A Study on the Kinetic Energy of the Laser-Ablated Cation Using Time-of-Flight Mass Spectrometry

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The initial kinetic energy of laser-ablated Zn cation has been investigated via time-of-flight mass spectrometry. The flight times of the ions have been measured with a high voltage pulse on the extract electrode in the mass spectrometer, which has been delayed from the laser pulse. The time-of-flight equation including the initial kinetic energy term of the ion has been derived for the mass spectrometer. The optimum value of the initial kinetic energy has been extracted by fitting the measured flight times into the time-of-flight equation. The initial kinetic energy of the ions generated by Nd:YAG laser (532 nm) at the power density of 5×10^7 W/cm^2 has been determined to be 22-44 kJ/mol.

Introduction

Laser ablation of a solid sample by collimated high power laser has been applied to analyze the compositions of the solid surface[1] and to deposit thin films.[2] The method has attracted the special attention of many workers for chemical analysis of solid samples[3-5] due to its omission of a preliminary sample preparation steps. The pulsed laser deposition method also has several merits over other techniques including its durability in severe operating conditions and the stoichiometric deposition.[6]

Although the technical aspect of laser ablation has made remarkable progress in recent years, the complexity of the technique has yet to be studied further for full understanding of the phenomena. It requires a deep understanding of the laser ablation mechanism, including the interaction between photons and solid surface. Some of the experimental information[1,2,7-10] on the interaction have been utilized for theoretical development to describe the laser ablation of a solid sample. These theories, however, have not enjoyed universal success in describing every system. A typical example may be the thermal process that describes the laser ablation phenomena fairly well for metal but is not as successful for insulating materials.[6] The observed kinetic energies for ablated particles also vary from several eV to several hundreds eV depending on the measuring techniques and samples.[11-15]

The properties of particles in laser ablation of a solid sample have been characterized by kinetic energy distribution, internal state, sizes, and number density. Among these properties, kinetic energy distribution of particles is important to understand the evaporation phenomena since it provides the information on the temperature of solid surface in the process. The precise measurement of kinetic energy helps to improve the laser ablation processes by correctly controlling the vaporization and the ionization.

In the time-of-flight mass s pectrometer (TOFMS), the position of an ion in the ionization region affects the ion flight time since the effective electric field strength is determined by its position. The ion movements are only related to the electric field since the ions gain their kinetic energies from the electric field in the TOFMS. An ion with initial kinetic energy and no external electric field will fly some distance in the ionization region. At that position, if high extracting voltage is applied, an ion will then gain additional kinetic energy by an effective electric field strength. If the high extracting voltage is applied with a different time lag, differences in the ion flight time will be observed. From this observation, the initial kinetic energy of an ion can be determined.

In this work, we have studied the initial kinetic energies of the laser ablated Zn^+ ions in terms of the time delay between the laser and extracting pulses. The resolution between the initial kinetic energy and kinetic energy obtained by the extracting electric field in laser ablation has been achieved by applying a high voltage pulse to the extraction electrode after the ablation laser pulse. The flight times of Zn^+ ions generated by laser ablation have been measured as a function of the time delay. The theoretical flight time of the ion has been calculated from the time-of-flight equation to obtain information about the initial kinetic energy of ablated cations.

Experimental

The TOFMS in this study was Wiley and McLaren type in its design.[16,17] In brief, it consists of three parts: an Nd:YAG laser for ablation, the ionization chamber and the time-of-flight chamber/detector. Each chamber was pumped differentially to about 10^{-6} Torr with an oil diffusion pump.

A frequency-doubled Nd:YAG laser beam (Quanta-Ray GCR3) was used to ablate solid sample. This laser beam was focused onto sample surface using f=500 mm lens and the incidence angle of 45 degrees. The shape of focused laser beam on sample surface was showed to be an elliptical shape with diameters of 300 and 500 μm due to the 45° incidence angle. Since ions have been generated aptly at low laser power, the power was attenuated by the diaphragm of

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1 mm diameter to obtain a working power of about 5×10^7 W/cm^2 at the sample surface.

The ionization region is composed of a sample holder, an ion extraction electrode (E1) and other ion optics. Zinc metal of about 10 mm diameter (Johnson Mathey Co.) was positioned at the center of the Teflon sample holder whose tip is held with a linear and rotary motion feedthrough. The sample holder could be in the same ionization position in all cases by attaching to E1. The stainless steel cap covered the sample in the sample holder. This itself is part of a repelling electrode for minimizing the distortion of an extracting electric field generated due to the center hole of E1. There are two other electrodes and X-Y deflectors in the ionization region; accelerating (E2) and ground electrodes (E3) that establish the extracting and accelerating fields from a conventional Wiley and McLaren type.[17] In this study, however, high-voltage pulse is applied only to E1 in order to determine the kinetic energy of ablated ions. Both E2 and E3 are used to ground electrodes in which E3 has a small center hole (1 mm in diameter) to select the central part of the ion packet generated by the laser. X-Y deflectors direct the ions toward the detector.

