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Short communication

Resonance enhancement of ion signals in direct isotope analysis of metal samples by adopting 2-color resonant laser ablation mass spectrometry

Kyuseok Song *, Euochang Jung, Hyungki Cha

Laboratory for Quantum Optics, Korea Atomic Energy Research Institute, P.O. Box 105, Yusong, Taejeon 305–600, Republic of Korea

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Abstract

The enhancement of ion signals by the resonant laser ablation (RLA) process was investigated by using a 2-color RLA mass spectrometry for samples containing Pb and Ni. Two laser beams, a second harmonic of Nd:YAG laser (532 nm) and a UV beam of frequency tunable dye laser, were used for either simultaneous ablation by directing both lasers to the target sample or laser ablation followed by a resonant ionization. In both cases, the resonant enhancement of the ion signal was observed, but the mass resolution was much better when two lasers contribute to the laser ablation process by arranging both beams hit the sample at the same position. The enhancement factor was more prominent when the laser power was kept at low. The maximum resonance enhancement was more than 160 times for the Pb case when compared to the non-resonant laser ablation. Several NIST standard reference materials were analyzed by adopting RLA.

Keywords: Resonant laser ablation; Isotope analysis; Laser-induced plasma

1. Introduction

Laser ablation mass spectrometry has been used for the direct isotope analysis of solid sample. But the detection sensitivity of this technique needs to be improved in order to apply for the ultra trace detection. A resonant laser ablation (RLA) is one of the techniques in improving detection sensitivity of laser ablation mass spectrometry owing to the resonance enhancement of ion signals. Since the resonance ionization spectroscopy (RIS) or resonance ionization mass spectrometry (RIMS) has been used for more than two decades in trace detection of isotopes, RLA has been rather easily developed based on the information obtained through the investigations on RIS and RIMS.

The RLA has been applied for the microanalysis of solid materials for some time now [1–12]. The reported investigations include the thin film microanalysis using RLA by Odom and Schuler [1], the trace detection of Al in steel samples by Borthwick et al. [2], the two-photon spectrum of iron and silicon detected by RLA by Eiden and Nogar [3]. Gill et al. investigated the one-color RLA ion trap mass spectrometry for several elements including Co, Ni, Mg, Al, Si, Fe, etc. [4,5]. They were able to detect ~26.5 ppm of a lead content in standard reference materials (SRMs) 494. Aubriet et al. adopted RLA as a tool to investigate a matter transfer during a pulsed-laser deposition experiment [6]. Watanabe et al. thoroughly investigated the RLA, experimentally as well as theoretically [7–10]. Their theoretical model described the RLA process fairly well. The RLA was also applied for the microanalysis of copper by adopting a two-photon resonance ionization with the wavelength of 463.86 nm [11] and an investigation of the internal energy disposal information for Ni by Rothschopf et al. [12]. In most of these papers, either one-color RLA with a two-photon resonance or a two-color RLA arranging one laser for ablation and the other for resonant ionization by dividing one laser beam was adopted. The reported detection sensitivities were dependent on the type of sample, target element and adopted resonant ionization schemes. There are little investigations on the RLA process adopting both lasers on the ablation process.

In the present study, the main focus of the investigation is concentrated on the resonance enhancement of the detection sensitivity by the 2-color RLA processes. We have used two laser beams, 532 nm and a frequency tunable UV laser beam for the RLA process. Two laser beams were arranged for either simultaneous contribution to the ablation process or resonant ablation

* Corresponding author. Tel.: +82 42 868 8226; fax: +82 42 868 8230.
E-mail address: sks@kaeri.re.kr (K. Song).

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followed by a resonant ionization of the generated laser-induced plasma. The use of 532 nm in ablation process in addition to the frequency tunable laser provides additional flexibility in applying RLA for sample analysis, since most of the pumping lasers for dye lasers or OPOs generate 532 nm which can be used for the ablation process. The time delay between the two laser beams was varied and optimized in order to understand the dynamics of the laser-induced plasma, such as velocity of laser-induced plasma and the effect of UV laser pulses in RLA process. The resonance enhancement of the ion signal for the Pb and Ni samples were obtained as big as 160 times for the Pb case when compared to the ion signal generated by a non-resonant laser ablation. The technique was applied for the trace detection of Pb isotopes and Ni isotopes in several NIST SRMs.

