Diamond & Related Materials 63 (2016) 69–74

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Application of femtosecond laser technique in single crystal diamond film separation

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ARTICLE INFO

Article history:
Received 15 July 2015
Received in revised form 23 November 2015
Accepted 26 November 2015
Available online 30 November 2015

Keywords:
Diamond film
Semiconductor
Chemical vapor deposition
Single crystal growth

ABSTRACT

In this paper, we report on an attempt to separate single crystal (SC) diamond film from diamond substrate by femtosecond laser treatment and electrochemical etching techniques. Firstly, femtosecond laser was focused on about 20 μm below the surface of diamond substrate to form a non-diamond layer. Secondly, a thick SC diamond film was grown on this substrate by microwave plasma chemical vapor deposition system. Finally, an electrochemical etching treatment was performed to separate the SC diamond film from its substrate. The results indicate that femtosecond laser technique has provided a potential way for the separation of grown diamond film from its substrate.

1. Introduction

Single crystal (SC) diamond has excellent properties such as wide band gap, highest thermal conductivity, high breakdown field, high electron and hole mobility [1]. These properties endow diamond to possess potential applications in the field of electron devices such as high frequency, high temperature, and high power [2]. For several decades, researchers have used natural and high-pressure high-temperature (HPHT) diamonds to develop electron devices. While, natural and HPHT diamonds are limited for high cost, low growth rate and small size [3]. In order to fabricate diamond devices, it is necessary to develop high quality SC diamond films.

In 2002, Yan et al. [4] introduced a small flow rate of N_2 into microwave plasma chemical vapor deposition (MPCVD) chamber during diamond growth and increased the growth rate from few microns per hour to above 150 μm/h, which enables the large-area SC diamond to be developed. However, when getting free standing SC diamond film to form high quality substrate, there are still difficulties in how to separate the grown film from its initial substrate. Traditionally, laser cutting and substrate polishing techniques were used. Alternatively, Fairchild et al. [5] successfully used ion implantation technique to separate the grown diamond film from its substrate and applied it into the fabrication of ultra-thin single-crystal diamond membranes. However, ion implantation technique alone could not meet the increasing need of diamond substrates for electronic devices and research applications. Thus, seeking for an alternative and possible method is very important.

Femtosecond laser (fs-laser) process has been of great interest for semiconductor materials micromachining in recent years, and a number of groups have reported on fs-laser ablation thresholds and fs-laser induced surface modifications in SC diamond [6–8]. While, few results on fabrication of a non-diamond layer below the surface of diamond substrate were reported. Moreover, the application of fs-laser technique in diamond film lift-off process has not been reported yet.

In this paper, we report on an attempt to separate SC diamond film from diamond substrate using fs-laser treatment and electrochemical etching techniques.

2. Experimental procedure

Before fs-laser treatment, the polished HPHT Ib (001) SC diamond substrate ($3 \times 1.5 \times 0.3$ mm^3) was subjected to a series of chemical cleaning processes [9]. Then, the substrate was put on a 3D translation stage and treated by the fs-laser system with 100× objective lens and NA of 0.95, as shown in Fig. 1. The fs-laser is a regenerative amplified mode-locked Ti: sapphire laser, which has the properties such as 800 nm wavelength, 9 mW average laser power at pulse repetition rate of 1 kHz. The laser beam was adjusted perpendicularly to the diamond substrate, and sharply focused at a certain depths below the surface. Furthermore, a line-by-line serial scanning process was performed with a scanning speed of 40 μm/s and the laser power density on the sample surface and in the focused area were 0.19 J/cm^2 and 3.2 J/cm^2 respectively. Two substrates were prepared with about 2 and 20 μm

