Multigraphene growth on lead-pencil drawn sliver halide print paper irradiated by scanning femtosecond laser

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Drawings were made on various types of paper using lead pencils of grades from 4H through 10B. Raman spectroscopy verified both G and D peaks on all the drawings on PC print paper, PC photopaper, kent paper, and paper for silver halide print. After irradiation with a scanning femtosecond laser, silver halide paper drawn on with a 10B lead pencil maintained its surface flatness compared with the other types of paper. Raman spectroscopy on silver print paper showed a high-intensity G peak and a low-intensity D peak. After irradiating the scanning femtosecond laser on silver halide paper drawn on with a 10B lead pencil, Raman spectroscopy showed a high-intensity G peak and a low-intensity D peak. A 2D peak was observed at 2,700 cm⁻¹ corresponding to the existence of multigraphene. © 2016 The Japan Society of Applied Physics

1. Introduction

After the discovery of graphene1–3 prepared by peeling Scotch tape off graphite, graphene has been prepared by other methods such as thermal decomposition of SiC4–6 and chemical vapor deposition with catalysts such as Ni, Cu, and Fe.7–11 In this study, we propose another method of preparing graphitic carbon: irradiating pencil-drawn print paper using a femtosecond laser.

Pulsed laser deposition is one of most versatile methods of growing metals,12–15 oxides,13–15 and multilayers16,17 including graphene18,19 and diamond.20 In this technique, an incident laser beam irradiates a target in a vacuum chamber, and the vaporized materials from the target surface reach a substrate placed against the target, resulting in the growth of film. A femtosecond laser is often used as a laser source.21,22 We drew on a sheet of printing paper with a lead pencil, and irradiated the drawn paper with a femtosecond laser at room temperature. Compared with conventional methods, this simple method of using pencil lead as a source material does not require either a high-vacuum atmosphere or high temperature. A vacuum chamber is not required and the scanned area is only dependent on the movement of the X–Y stage (sample holder), resulting in the large advantages of high productivity and large sample size.

The solid core of a pencil is made of graphite mixed with a clay binder, and is “harder” with more clay in the solid core and soft with more graphite. The ratio of graphite to clay determines the grade of the pencil from “H” for hardness to “B” for blackness, and an intermediate grade “F” for fine. A set of pencils ranging from a very hard, light-marking pencil to a very soft, dark-marking pencil usually ranges from hardest to softest with different amounts of carbon, clay, and wax.23 As shown in Fig. 1, the grade 10B was not available until Mitsubishi Corp. produced the 10B lead pencil, which is available only in some regions of Japan.

Although paper and pencil are literally primitive materials, an interesting approach has been presented24–27 Lin et al. used pencil traces drawn on print paper as strain gauges and as chemiresistors. Graphite particle chains in a U-shaped pencil trace have varying resistance depending on the deformation of the paper. As shown in Fig. 1, the grade 10B with a high graphite content was mainly used for drawing on a sheet of paper in this study. Various types of paper were also prepared for this study: printing paper for a PC printer, photo print paper for a PC printer, kent paper, and print paper for silver halide prints. The paper for silver halide prints showed lower background fluorescence in Raman spectroscopy compared with other types of paper; thus, the grade 10B lead pencil was used for drawing on the back of the silver halide print paper in this study.

2. Experimental procedure

The types of paper used in this study were (1) print paper for a PC printer (PC paper), (2) photo print paper for a PC printer (PC photo paper), (3) kent paper, and (4) paper for silver halide print paper.

Fig. 1. Grades of lead pencils. “H” (for hardness) to “B” (for blackness), as well as “F” (fine), a letter arbitrarily chosen to indicate midway between HB and H.
halide prints (print paper). After drawing on paper (roughly size of 10 × 20 mm²) with each grade of lead pencil, Raman spectroscopy with a wavelength of 632.8 nm was employed to observe G, D, and 2D Raman peaks, which correspond to ∼1,600, 1,350, and 2,700 cm⁻¹, respectively. Resistance was also measured by using a multimeter for reference.

A femtosecond laser (Cyber Laser IFRIT) was employed to irradiate the area of the drawing made using lead pencil on the paper, as shown in Fig. 2. The maximum power of the laser was 5 mW with a wavelength of 800 nm at a repetition rate of 1 kHz. The laser spot with a diameter of 50 µm was scanned over the graphite-drawn paper at a scan speed between 3,000 and 50 µm/s, which resulted in irradiation with a laser fluence of between 5 and 0.1 J/cm². A piece of paper fully covered with graphite from a pencil drawing was placed on the X–Y stage, and the femtosecond laser was scanned with a line pitch of 25 µm. The details of the irradiation conditions are shown in Table I.

