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레이저 에블레이션 분광을 이용한 고분자 표면의 나노미터 스케일 표면 분석

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Nanometer-Scale Surface Analysis of Polymers Using Laser Ablation Spectroscopy

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Abstract - In this study, laser ablation atomic fluorescence (LAAF) spectroscopy has been applied for a nanometer-scale surface analysis of Na-doped polymethyl methacrylate (PMMA). LAAF spectroscopy is a new sensitive element detection technique which involves atomizing of a sample by the laser ablation and detection of ablated plume by laser-induced fluorescence (LIF) spectroscopy. Using this technique in the detection of Na atoms with Na-doped PMMA, a detection limit is obtained as 36 fg for single laser shot. Further, the depth distribution in the sample is measured with a very high spatial resolution using a two-layer PMMA sample by observing the shot-by-shot LIF intensity from the Na atoms.

1. Introduction

A very sensitive atomic detection technique which is termed as laser ablation atomic fluorescence (LAAF) spectroscopy has been proposed. This technique involves laser-induced fluorescence (LIF) spectroscopy combined with the laser ablation[1]. Laser ablation is well established as a tool for surface processing and makes an accurate vaporization of a solid surface possible. Therefore, various types of materials ranging from polymers to inorganic crystals and metals can be extensively studied. [2].

In LAAF spectroscopy, the ablation process is used to atomize a sample surface, and the atoms in the ablated plume are detected by LIF spectroscopy. As a diagnostic tool, LIF spectroscopy gives time-resolved behaviour of the atoms and molecules which leave the solid surface at supersonic velocities during the laser ablation[3].

In this study, a very thin layer ablation of nanometer for a single laser shot is attained by using a pulsed UV laser with a nanosecond (ns) pulse width and by controlling a laser fluence irradiated onto the surface of samples. Further, an experimental investigation is performed related to the measurement of the detection limit and spatial resolution in the depth direction for PMMA sample, by using LAAF spectroscopy. This study clearly shows that an ablation rate on the order of nanometer -scale is possible with a stable LIF signal

2. Experiment

Figure 1 shows the experimental setup for LAAF spectroscopy. Initially, a solid PMMA sample doped with Na was mounted vertically on a remote-controlled stage in a vacuum chamber.

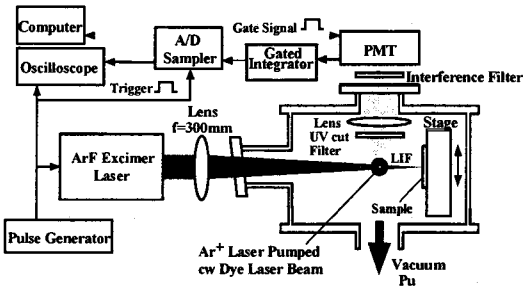

Fig.1 Experimental setup

The vacuum chamber was depressurized and filled with He as a buffer gas. Then the ablation was performed by a pulsed ArF excimer laser (Lambda Physik, LPX350ST, 193nm). The pulse duration was 24 ns FWHM and repetition rate was 2 Hz. The laser beam was focused onto the sample surface with a lens of 300 mm focal length. Na atoms in the ablated plume were excited by a two-level system with a cw dye laser (Spectra Physics, Model 375) as a probe laser. The probe laser was tuned to Na D_2 line (588.995 nm). The LIF signal for Na atoms was detected by a photo-multiplier tube (Hamamatsu, R-928) with a time-gated socket assembly (C1392-56) through a UV cut filter (Toshiba, L39S, T=2%@355, 93% @589 nm), a focusing lens (f=50 mm) and an interference filter (T=70% @589.7 nm, bandwidth 1nm FWHM).

Ablation was performed at the same position repeatedly. The ablation laser fluence was varied either by using a dielectric attenuator or by changing the sample-to-lens distance. Experiments were performed in the fluence range of 20~300 mJ/cm^2, and the range of illuminated spot area on the sample was 10~100 mm^2. After finishing the ablation with a constant number of laser pulses, the depth of ablated surface was measured with a stylus profilometer (Taly Step, Taylor Hobson, resolution 2nm) and the morphology of the

ablated area was investigated by a scanning electron microscopy (SEM, JEOL JSM-6320FZ).