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http://dx.doi.org/10.1016/j.diamond.2015.11.015
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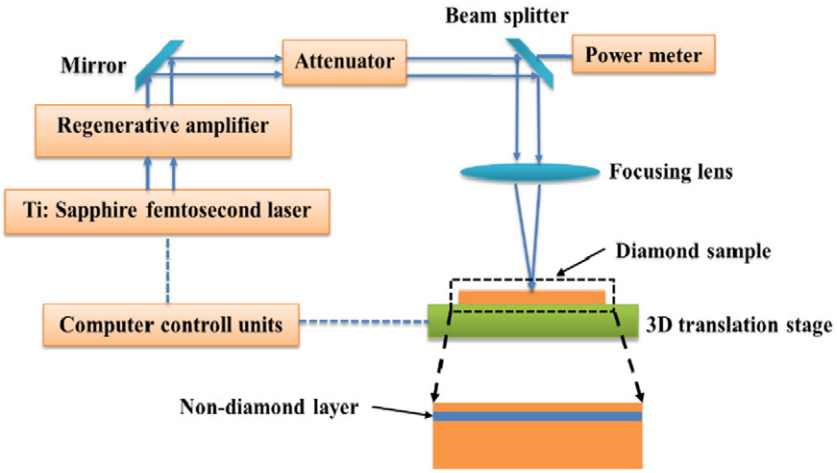

Fig. 1. Schematic of femtosecond laser system.

focused depths, which were denoted as sample A and sample B, respectively.

After fs-laser treatment, the samples were put into MPCVD chamber to grow SC diamond film. During growth, H_2 (500 sccm, 6N), CH_4 (50 sccm, 6N) and N_2 (0.5 sccm, 6N) were used as the reaction gases. The chamber pressure, microwave power and substrate temperature were 16 kPa, 5 kW and 1175 °C, respectively. The growth time and thickness were 6 h and 300 μm. After growth, the electrochemical etching treatment was performed on the sample by our system. In this system, an alternating-current (AC) power supply with a maximum voltage of 6000 V, a neutral solution with low electrical conductivity and the electrodes with chemical stability were used. Surface morphologies were characterized by optical microscopy (OM) and scanning electron microscope (SEM). The crystal qualities were investigated by Raman system with a 100× objective lens and a 532 nm wavelength laser, and high-resolution X-ray diffraction (HRXRD) systems which use the Cu Kα X-ray radiation and four-crystal Ge (440) monochromator.

3. Results and discussion

Fig. 2(a) indicates the SEM image of sample A after fs-laser treatment, showing a rough surface. Fig. 2(b) presents an enlarged image which exhibits almost uniform scanning traces along the scanning direction, and the laser scanning pitch is about 1 μm, indicating a strip like pattern. Fig. 2(c) exhibits the image of the as grown diamond film on sample A, showing a rough surface, on which there are many hillocks, indicating that the surface of sample A is not suitable for growth of SC diamond.

Fig. 3 (a) shows the SEM image of sample B after fs-laser treatment, presenting a smooth surface. Fig. 3(b) exhibits the magnified image with only several defect points. Fig. 3(c) presents the image of as grown diamond film on the surface of sample B, illustrating "orange peel" appearances, which are due to accumulation of step to bunching pattern [10]. Fig. 3(d) indicates the SEM image of the step-flow growth, and the step bunching is clear, exhibiting a typical SC diamond film growth on Sample B.

Sample A and sample B were treated with the same fs-laser treatment condition, and the only difference is the focused depth. From the SEM image of Sample A, it can be seen that the fs-laser treatment could form almost uniform scanning traces along the scanning direction. Although there is no scanning trace can be seen in the surface of Sample B, it could be thought that the traces at the depth of 20 μm have the same scanning pattern as that of Sample A. Since the as grown film on Sample B has a smooth surface, we will concentrate on investigation of only sample B in later discussion.

Fig. 4 shows the color variation images of the sample B before and after fs-laser treatment. Fig. 4(a) indicates a normal transparent diamond substrate before treatment. Fig. 4(b) exhibits an opaque diamond substrate after treatment, illustrating that there were some reactions happened in the substrate during treatment. Fig. 4(c) presents Raman measurement results which were taken from four points on the surface of Sample B after fs-laser treatment. The peaks at around 1332 cm^{-1} indicate that the sample surface is fully composed of sp^3 carbon bonds, which reveals that no composition change took place on Sample B surface and the crystalline quality of it is good as well.

