PHOTOLUMINESCENCE AND OPTICAL ABSORPTION BANDS INDUCED BY EXCIMER LASER IRRADIATION IN SILICA GLASSES

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ABSTRACT

Photoluminescence and optical absorption bands in silica glasses excited by VUV laser (7.9-eV) are reported. Luminescence spectra of various types of silicas, prepared under different conditions, exhibit sample-to-sample variations. Several luminescence bands (1.9-eV, 2.7-eV, 3.1-eV, 4.2-eV, 4.3-eV, and 2-4-eV band) were observed at room temperature. The 2.7-eV band, previously ascribed to a triplet-to-singlet transition of neutral oxygen vacancy, show a slow decay rate of $\tau \simeq 10$ ms. Relatively slow decay rates of $\tau \simeq 13$ μs and $\tau \simeq 110$ μs were obtained for the 1.9- and 3.1-eV bands, respectively. Optical absorption spectra after the 7.9-eV irradiation also show sample dependence. Interestingly, the growth of 5.0-eV band was observed in oxygen-deficient samples in addition to the previously reported bands (4.8-eV

and 5.8-eV). This suggests that oxygen vacancy defects are induced from oxygen-deficiency-related precursors.

1. INTRODUCTION

Defect generation mechanisms in SiO_2 have been a subject of interest in recent years[1-4]. They can be divided into two types; the intrinsic and extrinsic mechanisms. There have been several reports on the intrinsic defect generation mechanism involving the nonradiative decay of self-trapped exciton[1,2,5]. Although the transient oxygen displacement seems to be established, the displacement leading to the formation of permanent E' center in SiO_2 is still not yet confirmed.

On the other hand, Arai et al.[3] and the authors[4] have recently reported the extrinsic mechanism involving the precursor transformation driven by the decay of the electron-hole pair or exciton at the precursor sites such as neutral oxygen vacancy(≡Si-Si≡). The ESR investigation on wide ranges of silica glasses irradiated by ArF (6.4 eV) excimer laser shows the sample-to-sample variation of defect species and yields[4].

In either case of the defect process, excited states such as excitons produced by the cross-band-gap excitation play an important role. Although ESR is a structure sensitive probe, it can reveal only the paramagnetic defects in the ground state. Photoluminescence and optical absorption measurements, on the other hand, can give informations regarding energy levels of the excited states.

We report here the observation of the photoluminescence and optical absorption induced by VUV excimer laser irradiation in various types of high-purity silicas.

2. EXPERIMENTAL PROCEDURES

Characteristics of the samples are shown in Table I. They are high-purity silicas with the diverse contents of impurities such as chlorine and hydroxyl. The low-OH silicas are classified into oxygen-deficient and oxygen-surplus silicas, as previously reported[6].

Samples were placed in a chamber and excited with an VUV (7.9 eV, F_2) excimer laser through optical path under vacuum ($\simeq 10^{-3}$ Torr). The luminescence is dispersed by a monochromator and detected by a photomultiplier (PM, Hamamatsu R212UH and R955). Signals from the PM are then fed into an oscilloscope (Iwatsu DS-6121) and stored in a computer. Before measurements, samples were not irradiated with any radiation other than the excitation laser. Measurements were made both at room temperature and around 110K. The time response of the present system is 10^{-7}s. Optical absorption measurements were performed before and after the 7.9-eV irradiation (50Hz, 5mJ/cm^2·pulse) at room temperature in N_2 gas atmosphere.

3. RESULTS

3.1. Photoluminescence spectra

Figures 1 (a), (b), (c), and (d) show the luminescence spectra of typical samples obtained at room temperature. The presence or not of luminescence bands shows sample dependency.

The oxygen-surplus low-OH silica exhibits 1.9-eV band and a broad band spreading from 2 to 4 eV at room temperature. The 1.9-eV band decays with a time constant of about 14 μs at room temperature, and somewhat more slowly at 110 K ($\tau \simeq 18$ μs).

