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High-energy electron scattering from TiO_2 surfaces

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ABSTRACT

Electron scattering experiments at keV energies from a TiO_2 surface are presented. The paper aims to give an overview of the wide variety of information that can be extracted from such experiments. If the elastic scattering cross sections are known these experiments give the sample composition, if the composition is known one can extract the ratio of the elastic cross sections. In the experiments described here the ratio of the Ti and O cross sections deviates noticeably from the one calculated from the Rutherford formula. The peak widths give access to the mean kinetic energies of the atoms present. We show that the mean kinetic energy of Ti atoms is less than that of O atoms, but both kinetic energies are still affected by quantum effects, i.e. are larger than $3/2\,kT$. We extract an estimate of the dielectric function of TiO_2 by extending the measurement up to 100 eV energy loss. At these high energies the determination of the dielectric function from the measured energy loss spectrum is relatively simple, as the contribution of surface excitations is small and the obtained loss function is closely related to the dielectric function in the optical limit. Finally, we use the technique to monitor the surface after sputtering with Ar^+ ions, and observe both differences in composition and electronic structure induced by sputtering that disappear again after annealing.

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1. Introduction

Large-angle scattering of keV electrons from surfaces at high energies provides a wealth of information. Under these conditions the recoil energies can be resolved, particularly for light atoms, and the technique is then usually referred to as electron Rutherford backscattering spectrometry (ERBS) [1,2]. As a consequence the elastic peak for compounds splits up into several components due to the different atomic constituents. Each component has a different intrinsic width, which is related to the momentum distribution of the scattering atom. Moreover, at larger energy losses we see the effect of electronic excitations. When these excitations are studied the spectroscopy is usually referred to as reflection electron energy loss spectroscopy (REELS). In REELS the elastic peak position is taken as the zero energy-loss position. This interpretation becomes ambiguous if the elastic peak splits up in several components of comparable magnitude. Such a case is TiO_2 where the oxygen elastic peak has ≈25% of the intensity of the Ti elastic peak. Here we present a subtraction procedure to remove this ambiguity. This procedure turns out to be competitive with a more traditional curve fitting approach for interpreting the elastic peak in terms of their separate components. The results show clearly that the differential elastic scattering cross sections (DCS) deviate significantly from those given by the Rutherford formula.

Both the experimental resolution and Doppler broadening due to atomic vibrations contribute to the elastic peak width. The experimental resolution is determined by evaporating a small amount of Au on the surface. This results in a third elastic peak (besides the ones due to Ti and O) but the intrinsic width of the Au peak is well-understood. It can thus be used to determine the spectrometer resolution. Provided with this information we are able to determine the mean kinetic energy of O and Ti atoms in TiO_2, which turns out to be significantly higher than what is expected in the classical limit: $3/2\ kT$. Surprisingly, few measurements exist of this basic quantity and we compare our results with some theoretical models.

Next we obtain an estimate of the dielectric function $\epsilon(k,\omega)$ for TiO_2 (where k is the momentum of the electronic excitation and ω the energy loss). Here several estimates already exist, but the theoretical and experimental estimates of this important property vary considerably. We argue that our measurement is close to the optical limit, and hence our estimate of the dielectric function at $k = 0$ should be quite reliable.

Finally it is demonstrated how one can monitor effects of sputtering with this technique. Ar ions remove preferentially O atoms.

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As a consequence both changes in composition and electronic structure are observed, but the initial spectra are largely recovered after annealing.

This study is in many ways a follow-up of our work on HfO_2 and shows that much of the physics revealed for HfO_2 is also present for TiO_2. A more extensive discussion can often be found in the papers on HfO_2 [3–5].

2. Theory

Fast electrons (with energy E_0) moving through a material can lose energy by creating inelastic (i.e. electronic) excitations or change direction by deflection from a target atom. It is often assumed that the creation of inelastic excitation does not affect the direction of propagation of the electron, and that deflection from a target atom does not change its energy. Both assumptions are approximations only, the first one becomes better, the second one worse, with increasing E_0 values. The deflection from a nucleus results in a momentum transfer q to the scattering atom, and, if the atom was initially at rest, it acquires a kinetic energy $q^2/2M_i$ with M_i the mass of the atom i. If the atom had a momentum p before the collision, then the recoil energy E_r (i.e. the change kinetic energy of the atom due to the recoil) is given by:

$$E^i_{\rm rec} = \frac{(p+q)^2}{2M_i} - \frac{p^2}{2M_i} = \frac{q^2}{2M_i} + \frac{p\cdot q}{M_i}. \quad (1)$$

The projectile energy is reduced by this amount. The elastic peak is thus centred on the mean recoil energy $\overline{E^i_{\rm rec}} = q^2/2M_i$ but its shape is a Compton profile of the atomic motion. If the target contains two elements with substantially different masses M_i then the elastic peak splits up in two components, each related to a different element, and with a width that is determined by the momentum distribution of that element [1].

