

# Pulsed UV laser irradiation of polymer surfaces

H. Hiraoka

Department of Chemistry, The Hong Kong University of Science and Technology, Clearwater Bay, Kowloon, Hong Kong

## Abstract

Pulsed UV lasers, such as the fourth harmonic emission of an Nd:YAG laser at 266 nm and an ArF excimer laser at 193 nm, were used to obtain modification of polymer surfaces, nanostructure fabrications on polymer and silicon substrates and diamond deposition using photoablated polymer plumes. The results are reported here.

**Keywords:** Pulsed UV-laser irradiation; Polymer surfaces; Nano-structure fabrications; Diamond deposition

## 1. Introduction

Pulsed lasers have been used for surface modification for many years. In particular, carbon dioxide lasers have been used for hole drilling, welding, cutting, surface melting, etc. However, with the increasing use of pulsed UV lasers, such as excimer lasers and Nd:YAG lasers in the third and fourth harmonic modes, surface treatments have become more precise and more chemical reactions are involved, as demonstrated by the clean ablated holes made by excimer lasers. In this paper, we report the results obtained using pulsed UV lasers to fabricate nanostructures, improve the wettability and adhesion and deposit diamond from photoablated polymer plumes (see Table 1).

## 2. Nanostructure fabrication

Fabrications of nanostructures on substrates such as polymers, SiO<sub>2</sub> and GaAs are very important both scientifically and technically. These structures are useful for the alignment

of liquid crystalline molecules, the fabrication of quantum devices and fine gratings and other applications. Submicrometre periodic structures on polymers have been induced with the use of a quartz polarizer to produce polarized excimer laser beams [1,2]. These submicrometre-sized periodic structures are obtained using 193 nm and 248 nm excimer laser irradiation with a fluence of 2–3 mJ cm<sup>-2</sup>, i.e. far below the photoablation threshold. However, repetitive exposures of up to about 1000 pulses are required. With a fluence exceeding the ablation threshold, a few micrometre-sized periodic patterns have been reported using excimer lasers on polymer surfaces such as poly(ethylene terephthalate) (PET) [3,4]. These larger periodic patterns are the result of the combined effects of many factors. Periodic ripple structures have also been generated on metallic films [5] and semiconductor films, such as GaAs [6] and Si [7], using polarized laser irradiation.

Our purpose was to find a simple way to fabricate nanostructures on polymer, silicon and other semiconductor surfaces. We used, primarily, an Nd:YAG laser in its fourth harmonic mode (266 nm) (single beam or double beam mode), with polarization planes orthogonal to each other, for the generation of dot patterns [8,9]. Examples of line and dot patterns are shown in Figs. 1 and 2. The polarized pulsed laser exposure at 266 nm was carried out with a fluence of 3–5 mJ cm<sup>-2</sup> at a repetitive rate of 10 Hz with a total pulse number of about 1000. Periodic linear structures start to appear after the polymer surface has been exposed to a few hundred pulses. The periodicity  $\Gamma$  depends on the laser wavelength  $\lambda$ , the refractive index  $n$  of the material used and the sample angle  $\theta$  relative to the laser beam, as expressed by the following equation

Table 1  
Pulsed UV laser process

Process	Required fluorescence
Nanostructure fabrications with polarized beams and reactive ion etching (RIE)	2–5 mJ cm <sup>-2</sup> , below photoablation threshold
Surface chemical changes; wettability; selective metal deposition	10–50 mJ cm <sup>-2</sup> , around ablation threshold
Photoablation: diamond deposition from ablated polymer plumes	> 80 mJ cm <sup>-2</sup>

