Formation and photobleaching of 5 eV bands in ion-implanted SiO_2:Ge and SiO_2 glasses for photosensitive materials

LETTER TO THE EDITOR

Formation and photobleaching of 5 eV bands in ion-implanted SiO$_2$:Ge and SiO$_2$ glasses for photosensitive materials

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Abstract. Formation and photobleaching of optical absorption bands in the 5 eV region were examined in proton-implanted 5GeO–95SiO$_2$ glasses and SiO$_2$ glasses implanted with Si, Ge, B or P ions. A conspicuous increase in the intensity of the 5 eV band, which is attributed to oxygen vacancies, was seen in both substrates after implantation. However, a distinct difference was observed in bleaching with 5 eV light between the H-implanted SiO$_2$:Ge glasses and the implanted SiO$_2$ glasses. In the former the 5 eV band was bleached and intense absorptions above 5 eV emerged, whereas in the latter bleaching occurred in the whole UV region. This distinct bleaching nature provides implanted glasses with the possibility of modification of refractive index by UV illumination.

Ion implantation into glasses attracts much interest as a fabrication technique of glasses with novel photonic functions such as nonlinear optical properties and wavelength conversion of light (Townsend 1987, 1992). Enormous concentrations of point defects in glasses are produced by implantation and information on chemical interaction of implanted ions with substrate structures can be obtained through the characterization of these defects (Hosono and Matsunami 1993, Hosono and Imagawa 1994). Although these defects degrade properties of substrates in many cases, they can be the primary source of new functionality in some cases. Build-up of Bragg reflection grating effects (Hill gratings) (Hill *et al* 1978, Meltz *et al* 1989) and second-harmonic generation (SHG) (Osterberg and Margulis 1986) are novel photonic properties of Ge-doped SiO$_2$ glasses and various applications are being examined now.

