



# Ultraviolet-irradiated precision polishing of diamond and its related materials



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## ABSTRACT

In this study, a novel ultraprecision polishing process for single-crystal diamond substrates was developed utilizing ultraviolet (UV) irradiation. This polishing is basically a mechanochemical polishing (MCP) process combined with a UV-induced photochemical reaction. Carbon atoms on the topmost surface of diamond are oxidized by active species such as hydroxyl radicals (OH radicals) and oxygen radicals at localized high temperature and finally removed as CO and CO<sub>2</sub>. This polishing process was applied to diamond substrates, chemical vapor deposition (CVD) diamond-coated films and polycrystalline diamond (PCD). The results showed that the surface roughness of the entire substrate reached 0.2 nmRa within 1–3 h at a comparatively high removal rate. The characteristics and removal mechanism of UV polishing were also discussed.

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## 1. Introduction

Diamond is a good candidate material of semiconductor devices and sensor elements because it can perform even in extreme environments. Among various materials, single-crystal diamond has the highest hardness and the greatest fracture strength as well as excellent chemical, heat and radioactive resistance. The original crystalline structure and chemical composition of diamond beneath a polished substrate do not essentially change before and after mechanochemical polishing (CMP). However, the above excellent characteristics of diamond basically prevent the application of CMP to a diamond substrate.

Diamond substrates are polished by various techniques, such as thermochemical polishing [1,2], plasma etching [3,4] and polishing using powerful oxidizing agents [5]. Unfortunately, these techniques are impractical. Although laser abrasion using ultraviolet lasers has been described in many patents, it does not provide the high machining accuracy required for semiconductor substrates. Research and development of the mechanism of etching techniques for SiC or GaN substrates in UV-irradiated alkaline solution have been conducted with the purpose of forming oxide films mainly via the oxidation of holes generated by excitation under UV irradiation [6]. Then, such oxide films are subsequently removed by etching in alkaline solution. When this mechanism is applied to a diamond semiconductor, it is extremely difficult to etch carbon atoms on the surface, even if the atoms can be terminated as C–O and C–O<sub>2</sub>.

In this study, a UV-excited polishing process for diamond substrates (abbreviated as UV polishing hereafter) was developed [7–9]. In this

process, carbon atoms on the topmost surface are oxidized by UV irradiation and finally removed mechanically as CO<sub>2</sub> or CO. UV polishing with high-efficiency machining can achieve superior surface smoothness, thereby maintaining the original crystalline structure. The difference in polishing performance between some crystalline planes can be suppressed by UV polishing. The polishing characteristics and removal mechanism of UV polishing were also discussed.

## 2. Proposed mechanism of UV polishing of diamond substrates

Diamond has a band gap energy of 5.45 eV and thus can be excited by UV irradiation with a wavelength shorter than 225 nm. Fig. 1 shows a schematic of an oxygen-terminated diamond surface. Holes and electron pairs can be generated by photoexcitation under UV irradiation, and bond immediately with oxygen and water molecules in the atmosphere. The bonding reactions generate many atomic oxygen and OH radicals, which are highly active species with high oxidation potentials, and result in the oxidation of the topmost surface of diamond [10]. These bonded oxygens are not eliminated independently, but are outgassed from the surface as CO or CO<sub>2</sub> above 730 K [11]. In the process indicated in Fig. 1, as electron and hole pairs usually recombine at rates of 98–99%, they contribute little to the formation of OH and oxygen radicals. Also, oxygen and water molecules, which strongly adsorb onto photoexcited diamond atoms, can only react with hole and electron pairs. Note that the temperature of restricted areas on a diamond substrate is increased by the strong friction between the hard plate and the diamond substrate. This is effective for the formation of oxygen radicals and for their diffusion into two or three carbon layers and their chemical reactions with carbon atoms, as well as for the elimination of oxide films. Furthermore, as these reactions are restricted to narrow

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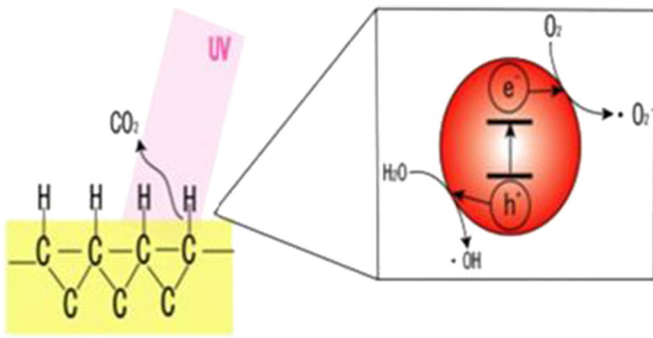


Fig. 1. Schematic drawing of oxygen-terminated diamond surface induced by UV irradiation.

contact areas on the diamond substrate, it is often helpful to achieve the microplanarization of the diamond substrate. These mechanisms suggest the distinct practical and feasible application of diamond UV polishing with high removal rate and excellent surface roughness.

