Ultrafast ablation dynamics in fused silica with a white light beam probe

Ping-Han Wu,¹ Xuan-Yu Yu,² Chung-Wei Cheng,¹ Che-Hao Liao,³ Shih-Wei Feng,⁴ and Hsiang-Chen Wang¹,²,*

¹ITRI South, Industrial Technology Research Institute, No. 8, Gongyan Rd., Liujia District, Tainan County 73445, Taiwan
²Graduate Institute of Opto-Mechatronics, National Chung Cheng University, 168, University Rd., Min-Hsiung, Chi-Yi County 62102, Taiwan
³Institute of Photonics and Optoelectronics, National Taiwan University, 1, Roosevelt Rd., Section 4, Taipei 10617, Taiwan
⁴Department of Applied Physics, National University of Kaohsiung, 700, Kaohsiung University Rd., Nanzih District, Kaohsiung 81148, Taiwan

*hcwang@ccu.edu.tw

Abstract: This study demonstrates a non-degenerate pump-probe spectroscopy with a white light beam probe based on a regenerative, amplified, mode-locked, Ti:sapphire laser. This white light beam probe is produced by supercontinuum generation of sapphire crystal after ultra-short pulse excitation. To implement the pump-probe experimental operation, the ablation dynamics with and without fresh spot measurements in fused silica samples are demonstrated. Combining the time-resolved differential reflection profiles in the white light range and X-ray photoelectron spectroscopy spectra of fused silica, the following ablation dynamics processes can be observed: Without fresh spot measurements, once carriers are excited, first, the three absorption bands of the intrinsic defect sites are observed within 750 fs. Then, a fast recovery is observed. This recovery comes from defect-trapped carriers excited to conduction bands through hot-carrier-phonon interactions. In the final step, a rapidly rising signal is observed after 800 fs. This signal rise comes from the creation of free-electron plasma, the density of which increases with increasing excitation energy accumulation. With fresh spot measurements, time delay of carrier dynamics among the three bands can be identified clearly within 750 fs. The intrinsic defect sites of fused silica play the key role during the ultrafast laser ablation process.

© 2011 Optical Society of America

OCIS codes: (140.3440) Laser-induced breakdown ; (320.7130) Ultrafast processes in condensed matter, including semiconductors; (320.7150) Ultrafast spectroscopy.

References and links

1. Introduction

Over the past decade significant progress on femtosecond laser ablation has been made for higher accuracy and shorter process time. Femtosecond laser processing in state of the art machining on metal, semiconductor, transparent, and organic materials has high quality processing that traditional nanosecond laser processing cannot match. For traditional laser processing on hard and brittle materials, the fractures of material extend in the direction of the crystal line rather than the direction of laser processing. Femtosecond laser processing overcomes this problem, and it also increases aspect the ratio of laser drilling. Femtosecond laser induced nano-periodic surface structure introduces more novel applications to the machining industry [1]. Guo et al. developed the creation of colored metals using the femtosecond laser processing technique that produces nano- or micro-structures with pits, balls, and rope sharply on metal surfaces. This metal colorization technique will ultimately allow people to control the optical properties of metals from UV to terahertz [2]. Shieh et al. demonstrated that amorphous silicon was crystallized by femtosecond laser annealing using a near-infrared ultrafast laser system. The intense ultrashort laser pulses lead to efficient nonlinear photoenergy absorption and the generation of very dense photoexcited plasma in irradiated materials, enabling nonlinear melting of transparent materials on silicon [3]. Burmester et al. reported a new cleaning method for antique metallic artworks with temperature-sensitive surfaces using femtosecond laser technology to avoid damage or discoloring of the original surface [4]. Wagner et al. showed an advanced femtosecond laser mask repair tool that utilizes DUV optics which allow ~100 nm mask features to be imaged. The laser beam is focused on a round, Gaussian spot. This Gaussian spot is scanned over the defect, thus allowing arbitrarily- shaped repairs to be performed with a spatial resolution of ~100 nm [5]. From the above examples it can be seen that ultrafast laser processing can be very broadly applied in industry. The study of ultrafast ablation dynamics is important for accurate machining in the nm scale.

