電気通信大学大学院電子工学専攻光エレクトロニクス講座
博士課程前期修士論文資料

Investigation of carrier dynamics in CVD diamond thin film with ultra-short pulse laser

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1. Introduction

Chemical vapor deposited (CVD) diamond is expected to be used for ultra-fast electric-optical devices. Because of its high breakdown threshold, high carrier saturated velocity and low dielectric constant properties; attractive features are achieved for high electrical field application, such as emitter of electromagnetic wave radiation (THz) [1]. For these applications, it is important to understand the carrier dynamics of CVD diamond. Specially, it has the grain boundary that is considered to affect largely on the dynamics.

Therefore, the purpose of this study is to clarify the details of carrier dynamics in the grain boundary of CVD diamond under high electric field. There are also diagnostics tools are developed, such as micro Raman system having an ultra fast laser pump-probe ability, and deep ultraviolet radiation with several other photoconductive monitors.

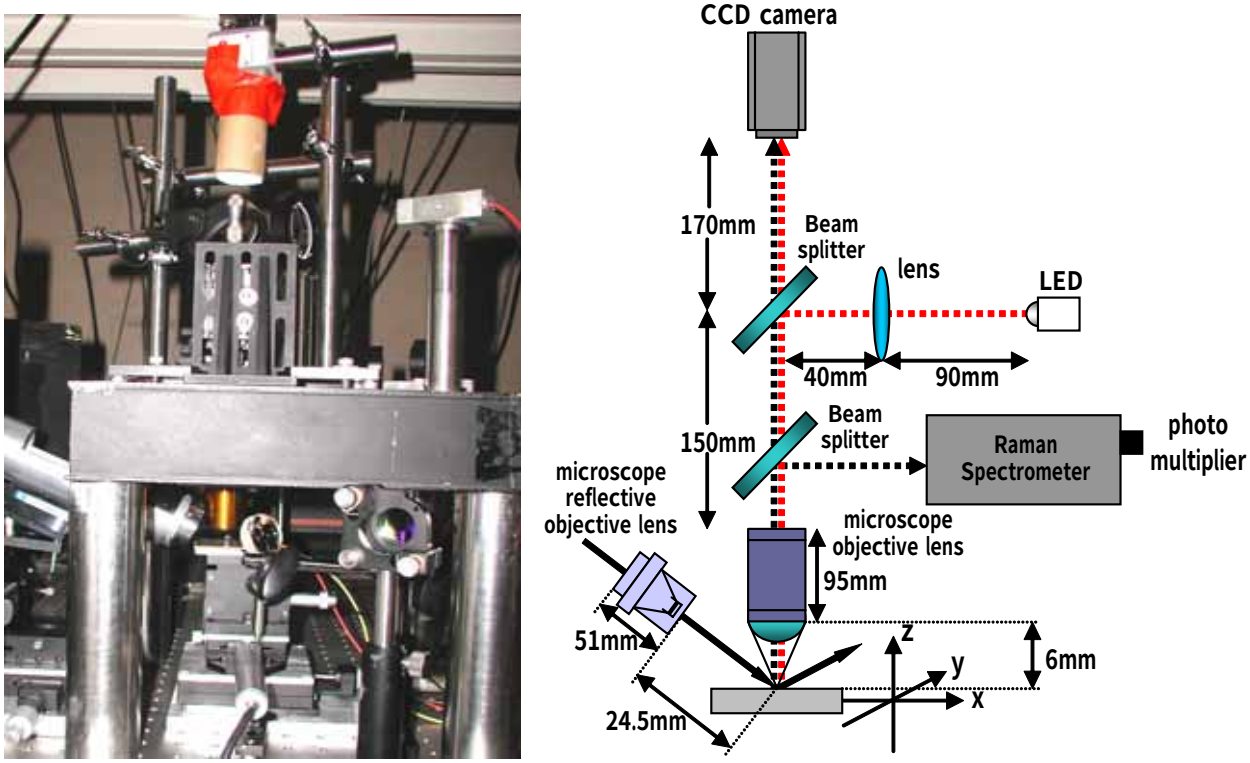


Fig. 1 Image and schematic of pump-probe micro Raman measurement system

2. Experimental setup

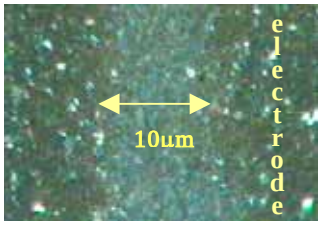
A. Micro Raman measurement system

For investigation of grain boundary, with ultra-fast temporal resolution, the micro Raman measurement system using various pump-probe lasers are constructed.

