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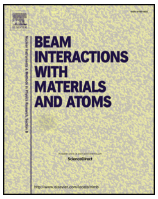

Secondary ion formation during electronic and nuclear sputtering of germanium

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ABSTRACT

Using a time-of-flight mass spectrometer attached to the UNILAC beamline located at the GSI Helmholtz Centre for Heavy Ion Research, we investigate the formation of secondary ions sputtered from a germanium surface under irradiation by swift heavy ions (SHI) such as 5 MeV/u Au by simultaneously recording the mass spectra of the ejected secondary ions and their neutral counterparts. In these experiments, the sputtered neutral material is post-ionized via single photon absorption from a pulsed, intensive VUV laser. After post-ionization, the instrument cannot distinguish between secondary ions and post-ionized neutrals, so that both signals can be directly compared in order to investigate the ionization probability of different sputtered species. In order to facilitate an in-situ comparison with typical nuclear sputtering conditions, the system is also equipped with a conventional rare gas ion source delivering a 5 keV argon ion beam. For a dynamically sputter cleaned surface, it is found that the ionization probability of Ge atoms and $\mathrm{Ge_n}$ clusters ejected under electronic sputtering conditions is by more than an order of magnitude higher than that measured for keV sputtered particles. In addition, the mass spectra obtained under SHI irradiation show prominent signals of $\mathrm{Ge_nO_m}$ clusters, which are predominantly detected as positive or negative secondary ions. From the *m*-distribution for a given Ge nuclearity *n*, one can deduce that the sputtered material must originate from a germanium oxide matrix with approximate GeO stoichiometry, probably due to residual native oxide patches even at the dynamically cleaned surface. The results clearly demonstrate a fundamental difference between the ejection and ionization mechanisms in both cases, which is interpreted in terms of corresponding model calculations.

1. Introduction

The formation of secondary ions during ion sputtering of solid surfaces represents the physical basis of secondary ion mass spectrometry (SIMS). A key quantity in such experiments is the ionization probability of a sputtered particle, and significant effort has therefore been devoted to investigate this quantity under so-called *nuclear sputtering* conditions, where the surface is bombarded with keV projectile ions and the primary energy transfer is dominated by nuclear stopping. Much less is known about secondary ion formation in the *electronic sputtering* regime, where the solid is irradiated with swift heavy ions (SHI) and the primary energy transfer occurs via electronic stopping of the projectile. While the ionized particles ejected from the surface under these conditions have been characterized for a few target materials (mainly ionic crystals such as LiF [1–23]), including measurements of secondary ion yields as well as the emission velocity and angle distributions of sputtered atomic and cluster ions [12,14,15,18,20,21], to date practically no such information exists about the sputtered material which is emitted in the neutral charge state. Using collector techniques, total sputter yields as well as angular distributions of the sputtered material have been measured for some ion-target combinations (for a review see [24]), which – provided the instrumental transmission and detection efficiency for the secondary ions is known – in principle allow to estimate the total ion fraction of the sputtered material. A fundamental open question, however, regards the ion fraction of specific components in the sputtered flux. In that context, it is useful to define the ionization probability of a sputtered species X as

$$\alpha_X^{+,-} = \frac{Y_X^{+,-}}{Y_X}, \tag{1}$$

where X can stand for an emitted single atom, molecule or cluster, respectively. The quantity $Y_X^{+,-}$ denotes the secondary ion yield, i.e., the average number of secondary ions $X^{+,-}$ which is emitted per projectile impact, while Y_X represents the respective partial sputter yield of all emitted particles X regardless of their charge state. It should be stressed that this definition of $\alpha_X^{+,-}$ does not necessarily imply the emission and

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ionization processes to be decoupled from each other. While this may in some cases be true, e.g. for single atoms emitted from a clean metallic surface under nuclear sputtering conditions, one could imagine a strong coupling between the ejection and ionization mechanisms in other cases, for instance via a charge related emission process such as Coulomb explosion. Particularly for molecular emission, the fragmentation or survival of a sputtered molecule may also be closely coupled to its charge state, so that the factorization according to Eq. (1) may represent an oversimplification. Moreover, both the emission velocity and angle distributions of secondary ions may in principle differ from those of the respective neutral particles, thereby defining a velocity or trajectory dependent ionization probability of a sputtered particle.

The goal to obtain quantitative information regarding the ionization probability of sputtered particles ultimately requires the mass resolved detection of emitted neutral species in addition to the corresponding secondary ions under otherwise identical experimental conditions. This is a difficult task, since neutral particles must be post-ionized in order to render them accessible for mass spectrometric analysis. Several post-ionization schemes have been employed, including electron impact ionization (using either an electron beam [25] or the electron component of a low pressure plasma [26]), surface ionization (involving scattering of the particles at a heated surface) or photoionization (using resonant or non resonant multiphoton or strong field ionization [27]). Among these, single photon ionization (SPI) using an intense VUV laser has been demonstrated as a promising tool for efficient post-ionization of atoms and molecules, provided the photon energy is above the ionization potential of the investigated species [28–33]. If combined with time-of-flight (ToF) mass spectrometry, it was shown that this technique allows the detection of secondary ions and their neutral counterparts under otherwise identical experimental conditions regarding the detection probability as well as the sampled emission angle and velocity window [27]. Moreover, it is often possible to drive the photoionization process into saturation, thereby gaining quantitative information about the post-ionization efficiency which is essential for a determination of absolute ionization probability values.