The pump-probe techniques are commonly used to understand the different processes during ultrafast laser machining. Generally, laser ablation in materials is described in terms of three major processes: (i) multiphoton ionization (MPI) and/or tunneling causing the excitation of electrons to the conduction band, (ii) electron-electron collisional ionization (avalanche process) due to Joule heating, and (iii) plasma energy transfer to the lattice [6]. Through the pump-probe study, the time periods of these three major processes can be measured and the transient mechanism of femtosecond laser ablation can be understood. For traditional pump-probe measurement, the excitation beam is the fundamental wavelength and the probe beam is either the same or the second-harmonics wavelength. In this kind of measurement, the explanations for time-resolved transmission and reflection changes are the formation of free-electron plasma within 1 ps and rapid structural damage on the order of a few picoseconds [7–9]. As indicated above, for transparent materials, the changes in the measurements of the signals are shown to not be entirely functions of the photon energy of the probe beam due to these pump and probe photon energies being smaller than the bandgap energies of the materials. Those signals coming from the changes of surface topography are different mechanisms than traditional carrier dynamics (carrier relaxation, band filling etc.). This approach seems not very intuitive for studying the basically physical origins of femtosecond laser processes [10]. Recently, Mermillod-Blondin et al. reported the dynamics of femtosecond-laser-induced voidlike structures in fused silica by using time-resolved phase contrast microscopy [11]. The imaging observations allow the extraction of the transition relative refractive index change with respect to the background when the laser pulse excited the sample. But this method does not directly show carrier dynamics (electron-phonon collisions, electron-vibrational relaxation) during femtosecond laser processes. Usually in femtosecond laser processes in the infrared energy range, first the blue light of scattering, then the white light, can be seen. This process is considered to be caused by nonlinear optical phenomena that include second harmonic generation and supercontinuum generation (SCG) etc. The purpose of this study is to clarify what this process is, through measurement with an 800 nm pump and a white light beam probe.

This paper reports on the study of ablation dynamics in fused silica with a white light beam probe. An objective lens (10x, numerical aperture 0.26, M Plan Apo NIR, Mitutoyo) and focal lens with a 10 cm focal length are used to find the parameters of femtosecond laser processes that include the laser induced periodic surface structure (LIPSS) and material damage. In order to make the ultrafast optical measurements with a pump and white-light-probe system, the most suitable bandwidth and most stable spectral profile of SCG were determined by using different nonlinear optical crystals (materials) and focal-length lenses. Finally, a rotator stage is used to study the ultrafast ablation dynamics with and without fresh spot measurements. Comparison between the pump-probe measurement results and the X-ray photoelectron spectroscopy (XPS) measurements results reveal that the material damage induced by ultrafast laser processes first come from trapped carriers in the intrinsic defect sites of the materials.

This paper is organized as follows: In Section 2, for LIPSS and material damage, the parameters of femtosecond laser processes and scanning electron microscope (SEM) images of surface morphology on fused silica are presented. The spectra of SCG with different crystals and the implementation of the non-degenerate pump-probe experiment are reported in Section 3. Section 4, the discusses all the spectroscopy, and XPS results are given. Finally, the conclusions are drawn in Section 5.

2. Parameters and SEM images of femtosecond laser processes in fused silica

Ablation thresholds are core parameters for the durability of optical components and laser safety equipment. Moreover, the determination of ablation rates is of key importance for femtosecond laser processes applications. A threshold energy fluence was found as the characteristic physics value for ablation, which is constant for a given set of experimental conditions (pulse number, repetition rate, pulse duration, focal length of lens). For pulse number dependence, damage fluence is in inverse proportion to pulse number below several
pulses. Precatastrophic changes in the absorption behavior during multiple-shot irradiation are related to the laser induced generation of defects [12]. The damage fluence will be constant when the pulse number is sufficient to generate the saturation of defects. For repetition rate dependence, high repetition rate laser processing of materials leads to considerably lowered ablation thresholds accompanied by higher ablation rates. The explanation for this, is that heat accumulation caused by higher repetition rates was assumed to be mainly ablation behavior influencing effect, but in fact thermal material properties have to be considered [13]. For pulse duration dependence, in wide band-gap materials initial free electrons are provided by multi-photon ionization, which then are further heated by the remaining part of the ultra-short laser pulse leading to avalanche processes. As the laser pulse duration decreases, the multi-photon excitation becomes more dominant, which has important consequences for the damage threshold [13]. For spot-size dependence of the laser processes, the large area of those processes is an important issue in industrial applications, especially for increasing productivity. In general, the damage threshold decreases as the laser beam radius increases due to the increased probability of the laser beam hitting defects [14]. In order to select the most suitable laser power for conducting this pump-probe study, various laser pulse energies with two different kinds of lenses are used to irradiate fused silica samples. Figure 1 shows the dependence of the squared ablation diameter with the pulse energy that is depicted for two measurements by different focal-length lenses. A regenerative amplified modelocked Ti:sapphire laser (SPIT FIRE, Spectra-Physics) with a repetition rate of 1 kHz, a pulse duration of ~120 fs, a central wavelength of 800 nm, and a maximum pulse energy of ~3.5 mJ was used for the experiments. The sample was placed at a translation stage in the x- and y-directions under the control of a PC-based micro-positioning system for automatic laser ablation with various pulse energies on the different positions of the sample. The diameter of the ablation area was measured by a scanning electron microscope (SEM; JEOL, JSM-7001F). Commercially available fused silica served as the target. The blue and green points represent the experimental results for 1,000 laser shots with the 10 cm focal-length lens and 5 laser shots with the objective lens, respectively. The red lines represent fitting results obtained with equation for femtosecond laser ablation, as shown in Eq. (1).