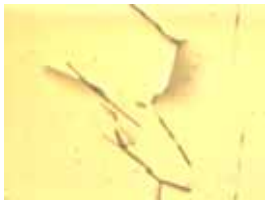
In this system, there are two set of micro-optics for UV pump and visible –IR probe beam. They have 2.6 μm spatial resolution for visible and IR with refractive objective and 4 μm x 10 μm resolution for UV with reflective objectives. This resolution is high enough to distinguish the difference between grain boundary and the grain bulk material for high mobility CVD diamond. The resolution of microscope objective is 2.6 μm and 4 μm x 10 μm resolution for reflective objective was achieved. In order to detect small signal of Raman spectrum, double monochromator as Raman spectrometer, photo multiplier and dual phase lock-in amplifier were used. The sizes of Raman spectrometer are 90 cm x 40 cm x 55 cm and its resolution and reproducibility are 1 cm^{-1} and 0.3 cm^{-1}, respectively. About 30 – 50 kV/cm of electric field was applied to the sample. Fig. 1 shows the image and schematic of pump-probe micro Raman measurement system.

Diamonds having different grain boundary features were investigated with this system. There are diamonds that have different size of grain (100, 5 μm) and single natural crystals. In addition, in order to change the grain boundary conditions, Li-ions also doped into CVD diamond with thermal diffusion method (LiO_2, T=500°C) for 4, 10, 20, 40 hours. Fig. 2 shows the CVD diamond samples that used in this experiment. In large grain size CVD diamond, 21 detection points on the sample with 8 μm distances, started from position near grain boundary that is clearly seen, were detected. Only 1 point, which is located between electrodes, was detected in 5 μm grain size CVD diamond film. The distance between the electrodes is 10 μm. There were 2 detection angles of Raman signal, as seen in Fig. 3. One, detected by microscope objective, has 70° angle from pump laser and another one having 115° angle was detected by lens.

(a)



(b)

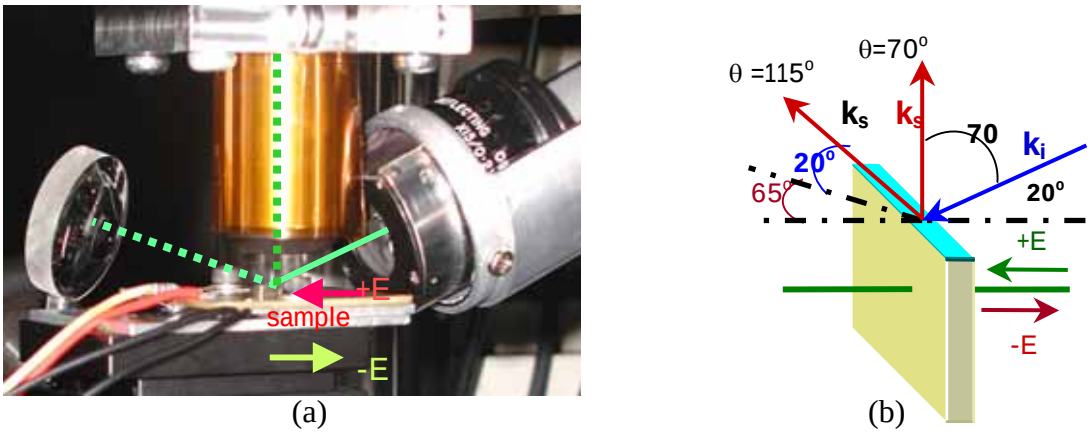


undoped diamond

40h–doped diamond

(c)

Fig. 2 Diamond samples (a) large grain size of CVD diamond (100 μm grain size), (b) small grain size of CVD diamond (5 μm grain size), (c) undoped and 40 hours Li-doped CVD diamond

