# IMPROVEMENT OF EXCIMER LASER DURABILITY OF SILICA GLASS

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ABSTRACT

The effects of dissolved hydrogen on fluorescence emission behavior and on degradation of transmission (solarization) under irradiation of KrF excimer laser ray were investigated for a silica glass that was synthesized from high purity silicon tetrachloride by the oxy-hydrogen flame hydrolysis method. One half of the samples thus made was left hydrogen-free (Sample B), while the other half was doped with hydrogen to ca. $4 \times 10^{18}$ molecules/cm$^3$ (Sample A), both containing OH groups to 750 ppm by weight.

It was observed that both Samples A and B exhibited two fluorescence spectra: a broad one with its peak at ca. 2.8 eV (450 nm) and another with the peak at ca. 1.9 eV (650 nm), of which the 1.9 eV spectrum was about ten times stronger for Sample B than for Sample A, suggesting its close relationship to the oxygen-excess type defects; that both samples formed the 5.8 eV (214 nm) absorption band, which is due to formation of the E' centers; that the 5.8 eV absorption band was formed at markedly smaller laser energy input for Sample B than for Sample A, attesting to the beneficial effect of dissolved hydrogen to hold back the formation of E' centers; and that for both samples and for a given total laser energy input, the extent of E' center formation was the greater, the larger

the pulse energy density, suggesting the involvement of multiple photon absorption in the mechanism of damage.

## 1. INTRODUCTION

The UV rays, particularly those of KrF excimer laser (5 eV), ArF excimer laser (4.7 eV), and YAG laser (4th harmonic, 4.7 eV), are drawing attention as the working light for LSI making, photochemical processing, optical molding, and nuclear fusion. In these services, fluoride crystals (e.g., magnesium fluoride, calcium fluoride, barium fluoride) and silica glass have been used for the material of UV optics components, such as lenses, prisms, mirrors, etalon plates, fiberoptics, and the likes. Of these materials, silica glass is regarded as most usable for its superior workability, commercial availability (both in quantity and size), and uniformity in the striae and refractive index.

One drawback of silica glass for these services is that it is prone to optical damage when irradiated with UV rays of an energy greater than ca. 4.8 eV (shorter than ca. 260 nm in wavelength), becoming conspicuous on prolonged irradiation as degradation in such optical properties as listed in Table 1. Of these, decrease in transmission in the range of ca. 360 nm to 160 nm and increase in the intensity of UV-excited fluorescence should be noted with particular interest, because they are more directly related to the service performances of the silica glass. Here, the degradation of transmission, called solarization, is ascribed to formation of the 5.8 eV absorption band, i.e., the so-called E' centers, and the 4.8 eV absorption band, a process which is believed to take place on disruption of glass network structure by the UV ray.

As for the causes of these various sorts of degradation, there has been a number of studies made from the viewpoint of oxygen-related defects[4, 6-11]. Also, there are several studies on the behavior of hydrogen dissolved in silica glass under irradiation of γ-ray[1, 2, 3].

We at the Shin-Etsu Quartz Products, on the other hand, have been examining the durability of silica glass —namely, the number of shots of UV laser rays to bring about a chosen degree of degradation in the optical property of immediate interest— in terms of expected service conditions, such as the kind of laser ray, the pulse energy density, and the species and concentration of dissolved gas.

In this communication, I intend to discuss the durability of silica glass under KrF excimer laser irradiation with regard to fluorescence emission and solarization. Also, the effects of hydrogen dissolved in an OH-containing oxygen-defect free high purity sample on durability will be reported.

## 2. EXPERIMENTAL

### (1) Method of sample making

The silica glass was synthesized from a high purity silicon tetrachloride by the direct oxy-hydrogen flame hydrolysis method, i.e., the direct method. Ingots thus made were then subjected to stress-relief annealing in an electric furnace (made of high purity alumina bricks as insulator and silicon carbide as heating element) at 1,100°C for 1 h and slowly cooled at 5 °C/h to room temperature, all in ambient air. Then several test pieces were machined to 40 × 30 × 30 (thick) mm, and were ground on both surfaces to mirror finish. These test pieces will be referred to as Sample B.

