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Crystallite Phase and Orientation Determinations of (Mn, Ga) As/GaAs-crystallites using Analyzed (Precession) Electron Diffraction Patterns

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Crystallite phase and orientation determinations of (Mn,Ga)As/GaAs-crystallites using analyzed (precession) electron diffraction patterns

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Outline

1. Material system: (Mn,Ga)As/GaAs-crystallites
2. Structure analysis using
   Nano-beam Diffraction (NBD)
   Precession Electron Diffraction Technique (PED)
   → Structure type I + II
3. Phase and orientation mapping using ASTAR
4. Conclusion
Material system: MnAs/GaAs

Motivation
- $\alpha$-MnAs: ferromagnetic properties (Curie temperature above room temp.)
- combination of $\alpha$-MnAs and paramagnetic semiconductor materials (e.g. GaAs) for spintronic devices
  \[ \rightarrow \text{fast information transport} \text{ basing on the intrinsic electron spin} \]

Growth process
- Metal-organic chemical vapor deposition (MOCVD)
- [001]-oriented GaAs substrate
- Deposition of Ga, Mn and As at 870K
- Formation of crystallites during cooling process
Phases of MnAs

α–MnAs
hexagonal
ferromagnetic
Space group: P6₃/mmc

β–MnAs
orthorhombic
paramagnetic
Space group: Pnma
Phases of MnAs

α–MnAs
hexagonal
ferromagnetic
Space group: P6₃/mmc

β–MnAs
orthorhombic
paramagnetic
Space group: Pnma

313 K
Phases of MnAs

α–MnAs
hexagonal
ferromagnetic
Space group: P6₃/mmc

β–MnAs
orthorhombic
paramagnetic
Space group: Pnma

313 K

[Image of crystal structures for α–MnAs and β–MnAs]
**Instrumentation**

JEOL JEM-2200FS @ HU Berlin

- Field-emission gun
- In-column energy filter
- Energy dispersive X-ray detector (EDXS)
- High angle annular dark-field (HAADF) detector
- Beam precession unit
- Electron biprism

Accelerating voltage: 200 kV
Energy resolution: 0.7 eV
Point resolution: 0.19 nm
Probe size STEM: 0.14 nm
Probe size NBD: 0.5 nm
Energy dispersive X-ray spectroscopy

HAADF STEM

Elemental mapping

Mn-K

Ga-K

GaAs

Mn_xGa_{1-x}As crystallite

Ga-L

As-L

Ga-Kα

As-Kα

Ga-Kβ

As-Kβ

Ga-L

Mn-Kα

Mn-Kβ

Ga-Kα

As-Kα

As-Kβ
Energy dispersive X-ray spectroscopy

HAADF STEM  Elemental mapping

$\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As}$

GaAs crystallite
**Assumption:** Statistically distribution of Manganese atoms (75%) and Gallium atoms (25%) at cation positions

\[ \text{Short: } \alpha-\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As (hex)} \]

\[ \text{Short: } \beta-\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As (orth)} \]
Nano-beam electron diffraction (NBD)

Poly-crystalline sample

Parallel beam

Nano-probe mode

Electron beam

Probe size: 0.5 - 1.5 nm

Nano-beam electron diffraction

Diffraction pattern
Structure analysis of Mn$_{0.75}$Ga$_{0.25}$As
Nano-beam electron diffraction

Nano-beam mode
Spot size: 1.0 nm
Structure analysis of Mn$_{0.75}$Ga$_{0.25}$As
Nano-beam electron diffraction

Nano-beam mode
Spot size: 1.0 nm

Crystallite A

Crystallite B

Templates

α-(Mn,Ga)As

β-(Mn,Ga)As
## Reflection conditions (kinematic)

### Hexagonal

<table>
<thead>
<tr>
<th>Space Group</th>
<th>Reflection Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P6_3/mmc)</td>
<td>General: (hh2hl : l = 2n) (000l : l = 2n)</td>
</tr>
</tbody>
</table>

No. 194

\(P 6_3/m 2/m 2/c\)

