Potential effect in Balmer light emission near surface irradiated with highly charged ions

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Abstract. The interaction between highly charged ions (HCIs) and the solid surface causes various phenomena due to high potential energy of HCIs. Luminescence is also included in them. In order to investigate the origin of the light emission from the surface irradiated with HCIs, we conducted spectroscopic measurements and then we investigated characteristics of Balmer light emission because potential effect of HCI was remarkable in Balmer light emitted from hydrogen atoms desorbed from the surface. In the present study, the Balmer light intensity was revealed to increase rapidly with the charge state of HCIs.

1. Introduction
The highly charged ion (HCl) possesses large potential energy increasing with its charge state. When a HCl is incident on the solid surface, emission of photons in the range of visible to X-ray, hundreds of secondary electrons, sputtering of secondary ions and modification of surface structure in nanometer scale are caused. The effect of potential energy concentrates on only a few atomic layers of the topmost surface [1,2].

In the previous experiments, measurement of luminescence of Er₂O₃ irradiated with HCIs had been performed. The emission intensity from the region of 607–680 nm strongly depended on charge state of HCIs. In addition, the emitted light was not dependent on kinetic energy. The luminescence caused by the potential effect of HCIs. The luminescence from Er₂O₃ irradiated with HCIs nonlinearly increased depending on the charge state of HCIs. The light emission of particles sputtered from the surface by HCIs is dominant [3,4]. In the present study, spectroscopic measurements and secondary ion mass spectrometry (SIMS) were performed in order to specify atoms participating in the luminescence. In addition, the characteristics of the Balmer light emission was investigated since the light emission from the adsorbed hydrogen atoms is remarkable at spectroscopic measurements. We investigated the dependence of Balmer light emission on charge state and temporal change of the emission intensity.

2. Experimental
HCIs were produced by using an electron beam ion source (EBIS) installed at Kobe University, Japan [5-7]. The Kobe EBIS comprises an electron gun, drift tubes, an electron collector and a superconducting magnet. HCIs are created by successive ionization processes in the collision of electrons focused by the strong magnetic field (3 T) with ions. The current density of electrons at drift tube region is in the order of 1000 A/cm². The potential of drift tubes (the acceleration voltage to
HCl is 3 kV. The ultimate pressure of the Kobe EBIS is in the range of 10⁻⁸ Pa. A sector magnet is used to select charge state of HCl extracted from the ion source. HCl with specific charge state enter the irradiation chamber maintained at ultrahigh vacuum of about 10⁻⁷ Pa. Primary ion current is monitored by a Faraday cup and ion beam shape and position are monitored by a micro-channel plate (MCP). Incident ion current to the sample during irradiation is also monitored.

In the present measurement, the light emission caused by the interaction between HCl and samples was measured with a liquid nitrogen cooled CCD. In order to keep kinetic energies of HCl incident on the surface constant (16 keV) for each measurement, the retarding voltage was applied to the sample. The diameter of HCl beam was about 3 mm for each experiment. Spectroscopic measurements were conducted using a polychromator. Wavelength distribution for the range of 420–670 nm and spatial distribution of horizontal direction were measured from the two-dimensional CCD image. Er₂O₃, Si, highly oriented pyrolytic graphite (HOPG) and Cu were used as samples. We used commercially available Si wafer for Si sample. Because no cleaning or passivation procedure was done, the native oxide film was formed on the Si surface. These samples were stored in the atmosphere before each measurement, and were irradiated with HCl (Ar⁶⁺ and Ne⁶⁺). For HOPG, the surface was cleaned before introduction to the irradiation chamber by peeling-off procedure. In spectroscopic measurements, the exposure time was 2 hours. SIMS was performed using a quadruple mass analyzer (QMS). In the Balmer light measurement, the distribution of light emission in two-dimensional space was obtained using a filter instead of a polychromator. The emission intensity in the 656 ± 5 nm region (Hα) was evaluated and the exposure time was 10 minutes.

3. Results and discussions

Figure 1 shows the spectrum of Si irradiated with Ne⁶⁺. The emission intensity is calculated as a summation of count at the pixels corresponding to each wavelength. Since many noises appeared in the spectrum due to cosmic rays during measurement, data points which are remarkably stronger than that of adjacent pixels are replaced with average values of data on both sides in order to remove noises. In figure 1, emitted light lines are observed around 486 nm, 590 nm and 656 nm. These lines also appeared in the spectra of Er₂O₃ irradiated with Ar¹¹⁺ [4]. From these results, it is suggested that these peaks are not derived from irradiated ions or samples since three emitted light lines appear in common.