In the oxygen-deficient low-OH silicas, we observed 2.7- and 4.3-eV bands both at room temperature and 110 K. The 2.7-eV band decays with a time constant of about 10 ms. The 4.3-eV band decays faster than the response time of present system (10^{-7} s).

High-OH silica shows the luminescence bands at 1.9 eV, and 4.3 eV. The 1.9-eV and the 4.3-eV bands have the same decay constant as the corresponding bands observed in the oxygen-surplus and oxygen-deficient samples, respectively.

The $B_2\beta$-type sample has 1.9-, 3.1- and 4.2-eV bands. The 3.1-eV band has a decay constant of 110 μs. At 110 K, the intensity grows stronger, while the decay constant does not change.

Table II summarizes the presence or not of the luminescence bands in various types of silicas.

3.2. Optical absorption bands

Figures 2 (a) and (b) show the absorption spectra of oxygen-surplus silica P3F and oxygen-deficient silica SA2,

respectively, which were obtained before and after the 7.9-eV laser irradiation. As in the case of photoluminescence, optical absorption spectrum also shows sample dependency.

In the oxygen-surplus low-OH silica, we observed absorption bands at 4.8 and 5.8 eV. The intensity of the 5.8-eV band is much smaller than that observed in the oxygen-deficient silica.

In the oxygen-deficient low-OH silica, the 5.8-eV band is induced. Curiously, we observed the growth of 5.0-eV band, in addition to that of the 5.8-eV band. This is clearly seen in the induced absorption spectra in Fig. 3. The newly created 5.0-eV band has a nearly identical shape (full-width at half maximum of about 0.3 eV) to the $B_2\alpha$ band observed before irradiation.

4. DISCUSSION

Before discussing the cause of the luminescence, we consider the excitation process of the luminescence. Figure 4 shows optical absorption in the VUV region of various types of silica[7]. As shown in Fig. 4, each type of silica shows a characteristic absorption band due to diamagnetic defects.

The oxygen-surplus silica has an optical absorption tail at 7-8 eV, reported to be due to peroxy linkages[8]. The oxygen-deficient silica exhibits the 7.6-eV band, due to neutral oxygen vacancy[7]. High-OH silica has an absorption band at 8 eV, possibly due to hydroxyl-group[9].

Since the F_2-laser line (7.9 eV) is within these energy

regions, the most likely excitation channel is direct excitation of these defect bands. Following energy transfer from one absorption center to another luminescence center is also possible in the present case.

Another possibility is cross band-gap excitation by two photon absorption achieved by high excitation density and subsequent energy migration in the form of excitons or electron-hole pairs.

4.1. Luminescence bands

We will discuss the defect responsible for each luminescence. As we mentioned in the Sec. 3, we see the sample dependence of luminescence bands.

4.1.1. 1.9-eV band

The 1.9-eV band is observed in the low-OH oxygen-surplus silica and in the high-OH silica. As previously reported, the 1.9-eV band is due to the NBOHC[9]. Since the samples were not exposed to any radiation other than the excitation laser, the luminescence centers should be induced by the excitation light. Namely, NBOHCs are first created as follows[4]:

$$\equiv Si\text{-}O\text{-}O\text{-}Si\equiv \rightarrow \equiv Si\text{-}O\cdot + \cdot O\text{-}Si\equiv \quad (1),$$

or

$$\equiv Si\text{-}OH \rightarrow \equiv Si\text{-}O\cdot + \cdot H \qquad (2),$$

and the subsequent excitation of the NBOHC results in the 1.9-eV luminescence.