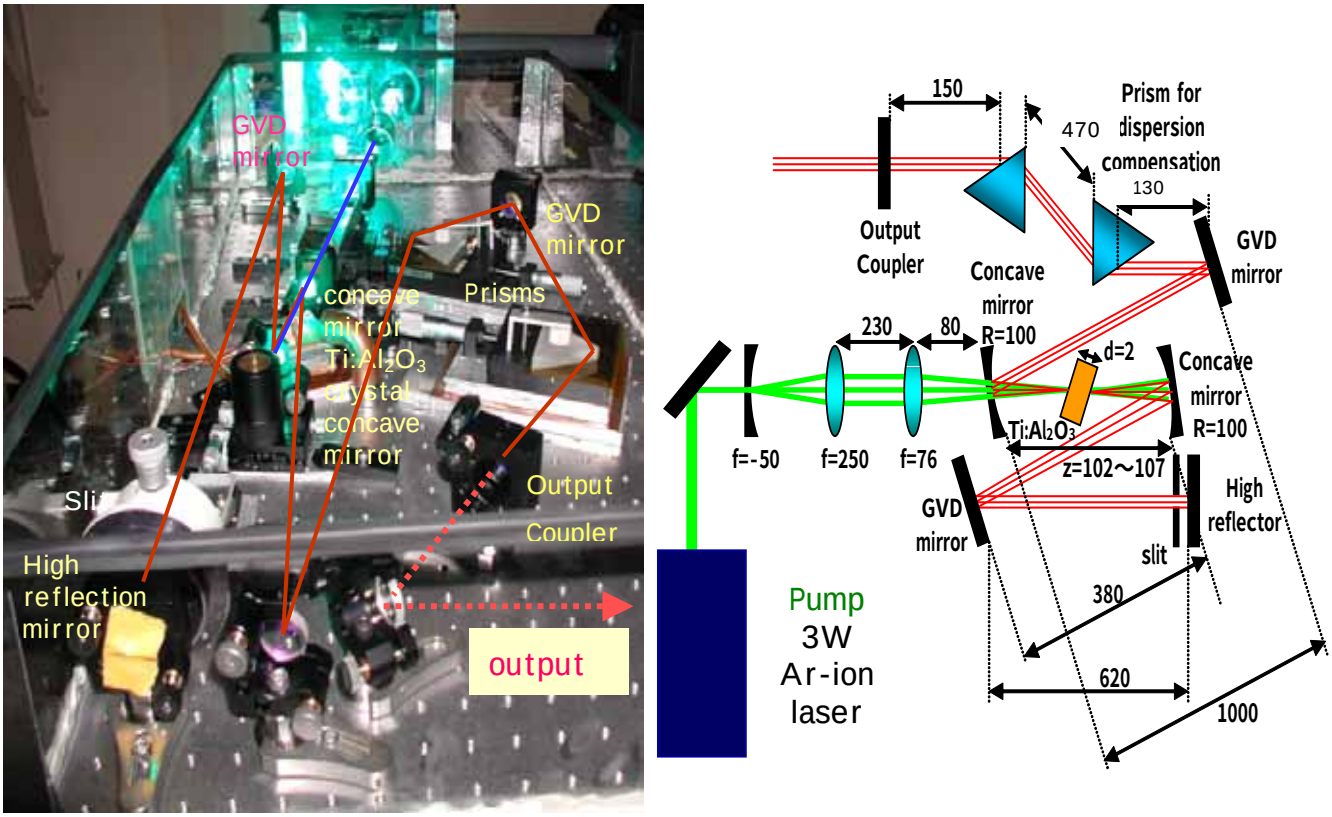


(a) (b)

Fig. 3 The image (a) and schematic (b) of detection angle of Raman signal

B. Ultra fast pulse laser

Ultra-fast Ti-Sapphire laser system was also been set up. Fig. 4 is ultra fast system image and its schematic. Argon-ion laser with 2-3 W power as pump laser and 2 mm of Ti-Sapphire crystal were used.



(a) (b)

Fig.4 The image (a) and schematic feature (b) of ultra fast Ti-Sapphire laser system

3. Experiment and Result

The typical Raman spectrum of single crystal natural diamond without electric field located at 1332 cm^{-1} wave number. The Full Width Half Maximum of this spectrum is 4.5 cm^{-1}. In natural single crystal diamond, we applied 2 directions of electrical field, positive

direction that has same direction with pump laser and negative field that has the opposite direction. Fig. 5a-d is the shifted of Raman peak due to applied electrical field. If we assumed 0 position is the position without electric field condition and red bars are errors due to spectrometer reproducibility, we made the schematic result of Fig. 5, as seen in Fig. 6.