Formation and photobleaching of optical absorptions peaking at ~5 eV (5 eV band) are now known to be a primary origin of both photoeffects (Vogel *et al* 1991, Tsai and Griscom 1991). The formation of refractive index gratings (leading to Hill gratings) and the periodic array of electrical dipoles (to SHG) are induced by spatially periodic bleaching of the 5 eV band due to oxygen vacancies with interference light. The refractive index change occurs via the Kromers–Kronig relation of complex refractive index ($\hat{n} = n - ik$, where n is the refractive index and k the extinction coefficient) (Hand and Russel 1990) and the dipoles are formed by photochemical conversion of the neutral oxygen vacancy coordinated by two Ge^{4+} ions into Ge-related charged defects. Enhancement of the efficiency of these photoeffects is an important issue to realize down-sizing toward optical integrated circuits.
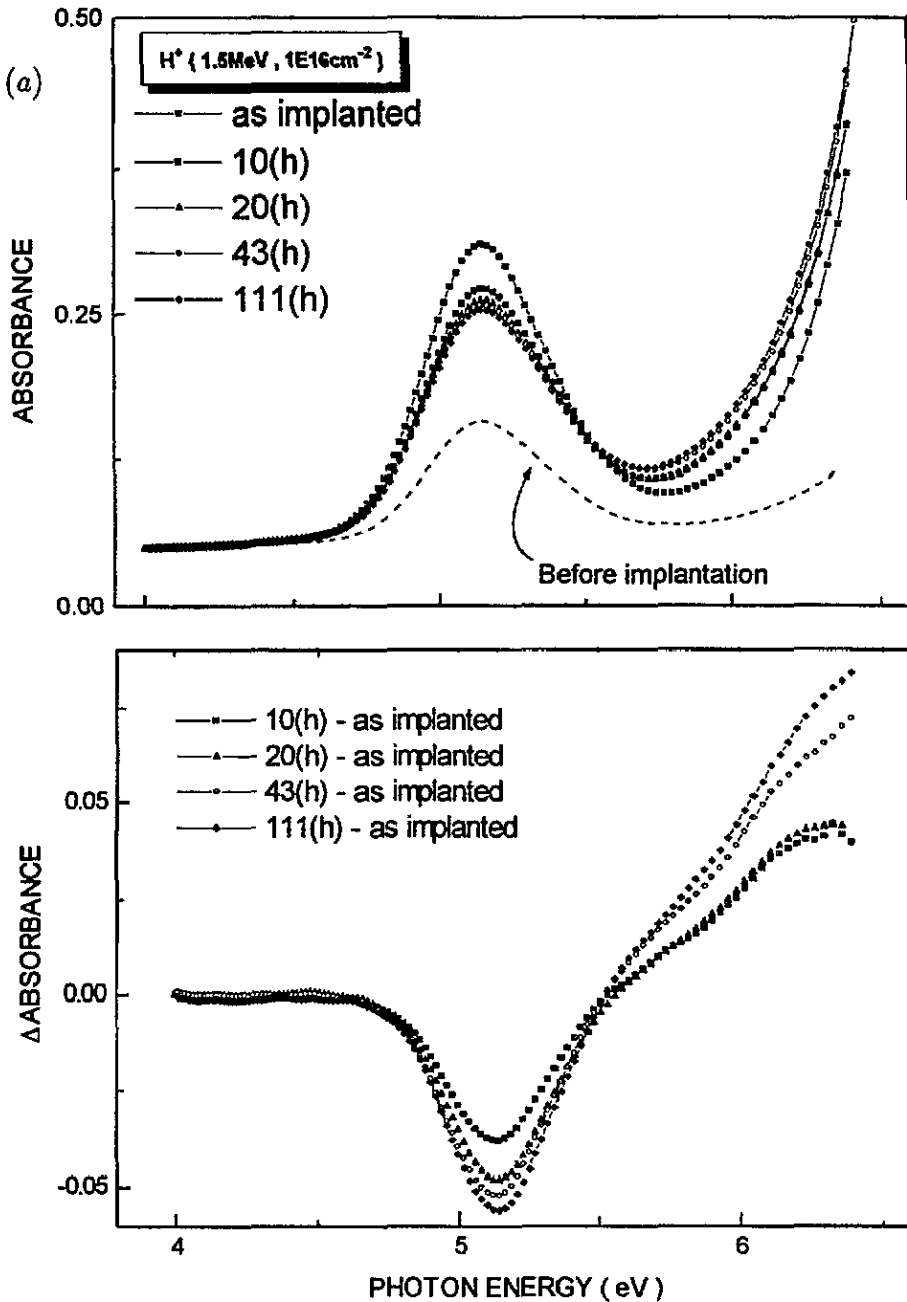
Figure 1. Changes in the optical absorption spectra of H^+-implanted $5GeO_2$–$95SiO_2$ glass with 5 eV light illumination. The lower panel shows the effectively changed spectrum with duration of illumination. (a) H^+ 1×10^{16} cm^{-2}; (b) 1×10^{17} cm^{-2}.

It is anticipated that ion implantation, which fits well with microelectronics, is a promising tool to achieve this goal because quite a large degree of formation and photochanges of the 5 eV band is expected to occur. Recalling that defects responsible for the photoeffects
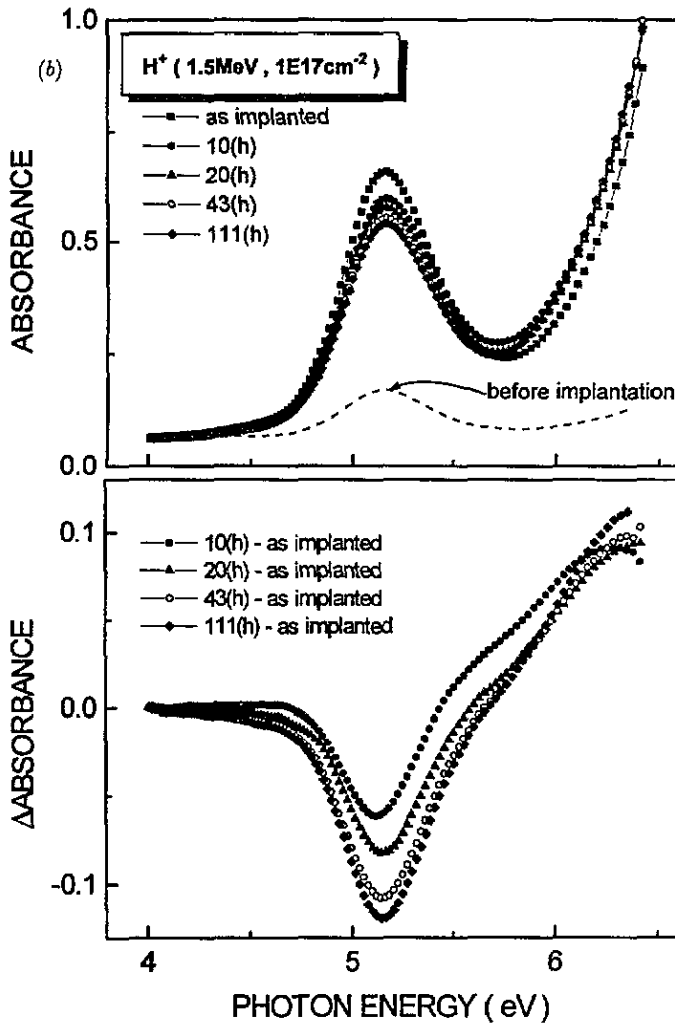
Figure 1. (Continued)

