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Study of optical and electronic properties of nickel from reflection electron energy loss spectra

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ABSTRACT

We use the classical Monte Carlo transport model of electrons moving near the surface and inside solids to reproduce the measured reflection electron energy-loss spectroscopy (REELS) spectra. With the combination of the classical transport model and the Markov chain Monte Carlo (MCMC) sampling of oscillator parameters the so-called reverse Monte Carlo (RMC) method was developed, and used to obtain optical constants of Ni in this work. A systematic study of the electronic and optical properties of Ni has been performed in an energy loss range of 0–200 eV from the measured REELS spectra at primary energies of 1000 eV, 2000 eV and 3000 eV. The reliability of our method was tested by comparing our results with the previous data. Moreover, the accuracy of our optical data has been confirmed by applying oscillator strength-sum rule and perfect-screening-sum rule.

1. Introduction

The physical properties of solids are commonly studied by the response of various kinds of particle beams. The optical and electronic properties are mostly studied employing photon- or electron- probing techniques. Typically, reflection spectroscopy, absorption spectroscopy and spectroscopic ellipsometry are the widely-used techniques to study optical properties of a sample, which are well-established [1–3] and nowadays are routinely carried out with commercial equipment. The handbook of optical constants edited by Palik [2,3] has included most elemental solids in the periodic table along with many compounds. However, with the demands of scientific development the optic techniques have reached their limitations. For instance, these measurements are usually performed under atmospheric condition. Surface cleanliness is thus definitely not guaranteed, and, reflection experiments tend to be sensitive also to the surface roughness. In addition, the energy region of the measured optical constants is directly constrained by the light source. To obtain data in a high photon energy region, synchrotron radiation source and ultra-high vacuum (UHV) have to be integrated, which makes a laboratory measurement difficult. Last but not least, advances in nanoscience requires characterization techniques with high spatial resolution. This is impossible by using a photon probe because it is hard to focus it into a sub-nanometer size. Since the advent of electron energy-loss spectroscopy (EELS), it was realized that the optical properties and electronic structure of a solid sample can be obtained from EELS spectra. EELS are routinely carried out under UHV condition and it is not as sensitive to surface roughness as optical reflection experiment. Furthermore, electrons can easily be focused into the sub-nanometer range. Most importantly, EELS technique allows the determination of optical data in a wide range of energy loss (or photon energy) in one measurement, which is typically 0–100 eV or larger. Historically EELS was developed and studied firstly at the transmission mode with a transmission electron microscope and various theoretical models and approaches [4,5] have been proposed during the last decades. But, such a transmission mode requires very high incident beam energy and thin, free-standing film sample. Considering these limitations, the EELS in the reflection mode, i.e. reflection electron energy loss spectroscopy (REELS) has shown an advantage. In a REELS experiment, typical incident energy of primary electrons would be several hundreds of or several thousands of eV with a surface electron spectrometer. There is no special requirements for the sample thickness.

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To derive the photon energy or frequency ω-dependent optical constants from a measured REELS spectrum, where the energy loss is $\Delta E = \hbar\omega$, it is necessary to establish a theoretical model for relating the dielectric function $\varepsilon(\omega)$, or specifically in this work the bulk energy loss function (ELF), $\mathrm{Im}[-1/\varepsilon(\omega)]$, of the sample with the measured spectrum shape and intensity. Because of the presence of sample surface and the oblique incidence geometry of experiment, the surface excitation effect is profound and complicates the theoretical description of REELS data. In the past twenty years, several models and approaches are proposed to deal with this issue [6–15]. Some of the works [6–8,15] employed an analytical algorithm [16] to remove multiple scattering effects, where REELS spectrum is analytically expressed as multi-convolutions of a single inelastic scattering distribution, i.e. the differential inverse inelastic mean free path (DIIMFP), excluding elastic scattering. A modification has been made by simply applying a scaling factor to account for elastic scattering effect [9,10]. In this way an effective ELF with ambiguous physical meaning, i.e. the bulk ELF mixed with surface ELF, would be obtained. Further, a REELS spectrum was analytically separated into surface- and bulk-excitations in order to obtain the pure bulk ELF [11,17,18]. In spite of these advances promoted in understanding of electron-solid interactions and in providing valuable optical data for some metals [18], the analytical modeling has serious problems: calculation requires pre-knowledge of electron inelastic mean free path (IMFP) and surface excitation parameter (SEP) as input parameters, which behaves as logical contradiction since such parameters should be determined by ELF. Another problem is the assumption of homogenous scattering property of the sample, while, for example, the surface excitation is in fact depth dependent. In addition, a non-physical scaling factor is frequently introduced for compensation to the absent or insufficient description of elastic scattering. Furthermore, the REELS spectrum shape is actually sensitive to the ratio of scattering cross sections between elastic scattering and inelastic scatterings and thereby also the ELF.

