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ION-INDUCED PARTICLE DESORPTION IN TIME-OF-FLIGHT MEDIUM ENERGY ION SCATTERING

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Abstract

Secondary ions emitted from solids upon ion impact are studied in a time-of-flight medium energy ion scattering (ToF-MEIS) set-up. In order to investigate characteristics of the emission processes and to evaluate the potential for surface and thin film analysis, experiments employing TiN and Al samples were conducted. The ejected ions exhibit a low initial kinetic energy of a few eV, thus, requiring a sufficiently high acceleration voltage for detection. Molecular and atomic ions of different charge states originating both from surface contaminations and the sample material are found, and relative yields of several species were determined. Experimental evidence that points towards a predominantly electronic sputtering process is presented. For emitted Ti target atoms an additional nuclear sputtering component is suggested.

Keywords: desorption, electronic sputtering, TOF-MEIS, TiN

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1. Introduction

Understanding the interaction of medium energy ions with matter is of fundamental physical interest as well as essential for a variety of applications such as ion beam analysis, sputtering and ion implantation [1]. When charged energetic particles enter a solid, they interact with the target nuclei as well as with the target electrons. The resulting energy loss per path length (dE/dx) is called stopping power S [2]. The energy transfer from the incident ion to the solid can lead to the ejection of target particles. This process can, on the one hand, be of nuclear nature when binary collisions between projectile and target nuclei, i.e. direct momentum transfers, lead to knock-on sputtering [3]. Electronic sputtering or desorption, on the other hand, is a process where energy transferred to the electronic system of the target induces emission of surface species [4].

One well-established experimental method to assess sputtered particles is secondary ion mass spectrometry (SIMS) [5]. Typically, a focused beam of ions or neutral particles with energies of at most a few keV/u is employed to sputter the sample surface of interest, and ejected ions are analysed according to their mass. Separation of ions of different mass to charge ratios is achieved by one of three techniques: sector mass spectrometry, quadrupole mass spectrometry or time-of-flight (ToF) [6]. The last mentioned method has shown great potential in particular for the characterisation of sensitive systems [7]. Recently, ToF-SIMS has also been incorporated into a helium ion microscope, thus, combining high resolution imaging with elemental mass spectroscopy [8]. Another current development is MeV-SIMS, which is targeted at detecting large molecular species and analysis at ambient conditions [9,10]. The physical basis for this method is the large amount of energy deposited into the target electronic system by the employed energetic heavy ion projectiles, thus, exciting a large area around the impact site [11].

Medium energy ion scattering (MEIS) typically employs light ions with energies of several ten to a few hundred keV as probes with the aim to obtain depth profiles with high resolution. For these energies of the primary ions, the inelastic deceleration caused by the electronic system dominates over energy loss due to elastic collisions with nuclei [12]. In other words, the electronic stopping power S_e is much larger than the nuclear stopping power S_n . By studying desorption and sputtering processes, information on the specific energy transfer mechanisms in this

regime can be obtained. Data obtained in the MEIS energy regime also bridges a gap in energy between the commonly employed keV ions and the ongoing developments in MeV-SIMS.

In the present work, which is a follow-up study on [13], secondary ions emitted from the target have been studied in a ToF-MEIS system. A pulsed ion beam and a detector mounted in backward geometry allow for combining conventional high-resolution backscattering experiments for depth profiling with mass spectrometry. Experiments employing hydrogen and helium ions as probes and aluminium and TiN as samples were performed to investigate characteristics of the emission processes and to evaluate the potential for surface and thin film analysis. The initial energy and energy spread of desorbed hydrogen is determined and desorption yields of selected species are quantified.

2. Experiment and Analysis

The ToF-MEIS system at Uppsala University is based on a 350 kV Danfysik implanter, which can provide atomic and molecular beams of almost all elements with typical energies between 20 keV and 350 keV [14]. Pulsing of these ion beams and a ToF detection system are used to determine the energy of charged and neutral particles. The typical time resolutions Δt of (1.0 - 2.0) ns (non-bunched) and 0.3 ns (bunched) lead to relative energy resolutions $\delta E/E$ of about 0.01 - 0.02 [15]. The repetition rate of the gate pulses used for chopping the beam is adjustable, but for experiments presented here set to 1/16 MHz. Figure 1 illustrates the experimental set-up inside the MEIS scattering chamber. The position sensitive detector (DLD120 from Roentdek) consists of two stacked microchannel plates (MCPs) (diameter 120 mm) and two delay line anodes, and covers a solid angle of 0.13 sr. In front of the detector, facing the sample, a grid is mounted, to which a voltage between -500 V and 500 V can be applied. The whole detector can be rotated around the scattering point on a circular path with a radius of 290 mm enabling measurements under different scattering angles θ . The sample itself is mounted on a 6-axis goniometer allowing for three translational and three rotational movements. The base pressure in the scattering chamber is found to be below 5×10^{-9} mbar.

