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The interaction of water and hydrogen with nickel surfaces

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Citation

Shan, J. (2009, November 11). *The interaction of water and hydrogen with nickel surfaces*. Retrieved from <https://hdl.handle.net/1887/14365>

Version: Corrected Publisher's Version

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Chapter 2

Experimental setup and techniques

2.1 Ultra-high vacuum system

The experiments described in this thesis are carried out in an ultra-high vacuum system. The system consists of two chambers, the top level and the lower level, separated by a gate valve. The top chamber contains a quadrupole mass spectrometer (Balzers QMS 422), an ion sputter gun, an atomic hydrogen source (tectra), a stainless steel gas doser, and a home-built capillary array doser [1]. The lower level contains an upgraded ELS22 high resolution electron energy loss spectrometer and an Auger Electron spectrometer ((Staib Instruments). A detailed description of the sample preparation and experimental procedures will be presented in subsequent chapters, hence only a brief description is given here.

The top level is also called the preparation chamber, which consists of a stainless steel cylinder with a length of 0.178 m and a diameter of 0.2 m, vertically mounted on top of the lower level. A base pressure of 3×10^{-11} mbar is achieved in this chamber by running a turbodrag pump (230 l s^{-1} for N_2). The turbodrag pump is backed by a rotary vane pump. The quadrupole mass spectrometer is used for analysis of the residual gas, as well as to perform temperature-programmed desorption experiments. The cleaning of the sample and the gas dosing is also performed in this chamber.

The lower level is also called the characterization chamber, which also consists of a stainless steel vessel with a nearly cylindrical shape. The length of the vessel is 0.55 m and the diameter is 0.57 m. A turbodrag pump (230 l s^{-1} for N_2) in combination with a rotary vane pump pumps the characterization chamber. The chamber is also equipped with a titanium sublimation pump, and an ion pump. These pumps keep the base pressure at approximately 2×10^{-10} mbar for the lower chamber with the gate valve closed. With the gate valve open, the base pressure drops to below 1×10^{-10} mbar.

The sample is mounted vertically on a manipulator allowing for sample movement. Translation along the axis of the two cylinder vessels is motorized, while translation in the

two perpendicular directions to the axis of the two cylinders can be performed manually over a range of 2.5 cm. A rotary feedthrough, pumped with a rotary vane pump, allows for a motorized rotation of 360 degree. A copper block is mounted on the manipulator, through which liquid nitrogen can be flowed. The single crystal Ni(111), cylindrical with a diameter of 10 mm and a thickness of 1 mm, is fixed to two molybdenum legs. These two legs with the sample are screwed onto the copper block. Heating is performed from the back of crystal by a tungsten filament in combination with a high voltage applied to the sample, allowing electron bombardment. The sample can be heated to 1200 K and cooled to 85 K. The crystal temperature is measured by a chromel-alumel thermocouple spot welded to the edge of the crystal.

2.2 Temperature-programmed desorption

Temperature-programmed desorption (TPD) belongs to the larger class of the thermal desorption techniques. If a metal sample is heated in a vacuum, the rate of gas evolution from the metal surface changes noticeably with temperature and, moreover, there may be several temperatures for which the evolution rate goes through a relative maximum. The rate of gas evolution increases with surface temperature, resulting in an instantaneous rise of the gas density. The rise of pressure of a certain mass or masses is detected by means of a mass analyzer. There are two approaches to thermal desorption techniques [2]. First in flash desorption, the increase in the temperature of the sample is such that the desorption rate is much higher than the rate at which gas is pumped out of the system. The data analysis is similar to that of desorption performed in a closed system with no pumping. Second, one can use a lower rate of temperature increase of the sample (between 15 seconds to several minutes). As the temperature rises, particular species are able to desorb from the surface of the sample to gas phase. Since the temperature increase is rather slow, the partial pressure due to desorption continues to increase. As the temperature increases still further the amount of species on the surface will reduce. Thus the relative pump rate increases, causing the pressure to drop again. This results in a peak in the pressure versus temperature plot. In contrast to flash desorption, the desorption of a particular binding state

results in a peak in the pressure-temperature curve rather than the rise to a plateau. Such technique is called the TPD technique.

