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Detection of hydrogen isotope atoms by mass spectrometry combined with resonant ionization

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Abstract. We examined the application of mass spectrometric methods using resonant ionization by a tunable laser and proposed its use for analyzing hydrogen isotopes. We conducted resonance ionization mass spectrometry (RIMS) to detect gas-phase hydrogen isotope atoms. The ionization efficiency was increased by more than 1000 times that obtained with conventional methods using nonresonant ionization. Resonant laser ablation mass spectrometry (RLAMS) was applied for deuterium detection in solid samples. A graphite substrate implanted with deuterium was used for ordinary laser ablation mass spectrometry (LAMS) and RLAMS. The deuterium signal was observed very clearly by RLAMS, in contrast to LAMS. Mass spectrometry combined with resonance ionization was very useful for hydrogen isotope detection, because components with equal mass numbers were resolved and the method demonstrated higher ionization efficiency.

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The ability to detect hydrogen atoms in solid materials is very important in various fields, especially for evaluating the material properties in fusion technology. Mass spectrometry has advantages over other techniques, such as chemical analysis, due to the short analyzing time. However, mass spectrometry is problematic for trace hydrogen isotope detection because it is hard to resolve equal mass-number components, such as deuterium atoms (D) and hydrogen molecules (H_2). Therefore, it is very difficult to distinguish trace deuterium atoms from a background of hydrogen molecules. Another problem involves the ionization efficiency. The ionization efficiency of hydrogen atoms is relatively low because of the high ionization energy. This problem might be solved in resonance ionization mass spectrometry (RIMS), that is well known for detection of gas-phase trace components. In RIMS, the trace components are ionized by tunable laser light that is tuned to the resonant transition of the trace component.

For solid material analysis, the sample is vaporized and then ionized. Laser ablation is one of the best methods for this because the spatial resolution is very high, the amount of sample required for measurement is very low, and the sample can be ionized immediately. This is known as laser ablation mass spectrometry (LAMS). LAMS is generally performed using fixed wavelength lasers such as Nd:YAG and excimer lasers. Resonant laser ablation (RLA) was recently investigated [1, 2]. In RLA, the wavelength of the laser for ablation is tuned to the resonant transition of the atom to enhance ionization efficiency. RLA is applied to the ionization of mass spectrometry (RLAMS). RLAMS is very suitable for detecting trace components, as is RIMS. RLAMS was investigated for some metal atoms, such as Al, Fe, Ni, Mg, Si, etc. [3–6]. RIMS and RLAMS have the potential to overcome the problems in hydrogen isotope detection related to the detection limit and resolution. In this work, we investigated the detection of hydrogen isotope atoms using RIMS and RLAMS with a tunable laser.

1 Experiment

The experimental apparatus is shown in Fig. 1. The light source consisted of a third-harmonic Nd:YAG laser (Spectra Physics, GCR 230), pumping a dye laser (Lumonics, HD500), and a BBO crystal for frequency doubling. The laser light wavelength was tuned to 243 nm, which caused two photon excitations of the $1S-2S$ transition of the hydrogen