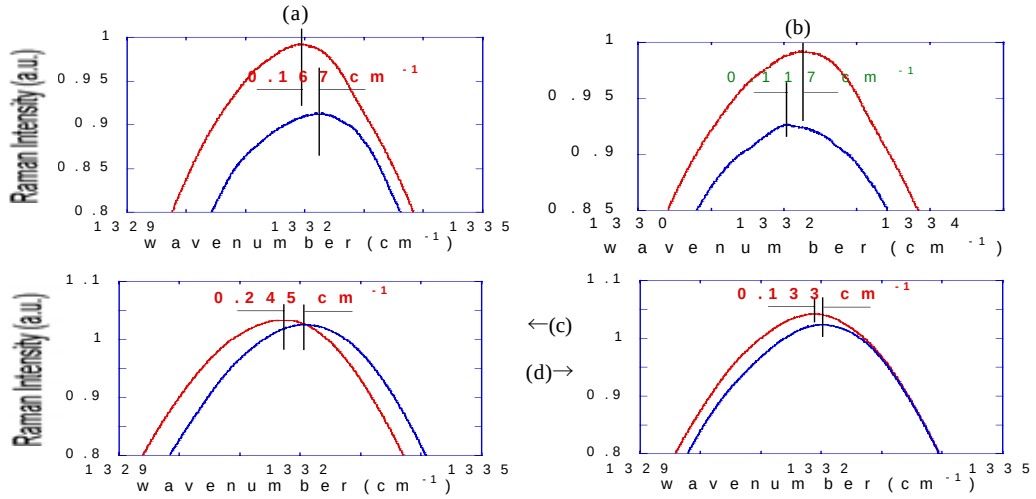


Fig. 5 Comparison of Raman spectrum with (red) and without (blue) electrical field in natural diamond sample from 70^{o} angle detection with +E (a), with –E (b), from 115^{o} angle detection with +E (c), with –E (d)

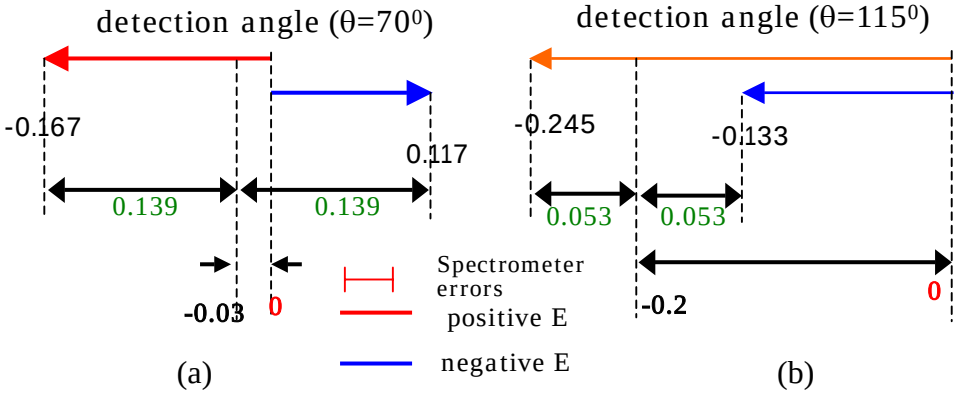
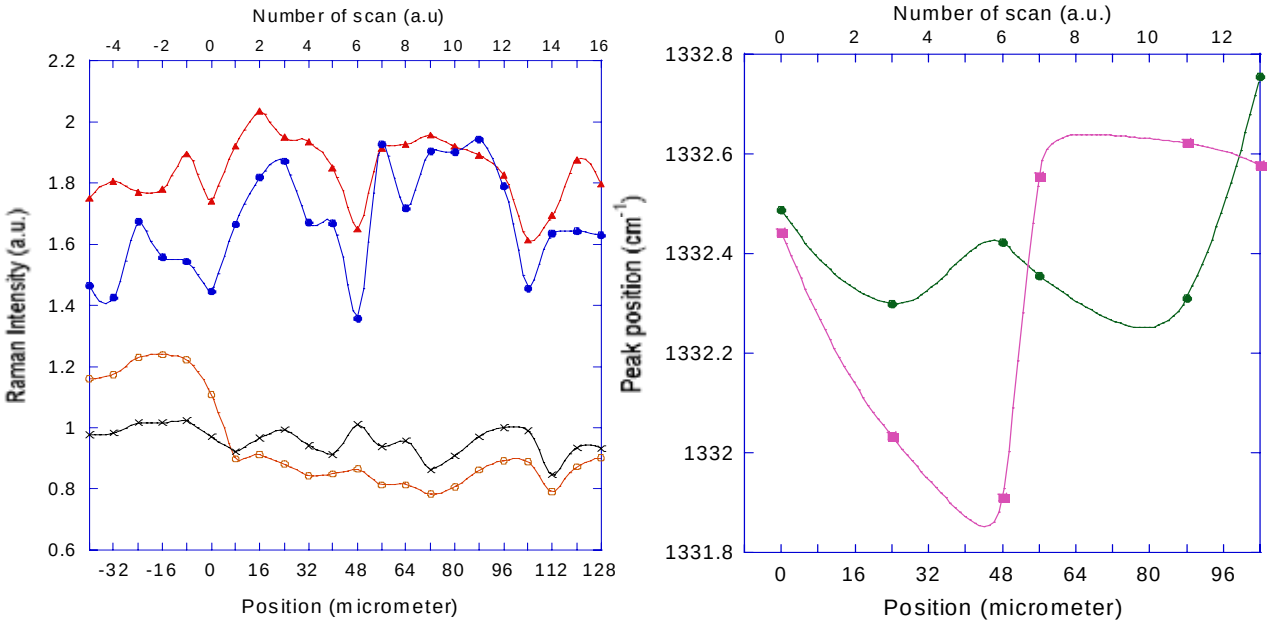