In order to evaluate the quality of sample B, the XRD investigation has been carried out. Fig. 5 shows the XRD measurement results of (400) ω

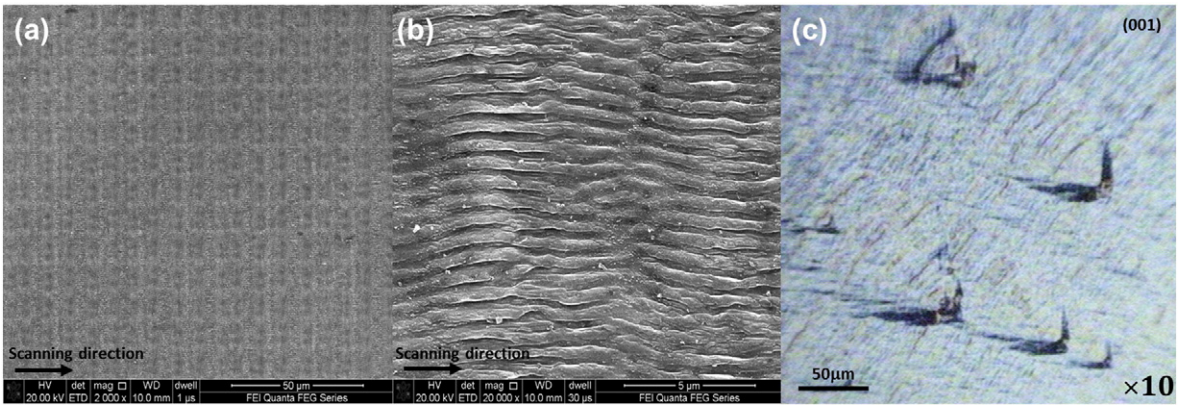

Fig. 2. (a) SEM image of sample A after fs-laser treatment. (b) enlarged SEM image of (a). (c) OM image of the as grown diamond film.

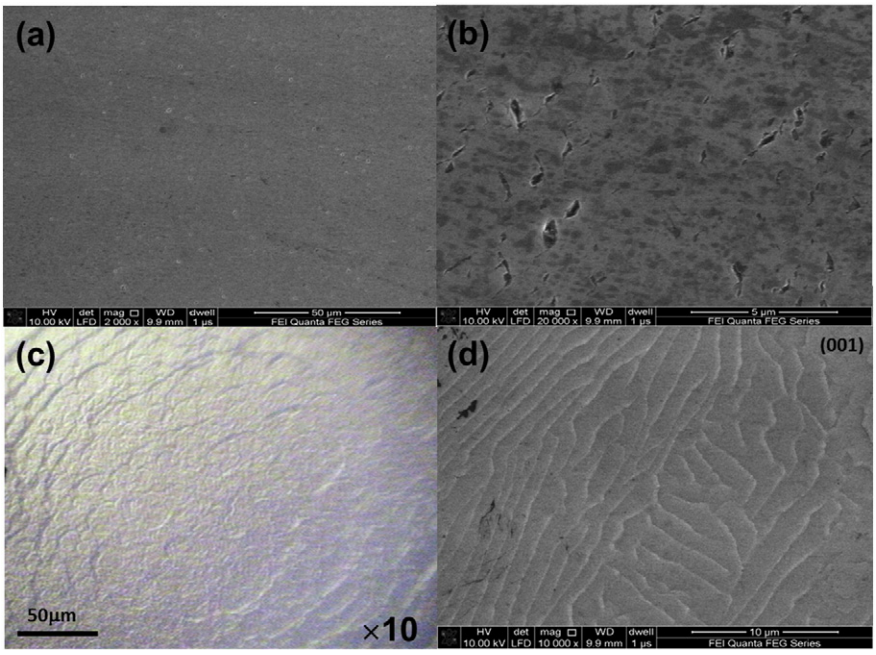

Fig. 3. (a) SEM image of sample B after fs-laser treatment. (b) magnification SEM image of (a). (c) OM image of as grown sample. (d) SEM image of as grown sample.