For regular backscattering experiments the sample holder as well as the grid are grounded. In order to detect desorbed charged particles of initially low kinetic energy (apart from protons) within the measurement time window (determined by the gate pulse repetition rate; maximum 16 000 ns), an electric field has to be applied between sample holder and grid. Therefore, a positive voltage V_S ($V_S \leq 500$ V) is applied to the goniometer. Note that at present the front MCP lies at a potential of $V_{MCP} = -2400$ V, thus, only positive desorbed ions can be detected. To ensure a defined field geometry, indicated by symmetric patterns on the position-sensitive detector, the sample and the detector surfaces must be parallel to each other, which means that the incident angle of the beam will be equal to the detector angle θ_{det} ($\theta_{det} = 180^\circ - \theta$). If not otherwise stated, let $\theta_{det} = 30^\circ$.

The TiN thin film employed as a target has a NaCl-like B1 cubic structure and was deposited on a Si(100) wafer via cathodic arc evaporation. For the synthesis in an Ar/N₂ atmosphere (at 420 °C, 2×10^{-6} mbar) an Oerlikon Balzers INGENIA P3e industrial batch coating system was used. The film was characterised by Rutherford backscattering spectrometry (RBS) and ToF elastic recoil detection analysis (ToF-ERDA) experiments employing the 5 MV 15SDH-2 Pelletron tandem accelerator at the Ångström laboratory at Uppsala University. By using a 2 MeV $^4\text{He}^+$ beam and detecting backscattered ions under a scattering angle of 170° with a surface barrier detector, the areal thickness of the film could be determined with an accuracy of about 4 %. A ToF-ERDA analysis with a $^{127}\text{I}^{8+}$ beam verified the absence of significant impurities and the stoichiometry of the TiN film.

The purity of the aluminium sample was likewise examined with the help of ToF-ERDA. The surface is found oxidised with an oxygen content of about 70 %. In addition, a very small carbon contamination can be detected on the surface.

In order to obtain quantitative results on desorption yields, the number of detected counts has to be normalised to the number of incident ions. The current of the pulsed ion beam is difficult to measure directly since it is only of the order of a few pA and leakage currents from the applied voltage deteriorate measurements. Thus, normalisation was attempted from the spectrum of backscattered primary particles. Figure 2 shows the time-to-energy-converted spectrum of backscattered primary particles. 120 keV $^4\text{He}^+$ ions served as projectiles and the target was a 189 Å TiN film on Si substrate (assuming bulk density). Also shown is a SIMNRA simulation

[16] of the experiment (blue full line). The SIMNRA simulation is scaled in such a way that the integral over the Ti peak is the same for experiment and simulation. This way, the number of incident ions for the experiment can be determined via the simulation with an accuracy of better than 5 %.

The sample holder was on a potential of 500 V during the whole measurement, while the grid was on ground. By comparing the experimental data with the simulation, it can be clearly seen that this potential difference leaves the backscattering spectrum undisturbed, as expected from the primary and final energy of the ions.

3. Results

3.1 Mass identification and energy determination

A ToF spectrum of backscattered and desorbed ions, as it is obtained when applying 500 V to the sample holder, is shown in Fig. 3. Here, again a 120 keV $^4\text{He}^+$ beam provided projectiles, and the target was a 189 Å TiN film. Note, however, that ToF spectra measured with different primary energies or using an H_2^+ incident beam look qualitatively similar, i.e. most structures appear at similar time-of-flight. Before the measurement the sample was sputter-cleaned with a 60 keV $^4\text{He}^+$ beam (incident angle 45° , 0.3 mA/cm^2) for 30 minutes. At the very left of the spectrum a narrow ion-induced prompt photon peak (ToF = 1 ns) can be seen, which is used to determine both the time resolution of the measurement and the origin of the time axis [17]. The next peak structure comprises of particles backscattered from the thin TiN film followed by the broad substrate signal. All other peaks are secondary ions leaving the sample on impact of the primary beam. The mass to charge ratio of the latter, m/q , which is shown on the top axis of Fig. 3 was calculated using Eq. 1 (after [13])²:

$$\text{ToF} = \frac{\sqrt{2m} \times L_1}{\sqrt{E_0} + \sqrt{E_0 + qV_S}} + \frac{\sqrt{m} \times L_2}{\sqrt{2(E_0 + qV_S)}} + \frac{\sqrt{2m} \times L_3}{\sqrt{E_0 + qV_S} + \sqrt{E_0 + q(V_S - V_{\text{MCP}})}}, \quad (1)$$

where E_0 is the (low) primary kinetic energy of the desorbed particles. The three distances L_1, L_2 and L_3 correspond to the region of initial acceleration close to the