We have frequently employed this technique in the past in order to measure the ionization probability of particles emitted under nuclear sputtering conditions [30,34–44]. For elemental targets, it is found that the ionization probability strongly depends on a possible surface contamination, an effect which is commonly described as the SIMS matrix effect. For thoroughly sputter cleaned surfaces, one usually finds relatively small values $< 10^{-3}$ for sputtered single atoms [45], which increase for clusters with increasing cluster size [30,34,37,46–48]. Oxidized surfaces, on the other hand, yield ionization probabilities which may be enhanced by orders of magnitude [49–51]. Only recently, a ToF spectrometer equipped with a VUV post-ionization laser was added to a high energy ion beam line [52], thereby allowing to adopt the technique to particles emitted under electronic sputtering conditions as well [53]. In this work, we present data collected on atoms and clusters ejected from a dynamically sputter cleaned germanium surface and compare the results obtained under SHI impact with those measured in-situ under low energy rare gas ion bombardment.

2. Experimental

The experiments were performed using a home-built reflectron time-of-flight (ToF) mass spectrometer installed at the M1 beam line of the UNILAC accelerator facility at the Helmholtz centre for heavy ion research (GSI) in Darmstadt, Germany. The system has been described in detail elsewhere [52], and therefore only a brief description of the features relevant for this work will be given here. The ToF spectrometer is mounted under 45° with respect to the UNILAC ion beam, and the sample is positioned in such a way that the sputtered particles are collected along the surface normal. For reference and alignment purposes, the system also includes a 5 keV Argon ion beam which impinges under the same polar angle (45°) with respect to the surface normal as the SHI projectiles. Projectile ions used in these experiments were ^{197}Au ions of a selected charge state (26 +) delivered by the accelerator with a specific energy of 4.8 MeV/u. We note that these conditions do not coincide with the equilibrium charge state of the gold ions (which is reached once the projectile penetrates a distance of typically several 10 nm into the solid), and therefore the energy deposition from electronic stopping of the projectile will vary as a function of penetration depth [54]. For the sputtering process investigated here, however, this variation is practically irrelevant since the mean emission depth of sputtered particles is only of the order of several nm. The UNILAC beam was shaped to a spot profile of typically about 6 mm diameter using a fluorescent target in place of the sample. The spot profile of the keV-beam was also examined by the fluorescent target and set to a diameter of about 2 mm FWHM.

Secondary ions released from the surface were swept into the ToF spectrometer using a pulsed extraction field, with the switching time marking the flight time zero for the detected ions. The reflector voltage (1450 V) was tuned slightly below the target potential (1600 V) in order to ensure that only ions originating from a minimum height of about 1 mm above the sample surface could be reflected and detected. In connection with the flight time refocusing properties of the ToF spectrometer, this setting determines a sensitive volume of about 1 mm diameter located at about 1 mm above the surface and centered around the ion optical axis of the spectrometer, from which ions could be extracted and contribute to the detected sharp flight time peaks [27].

Secondary neutral particles emerging from the bombarded surface were post-ionized using a pulsed F_2-laser operated at a VUV wavelength of 157 nm. The corresponding photon energy ensured that neutral atoms and molecules possessing ionization potentials up to 7.9 eV can be efficiently post-ionized via non resonant single photon absorption. The laser beam was directed parallel to the sample surface at a distance matching the location of the ToF sensitive volume. The beam was focused to a spot diameter of about 0.5 mm using a 250 mm focal length CaF_2 lens, which at the same time acted as the entrance window to the ultrahigh vacuum chamber housing the experiment. The laser delivered output pulses of about 4–7 ns duration and up to about 1.6 mJ pulse energy, which was monitored using its internal energy monitor and calibrated using a GenTech power meter. Due to geometrical restrictions, the laser beam had to be guided through an evacuated beam line of about 2 m length and then coupled into the vacuum system via a $\sim 120^\circ$ deflecting mirror, both leading to a significant intensity loss before being introduced into the experiment chamber. The intensity of the laser pulse actually entering the vacuum chamber was therefore monitored again with a fast in-vacuum photoelectric detector located behind the sample, the signal of which was also used in order to control the timing of the pulse.

During most of the experiments, the laser pulse was fired simultaneously with the ion extraction pulse. This way, the instrument cannot distinguish between intrinsic secondary ions and post-ionized neutral particles of the same species, thereby detecting both entities under otherwise the same experimental conditions regarding instrument transmission and detection efficiency. In order to distinguish between secondary ions and post-ionized neutrals, spectra were therefore taken with (SNMS) and without (SIMS) firing the laser beam, and the data corresponding to the secondary neutral particles alone were derived by subtracting both spectra. In the following, the spectra taken under irradiation with swift heavy ions during an UNILAC pulse will be referred to as “MeV-SNMS” and “MeV-SIMS”, respectively.

Inbetween subsequent UNILAC pulses, additional spectra were taken either with the keV argon ion beam bombarding the surface (“keV-SNMS/SIMS”) or without any ion bombardment at all. While the first deliver reference spectra which allow a direct comparison between electronic and nuclear sputtering processes, the latter are needed to ensure that the measured signals are actually related to the ion bombardment. In particular, the data taken with the laser beam alone reveals important information about the background signal arising from