scans on Sample B and as grown diamond film. Fig. 5(a) exhibits XRD result of Sample B with a sharp peak at 59.7567° and a FWHM of 0.008°, indicating a good crystal quality after femtosecond laser process. Fig. 5(b) presents XRD result of as grown diamond film with a sharp peak at 59.867° and a FWHM of 0.07°, confirming that the CVD diamond are single crystals. The slight broadening of FWHM stems from small degree of poly-crystal particles at sample edge [4]. All this indicates that the as grown diamond film has an accepted quality.

Fig. 6(a) shows the cross section SEM image of as grown diamond sample, which presents a sandwich structure with neat boundaries compared with diamond substrate and as-grown film. What's more, there are some dark lines and dark spots appeared in the image, which could be ascribed to the contaminations introduced in the cross-section preparation with laser cutting and machine grinding. Also, it is obvious that the B area and the A C area indicates different morphologies, which could be thought to be stemmed from the different compositions. In order to investigate the composition of the black strip in Fig. 6(a), the Raman measurement has been carried out. Fig. 6(b) illustrates the Raman spectra taken from three points in Fig. 6(a). The spectrum a taken at point A in diamond substrate side in Fig. 6(a) shows only a strong peak at 1332.7 cm^{-1}, revealing a diamond sp3 structure. The spectrum c taken at point C in as-grown diamond layer in Fig. 6(a) exhibits the typical result of SC diamond film grown with nitrogen introduction. The spectrum b taken at point B in the black strip in Fig. 6(a) shows two peaks at around 1350 cm^{-1} and 1580 cm^{-1}, indicating a typical graphite sp^2 structure, which means that the diamond structure was changed to graphite structure during fs-laser treatment.

In order to demonstrate that the position of black (graphite) strip could be roughly controlled by setting a fs-laser focused depth, another sample has been prepared by fs-laser treatment with a focused depth of about 20 μm. Fig. 7 shows the SEM image of its cross section. A black strip can be clearly seen at a depth of about 12 μm, by which it could be thought that there are some factors cause the movement of strip position from the fs-laser focused point. A possible reason would be that the crystal structure transformation was moved towards the laser beam during treatment. Therefore, the black strip position is at a position above the focused point.

The crystal structure transformation from sp^3 to sp^2 could be thought that the electrons absorb sufficient energy from fs-laser pulse

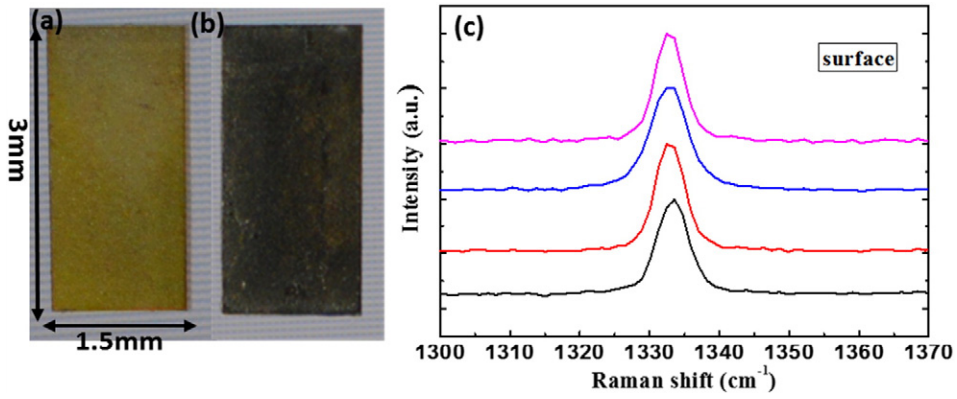

Fig. 4. Color variation images of sample B before (a) and after (b) fs-laser treatment. (c) Raman spectra image taken from four points on the surface of sample with only 1332 cm^{-1} diamond peak.