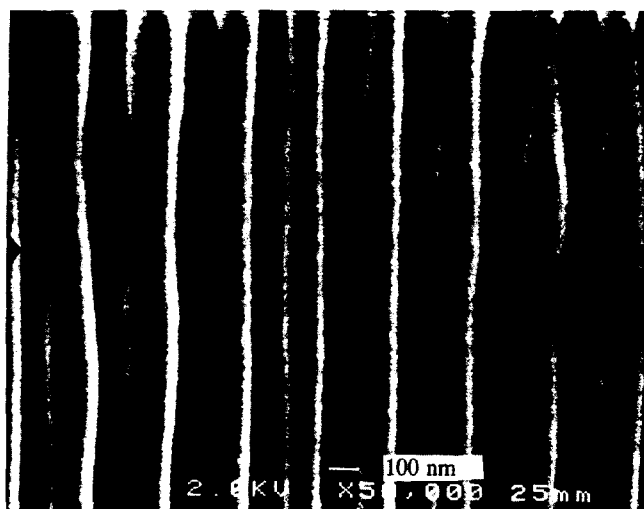


Fig. 1. Scanning electron micrograph of a typical periodic linear structure obtained with the fourth harmonic of an Nd:YAG laser on PET.

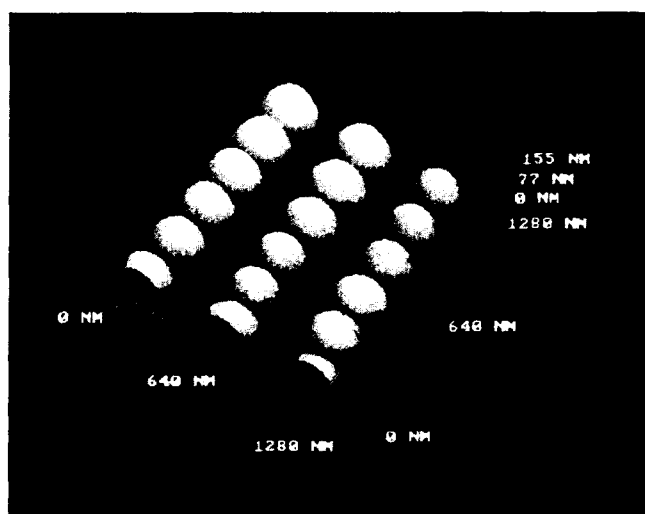


Fig. 2. An AFM micrograph of a dot pattern obtained with a single polarized beam of the fourth harmonic of an Nd:YAG laser on polyimide.

$$\Gamma = \lambda / (n - \sin \theta)$$

As shown in Fig. 1, a linewidth of about 100 nm is obtained. These lines are shallow, about 500 nm deep, with a sloped wall profile. If we continue to expose the polymer films, line patterns are converted to dot patterns after about 8000 pulses. Thus we can cover polymer surfaces with small dots of a few thousand angstroms in diameter. The total width of the dot patterns is larger than the linewidth.

The next step was to use such periodic patterns to generate nanostructures on silicon and other semiconductor surfaces. Although direct exposures of a polarized pulsed beam have been reported previously [6,7], the Si and GaAs lines obtained were shallow and not well defined. Our method is summarized in Fig. 3, which shows a thin film of polydimethylsiloxane placed on top of the periodic structure, filling all valleys produced, followed by back etching of the polydimethylsiloxane layer, except that filling the valleys, and then

