Secondary electron energy loss coincidence (e,2e) spectroscopy on Ag and Si surfaces

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Abstract. Qualitative information on the mechanism of secondary electron emission with respect to loss processes has been gathered by measuring the coincidences between secondary electrons and inelastically backscattered electrons on a polycrystalline silver (Ag) and an amorphised silicon (Si) sample using a specially designed (e,2e) coincidence spectrometer. Primary electrons impinge on the sample with an energy of 100 eV. Correlated emission of electron pairs was observed with a hemispherical mirror analyzer (backscattered electrons with losses up to 50 eV) and a time of flight analyzer (secondary electrons with energies up to 50eV). A comparison of these experimental data with a Monte Carlo (MC) simulation model is made. It is found that surface excitations play an important role in secondary electron emission mechanism. For Ag, low energy loss distributions were compared with calculations using linear response theory and agreed satisfactorily even though the expected limit of validity of this type of theories is for energies ≥100 eV.

1. Introduction

For electrons impinging on solid targets an important reaction channel involves a single collision event with a valence electron resulting in two electrons leaving the solid. Energy and angle resolved observation of these two electrons in coincidence is known as (e,2e) spectroscopy. The energy and momentum of the valence electron is determined from the known energies and momenta of the primary and the detected electrons using energy and momentum conservation. Early (e,2e) coincidence experiments were performed on gases [1]. The study of solids has always been more complicated. In a solid, before escaping from the surface, an unknown amount of energy can be lost in a "cascade" of subsequent scattering events. Besides this, the work function must be overcome. In case of transmission (e,2e) spectroscopy, high incident electron energy can help in reducing the additional scattering but it reduces the (e,2e) count-rate also and leads to poor statistics and long acquisition times. Also the transmission mode experiments are difficult to perform because of the need to prepare very thin samples. Experiments with thin foils and fast electrons in transmission geometry have the advantage that elastic processes are insignificant and the trajectory is more or less a straight line which can be interpreted entirely in terms of bulk scattering. An equally interesting application of (e,2e) spectroscopy is to use it in reflection geometry, first performed about 2 decades ago [2]. Use of a reflection mode involves electrons with low energies, where elastic scattering cannot be neglected. A mechanism of incoherent elastic reflection and inelastic collisions constitutes the framework for the interpretation of these experiments.

Secondary electron emission is a well-known phenomenon. This effect causes solid-state electrons to be emitted when a target is hit by an electron beam. This secondary emission effect was discovered a century ago [3] and has many important technological applications. In some areas (e.g. particle detectors) it is desirable to have large a secondary electron yield while in some cases (e.g. particle accelerators and storage rings [4]) a low secondary electron emission yield is desirable. A great effort has been made by Lin and Joy [5] in compiling measurements from over 80 years from more than hundred different groups.
They developed a universal formula in which certain parameters are fitted for different materials with experimental data. But analysis of this huge dataset reveals significant discrepancies for the same dataset measured by different groups. Thus the phenomenon of secondary electron emission is still a subject of research.

Experimentally it is difficult to deal with slow secondary electrons. Reflection electron energy loss spectroscopy (REELS) is a well established tool to observe energy loss distribution of reflected electrons. But the interpretation of these spectra is more difficult at low energies since the secondary electron peak and loss features overlap. Furthermore the secondary electron spectrum is a superposition of many different excitation processes which are superpositioned in the emitted secondary electron energy distribution making it very difficult to study the emission mechanism of secondary electrons experimentally. Thus the information on the secondary electron emission mechanism one can obtain only by measuring the secondary electron spectrum is limited. Detailed information on the dynamics of low energy electrons in solids can be accessed by means of electron coincidence spectroscopy. To investigate the mechanism of secondary electron emission, (e,2e) spectroscopy has been utilized by measuring the secondary electrons in coincidence with the reflected/transmitted electrons with a specific energy loss. In the present work double differential secondary electron spectra have been measured for a large energy loss range of backscattered electrons by using a specially designed (e,2e) coincidence spectrometer. The unique dataset, interpreted with the aid of state-of-the-art Monte Carlo (MC) simulations, gives detailed information on the emission mechanism of the secondary electrons from solids.

2. Experiment

The (e,2e) coincidence spectrometer consists of an electron gun and two electron analyzers flanged to a µ-metal shielded vacuum chamber with base pressure of ~ 10⁻¹⁰ mbar. The experimental setup is shown schematically in figure 1. A hemispherical mirror analyzer (HMA) with 5 detectors (channel electron multipliers CEMs) is used to record backscattered electrons with a polar opening angle of ±12° with an effective energy resolution of 1.25 eV for a pass energy of 50 eV. The secondary electrons are detected by a time of flight (TOF) analyzer with multichannel plate (MCP) detector. The acceptance angle of the TOF analyzer is 2π achieved by applying a positive bias to the outer two grids and the drift tube for fast acquisition (VG; VR; VD in figure 1). The plane of incidence describes an angle of 35°. The sample is mounted at the center of the vacuum chamber where it can be cleaned and in case of Si amorphised by sputtering with 4 keV Ar+ ions. The cleanliness of the sample is monitored by Auger electron spectroscopy before and after a coincidence measurement. This cleaning procedure was repeated every 24 h and subsequent a coincidence measurement was started.

