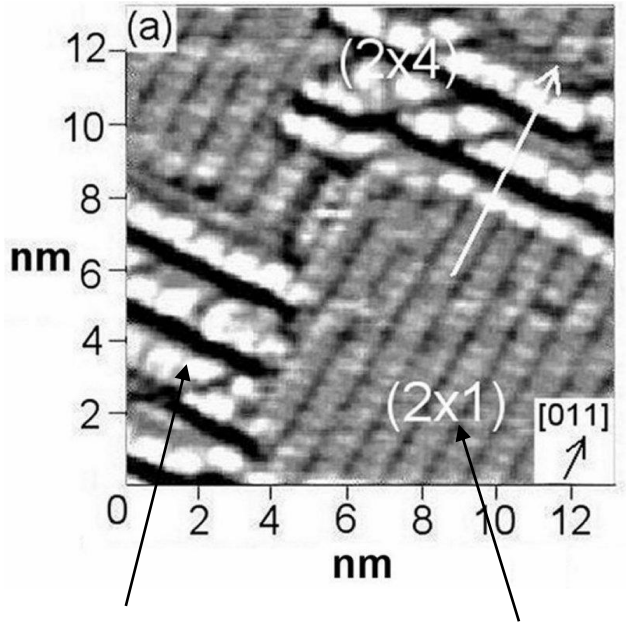
2. Density of states (DOS) near the Fermi energy decreases (i.e., pseudogap formation) as compared to hypothetical As- and Sb-induced (2x1) reconstructions.

(2x1)-Bi reconstruction might be a useful growth front:

- Its metallic nature can increase the surface diffusion (please find, e.g., Neugebauer et al. PRL 90, 056101).

- (2x1)-Bi surface is also atomically smoother than III-V reconstructions usually → an improved surface diffusion.

GaInAs(100)-Bi surface which includes both (2x1) and (2x4) areas



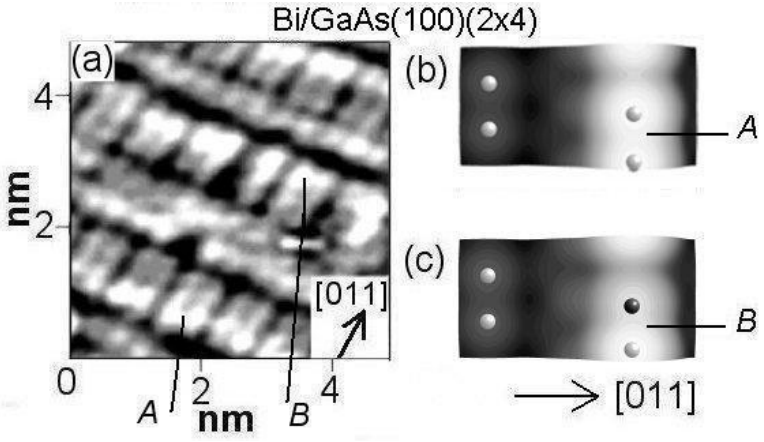
(2x4)-Bi area

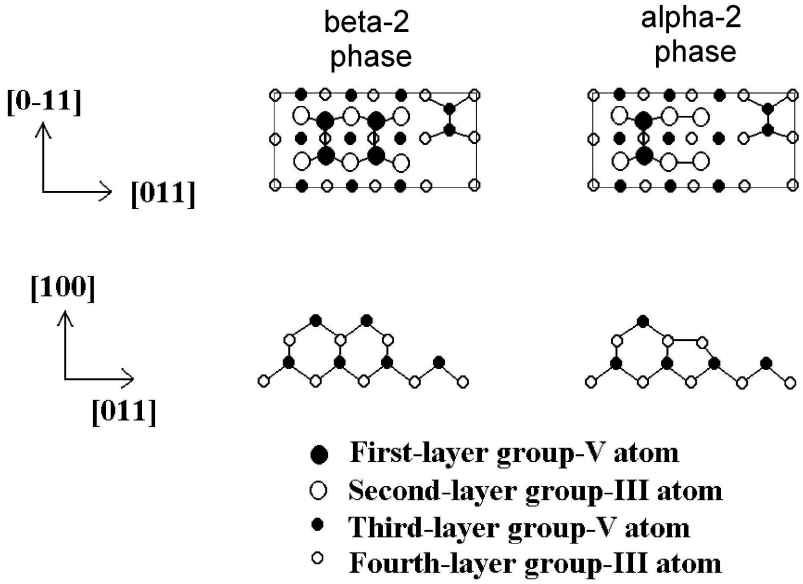
(2x1)-Bi area

Bi-induced change in (2x4) reconstruction of III-V's:

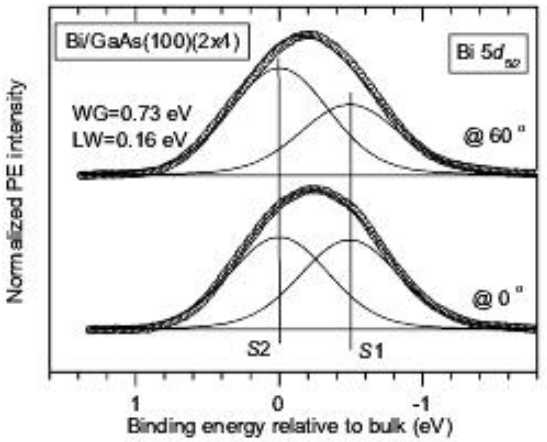
STM measurements show that Bi induces only the alpha-2 phase of the (2x4) reconstruction, in contrast to the As-induced (2x4) surface on which beta-2 appears usually.

This agrees well with ab initio calculations which reveal that rearrangement of the subsurface layers due to the Bi atom size leads to the absence of the Bi-induced III-V(100)(2x4)-beta-2 phase.





Comparison of measured and calculated core-level shifts demonstrates that Bi atoms occupy both the 1. and 3. layer dimer sites in (2x4). Also the presence of Bi-As dimers is supported.



Bi/GaAs(100)(2×4)	**Bi 5*d***	**Ga 3*d***	**As 3*d***
Measured SCLS	-0.49 (*S*1), 0 (*S*2)	-0.23 (*S*1), +0.25 (*S*2)	-0.35 (*S*1), -0.16 (*S*2), +0.17 (*S*3)
Calc.: (2×4)-α2 (2BiBi in Fig. 1) **1.layer:Bi-Bi, 3.layer:Bi-Bi**	-0.44, 0	-0.15, -0.12, +0.28, +0.50	-0.18, +0.16, +0.29
Calc.: (2×4)-α2 **1.layer:Bi-Bi, 3.layer:Bi-As**	-0.36, -0.01	-0.18, +0.26, +0.60	-0.25, -0.18, +0.16, +0.30
Calc.: (2×4)-α2 (BiBi in Fig. 1) **1.layer:Bi-Bi, 3.layer:As-As**	-0.03	-0.16, -0.12, +0.27, +0.50	-0.35, -0.18, +0.15, +0.31
Calc.: (2×4)-α2 **1.layer:Bi-As, 3.layer:Bi-Bi**	-0.44, +0.09	-0.15, -0.11, +0.27, +0.50	-0.20, +0.16, +0.32
Calc.: (2×4)-α2 **1.layer:Bi-As, 3.layer:Bi-As**	-0.35, +0.08	-0.17, -0.11, +0.26, +0.50	-0.34, -0.21, +0.14, +0.34
Calc.: (2×4)-α2 **1.layer:Bi-As, 3.layer:As-As**	+0.05	-0.18, -0.13, +0.25, +0.49	-0.24, +0.17, +0.33

(2x4)-Bi reconstruction might be a useful growth front:

Formation of alpha-2 instead of beta phase of (2x4) reduces harmful effects of dimer-row kinks (meandering dimer rows) on the growth front

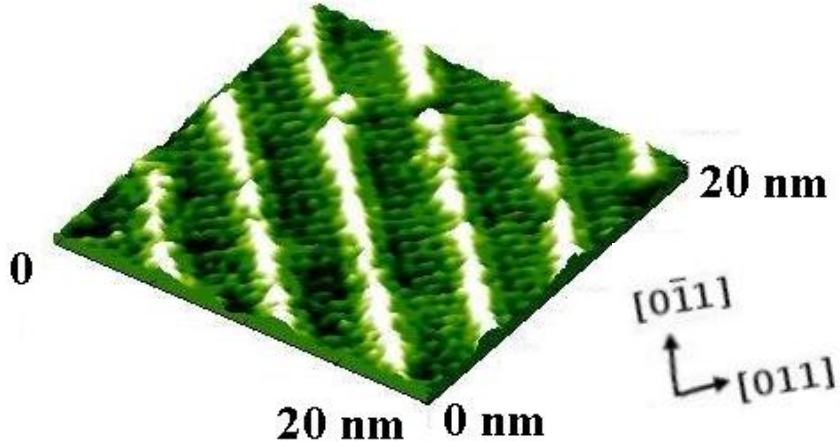
→ diffusion of group- III atoms along the dimer rows improves.