4.1.2. 2.7-eV band

The 2.7-eV band is only observed in the oxygen-deficient silicas. We have reported that the 2.7-eV luminescence is also observed in the same type of silica when excited at 5.0 eV ($B_2\alpha$ band), and that its lifetime is 10.2 ms[7,10]. Ab-initio molecular orbital calculations have shown that the 2.7-eV band is due to transition from the triplet to the singlet states. As seen in Fig.4, the 7.6-eV band, ascribed to the singlet-to-singlet transition at oxygen vacancies, is observed in the oxygen-deficient silica. Therefore, the observed 2.7-eV luminescence can be described as follows. First, the 7.9-eV photon is absorbed by the singlet-to-singlet transition at oxygen vacancies. Then the intersystem crossing occurs between the excited singlet and the triplet states. Finally, the 2.7-eV light is emitted through the transition from the triplet to the singlet states. The lifetime of the luminescence by 7.9-eV excitation is about 10 ms, which is consistent with the present view.

4.1.3. 4.3-eV band

In oxygen-deficient silica, the 4.3-eV band is observed along with the 2.7-eV band as previously reported (See Fig.

1(b))[7,10]. In the case of high-OH silica, only the 4.3-eV band is observed while the 2.7-eV is absent. This suggests that the defect responsible for the 4.3-eV band is different from that responsible for the 2.7-eV band. However, since the 4.3-eV band is not seen in oxygen-surplus silica, the oxygen deficiency plays a role, to some extent, in the appearance of this band. The decay of the luminescence is faster than the time response of our system ($\simeq 10^{-7}$s).

4.2. Optical absorption bands

4.2.1. 4.8-eV band

The 4.8-eV absorption band is observed in the oxygen-surplus low-OH and in the high-OH silicas. We have reported that the 4.8-eV band is due to negatively-charged nonbridging oxygen hole centers($\equiv Si-O^-$)[9]. Possible mechanism of the formation of $\equiv Si-O^-$ are as follows:

$$\equiv Si-O-O-Si\equiv + e^- \rightarrow \equiv Si-O^- + \cdot O-Si\equiv \quad (3),$$

or

$$\equiv Si-OH + e^- \rightarrow \equiv Si-O^- + \cdot H \quad (4).$$

4.2.2. 5.0-eV band induced by 7.9-eV irradiation

The 5.0-eV band is induced newly by the 7.9-eV irradiation, only in the oxygen-deficient silica which has an absorption

band at 5.0eV even before irradiation. This newly created 5.0-eV band has almost the same peak energy and full width at half maximum (≃0.3 eV) as the preexisting 5.0-eV band. Therefore, the new and old 5.0-eV bands seem to be identical, and the growth of the new band is due to the creation of neutral oxygen vacancy (≡Si-Si≡). One possible precursor is ≡Si-Cl or ≡Si-F bonds which presumably exist in pairs in the Ar-plasma sample (Cl:3200 ppm) or in the F-doped samples (F:2000 ppm), respectively:

$$\equiv Si\text{-}Cl\ \ Cl\text{-}Si\equiv \rightarrow \equiv Si\text{-}Si\equiv + Cl_2 \qquad (5),$$

or

$$\equiv Si\text{-}F\ \ F\text{-}Si\equiv \rightarrow \equiv Si\text{-}Si\equiv + F_2 \qquad (6).$$

4.2.3. 5.8-eV band

The 5.8-eV band was previously ascribed to the E' center[11]. The intensity of this band observed in oxygen-deficient silica is stronger than in other types of silicas. This is consistent with the proposed mechanism of E' centers from oxygen vacancies in oxygen-deficient silicas[12]:

$$\equiv Si\text{-}Si\equiv \rightarrow \equiv Si\cdot + {}^{+}Si\equiv + e^{-} \qquad (7).$$

5. SUMMARY

We have demonstrated the sample dependence of the luminescence and the optical absorption bands induced by VUV (7.9 eV) excimer laser irradiation.