It can be shown that for isotropic targets (e.g. polycrystalline samples) the intrinsic width of a peak is related to the mean kinetic energy $\overline{E^i_{\rm kin}}$ of element i by the following equation [6]:

$$\sigma_i = \sqrt{\frac{4}{3}\overline{E^i_{\rm rec}}\,\overline{E^i_{\rm kin}}}. \quad (2)$$

In the previous we assumed implicitly that the scattering of an electron by an atom can be described as incoherent (the electron scatters from a single atom) and that the atom behaves as a free particle, i.e. we neglected the fact that the atom is bound to the target. Especially the latter assumption is far from obvious as the transferred energy is usually less than the binding energy of the atom. Nevertheless this assumption, referred to as the impulse approximation, works quite well under the present conditions. The impulse approximation is discussed extensively for neutron scattering at similar momentum transfers (then usually referred to as neutron Compton scattering) [7,8] which is in many ways the neutron-analogue of the present experiment.

For compounds the ratio for the elastic peaks is proportional to the relative concentration of the different elements *and* their DCS values. As a first approximation the DCS can be obtained from the Rutherford formula, but partial wave calculations [9] show that under these conditions the DCS for scattering of electrons from heavy atoms is enhanced relative to the Rutherford DCS values. For scattering from TiO_2 at 40 keV and 135° the expected elastic peak ratio for the partial wave cross sections differs by 10% from the expectations based on Rutherford, and the difference increases with decreasing E_0 values. For a target of known composition these measurements can thus be used to verify the partial wave calculations. Relevant values of the DCS are given in Table 1 as well as the mean recoil energy $\overline{E^i_{\rm rec}}$.

Table 1
The differential cross section as calculated from partial wave calculations as implemented in ELSEPA [9] for Ti and O at the energies indicated, as well as the ratio of their cross section. Note that this ratio is energy dependent and deviates from $(Z_{\rm Ti}/Z_{\rm O})^2 = 7.56$ as obtained for the Rutherford cross sections. The mean recoil energy $\overline{E^i_{\rm rec}}$ for scattering from Ti or O over 135° are given in the last columns.

E_0 (keV)	DCS O (cm^{-2})	DCS Ti (cm^{-2})	Ratio	$\overline{E^i_{\rm rec}}$ Ti (eV)	$\overline{E^i_{\rm rec}}$ O (eV)
5	5.04E−21	4.79E−20	9.50	0.20	0.59
25	1.82E−22	1.55E−21	8.51	1.00	3.00
40	6.93E−23	5.79E−22	8.35	1.62	4.86

An example of a spectrum of 40 keV electrons scattered over 135° from TiO_2 is given in Fig. 1. The two elastic peaks are followed by a feature-rich energy loss spectrum. In the following we try to uncover the information that is contained in such a spectrum.

3. Some experimental details

ERBS measurements were done with our spectrometer described extensively elsewhere, see e.g.[2,10]. Briefly, 40 keV electrons are scattered over 135° from a target and the scattered electrons are energy-analysed with a resolution of 0.3 eV. This is good enough to separate the contributions of Ti and O to the elastic peak and their intrinsic width. The zero point of the energy scale is not exactly known and we use the energy peak of the heaviest peak (in this case Ti) to fix the zero position by assuming that it has a recoil energy as calculated for an electron scattering from a free atom (1.62 eV for electrons scattering from free Ti under these conditions). When electronic excitations are studied it is more convenient to align the Ti peak with zero energy loss, as then the energy loss scale corresponds directly to the energy of the electronic excitation created.

The TiO_2 sample was grown by annealing a high-purity Ti foil for 5 h at 650 °C under a flow of high purity oxygen. The thickness of the polycrystalline (mainly rutile) oxide film grown in this way is several 1000 Å. For one experiment 2 Å of Au was evaporated from a W coil and the thickness was determined from a crystal thickness monitor reading.

4. Subtraction procedure for the contribution of electrons scattered from Oxygen

All detected electrons have been scattered elastically at least once, as inelastic excitations basically do not affect the direction of propagation of the projectile electron. The fact that we see two well-defined peaks in the spectra with a separation within 1–2% of what is predicted by Eq. (1) is a strong indication that the vast majority of detected electrons had basically a v-shaped trajectory with only a single large-angle elastic deflection. Assuming v-shaped trajectories and a *spatially homogeneous* target then for TiO_2 the spectrum can be separated into a part that is due to electrons scattered elastically from Ti and a part due to electrons scattered elastically from O. The intensity ratio of both contributions is determined by their relative concentration and the ratio of their DCS at the scattering angle dictated by the experimental geometry. Thus all detected electrons have lost energy due to the recoil, and many have lost additional energy due to inelastic excitations.

The contribution of electrons scattered elastically from O is shifted to larger energy losses by the difference of the Ti and O mean recoil energy. The Ti part of the spectrum is broadened by the Doppler broadening due to the Ti atom motion, whereas the O part is broadened by the Doppler broadening of the O atom. From Eq. (2) it is clear that for the lighter element the Doppler broaden-

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