![Figure 1: Squared ablation diameter as a function of the laser energy with two different lenses.](image)

The insert images are the SEM images of fused silica surfaces with the 10 cm focal-lens (c, e) and the objective lens (a, b, d) at various excitation energies.

\[ D^2 = 2\omega_0^2 \ln \left( \frac{F_0}{F_{th}} \right) \]  

(1)
For femtosecond laser ablation, many materials have a distinct power density threshold, and if the maximum fluence ($F_0$) exceeds the ablation threshold fluence ($F_{th}$), the fused silica is removed from an area with the diameter ($D$). The $\omega_0$ is the focus spot radius. The slope and x-axis intercept of these two plots allow calculation of the focus spot radius and ablation threshold fluence, respectively. For the 1,000-laser-shot condition, the equation is $y = -904.7 + 1,636.2x$. The focus spot radius and ablation threshold energy are 28.6 $\mu$m and 1.74 $\mu$J. For 5-laser-shot condition, the equation is $y = -157.2 + 85.7x$. The focus spot radius and ablation threshold energy are 6.5 $\mu$m and 6.26 $\mu$J. The ablation with the objective lens has the smaller spot radius than the one with the focal lens. But the ablation threshold energy will increase when the number of laser shots is decrease. When the laser energy is above and close to the ablation threshold energy, then periodic lines (a high spatial frequency LIPSS) on the fused silica surface can be found. Figure 2 shows magnified images of the inset images in Fig. 1. The SEM images (a) and (c) show the LIPSS surface under different laser ablation conditions. The direction of the lines is orthogonal to the polarization of the laser beam. When the laser energy is above the ablation threshold energy, damage is observed. However, the LIPSS can be found slightly at the bottom of hole (see image (d)). For images (b) and (e), the number of layers inside the hole increases with the number of laser shots.

3. Set-up of the non-degenerate pump-probe experiment and supercontinuum generation

The non-degenerate pump-probe experimental setup is shown in Fig. 3. Here, the Spit Fire laser is split into two beams with a beam-splitter (BS, 20/80 split ratio for transmission/reflection), one for the probe and the other for the pump. The laser in each beam passes through a half-wave ($\lambda/2$) plate of a certain rotation angle and a polarizer plate for the desired incident laser power. The pump-probe delay was controlled by a translation stage of 1.0 $\mu$m in step size. This step size corresponds to the time delay resolution of 6.6 fs. The temporal resolution of the pump-probe experiment is determined by the larger one of the delay resolution and the pulse width that is used. In this study, the pulse width of the pump and probe beams are about 170 fs and 210 fs respectively at the sample location with autocorrelator measurements (Spectra-Physics, PSCOUT HR). In the probe beam path, the first iris is used to control spot size for generating the white light probe beam stably, and then, in conjunction with the lens with specific focal length, the white light can be generated. The details of SCG will be discussed in the next section. The second iris is used to stop the unwanted blue and red light at the outer ring of the white light beam [15]. An aspherized
achromatic lens (Edmund Optics, A49-665), after the second iris, focuses the white light on the sample and corrects the axial color aberration. The color filter (Lambda Research Optics, SWP-750) after the aspherized achromatic lens is used to stop the fundamental laser energy. For reflection-type pump-probe measurements, the probe beam reflected from the sample has been guided to the spectrometer. The color filter (the same as above) and iris after the sample are used to stop the light scattering of the sample from the pump beam. After the sample, the probe signal is collected by a light guide and monitored with a CCD-mounted spectrometer (Ocean Optics, QE65000). In the pump-probe experiment, the probe power is quite low (but the spectrometer can detect it) and the pump power is fixed at 5 mW with 1,000 laser shots per measurement. The diameters of the pump and probe beams are 150 µm and 100 µm, respectively. That ensures the uniform pump illumination of the probe region. In order to check the laser-exposed position on the sample precisely, the sample was placed on a translation-rotation stage in the x-, y-, z-, and θ- directions combined with a visual system based on the CCD camera behind the sample.