3. Results and Discussion

First, the effect of He buffer gas pressure on the LIF signal intensity was investigated experimentally. Fig. 2 shows plots of the LIF signal with respect to time, for different He gas pressure, where the same point on the sample was ablated at the fluence of 64 mJ/cm^{2}and the irradiated spot area was 17 mm^2. He gas pressure was changed from 0.01 to 10 Torr. The profiles of the LIF signal in Fig. 2 are proportional to the number of Na atoms in the observing region. At a pressure of 0.3 Torr, the peak of the LIF signal shows a maximum value since the LIF signal could be separated temporally from the plume. At the higher pressure values, the LIF signal intensities decrease due to the collisional dissipation. On the other hand, with the lower pressure values, the signal intensities also decrease due to the shortening of the time of flight of Na atoms. Fig. 2 indicates that the optimal range of He gas pressure is between 0.1 and 0.5 Torr. Therefore, in the subsequent experiments, He gas pressure was maintained around 0.3 Torr.

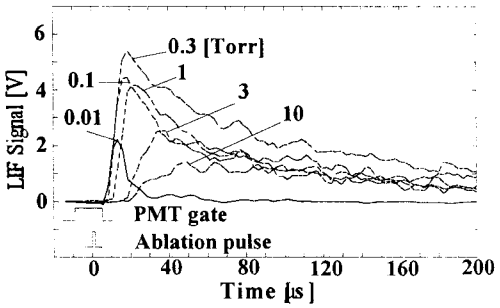

Fig.2 Effect of He gas pressure on LIF intensity.

Next, the correlation between the LIF signal and Na concentration was investigated. Fig. 3 shows the intensity of the integrated LIF signal as a function of Na concentration in PMMA, where the ablation laser fluence was ≈ 30 mJ/cm^2 with the irradiated spot area of 11 mm^2. The intensity of the integrated LIF signal is proportional to the concentration of Na in Fig. 3, which implies that the dopant Na was distributed uniformly in the bulk of PMMA and the ablation per laser shot progressed uniformly with a very small fluctuation shown by error-bars.

The LIF signal also depends on the ablation laser fluence. The relationship between the integrated LIF intensity and the ablation laser fluence is shown in Fig. 4, where the irradiated spot area was 18 mm^2, and Na concentration was 450 μg/cm^3. A clear threshold in the fluence was observed, and it was measured as ≈ 20 mJ/cm^2. The values of standard deviation which represent error in measurements with respect to the ablation laser fluence are also plotted in Fig. 4. From this measurements, it is apparent that the fluence of around 30 mJ/cm^2 is required to obtain a stable LIF signal. This fluence value was used in the subsequent experiments.

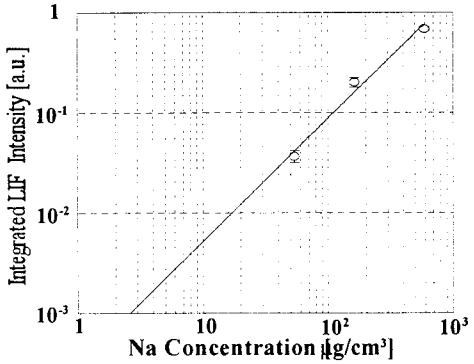

Fig.3 LIF intensity vs. Na concentration in PMMA samples. (Fluence≈30 mJ/cm^2)

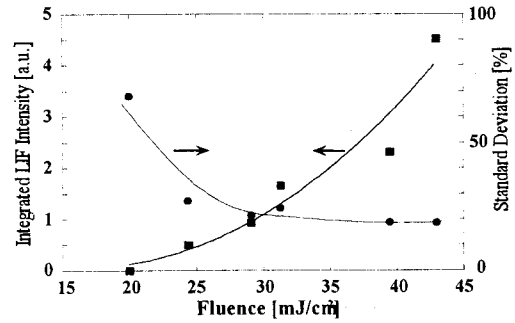

Fig.4 LIF intensity vs. laser fluence (Na concentration in PMMA, 450 μg/cm^3).

Next, the study was made for the ablation depth per laser shot, which is termed as an ablation rate and can be expressed as nm/shot. Fig. 5 shows the plots of the ablation depth versus the number of ablation laser shots for different fluence values. The ablation depth was measured with a stylus profilometer. Based on the least-squares method, the slope representing the ablation rate, was obtained. In general, the plots of the ablation depth versus the number of shots show good linearity. In some cases, however, the spots irradiated with a large number of shots give smaller ablation rate than the spots with fewer shots at the same fluence. This phenomenon seems to be attributed to the redeposition of the ablated material into the ablated pit, where a large number of shots at a relatively higher fluence cause subsequent increase in the quantity of fragments. An increased redeposition of the ablated fragments back onto the sample can reduce ablation efficiency and the photo-fragments absorption of the laser beam can lower its fluence on the sample.

