History of improvement in performance of MTJ devices (magnetoresistance ratio)

Increased performance by improving and controlling the crystallographic order at the interfaces

We need the ability to check the crystallographic structure of our media:
  a) on a large scale
  b) in real time

Electron diffraction
The outcoming electrons are diffracted by the atomic planes in the sample.

The outcoming electron beam contains information about the atomic arrangement in the sample.

Example: real time lattice relaxation

Fig. 12. (a) Coherent phonon generation in nonmagnetic metals. (b) Temporal evolution of coherent phonon amplitude. The open circles are arithmetic averaging of the vibration data of all Bragg peaks. The solid curve is a fit using Eqs. 7 and 10.
femtosecond electron pulses to study the structural evolution of aluminum as it underwent an ultrafast solid-liquid phase transition.

At $t = 6$ ps the highly modulated structure of $H(r)$ that is due to the fcc lattice is replaced by the simple coordination shell structure of liquids.

$$H(r) = 4\pi r^2 [\rho(r) - \rho_0] = 8\pi r \int_0^\infty s [K(s) - 1] \sin(2\pi rs) \, ds; \quad K(s) = \frac{I(s)}{f^2(s)}$$

$H(r)$ is the pair correlation function, $I(s)$ is the coherently diffracted intensity in electron units, $f(s)$ is the atomic scattering factor, $\rho(r)$ is the atomic density, and $\rho_0$ is the average atomic density.
Structure analysis: Electron diffraction

LEED: Low Energy Electron Diffraction
SPA-LEED: Spot Profile Analysis Low Energy Electron diffraction
RHEED: Reflection High Energy Electron Diffraction
TEM: Transmission Electron Microscopy

LEED

RHEED

TEM

\[ k_i \rightarrow k_f \]

\[ k_i \rightarrow k_f \]

\[ k_i \rightarrow k_f \]

\[ E = 10 - 500 \text{ eV} \]

\[ E = 10 - 200 \text{ keV} \]

\[ E = 10 - 200 \text{ keV} \]

Electron mean free path

\[ \lambda \text{ (monolayer)} \]

Energy (eV)

\[ 1 \text{ to } 1000 \]

\[ 1 \text{ to } 1000 \]

\[ 1 \text{ to } 1000 \]
By the principles of wave-particle duality, the beam of electrons may be equally regarded as a succession of electron waves incident normally on the sample. These waves will be scattered by regions of high localized electron density, i.e. the surface atoms, which can therefore be considered to act as point scatterers.

The wavelength of the electrons is given by the de Broglie relation:

\[ \lambda = \frac{h}{p} \]  

where \( p \) - electron momentum

Now,

\[ p = m v = (2 m E)^{1/2} = (2 m e V)^{1/2} \]

\[ \lambda = \frac{h}{(2 m e V)^{1/2}} \]

\( h \)  Planck constant  = 6.6 \( 10^{-34} \) J s

\( m \)  electron mass  = 9.1 \( 10^{-31} \) Kg

\( v \)  electron velocity

\( E \)  electron kinetic energy

\( e \)  electron charge  = 1.6 \( 10^{-19} \) C

Example:

1) Electron energy = 20 eV -> Wavelength = 2.7 Å
2) Electron energy = 200 eV -> Wavelength = 0.87 Å

\( \lambda \) comparable to the atomic spacing

N.B.: Electron energy = 2 eV -> Wavelength = 8.5 Å i.e. the hypothetical ‘RLEED’ would have low resolution
Plane wave scattered by a point

In the case of many scatter points the scattered wave is given by:

\[ S_j f_j(q, r_j) e^{i r_j k_f} \]

\[ k_f \]

\[ f_j(\theta, r_j) \] is the atomic structure factor

In the case of many scatter points the scattered wave is given by:

\[ \Sigma_j f_j(\theta, r_j) e^{i r_j k_f} \]

Diffraction spots are the result of the interference pattern generated by the spherical waves scattered by the atoms in the crystal lattice

Thomas Young's sketch of two-slit diffraction, which he presented to the Royal Society in 1803.
Elastic scattering: $|\mathbf{k}_i| = |\mathbf{k}_f|$ or the incident and reflected rays have the same wavelength $\lambda$

Constructive interference: $d \cos \theta_i + d \cos \theta_f = d (n_i - n_f) = m \lambda$

or

$d (\mathbf{k}_i - \mathbf{k}_f) = 2\pi m$ \hspace{1cm} m integer

This is also equivalent to: $e^{-id (\mathbf{k}_i - \mathbf{k}_f)} = 1$

**Bravais lattice**

The condition of constructive interference has to be verified by all the lattice points, i.e.

