

Surface Microscopy and Spectroscopy

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One of the most remarkable aspects in the study of surfaces is that their properties can be extremely different from those of the corresponding bulk material. The broken symmetry at the surfaces is reflected on electronic properties. For example, electron can be trapped between two barriers: image potential barrier introduced by surface, and a gap in the projection of bulk electronic on the particular surface, resulting in 2D surface states. Also on some surfaces surface reconstruction may take a place.

In addition to this, the relative importance of the surfaces increases for smaller structures. This is particularly relevant for nano-technology where surfaces are often used as templates for assembling nano objects.

Methods

There is a great variety of surface experimental techniques giving information about: atomic structure, electronic structure, thermal excitations, chemical composition, adsorption and desorption phenomena.

Several surface sensitive techniques used in our research are:

- X-ray Photoemission Spectroscopy (XPS - 200 to 2000 eV source),
- Ultraviolet Photoemission Spectroscopy (UPS - 10 to 50 eV source),
- Auger Electron Spectroscopy (AES),
- Low Energy Electron Diffraction (LEED),
- Scanning Tunneling Microscopy (STM).

Photoemission spectroscopy is the main powerful technique to gain information of the electronic structure on the surfaces.

Electron beams are often used to create core hole in the atom. Auger spectroscopy is based on the analysis of electrons emitted from an excited atom after internal relaxation events. The energy of the Auger electron is characteristic of the chemical element.

To access information on surface structure, Low Energy Electron Diffraction (LEED) is often used. In LEED experiments, the diffraction pattern of elastically scattered electrons on well ordered surface layers reflects the symmetry of the surface structure in reciprocal space. Information is integrated over a millimeter scale.

Finally, Scanning tunneling microscopy (STM) and Atomic force microscopy (AFM) were developed for structural investigation of surfaces on atomic level in real space and today these techniques are employed to investigate much broader area of surface properties (ranging from electronic structure performed by STM to identification of chemical character of individual atoms performed by AFM).

The common concept of all Scanning probe microscopy (SPM) techniques is that the scanning across the surface is performed by an extremely sharp tip, giving information on surface structure. STM enables real space imaging of conducting and semi-conducting surfaces down to the atomic scale. The AFM allows the imaging of the topography of conducting and insulating surfaces.

In this contribution the focus is on angle-resolved photoemission spectroscopy (ARPES) and STM experimental techniques.

ARPES

In photoemission spectroscopy the penetration depth of photons is around 500 to 1000 Å, but because of the short mean free path of electrons, only electrons created near the surface (in few atomic layers) are able to escape in vacuum and reach the analyzer. That makes the technique surface sensitive [1].

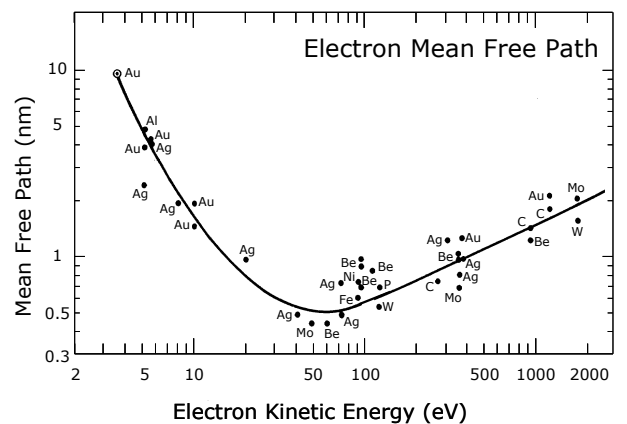


Figure 1. Electron mean free path (“Universal curve”).

The main characteristic of ARPES is its momentum selectivity. This allows the dispersion of the electronic bands of atomically ordered surfaces to be measured.

The electronic band structure is mapped from kinetic energy of emitted electrons and direction of emission or more precisely, wave vectors of emitted electrons. The band dispersion is accessible by subsequent measurements of photoemission intensities at different polar angles, which are changed by rotation (changing of polar angle) of the sample with the respect to the entrance slit of the analyzer.

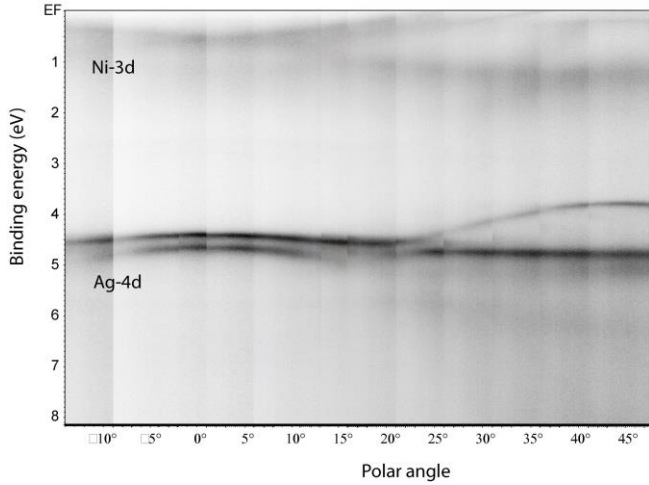


Figure 2. The photoemission intensity map of 1 ML of Ag on Ni(111) measured along Γ -M high symmetry line .

Of general interest in Surface Science lab is studying of low dimensional electronic systems on metallic surfaces. Ultrathin films (UTF) are representative examples of two-dimensional nanosystems. Due to existence of gap in the projection of substrate bulk electronic structure on surface or even symmetry gap (bands of different symmetries with respect to the states in the film exist), perpendicular to the surface the UTF electronic system may be quantized (k_{\perp} is fixed) and the quantum well (QW) states may be formed. Several examples are given in Figure 3.