Experimentally, TPD consists of applying a constant temperature ramp (typically in the range of $0.5\text{-}6\text{ Ks}^{-1}$) to the crystal and detecting the desorbing species in the gas phase as a function of surface temperature. The desorption temperature is related to the bond energy of bound species; a higher desorption temperature normally indicates the larger bonding energy of the adsorbate to the surface. In the case of a multilayer system, the bond energy of the first layer bonded to the substrate is generally larger than that experienced in between layers. For this reason, as described in Chapter 3, a multilayer peak usually occurs in the TPD spectrum at distinctly lower temperature than the (sub)monolayer peak. In addition, TPD measurement can also provide information about intermediate species and reaction products, in connection with a particular surface reactivity [3].

In this thesis, the TPD experiments were carried out using a quadrupole mass spectrometer together with a temperature controller (Eurotherm). The temperature controller can regulate the sample temperature by adjusting the current flowing through the filament behind the crystal. Typically, linear heating rates of 1 Ks^{-1} are used. With the QMS used here, 16 masses can be measured simultaneously in a mass range from 1 up to 511 atomic mass units (a.m.u.).

2.3 High resolution electron energy loss spectroscopy

In surface science, many techniques use electrons, as the probe. For example low energy electron diffraction (LEED), reflection high energy electron diffraction (RHEED), Auger electron spectroscopy (AES), and electron energy loss spectroscopy (EELS) are included in such techniques. Among these techniques, EELS employs the electrons both as the probe and the analyzed particles, which means that the electrons are used as a means of excitation, as well as the entities that carry information back from the surface. Using EELS, localized vibrational and rotational modes of adsorbed molecules can be studied as well as electronic transitions, with high resolution, which makes EELS an indispensable tool in surface science. The study of vibrations by electron energy loss is often called High Resolution

Chapter two

Electron Energy Loss Spectroscopy (HREELS) to differentiate it from the study of electronic transitions.

The primary energy of the electrons in HREELS is typically only between 4 and 100 eV, and the energy losses go up to a few hundred meV when only considering vibrational modes. Therefore, not only must the analyzer be capable of high-energy resolution, but also the incident beam must be highly monochromatic. Monochromators are used to obtain a narrow distribution of the electron energy. These electrons are thus within an energy window not broader than a few meV. Both hemispherical and cylindrical electrostatic electrons can be used as the monochromator. Monochromatic electrons are focused in a well defined direction onto the sample surface. The majority are elastically scattered, while, a small number of electrons will lose or gain a certain amount of energy in the interaction with the sample. Energy gain processes are very weak and can be neglected in most studies [4]. For the electrons scattered from the surface, there are two scattering mechanisms, impact scattering and dipole scattering.

In impact scattering, the electron is scattered by a local atomic potential. The electron bounces off the scatterer (adsorbate or surface phonon), experiencing a short range interaction and exchanging momentum. The momentum exchange is observed by a quasi-isotropic distribution of the scattered electrons. The scattering cross-section increases with increasing primary electron energy in impact scattering. In dipole scattering, the electron is scattered by the interaction of the electric field of the moving electron with the dipole field of the surface excitations. This is therefore a long range interaction. The momentum transfer in the dipole scattering is very small. Therefore the scattered electron pathway is very close to the specular direction. To be precise, dipole inelastically scattered electrons are distributed within a narrow lobe around the specular direction. In dipole scattering, the scattering cross-section decreases with increasing primary electron energy. It is evident that impact scattering and dipole scattering can be distinguished experimentally by the angular distribution of the inelastically scattered electrons around the specular direction. Strong peaking of the scattered intensity in this direction clearly indicates scattering in dipole fields. HREELS measurements are most often performed at or in the near vicinity of the

specular direction. These two different scattering mechanisms are shown in figure 2.1. The detailed description of the theory of HREELS can be found in Ref 4.

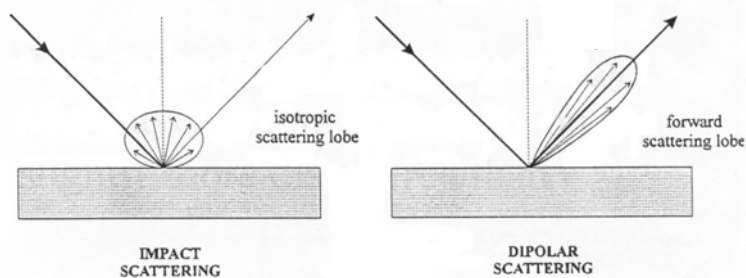


Figure 2.1 Impact scattering and dipole scattering.

