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) at different depths
c) 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.

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

\( H(r) \) 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

\[ k_i \quad k_f \]

E = 10 – 500 eV

RHEED

\[ k_i \quad k_f \]

E = 10 – 200 keV

TEM

\[ k_i \quad k_f \]

E = 10 – 200 keV

Electron mean free path

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

Energy (eV)

\[ 1 \quad 10 \quad 100 \quad 1000 \]
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,

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

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

- \( h \) Planck constant = 6.6 \( \times \) 10\(^{-34}\) J s
- \( m \) electron mass = 9.1 \( \times \) 10\(^{-31}\) Kg
- \( v \) electron velocity
- \( E \) electron kinetic energy
- \( e \) electron charge = 1.6 \( \times \) 10\(^{-19}\) C

Example:

1) Electron energy = 20 eV \( \rightarrow \) Wavelength = 2.7 Å
2) Electron energy = 200 eV \( \rightarrow \) Wavelength = 0.87 Å

\( \lambda \) comparable to the atomic spacing

N.B.: Electron energy = 2 eV \( \rightarrow \) Wavelength = 8.5 Å i.e. the hypothetical ‘RLEED’ would have low resolution
In the case of many scatter points the scattered wave is given by:
$$\sum_j f_j(\theta, r_j) e^{i r_j k_f}$$

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.
Two points scattering

\[ d \cos \theta_i = d \mathbf{n}_i \]
\[ d \cos \theta_f = -d \mathbf{n}_f \]

Elastic scattering: \[ |\mathbf{k}_i| = |\mathbf{k}_f| \] or the incident and reflected rays have the same wavelength \( \lambda \)

Constructive interference: 
\[ d \cos \theta_i + d \cos \theta_f = d (\mathbf{n}_i - \mathbf{n}_f) = m \lambda \]
\[ \text{or} \]
\[ d (\mathbf{k}_i - \mathbf{k}_f) = 2\pi m \quad m \text{ integer} \]

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.
\[ \mathbf{R} (\mathbf{k}_i - \mathbf{k}_f) = 2\pi m \quad \text{with } \mathbf{R} \text{ Bravais lattice vector}, \]

\[ (\mathbf{k}_i - \mathbf{k}_f) = \mathbf{G} \quad \text{with } \mathbf{G} = 2\pi/\mathbf{R} \text{ is a vector of the reciprocal lattice} \]
Laue’s diffraction condition: \( \mathbf{k}_f = \mathbf{k}_i \pm \mathbf{G} \)

Given an incident wave \( \mathbf{k}_i \), the diffraction spots are located by the \( \mathbf{k}_f \) vectors verifying:

1) \( |\mathbf{k}_i| = |\mathbf{k}_f| \)
2) \( \mathbf{k}_f = \mathbf{k}_i \pm \mathbf{G} \)

2D case or the case of a surface

2D lattice described by \( \mathbf{R}_s \) implying \( \mathbf{R}_s (\mathbf{k}_i - \mathbf{k}_f) = 2\pi m \)
or \( (\mathbf{k}_f - \mathbf{k}_i)_{\parallel} = \Delta \mathbf{k}_{\parallel} = \pm \mathbf{G}_s \) with \( \mathbf{G}_s \) vector of the 2D reciprocal lattice

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

Example

\( \mathbf{R}_s = 1 \mathbf{a}_1 + 1 \mathbf{a}_2 = (\mathbf{a}_1, \mathbf{a}_2,0) \)
\( \mathbf{G}_s = s (1 \mathbf{a}_1^* + 1 \mathbf{a}_2^*) = s (2\pi/\mathbf{a}_1, 2\pi/\mathbf{a}_2,0) \)

\( \mathbf{k}_i = (0,0,1) \)

\( \mathbf{k}_f = (2\pi s/\mathbf{a}_1, 2\pi s/\mathbf{a}_2, c) \)

with \( c^2 = 1 - (2\pi s/\mathbf{a}_1)^2 - (2\pi s/\mathbf{a}_2)^2 \)

\( \mathbf{k}_f \) stays on the surface of a sphere
Example: fcc(100)

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

fcc(110)

\[ a_1^* = \frac{2\pi}{a_1} \]
\[ a_2^* = \frac{2\pi}{a_2} \]
fcc(100) (2x2)

Diffraction Pattern

fcc(100) (√2x√2) R45 [c(2x2)]

Diffraction Pattern
Graphene/Ir(111)

10 x 10 C atoms over 9 x 9 Ir atoms

\[ a_{Ir} = 0.27 \text{ nm} \]
\[ a_c = 0.245 \text{ nm} \]
Graphene/Ir(111)

The diffraction pattern contains information on the structure of Ir(111), graphene, and the moiré structure.

