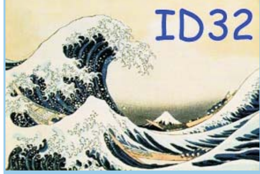

In-situ diffraction study of Cu deposited on UHV prepared GaAs(001)

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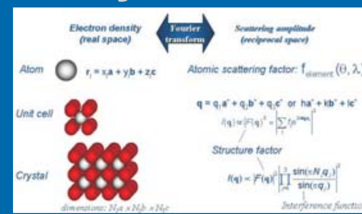
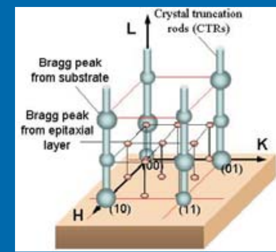
ESRF

Introduction & Motivation

Major interest in solid/electrolyte Interfaces (etching, plating, corrosion,...)
Metal interfaces are electrochemically well-understood.
Semiconductor (SC)/electrolyte interfaces are interesting for industrial processes (Ohmic contacts, etching,...) and for solar energy conversion (hydrogen technology, but corrosion problems)
But: Band-Gap in SC & Band-Bending at SC/Electrolyte interfaces
→traditionally electrochemical tools are difficult to apply
→STM-Imaging very problematic
⇒ Electrochemical processes on semiconductors are scarcely studied on atomic scale but increasingly important for nanoscale-devices and a global understanding of chemical mechanisms on surfaces

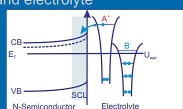
X-Ray diffraction

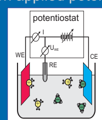


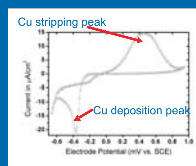


SC in Electrolyte

Band-Bending at SC/Electrolyte-Interface due to Fermi-niveau equalisation through e--transfer ⇒Space Charge Layer
Band-bending in SC at Electrolyte interfaces depends on applied potential (EF=Uapp), SC doping and electrolyte







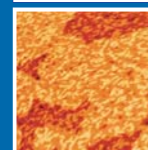
Voltammograms .5M H_2SO_4 +1mM $CuSO_4$ of an GaAs/As surface after removing the As-cap

GaAs/As

Clean (and smooth) surfaces are needed for electrochemical processes in electrolytes.
⇒ GaAs(001) protected by an armorphous arsenic cap

"Decapping"...

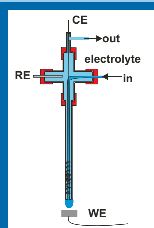
... via heating in UHV: different reconstructions with different surface termination are obtainable depending on temperature

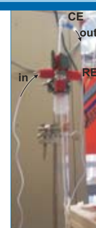


STM-image of a GaAs(001)-(2x4) surface

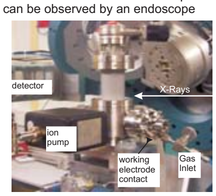
In-Situ X-Ray Droplet Cell

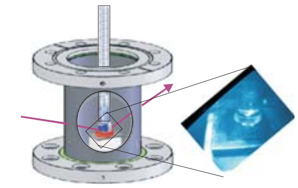
The sample can be prepared and characterised (STM, LEED, AES) in UHV in the surface characterisation lab. It is then transferred under UHV into the portable chamber (equipped with a Be-cylinder and an ion-pum) and mounted on the diffractometer. The sample is investigated by GIXRD, and again after venting the chamber with inert gas. Finally the capillary of the electrochemical droplet cell, containing counter and reference electrode, is introduced through a valve, lowered down (in inert gas) and contacting the surface with the droplet of electrolyte.





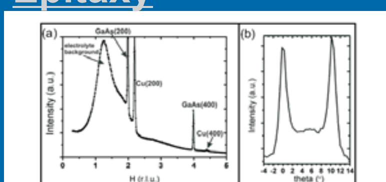
The droplet cell is used in combination with a portable UHV chamber, which can be mounted on the ID32 diffractometer. The droplet is kept stable by a computer controlled syringe system and can be observed by an endoscope



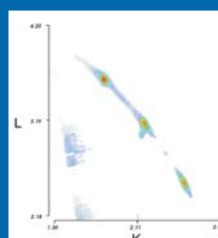


Cu depositon on UHV prepared GaAs(001)

Epitaxy

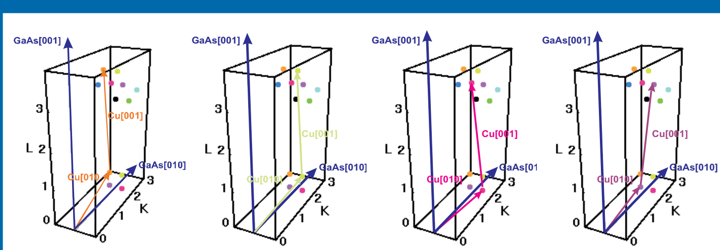


(a)In-plane scan along the GaAs [100]-direction (surface coodinates)
(b) Rocking scan through the copper (200)-reflection reveals an in-plane rotation of the copper lattice with respect to the GaAs lattice



A reciprocal space map taken around the Cu(022)-reflection. The Cu(010) direction is taken as x-axis, the Cu(001)-direction is the z-axis. Two additional Cu(022) reflections from domains with another tilting direction appear.

The copper lattice is found to be rotated by an angle θ about the GaAs(001)-axis and has an additional tilt ϕ in the GaAs(100) or the GaAs(010) direction. In total eight different equivalent domains can be observed, resulting from one of two possible in-plane rotations combined with one of four possible tilting directions.