Fig. 6 Schematic result of spectrum shifted in natural diamond with +E (r) and –E (b) from 70^{o} (a) and 115^{o} (b) detection angle

According to Fig. 5 and 6, two types of origin for shifting the Raman peak were observed with applied electrical field. One has E-field directional dependence and the other only has field strength dependence. The possible explanations to analyze these shifted are the interaction between the carriers and phonon induce phonon shift and the stress that is induced by applied electrical field.

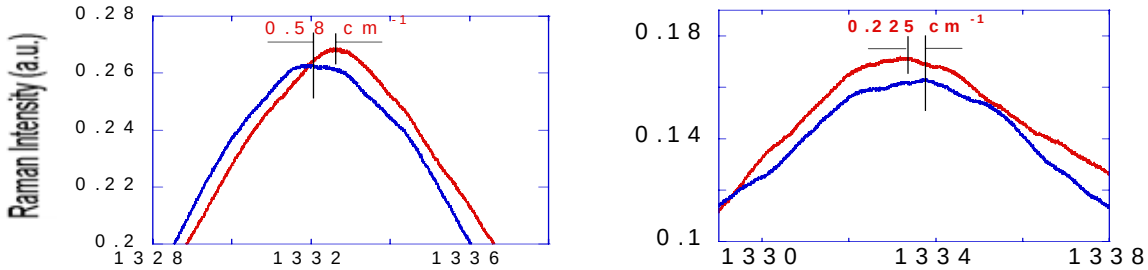
Generally, Raman shift near the grain boundary are considered due to the residual stress changed in the polycrystalline crystals [2], also seen in Fig. 7b in without electrical field condition. Effect of electrical field was also observed in CVD diamond samples, as seen in Fig 7 and 8. This measurement data (Fig. 7a) shows the grain boundary at position 0 has smaller peak intensity and it is also observed at position 48 μm and 104 μm. We assumed that these positions are also grain boundary areas. Therefore, the grains having 48 μm and

56 μm were detected. Full Raman spectrum at specific positions (Fig. 7b) shows that Raman peak position near grain boundary at position 48 μm changed by applied electrical field. To clarify the physical meaning of this effect, need farther investigation such as UV pump-probe experiment or direct measurements of carriers.



(a) (b)

Fig. 7 (a) Scanning Raman peak measurement of large grain CVD diamond sample with 8 μm distance (b) Raman peak position with (green) and without (pink) E from 70° detection angle