The coincidences are detected by standard coincidence electronics. The signals from CEMs and MCP/DLA are processed by respective constant fraction discriminators (CFD). A time to digital convertor (TDC), started by a periodic signal from a PCI card, is used to store timing information of the events to computer hard disk. The evaluation software searches for coincidences by subtracting arrival times of electron events at both detectors. The flight times in the TOF analyzer are calibrated by a calibration measurement performed before each coincidence measurement. The time scale is converted to energy scale using the equations of motion of an electron inside the TOF analyzer. The outcome is a secondary electron coincidence spectrum for an energy loss of reflected electrons. These spectra have been measured for a range of energy losses between 0 and 50 eV in steps of 0.25 eV to obtain the double differential coincidence yield.
3. Results and Discussion

The measured double differential coincidence spectra for polycrystalline Si and Ag for primary energy of 100 eV are shown in figure 2. Panel (a) shows REELS for polycrystalline Si measured with 100 eV primary energy. The spectrum shows a peak at 12 eV corresponding to excitation of one surface plasmon (label “1s”) and the peak seen at 17 eV corresponds to excitation of one bulk plasmon (label “1b”). The peak near 30 eV corresponds to reflected electrons that have excited a surface as well as a bulk plasmon excitation. Coincidence spectra for correlated electron pairs for Si is shown in panel (b) where the energy distribution of the secondary electrons is shown on a time of flight scale. The same dataset with the secondary electrons energy distribution on a kinetic energy scale is presented in panel (c). The red line in this curve represents the secondary electrons which are exactly at the Fermi edge originally and are excited by a collision with incoming primaries and escaping from the solid without any energy loss. The signal in these spectra represents the number of true coincidences obtained by subtracting at background of false coincidences. Panels (d)-(f) are the results of MC calculations based on the dielectric response theory of energy loss deep inside the solid and accounting for the influence of the vacuum-solid boundary (surface excitations)[11]. figure 2(d) shows MC results in which the surface excitations are neglected while panel (e) are MC simulations produced with surface excitations accounted only for the primary electrons. In the lower panel (f) surface excitations are accounted both for the primary and secondary electrons.

Figure 1. (e,2e) coincidence spectrometer
Figure 2. (a) Reflection Electron Energy Loss Spectrum (REELS) of Si; (b) Double differential coincidence yield for Si with the secondary electron energy distribution represented on a time of flight scale; (c) same as (b) using after conversion of the time of flight scale to an energy scale; (d) MC calculations in which surface excitations are neglected; (e) MC simulations in which surface excitations are taken into account for the primaries only; (f) MC results for which surface excitations of both primaries and secondaries are considered; (g) REELS of Ag; (h) same as (b) for Ag; (i) same as (c) for Ag; (j) MC results with surface excitations included both for the primary and secondary electrons; (k) Inelastic mean free path (IMFP) as a function of the energy for Ag and Si

Inspection of the measured spectra figure.2(b) and (c) reveals a region of high intensity between the red lines labelled "1s" and "1b". This region has its maximum exactly at the energy corresponding to excitation of a single surface plasmon ("1s"). For larger energy losses the intensity decreases rapidly
reaching a minimum for $\Delta E - \hbar \omega_b$, as observed earlier in the case of Al \[9, 10\]. For the energy loss greater than twice the surface plasmon excitation energy, a broad region with gradually increasing intensity is seen. The narrow ridge between the lines labeled "1s" and "1b" can be understood by inspection of figure 2(k) which shows that for energies below the bulk plasmon excitation energy, the value of inelastic mean free path (IMFP) is very large. In consequence, when a primary liberates a solid-state electron by transferring an energy less than the bulk plasmon energy, the probability for the secondary to be scattered again is very small: in the majority of cases it will escape with the full energy transfer. This explains the ridge-like structure of this feature. The intensity of the secondary electrons for this region is due to the decay of the surface plasmons. For energies above the bulk plasmon loss the IMFP is small, therefore if a bulk plasmon decays, most probably the secondary electron can lose energy by multiple inelastic collisions in particular surface excitations. This also explains why the intensity of secondary electrons drops rapidly for secondary electron energies larger than the bulk plasmon energy (minus the work function).