**3. Experimental procedure and polishing model validation of UV polishing of single-crystal diamond and polycrystalline diamond**

The UV polishing of the single-crystal diamond Ib (100) plane was performed using the laboratory-built horizontal type polishing machine shown in Fig. 2(a). The substrate was 3 mm × 3 mm × 1 mm. The

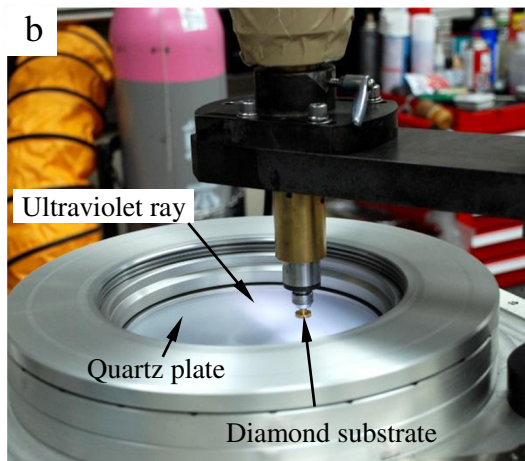
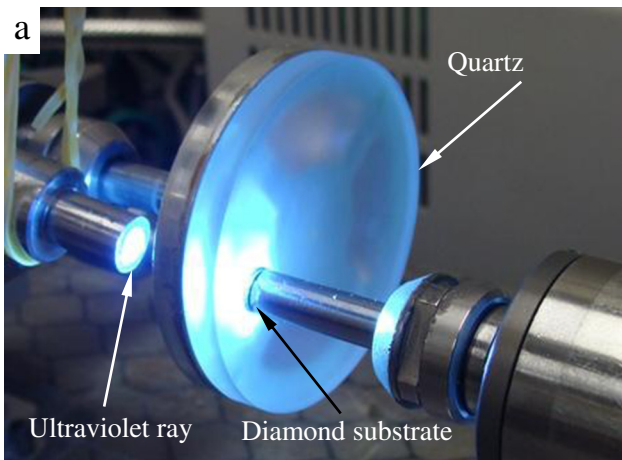


Fig. 2. Photograph of laboratory-built experimental setup for UV polishing. (a) Horizontal type UV polishing machine for single crystal diamond. (b) Vertical type UV polishing machine for polycrystalline diamond.

polishing plate with a 50 mm diameter was artificial quartz with a UV transmittance of more than 85% at a UV wavelength of approximately 200 nm. The UV wavelength and UV intensity used in Fig. 2(a) are 200 – 400 nm and 1200 mW/cm<sup>2</sup> measured at the exit of the optical fiber. Although the UV intensity decayed to 300 mW/cm<sup>2</sup> on the sample surface due to absorption of by the artificial quartz plate and the air, this UV intensity is sufficient to induce the photochemical reaction in the UV polishing. Rotational speed and polishing pressure were set at 600 – 2000 rpm and 0.2 – 1.0 MPa, respectively.

The UV polishing of polycrystalline diamond was performed using a vertical type polishing machine as shown in Fig. 2(b). This machine was developed to correspond with diamond substrates with a large diameter (50 mm maximum diameter). A UV light source with shorter wavelength was applied and an artificial quartz plate with 200 mm in diameter was used. The UV wavelength and intensity used in this machine were 172 nm and 50 mW/cm<sup>2</sup> at the top of the UV source. The UV intensity also decayed to 3.6 mW/cm<sup>2</sup> on the sample surface. Surface morphology, surface roughness and removal depth were measured and evaluated using an interferometric microscope and a laser microscope.

Fig. 3 shows the effects of the UV irradiation and rotation of the quartz disk/workpiece on the CO concentration detected during the UV polishing of the single-crystal diamond Ib (100) plane. A highly sensitive gas sensor was used to measure CO concentration, and the temperature around the diamond substrate was also recorded at the same time. After UV irradiation started at a processing time of 10 min, CO concentration increased rapidly before reaching a steady state. When the rotation of the substrate was turned off at 30 min, CO concentration decreased gradually with the detection of residual CO and finally reached zero at approximately 40 min. After the rotation was restarted at 50 min, CO concentration immediately increased to the same value as that at 10 – 30 min. The termination of UV irradiation results in a zero CO concentration after 70 min despite the fact that the diamond substrate and quartz plate were continuously rotated. Experimental results in Fig. 3 qualitatively indicate the validity of the UV polishing model shown in Fig. 1.

Matsumoto et al. [10] detected CO<sub>2</sub> gas using chromatography when UV was irradiated on diamond powder completely mixed with TiO<sub>2</sub> powder. The mixed powder was inserted into a quartz cell. According to their experiment, in the case of using pure diamond powder, CO<sub>2</sub> gas could not be detected by UV irradiation for 120 min. In the case of using a mixture of diamond powder with TiO<sub>2</sub> powder, CO<sub>2</sub> concentration increased up to 20% by UV irradiation for only 30 min.

On the other hand, a strong mutual sliding of the quartz plate and diamond substrate under high pressure could increase CO concentration up to 17 ppm within 3 – 5 min of UV irradiation. From this point of view, it is clear that a polishing process with high removal efficiency that entails both the oxidation of the diamond surface and the outgassing of CO or CO<sub>2</sub> can be achieved by high-pressure sliding under UV irradiation. Namely, it can be interpreted that each step of the polishing process, illustrated in Fig. 1 is enhanced by high temperature and high pressure. Therefore, the UV polishing process developed here is clearly different

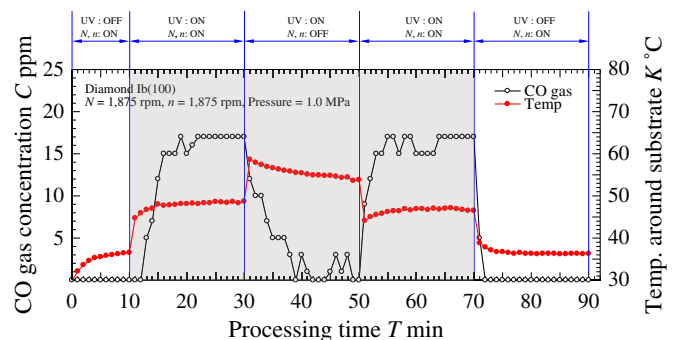


Fig. 3. CO gas concentration and temperature around diamond substrate are plotted against processing time. UV-irradiated between 10 min and 70 min.

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