Optical emission spectroscopy of excited atoms sputtered on a Ti surface under irradiation with multicharged Ar ions

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Abstract. Optical emission spectroscopy of excited atoms was carried out in order to investigate the sputtering processes on solid surfaces under irradiation of slow, multicharged ions. Many atomic lines of Ti I (neutral) and Ti II (single-charged ions) were observed in wavelengths from 250 to 750 nm with irradiation by Ar³⁺ (30 keV) on a Ti surface which was placed in a low pressure O₂ atmosphere. The emission intensity of Ti I (520 nm) decreased monotonically with an increase of O₂ partial pressure, whereas that of Ti I / II (670 nm, a 2nd order wavelength of 335 nm) slightly increased. From a semi-logarithmic plot of emission intensity for the 670 nm spectrum as a function of distance from the surface, the mean velocity of the excited Ti atoms and ions in a normal direction parallel to the surface, or \(<v_\perp>\), is estimated.

1. Introduction

Electron capture by multicharged ions often induces desorption [1], sputtering [2], and nano-structure formation [3]. It is generally recognized that nano-structure formation is triggered by the electronic excitation of target materials followed by explosive secondary particle emissions. Positive secondary ions produced by multi-electron capture have been considered to play important roles in the initial stage of the Coulomb explosion [4]. Numerous papers have reported in the last decade that secondary ion yields increase with an increase of the charge state of multicharged ions [5]. However, few studies report the velocity, momentum, or kinetic energy of secondary particles, though the importance of the recoil momentum of secondary ions is widely admitted. Neutral atoms, as a majority of secondary particles especially might play key roles in nano-structure formation processes. Therefore, we focused in this study on the velocity measurements of neutral particles produced by low energy collisions of multicharged ions. In order to measure the mean velocity of sputtered atoms on solid surfaces, we performed optical emission spectroscopy. In our previous study [6], no noticeable change of mean velocity parallel to the surface, or \(<v_\parallel>\), among different charge states was observed in the Al⁺ atoms which were emitted from Al and Al₂O₃ surfaces interacting with Ar⁺⁺ (q = 1–9). Results were obtained by analyzing the Doppler broadening in the emission spectrum.
2. Experimental details

A schematic illustration of the experimental setup is shown in figure 1. The multicharged Ar ions were extracted from a 10 GHz electron cyclotron resonance ion source [7], and their mass to charge ratios \((m/q)\) were analysed by 90° sector magnets after being focused with an electrostatic lens. The ion beam irradiated a polycrystalline Ti surface at a normal angle after passing through a hole with a 10 mm inner diameter. One can adjust the surface linearly along the beam axis with a motion feedthrough. Light emitted from the surface was focused by an optical lens of magnification 1. Light was dispersed with a visible monochromator and detected with a photo-multiplier tube.

The hole was negatively biased (~ -100V) to repel secondary electrons emitted from the surface. The current of the ion beam (~ 2 µA) was measured with a current-voltage conversion amp (1 V/µA). The background pressure was 1×10^{-6} Pa, whereas the partial pressure of oxygen molecules in the collision chamber was 1×10^{-5}–1×10^{-4} Pa. The vacuum was monitored with a cold cathode ion gauge. To eliminate any pre-existing oxidized layer and other impurities, the surface was cleaned by irradiation of an Ar+ (10 keV) beam for an hour.

3. Results and discussion

Figure 2 shows the visible emission spectra measured on the Ti surface interacting with Ar^{3+} (30 keV). The vertical axes of the figures indicate the number of photons normalized with the ion beam current. A number of atomic lines were clearly observed. The assigned spectra are summarized in Table 1. The lines observed in the present study correspond well with the results of pulsed laser [9] and O \(^+\) [10] irradiation with TiO\(_2\) surfaces except for some oxygen lines.

It is interesting that the spectra in the figure divide into two types, with type A including the spectra whose intensity increased with an increase in oxygen pressure, and type B including those whose intensity decreased with an increase in oxygen pressure. Most of the lines in the wavelength range of 300–380 nm belong to the former case, whereas those in 390–530 nm belong to the latter case. The 648 and 670 nm lines are the spectra of 2nd order wavelengths of 324 and 335 nm lines, respectively. From supplementary obtained results of high resolution wavelength scanning of the monochromator with a narrower slit width, we concluded that the spectra of Ti II belong to type A whereas those of Ti I belong to type B, though some Ti II spectra overlap with Ti I in figure 2.