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

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

Surface sensibility if $\cos \varphi = \frac{d}{\lambda}$ with $d = 1$-$2$ atomic layers or

$\varphi$ 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 of the specular spot 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 drawback is that magnetic fields can not 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 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

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Figure 1 | Charge distribution, projected potentials and TEM simulations for nitrogen-doped graphene. a, Relaxed atomic configuration for a nitrogen substitution in graphene. Bond lengths are given in angstroms. b, Projected potential based on the IAM, with the periodic components of the graphene lattice removed, and bandwidth-limited to our experimental resolution (about 1.8 Å). Dark contrast corresponds to higher projected potential values, in accordance with our TEM imaging conditions. c, TEM simulation based on the IAM potential, for two experimental conditions ($f_1$ and $f_2$, see text). Filters are: (i) unfiltered, (ii) periodic components removed by a Fourier filter, and (iii) low-pass filtered. d, Atomic structure (same bond lengths), with the changes in projected electron density due to bonding shown in colour. Blue corresponds to a lower, red to a higher electron density in the DFT result as compared with the neutral-atom (IAM) case. e, Projected potential, filtered as in b, based on the all-electron DFT calculation. f, TEM simulations using the DFT-based potentials. The greyscale calibration bar applies to columns (ii) and (iii), which are all shown on the same greyscale range for direct comparison. The scale bars are 5 Å.

The dopant atom change the local scattering potential.
Changing the focus conditions one gets different chemical contrast
Magnetic nanoparticles

Particles with organic capping

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: \( \text{HWHM} = 15-20 \% \)

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

FCC chemically desordered A1 phase

As prepared

Tetragonal chemically ordered L1₀ phase

Different contrast for the different atomic planes

Problem: order loss after annealing

T=20°C  

T=530°C  

T=600°C
Enzymes are proteins that catalyze (i.e., 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 CO\textsubscript{2} concentration)

\[
\text{H}_2\text{CO}_3 \xrightarrow{\text{Carbonic anhydrase}} \text{CO}_2 + \text{H}_2\text{O}
\]  
(in lungs with low CO\textsubscript{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.
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) however Methanotrophs bacteria use methane monooxygenase (MMO) enzymes to convert methane to methanol at ambient conditions !!!
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, Copper in blue

Oxidation at the dinuclear copper center


Copper edge EXAFS data and simulations for MMO
Convention:
- EXAFS $\rightarrow$ about 100 eV above absorption edge
- XAS $\rightarrow$ around the absorption edge

The electrons emitted in vacuum are diffracted by the atoms $\rightarrow$ information about the local structure
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 -> $E_{\text{kin}} = h\nu - E_{\text{edge}} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{(2m\lambda^2)}$
\[ \lambda = \frac{h}{2m(h \nu - E_K)^{1/2}} \]

Interference conditions depend on the in-coming photons

**EXAFS expression**

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

<table>
<thead>
<tr>
<th>Amplitude factor</th>
<th>Attenuation factor:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>reduced electronic mean free path</td>
</tr>
<tr>
<td>Debye-Waller term:</td>
<td>thermal vibrations and crystallographic disorder</td>
</tr>
<tr>
<td>Phase factor</td>
<td></td>
</tr>
</tbody>
</table>

\( kR_i \rightarrow \) phase due to the distance between absorbing and diffusing atom \( \delta_i \rightarrow \) phase due to the propagation in the potential of the absorbing atom \( \phi_i \rightarrow \) phase due to the propagation in the potential of the diffusing atom

\( k \chi(k) \) 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 \((\text{Ge}_2\text{Sb}_2\text{Te}_5, \text{or GST})\) 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>From XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallized state</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge–Te</td>
<td>2.83 ± 0.01</td>
<td>3.0(1) ± 0.3</td>
</tr>
<tr>
<td>Sb–Te</td>
<td>2.91 ± 0.01</td>
<td>3.0(1) ± 0.3</td>
</tr>
<tr>
<td>Te–Te (2nd)</td>
<td>4.26 ± 0.01</td>
<td>4.2(6) ± 0.2</td>
</tr>
<tr>
<td>Laser-amorphized state</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge–Te</td>
<td>2.61 ± 0.01</td>
<td>2.61*</td>
</tr>
<tr>
<td>Sb–Te</td>
<td>2.85 ± 0.01</td>
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