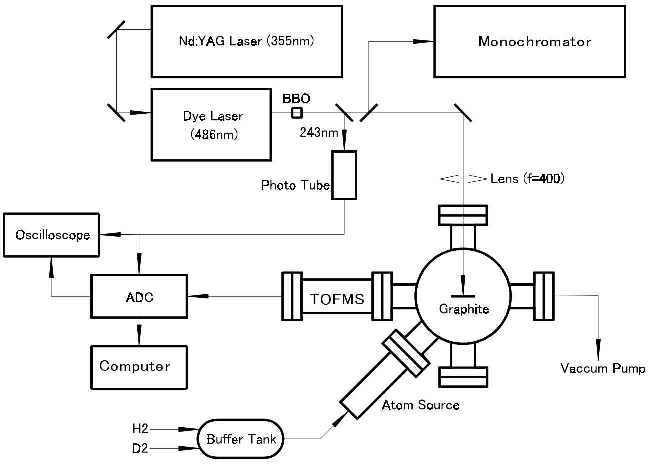

Fig. 1. Experimental apparatus

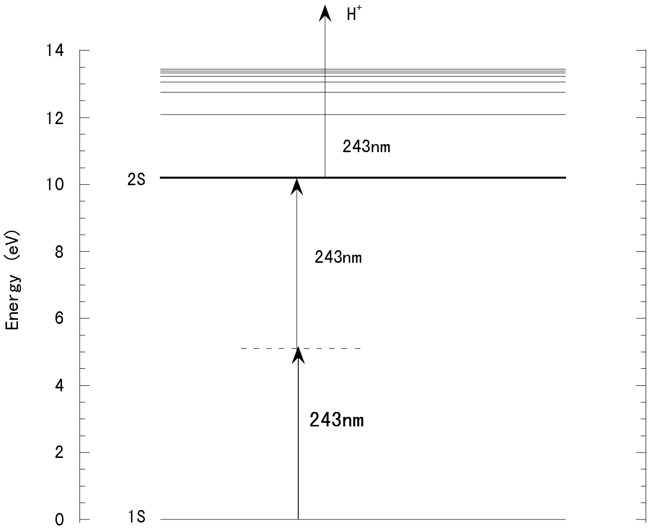

Fig. 2. Energy diagram of hydrogen atom. A 2 + 1 (2 photons to resonantly excite +1 photon to ionize) ionization process was conducted with a 243-nm wavelength

atoms (Fig. 2). The typical output energy was 100 μJ with a 10-ns pulse duration at 10 Hz. The laser light was focused into a sample chamber by a fused silica lens (focal length 400 mm). The sample chamber was pumped by a turbo molecular pump, and the operating pressure of the chamber was 10^{-8} Pa. The focused spot size on the samples was 100 μm in diameter; therefore, the average intensity was $100\,\mathrm{MW/cm^2}$. We used a time-of-flight mass spectrometer (TOFMS) for the mass spectrometry. The TOFMS consisted of three electrodes and an ion detector. Ions were accelerated by an electric field and subsequently injected into the drift region. The acceleration high voltage was −2000 V and the length of the drift region was approximately 30 cm. We used a micro-channel plate (Galileo, TOF-2003) for the ion detector. The signal from the detector was monitored by a digital oscilloscope, and the TOFMS signal in an appropriate time window was measured by a 10-bit charge-sensitive analog-to-digital converter (ADC). The laser light energy was measured simultaneously with a calibrated biplanar phototube. We stored the data from the ADC in a computer. A quadrupole mass spectrometer (Stanford Research Systems) were used on the sample chamber for calibration. A thermal cracking hydrogen atom source (EPI) was used to generate hydrogen atoms. In the equipment, hydrogen atoms were generated by dissociation of hydrogen molecules with a hot tungsten filament [7]. The TOF system was calibrated and confirmed to measure H, D, C, N, O, H_2O, C_2, N_2, O_2, and C_3. We calibrated the wavelength of the light source by comparing the measured resonant wavelength of the hydrogen atom with the known resonant wavelength [8].

2 Result and discussion

2.1 RIMS for gas-phase hydrogen isotope atom

Figure 3a shows the correlation between the ion signal intensity and the excitation wavelength. Strong resonant peaks that corresponded to the hydrogen and deuterium atoms were observed. Each resonant wavelength corresponded to a 2 + 1 (2 photons to resonantly excite +1 photon to ionize) ionization process for hydrogen and deuterium atoms [9, 10]. The hydrogen atoms and deuterium atoms were very clearly resolved by their distinctive resonant wavelengths with the light source we used. Furthermore, these resonant wavelengths were nearly isolated from any resonant wavelengths of hydrogen molecules. For example, the E-X band of the H_2 molecule was 193 nm for 2-photon excitations [11]. Therefore, it is possible to resolve all the hydrogen isotope atoms and hydrogen molecules by resonance ionization.