The 1.9-eV band is observed in the oxygen-surplus and the high-OH silicas and considered due to the NBOHCs. The 2.7-eV luminescence is observed in oxygen-deficient silica when the 7.6-eV band is excited. The observed slow decay ($\tau \simeq 10$ ms) of the 2.7-eV band is due to the triplet-to-singlet transition, as theoretical calculations have shown. The 3.1- and the 4.2-eV bands are observed in $B_2\beta$-type silica. The lifetime of the 3.1-eV band is relatively slow ($\tau \simeq 110$ μs), while that of the 4.2-eV band is faster (less than about 10^{-7} s). From the sample dependence of the 4.3-eV band, it is suggested that this band is not directly correlated with oxygen vacancies. The growth of the 5.0-eV ($B_2\alpha$) band was observed in the oxygen-deficient silicas after the 7.9-eV irradiation. This suggests that the oxygen vacancies are produced from oxygen-deficiency-related precursors by laser irradiation.

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Table I. Sample list

Sample name	Category	Manufacturing method	Impurity (ppm) Cl	OH
P3F	Oxygen-surplus	$Ar+O_2$ plasma	370	0.46
SA2	Oxygen-deficient	Ar plasma	3200	0.75
SFF	Oxygen-deficient	Soot	N.D. (F: ≃2000 ppm)	N.D.
S1F	Oxygen-deficient	Soot	0.3 (F: ≃2000 ppm)	N.D.
DF8	High-OH	Direct	N.D.	1000
SF1	Unknown ($B_2\beta^a$)	Soot	0.3	270

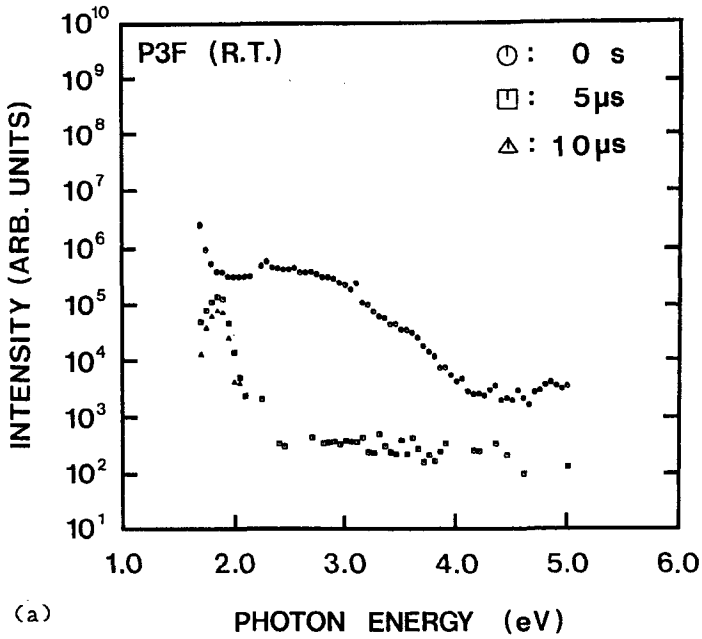
N.D.: Not detected.

[a] See Ref. 7.

Table II. Photoluminescence bands observed in various types of silicas.

Type	Photoluminescence bands					
	1.9 eV	2.7 eV	3.1 eV	4.2 eV	4.3 eV	2-4 eV
Oxygen surplus	D	N.D.	N.D.	N.D.	N.D.	D
Oxygen deficient	N.D.	D	N.D.	N.D.	D	N.D.
High-OH	D	N.D.	N.D.	N.D.	D	N.D.
$B_2\beta$	D	N.D.	D	D	N.D.	N.D.

D: Detected, N.D.: Not Detected.