In this study, we used a commercial high-voltage pulse generator (Avtech Electro System; AVRH-3) which provided the output amplitude of about 1500 V and a pulse width in the range of 1.0-2.2 μs at the top flat region. The rising time of the high voltage pulse is less than 50 nsec. This is fast enough to avoid the distortion of the ion flight. The pulse generator can be synchronized to the output pulse of the Nd:YAG laser through the digital delay generator (Stanford Research System; DG535). The delay between laser ablation and ion extracting pulses can be controlled with a precision of a nanosecond.

Ion detection was made by a pair of microchannel plates (MCP) in the Chevron configuration. Transient ion signals were recorded on a 300 MHz digital oscilloscope (LeCroy; 9310M) coupled with PC. The experiments was performed at 10 Hz and TOF mass spectra typically accumulated for 500 pulses.

Results and Discussion

Calculation. In Figure 1 the ionization region consists of three plates (E1, E2 and E3). The d_1 and d_2 designate two sets of separations, the former from plate E1 to E2 and latter from plate E2 to E3. A positive voltage is applied to E1 to form an extracting field between E1 and E2, where E2 is electronically grounded. The ion generated by the laser is extracted promptly from the sample surface to E2 and passes through the field free region arriving at the detector.

High voltage pulses are applied to the E1 electrode with time delay between the laser pulse and extraction pulse. In the delay period, the formed ion moves only with initial kinetic energy obtained during laser ablation process. The final kinetic energy of an interested ion varies with its spatial position in the extraction region. Consequently, the flight time of the ion varies with the time delay. The effect of initial kinetic energy U_o of the ablated ion can be obtained from an accurate measurement of the flight time as a function of the delay time.

If an ion with an initial velocity v_o is formed by the laser

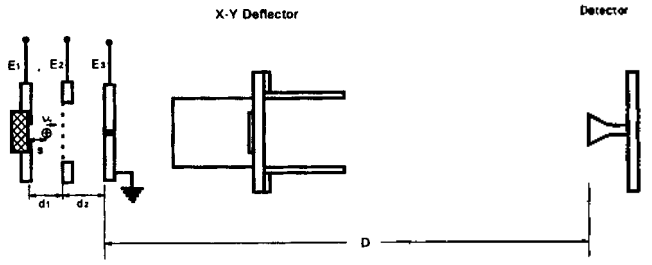

Figure 1. Schematic drawing time-of-flight mass spectrometer (TOFMS) for the determination of the initial kinetic energy of the laser-ablated cations.

light, the flight time, t_1, of the ion from the sample surface to E2 electrode is given by,

$$t_1=\frac{\sqrt{2M}}{qE}\left(\sqrt{U_o+qd_1E}-\sqrt{U_o}\right) \tag{1}$$

where U_o is the initial kinetic energy of the ion, 1/2 Mv_o^2, E the electric field strength in the extraction region between E 1 and E2 electrodes, and M and q the mass and charge of the ion, respectively. The arrival time, t_2, of the ion to the detector after passing through the extraction region is given by Eq. (2).

$$t_2=\frac{\sqrt{M}D'}{\sqrt{2(U_o+qd_1E)}} \tag{2}$$

where D' designates the total length of the field-free region d_2+D. The total flight time of the ion from the sample surface to the detector is given by adding up two flight times of the ion, t_1+t_2, when the continuous high voltage is used for the extracting voltage.

When the high voltage pulse is applied to E1 after the delay time, Δt, the ion moves from the sample surface to some distance, $s=v_o\cdot t$. The electric field strength of the ion at this position changes to $(d_1-\Delta t\sqrt{2U_o/M})qE$. The total flight time, t, also changes to Eq. (3);

$$\begin{aligned} t&=\Delta t+t_1+t_2\\ &=\Delta t+\frac{\sqrt{2M}}{qE}\left(\sqrt{U_o+(d_1-\Delta t\sqrt{2U_o/M})qE}-\sqrt{U_o}\right)\\ &\quad+\frac{\sqrt{M}D'}{\sqrt{2(U_o+(d_1-\Delta t\sqrt{2U_o/M})qE)}} \end{aligned} \tag{3}$$

For the given potential and geometry, the initial kinetic energy of an ion can be obtained from Eq. (3). In this equation, D' can be expressed with the known parameters and U_o since D' is actually the exact ion flight path in the field free region. In the case of Δt=0, the flight time of an ion, t_o, is equal to that obtained using the continuous extracting voltage. Therefore, we can obtain t_o with the continuous high voltage power supply by adjusting the voltage in the order of ten volts. With this method, we also estimate the exact value of the extracting voltage pulse. By rearranging Eq. (3) , the total flight time becomes Eq. (4).