The analysis of ions produced by irradiation with HCl was performed using a QMS to identify the origin of the light emission. Figure 2 shows a secondary ion mass spectrum of Si irradiated with Ar¹¹⁺. A very strong signal of H with a mass number of 1 and a signal of Na with a mass number of 23 are observed in the spectrum in addition to Si as a sample and Ar as a primary ion. It should be noted that the intensity of mass number of 1 (H⁺) is overwhelmingly more than that of 2 (H₂⁺) in the spectrum. This result is completely different from the quadruple mass spectrum of the residual gas [8]. These results indicate that hydrogen atoms contained in molecules on the surface are ionized and desorbed as an interaction of molecules with HCl. From these results, it seems that emitted light lines observed by
spectroscopic measurements come from H and Na, i.e. Balmer series (Hα and Hβ) and the resonance line of Na (D line). It is considered that H is originated from either water or hydrogen adsorbed or occluded on the sample surface. The peak at 590 nm did not appear in the emission spectrum of HOPG, therefore the origin of Na is contamination.

To investigate the nature of Balmer light produced by the injection of HCIs, the emission intensities at the 656 ± 5 nm region (Hα) were evaluated for various experimental conditions. The emission intensity was obtained from the summation of data points at light emitting part subtracting background in the CCD image, and normalized by incident ion current divided by the charge state of HCIs. Finally, the intensity was converted to the emission intensity per single ion. Figure 3 shows the dependence of emission intensities per single HCI on the charge state of Arq⁺ (q = 6, 8, 11, 14, 16). The intensities increase with charge state. It is considered that the transfer of electrons caused by large potential energy leads to the excitation of more hydrogen atoms. Figure 4 and figure 5 present temporal changes of emission intensities from Si and HOPG surfaces per the injection of single HCI. Here, the time is converted to the number of incident ions since the number of incident ions per unit time is different for each measurement. The intensities tend to decrease by continuous irradiation with HCIs. It is suggested that the number of hydrogen atoms on the surface decreased by the irradiation.

**Figure 3.** Dependence of emission intensities per single ion on charge state of Arq⁺ (q = 6, 8, 11, 14, 16).

**Figure 4.** Temporal changes of emission intensities of Si irradiated with Arq⁺.

**Figure 5.** Temporal changes of emission intensities of HOPG irradiated with Arq⁺.

It is suggested that water or hydrogen are desorbed and decreased from the surface by HCI injection, since the SIMS spectrum indicates that atomic hydrogen ions are produced by irradiation with HCIs. Comparing temporal changes of Si and HOPG, decrease of emission from HOPG is slower than that from Si. This is probably because the Si sample is stored in the atmosphere, while the HOPG surface was prepared a new surface for every measurement, so that exposure time of HOPG to air is
shorter than that of Si. Therefore, it is considered that the origin of emission is both hydrogen attached to the sample in the irradiation chamber and water adsorbed in the atmosphere. However, the number of molecules present on the surface is unknown in these measurements due to the difference of exposure time to air. Figure 6 shows temporal changes of the emission from HOPG irradiated with Ar^{11+} for various exposure time to air after peeling-off procedure. Because the emission intensity of the sample exposed to air for 7 days is stronger than that of the sample exposed for 1 day, it is considered that water in air was adsorbed to the HOPG surface.

Water molecules seem to mostly contribute to the Balmer light emission, however, there remains a possibility of contribution from adsorbed hydrogen molecules which come from residual gas. It is essential to control the condition of the surface in order to identify the origin of Balmer light. As future prospects, in order to reduce the influence of water, the sample surface will be cleaned using an ion gun in vacuum before measurement.

![Figure 6](image_url)

**Figure 6.** Temporal changes of emission intensities of HOPG irradiated with Ar^{11+}. HOPG surfaces were exposed to air for 0.5 hours, 24 hours (1 day) and 168 hours (7 days).

4. Conclusions
The emission light from the surface irradiated with HCIs was observed. The origin of luminescence was identified as H as the main light emission species from the spectroscopic measurement and SIMS. The emission intensity of Balmer light increases with the charge state of HCIs and decreases as the irradiation continues.

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