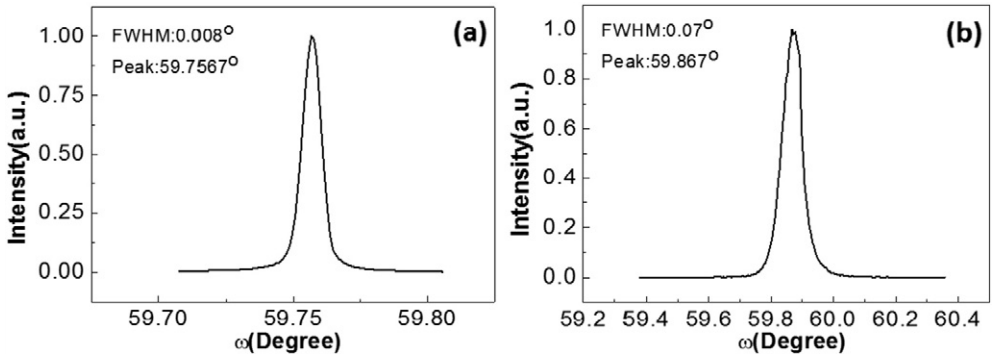

Fig. 5. XRD (400) ω scan spectra of laser processed substrate (a) and as grown diamond film (b).

and as the femtosecond regime is reached, materials are capable of producing quite high enough electron densities [11]. Moreover within an fs time scale, the absorbed energy is distributed among the excited electrons by electron–electron collisions leading to a rapid thermalization of the excited electrons while the lattice remains cold. This is induced by the high intensity and the nonlinear effect (multiphoton absorption) of the fs-laser [12,13,14]. And the probability of multiphoton absorption is proportional to the laser light intensity of n (n is the photon number), the enormous intensity that fs-laser pulses achieve at their focus could increase the possibility of the multiphoton absorption [15,16]. Because of this, electrons are excited from valence band to the conduction band. Those excited electrons will jump from bonding state to antibonding state, which leads to a creation of unbalanced repulsive force [17]. When a high enough fraction of the valence electrons is excited from bonding state to antibonding state, the crystals will become unstable and the structural phase transition occurs [18,19]. It could be suggested that under the traditional laser thermal ablation treatment (e.g. ps-laser), no enough density of antibonding state electrons can be excited to induce a structural phase transition. However, during the fs-laser treatment, since large number of electrons are in antibonding state, the strong covalent bonds in diamond can be destroyed, and the phase transition from diamond sp3 bond to graphite sp2 bond has occurred. In this way, if the power density of fs-laser is increased, the number of excited electrons would be increased and the phase transition becomes faster. Observing from the SEM image (shown in Figs. 6(a) and 7), the clear interface between diamond film and graphite strip could make the grown diamond film possibly be separated from its substrate.

After investigation, the sample (sample B) was treated by electrochemical etching system whose schematic is shown in Fig. 8(a). And Fig. 8(b)–(e) exhibits the sample color variation images during electrochemical etching process. Fig. 8(b) presents that more than half area was changed from black to transparent, and then the black area becomes less as shown in Fig. 8(c). During etching process, about half of the sample was inserted in an open Teflon holder. Since the difference of dielectric constant between solution and Teflon, the local electrical field strengths in the solution and the Teflon holder are different, leading to different etching rates of non-diamond layer in the solution and in the Teflon holder, which results in a distorted etching area.