Some of Sample B were further subjected to hydrogen doping (Sample A). Laser Raman scatter spectroscopy[5] showed Sample A specimens to contain hydrogen to about 4 × $10^{18}$ molecules/$cm^3$, whereas Sample B samples' hydrogen content was below 5 × $10^{16}$, which was the detection sensitivity of the instrument.

The content of OH groups was 750 ppm (by weight) for both.

(2) Laser irradiation conditions

KrF excimer pulse laser (Lambda Physik Model EMG 103 MSC) was used for irradiation with a pulse energy of 175 mJ, repetition frequency of 100 Hz, pulse duration of 23 ns, and with the pulse energy density varied between 100 to 1,000 mJ/$cm^2$.

## 3. RESULTS AND DISCUSSION

(1) Fluorescence characteristics

The fluorescence spectroscopy was conducted during laser irradiation, which was conducted with the beam of 140 mJ/$cm^2$ (100 Hz) and focused to ca. 20 × 7 mm. Figure 1 presents the measuring system (Princeton Instrument's SMA System), and Figs. 2 and 3 illustrate the spectra for Samples A and B, respectively. It will be noted that both samples fluoresce in pale blue (peak at ca. 2.8 eV, or ca. 450 nm) and in red (peak at ca. 1.9 eV, or ca. 650 nm), and that the peak intensity of red fluorescence of Sample B is about ten times as strong as that of Sample A.

Inspection conducted on the laser irradiated spot immediately after completion of fluorescence spectroscopy revealed occurrence neither of mechanical strain nor of transmission degradation in the 4.8 eV (260 nm) band. On extended irradiation, however, the intensity of 1.9 eV fluorescence was seen to increase not only continually but also in clear proportion to the degradation of the 4.8 eV band transmission.

Now, the present author has found in a separate series of experiments that silica glass that contains oxygen-deficient type defects does not form the 4.8 eV absorption band nor emits out the 1.9 eV fluorescence on irradiation of KrF excimer laser ray, even though it does form the 5.8 eV (E' center) absorption band. Also, it is known that silica glass that contains oxygen-excess type defects not only forms under extended KrF excimer laser irradiation both the 4.8 eV and the 5.8 eV absorption bands, of which the former is the stronger one, but also fluoresces in the 1.9 eV band in correspondence to the strength of absorption at 4.8 eV band.

It has been concluded, therefore, that the 1.9 eV fluorescence is closely related to occurrence of the oxygen-excess type defects.

(2) Solarization

As mentioned earlier on, silica glass forms on extended KrF excimer laser irradiation an absorption band at about 5.8 eV, i.e., the so-called E' center absorption band, and another at about 4.8 eV (Fig. 4), degrading the transmission in the combined wavelength range. Moreover, oxygen-related defects were detected neither in Sample A nor in B as far as the examination by the methods of VUV transmission, UV transmission, and laser-induced fluorescence[4, 7 - 11] could discern.

Noting the degradation in the internal transmission in the 5.8 eV band as particularly indicative of the performance of the glass in services under KrF excimer laser irradiation, we have taken the number of shots to give rise to a 2 % reduction in the transmission of 30 mm thick test piece as the durability, and have examined it by varying the laser pulse energy density.

The results are shown in Fig. 5, where it will be seen that the durability, both for Sample A and for Sample B, is linearly related to the pulse energy density on log-log scale. This observation, namely, for the same total energy input, damage is the greater, the greater the pulse energy density, suggests that the multiple photon absorption is involved in the degradation process. It will be also seen that Sample A is far more durable than B (e.g., $1 \times 10^6$ shots vs latter's $2 \times 10^4$ shots at 600 mJ/cm$^2$), attesting to the beneficial effect of dissolved hydrogen.

Furthermore, Sample A exhibited recovery effect over a period of several hours after irradiation, whereas Sample B showed no such tendency. Namely, the 5.8 eV band transmission of Sample A, once degraded by 3 %, recovered to 2 % decrease in 30 min, and regained the pre-irradiation value in 3 h. On re-irradiation with a small number of shots, however, the apparently recovered transmission decreased again to the post-irradiation value. This observation has been taken as indicating that structurally silica glass does not recover, not perfectly anyway, to the original state on mere aging.