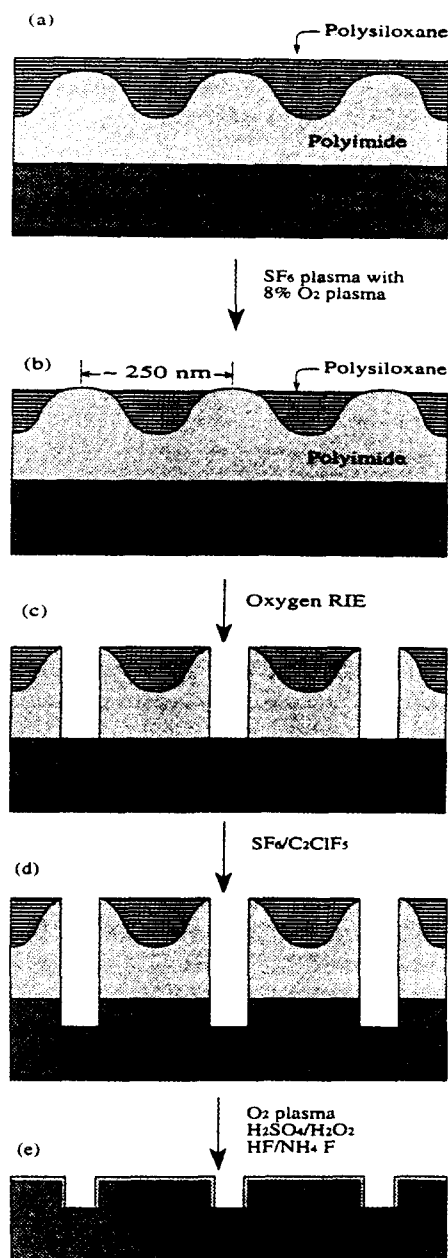


Fig. 3. Image transfer process used to transfer periodic polymer pattern to Si surface: (a) polysiloxane layer coating; (b) back etching by  $\text{SF}_6$  plasma; (c) oxygen RIE for anisotropic etching of polyimide layer; (d)  $\text{SF}_6$ -halo-carbon RIE for silicon anisotropic etching; (e) removal of polyimide layer; double layer on silicon indicates contamination layer.

straight oxygen reactive ion etching (RIE) for polyimide etching and  $\text{SF}_6$  RIE for silicon etching. After silicon etching, the organic and siloxane layers were removed with a solvent [10]. This kind of image transfer process has been used in integrated circuit fabrication in submicrometre dimensions [11], but has never been reported on a scale of 100 nm. The result is shown in Fig. 4. The silicon lines are 100 nm wide with a vertical wall profile. These Si lines were generated with the 266 nm laser beam. With the polarized ArF laser beam at 193 nm, we can expect to obtain a narrower linewidth. The linewidth can also be controlled to a certain degree by



Fig. 4. Si(100) surface pattern after image transfer.

back etching as shown in Fig. 3. Our result demonstrates the feasibility of the fabrication of 100 nm scale periodic patterns on wide surface areas of polymer, silicon and other substrates without the use of expensive photo- or X-ray masks or slow scanning electron beam systems.

### 3. Polymer surface modification

The KrF/ArF excimer-laser-exposed areas of thermostable polymers with high  $T_g$  values, such as polyimides (PI) and poly(phenylquinoxaline) (PPQ), become highly hydrophilic and can retain a water film resulting in imagewise wetting, while unexposed areas repel the water [12]. Increased electrical conductivity is also observed. Increased hydrophilicity is demonstrated by the diminished receding contact angle [12]. Such an increased hydrophilicity is also observed with low  $T_g$  polymers, such as polystyrene, due to photo-oxidation when exposure is carried out in air. However, the imagewise wetting and increased electrical conductivity have been observed only with polymers of high thermal stability and with very high  $T_g$  values. The imagewise wettability lasts for several months when kept in air, and the same sample film was tested successfully many times during this period.

A positively charged surface potential of polymer films after excimer laser ablation has been reported with PET, poly(ether sulphone) and PI [13]. The change to a positive potential on the films is caused by the redeposition of cationic fragments onto the ablated surface. This change in surface potential can be applied to area-selective electroless plating of copper and nickel, replacing chemical activation processes used in conventional electroless plating. The surface potential of a polymer after exposure to an excimer laser can be negative, since positively charged species are carried away while negatively charged species, mostly electrons, are trapped by functional side groups. Acrylonitrile-butadiene-styrene (ABS) polymer shows a minor carbon core level signal peak at 282.3 eV in addition to the main 284 eV peak after irradiation with an ArF excimer laser at 193 nm in air with a fluence of  $100 \text{ mJ cm}^{-2}$ , as shown in Fig. 5. This peak does not appear when the ABS film is exposed to the fourth harmonic of an Nd:YAG laser at 266 nm in air. We attribute this newly