As the time increases, the black area just remains a little (shown in Fig. 8(d)), and finally the black area has disappeared (shown in Fig. 8(e)). Compared with that in Fig. 4(b), it can be seen that the sample changed from opaque to transparent, indicating that the visually observed graphite has been etched. This illustrates that the graphite has been removed and the as-grown diamond film could be separated. During etching process, the current was always set at a certain value, and the applied voltage was varied. When the applied voltage was changed from 1000 to 3000 V and the current was kept in a range from 10 to 50 mA, the time of sample color being changed from opaque to transparent was varied from 10 to 6 h, which means that at a certain current, the etching rate was enhanced with applied voltage increasing.

Fig. 9(a) displays the cross section OM image of the sample after electrochemical etching, which could be seen that there was a gap between the substrate and as-grown film. Fig. 9(b) presents a SEM image which exhibits an obvious gap (as shown around the red line

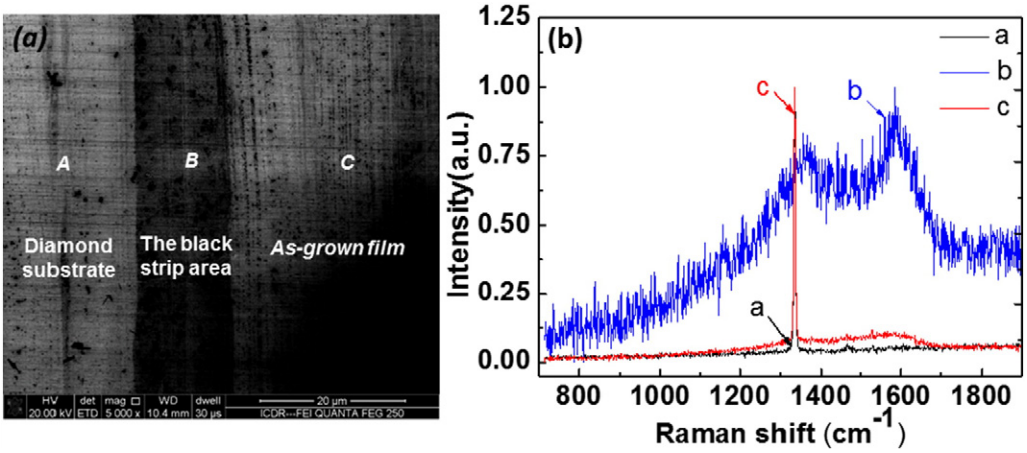

Fig. 6. The cross section SEM image (a) and Raman spectra (b) of diamond sample after CVD growth. (a) Presents a sandwich structure and neat boundaries. (b) Line a exhibits diamond substrate side, line c fingers as-grown diamond film, line b stands fs-laser focused area.

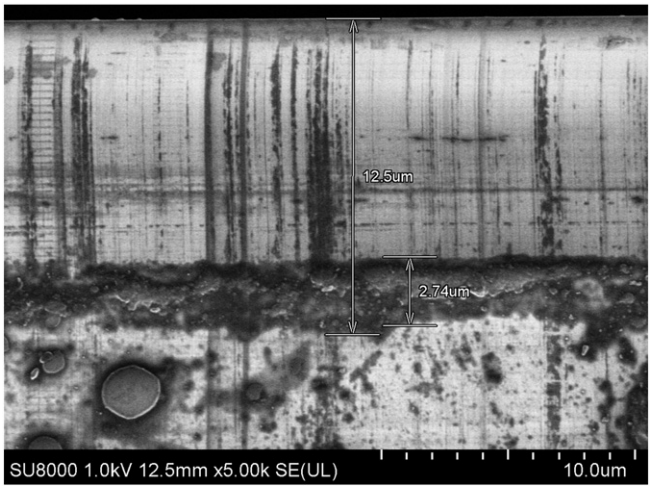

Fig. 7. The cross section SEM image of diamond sample after fs-laser treatment.

area) and a diamond joint point (as the white arrow pointing). It is because that the existence of this diamond joint point, the diamond film has not been separated yet. While this method has provided a potential way for the separation of grown diamond film from its substrate. Further work is underway to modify the fs-laser process condition to obtain a free standing SC diamond film from its substrate so as to use this technology for large area diamond substrate preparation etc.