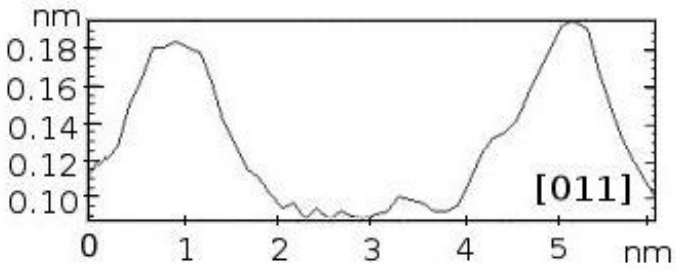
Please see K. Shiraishi, APL 60, 1363 and
J. Pakarinen et al. Appl. Surf. Sci. 255, 2985.

Bi nanowires are formed by self-assembly on InAs(100)(2x1)-Bi starting substrate

•This is an interesting example of the growth which starts with 2D layer formation, i.e., (2x1)-Bi formation, and which changes to 1D growth after the first atomic layer.

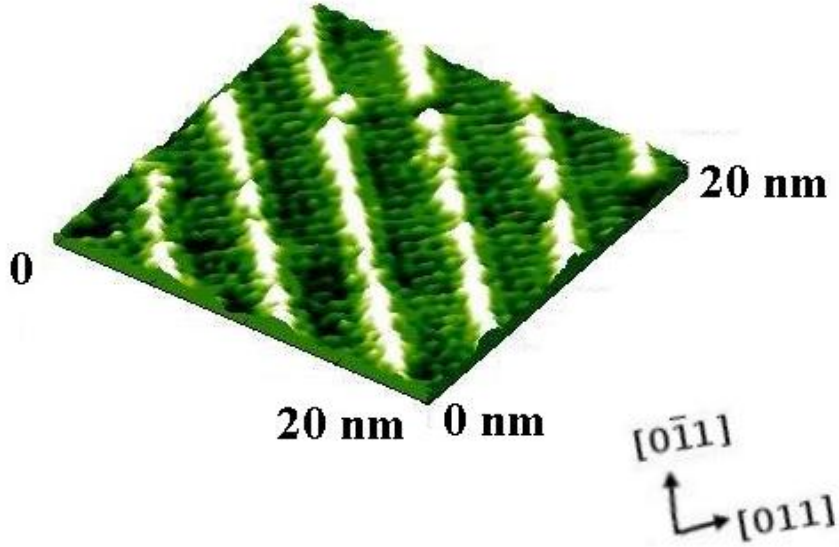
• Meandering of Bi nanowires causes (2x6) LEED pattern. Heating around 250 °C leads to straightening of wires and Bi induced (2x10) reconstruction.

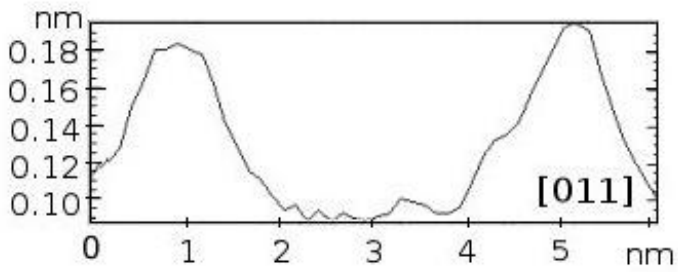




- The resulted Bi-nanowire surface is uniform in large scale and single domain (please compare, e.g., with double- and triple-domain Si substrates.

- It might be so that the Bi-(2x1)-reconstructed areas between nanowires are metallic but the wires itself are non-metallic.





SUMMARY

• Processing III-V surface properties is useful, and most likely its role increases in the device development.

• Knowledge of properties of Bi-induced surface structures is helpful to understand and control Bi-surfactant growth and III-V-Bi epitaxy.

• Metallic nature and atomic smoothness of (2x1)-Bi reconstruction might make it useful growth front, e.g., Bi surfactant growth of device heterostructures in which GaAs layers must be grown at low temperature like GaInAsN /GaAs quantum wells.

SUMMARY

- Bi induces the different (2x4) growth front as compared to the normal As-induced one, which might improve diffusion of group- III atoms along the dimer rows.

- Bi-nanowires on the InAs(100)(2x1)-Bi surface might provide a good template to study various phenomena.

Thank You Very Much and Have a Sunny Summer and Good Surface Problems To Be Solved !!!