(3) Improvement of durability

The factors that are considered to affect the durability of silica glass in the services under excimer laser irradiation are summarized in Table 2.

Of these, the effect of dissolved hydrogen is to improve the durability for KrF excimer laser irradiation as described above, but we have shown that, for ArF excimer laser irradiation, there is an optimum range for it to develop its beneficial effect[12)].

The effect of the oxygen-related defects is generally adverse, so that less of them, the better: the oxygen-deficient type defects appear to become the precursors of E' centers, while the oxygen-excess type defects to become the precursors of E' centers and of the 4.8 eV absorption band.

Besides the effects of dissolved hydrogen and oxygen-related defects discussed in the foregoing sections and summarized above, we have experimental evidences to show that concentrations of certain impurities and OH groups as well as the state of glass network texture can affect the durability of silica glass.

The major impurities are Na, K, and Li of the alkali metal group, Ca and Mg of the alkaline earth, and Fe, Cr, Ni, Ti, and Cu of the transition metal group, all of which can contaminate the silica glass during its synthesis and while it is heat treated. Naturally, then, the less of them, the better, but the practical measure of allowance is 50 ppb by weight for each.

The presence of OH groups to certain concentration appears to be necessary. This is probably because the OH radical is one of the glass network terminators, and function of OH group as a terminator is to relax the strains in the interatomic distance and angle of Si-O bonds, thereby stabilizing the glass network structure. Similar effects should then be expected of F and Cl, which are also the network terminators.

Besides these, there are the effects of the glass network structure, particularly the ring structure, and those of other dissolved gases than hydrogen and oxygen to be examined. They will constitute the subject of our future research.

## 4. SUMMARY

The effects of dissolved hydrogen on fluorescence emission behavior and on degradation of transmission (solarization) under KrF excimer laser irradiation were investigated for a silica glass that was synthesized from high purity silicon tetrachloride by the oxy-

hydrogen flame hydrolysis method. Of the silica glass thus made, one half of the sample was left hydrogen-free (Sample B), while the other half was doped with hydrogen to ca. 4 × $10^{18}$ molecules/$cm^3$ (Sample A), both containing OH groups to 750 ppm by weight.

It was observed:

(1) that both Samples A and B exhibit two fluorescence spectra: a broad one of pale blue fluorescence with its peak at ca. 2.8 eV (450 nm), and the other, a sharper band of red fluorescence with the peak at ca. 1.9 eV (650 nm);

(2) that, of these two fluorescence bands, the 1.9 eV spectrum of Sample B is about ten times stronger than that of Sample A; this appears to be related to the oxygen-excess type defects;

(3) that both samples form the 5.8 eV (214 nm) absorption band, which is due to formation of the E' centers;

(4) that the 5.8 eV absorption band (i.e., solarization) starts appearing at markedly smaller laser energy input for Sample B than for Sample A, attesting to the beneficial effect of dissolved hydrogen to hold back the formation of E' centers; and

(5) that for both samples and for a given total laser energy input, the extent of E' center formation is the greater, the larger the pulse energy density, suggesting the involvement of multiple photon absorption in the mechanism of damage.