For implementing the non-degenerate pump-probe measurements with a white light beam probe, the SCG of different materials at the location of the sapphire crystal in the Fig. 3 is studied. Table 1 shows the relative parameters of various materials. The threshold power means the threshold of the SCG with the 10 cm focal-length lens and 800 nm excitation wavelength. Figure 4 shows the SCG spectra of different materials after the color filter. The spectral broadening is proportional to each medium’s bandgap with the exception of the D2O and Ti:sapphire materials in this study. For D2O, the larger spectral broadening is found to be due to that material’s larger thickness. The larger spectral broadening also caused the lower stability of SCG spectra that can increase the noise distribution in pump-probe measurements. The main characteristic of the supercontinuum is that the spectral broadening is symmetric when the incident pulse energy is below and close to the threshold of self-focusing. The spectral broadening can reach several hundred nm when the incident pulse energy is above the threshold of self-focusing, but still below the damage threshold [16]. As the focus tightens, the SCG spectrum widens, but the spectral shape becomes less stable. This study demonstrates that for the non-degenerate pump and white light probe, a focus length between 10 cm and 13 is the most suitable for SCG.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Thickness (mm)</th>
<th>Threshold power (mW)</th>
<th>Eg (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D2O</td>
<td>10.0</td>
<td>1,000</td>
<td>7.5</td>
</tr>
<tr>
<td>fused silica</td>
<td>1.5</td>
<td>3.00</td>
<td>9.0</td>
</tr>
<tr>
<td>Ti:sapphire</td>
<td>5.0</td>
<td>4.00</td>
<td>5.6</td>
</tr>
<tr>
<td>sapphire</td>
<td>2.3</td>
<td>0.80</td>
<td>8.7</td>
</tr>
<tr>
<td>CaF2</td>
<td>2.2</td>
<td>0.98</td>
<td>10.2</td>
</tr>
</tbody>
</table>
4. Non-degenerate pump-probe experimental and XPS results

