Field Evaporation of Carbonaceous Materials in Laser-Assisted Atom Probe (Effects of the Laser Wavelength and Power)*

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We have observed the laser wavelength (1064, 532, 355 nm) and power (2, 10, 20 nJ per pulse) dependence of field evaporation of carbonaceous material on a tungsten needle by a three dimensional atom probe (3DAP). Carbonaceous materials were deposited by gallium focused ion beam-chemical vapor deposition. Several peaks corresponding to low mass carbon compounds were highest at 355 nm. On the other hand, predominant gallium peaks were observed with 20 nJ per pulse. These results indicate that incident photon energy and tip temperature rising should be taken into consideration when using a femtosecond pulsed-laser atom probe.

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I. INTRODUCTION

Pulsed-laser atom probe is widely used to investigate metals and semiconductors on a nearly atomic scale and in three dimensions [1]. The atom probe is a combination of a field ion microscope and a mass spectrometer. The basic principle of this technique is field evaporation of surface atoms in the needle whose apex is typically 100 nm in radius. These atoms are chemically identified by time-offlight method. Three dimensional position of each atom is calculated from the coordinates on the position-sensitive detector and the sequence of detection. Field evaporation is induced by the application of a standing voltage and laser or voltage pulses.

Formerly, pulsed-laser atom probes were performed with nanosecond laser pulses. It was confirmed that field evaporation occurs by thermal effects originated from nanosecond pulsed-laser [2, 3]. Recently, femtosecond pulsed-laser is employed on an atom probe because it is considered that an increase of tip temperature is too low to achieve the evaporation [4]. From the experiments with femtosecond laser pulses, Gault et al. [5] have proposed that field evaporation occurs by the electric field developed at the specimen apex. However, Cerezo et al. [6] has observed thermal effects with femtosecond pulsed-laser. Whether the dominant mechanism of field evaporation with femtosecond pulsed-laser is thermal or athermal is still controversial.

Meanwhile, Gilbert et al. [7] measured silicon materials at two different laser wavelengths and observed differences of the ionized species. This fact results in serious problem for the quantitative three dimensional analysis because analysis conditions have to be optimized at every measurement.

We are currently developing a femtosecond pulsed-laser atom probe which aims for analyzing electronic devices [8, 9]. Objective of this project is to establish the field evaporation mechanism to define the best evaporation conditions for the correct measurements [10]. In this study, the laser wavelength and power dependence of field evaporation of carbonaceous material has been observed.

II. EXPERIMENTAL

A. Sample

The samples analyzed in this study were carbonaceous materials which were deposited on tungsten needles by gallium focused ion beam-chemical vapor deposition (FIB-CVD) from phenanthrene (C_{14}H_{10}). It has been reported that the film prepared by FIB-CVD is amorphous diamond-like carbon containing a few at% gallium [11]. Meanwhile, photon-induced field evaporation of ethylene on silver by laser excitation has been reported [12]. Therefore, we considered that carbonaceous material prepared by FIB-CVD was appropriate for investigating the relation of incident photon energy and carbon bond energy because diamond-like carbon contains both sp^{2} and sp^{3}
The samples were prepared by following three procedures. Firstly, tungsten wire (diameter 0.1 mm; NILACO #W-461167) was electropolished in 1 mol/L sodium hydroxide solution. Secondly, phenanthrene gas was deposited on the front of the tip by a 30 kV and 80 pA gallium FIB (SII NanoTechnology, SMI3050SE). Vertical thickness of deposition was about 0.5 µm. Finally, the sample was fabricated to a needle shape by annular milling methods [13]. This procedure was performed in a series of steps, with decreasing annular masks and ion currents from 180 to 80 pA (30 kV). The samples were observed with a scanning electron microscope (SEM) (SII NanoTechnology, SMI3050SE). The SEM image of the sample is shown in Fig. 1.

B. Probing conditions

1. Laser wavelength dependence

A neodymium YAG laser (λ = 1064 nm, pulse width = 50 ps) with second (λ = 532 nm) and third (λ = 355 nm) harmonic generators fitted to a three dimensional atom probe (3DAP) of Kanazawa Institute of Technology [14] was used to observe the laser wavelength dependence of field evaporation. The repetition rate of laser pulses was 700 Hz and the laser power were approximately 16, 1.5 and 0.8 µJ per pulse for λ = 1064, 532 and 355 nm, respectively. A standing voltage was 4 kV. Pressure of the main chamber was lower than 10^-7 Pa at room temperature.