$R (\mathbf{k}_i - \mathbf{k}_f) = 2\pi m$ \hspace{1cm} with $R$ Bravais lattice vector,

or

$(\mathbf{k}_i - \mathbf{k}_f) = \mathbf{G}$ \hspace{1cm} with $\mathbf{G} = 2\pi/R$ is a vector of the reciprocal lattice
Laue’s diffraction condition: $k_f = k_i \pm G$

Given an incident wave $k_i$, the diffraction spots are located by the $k_f$ vectors verifying:

1) $|k_i| = |k_f|$
2) $k_f = k_i \pm G$

**2D case or the case of a surface**

2D lattice described by $R_s$ implying $R_s (k_i - k_f) = 2\pi m$
or $(k_f - k_i)_\parallel = \Delta k_\parallel = \pm G_s$ with $G_s$ vector of the 2D reciprocal lattice

The diffraction spots is a map of the 2D reciprocal lattice

Example

$R_s = 1 \ a_1 + 1 \ a_2 = (a_1, a_2, 0)$
$G_s = s (1 \ a_1^* + 1 \ a_2^*) = s (2\pi/a_1, 2\pi/a_2, 0)$

$k_i = (0,0,1) \quad a_1^* = 2\pi/ a_1 \ a_1/ a_1$

$\quad a_2^* = 2\pi/ a_2 \ a_2/ a_2$

$k_f = (2\pi s/a_1, 2\pi s/a_2, c)$
with $c^2 = 1 - (2\pi s/a_1)^2 - (2\pi s/a_2)^2$
fcc(110)

(0,0) represents the reflected beam along the surface normal

fcc(100)

\[ a_1^* = \frac{2\pi}{a_1}, \quad a_2^* = \frac{2\pi}{a_2} \]
fcc(100) (2x2)
Graphene/Ir(111)

10 x 10 C atoms over 9 x 9 Ir atoms

$a_{Ir} = 0.27$ nm
$a_{c} = 0.245$ nm
Graphene/Ir(111)

$a_{Ir} = 0.27$ nm
$a_c = 0.245$ nm

10 x 10 C atoms over 9 x 9 Ir atoms -> Moiré structure
Electron penetration depth \( \lambda = 10-30 \text{ nm} \) at 40 keV for normal incidence

Surface sensibility if \( \cos \varphi = d/\lambda \) with \( d = 1-2 \) atomic layers

or

\[ \varphi \text{ about } 89^\circ \]

Vertical bars in place of spots because due to the geometry the technique is strongly sensible to surface defects (in the impinging direction)

Due to the grazing incidence the surface is seen as a continuous along the incidence direction (no diffraction) and consequently only the periodicity perpendicularly to the incidence direction is detected
The spectrum is visible only if the incident beam is aligned with a symmetry direction of the substrate.
RHEED sensibility to surface defects

Growth of GaAs(100) by Molecular Beam Epitaxy (MBE)


The intensity oscillations are a measure of the surface disorder

Oscillation period: 1 atomic layer
Intensity: decreasing with the number of deposited layers

Imperfect layer by layer growth

Maximum disorder at 0.5 ML during layer by layer growth
What advantages does RHEED offer over LEED?

Pro: 1) The geometry of the experiment allows much better access to the sample during observation of the diffraction pattern. This is particularly important if it is desired to make observations of the surface structure during growth of a surface film by evaporation from sources located normal to the sample surface or simultaneous with other measurements (e.g. AES, XPS).  
2) Experiments have shown that it is possible to monitor the atomic layer-by-atomic layer growth of epitaxial films by monitoring oscillations in the intensity of the diffracted beams in the RHEED pattern.

Con: 1) quality of the diffraction pattern frequently lower  
2) diffraction patterns have to be observed for at least two sample alignments with respect to the incident beam in order to determine the surface unit cell.
Transmission Electron Microscope (TEM)

Conceptually is identical to an optical microscope where electrons are used in place of photons.

\[ E = 75 \text{ keV} \rightarrow \lambda = 0.05 \text{ Å} \]

Theoretical resolution about hundred thousands times better than that of light.
Unfortunately, this theoretical resolution has never come even close to being attained. The basic draw back is that magnetic fields cannot be manipulated, shaped and grouped the way an optical engineer does with glass lenses.