A schematic drawing of the HREELS apparatus used in our studies is shown in Figure 2.2. The electron source (emission gun) and the two monochromators, pre-monochromator and main monochromator are on the right hand side. The scattering chamber is in the centre and the analyzer unit is on the left. The unit on the right side is rotatable, and the unit on the left side is fixed. The electrons are emitted from a filament and then selected and focused by the two monochromators thus allowing only electrons in a small energy range to reach the sample. Following interaction with the sample, the majority of the electrons enter the analyzer. After passing through the analyzer, electrons are directed towards the detector which is a channel electron multiplier. Data of the HREELS are acquired with the help of computer programs.

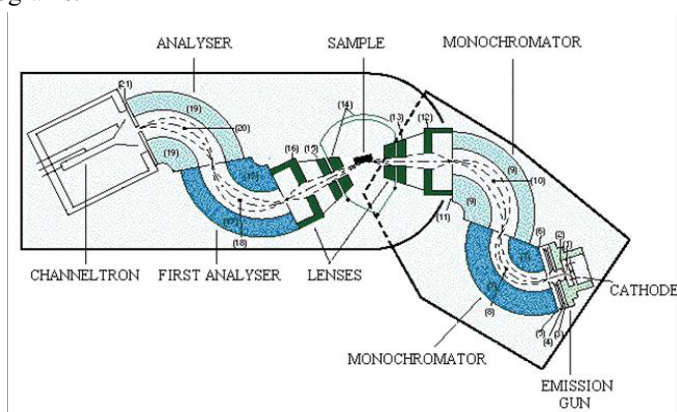


Figure 2.2 Schematic drawings of the HREELS apparatus, adopted from Ref 5.

2.4 Auger electron spectroscopy

Auger Electron Spectroscopy (AES) was developed in the late 1960's, and has become a popular technique for determining the composition of the top few layers of a surface. It cannot detect hydrogen or helium, but is sensitive to all other elements, being most sensitive to the low atomic number elements.

The theory of AES is based on the process of relaxation of the Auger electron, which is first discovered by Pierre Auger, a French physicist. In this process, electrons with energy of 3-20keV are incident upon a sample. These electrons cause core electrons from atoms contained in the sample to be ejected, which results in a photoelectron and an atom with a core hole. The atom then relaxes via electrons with a lower binding energy dropping into the core hole. The energy thus released can be converted into an X-ray or emit an electron. This electron is called an Auger electron. This scheme of this process is illustrated in Figure 2.3. After the emission of the Auger electron, the atom is left in a doubly ionized state. The energy of the Auger electron is characteristic of the element that emitted it. Thus in AES, measuring the energy of the Auger electron can identify the element in the sample.

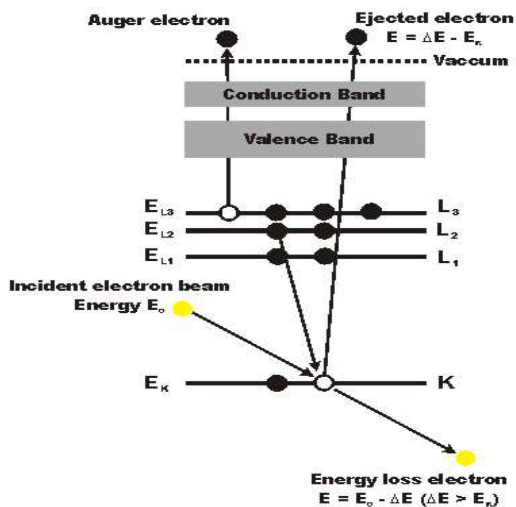


Figure 2.3 A scheme of the process of relaxation of the Auger electron.

Quantitative compositional and chemical analysis of a sample using AES is dependent on measuring the yield of Auger electrons during a probing event. Electron yield, in turn,

depends on several critical parameters such as electron-impact cross-section and fluorescence yield. Since the Auger effect is not the only mechanism available for atomic relaxation, there is a competition between radiative and non-radiative decay processes to be the primary de-excitation pathway. Generally, for heavier elements, x-ray yield becomes greater than Auger yield, indicating an increased difficulty in measuring the Auger peaks for large Z-values. Conversely, AES is sensitive to the lighter elements. For detailed descriptions of AES see Ref 6.

2.5 References

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