To solve these problems, the Monte Carlo (MC) modeling of REELS spectrum is the most powerful theoretical tool which can provide the spectrum intensity in agreement with experimental measured one, based on a complete physical model of electron elastic and inelastic scattering (including bulk- and surface-excitations), once the bulk ELF is known [19–21]. This allows the determination of bulk ELF through the comparison of the simulated REELS spectrum based on an assumed ELF with experimental spectra. For this a reverse Monte Carlo (RMC) technique has been recently developed; it was demonstrated for SiO_2 that the obtained dielectric function agrees with Palik's optical data [14]. In the present work, this RMC method is further improved and applied for the determination of ELF of Ni metal for which the previous data obtained with REELS spectrum and by optical methods have shown a large discrepancy.

The RMC technique is based on a pure physical modeling of electron transport in the solid. However, to save computation consumption a simplification has been made in the previous work on the modeling of electron inelastic scattering by assuming that DIIMFP can be expressed as a simple linear combination of the surface- and bulk-ELFs, and hence ignoring the depth dependence of the surface excitation [14]. In this work, the surface excitation is fully described by the depth-dependent DIIMFP, which is obtained from a semi-classical dielectric response theory [22,23]. The aim of the work is to determine optical constants of Ni in a wide energy range between 0 and 200 eV. The validity of the present optical constants is verified with the *f*- and *ps*-sum rules, showing the high accuracy and applicability of the present RMC approach.

2. Experimental

Three REELS spectra for a magnetron deposited nickel film of 100 nm thick were recorded at primary electron energies of 1000, 2000 and 3000 eV in an energy loss range of 0–200 eV by a home built electron spectrometer (ESA-31) in ATOMKI [24]. The sample was cleaned with Ar^+ ion etching at 3 keV with the beam intensity of 40 $\mu A/cm^2$ for 1–2 min before each measurement. The incident angle of the Ar^+ ion beam was 40° relative to the surface normal. The analyzer works in a fixed retardation ratio mode with a relative energy resolution of 5×10^{-3}. In the present experiment, the used pass energies were around 100 eV, and in this way the analyzer energy resolution was around 0.5 eV. The full widths at half maximum, being the convolution of the analyzer and the electron source generated widening of the elastic peak, were around 0.6–0.7 eV. The incident angle of the primary electron beam is 50° with respect to the surface normal of the sample and the angle of the analyzed electrons is 0° relative to the surface normal. Measurement time at each primary energy was about 30–35 min, during which surface cleanness was checked by XPS in several cases after the REELS measurements. From the XPS, C 1s, O 1s and Ar 2p peaks demonstrate surface contamination of about 2–2.5 atomic percent (relative to the Ni). The vacuum level during the measurements maintained stable at about 1.5×10^{-9} mbar.

3. Reverse Monte Carlo method

Many researches were carried out in the past to describe the electron transport processes in a solid, and numerous analytical expressions were proposed under certain approximations [16,17,25,26]. In the present work a MC simulation method is employed whose obvious advantage is that all interaction channels including elastic scattering, bulk- and surface- plasmon excitations, interband transitions as well as multiple scattering and secondary electron production [27,28] can be treated conveniently and more exactly during the simulation. For the deep mining of the internal information of a sample from the measured REELS spectra it requires a combination of this MC simulation of electron transport in solid with a powerful searching technique to optimize the parameters characterizing the material. By the RMC method, providing an accurate description of electron transport and a test ELF as input, we try to reproduce the experimental spectra and hence able to amend the test ELF. For this purpose, we firstly parametrize a trial ELF with several Drude-Lindhard type oscillators. The ELF is iteratively updated by modifying the values of the composing oscillator parameters so that a new comparison can be made between the simulated REELS spectrum and experimental spectrum. The calculation is terminated when the difference between the simulated and experimental spectra are negligibly small and we accept the final ELF as the true ELF. Specifically, several dozens of parameters are employed in the case of transition metal nickel. Then it is necessary to have a fast parameter updating algorithm; here we have used a simulated annealing global optimization technique [29] to accelerate the searching process.

As an electron is crossing the interface, the surface and bulk plasmons can be excited and the speed of the electron will be damped due to electronic excitations. Typical treatments of such an electron inelastic interaction with surface were either in the framework of classical electrodynamics [30] or that of quantum mechanics [31,32]. In this work we have employed a semi-classical model for it is numerically more efficient than the quantum model and also provides a similar accuracy as the latter [23]. The depth-dependent DIIMFP thus can be derived as,

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