2. Laser power dependence

An ytterbium doped fiber laser (λ = 1064 nm, 60 nJ per pulse, pulse width=300 fs) fitted to a home made three dimensional atom probe of The University of Tokyo was used to observe the laser power dependence of field evaporation. The repetition rate of laser pulse was 5 kHz, the spot size of the laser was approximately 20 µm and the laser powers were 2, 10 and 20 nJ per pulse, respectively. A standing voltage was 3.8 kV. Pressure of the main chamber was lower than 10^-8 Pa at room temperature. Schematic of laser system at Kanazawa Institute of Technology is shown in Fig. 2 and whole experimental conditions are comparatively shown in Table I.

FIG. 1: SEM image of a sample prepared by FIB-CVD.

FIG. 2: Schematic of pulsed-laser system at Kanazawa Institute of Technology. BE, HWP stand for beam expander, half-wavelength plate, respectively.

FIG. 3: Mass spectra of carbonaceous material on W by FIB-CVD at three different laser wavelengths.
TABLE I: Probing conditions to observe the laser wavelength and power effects of field evaporation. KIT and UT stand for Kanazawa Institute of Technology and The University of Tokyo, respectively.

| Dependence                  | Laser wavelength | Laser power |
|-----------------------------|------------------|-------------|
| 3DAP affiliation            | KIT              | UT          |
| Pressure of main chamber (Pa)| $<10^{-8}$       | $<10^{-7}$  |
| Tip’s temperature (K)       | 298              | 298         |
| Standing voltage (kV)       | 4.0              | 3.8         |
| Pulses                      | Nd YAG laser     | Yb-doped fiber laser |
| Pulse width: 50 ps          | 1064, 532, 355   | 1064        |
| Repetition rate: 700 Hz     | 10 nJ/pulse      | 20 nJ/pulse |

III. RESULTS AND DISCUSSIONS

A. Laser wavelength dependence

Firstly, we observed laser wavelength dependence of carbonaceous materials to investigate the effect of photon energy.

Mass spectra at the three different laser wavelengths are shown in Fig. 3 with a mass resolution of $m/\Delta m \sim 200$ at full width half-maximum. The three major mass peaks at 18, 28 and 44 were assigned to low mass carbon compounds because $C_2^+$, $C_4^+$ ($m/z = 6, 12$) and the several satellite peaks around the three major peaks appear in typical mass spectrum of carbon compounds [15]. Although there is a possibility that the three major peaks could be also assigned to $H_2O^+$, $CO^+$ and $CO_2^+$, respectively, which were originated from residual gas, it seems hard to understand that relative peak intensity of $CO_2^+$ is higher than that of $CO^+$. Therefore, the three major mass peaks ($m/z = 18, 28$ and 44) could be assigned to low mass carbon compounds.

The several low mass peaks ($m/z = 15-50$) corresponding to low mass carbon compounds were the highest at 355 nm. In contrast, the relative mass peaks of gallium ions were the highest at 1064 nm. The ratios of the total detected number of carbon to gallium were 5, 2.5 and 0.1 at 1064, 532 and 355 nm, respectively.

It is considered that the photon energies affect the evaporation behavior of each species because the photon energies were 1.2 eV, 2.3 eV and 3.5 eV at 1064 nm, 532 nm and 355 nm, respectively, while it is well known that the bond energies of $sp^2$ and $sp^3$ carbon are 6.3 eV and 3.5 eV, respectively [16]. Thus, it is reasonable that photon energy at 355 nm might break the carbon bond.

The predominant gallium peaks at 1064 nm might be explained by tip temperature rising because the laser power at 1064 nm (16 µJ) was much larger than 355 nm (0.8 µJ).

B. Laser power dependence

Secondly, to confirm the laser power effects on gallium, the laser power dependence was observed with constant wavelength. Mass spectra which were taken independently at the three different laser powers are shown in Fig. 4. The ratio of detected gallium ions to other ions increased with the laser power.

This result suggests that femtosecond pulsed-laser raised the tip temperature because it is considered that gallium atoms moved to the site where gallium is easy to evaporate. Thus, the predominant gallium peaks were observed at 20 nJ per pulse.

From this result, it is suggested that even a femtosecond pulsed-laser could raise the tip temperature.
IV. CONCLUSIONS

In a three dimensional atom probe experiment, the laser wavelength and power effects of field evaporation at carbonaceous material were observed. The detected fragments of carbonaceous materials could be explained by the relation of carbon bond energy and incident photon energy because incident photon energy at 355 nm almost corresponds to the carbon-carbon single bond energy. These results indicate the importance of incident photon energy to analyze carbonaceous material by a pulsed-laser atom probe.

On the other hand, predominant gallium peaks were observed with strong laser power. These results suggest that the tip temperature rising could not be ignored when using even a femtosecond pulsed-laser.

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