Comparison of the simulated spectra with the experimental data clearly reveals the role of surface excitations played in secondary electron emission: when only volume scattering is accounted for in the simulations, the ridge at low energies appears at energy losses corresponding to the bulk plasmon energy (panel (d)). When surface excitations of the primaries are "switched on" the width of the ridge in the simulated data increases towards lower energies (panel (e)), but only when surface excitations of both the primaries and secondaries are accounted for (panel (f)), does the width of the ridge match the experimental data.

Essentially the same dataset is presented for polycrystalline Ag in figure 2 (g)-(j) (except panels (c) and (d)). The REELS of Ag presented in panel (g) has characteristic losses at ~4 and ~7 eV that correspond to surface plasmon excitations. Three distinct regions are observable in the double differential spectra presented in figure 2 (i) and (j): a narrow ridge-like region centered around the surface excitation energy (~7eV), a second narrow ridge extending from $\Delta E \sim 10 - 20$ eV and a broad region above $\Delta E \sim 20$ eV with extending up to the energy conservation line ($E_{sec} = E_{Loss} - \Phi$). There is no intensity around 4 eV in these spectra. The secondary electrons generated due to an energy loss of 4 eV cannot come out of the solid due to the work function barrier, which amounts to $\Phi = 4.5$ eV for Ag. The region around 7 eV corresponds to the secondary electrons generated due to a decay of surface plasmon without further inelastic collision on their way out from the solid as the IMFP at this kinetic energy is very large. The width of this region corresponds to the width of the surface excitations in the REELS of Ag. It is therefore concluded, just as in the case of Si (and Al, see Refs. \[9, 10\]) that the sharp ridge-like structures in the double differential coincidence yield for energy losses just in excess of the work function are due to surface excitations. The intensity of the second region between 10 and 20 eV matches the white line $E_{Loss} - 4 - \Phi$ which corresponds to the secondary electrons originally created with an energy equal to the energy loss of the primary that are emitted after suffering exactly one inelastic collision before they come out of the solid. The IMFP for Ag is gradually decreasing till 50 eV kinetic energy which explains why the width of the coincidence spectra extends up to the line $E_{Loss} - \Phi$. The simulated spectra shown in panel (j) nicely reproduce the experimental results for Ag, at least qualitatively. Thus to correctly model the secondary electron coincidence spectra it is necessary to include the surface excitation loss channel both for the primary and the secondary electrons.
Figure 3. Qualitative comparison of experimental coincidence spectra for a specified secondary electron kinetic energy indicated in each panel with corresponding calculated differential inelastic inverse mean free paths (DIIMFP) for Ag. Line with points (black): Measured coincidence spectra, Line (red): Calculated DIIMFP, Dashed (blue): Zero energy loss without accounting for the work function.

The inelastic cross section is an important parameter used for the quantitative understanding of the change in energy distribution of electrons as they move in solids. This quantity has been extracted experimentally [12, 13, 14] as well as theoretically [15, 16] for kinetic energies in the range 50 eV-10 keV. For kinetic energies below 50 eV, it is difficult to obtain experimental results for the differential inverse inelastic mean free path. Since the mean free path for secondary electrons in this energy range is very large, the coincidence data at any given energy loss should be very similar to the single scattering loss distributions for the secondary electrons traveling with this energy. This is confirmed by the coincidence spectra shown in figure 3 that are compared with the energy loss probability for single
inelastic collision (differential inverse inelastic mean free paths, DIIMFP) calculated by the present model. This comparison indeed gives a good agreement with the experimental coincidence spectra for kinetic energies \( \leq 20 \) eV. Discrepancies appear in the calculated DIIMFP and experimental distribution for energies \( \geq 20 \) eV. The coincidence spectra at these energies become broader due to multiple scattering. The calculations based on dielectric theory correctly predict the single scattering loss distributions for very low energies at least qualitatively.

4. Conclusions
Double differential spectra of electron energy losses and secondary electrons emitted as a result have been measured and compared with MC calculations taking into account both volume and surface losses. Good qualitative agreement is found in general explaining the importance of surface excitation for secondary electron emission. Comparison of individual coincidence spectra for a given energy loss with calculations of the single scattering loss distributions gives reasonable agreement indicating that the employed theory is useful even for very low electron energies (~ 5 eV) being much lower than the assumed lower limit of validity of the theory (~100 eV).

Acknowledgments
The present work was supported by the Austrian Science Foundation FWF (Porject P20891- N20). A research scholarship of the Higher Education Commission of Pakistan via Österreichischer Austauschdienst in Vienna is gratefully acknowledged by the first author. F. Salvat-Pujol is grateful to Fundaci_ on Caja madrid for PhD grant and a travel grant of the Fundacion Agusti Pedro i Pons.

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