Figure 5(a) shows the differential reflection intensity distribution (ΔR/R) of the probe in the spectrum-delay time space when the pump central wavelength is 800 nm without the fresh spot measurements. Each measurement condition is 1,000 ms integral time (1,000 laser shots), 30 µm delay step (198 fs delay step), and below the ablation threshold probe on the same position of the fused silica. In order to eliminate the noise of measurement, Fig. 5(a) is an average result for thirty measurements with different exposure positions. Here, the color level represents the relative differential reflection intensity at various emission photon energies and various pump-probe time delays. The blue color and red color represent the negative and positive values of the differential reflection intensity, respectively. In Fig. 5(a), three signal bands can be found at 460 nm, 560 nm, and 630 nm. Previous studies, based on absorption spectrum measurement after femtosecond laser irradiation, determined that the defects of fused silica are the oxygen-deficient center, the peroxy radicals, and the nonbridging oxygen hole center (NBOHC), for which the absorption bands are 460 nm, 560 nm, and 630 nm, respectively [17–19]. To carefully examine the ablation dynamics process, in Fig. 5(b), the time-resolved differential reflection profiles at three spectral locations are plotted. All of the traces show consistent phenomena. In this figure, all three curves show fast decay times of around 250 fs, which is close to the temporal resolution of the system before the zero time delay, with the 460 nm curve having the deepest dip. Then the recovery of each trace is shown. At the 800 fs delay time, a fast rise of each trace is observed, and then a slower rise exists after this fast rise. In the reflective pump-probe measurement, it is well known that the negative component of each trace represents the absorption induced by some defects of fused silica and the recovery of each trace represents the carriers trapped by defects excited to the conduction band due to the hot-carrier-phonon interactions [20,21]. Meanwhile, the fast rise after the initial recovery of each trace represents the generation of free-electron plasma after laser excitation, which indicates the occurrence of laser ablation on the sample at the 800 fs delay time [7,8]. The trace at 630 nm has only small changes, indicating the NBOHC defects make only a small contribution to this condition. Such behaviors can be seen in Fig. 5(c), in which the probe spectra at several delay times are plotted. Here, it can be seen that the absorption of each trace occurs before 1,000 fs, then after 1,000 fs the ablation of the sample can be seen. The peak intensity of three bands in spectra increased with time, which represents the increasing generation of free-electron plasma on the sample with excitation energy accumulation. Comparing with three bands, the defects of the oxygen-deficient center dominate in these laser ablation processes, which can explain why the blue scattering of light can be seen in the early femtosecond IR laser irradiation.
In order to study the mechanism of the three bands’ generation from pump-probe measurement, high-resolution x-ray photoelectron spectroscopy (XPS, Kratos, Axis Ultra DLD) with Al Kα exciting the X-ray source ($h\nu = 1,486.7$ eV) at 15 kV and 450 W was utilized to determine the changes of binding structure of the fused silica sample before and after femtosecond laser irradiation. All binding energies were calibrated to C 1s at 285 eV, as the hydrocarbon content present in the sample. Standard curve fitting procedure was carried out for quantitative analysis. Convolution of Gaussian and Lorentzian functions with Shirley background was utilized. The quantitative analyses of the O 1s and Si 2p spectra of the fused silica were carried out using the X-ray photoelectron peak fitting program, XPSPEAK, version 4.1, created by Raymond Kwok’s group [22]. The XPS Si 2p spectra of the fused silica before laser irradiation are shown in Fig. 6(a). The full width at half maximum (FWHM) of the XPS Si 2p peak is 1.545 eV. A signal at 104.0 eV was attributed to Si$^{4+}$ which was bounded by four oxygen atoms [23]. Figure 6(b) shows the XPS Si 2p spectra of the fused silica after laser irradiation under 5 mW incident power and 10,000 laser pulses. The FWHM and peak position of the XPS Si 2p peak is 1.681 eV and 104.3 eV, respectively. The XPS Si 2p spectrum of the sample after laser irradiation does not contain only one binding structure. The black line represents the experimental data that can be deconvoluted into three components (peaks 0, 1, and 2). The three dashed-line arrows represent the possible binding structures that exist after laser irradiation. From the XPS Si 2p spectra, it can be seen that the sub-stoichiometric structure of SiOx ($0<x<2$) and suboxide Si$^{1+}$, Si$^{2+}$, and Si$^{3+}$ should exist on fused silica after laser irradiation. For the XPS O 1s spectra (not shown), the peak position and FWHM did not change after laser irradiation, which means that no oxygen ions were formed.
Many mechanisms have been proposed to account for the generation of laser-induced defects. The most commonly reported three possible scenarios are [17]:

\[
\begin{align*}
\text{Si} - \text{Si} & \rightarrow \text{Si}^+ + e^- \quad (2) \\
\text{Si} - \text{O} - \text{H} & \rightarrow \text{Si} - \text{O} + \cdot \text{H} \quad (3) \\
\text{Si} - \text{O} + \text{Si} & \rightarrow \text{Si} - \text{O} + \cdot \text{Si} \quad (4)
\end{align*}
\]

Equation (2) represents the oxygen-deficient center in fused silica binding structures after laser irradiation corresponding to blue band luminescence at 460 nm. Equations (3) and (4) represent the nonbridging oxygen hole center generation corresponding to red band luminescence at 630 nm. Equation (3) also shows the binding between oxygen and hydrogen to form the green band luminescence with complex energy transfer and electron transition. From the XPS results after laser irradiation, for the Si 2p spectra, the suboxide Si\(^{1+}\), Si\(^{2+}\), and Si\(^{3+}\) can be measured, and those measurements indicate that the oxygen-deficient center dominates the defect formation after femtosecond IR irradiation. But the XPS O 1s spectra had no distinct changes, which indicates that the nonbridging oxygen hole center made little contribution. Based on the above discussion, a clear scenario to explain the three bands’ generation and the relative response strengths of these bands from the pump-probe measurements has been demonstrated. In addition to the discussion of changes in the binding structures after femtosecond laser irradiation, the consistent results between transient pump-probe measurement and steady state XPS measurement indicate that the transient optical measurement cannot be implemented in the excitation energy accumulation condition.