There are several disadvantages of electron optics.
1) Electrons are easily effected by any mater they encounter. When they do encounter mater the interaction results in the emission of all the lower forms of energy. Such as x-rays, secondary electrons, ultraviolet, heat etc.
2) Complicate to describe the scattering process inside the object
3) The wave function resulting from the scattering process is falsified by the optical system
4) The electrons can not pass through air. As a result the microscope has to be kept in a high vacuum.
5) Our eyes are not sensitive to electrons so the operator must learn to focus the instrument using different focal clues than he is used to.

Advantages of TEM over light microscopes:
1) about a thousand fold increase in resolution
2) a hundred fold increase in depth of field.

TEM image of DNA
TEM images of a single-crystal MTJ with the Fe(001)/MgO(001)(1.8 nm)/Fe(001) structure. b is a magnification of a. The vertical and horizontal directions respectively correspond to the MgO(001) (Fe(001)) axis and MgO(100) (Fe(110)) axis. Lattice dislocations are circled. The lattice spacing of MgO is 0.221 nm along the [001] axis and 0.208 nm along the [100] axis. The lattice of the top Fe electrode is slightly expanded along the [110] axis.

Experimental analysis of charge redistribution due to chemical bonding by high-resolution transmission electron microscopy

Jannik C. Meyer\textsuperscript{1*,†}, Simon Kurasch\textsuperscript{1}, Hye Jin Park\textsuperscript{2}, Viera Skakalova\textsuperscript{2}, Daniela Künzel\textsuperscript{3}, Axel Groß\textsuperscript{3}, Andrey Chuvilin\textsuperscript{1,4}, Gerardo Algara-Siller\textsuperscript{1,5}, Siegmar Roth\textsuperscript{2,6}, Takayuki Iwasaki\textsuperscript{2}, Ulrich Starke\textsuperscript{2}, Jurgen H. Smet\textsuperscript{2} and Ute Kaiser\textsuperscript{1*}
Changing the focus conditions one gets different chemical contrast.

Figure 2 | Nitrogen dopants in graphene. Imaging conditions and filters in a-f are the same as in Fig. 1c,f. The red lines in the CTF plots (insets in a,d,h) indicate the 2.13 Å graphene lattice spacing. a-c, Scherzer defocus images. The dark contrast can be directly interpreted as atomic structure. However, the nitrogen substitution defects are not significantly above the noise (red circles). d-f, Larger defocus images (f2) of the same area as shown in a-c. The nitrogen defects are clearly detected as a smooth dark contrast (in any case, a filter (e,f) is needed to discern the N dopants against the much stronger signal of the single layer graphene lattice). The extended defect (red dashed line in a) allows us to compare the same atomic position in both focus values.
Magnetic nanoparticles

Particles with organic capping

![Diagram of Co$_2$(CO)$_8$ reaction and self-assembly via solvent evaporation]

Self-assembly via solvent evaporation

Assembly onto functionalized substrate via ligand exchange

Tunable size in the range 1-10 nm

Control of the particle volume:

HWHM = 15-20 %

Organic capping used as a spacer to define the array density
Annealing to about 600°C

Different contrast for the different atomic planes.

FCC chemically desordered A1 phase

As prepared

Tetragonal chemically ordered L1₀ phase

Problem: order loss after annealing

T = 20°C

T = 530°C

T = 600°C
**Enzymes** are proteins that catalyze \( (i.e., \text{increase the rate of}) \) chemical reaction

Interconvert carbon dioxide and bicarbonate to maintain acid-base balance in blood and other tissues, and to help transport carbon dioxide out of tissues.

\[
\text{CO}_2 + \text{H}_2\text{O} \xrightarrow{\text{Carbonic anhydrase}} \text{H}_2\text{CO}_3
\]

(in tissues with high \( \text{CO}_2 \) concentration)

\[
\text{H}_2\text{CO}_3 \xrightarrow{\text{Carbonic anhydrase}} \text{CO}_2 + \text{H}_2\text{O}
\]

(in lungs with low \( \text{CO}_2 \) concentration)

In humans the process works nicely
Can we understand how does it work?
Increasing the rate of chemical reaction is the dream of industry
Oxidation of methane to methanol

The methane oxidation is a difficult and expensive reaction because the methane is the most inert hydrocarbon (C-H bond is one of the most strong)

but

Methanotrophs bacteria use methane monooxygenase (MMO) enzymes to convert methane to methanol at ambient conditions !!!
monooxygenase (MMO)