are oxygen-deficient-type defects (ODCs) (more specifically neutral oxygen monovacancies) (Hosono *et al* 1992), we expect a conspicuous concentration enhancement of these defects in Ge-doped SiO_2 glasses by H^+ implantation as a consequence of chemical interactions of implanted H^+ and substrate structures. It has already been reported (Hosono and Matsunami 1993, Hosono and Imagawa 1994) that the predominant defects in SiO_2 glasses implanted with ions with electropositive nature are two types of ODC (Imai *et al* 1988), an Si–Si homobond (Hosono *et al* 1991) and a neutral oxygen vacancy (Arnold 1973). In this work we examine the formation and photobleaching of the 5 eV bands for H^+-implanted SiO_2:Ge glasses and SiO_2 glasses implanted with ions with electropositive nature as a first step of application of implanted glasses to a photorefractive material.

Substrates used are SiO_2 glasses and $5GeO_2$–$95SiO_2$ (SiO_2:Ge) glasses prepared by the vapour axial deposition technique. Silica glass plates 0.5 mm thick) and SiO_2:Ge glass plates (0.3 mm) were implanted with 160 keV Si^+, Ge^+, B^+ or P^+ (all are implants with electropositive nature) and 1.5 MeV H^+, respectively. Substrates were wrapped with Al

foils except for implanted portions to avoid charging during implantation. Light illumination of implanted glasses with 5 eV light was carried out at room temperature using a 500 W Hg/Xe lamp through a band pass filter (centre wavelength, 248 nm; width, 5 nm). The light intensity measured by a thermopile was $\sim$8 mW cm^{-2} (corresponding to photon flux of $\sim 1 \times 10^{16}$ cm^{-2} s^{-1}). Changes in optical absorption in UV–visible regions were measured by a conventional spectrophotometer. Formation of paramagnetic defects and their concentrations were determined by measurements of EPR spectra.

Figure 1 shows changes in UV absorptions of SiO_2:Ge glasses by implantation of H$^+$ ions and UV illumination. Figure 2 exemplifies changes in implanted SiO_2 glasses with implantation and UV illumination. In SiO_2:Ge glasses absorption bands centred at $\sim$5 eV were seen in the as-prepared state and their intensities increased conspicuously on H$^+$ implantation, by a factor of $\sim$2.5 for a fluence of 1×10^{16} cm^{-2} or by $\sim$7 for 1×10^{17} cm^{-2}. An absorption band peaking at 5.1 eV was bleached and intense absorptions at >5 eV emerged with illumination with 5 eV light. In the case of SiO_2 glasses (figure 2) implantation induces absorptions peaking at $\sim$5 eV having a tail extended to VUV regions s in H$^+$-implanted SiO_2:Ge glasses. However, the photobleaching behaviour of these absorptions differed from that in H$^+$-implanted SiO_2:Ge glasses, i.e., the absorptions induced by implantation were bleached over the whole UV range. No changes in optical absorption spectra were perceived in SiO_2:Ge or SiO_2 glasses after implantation of He$^+$.