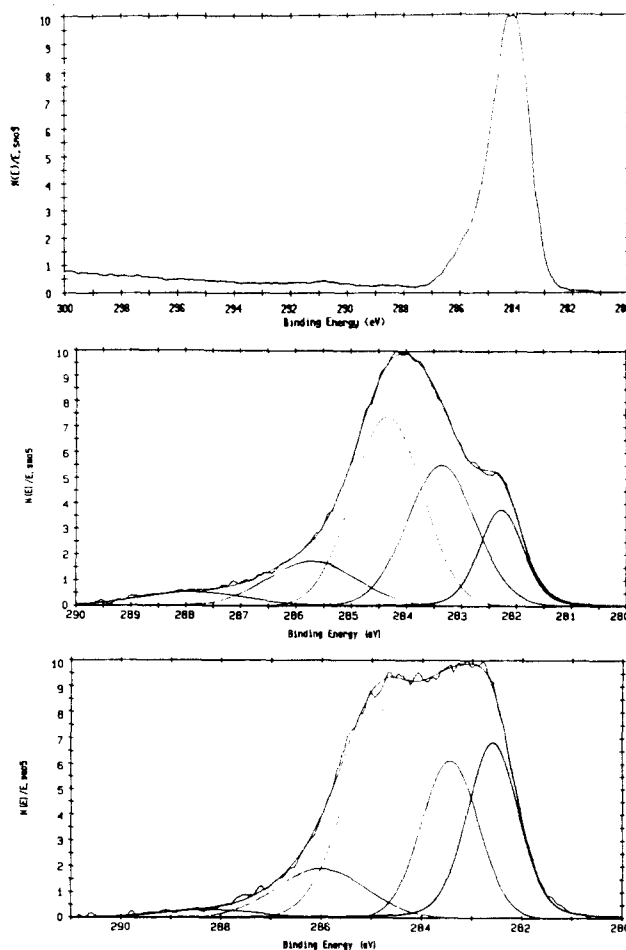


Fig. 5. (A) Carbon core level signal of unexposed ABS film. (B), (C) Change in the carbon core level signal with changing laser fluence.

found carbon core level peak to electron-trapping carbonyl carbons.

We have reported the successful surface modification of poly(tetrafluoroethylene) (PTFE) for Cu electroless plating [14]. Polymer surfaces were exposed to the fourth harmonic of an Nd:YAG laser in an aqueous basic solution, such as tetramethylammonium hydroxide, followed by metal deposition in electroless plating or vapour deposition [14]. The deposited Cu or Ni layers show excellent adhesion on PTFE.

### 4. Photoablation: diamond deposition from polymer plumes

The plumes generated during the photoablation of a polymer by an excimer laser travel at a high velocity with a shock wave front at high temperature and pressure. This feature makes diamond deposition easier than with other conventional methods, e.g. using a hydrogen-methane plasma, hot filament or acetylene torch. It also gives better adhesion to the substrate surface. Although the attempt to produce diamond films from polymers is not new, and others have reported diamond-like carbon (DLC) films [15], no crystalline diamond has been reported with an excimer laser with