MMO metal centers. (A) Mononuclear copper center. (B) Dinuclear copper center. (C) Zinc center. Oxygen atoms are colored red; nitrogen atoms are colored blue; Zinc atom in grey

Oxidation at the dinuclear copper center

Copper edge EXAFS data and simulations for MMO

Convention:
- EXAFS -> about 100 eV above absorption edge
- XANES -> around the absorption edge
EXAFS: Extended X-rays absorption fine structure

**Principle:**

1) photon in - electron out in vacuum
2) The emitted electron (described by a wave) is diffused by the neighboring atoms
3) Interference between emitted and diffused wave

The interference between emitted and diffused wave is constructive or destructive depending on:

1) The distance between the absorbing and diffusing atoms -> information on the crystallographic structure
2) The reflection coefficient of the diffusing atom -> information on the chemical environment
3) The wavelength of the emitted electron -> $E_{\text{kin}} = h\nu - E_{\text{edge}} = \frac{\hbar^2k^2}{2m} = \frac{\hbar^2}{2m\lambda^2}$
\[ \lambda = \frac{h}{2m(h\nu - E_K)^{1/2}} \]

Interference conditions depend on the in-coming photons

**EXAFS expression**

\[ \chi(k) = \frac{(\mu(k) - \mu_0(k))}{\mu_0(k)} = 1/k \sum_{i}^{\text{atoms}} S_0^2 N_i(e_i)/R_i^2 A_i(k) \exp(-2R_i/\lambda(k)) \exp(-2k^2\sigma_i^2) \sin(2kR_i + 2\delta_i + \phi_i) \]

Amplitude factor
Attenuation factor:
- reduced electronic mean free path
- Debye-Waller term:
- thermal vibrations and crystallographic disorder
- Phase factor

\[ kR_i \rightarrow \text{phase due to the distance between absorbing and diffusing atom} \]
\[ \delta_i \rightarrow \text{phase due to the propagation in the potential of the absorbing atom} \]
\[ \phi_i \rightarrow \text{phase due to the propagation in the potential of the diffusing atom} \]

\[ k \chi(k) \text{ is a summation over sinusoid functions} \]

The Fourier transform of \( k \chi(k) \) gives information on the phase factor or on the atomic distance.
Present interest in chalcogenide glasses is driven by the ability of a particular composition (\(\text{Ge}_2\text{Sb}_2\text{Te}_5\), or GST) to be repeatedly switched between crystalline (c) and amorphous (a) states by application of light or electrical pulses of suitable intensities and durations. Differences in the properties of the a and c materials (e.g., reflectivity) allows for device applications.

**Fragments of the local structure of GST around Ge atoms in the crystalline (left) and amorphous (right) states.** Stronger covalent bonds are shown as thicker lines whereas weak interblock bonds are shown as thinner lines.

**The crystal structure of laser-amorphized GST.** A schematic twodimensional image of the lattice distortion of the rocksalt structure due to charge redistribution between the constituent elements; atoms that form the building block of the GST structure are shown using thick lines. The arrows indicate displacements of atoms from the ideal rocksalt positions.
Spectra measured at the K-edges of: a) Ge, b) Sb and c) Te. On amorphization the bonds become shorter (as shown by shifts in the peak positions) and stronger, that is, more locally ordered (as shown by increases in the peak amplitudes and concurrent decreases in the peak widths). The peak positions are shifted from the actual interatomic distances towards lower r because of the photoelectron phase shift $\delta(k)$ in the phase factor of the EXAFS oscillations. Additionally, contributions from different nearest neighbors interfere producing extra features in the FTs.

<table>
<thead>
<tr>
<th>Bond</th>
<th>From EXAFS</th>
<th>Bond length (Å)</th>
<th>From XRD</th>
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<tbody>
<tr>
<td>Ge–Te</td>
<td>$2.83 \pm 0.01$</td>
<td>$3.0(1) \pm 0.3$</td>
<td></td>
</tr>
<tr>
<td>Sb–Te</td>
<td>$2.91 \pm 0.01$</td>
<td>$3.0(1) \pm 0.3$</td>
<td></td>
</tr>
<tr>
<td>Te–Te (2nd)</td>
<td>$4.26 \pm 0.01$</td>
<td>$4.2(6) \pm 0.2$</td>
<td></td>
</tr>
<tr>
<td>Ge–Te</td>
<td>$2.61 \pm 0.01$</td>
<td>$2.61^*$</td>
<td></td>
</tr>
<tr>
<td>Sb–Te</td>
<td>$2.85 \pm 0.01$</td>
<td></td>
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