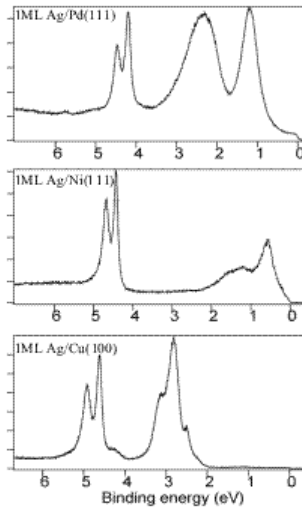


Figure 3. Energy distribution curves (EDC) extracted from ARPES spectra displaying QWS (double peak structure) in 1ML Ag films.

Recently the focus of research is aimed on graphene (Nobel prize 2010.), the material specific by its electronic structure (Dirac cones) that is characterized by zero effective mass for electrons and holes (acting as relativistic Dirac fermions) near the six corners of the 2D hexagonal Brillouin zone near the Fermi level. The electronic structure of graphene can be modified (to larger or minor extent) when graphene layer is supported by metal surface. ARPES measure the degree of hybridization with substrate states. Experiments with graphene on Ir(111) show that graphene

electronic structure is barely affected by the substrate [2]. Furthermore, decoupling of graphene is investigated through alkali metal intercalation.

Besides mapping of surface valence band structure, one can extract other valuable information from ARPES spectra. High energy and momentum resolution ARPES instrumentation allows a study of the lifetime of states near Fermi level.

In “one electron model” [3] in which quasiparticle states are introduced the intensity of photocurrent is given by:

$$I(\vec{k}, E) = |M|^2 A(\vec{k}, E) f(E)$$

where M is the matrix element between initial and final state, f represents Fermi function excitation from occupied states, and A is single particle spectral function of the hole state.

The spectral function is what we actually measure in ARPES spectra:

$$A(\vec{k}, E) = \frac{1}{\pi} |G(\vec{k}, E)|.$$

In interacting electron system spectral function is:

$$A(\vec{k}, E) = \frac{1}{\pi} \frac{\text{Im} \Sigma(\vec{k}, E)}{[E - E_{\vec{k}}^0 - \text{Re} \Sigma(\vec{k}, E)]^2 + \text{Im} \Sigma(\vec{k}, E)}$$

Complex self-energy contains the effect of many-body interactions:

$$\Sigma(\vec{k}, E) = \text{Re} \Sigma(\vec{k}, E) + i \text{Im} \Sigma(\vec{k}, E)$$

Re-gives a shift in energy and mass enhancement, Im-gives a lifetime broadening.

Recently Laser-ARPES system [4] has been developed to study electron band dispersion with increased spectral resolution and to access bulk bands at low kinetic energy side of “Universal curve” (Electron mean free path curve). Another aspect of using Laser-ARPES is to get the electron dynamics through pump-probe experiments.

STM

STM is based on quantum tunneling between two electrodes, atomically sharp tip and a conducting surface separated by less than a nanometer. Applied bias voltage between electrodes gives rise to the tunneling current.

According to Bardeen approach the probability of tunneling is given by matrix element (actually M^2) containing overlap of the wave functions of tip and sample. In simplified Tersoff-Hamann model, the tip wave function is approximated by s-wave function. Following from this approximation, tunneling current is proportional to LDOS of the sample:

$$I \propto V \sum_v |\Psi_v^s(\vec{r}_0)|^2 \delta(\varepsilon_v - \varepsilon_F)$$

where V is bias voltage and Ψ_v^s is a wave function of the sample.

In STM experiments, the tip is moved by applying voltage on piezo elements. Scanning the surface results in curves which present LDOS corrugation.

The electronic properties of UTF may be significantly affected by their growth and structural

properties. One such example is the formation of 1 monolayer Ag film on Cu(100) substrate, where the increase in splitting of two peaks in photoemission spectra is due to the structural changes that take place during the growth process [5].

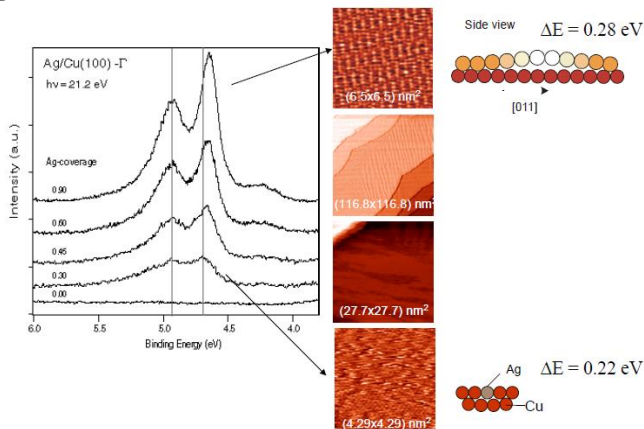


Figure 4. Photoemission spectra of Ag 4d region showing the increase of peak splitting when the system changes from individually alloyed Ag atoms in Cu matrix to separated Ag layer on the Cu surface, as visualized by STM images.

In some STM experiments forces between tip and sample are used to manipulate atoms on surfaces, which is particularly useful at low temperatures (at which atom diffusion on surface is suppressed) allowing assembling of nanostructures atom by atom (e.g. quantum corrals).

Besides LDOS corrugation obtained in STM experiments, information on the electronic structure at a given location in the sample can be obtained in Scanning tunneling spectroscopy (STS) experiments. In the most frequently used mode by sweeping voltage at a constant height over sample surface and measuring current at a specific site, dI/dV signal directly proportional to LDOS at distinct energies is recorded. The proportionality holds for small bias voltages.

The latest topic to gain fundamental information on electronic structure will be dedicated to topological insulators.

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