### Orthorhombic

<table>
<thead>
<tr>
<th>Space Group</th>
<th>Reflection Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Pnma)</td>
<td>General: (0kl : k + l = 2n) (hk0 : h = 2n) (h00 : h = 2n) (0k0 : k = 2n) (00l : l = 2n)</td>
</tr>
</tbody>
</table>

No. 62

\(P 2_1/n 2_1/m 2_1/a\)

* International Tables for Crystallography: Volume A – space group symmetry; ed. Th. Hahn
Kinematic versus Dynamic ED

**Kinematic Electron Diffraction:**
- Only single scattering processes take place
- No double diffraction
- Each individual diffraction event acts independently of the others
- Two-beam condition (just the undiffracted beam and one diffracted beam are only excited)

**Dynamic Electron Diffraction:**
- Interaction of waves
- Multiple scattering effects
- Double diffraction possible (strong reflections behave like new primary beams)
- Dynamical effects increase with the number of excited reflections

Very thin crystals

Thick crystals
Precession Electron Diffraction (PED)

- Tilting the incident electron beam away from the zone axis (tilting angle = precession angle $\varepsilon$, typically $1^\circ$-$3^\circ$) → less beams are simultaneously excited
- Continuous integration of the reflections over the entire range of angle $\omega$
Precession Electron Diffraction (PED)

Advantages:

- Symmetrical precession patterns are obtained also for off-zone orientation tilted by less than 1°
- Dynamical effects are reduced due to the off-axis beam inclinations because less beams are simultaneously excited
- The number of reflections is higher than in conventional electron diffraction
Precession Electron Diffraction (PED)

Problems:

- The loss of the spatial resolution (depends on the precession angle and spherical aberation)
- Overlaps between Laue zones are possible for high precession angles
- Information about the shape of the reflections is lost by integration over $\omega$
- Reflections at low angle stay in Bragg condition for longer time than reflections at high angles (Lorentz effect)
Instrumentation – ASTAR

JEOL JEM-2200FS @ HU Berlin
PED Simulation of Mn$_{0.75}$Ga$_{0.25}$As Structure Type I

ZA: [0 21 22]

jem - Simulation
Precession angle: 0.00 deg  Thickness: 100 nm

β-Mn$_{0.75}$Ga$_{0.25}$As
space group: Pnma (orthorhombic)
Structure analysis of (Mn,Ga)As

Nano-beam mode, spot size: 1.0 nm

Precession OFF

Precession ON: 0.96°

Crystallite A

Crystallite A

Precession ON: 0.95°

Crystallite B

Crystallite B

Simulation

Precession angle: 0.95 deg
Thickness: 100 nm
ZA: [0 21 22]

β-Mn<sub>0.75</sub>Ga<sub>0.25</sub>As
Space group: Pnma (orthorhombic)
Structure analysis of (Mn,Ga)As

Nano-beam mode, spot size: 1.0 nm

Precession OFF

Precession ON: 0.96°

As

Mn 75%, Ga 25%

Crystallite A

Crystallite A

Crystallite B

Crystallite B

Superlattice reflections

Modification of structure
**Assumption: Superstructure**

Each second cation lattice plane of the superlattice is completely occupied with Manganese atoms. 50% of Manganese and 50% of Gallium are statistically distributed on the other cation lattice planes.

**α–superstructure** \(\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As} \)  
trigonal  
Space group: \(\overline{\text{P}3\text{m}1}\)

Short: \(\alpha\text{–Mn}_{0.75}\text{Ga}_{0.25}\text{As (tri)}\)

**β–superstructure** \(\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As} \)  
monoclinic  
Space group: \(\text{P}2_1/m\)

Short: \(\beta\text{–Mn}_{0.75}\text{Ga}_{0.25}\text{As (mono)}\)
PED Simulation of Mn$_{0.75}$Ga$_{0.25}$As
Superstructure Type II

ZA: [0 21 22]

jemS - Simulation
Precession angle: 1.00 deg
Thickness: 1 nm

β-superstructure Mn$_{0.75}$Ga$_{0.25}$As
space group: P2$_1$/m (monoclinic)
Structure analysis of (Mn,Ga)As