<u>References</u>

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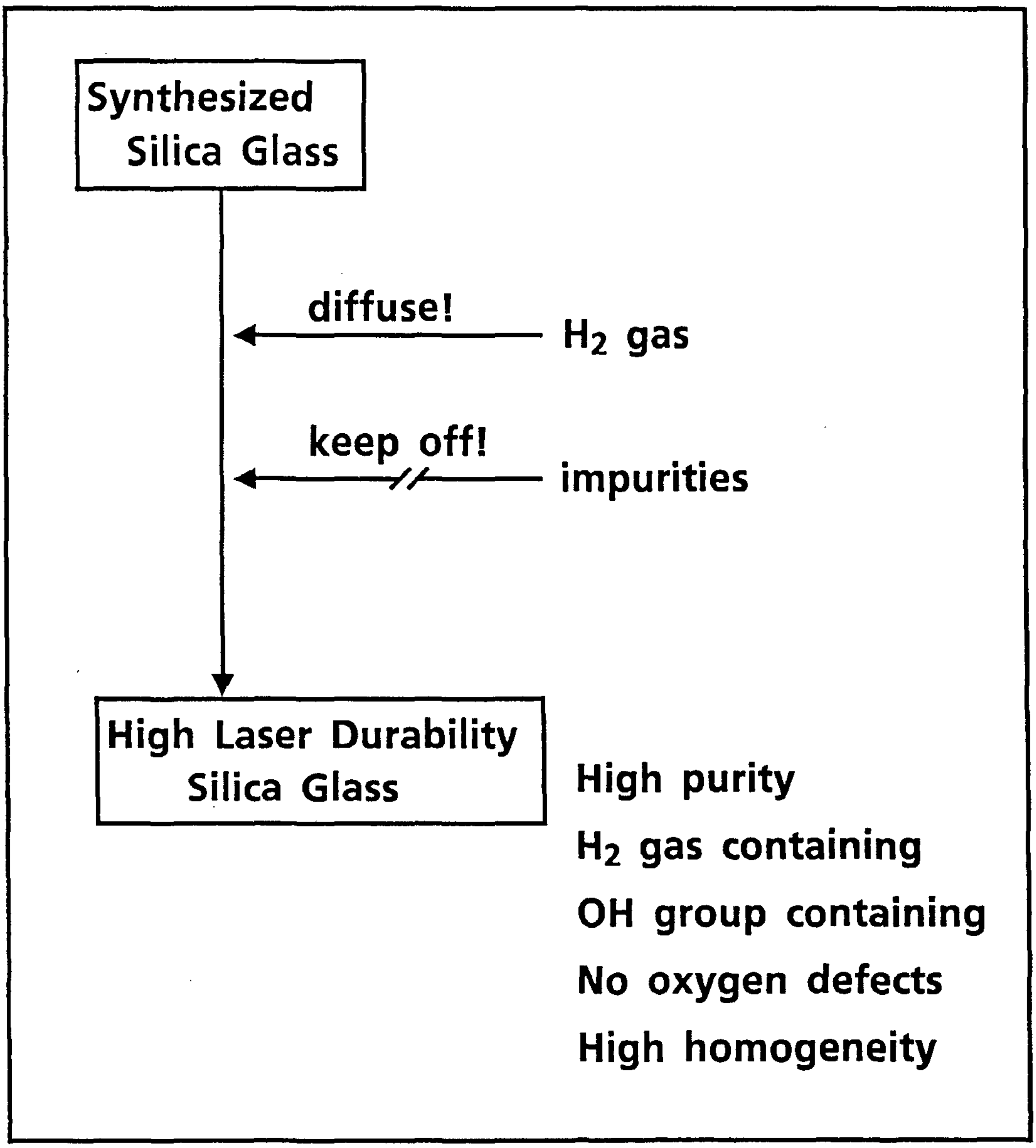
**Table 1** **Changes in Optical Properties of Silica Glass given Rise to on Extented Irradiation of UV Laser**

| |
|---|
| Degradation of Optical Property of Silica Glass on Laser Irradiation |
| Birefringence: increase |
| Refractive index: increase |
| Homogeneity:decrease |
| Transmission: decrease |
| Fluorescence: increase |

Table 2 Factors Affecting the Excimer Laser Durability of Silica Glass

- Content of impurities
- Content of $H_2$ gas
- Content of OH radicals
- Content of oxygen defects
  - Oxygen deficient type
  - Oxygen excess type
- State of network texture
- Others

