Structural instability in SiO_2 films prepared by photochemical vapor deposition

H. Nonaka and K. Arai,
Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba,
Ibaraki 305 Japan

J. Isoya,
University of Library and Information Science,
1-2 Kasuga, Tsukuba, Ibaraki 305 Japan

Abstract

We have studied the effects of irradiation of D_2 lamp on the films prepared by D_2-lamp-photo-CVD with/without F-doping. The irradiation was done by exposing the films to the lamp in vacuum at the same substrate temperature used in the process. It was found that the point defects such as ≡Si-H , ≡Si-Si≡, and the defect related to the 880 cm^{-1} peak in IR spectra were gradually decreased by the irradiation. The E' centers which were observed in the as-deposited films without F-doping were almost extinguished after the long UV exposure, whereas the films with F-doping originally had no E' centers, even having some point defects. Results were discussed on the concepts of the optical and the chemical annealing.

Introduction

Photochemical vapor deposition (photo-CVD) has a potential as low-temperature and ion-damage free process on amorphous silica (a-SiO_2) films in, for instance, very-large-scale integration technology [1]. However, the photo-CVD has its inherent problems due to a low-temperature process; structural imperfections including point defects sucu as ≡Si-H, ≡Si-OH, and ≡Si-Si≡ (oxygen-deficient centers; ODC) tend to remain in the films and may affect reliability in the electronic uses. Thus further development of the process will demand not only electronic but also structural characterization on the films. Recently, we have developed fluorine(F)-doped a-SiO_2 films using a deuterium(D_2)-lamp CVD [2] and shown that the as-deposited films without fluorine have E' centers of the order of 10^{18} cm^{-3}, slowly decaying at room temperature, whereas the films with F-doping had substantially E' centers under detection limit [3]. In bulk silica glasses, it is known that the point defects have relation to the occurrence of paramagnetic centers induced by high energy excitation [4] and by VUV (vacuum ultraviolet) irradiation [5-8]. There is apprehensions that UV irradiation involved in photo-CVD itself might be responsible for the high density of E' centers observed.

In this paper, we have studied structural stability of the films after preparation on the effects of the D_2-lamp irradiation and F-doping.

Experimental

The procedure for preparation of the films has been described in detail [2]. In brief, amorphous SiO_2 films were deposited from Si_2H_6 and O_2 using the D_2-lamp photo-CVD method at 200 °C on Si(100) wafer. The VUV light from the D_2-lamp was irradiated perpendicular to the substrate. A small portion of fluorine (F) was incorporated into the film by admixing Si_2F_6 with the source gases. The deposition conditions for each film including the film thickness are listed in Table I along with the characteristics of the films such as impurities and fluorine content estimated mainly from infrared spectra of the films (see Fig. 1). The films thus prepared could be categorized as follows:

A. Slowly-deposited without F.

B. Slowly-deposited with F.

C. Fast-deposited without F.

D. Fast-deposited with F.

In order to investigate the effect of direct irradiation of VUV light on the film, the films were exposed to the D_2-lamp irradiation. The experimental set up was the same as that of the film deposition except that there was no gas introduction into the reaction chamber. Before the irradiation experiment, the films had been left at room temperature till their EPR signal intensity decayed almost to a constant value.

The infrared (IR) spectra of the films were taken by a Fourier transform IR spectrometer (DIGILAB FTS-60). The VUV absorption spectra were taken by a VUV spectrometer with a D_2 lamp.

The EPR spectra of the films were measured at the liquid nitrogen temperature using an EPR spectrometer (Bruker ESP 300).

The films were deposited on Si wafer of high resistivity of 7000-20000 Ω cm in order to keep the Q-value of the cavity within a right level for the measurement. After deposition, the sample was cut into pieces (5×3 mm on the average) and placed in a silica sample tube (5 mm ϕ) as soon as possible and kept at liquid nitrogen temperature to prevent paramagnetic centers of a short life time, if existed, from decaying at room temperature. The sample tube was set in the microwave cavity so as to make the magnetic field perpendicular to the film surface. Non-saturating microwave power of 0.2 mW was applied for evaluation of the spin density of the resonance. Pure hydrous copper sulfate, $CuSO_4 \cdot 5H_2O$, whose total spin number was estimated to be 3.16×10^{19}, was used as a standard to estimate the absolute values for the spin density of the samples.

Results

Figure 1 shows the IR spectra of the film C before and after D_2-lamp irradiation. As-deposited film as absorption peaks due to point defects at 3650 cm^{-1} (≡Si-OH), 2270cm^{-1} (≡Si-H), and 880 cm^{-1} which we tentatively assigned to a pair of ≡Si-H [2], besides ≡Si-O-Si≡ vibrational modes at 1070-1090 cm^{-1}, 810 cm^{-1}, and 450 cm^{-1}. It is observed that the ≡Si-H and the 880 cm^{-1} peaks decrease with the irradiation. In fig. 2, the irradiation-time dependence of the peak height of the 880 cm^{-1} band and the defect densities of ≡Si-H and ≡Si-OH in the films C are plotted. The ≡Si-H and the 880 cm^{-1} defect rapidly decreases, while ≡Si-OH does not change at all. It is noted that without irradiation the

effect is negligible at 200 ℃ (see fig. 2) and therefore the irradiation plays an essential role in reducing the point defects rather than the thermal effect. For other samples, the bands due to defects, if existed, more or less decreased in a similar way.