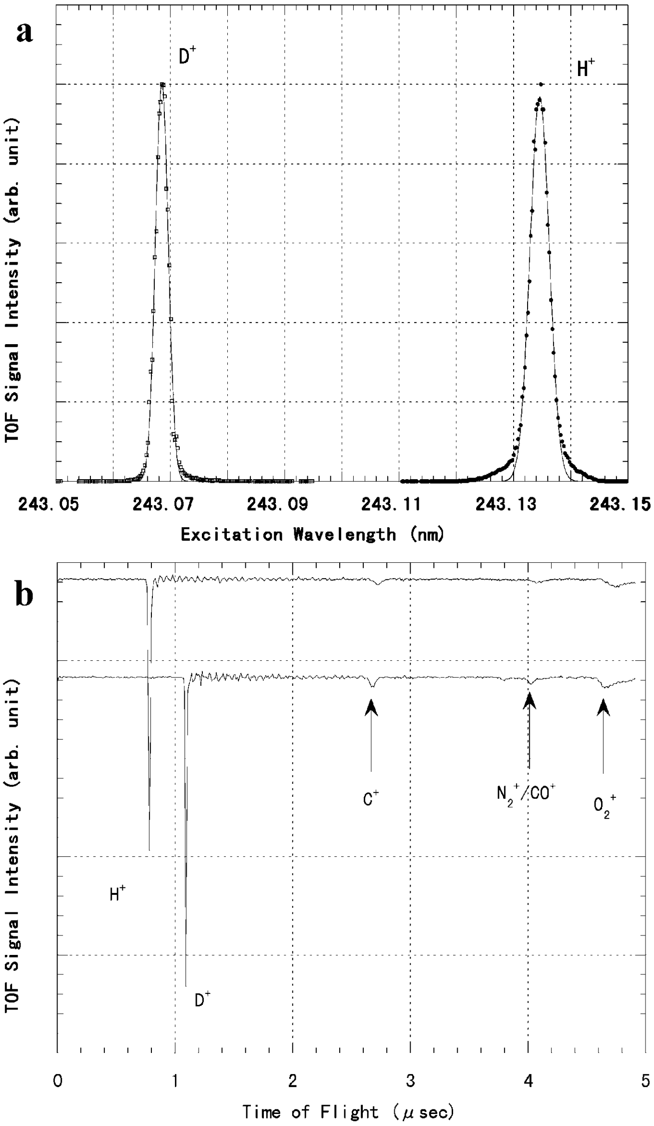

Fig. 3a,b. TOF measurement of H^+ and D^+ of a free hydrogen and deuterium atom. **a** Correlation between TOF signal intensity and excitation wavelength for the hydrogen and deuterium atom. **b** RIMS spectra for hydrogen and deuterium atom

RIMS was conducted for a hydrogen and deuterium atom mixture using the 2 + 1 ionization scheme. The density of each atom was evaluated as 10^9–10^{10} atom/cm^3 using the quadrupole mass spectrometer. Figure 3b shows the RIMS mass spectra. Each spectrum was obtained by resonance ionization of the hydrogen atom and deuterium atom. In contrast to the resonance ionization of a hydrogen atom, a strong peak was observed corresponding to mass number = 2 when the laser was tuned for resonance ionization of a deuterium atom. Therefore, this peak was assigned to the deuterium atom, not the hydrogen molecule. A deuterium atom is difficult to distinguish from a hydrogen molecule using conventional mass spectrometry. It is possible to resolve identical-mass components using RIMS. Comparing the two spectra indicates that ionization efficiency was enhanced at least three orders using resonance ionization.

2.2 *RLAMS for deuterium-implanted graphite*

A graphite target was implanted with deuterium to a dose of $6 \times 10^{15}\,\mathrm{cm}^{-2}$ by a cyclotron (Sumitomo Heavy Industries, Cypris) and was used for the measurements in this section. We calculated the depth profile of deuterium to be 10 µm.

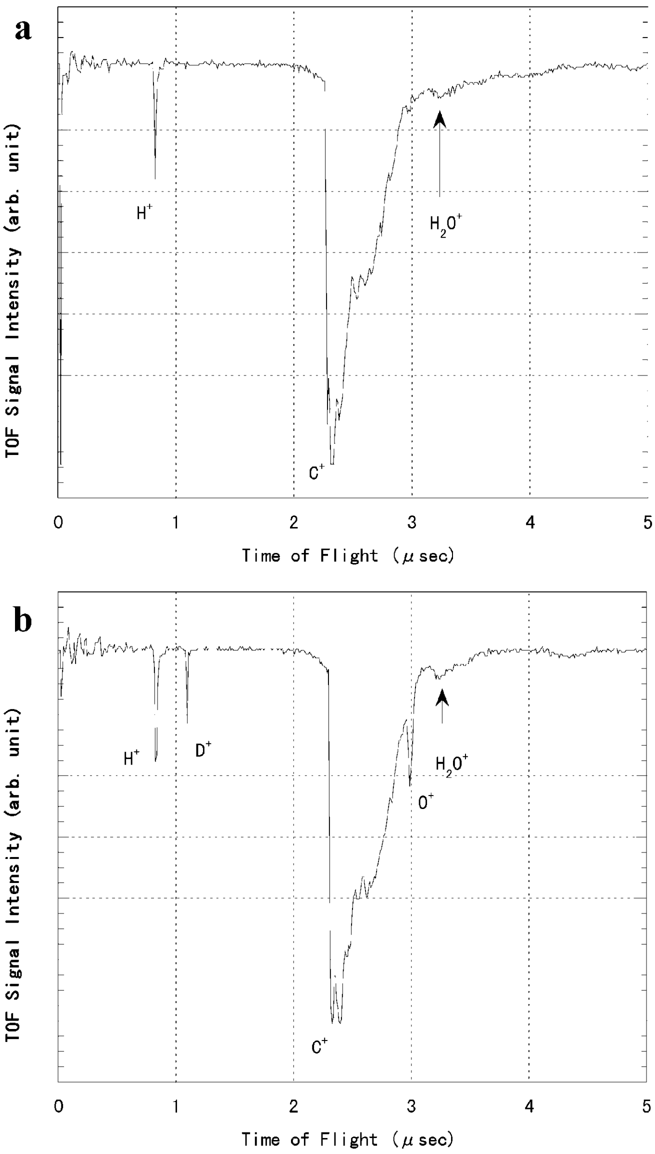

Fig. 4a,b. TOF signal of laser ablation of deuterium-implanted graphite. **a** LAMS spectrum. A large amount of hydrogen was caused by fragmentation of water molecules. **b** RLAMS spectrum for a deuterium atom. Deuterium was observed clearly