P3F (R.T.)
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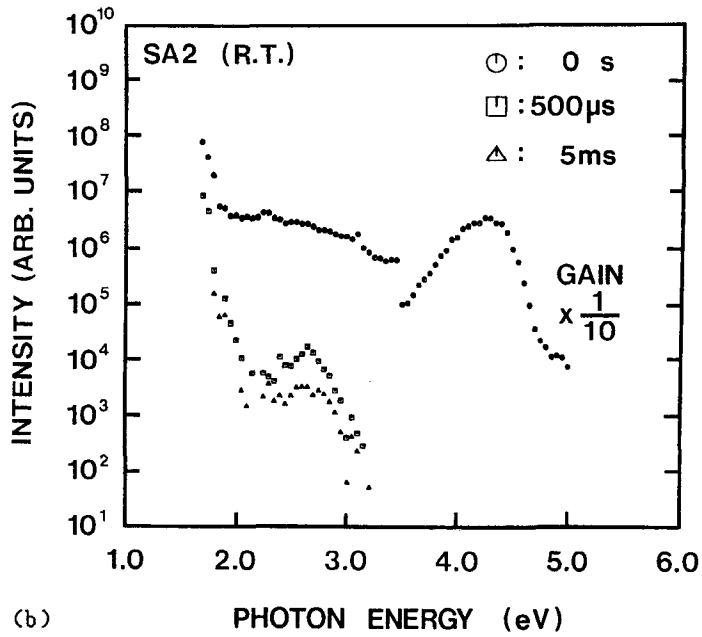
⊡: 5μs
△: 10μs
INTENSITY (ARB. UNITS)
PHOTON ENERGY (eV)

(a)


SA2 (R.T.)
⏲: 0 s
⊡: 500μs
△: 5ms
GAIN
x 1/10
INTENSITY (ARB. UNITS)
PHOTON ENERGY (eV)

(b)