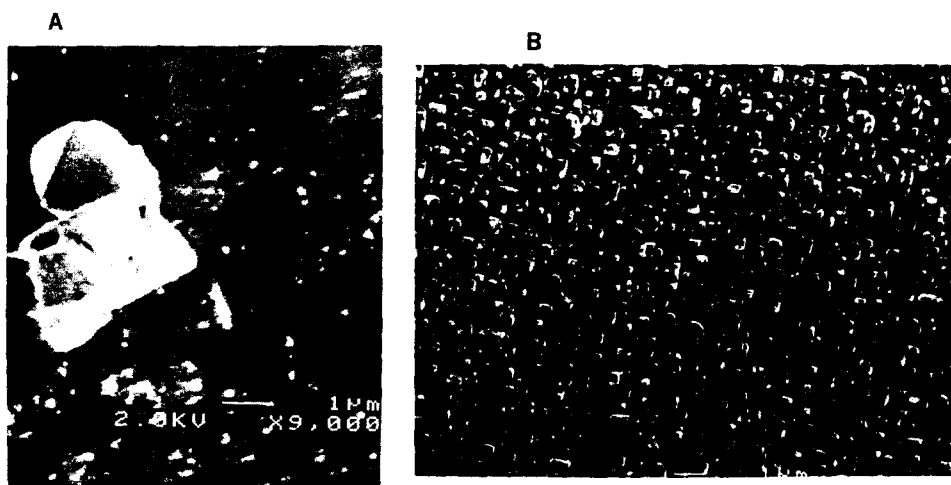


Fig. 6. (A) Octahedral diamond crystal on a Si{111} surface. (B) Block-shaped diamond crystals on Si{100} surface.

the exception of our work [16]. Our experimental apparatus can control the gas phase composition by addition of a reactive gas to the chamber. Initially, we used poly(methyl methacrylate) (PMMA) as target polymer. The chemical composition of PMMA alone is not sufficient to generate crystalline diamond, and additional oxygen or hydrogen is required according to a phase diagram established for the chemical vapour deposition of diamond [17].

All experiments were conducted with an ArF excimer laser at 193 nm with a fluence ranging from 80 to 200 mJ cm<sup>-2</sup>. The reflected plume was adjusted to hit the silicon substrate at a maximum superficial area. The substrate itself was fixed onto a thermal element which could be heated up to 800 °C. A negative bias potential of 50 V was applied to accelerate the smaller carbon ions. The important parameters are the substrate surface, temperature, laser fluence and target polymer composition.

Fig. 6(A) shows an octahedral diamond crystal deposited on a {111} silicon surface heated at 680 °C. Better growth was achieved on a {100} silicon surface with the deposition of block-shaped crystals, as shown in Fig. 6(B). The dia-

mond crystals of Fig. 6(B) have a micro-Raman spectrum consisting of two peaks: a major peak at 1330 cm<sup>-1</sup> and a minor peak at 1597 cm<sup>-1</sup>. The latter peak is clearly due to graphite contamination. The peak at 1330 cm<sup>-1</sup> is broad with a full width at half-maximum (FWHM) of 80 cm<sup>-1</sup> [16]. We believe that this peak at 1330 cm<sup>-1</sup> is due to diamond, but its broadness is due to its microcrystalline nature and the defects inherently present in diamond deposited in this way.

We can remove the graphite peak at 1597 cm<sup>-1</sup> and can obtain a very sharp peak at 1332.9 cm<sup>-1</sup> with a FWHM of 1.2 cm<sup>-1</sup>, as shown in Fig. 7. A jewel diamond used as a standard gave a Raman peak at 1332.3 cm<sup>-1</sup> with a FWHM of 4.5 cm<sup>-1</sup>. The best diamonds deposited from methane-hydrogen plasmas have been reported to have a FWHM of 5 cm<sup>-1</sup> (natural diamond: FWHM = 2 cm<sup>-1</sup>; GE diamond: FWHM = 1.7 cm<sup>-1</sup> [18]). Several parameters are involved in the deposition of these pure diamond crystals with micro-metre-sized tetrahedral shapes shown in Fig. 7. A study is in progress to determine the parameters. Both PMMA and poly(methacrylic acid) doped with TiCl<sub>4</sub> were used to obtain this sharp diamond peak. Other parameters different from previous experiments are the substrate surface (the substrate surface had 100 nm Si lines fabricated on Si{100} as previously shown in Fig. 4) and a lower laser fluence (in the range 80–100 mJ cm<sup>-2</sup>). Details will be reported in a future publication.