Nano-beam mode, spot size: 1.0 nm

- Precession OFF
- Precession ON: 0.96°

Crystallite A

- Structure type I
  - Mn 75%, Ga 25%

Crystallite B

- Superlattice structure type II
  - Mn 50%, Ga 50%

Phases of $\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As}$

\[ \alpha-\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As}(\text{hex}) \]

space group: $\text{P6}_3/\text{mmm}$ (hexagonal)

Laue class: $\begin{array}{ccc} 6 & 2 & 2 \\ m & m & m \end{array}$

2701 templates

\[ \beta-\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As}(\text{orth}) \]

Space group: $\text{Pnma}$ (orthorhombic)

Laue class: $\begin{array}{ccc} 2 & 2 & 2 \\ m & m & m \end{array}$

8001 templates

\[ \alpha-\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As}(\text{tri}) \]

space group: $\text{P}3\text{m}1$ (trigonal)

Laue class: $\overline{3}m$

10404 templates

\[ \beta-\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As}(\text{mono}) \]

space group: $\text{P}2_1/\text{m}$ (monoclinic)

Laue class: $\begin{array}{c} 2 \\ m \end{array}$

16129 templates
Phases of Mn$_{0.75}$Ga$_{0.25}$As

$\alpha$–Mn$_{0.75}$Ga$_{0.25}$As(hex)
space group: P6$_3$/mmm (hexagonal)
Laue class: 6 2 2
m m m

$\beta$–Mn$_{0.75}$Ga$_{0.25}$As(orth)
Space group: Pnma (orthorhombic)
Laue class: 8001 templates

$\alpha$–Mn$_{0.75}$Ga$_{0.25}$As(tri)
space group: (trigonal)
Laue class: 10404 templates

GaAs
space group: F$\bar{4}3m$ (cubic)
Laue class: $\frac{4}{m} \frac{3}{m} \frac{2}{m}$

$\beta$–Mn$_{0.75}$Ga$_{0.25}$As(mono)
space group: P2$_1$/m (monoclinic)
Laue class: $\frac{2}{m}$
16129 templates

Mn 75%, Ga 25%
As

1 m 3 $\bar{P}$
2 m 2 m 2 m

Mn 50%, Ga 50%
GaAs
m 3 4 $F$
23m 4
Phases of $\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As}$

$\alpha$-$\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As}$ (hex)
- Space group: $\text{P6}_3/\text{mmm}$ (hexagonal)
- Laue class: $6\ 2\ 2$

$\beta$-$\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As}$ (orth)
- Space group: $\text{Pnma}$ (orthorhombic)
- Laue class: $8\ 0\ 0\ 1$

$\alpha$-$\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As}$ (tri)
- Space group: $\text{R3}$ (trigonal)
- Laue class: $10\ 4\ 0\ 4$

$\beta$-$\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As}$ (mono)
- Space group: $\text{P2}_1/\text{m}$ (monoclinic)
- Laue class: $16\ 1\ 2\ 9$

GaAs
- Space group: $\text{F}4\text{3}m$ (cubic)
- Laue class: $4\ \frac{3}{2}\ \frac{2}{m}$

\[ \Sigma \ 38561 \ templates \]

Mn 50%, Ga 50%

$\text{Mn} \quad \text{Ga}$

As 1 m 3 P

$\text{GaAs}$
Scanning nano-beam diffraction (SNBD)