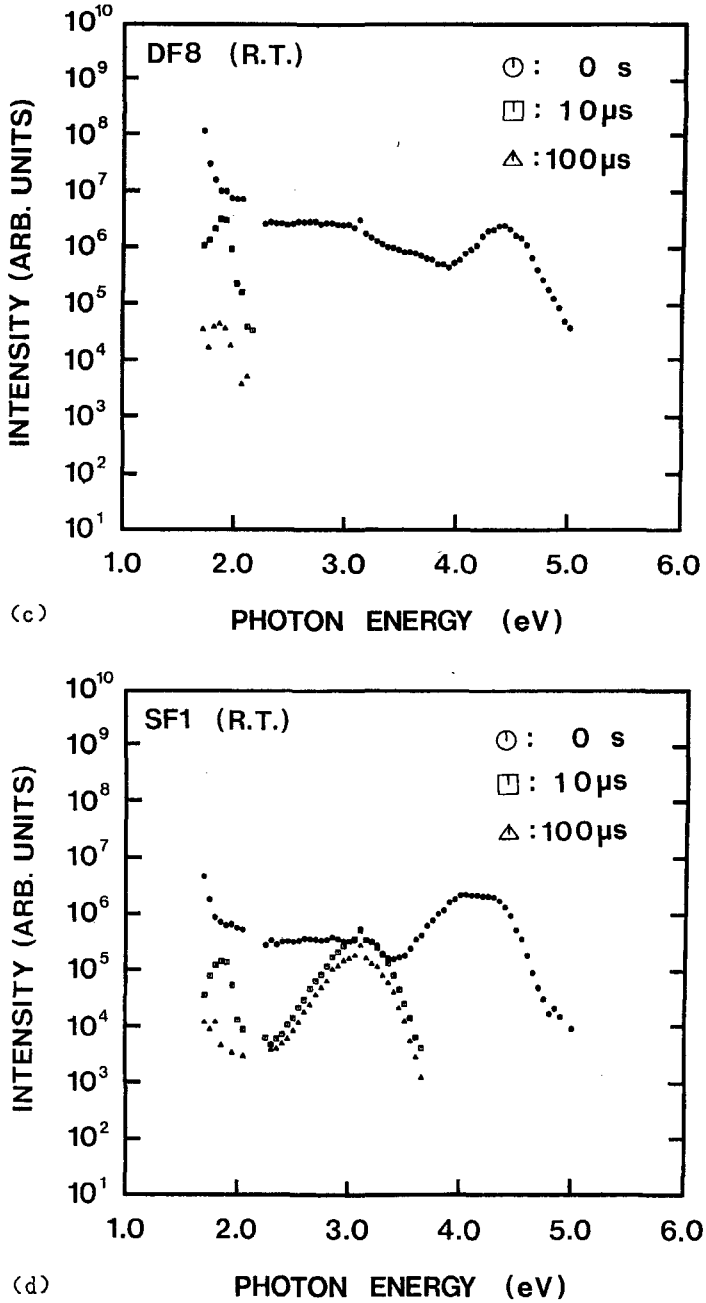


FIG. 1. Photoluminescence spectra obtained at room temperature when excited at 7.9 eV for (a) the oxygen-surplus silica P3F, (b) the oxygen-deficient silica SA2, (c) the high-OH silica DF8, and (d) the $B_2\beta$-type silica.

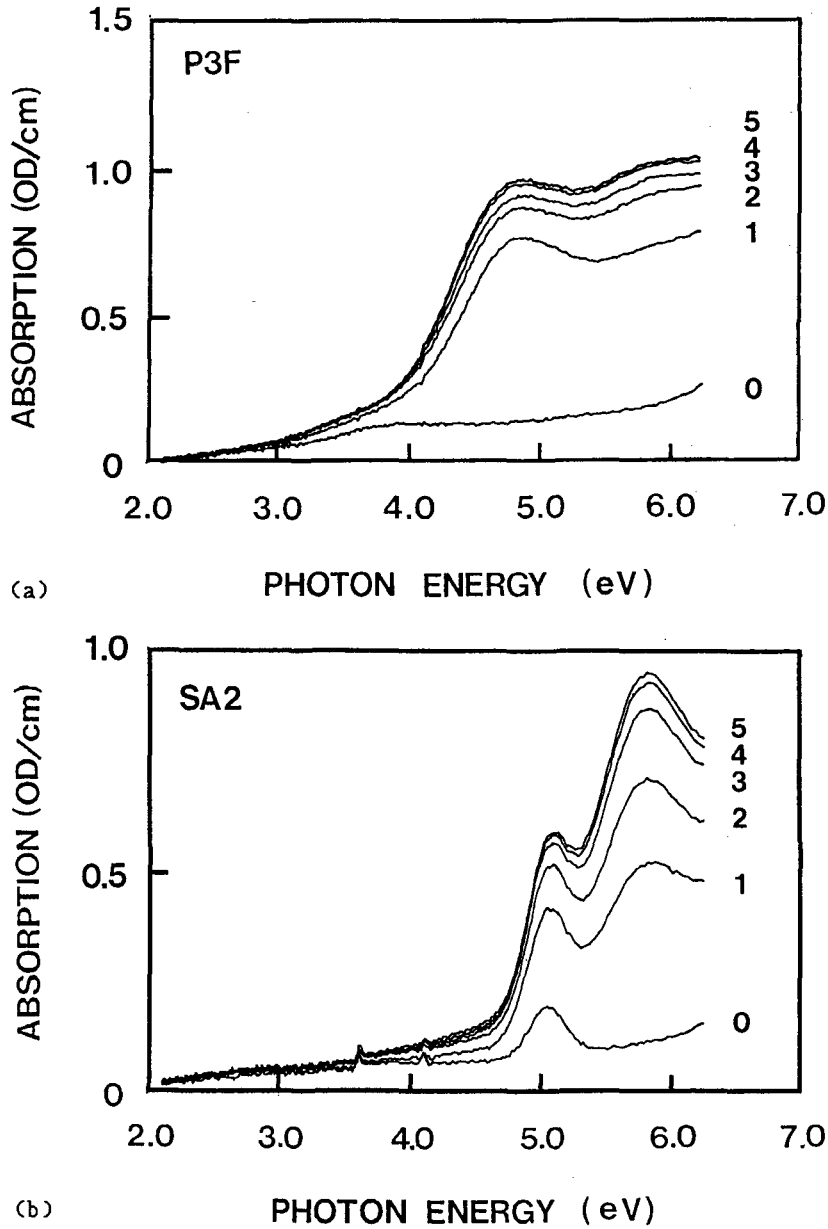


FIG. 2. Optical absorption spectra obtained for (a) the oxygen-surplus P3F and (b) the oxygen-deficient SA2, before and after 7.9-eV irradiation (50 Hz, 5 mJcm^{-2}/pulse, 0: 0 min., 1: 5 min., 2: 10 min., 3: 15 min., 4: 20 min., and 5: 25 min.).