Si 3E16(160 keV)

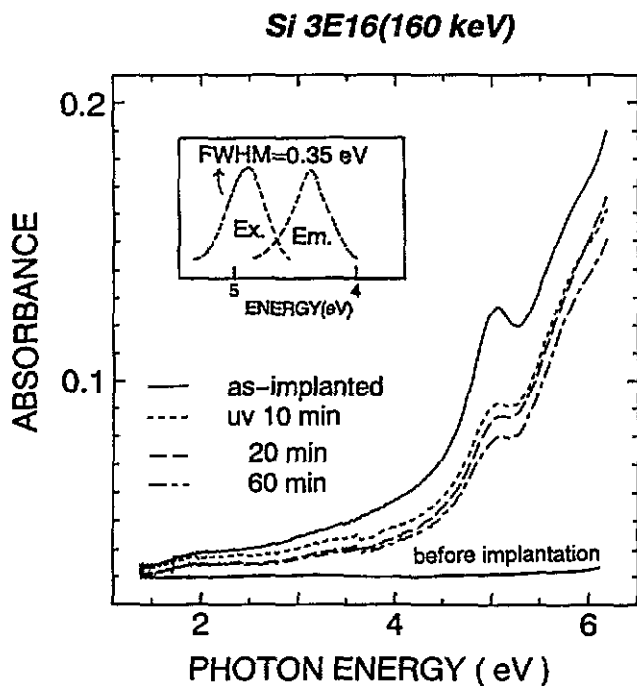
Figure 2. Changes in the optical absorption spectra of Si$^+$-implanted SiO_2 glass with 5 eV light illumination. Similar changes were observed also for SiO_2 glasses implanted with other ions examined. Note that absorption decreases over the whole UV region with illumination. The inset shows photoluminescence and photoexcitation spectra.

An increase in concentrations of Ge E' centres ($\cdot$ Ge $\equiv$: $\cdot$ and – denote an unpaired electron and a bond with an oxygen) was observed for H$^+$-implanted SiO_2:Ge glasses. A
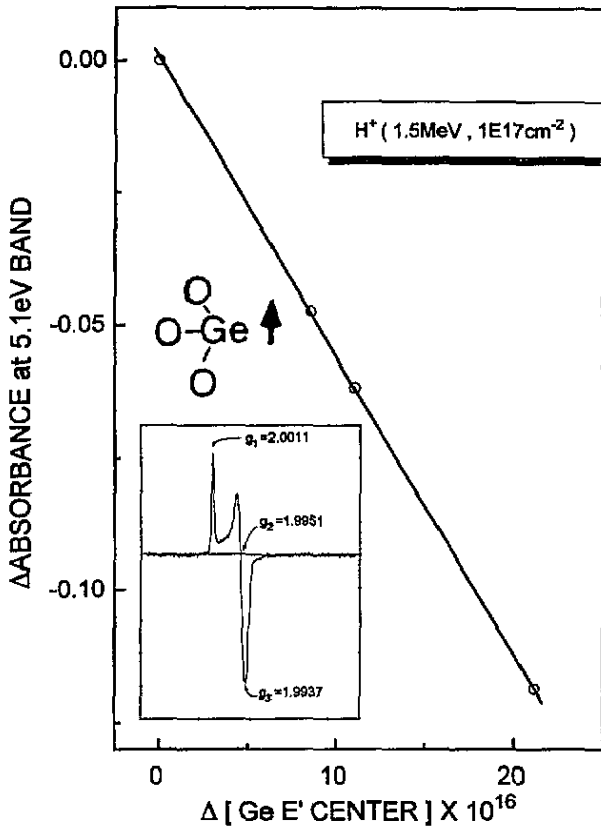
Figure 3. The correlation between the concentrations of UV-induced Ge E′ centres and the absorptivity of the UV bleached 5 eV band. The inset shows the EPR signal and the structure of the UV-induced Ge E′ centre.

linear relation is obtained as shown in figure 3 between intensities of the bleached band and concentrations of photoinduced Ge E′ centres. No significant changes ($< \pm 20\%$) were seen for the implanted SiO_2 glasses with photobleaching.