4. Conclusion

In this paper, we have tried to experimentally separate the as grown single crystal diamond film from diamond substrate by fs-laser treatment and electrochemical etching techniques. The fs-laser focused depth has seriously influenced on the surface morphologies of the treated substrate and the quality of as grown SC diamond film. The cross section SEM image indicates that a black strip with a neat boundary was formed at a depth above the focused point, which is identified to be graphite composition by Raman spectra. By electrochemical etching technique, it can be seen that the diamond sample is changed from opaque to transparent, indicating that the graphite strip has been removed. This method has provided a potential way for the separation of grown diamond film from its substrate.

Acknowledgments

This paper was supported by National High-tech R&D Program of China (863 Program) (Grant No. 2013AA03A101). The authors acknowledged the assistance given by the members of Institute of wide band gap semiconductors, Xi'an Jiaotong University.

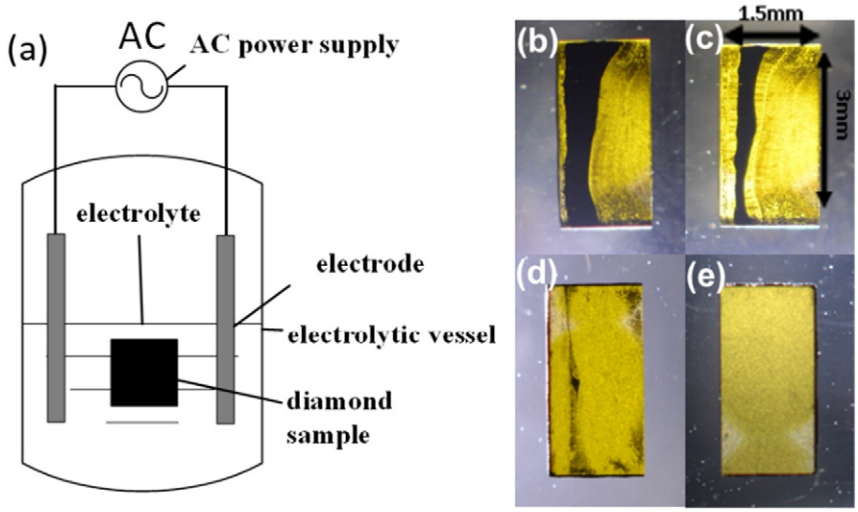

Fig. 8. Schematic of electrochemical etching system (a) and the color variation images of the sample during electrochemical etching (b)–(e): (b) More than half area changed. (c) The black area becomes less. (d) The black just remains a little. (e) The black has disappeared.

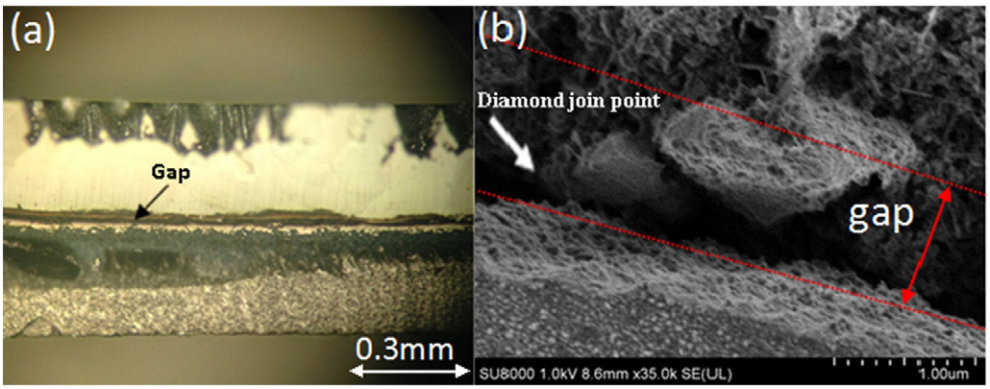

Fig. 9. (a) The cross section OM image after electrochemical etching process, (b) the magnified SEM image.

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