Next, detection limit for Na contained in

Na-doped PMMA was estimated by using LIF signal variation shown in Fig. 6. In this case, the ablation rate was estimated to be 4.4 nm/shot and the absolute quantity of Na contained in the ablated PMMA for each laser shot can be calculated as 230 fg. The S/N ratio under this ablation condition was 6.5 as calculated from Fig. 6. Considering the S/N ratio of unity, the limit of detection can be estimated as 36 fg ($\approx 1.85\mu g/cm^3$). It is also possible to improve the limit of detection further by shot-by-shot averaging.

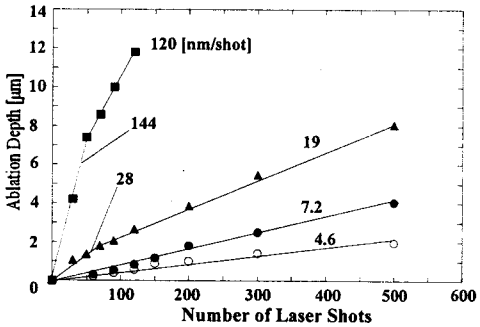

Fig.5 Ablation depth vs. number of laser shots for different fluences of ablation laser: (○) 30mJ/cm^2, (●) 37 mJ/cm^2, (▲) 43 mJ/cm^2, (■) 85 mJ/cm^2).

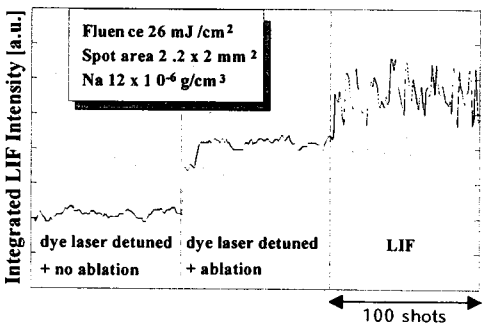

Fig.6 LIF signal variation due to the cw dye laser tuning.

Finally, in order to evaluate the spatial resolution of Na distribution in the depth direction, a two-layer structured sample was preparedas, where MMA, without Na, was spin coated on the PMMA substrate already doped with 140 $\mu g/cm^3$ of Na for 30 s at 1500 rpm. Fig. 7 shows the integrated LIF signal intensity for the two-layer structured sample. The ablation fluence was 31 mJ/cm^2, the spot area was 2.4 mm^2 and the number of ablation laser shots were 220. The ablation rate was calculated to be 7.5 nm/shot from the depth of the ablated region. As shown in Fig. 7, the LIF signal has clearly changed corresponding to the concentration distribution in the depth direction. The spatial resolution is estimated to be 50 nm from the straight line plot in Fig. 7. However, this value is larger than 7.5 nm which is the depth removed by single laser

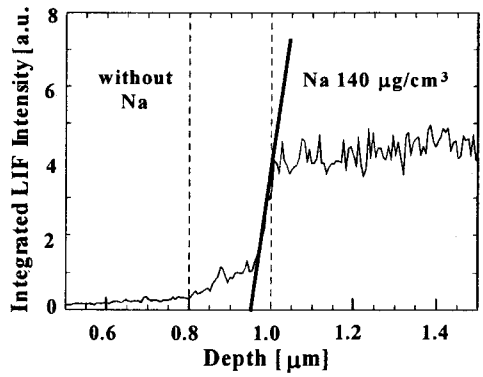

Fig.7 LIF intensity for two-layer structured PMMA having different Na concentration in depth direction. (Fluence ≈ 30 mJ/cm^2, spot area 2.4 mm^2, laser shots 220).

shot. One of the reason for the decrease in the spatial resolution is due to non-uniform ablation. The non-uniform ablation is partly caused by non-uniform illumination due to the laser beam itself and the diffraction effect.

4. Conclusions

In the study, laser ablation atomic fluorescence (LAAF) spectroscopy has been applied for analysis of trace elements in the nanometer-scale solid surface. LAAF spectroscopy involves atomizing of sample by laser ablation and detection of the ablated plume by laser-induced fluorescence (LIF) spectroscopy and possesses higher sensitivity than LAAE spectroscopy. Following results were obtained in the study.

1. In the case of Na-doped PMMA irradiated by the ArF excimer laser, the sensitivity of LAAF spectroscopy was demonstrated. A detection limit for Na atoms contained in the ablated PMMA was attained as 36 fg for single laser shot, considering the S/N ratio of unity.
2. A spatial resolution in depth direction for two-layer Na-doped PMMA with different Na concentration was about 50 nm, which was greater than the ablation rate of 7.5 nm/shot.

(References)

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