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Matrix effects in the neutralization of He ions at a metal surface containing oxygen

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ABSTRACT

Charge exchange between He ions and a Ni(111) surface containing oxygen was studied by Low-Energy Ion Scattering, using 1.25 keV He^+ as primary ions. The energy resolved yield of positive ions was detected after backscattering from Ni or O for different exposures of Ni(111) to molecular oxygen. Pronounced changes in the neutralization efficiency due to the presence of oxygen are observed for both, the adsorbate phase at low oxygen dose, and the NiO phase at high dose. The presence of O in the surface makes resonant charge transfer in a close collision possible. Evidence for a strong matrix effect is found: O in NiO neutralizes much more efficiently than O in the adsorbate phase. Independently, the different interaction stages of Ni–O and the surface structure were monitored by Photoelectron-Emission-Microscopy and Low-Energy Electron Diffraction.

1. Introduction

In the interaction of slow ions with solid surfaces or gas atoms, charge exchange has been a very interesting physical phenomenon being studied ever since the early days of ion physics [1–3]. Electron capture and loss are of importance for a fundamental understanding of ion–solid interaction [4], in astrophysics [5], and in plasma physics [6]. Last but not least, it is of great relevance in manifold applications successfully employed to study morphology and composition of surfaces or near-surface structures [7,8]. In these contexts neutralization of noble gas ions at metal surfaces has been investigated extensively in the last decades [9–11]. The good qualitative and quantitative understanding of the underlying processes has led to a wide field of applications for techniques like Low-Energy Ion Scattering (LEIS) or Secondary Ion Mass Spectrometry (SIMS). However, for both systems matrix effects have been reported, which means that the efficiency of active charge exchange processes is influenced by the chemical environment [12,13]. Oxygen is an abundant constituent on surfaces of technological or scientific interest, no matter whether as a contaminant or as an inherent part of the system of interest, and it is known to change ion fractions in SIMS drastically [14]. In fact, a change in the O concentration of less than a percent can increase ion yields by an order of magnitude [15]. In LEIS, only insufficient knowledge on the role of oxygen in charge exchange of slow light ions is available. This represents a striking lack of basic knowledge about charge exchange processes, and is a handicap for quantification in applications of LEIS to oxide surfaces [7,16]. Thus, a deeper understanding of the role of oxygen in ion neutralization at surfaces is not only of fundamental interest, but could also break the ground for an even wider field of application of the surface analytical techniques mentioned before.

In the present study we investigated charge exchange of He^+ ions with Ni and O atoms for both, O chemisorbed on Ni(111), and a NiO surface oxide on Ni(111). To this aim we applied LEIS, Photo-Electron Emission Spectrometry (PEEM) and Low-Energy Electron Diffraction (LEED). The Ni(111)–O system represents an ideal case for our study, since it has been extensively studied in the past (see e.g. [17–21] and references therein). Thus, a profound understanding of the mechanisms of chemisorption and surface oxidation is available today. This allows us to extract information on the role of O in ion neutralization by metal atoms, and on charge exchange between helium ions and oxygen in different chemical states.

For He ions with a kinetic energy of several keV, the dominant charge exchange processes in the interaction with surface atoms are well known. For most chemical elements, only two different types of charge exchange processes prevail: Auger neutralization and resonant charge transfer in a close collision [22]. Auger neutralization (AN) is nonlocal, acts along the trajectory, is due to interaction of the projectile ground state with the valence-conduction band of the sample, and is governed by a transition rate Γ_A. Via the rate equation for the ion fraction P^+ this leads to $P^+ = \exp(-v_c/v_z)$, where $v_c = \int \Gamma_A dz$ is a measure for the AN efficiency, and v_z is the perpendicular component of the ion velocity [23]. If AN is the only process, P^+ represents a survival probability which is $\ll 1$ even for scattering at the

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outermost surface atoms, leading to a superb surface sensitivity of $\approx$1 atomic layer, for which LEIS is known.

Resonant processes refer to a situation where the He ground state level is resonant with occupied or unoccupied states of the conduction band: Only a small number of elements like Ge, In or Pb exhibit electrons with similar binding energies than the unperturbed He 1s level. For the prevailing part of the elements, resonant charge transfer is only possible in a close collision – at an interatomic distance, *r*, smaller than a critical value R_0 – as a consequence of electron promotion of the projectile level due to interaction with atomic levels of the target atom. Resonant charge transfer may lead to (resonant) neutralization (RN) when He^+ enters the collision, or even to (re)ionization (RI) when He^0 is scattered [24,25]. For a fixed scattering angle, the probabilities for these processes, P_{RN} and P_{RI}, depend on the ion energy, and vanish for energies lower than a threshold energy E_{th}, which is characteristic for the specific choice of projectile and scattering center. For instance, for He and Ni, $E_{th} = 1500$ eV, while for He and O, a value of 700 eV has been reported for E_{th} [25–27].

For $E > E_{th}$, the ion fraction consists of two contributions: "*survivals*" and "*reionized projectiles*". *Survivals* are projectiles that did not undergo any charge exchange process; *reionized projectiles* have first been neutralized and then reionized on their way out in a collision close to the surface. In this regime, the information depth may exceed one atomic layer, but for polycrystalline samples, excellent surface sensitivity can be maintained if the LEIS signal is properly evaluated [28]. For typical LEIS energies, an information depth of less than 2 or 3 atomic layers can be obtained, details depending on the investigated system.