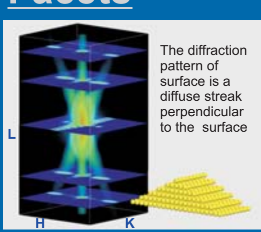
Four of the eight possible tilting and rotations of the copper lattice with respect to the GaAs-lattice are indicated.
Eight copper (022) and four copper (020) reflections are observed due to the different rotation and tilt directions.

The tilting and rotation angles as well as the copper in- and out-of-plane lattice constants could be determined for different nucleation potentials for As-rich and Ga-rich starting surfaces.
No dependence on the nucleation potential could be observed. However the tilting and rotation angles for copper deposited on a Ga-rich surface are smaller.

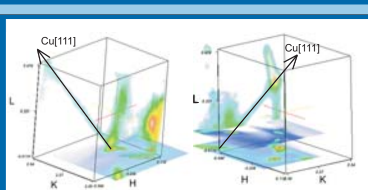
starting surface	deposition potential in mV	θ in °	ϕ in °	$d_\parallel$ in Å	$d_\perp$ in Å
2x4 As-rich	-350	5.05	9.53	3.629	3.614
	-500	4.77	9.16	3.626	3.624
	-900 → -350 [1]	5.09	9.55	3.618	3.613
	-1200→ -350 [1]	4.92	9.26	3.616	3.612
4x2 Ga-rich	-350	4.43	8.78	3.62	3.612
	-600	4.31	8.75	3.62	3.616

[1]a step potential of -900 mV (-1200mV) has been applied for one second before jumping to -350 mV

Facets



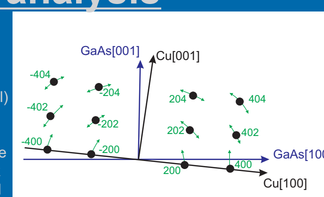
The diffraction pattern of surface is a diffuse streak perpendicular to the surface



A reciprocal space map taken around the Cu(-200)-reflection is shown. The Cu(110) direction is taken as x-axis, the Cu(001)-direction is the z-axis. A diffuse streak in the copper (111) direction is indicating that the copper clusters are facetted.
No diffuse streak from the Cu/GaAs interface can be observed.

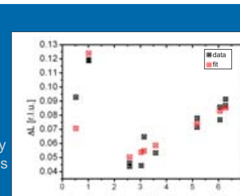
Line-shape analysis

The copper peaks are broadened by several effects. The domain size is contributing to the width in all directions. In addition the peak width in radial) and the L-direction have a contribution from the mosaicity of the tilt and the variation of the copper lattice constant. A peak on a rocking scan is broadened by the mosaicty of the in-plane rotation.



Projection of the plane defined by the Cu(100) and the Cu(010) direction in the HL-plane. The Cu(H0L)-Bragg reflections are indicated for the case of a tilt of the Cu(001)-axis in the GaAs(100)-direction. The peak broadening due to the mosaicity of the tilt is schematically shown by the green arrows.

The peak widths were fitted for different nucleation potentials and starting surfaces (As-rich and Ga-rich). The mosaicity of the tilt and the variation in the out-of-plane lattice constant are increasing with more negative nucleation potential. The mosaicity of the tilt and the in-plane rotation as well as the variations of the lattice constant are bigger on a Ga-rich starting surface.



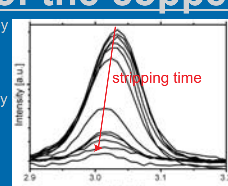
The measured peak width in the L-direction as well as the corresponding values obtained from the the fit are plotted. At low L the mosaicity of the tilt is determining the peak width, at high L the peak-broadening is basically due to the variation of the out-of-plane lattice constant.

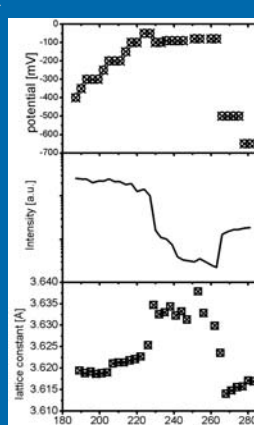
starting surface	deposition potential	$\Delta\phi$	$\Delta\theta$	$\Delta d_\parallel/d_{Cu}$	$\Delta d_\perp/d_{Cu}$	$D_\parallel$	$D_\perp$
As-rich	-350mV	0.65°	0.7°	0.84%	1.4%	125Å	150Å
	-900mV → -350mV [1]	0.81°	0.7°	1.4%	1.7%	190Å	168Å
	-1200mV→ -350mV [1]	1.1°	0.84°	0.86%	1.8%	130Å	140Å
Ga-rich	-350mV	0.93°	1.0°	1.1%	1.8%	107Å	109Å

[1]a step potential of -900 mV (-1200mV) has been applied for one second before jumping to -350 mV

Stripping of the copper

The copper was stripped by slowly changing the potential to more positive values. The copper (202) reflection was continuously scanned to monitor its position and intensity. During the stripping of the deposited copper the positions of the copper peaks are changing to smaller Q





The copper at the interface seems not to be relaxed. It has a bigger lattice constant than natural copper. This is probably due to interdiffusion at the interface and would also explain the peak broadening observed due to the variation of the copper lattice constant.
CuAs- and CuGa-alloys with an atomic percentage of arsenic and gallium respectively up to 25% exist (fcc).
In both cases the lattice constant is (starting with the one for natural copper) increasing with increasing arsenic (gallium) content.