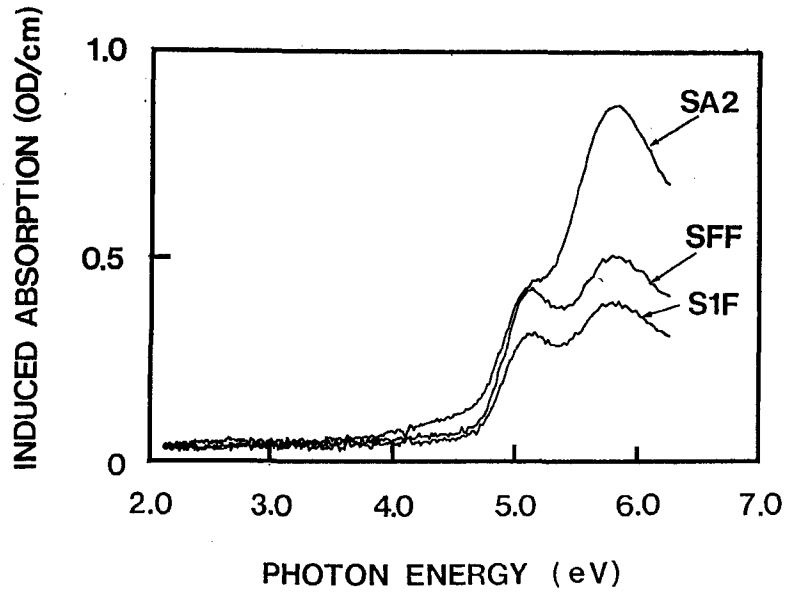


FIG. 3. The 7.9-eV induced optical absorption spectra obtained for the Ar-plasma silica (SA2) and F-doped silicas (SFF and S1F).

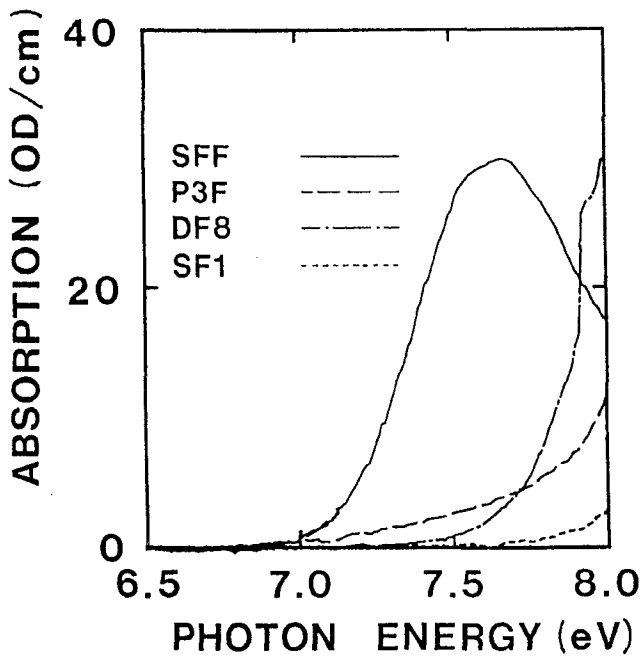


FIG. 4. VUV-absorption spectra obtained for the oxygen-deficient silica SFF, the oxygen-surplus silica P3F, the high-OH silica DF8, and the $B_2\beta$-type silica SF1.