2. Experiment

We performed the experiments using the ESA-LEIS setup MINIMOBIS [29] at the Institute of Experimental Physics at the Johannes Kepler University Linz. In this setup a mass selected beam of He ions with primary energies in the range of 0.2–4 keV can be directed towards the sample surface in perpendicular incidence. Primary beam currents range from 0.05 to 2 nA. Ions that are backscattered by $\theta = 136°$ pass a cylindrical mirror analyzer (CMA) with an azimuthal acceptance angle of 2π and are detected by micro channel plates (MCP). As a sample, a polished Ni(111) single crystal with a roughness below 0.03 μm and a precision of the orientation of $\pm 0.1°$ was used. We prepared a clean crystalline surface by cycles of Ar^+-sputtering and annealing (up to 700 °C). Surface crystallinity was checked by Low-Energy Electron Diffraction (LEED). After preparation, LEIS spectra did not show any surface impurities. To study the influence of oxygen on charge exchange, the sample was exposed to molecular oxygen at room temperature. LEIS spectra were recorded for 1.25 keV He^+ ions for oxygen exposures in the range from 0.1 to 10,000 L. Photo-electron Emission Microscopy (PEEM) and LEED were used to study changes in electronic properties and surface structure; PEEM and LEED images were recorded for Ni(111) as a function of oxygen exposure, in another UHV-setup but with identical sample preparation. For the excitation of photoelectrons a D_2 lamp with a MgF_2 window was used. This lamp delivers photons up to 11 eV with a major emission line in the deep UV at 7.7 eV (160.8 nm). LEED pictures were taken at an electron energy of 83.6 eV.

3. Experimental results

PEEM intensities averaged over a field of view of ~145 μm are plotted in Fig. 1 for oxygen exposures from 0.1 to 3000 L. The figure also includes characteristic LEED patterns recorded in the course of the experiment. These results permit to identify the individual stages of the interaction of Ni(111) with oxygen.

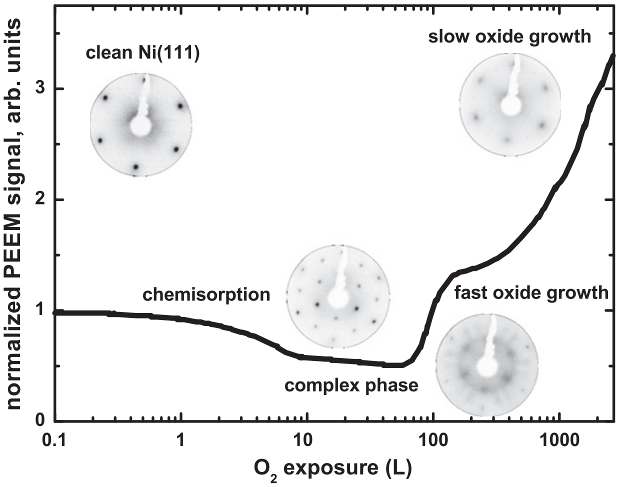

Fig. 1. Normalized electron emission yield extracted from PEEM images during exposure of a Ni(111) surface to molecular oxygen. Also shown are LEED images recorded for selected oxygen doses.

At exposures of about 1 to 5 L, the decrease of the normalized intensity corresponds to the adsorption of O in a (2×2) superstructure, which is known to lead to an increase in work function from about 5.3 to 6.0 eV [30,31]. This interpretation is also in accordance with the LEED pattern recorded for an exposure of 2 L. For higher exposures, the PEEM intensity remains constant, whereas the LEED pattern continuously changes due to formation of more complex adsorbate structures [18]. For exposures above ~80 L, the PEEM intensity increases again, due to the onset of surface oxide formation, and a corresponding decrease in the work function. The final LEED pattern shows again a hexagonal surface structure, as expected for NiO on Ni(111). A comparison of the patterns for clean Ni(111) and NiO shows an increase by 15% in the size of the unit cell [32]. To summarize, all observations described so far are in accordance with literature, proving proper sample preparation.

As a next step, the Ni(111)–O system was investigated by LEIS, using 1.25 keV He^+ ions as projectiles. Spectra obtained for different O exposures are shown in Fig. 2. The peaks around 950 and 480 eV correspond to ions which were backscattered in a single collision from Ni or O (if present), respectively. The integral peak areas, i.e. the ion yields, can be evaluated independently for Ni and O, yielding $Y_{Ni}{}^+$ and $Y_O{}^+$, respectively. From $Y_{Ni}{}^+$ and the corresponding surface atom density of Ni(111), the ion fraction P^+ can be deduced, i.e. the percentage of positively charged helium ions when backscattered from a Ni atom in a Ni(111) surface. For the clean Ni(111) surface and 1.25 keV He ions, this results in $P^+ = 0.18$. A detailed description of the evaluation

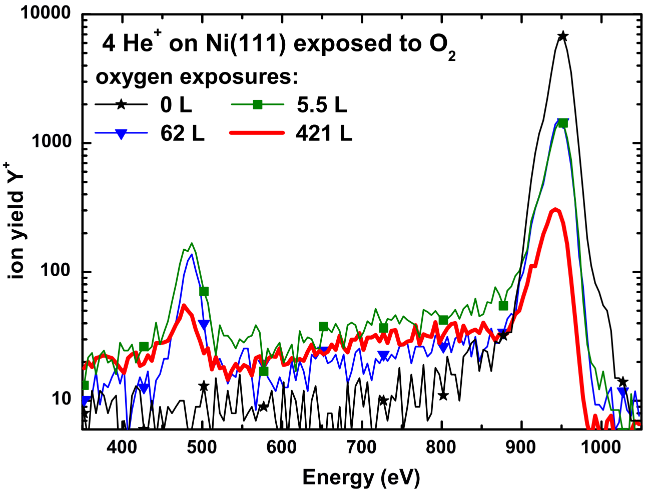

Fig. 2. Energy spectrum of He^+ ions backscattered from Ni(111) exposed to O_2 for different doses of O_2 (see inset) and normalized for the same primary ion fluence. The primary ion energy was 1.25 keV.