Electron beam

Probe size: 0.5 - 1.5 nm

Poly-crystalline sample

Diffraction pattern

Probe size: 0.5 - 1.5 nm
Virtual BF

300 nm

without precession
Phase map

GaAs (cubic)
$\alpha$–Mn$_{0.75}$Ga$_{0.25}$As(hex)
$\beta$–Mn$_{0.75}$Ga$_{0.25}$As(orth)
$\alpha$–Mn$_{0.75}$Ga$_{0.25}$As(tri)
$\beta$–Mn$_{0.75}$Ga$_{0.25}$As(mono)

without precession
ASTAR: Phase and Orientation Maps

Phase map

Orientation maps

GaAs matrix (cubic)

without precession

Legend:
- Red: GaAs (cubic)
- Blue: α-Mn_{0.75}Ga_{0.25}As (hex)
- Green: β-Mn_{0.75}Ga_{0.25}As (orth)
- Pink: α-Mn_{0.75}Ga_{0.25}As (tri)
- Yellow: β-Mn_{0.75}Ga_{0.25}As (mono)
ASTAR: Phase and Orientation Maps

Phase map

Orientation maps

GaAs (cubic)
α–Mn$_{0.75}$Ga$_{0.25}$As (hex)
β–Mn$_{0.75}$Ga$_{0.25}$As (orth)
α–Mn$_{0.75}$Ga$_{0.25}$As (tri)
β–Mn$_{0.75}$Ga$_{0.25}$As (mono)

without precession
ASTAR: Phase and Orientation Maps

**Phase map**

**Orientation maps**

- **GaAs (cubic)**
- **α–Mn_{0.75}Ga_{0.25}As (hex)**
- **β–Mn_{0.75}Ga_{0.25}As (orth)**
- **α–Mn_{0.75}Ga_{0.25}As (tri)**
- **β–Mn_{0.75}Ga_{0.25}As (mono)**

Without precession
ASTAR: Phase and Orientation Maps

Phase map

Orientation maps

β–Mn$_{0.75}$Ga$_{0.25}$As (monoclinic)

<colors>
- GaAs (cubic)
- $\alpha$–Mn$_{0.75}$Ga$_{0.25}$As (hex)
- $\beta$–Mn$_{0.75}$Ga$_{0.25}$As (orth)
- $\alpha$–Mn$_{0.75}$Ga$_{0.25}$As (tri)
- $\beta$–Mn$_{0.75}$Ga$_{0.25}$As (mono)

without precession
ASTAR: Phase and Orientation Maps

**Phase map**

- GaAs (cubic)
- α–Mn$_{0.75}$Ga$_{0.25}$As (hex)
- β–Mn$_{0.75}$Ga$_{0.25}$As (orth)
- α–Mn$_{0.75}$Ga$_{0.25}$As (tri)
- β–Mn$_{0.75}$Ga$_{0.25}$As (mono)

**Orientation maps**

- β–Mn$_{0.75}$Ga$_{0.25}$As (monoclinic)

*without precession*
ASTAR: Phase and Orientation Maps

\[ \beta-\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As} \text{ (monoclinic)} \]

- As
- Mn
- Mn 50%, Ga 50%

GaAs matrix (cubic)

- As
- Ga
ASTAR: Phase and Orientation Maps

Phase map

Orientation maps

β–Mn$_{0.75}$Ga$_{0.25}$As (monoclinic)

GaAs (cubic)
α–Mn$_{0.75}$Ga$_{0.25}$As(hex)
β–Mn$_{0.75}$Ga$_{0.25}$As(orth)
α–Mn$_{0.75}$Ga$_{0.25}$As(tri)
β–Mn$_{0.75}$Ga$_{0.25}$As(mono)

without precession
ASTAR: Phase and Orientation Maps

\( \beta-\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As} \) (monoclinic)
Materials analysis:

• Chemical composition of crystallites as found by EDXS: $\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As}$

• Formation of superstructure in $\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As}$ as revealed by PED

• Proposal of structure models of a trigonal phase (derived from the hexagonal $\alpha$-phase of $\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As}$) and of a monoclinic phase (derived from the orthorhombic $\beta$-phase of $\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As}$)

• Phase and orientation mapping
  – Identification of two phases within the crystallites:
    monoclinic $\beta$-$\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As}$
    hexagonal $\alpha$-$\text{Mn}_{0.75}\text{Ga}_{0.25}\text{As}$
  – Oriented growth of (Mn,Ga)As with respect to the GaAs matrix
  – Multi-grain growth found for individual crystallites
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