In order to be clear about the ablation dynamics of fused silica, the pump-probe measurement was implemented with the fresh spot measurements. A sample was held on the translation-rotation stage in the x-, y-, z-, and \(\theta\) directions under the control of a PC-based micro-positioning system for automatic pump-probe measurement with various delay times on the different \(\theta\) positions of the sample. Figure 7(a) shows the differential reflection intensity distribution (\(\Delta R/R\)) of the probe in the spectrum-delay time space when the pump central wavelength is 800 nm with the fresh spot measurements. Each measurement condition is 1,000 ms integral time (1,000 laser shots), 30 \(\mu\)m delay step (198 fs delay step), and below ablation threshold probe at different positions of fused silica. In order to eliminate the noise of measurement, Fig. 7(a) is an average result for thirty measurements with different exposure positions. Here, the color level represents the relative differential reflection photon energies and various pump-probe time delays. The red color and blue color represent the positive and negative values of the differential reflection intensity, respectively. In this figure, the three bands at 460, 560, and 630 nm also can be seen. Compared with Fig. 5(a), in Fig. 7(a) all three bands have negative values of the
differential reflection intensity for their entire lengths (it is not clear that the yellow and orange above 2,000 fs delay time at 460 nm are not noise) and all three bands appear after a longer delay time. Negative values represent the absorption processes induced by some defects of fused silica. The free-electron plasma generation on the sample was not found all during the measurement with a fresh spot condition, which means the ablation processes of fused silica cannot have occurred. In Fig. 7(b), in order to carefully examine the difference in delay time among three bands, the time-resolved differential reflection profiles of three are plotted. The carrier dynamics of decay and recovery of each trace show the same mechanisms as in Fig. 5(b). In Fig. 7(b) it is seen that the transient absorption at 460 nm, induced by intrinsic defect sites such as the oxygen-deficient centers, occurred first, implying that an abundance of oxygen-deficient centers exist in fused silica. After the oxygen-deficient center defects become saturated with trapped carriers, the transient absorption at 560 nm, induced by the peroxy radicals, occurred at 500 fs delay time. Finally, the transient absorption at 630 nm induced by the NBOHC defects occurred after a 700 fs delay time. After the absorption, these three traces show the nonlinear recovery processes, each of which has two steps. The exact recovery times were calculated by fitting the differential reflection intensity distribution to a logarithmic scale. The first recovery step is from 4.71 ps to 7.63 ps, with three probe photon energies corresponding to the carriers trapped by defects excited to the conduction band with carrier-carrier scattering. The second recovery step is from 2.43 ps to 5.56 ps, with three probe photon energies corresponding to the carriers trapped by defects excited to the conduction band with hot-carrier-phonon interactions [24]. Such behaviors can be seen in Fig. 7(c), in which the probe spectra at several delay times are plotted.

Fig. 7. (a) Differential reflection intensity distribution of the probe in the spectrum delay time space when the pump central wavelength is 800 nm with the fresh spot measurements. (b, c) is cross sections of (a) at three spectral locations and several time delays.

5. Conclusions

In conclusion, the study of ultrafast carrier and ablation dynamics in fused silica based on a non-degenerate pump-probe spectroscopy with white light beam probe has been achieved. In
the pump-probe results, three bands can be identified corresponding to the absorptions of the carriers trapped by defects with the oxygen-deficient centers, the peroxy radicals, and the NBOHC, respectively. When the incident pump power is greater than the ablation threshold of fused silica, the pump-probe traces increase rapidly with the generation of free-electron plasma. Without the fresh spot measurements, all three bands generated simultaneously, and their signals changed from negative to positive values with time, corresponding to the processes changed from carrier dynamics to ablation dynamics. With the fresh spot measurements, the ablation processes cannot occur due to the incident power being less than the ablation threshold of fused silica. A delay among the three bands is seen, which indicates that an abundance of oxygen-deficient centers exist in fused silica. This explains the color changes during infrared fs laser ablation processes in fused silica, that first the blue light of scattering, followed by white light, come from carrier absorption by some intrinsic defect sites in fused silica.

**Acknowledgements**

This research was supported by the National Science Council, The Republic of China, under grant NSC 99-2221-E-194-020 and the Ministry of the Economic Affairs (MOEA), Taiwan, R.O.C. for performing this project.