² Note that it is strictly speaking not correct to talk about m/q values here since the flight time depends on the individual values of m and q and not just on the ratio. However, the deviation is caused by the initial kinetic energy E_0 , which is very small compared to the energy obtained through acceleration, thus, making the approximation reasonable.

sample, the drift region, which comprises most of the distance between sample and grid and the distance between the grid and the MCP, respectively. Note that for simplicity the grid is grounded for these measurements.

By measuring the flight time as a function of V_S , not only the mass to charge ratio but also E_0 can be determined. For $m/q = 1$, which corresponds to desorbed H^+ , a most probable initial kinetic energy of 11.3 ± 1.0 eV is found. For $m/q = 2$ (H_2^+), $E_0 = 6.4 \pm 1.2$ eV. The error takes into account the standard error from the fit (Eq. 1) and the uncertainty in the total length between sample and detector. Since the H^+ peak is also visible in the spectrum without any applied electric field, E_0 can in this case also be determined using this measurement only. The result of about 11 eV agrees very well with the fitted one. Kobayashi et al. reported a similar value ($13.4^{13.0}_{-5.6}$ eV) for measurements using a Li_2O target [13].

In addition, we have studied the energy distribution of the desorbed H^+ . However, a dependence on the applied sample voltage was found. The full energy width at half maximum increases from 5.3 eV at $V_S = 0$ V to 12.4 eV at 500 V. This observation might be caused by an inhomogeneity of the electric field in the scattering chamber.

The above equation is independent of the projectile type and initial energy, which is confirmed by experiments. Since for most m/q ratios the peak positions and peak shapes do not shift upon variation of these experimental parameters, E_0 must stay constant within our detection limits as well. This finding indicates that the energy transfer from the projectile to the desorbed ions is an electronic process and not caused by direct scattering of the atomic nuclei.

In order to learn more about the nature of the desorbed species, a comparison between a cleaned and a non-cleaned sample is helpful. Figure 4 shows details of two ToF spectra obtained by impinging a 100 keV $^4He^+$ beam on the TiN target. A voltage of 500 V was applied to the sample holder. The black full line corresponds to a spectrum obtained from the as-transferred sample, which had been exposed to ambient conditions. The same sample was then cleaned as described above, and the result from the subsequent measurement is depicted by the red dashed line. Note that for easier comparison the second spectrum is scaled such that the integrals over the backscattering spectra of both measurements are identical (cf.

Analysis – the signal from backscattering is at flight times not visible in this time window as can be seen also in Fig. 3).

It can be clearly seen that a majority of the peaks are reduced drastically after sputter-cleaning. Even desorbed H^+ after cleaning (not shown in detail) only yields about 70 % of the signal prior to cleaning. Most of the peaks that can be observed in the ToF spectrum must, therefore, be interpreted as surface contaminations. The peak we interpret as Ti^+ (at flight times corresponding to masses 46-49 after Eq. 1; marked with an arrow in Fig. 4), however, appears with similar intensity in both spectra. In general, ion fractions exhibit a matrix effect, and ion yields can depend strongly on surface contaminations [18,19] and even on the structure [20] or on the chemical state of the surface [21]. The now present observation that the Ti^+ yield hardly changes suggests that even the as-transferred sample was featuring only sub-monolayers of surface adsorbed species. Since we still observe significant desorption yields from contaminants, the method can be regarded as very sensitive to these species.

3.2 Yield quantification

Table 1 contains desorption yields of selected species for three different projectile-material pairs (180 keV $^4He^+$ - TiN, 100 keV H_2^+ - TiN and 100 keV H_2^+ - Al). Note that all targets were transferred from ambient conditions and that none of them was sputter-cleaned. For all three combinations, many more peaks are visible in the spectrum (cf. Fig. 3), but only light species that can be relatively easily identified are listed here. All yields are normalised to the number of incident ions as explained in Sec. 2.