The etching depth caused by laser ablation was measured by a laser microscope to estimate the etching amount. The etching depth was proportional to the number of laser shots and the etching rate was 0.1 µm per laser pulse. Therefore, it was estimated that 10^{14} carbon atoms and 10^{9} deuterium atoms were ablated by each laser shot, based on the etching rate and beam spot size.

We performed ordinary laser ablation mass spectrometry (LAMS) as the first step. Figure 4a shows the mass spectrum obtained by LAMS. Carbon produced by nonresonant ionization was observed clearly. Nonresonant ionization of hydrogen and water molecules was also observed. The same components were observed by the quadrupole mass spectrometer. The water molecules were contained in the sample and a large amount of hydrogen was from fragmentation of water molecules. The wavelength of the ablation laser was then tuned to the wavelength of the resonant ionization transition of the deuterium, and RLAMS was carried out. Figure 4b shows the mass spectrum in this measurement. Deuterium was clearly observed by the RLAMS. However, carbon and hydrogen were observed at a similar intensity as with LAMS. The observed signal intensity of deuterium was $1/10 - 1/100$ of the carbon signal intensity. Therefore, the ionization efficiency of deuterium was increased 10^3–10^4 times higher than that of carbon, based on the etching amount per laser shot for each component.

G.C. Eiden et al. [4] investigated the resonant wavelength of RLA for several kinds of metal atoms and observed a discrepancy in the resonant wavelengths between RLA and the known transition for silicon atoms. Figure 5 shows the precise measurements of the TOFMS signal and the excitation wavelength for gas-phase deuterium and RLAMS. The laser light energy was 100 µJ for both measurements. A small discrepancy between each resonant wavelength was observed in this measurement. A similar discrepancy was observed between a gas-phase hydrogen atom and the RLA of a hydrogen atom. G.C. Eiden et al. suggested that the discrepancy of the Si transition might be due to an ac Stark shift or to perturbations arising from the proximity of the surface. We think that

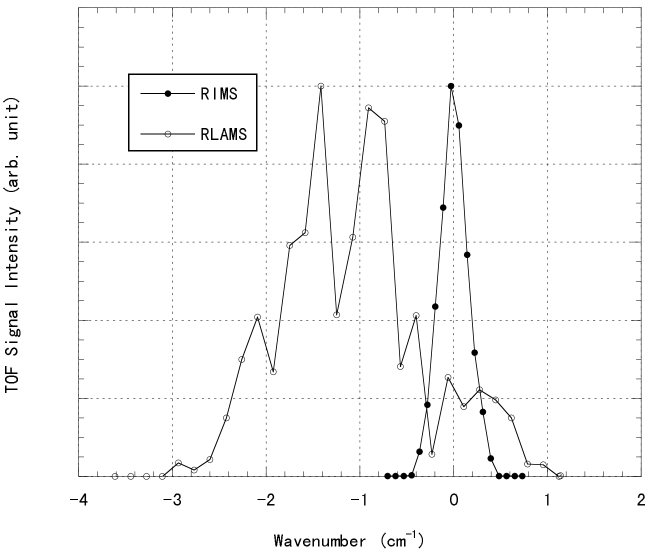

Fig. 5. The dependence of the excitation wavelength on RIMS for the gas-phase atom and RLAMS for a deuterium atom contained in a solid

the discrepancy was also caused by the Doppler shift of the high-speed components.

3 Conclusion

We demonstrated that RIMS, mass spectroscopy combined with resonance ionization using a tunable laser, is suitable for high-sensitivity detection of hydrogen isotope atoms, since the ionization efficiency was enhanced at least three orders. In addition, equal mass-number species, such as H_2 molecules and D atoms, were also resolved by RIMS. This is a very significant advantage for hydrogen isotope detection.

RLAMS is a very useful technique for detecting hydrogen isotope atoms contained in solid material, because RLAMS has the advantages of RIMS in addition to the advantages of LAMS, including high spatial resolution and minimal sample preparation. RLAMS may be applied to the distribution measurement by using the controllability of the etching depth of laser ablation.

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