### Table I. Irradiation condition by femtosecond laser. “Material” indicates print paper for PC printer (PC paper), photo print paper for PC printer (PC photo paper), kent paper, and paper for silver halide prints (print paper).

| Material (back) | Laser frequency | Wavelength | Power | Scanning speed | Spot size | Pencil |
|----------------|-----------------|------------|-------|----------------|-----------|--------|
| PC paper       | 1 kHz           | 800 nm     | 0–5 mW| 50–3,000 µm/s | 50 µm     | 9H–10B |
| PC photo paper |                 |            |       |                |           |        |
| Kent paper     |                 |            |       |                |           |        |
| Silver print paper |           |            |       |                |           |        |

#### 3. Results and discussion

All grades of lead pencils were used to draw and fill in an area (approximately 1 × 3 mm²). Then, resistance over a length of ∼20 mm was evaluated using a multimeter, as shown in Fig. 3. The multimeter could not measure the resistance of paper drawn on using pencils with a grade harder than 5H. Although the resistances were, of course, not inaccurate and unreliable, they can show the tendency relative to the grade of the lead pencil. While grades 8B and 10B showed slightly higher resistances than those of 6B and 4B, the resistance decreased with increasing content of graphite in lead pencil in a wide range of grades, between 4H and 6B. The resistances in the cases of 8B and 10B slightly increased because of the non-uniformity of the carbon thickness when drawing with a soft pencil. However, the trend relative to the grade was in agreement with that in a previous report.

Raman spectra of the drawing area before the irradiation of the femtosecond laser were observed, and are shown in Fig. 4. Although there existed strong fluorescence at around 1,500 cm⁻¹ on drawings made with harder lead pencils, such as 4H and 1H, all the Raman spectra showed both G and D peaks corresponding to sp² hybridization (graphitic signature of carbon) and disorder due to defects, respectively. It is difficult to recognize Raman peaks of even D and G in the case of lead pencils harder than 6H because of the thinner drawn line and the fluorescence of the print paper. While spectra in the case of grade between 4H and 2B showed a higher intensity of the D peak than that of the G peak and a large background fluorescence, 10B and 6B pencil lead resulted in clear Raman peaks with strong G peaks of greater intensity than those of D peaks. The grade 10B lead pencil was used hereafter in this study.

It should be noted that the excitation wavelength of 632.8 nm was used in Raman spectroscopy. It is common for the 2D peak corresponding to graphene to become stronger in Raman spectra with the stimulated wavelength of 532 nm.
The National Institute of Science and Technology (NIST) provides Standard Reference Materials (SRM) to correct the relative intensity of Raman spectra obtained with different excitation wavelengths. However, SRMs 2241 through 2243 provided by NIST cannot be used to correct spectra obtained with the wavelength of 632.8 nm, in this study. This wavelength of 632.8 nm is suitable for graphene on a catalyst such as Cu, but it might be unsuitable for graphene on silver print paper.

After filling an area of around $10 \times 20$ mm$^2$ using a 10B pencil, the femtosecond laser was employed to irradiate the papers. With high fluency and power, PC paper, including PC photo paper, became scorched and burnt. The high polymer content in PC glossy paper is highly reactive under laser irradiation. Figure 5 shows irradiated areas on (a) kent paper and (b) silver print paper. Although a finer structure clearly exists on kent paper, print paper shows a relatively smooth surface. Only silver print paper was used hereafter in this study.

Both the laser power and scan speed of the femtosecond laser were varied, and Raman spectra were examined to optimize the irradiation conditions. Figure 6 shows Raman spectra of samples prepared with scan speeds in the range between 0 and 3,000 $\mu$m/s at a laser power of 5 mW. At a scan speed of 50 $\mu$m/s, the excess power removed almost all the graphite drawn on silver print paper, and only G and D peaks remained in Raman spectra. When the laser power was less than 5 mW and the laser scan speed was 1,000 $\mu$m/s, the Raman D peak remained. The irradiation at 5 mW and a scan speed of 1,000 $\mu$m/s eliminated the D peak whereas the G peak remained, together with the 2D peak corresponding to the graphene.

Pencil lead consists of graphite, clay, and wax, as shown in Fig. 1. We assumed that the laser irradiation resulted in (1) the removal of impurities other than the components of graphite and (2) promoted the growth of graphene. The resistance, for instance, decreased by 10% after laser irradiation. The irradiated area became depressed because the thickness of the graphite layer on print paper decreased after the laser irradiation. Even though the resistance decreased by only 10%, the resistivity can be greatly improved because of the decrease of the graphite thickness. However, the graphite thickness on pencil drawing paper has not been clearly defined. Since the layer thickness is used to evaluate the mobility of the graphite layer, it is necessary to find a way to evaluate the thickness of the graphite layer drawn on print paper.

4. Summary
Various types of paper were drawn on using lead pencil with grades between 4H and 10B. Raman spectroscopy of the graphite layer verified both G and D peaks corresponding to $sp^2$ hybridization (graphitic signature of carbon) and disorder due to defects, respectively. After irradiating a scanning femtosecond laser on silver paper drawn on using a 10B lead pencil, Raman spectroscopy indicated that laser scanning eliminated the D peak while G and 2D peaks remained, indicating the growth of graphene on silver print paper.

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