2. Experimental

The experimental setups for laser-ablation and the resonance ionization are described in detail in previous publications [13,14]. In brief, two Nd:YAG lasers, one for the optical pumping of a dye laser and the other for the laser ablation, were used for the two color RLA. The dye laser output was frequency-doubled by using a frequency doubling system (Inrad autotracker II) for the wavelengths, 283.3 nm for Pb and 300.25 nm for Ni, respectively. One of the pumping laser was set as the master trigger for the delay generator and the second Nd:YAG laser. The second laser was frequency-doubled to generate 532 nm and this beam was introduced to the target sample at an angle of 45°. The UV laser was directed at the sample either at 45° (type 1, see also Fig. 1) or parallel to the sample surface (type 2, see also Fig. 1). In the type 1 arrangement both lasers contribute to the ablation process, while only one laser contribute to the ablation process in the type 2 optical arrangement. A home-made time-of-flight mass spectrometer (TOF-MS, linear type) with a flight length of 200 cm was used for the analysis of the generated ions. This TOF-MS system was equipped with an ion source assembly which consisted of eight electrodes, one for a sample mounting and acceleration of the ions, three for an ion optics, and four for an ion deflection in the *X*, *Y* directions. The mass spectrometer was kept under vacuum at $\sim 2 \times 10^{-7}$ Torr. Ions are detected by a dual microchannel plate and the detected signal is amplified by a fast preamplifier before sending it to the digital oscilloscope. The overall experimental scheme is shown in Fig. 1. Metal samples (Pb, Ni) were purchased from Nilaco Co. and used without any further treatment. Adopted SRMs (C-1248, 1155, 1262b) were purchased from NIST.

3. Results and discussion

3.1. RLA-MS with the type 1 laser arrangement

The resonance enhancement of the ion signals in laser ablation mass spectrometry has been a great asset in enhancing the detection sensitivity of the direct isotope analysis technique. The resonance can be achieved by one-step or multi-step, depending on the target element and the available laser wavelength. In the present study on Pb, 2-color RLA was adopted with 532 nm and UV laser. Both laser beams were directed to the same spot at the sample surface with the same angle (type 1 RLA). In this experiment, the size of the laser beam on the target plate was normally optimized as 1.2 mm × 3 mm by defocusing the laser beams. Fig. 2 is the RLA mass spectrum of the Pb obtained by using both the 532 nm and UV laser at two different wavelengths, on and off resonance (283.3 and 282.5 nm), respectively. The average power of 532 nm was adjusted to be relatively low (20 mW) in order to prevent any ion signals from the laser-induced plasma with 532 nm only. The addition of 1.7 mW of UV beam at 282.5 nm along with 532 nm laser generated a very week signal even at non-resonant condition. When the UV laser wavelength was adjusted to the resonant wavelength (283.3 nm) the ion signal was enhanced more than 160 times compared to the ion signal from the non-resonant ablation process.

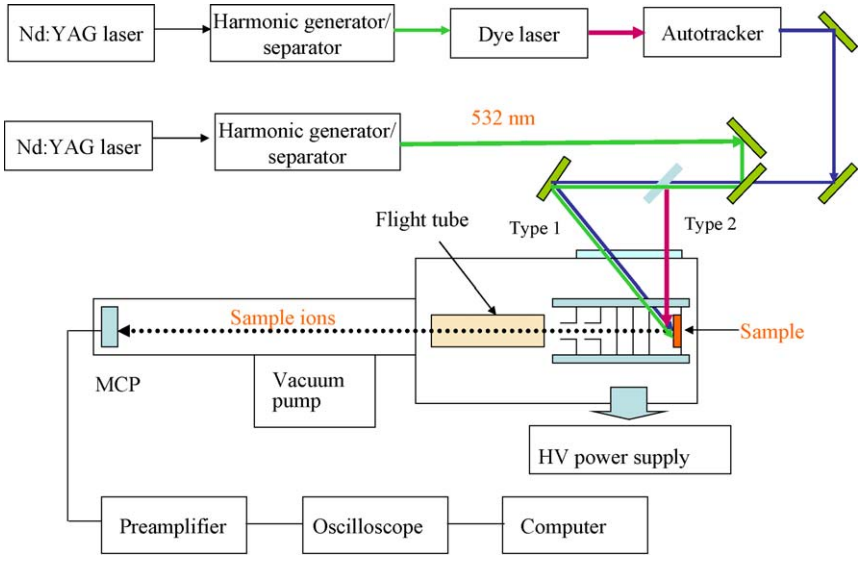

Fig. 1. A schematic diagram of experimental setup for the 2-color resonant laser ablation mass spectrometry.