Table 3. How to improve the durability



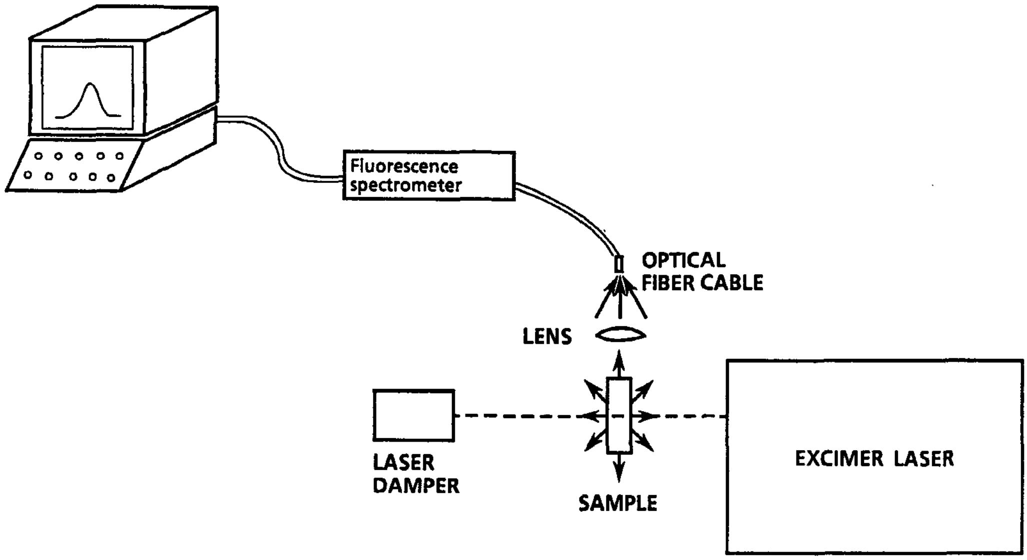



**Fig. 1 Fluorescence measurement system**

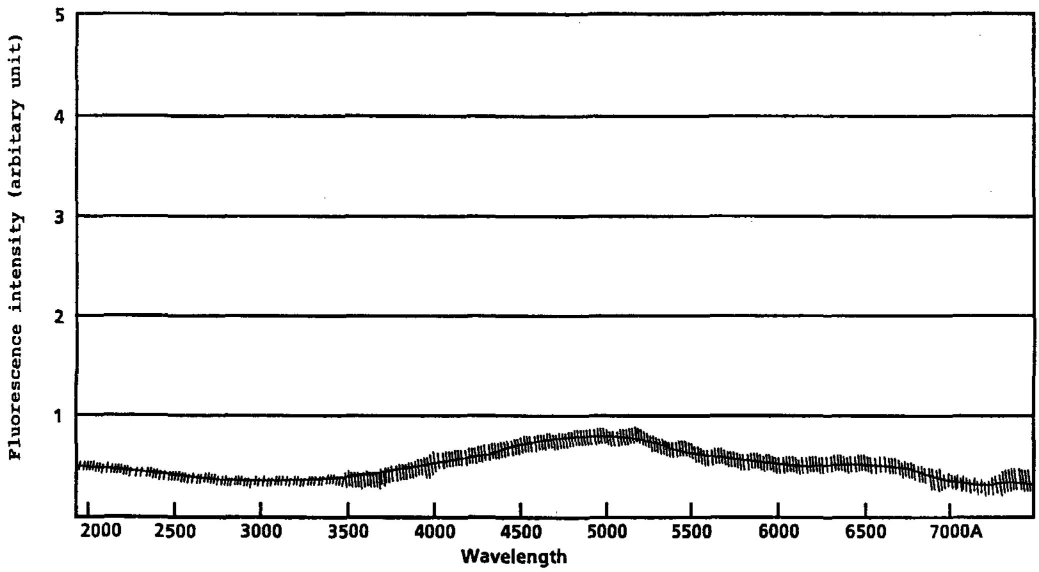



**Fig. 2 Laser-induced fluorescence spectrum of Sample A (KrF, 