As stated in the previous part, both surface contaminants and sample atoms can be detected when using the TiN target. Additionally, atomic and molecular ions and ions of different charge states are seen. The Ti^+ peak is quite pronounced, whereas N^+ yields very little signal (if anything at all). A complementary measurement using a LiF crystal as the target, confirmed that the target anion (in the form of F^+ , as negative ions cannot be detected with the present set-up) is not detected with the present set-up, while the cation (Li^+) shows a clear peak in the spectrum.

Quantification of yields from this measurement proves to be difficult, however, due to charging of the sample.

For the TiN sample, yields are given for a $^4\text{He}^+$ and a H_2^+ projectile of similar ion velocity (1.34 atomic units (a.u.) and 1.41 a.u., respectively). A comparison between the second and third column of Tab. 1 shows that the yields induced by He are higher. For Ti^+ and Ti^{2+} the yield differences comparing He^+ and H_2^+ ions are significantly greater than for the surface contaminants (factor >10 compared to factor 3-4).

The quantitative yields observed for the Al sample differ from yields from TiN, which is expected for different samples with different surfaces. The detected surface contaminant species and the order of magnitude of their yields are similar though. Note that Al^+ has the same mass to charge ratio as C_2H_3^+ ($m/q = 27$). Since hydrocarbons are ubiquitous on all samples used and their desorption yields are significant, quantification of the Al^+ yield was not attempted. Relative yields in SIMS for heavy ion projectiles with primary energies between 10 and 30 keV are of the order of 10^{-3} (lighter desorbed species) [22] or 10^{-8} - 10^{-6} (heavy desorbed molecules) [23] and MeV-SIMS yields of large desorbed biomolecules reach 10^{-3} / inc. ion [23]. Thus, numbers that can be achieved with the set-up described in this work using primary ions of intermediate energies are comparable with yields measured with established SIMS techniques.

All relative yields exhibit some kind of dependence on the incident ion velocity. For a He projectile all considered yields decrease with increasing ion velocity within the measured range (1.0 - 1.4 a.u.). H^+ yields induced by H_2 projectiles on Al and TiN likewise show a decrease for increasing ion velocity between 1.4 and 2.5 a.u. Measurements using a primary H_2^+ beam and the TiN sample indicate a maximum of the desorbed H^+ yield between 1.0 and 1.4 a.u. though. H_2^+ and H_3^+ yields follow similar patterns.

4. Discussion

The general observation that molecular species are present in high numbers in the detected yield of secondary particles indicates a non-nuclear desorption mechanism as the basis of the ionisation. In addition, the invariability of E_0 with incident ion

energy and the narrow and typically symmetrical energy distribution are other indications for electronic processes. The target bulk constituents, however, show a different behaviour, i.e. an asymmetric peak shape. As such a shape is also observed for the well-separated ^6Li and ^7Li cations in LiO_2 as described by Kobayashi et al. [13], multi-atomic clusters with different isotopes cannot explain the shape seen in the case of Ti^3 . On the other hand, the inverse-square-like decay towards higher energies (i.e. shorter flight times) as it is seen in Fig. 3 resembles the energy distribution of sputtered particles ejected by collision cascades [19,24]. Thus, for the observed ions originating from bulk constituents of the sample the energy from the primary ion is not transferred via electronic processes, but via nuclear collisions.

The explanation of the different peak shapes by two different emission mechanisms is also in good agreement with the observed yield ratios for the detected emitted species. When comparing 180 keV He with 100 keV H_2 projectiles, the energy deposition per unit path length into the electronic system is expected to differ by about a factor of 2.5 [25]. This ratio is in good qualitative agreement with the observed yield ratio $Y_{\text{He}}/Y_{\text{H}}$ of about 3 for most detected particle species. The noticeable exceptions are the intensities attributed to species from the bulk material, i.e. Ti. Data on ion-induced sputter yields of titanium in the medium-energy regime is scarce. Extrapolating from existing data, however, would yield a more than tenfold enhancement of the yield using a He instead of a H beam [26], which is indeed observed.

The observed dependence of the desorption yields on the incident ion velocity points towards the concurrence of several influences. Whereas a dependence of the yield on the deposited energy, i.e. the electronic stopping power, can be expected, a proportionality is not observed. Thus, other effects such as average excitation energies of electrons, secondary electron interactions and electron-phonon coupling must exhibit different scaling with incident energy.

5. Summary and Outlook

³ Note that in the case of the aluminium sample the bulk constituent signal (Al^+) overlaps with the signal from ubiquitous hydrocarbons, thus, its shape cannot be assessed without doubt.