$$\begin{aligned} t&=\Delta t+t_1+t_2\\ &=\Delta t+\frac{\sqrt{2M}}{qE}\left(\sqrt{U_o+(d_1-\Delta t\sqrt{2U_o/M})qE}-\sqrt{U_o}\right) \end{aligned}$$

$$+\left(t_o-\frac{\sqrt{2M}}{qE}(\sqrt{U_o+d_1qE}-\sqrt{U_o})\right)\times\frac{\sqrt{U_o+d_1qE}}{\sqrt{(U_o+(d_1-\Delta t\sqrt{2U_o/M})qE)}} \quad (4)$$

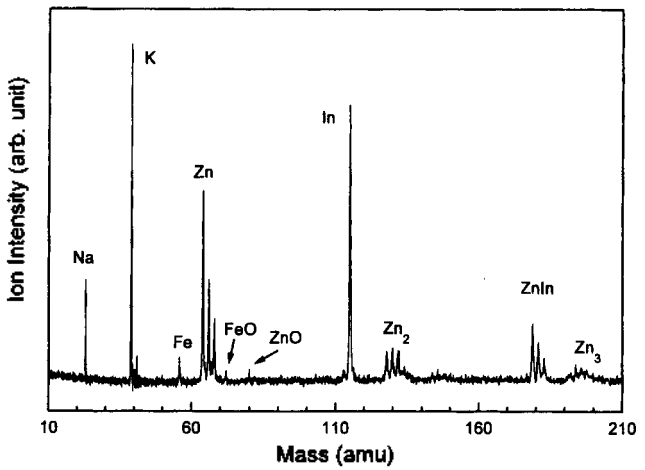

Figure 2. Mass spectrum of commercial Zinc (Zn) metal sample is obtained using laser ablation of 532 nm, in which the high voltage pulse to extract the ablated ions is applied to E1 without time delay between laser and extraction pulses.

Table 1. Measured and calculated Zn ion flight time using high voltage pulse height, 1550 V, and pulse width, 1.0 μsec. The result of calculated initial kinetic energy, U_o, is also shown

t (μsec)	t_{exp} (μsec)	t_{calc} (μsec)	t_{exp}-t_{calc}	U_o (kJ/mol)[a]
0.0	21.98	21.980	0.0	41.973[a]
0.1	22.15	22.106	0.045	
0.2	22.28	22.232	0.048	
0.3	22.39	22.359	0.031	
0.4	22.50	22.485	0.015	
0.5	22.62	22.612	0.008	
0.6	22.73	22.739	0.009	
0.7	22.84	22.866	−0.026	
1.0	23.19	23.247	−0.057	
1.4	23.79	23.757	0.033	

[a] Initial kinetic energy of Zn^+ obtained by using Eq. (4).

Table 2. Measured and calculated Zn ion flight time using high voltage pulse height, 1540 V, and pulse width, 1.2 μsec. The result of calculated initial kinetic energy, U_o, is also shown

t (μsec)	t_{exp} (μsec)	t_{calc} (μsec)	t_{exp}-t_{calc} (μsec)	U_o (kJ/mol)[a]
0.0	22.068	22.068	0.0	23.957[a]
0.1	22.20	22.187	0.013	
0.2	22.32	22.307	0.013	
0.3	22.44	22.427	0.013	
0.4	22.55	22.547	0.003	
0.5	22.67	22.667	0.003	
0.7	22.94	22.908	0.032	
0.9	23.15	23.148	0.002	
1.1	23.40	23.389	0.011	
1.5	23.863	23.872	0.009	

[a] Initial kinetic energy of Zn^+ obtained by using Eq. (4).

The initial kinetic energy of the ablated ion can be determined by fitting the measured flight times into Eq. (4) with the best fitted value of the initial kinetic energy.

Experimental measurement. Figure 2 displays TOFMS spectrum of positive ions formed during the laser ablation of Zn metal without time delay between a laser pulse and extracting pulse. The peak heights of Zn^+ isotopes ($^{64}Zn:{}^{66}Zn:{}^{67}Zn:{}^{68}Zn$=47.6 : 26.8 : 7.9 : 17.7) have been found to be in good agreement with their corresponding natural abundance Zn ($^{64}Zn:{}^{66}Zn:{}^{67}Zn:{}^{68}Zn$=48.6 : 27.9 : 4.1 : 18.8). Mass resolution, $R=\Delta m/m=\Delta t/2t$, is found to be about 190 at $^{64}Zn^+$ peak. A considerable amount of dimer and trimer ions, Zn^{2+}, $ZnIn^+$ and Zn^{3+}, are also detected. Some impurity peaks are also detected due to impurities in the sample. These impurity peaks, *i.e.*, Na^+ and K^+, were disappeared gradually in proportional to the ablation time. A trace amount of indium impurity in commercial high purity Zn has exhibited a very intense since In (I.P.=5.8 eV) has lower ionization potential than Zn (I.P.=9.4 eV).