140 mJ/$cm^2$, 100 Hz)**

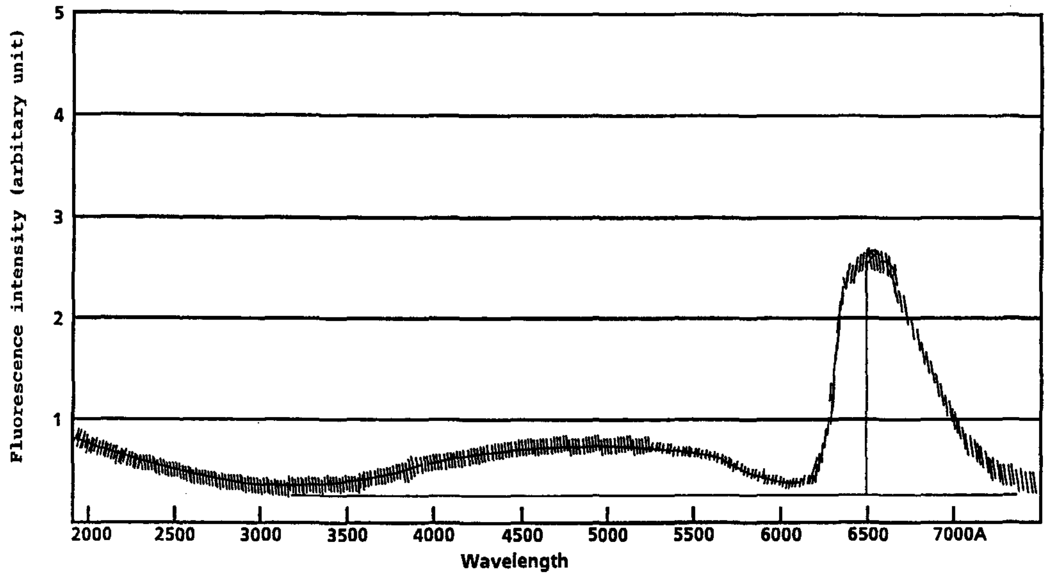



**Fig. 3 Laser-induced fluorescence spectrum of Sample B (KrF, 140 mJ/cm$^2$, 100 Hz)**

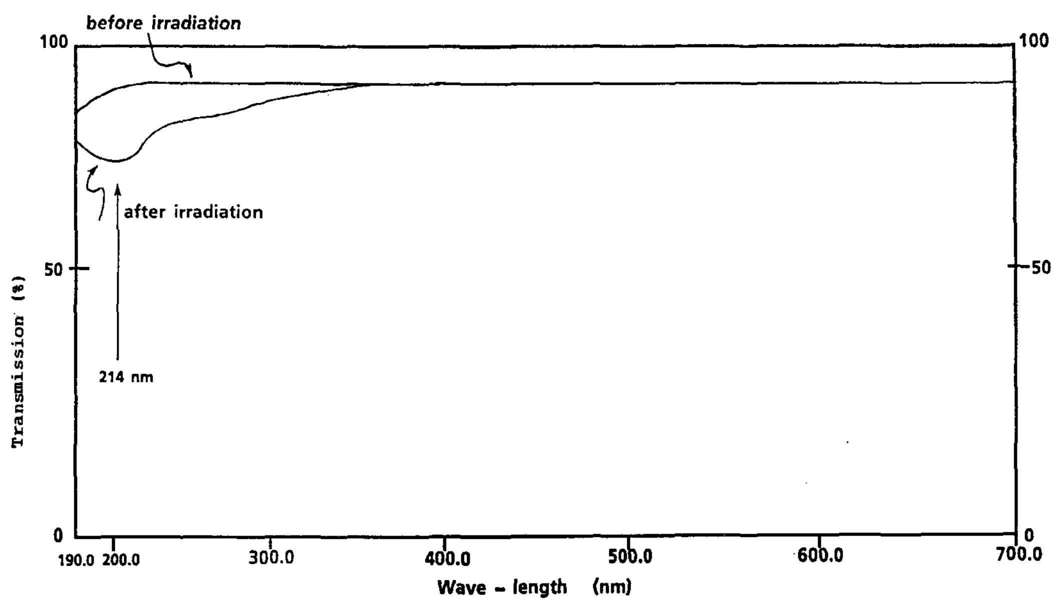