Mass spectroscopy was successfully integrated into a ToF-MEIS system by applying an electric field between the sample holder and a grid mounted in front of the detector. At present, emitted positive ions with mass to charge ratios up to 170 u and low initial kinetic energies (few eV) can be detected, and mass resolution is sufficient for distinguishing isotopes. Yields for emitted target material ions ($\text{Ti}^+/\text{Ti}^{2+}$) and several typical surface contaminants are presented for $^4\text{He}^+$ and H_2^+ projectiles. Experimental evidence such as the high number of emitted molecular ions, the yield ratio $Y_{\text{He}}/Y_{\text{H}}$ and the invariability of E_0 with projectile velocity indicate that the energy transfer to secondary particles is mainly of electronic nature. In contrast to desorbed surface contaminants, the asymmetric shape of the Ti peak points towards an additional nuclear-sputtering component for species originating from the target matrix.

Experiments investigating matrix effects by comparing desorption from TiN with VN or AlN with Al are planned. Additionally, comparisons between molecular and atomic projectile beams at similar energy/u could be of interest to investigate cluster effects.

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Figure captions

Fig 1: Sketch of the experimental set-up inside the MEIS scattering chamber. The detector is a delay line detector from Roentdek (DLD120), which consists of two stacked MCPs. In front of the detector a grid is mounted, to which a voltage V_{grid} can be applied ($-500\text{ V} \leq V_{grid} \leq 500\text{ V}$). The detector can be rotated on a circular path with a radius of 290 mm around the scattering point. This enables varying the angle θ , under which backscattered particles, desorbed ions and emitted photons are detected. A positive voltage up to 500 V can be applied to the sample holder, which is also rotatable. To ensure a defined field geometry the sample and detector surfaces are aligned parallel to each other for such experiments.

Fig 2: Converted energy spectrum from a ToF-MEIS experiment employing a 120 keV $^4\text{He}^+$ beam and a 189 Å TiN film on Si as the target. The incident angle was 30° and the scattering angle 150° , thus, aligning the sample surface parallel to the

detector surface. Note that, although a voltage of 500 V was applied to the sample, the backscattering spectrum is not affected by the electric field. Also shown is a simulation of the experiment obtained with SIMNRA [16] (blue full line). In order to find the total number of incident ions, the simulation was scaled in such a way, that the integral over the titanium peak was the same for the experimental and the simulated data.

Fig. 3: Time-of-flight spectrum of backscattered and desorbed particles obtained by directing a pulsed 120 keV $^4\text{He}^+$ beam onto a 189 Å TiN film on Si. The sample and detector surfaces were parallel to each other and 500 V were applied to the sample holder. The sample was sputter-cleaned with a 60 keV He beam for 30 minutes before the measurement. On the top axis the mass to charge ratio of the desorbed particles is shown, which can be calculated from the flight time with Eq. 1.

Fig.4: Comparison between desorption spectra from a non-cleaned (black full line) and a sputter-cleaned (red dashed line) TiN sample. Shown is a detail from the ToF spectra obtained by employing a 100 keV $^4\text{He}^+$ beam and applying 500 V to the sample holder. To simplify comparison, the spectrum from the cleaned sample is scaled so that the integrals over the backscattering spectra of both measurements are the same.

Table captions

Tab. 1: Desorption yields for selected mass to charge ratios (m/q) and three different projectile-material combinations: 180 keV $^4\text{He}^+$ on 189 Å TiN, 100 keV H_2^+ on the same target and 100 keV H_2^+ on aluminium foil (all of them transferred from air). The incident angle was 30° in all cases and an acceleration voltage of 500 V was applied to the sample holder. Note that the specified ion species are matched with the m/q value, but not confirmed by any other experimental method.

Figure 1

Figure 2

Figure 3

Figure 4

Table 1

m/q (ion species)	Yield 180 keV He ⁺ → TiN (10 ⁻⁸ / inc. ion)	Yield 100 keV H ₂ ⁺ → TiN (10 ⁻⁸ / inc. ion)	Yield 100 keV H ₂ ⁺ → Al foil (10 ⁻⁸ / inc. ion)
1 (H ⁺)	21 104	8 405	17 620
2 (H ₂ ⁺)	1 246	394	531
3 (H ₃ ⁺)	47	12	32
12 (C ⁺)	31	9	18
13 (CH ⁺)	24	8	23
14 (N ⁺ , CH ₂ ⁺)	57	21	82
15 (CH ₃ ⁺)	396	167	979
19 (H ₃ O ⁺)	635	183	51
23 (Ti ²⁺ ; TiN samples only)	259	14	308
46-49 (Ti ⁺)	4 539	364	—