The photon intensities of 520 and 670 nm spectra as a function of partial oxygen pressure are shown in figure 3. A mutually opposite pressure dependence was clearly observed between 520 and 670 nm spectra. The divergent pressure dependence of emission intensity between neutral atoms and
ions was also reported in an Mg surface irradiated with Kr⁺ (6 keV) in an oxygen atmosphere [11]. In low O₂ pressure, the intensity of Mg I lines increased with an increase in O₂ pressure, whereas that of Mg II lines decreased slightly with an increase in O₂ pressure. One possible conclusion is that the different pressure dependence is due to two different mechanisms which produce Mg* and Mg++. One is the bond-breaking model [12] in Mg I and the other is a kinetic process leading to electron capture [13] in Mg II. Note that the pressure dependencies of both Mg I and II also reversed themselves between the two limited cases of low and high oxygen pressure. This suggests that the reverse was due to a change in the chemisorption of oxygen atoms related to the oxidation of the surface. We can not conclude the excitation mechanism of Ti* and Ti++ at the present stage. The relative position of the energy levels to the different pressure dependence between Ti I and II. The term in which k = 0 of Ti* (3d₄4s₄p x 3G) to be 10.6 ns [15]. As a result, <τ> corresponds to the decay curve of emission species Transition

![Table 1. The assignments of the emission spectra observed in this study](image)

Figure 3. The emission intensities of Ti I 520 nm (▲) and Ti I / II 670 nm (●) as a function of partial oxygen pressure

![Figure 3](image)

\begin{equation}
I = \sum_k I_{0k} \exp \left( -\frac{Z}{\tau_k \cdot \langle v_0 \rangle} \right),
\end{equation}

where τₖ and I₀ₖ denote the life time and the spontaneous emission intensity at Z = 0, respectively, of the k-th excited state of the atom [14]. The terms in which k>1 define the cascade components. One can obtain the \(<v_0>\) value by fitting the eq. (1) with known life times into the decay curve in figure 4. The slow decay curve shown with the dashed-dotted curve in figure 4(b) is considered to be a cascade component with a long life time (> 10 ns). The dashed-double-dotted curve in figure 4(b) was drawn by assuming τₖ of Ti⁺ (3d₄4s₄p x G) to be 10.6 ns [15]. As a result, \(<v_0> = (7 ± 3) \times 10^7\) m/s was obtained for the Ti⁺ atoms. However, the spectrum might include a significant contribution from Ti II as mentioned above. If the mean life time of Ti⁺⁺ (3d₄4p z ⁴G₄ or ⁴F₄) (J = 3/2–11/2) is assumed to be
5.0 ns [16], the mean velocity becomes two times larger. Therefore we may conclude that the \( \langle v_{\perp} \rangle \) obtained in the present study was significantly larger than the \( \langle v_{\parallel} \rangle \) of Al* atoms which were emitted from Al and Al\(_2\)O\(_3\) surfaces interacting with Ar\(^{q+} \) (\( q = 1–9 \)) [6]. Generally speaking, a \( \langle v_{\perp} \rangle \) value depends on not only actual velocity of the sputtered atoms but also the escape probability of the corresponding electrons.

4. Conclusions
Optical emission spectroscopy of excited atoms emitted from a polycrystalline Ti surface interacting with Ar\(^{3+} \) (30 keV) ions was conducted. Numerous line spectra assigned to Ti I and II were observed. The emission intensity of Ti I and II showed mutually divergent O\(_2\)-pressure dependencies. This fact suggests different emission mechanisms of Ti\(^+\) and Ti\(^*\). The emission intensity of the 670 nm spectrum as a function of distance from the surface revealed a double exponential decay. The mean velocity \( \langle v_{\perp} \rangle \) of Ti\(^+\) atoms was estimated to be larger than the \( \langle v_{\parallel} \rangle \) of Al* emitted from Al and Al\(_2\)O\(_3\).

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