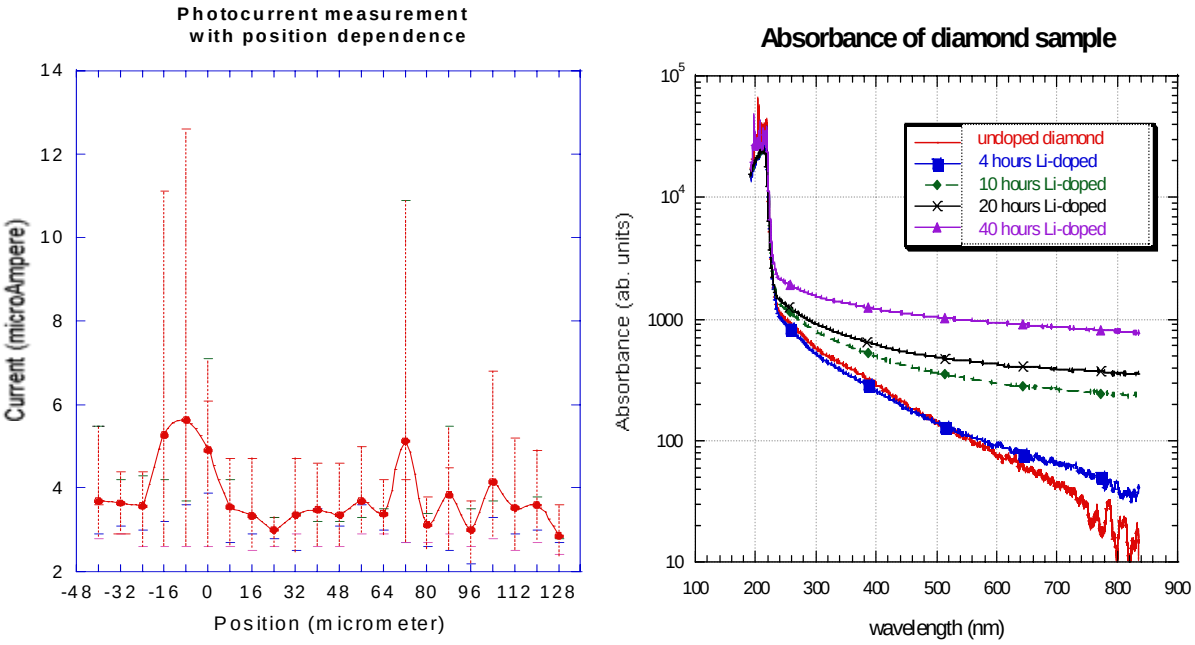
(a) (b)

Fig. 7 Raman peak position of small grain CVD diamond sample with (red) and without (blue) E from 70° (a) and 115° (b) detection angle

In addition, photocurrent experiment for micro spot illumination of 450 nm light at different positions is shown in Fig. 8a. This signal is proportional to the carrier density and mobility. According to Yoneda, et.al. [3, 4], lifetime and mobility are smaller near grain boundary. If we assumed E is uniform, so the increasing of photocurrent at grain boundary may be contributed by generation efficiency

Li-doped samples (Fig. 8b) have another evidence for carrier mobility and energy change of the grain boundary. From microscopic view of doped samples, the Li doped density is maximized at the grain boundary. With help of previous experiments about lifetime feature in the grain [3, 4], this result denoted carrier generation efficiency under the

nominal band gap photon increased with Li-doping. Therefore, band edge energy structure will be changed.



(a) (b)

Fig. 8 (a) Photocurrent measurement of large CVD diamond sample at different positions (b) Absorption spectrum of Li doped sample

In other hand, 30 mW ultra fast Ti-Sapphire with 19 ns (530 MHz) could be achieved by 2 W pump power. This smaller power might be caused by cavity losses, mode mismatching position inside the crystal, losses in prisms, air disturbance and vibration. In order to have stable and higher output power, the using of Brewster angle prisms, instead of 60^{o} apex angle, might have an effect. Reducing air disturbance by covering the laser is also suggested.

4. Conclusions

New types of shifts were observed under electrical field; E-field directional dependence that connects to carriers and E-field strength dependence that induced stress. Raman shift is significant near grain boundary in CVD diamond by applied electrical field. To clarify the physical meaning of this, investigation such as UV pump-probe experiment or direct measurements of carrier is needed. Li doping results denoted carrier generation efficiency change. It is considered that the energy band structure can be controlled selectively near the grain boundary.

5. References

[1] H.Yoneda et. al., Appl. Opt., 40-36, 6733 (2001)
[2] M. C. Rossi, Appl. Phys. Lett. 73-9 (1998)
[3] H. Yoneda et.al., Appl. Phys. Let. 77, 10 (2000)
[4] H. Yoneda et.al., J. Appl. Phys. 83, 3 (1998)