#### Acknowledgments

We thank the Hong Kong Government for research support through RGC grant UST 11/91, UST 627/94P and UPGC grant RI92/93.SC06.

#### References

- [1] M. Bolle, S. Lazare and M. Le Blanc, *Appl. Phys. Lett.*, 60 (1992) 674.

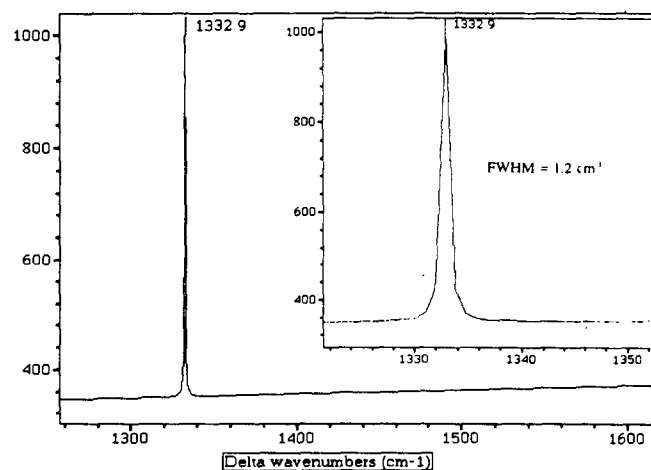


Fig. 7. Micro-Raman spectrum of tetrahedral crystals: a very sharp Raman peak is observed at 1332.9 cm<sup>-1</sup>; the inset shows a FWHM of 1.2 cm<sup>-1</sup>.

- [2] M. Bolle and S. Lazare, *Appl. Phys. Lett.*, 73 (1993) 3516.
- [3] H. Niino, M. Nakano, S. Nagano, A. Yabe and T. Miki, *Appl. Phys. Lett.*, 55 (1989) 510.
- [4] P. Dyer and R. Farley, *Appl. Phys. Lett.*, 57 (1990) 765.
- [5] J. Young, J. Preston, H. van Driel and E. Sipe, *Phys. Rev.*, 27 (1983) 1155.
- [6] H. Kumagai, M. Ezaki, K. Toyoda and M. Obera, *Jpn. J. Appl. Phys.*, 31 (1) (1992) 4433.
- [7] H. Leamy, G. Rozgonyi, T. Sheng and G. Celler, *J. Appl. Phys.*, 32 (1978) 535.
- [8] H. Hiraoka and M. Sendova, *Appl. Phys. Lett.*, 64 (1994) 563.
- [9] M. Sendova and H. Hiraoka, *Jpn. J. Appl. Phys.*, 32 (1993) 6182.
- [10] H. Hiraoka, M. Sendova and C.H. Lee, *Jpn. J. Appl. Phys.*, 33 (1994) 7135.
- [11] H. Hiraoka, *J. Microelectron. Eng.*, 6 (1988) 407.
- [12] H. Hiraoka and S. Lazare, *Appl. Surf. Sci.*, 46 (1990) 264.
- [13] H. Niino and A. Yabe, *Appl. Phys. Lett.*, 60 (1992) 2697; *Appl. Surf. Sci.*, 69 (1993) 1.
- [14] H. Hiraoka, S. Lätsch and M. Sendova, *J. Photopolym. Sci. Technol.*, 7 (1994) 299.
- [15] I.S. Athwal, A. Mele and E.A. Ogryzlo, *Diamond Relat. Mater.*, 1 (1992) 731.
- [16] S. Lätsch and H. Hiraoka, *J. Miner. Met. Mater. Soc.*, 46 (7) (1994) 64.
- [17] P.K. Bachmann, D. Leers and H. Lydtin, *Diamond Relat. Mater.*, 1 (1991) 1.
- [18] Y. Liou, A. Inspektor, R. Weimer, D. Knight and R. Messier, *J. Mater. Res.*, 5 (1990) 2305.