First, results on changes in H^+-implanted SiO_2:Ge glasses are discussed. It is accepted that the 5 eV band in SiO_2:Ge glasses is comprised of two components with different nature, photobleachable and unbleachable components, and the former and latter are attributed to a neutral oxygen monovacancy (NOMV) coordinated with two Ge^{4+} ions and a Ge^{2+} (with a lone pair) coordinated with two oxygens, respectively (Hosono *et al* 1992, 1993). The latter may be regarded as a neutral oxygen divacancy (NODV) when viewed from a GeO_4 structural unit. The NOMV is converted into a Ge E′ centre by illumination with 5 eV light, whereas the NODV, with a lone pair electron occupying the uppermost level, emits an intense blue luminescence but does not change chemically with 5 eV light at least via a one-photon process (Hosono *et al* 1992, Mizrahi and Atkins 1992, Nishii *et al* 1995). Thus, the presence of the NOMV is considered to be essential in the emergence of Hill grating with 5 eV light and the SHG. First to be evaluated is the concentration of the NOMV in H^+-implanted SiO_2:Ge glasses. Following the analysis described in the previous papers (Hosono *et al* 1992, 1993), first-order kinetics is assumed for the photoconversion process of the NOMV into a Ge E′ centre. Then, we obtain

$$\ln\left[1 - \Delta\alpha(t)/\Delta\alpha(\infty)\right] = -kt \qquad (1)$$

where $\alpha(t)$ denotes the absorptivity of the 5 eV band after light illumination for duration t and $\Delta\alpha(t)$ is defined as $\alpha(0) - \alpha(t)$. Here, $\Delta\alpha(\infty)$ can be evaluated through the least-squares fit of data (inset of figure 4) to the first-order kinetics plots shown in figure 4. Then, concentrations of the NOMV, N_{NOMV}, can be calculated from

$$N_{NOMV} = \Delta\alpha(\infty)/\varepsilon_{NOMV}d \qquad (2)$$

where ε_{NOMV} and d indicate the molar extinction coefficient of the NOMV and the thickness of implanted layers. Here, we use the reported value (4×10^4 L mol^{-1} cm^{-1} (Hosono *et al* 1992) of ε_{NOMV} and the calculated range (30 μm) of H$^+$ implanted at 1.5 MV as the value of d. Concentrations of the NODV can be evaluated from the value of $\alpha(0) - \Delta\alpha(\infty)$ employing the reported ε value (9×10^3 L mol^{-1} cm^{-1} (Yuen 1982) of ε_{NODV}. Table 1 summarizes the concentrations of the NOMV and the NODV in SiO$_2$:Ge glasses before and after H$^+$ implantation. It is evident that H$^+$ implantation enhances drastically the concentrations of both NOMV and NODV. The NOMV increased by a factor of about eight for a fluence of 1×10^{16} cm^{-2} or by a factor of $\sim$50 for 1×10^{17} cm^{-2} and the concentration ratio of the NOMV relative to the NODV remained constant (3%) for 1×10^{16} cm^{-2} but doubled (6%) for 1×10^{17} cm^{-2}.
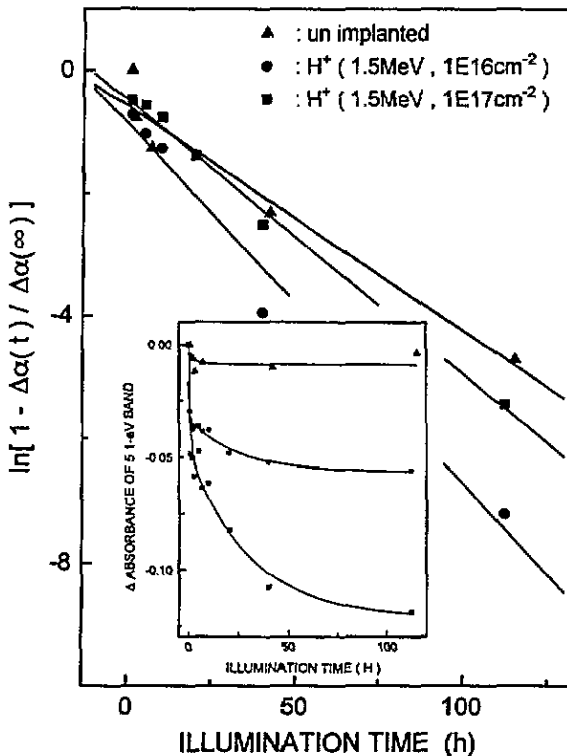

Figure 4. First-order kinetic plots for the intensity of the UV-bleached optical band. The inset shows the intensity of the UV-bleached band as a function of illumination time. $\Delta\alpha(t)$ denotes the absorptivity of UV-bleached band after 5 eV illumination of duration t.