**Fig. 4 Transmission of silica glass before and after KrF excimer laser irradiation. (400 mJ/cm$^2$, 4 × 10$^5$)**

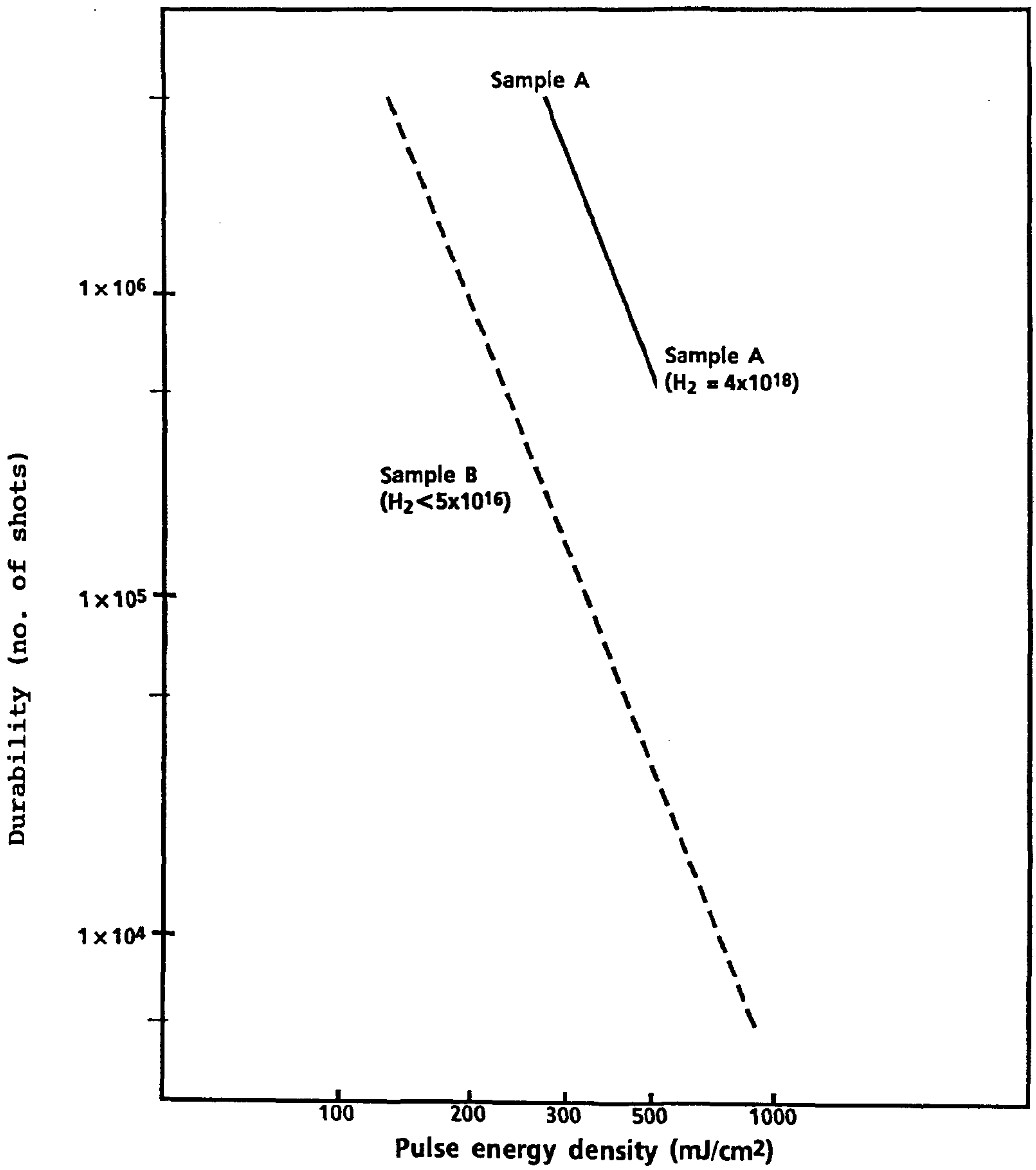



Fig. 5 Effect of dissolved hydrogen on formation of E' center absorption band by KrF excimer laser irratidation