Tables 1-4 represent Zn^+ (m/z 64) ion flight time as a function of the time delay between the laser pulse and the extraction pulse under four different experimental conditions. In order to determine the exact extracting voltage for each experiment, the fine controlled DC voltage has been applied to E1. Theoretical values listed in each Tables were calculated from the Eq. (4) by fitting into the experimental data using U_o as a variable. Computed average error of

Table 3. Measured and calculated Zn ion flight time using high voltage pulse height, 1510 V, and pulse width, 1.5 μsec. The result of calculated initial kinetic energy, U_o, is also shown

t (μsec)	t_{exp} (μsec)	t_{calc} (μsec)	t_{exp}-t_{calc} (μsec)	U_o (kJ/mol)[a]
0.0	22.265	22.265	0.0	37.912[a]
0.1	22.375	22.39	0.015	
0.2	22.51	22.515	0.005	
0.25	22.555	22.578	0.023	
0.3	22.63	22.641	0.011	
0.35	22.675	22.704	0.029	
0.4	22.75	22.766	0.016	
0.6	23.02	23.017	0.003	
1.1	23.66	23.647	0.013	
1.4	24.035	24.027	0.008	

[a] Initial kinetic energy of Zn^+ obtained by using Eq. (4).

Table 4. Measured and calculated Zn ion flight time using high voltage pulse height, 1570 V, and pulse width, 2.2 μsec. The result of calculated initial kinetic energy, U_o, is also shown

t (μsec)	t_{exp} (μsec)	t_{calc} (μsec)	t_{exp}-t_{calc} (μsec)	U_o (kJ/mol)[a]
0.0	21.84	21.84	0.0	22.010[a]
0.1	21.938	22.959	0.021	
0.2	22.055	22.078	0.023	
0.3	22.165	22.197	0.032	
0.4	22.285	22.316	0.031	
0.7	22.628	22.673	0.045	
0.8	22.745	22.792	0.047	
0.9	22.945	22.911	0.034	
1.0	23.017	23.031	0.024	
1.4	23.565	23.509	0.056	

[a] Initial kinetic energy of Zn^+ obtained by using Eq. (4).

these values is below 30 nsec for four experimental conditions (See Tables). The initial kinetic energy of Zn^+ ion is found to be 22-44 kJ/mol at laser power of about 5×10^7 W/cm^2. These values are equivalent to the velocities of 8×10^5-1.1×10^6 cm/s and the surface temperature of 2670-5100 K. Time-of-flight measurement of Zn^+ ion indicates that its energy is very low. Similar results for the initial kinetic energy also were obtained by the pulsed copper ablation.[18]

Conclusions

The flight time measurement of an ion as a function of the time delay between the ablation laser and extraction pulses has been demonstrated to be a useful method of obtaining the initial kinetic energy of an ion. The time-of-flight dependence of an ion on time delay has been formulated and fitted into experimental data to obtain the initial kinetic energy of the ablated ion. At 532 nm and about 5×10^7 W/cm^2 power, the initial kinetic energy of ablated ions have been found to be 22-44 kJ/mol.

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Synthesis and Properties of Terdentates with Extra Pyridine Ring and Their Ru(II) Complexes

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The synthesis and electronic as well as redox properties of four Ru(II) complexes based on the ligand 4'-(4-pyridyl)-3,3';5',3"-bis-dimethylene-2,2';6',2"-terpyridine are reported. Each new complex is of the type $[Ru(L)_2]^{n+}$ and $[Ru(tpy)(L)]^{n+}$, where L is the terdentate ligand with extra pyridine ring at 4'-position or is a N-methylated ligand and n=2, 3, or 4. Cyclic voltammetry indicates that the first electron added to the complex enters the viologen-type acceptor in N-methylated ligand.

Introduction

Importance of polypyridines, especially 2,2'-bipyridine (bpy) and 2,2';6',2"-terpyridine(tpy), stems from their abilities to form complexes with various transition metals. Ruthenium(II) complexes of these polypyridines, show somewhat unique spectroscopic,[1] electrochemical,[2] photophysical and photochemical[3] and biochemical properties[4] compared to other transition metals. Studies on the photophysical and photochemical properties of the ruthenium complexes have been directed toward electron transfer quenching process of the excited state to lead to energy storing redox products. Among the oxidative quenching agents, pyridinium ions, including viologen have most likely been employed. For the biochemical properties, some of ruthenium complexes exhibit intercalative binding to DNA and