Table 1. Changes in concentrations of neutral oxygen monovacancy (NOMV) and neutral oxygen divacancy (NODV) with H^+ implantation $\alpha(0)$ and $\alpha(\infty)$ denote the absorptivity of the 5 eV band before and after prolonged UV illumination, respectively. Molar extinction coefficients used are 4×10^4 L mol^{-1} cm^{-1} for the NOMV and 9×10^3 L mol^{-1} cm^{-1} for the NODV.

Sample	$\Delta\alpha(\infty)$ (cm^{-1})	N_{NOMV} ($\times 10^{16}$ cm^{-3})	$\alpha(0) - \Delta\alpha(\infty)$ (cm^{-1})	N_{NODV} ($\times 10^{17}$ cm^{-3})	[NOMV]/[NODV]
unimplanted	0.7	1.1	5.6	3.8	0.03
H^+ (1×10^{16} cm^{-1})	5.7	8.6	44.3	30	0.03
H^+ (1×10^{17} cm^{-1})	53	53	125	84	0.06

Second, results on implanted SiO_2 glasses are discussed. Absorption bands peaking at ~5 eV in amorphous silica are seen in many cases, such as synthetic OH-free silica prepared via the dehalogenation process and silica irradiated with high-energy ionizing radiation (Griscom 1991). It is in agreement that several intrinsic point defects with different nature give the 5 eV band, i.e. a neutral oxygen vacancy coordinated by Si^{4+} (the analogue of the Ge NOMV) (Imai *et al* 1988), an Si^{2+} centre (the analogue of the Ge MODV) (Silin and Skuja 1985) and a peroxy radical Si–O_2 or a molecular superoxide ion O_2^- (Hosono and Weeks 1990). Of these defects photobleachable defects are the neutral oxygen vacancy and the peroxy radicals. These defects can be discriminated from each other by photoluminescence and EPR: the former is diamagnetic (EPR silent) and emits a luminescence band at ~4.3 eV on excitation with 5 eV light (Griscom 1985, Imai *et al* 1988), whereas the latter is paramagnetic (EPR active) and emits no intense luminescence. A luminescence band peaking at 4.3 eV appears and its excitation peak is seen at ~5 eV (the band width also agrees with that of the absorption band) for all implanted SiO_2 glasses as exemplified in the inset of figure 2. Although a trace of the EPR signal of peroxy radicals was detected, their intensities calculated using the concentrations and the molar extinction coefficient (2700 L mol^{-1} cm^{-1} (Kim *et al* 1979)) were at most 5% of the observed intensity of the 5 eV band. It is, therefore, reasonable to consider that the photobleached component of the 5 eV band in the implanted SiO_2 glasses is due primarily to the neutral oxygen vacancy. However, no significant increase in concentrations of the Si E′ centre (which gives an optical band centred at 5.8 eV (see the review article by Griscom (1991))) was observed after photobleaching. Following the photochemical reaction proposed so far (Griscom 1985, Imai *et al* 1988, Hosono *et al* 1992), the neutral oxygen vacancy is converted into the pair of an Si E′ centre and a planar Si $\equiv$ O_3 upon exciting with 5 eV light. Thus, the present result does not agree with this model. A possibility of so far unknown photochemical reaction channels involving unidentified point defects is suggested.

Last, we discuss the possibilities of application of implanted SiO_2 and SiO_2:Ge glasses as photorefractive materials. The refractive index of SiO_2:Ge glasses (unimplanted) increases after UV illumination. This increase is explained by the Kramers–Kronig relation of complex refractive index ($\hat{n} = n - ik$) (Hand and Russel 1990), i.e., an emergence of intense absorptions above 5 eV (i.e., an increase in k) at the expense of bleaching of the 5 eV band results in an increase in refractive index n. Since spectral changes in H^+-implanted specimens with UV illumination are almost the same as those in the specimen before implantation except the magnitude, it is expected for the H^+-implanted specimens that the sign Δn is positive and its magnitude increases to a large extent in proportion to the concentration ratio of the NOMV. On the other hand, it is considered that the sign of Δn (compared with the as-implanted state) induced by UV illumination is reversed (negative) in implanted SiO_2 glasses. A detailed study of refractive index changes in these implanted

glasses is in progress along with bleaching of these 5 eV bands via two-photon absorption processes using excimer lasers in our laboratory.

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