We also measured the VUV spectra of the films before and after the D_2-lamp irradiation. Figure 3 shows the VUV spectra of the film C. Before the irradiation, the spectra had an absorption band at 7.6 eV, which is due to ODC (≡Si-Si≡) [2,9], but after 1-hour irradiation it disappeared. For the film D, we had similar results.

For the films without F (i.e., A and C), we observed E' centers (occasionally along with P_b centers) as shown in Fig. 4. where the densities of the centers were estimated to be $\sim 1 \times 10^{18}$ cm^{-3} and 2×10^{18} cm^{-3}, respectively. The spectral feature for the film A corresponds to that of E' centers of the usual type, whereas the shape of the peak for the film C is broadened, indicating a broad distribution of the bonding structures around the paramagnetic centers.

The intensity of the peak in EPR spectra for the film C decreased at room temperature as shown in Fig. 5(a). The absolute values for t=0 were not strictly equal to those of as-deposited films because it needed more than 10 minutes to take the films out of the deposition chamber and the films thus underwent a thermal annealing at about 200 ℃ before they were cooled down to the liquid nitrogen temperature. The decay curve for each film was featured as a double-exponential with a constant term. The E' centers in the films had at least two kinds of lifetime, 2-3 hours and 30-50 hours estimated through the curve fitting. The similar

double exponential decay features were obtained for both films A and C, irrespective of the difference in spectral shapes. For the film A, the peak intensity at t=0 after 1-hour irradiation was about one order smaller than that of the as-deposited film and after 2-hour irradiation the signal level became below the detection limit (=3 $\times 10^{16}$ spins cm^{-3}). It is noted that for the films with F (i.e., B and D), no signal above the detection limit was observed either before or after irradiation.

Figure 5(b) shows a decay curve of the peak intensity in EPR spectra for the film C after 1-hour D_2-lamp irradiation at 200 °C. The peak intensity was nearly recovered to that of the as-deposited film at t=0, then decayed with the same feature as shown in Fig. 5(a). However, after 3-hour irradiation the signal intensity was remarkably decreased as shown in fig. 5(d). With the decrease of the signal intensity , the shape of the peak became more alike that shown in fig. 4(a).

Discussion

The effects of the D_2-lamp exposure of the films shown in figs. 1-5. indicate that VUV light can remove the point defects such as ≡Si-H, ≡Si-Si≡, and the defect related to the 880 cm^{-1} peak, accompanying the E' centers generation, and finally can make the film stable to the irradiation. Since without exposure almost no effect was observed, the effect is attributable to the photo-effect rather than the thermal effect. The effects induced were larger in the fast deposited film (C) which had the larger amount of point defects, suggesting that the instability of the films is

partly attributable to the imperfection in the film structure due to incompleteness of the photochemical reaction in such photon-flux limited CVD process. The VUV light may cause additional photo-reactions in the films (including the reaction between partly unreacted Si_2H_6 and residual O_2 as an extreme case) to make more complete SiO_2 network without any other point defects, since there was no change in ≡Si-OH content after irradiation. The effect will be called "optical annealing".

The E' centers are most likely to be generated by the D_2-lamp irradiation during the photochemical reaction both in the preparation and in the irradiation. The number of the points defects decreased by the irradiation was greater by two to three orders of magnitude than that of E' centers generated and the E' centers were finally reduced below the detection limit, whereas the point defects like ≡Si-H still remained in the density of order of 10^{19} cm^{-1}. Although ≡Si-H-related defect is one of possible canidates of the precursors of E' centers under the irradiation [9], only a part of them, being more unstable, tend to turn to E' centers under irradiation.

As for the films B and D (containing F), as-deposited films showed substantially no E' centers and after irradiation ESR signal level of E' centers still remained below the detection limit. that is F-doping suppressed the E' center generation in the films. On the other hand, the film B has only a trace of ≡Si-H-related defects and the film D has reduced but comparable amount of the defects to that for film A as seen in table 1. Thus the incorporation of F into the film seems to have selectively removed the more unstable ≡Si-H-related defects in the films, which we

mentioned above. Such effect of F-doping will be called "chemical annealing". It is noted that the films with F-doping were more resistant to the electron beam than the undoped films or even thermally oxidated films [10]. The microscopic picture of "chemical annealing" is not yet clear but probably related to the chemical reactiveness of F-containing radicals which may occur during the photo-CVD [2]. Another possible explanation to the F-doping effects might be due to an relaxation of SiO_2 network induced by introducing the bond terminators such as ≡Si-F or due to a special role of electronegative nature of F, which could not be ruled out.

Summary

We have studied the effects of the D_2-lamp irradiation on the films prepared by the D_2-lamp photo-CVD with/without F-doping. The irradiation was done by exposing the films to the lamp in vacuum at the same substrate temperature used in the process. It was found that the point defects such as ≡Si-H, ≡Si-Si≡, and the defects related to the 880 cm^{-1} peak in IR spectra were gradually "optically annealed", suggesting incompleteness in the photochemical reaction in the CVD process. The E' centers which were observed in as-deposited films without F-doping were almost extinguished after the long VUV exposure, whereas the films with F-doping originally had no E' centers, even having some point defects, suggesting that F works in forming glass network during deposition as removing the precursors of E' centers, that is, "chemical annealing". The concepts of the optical and the

chemical annealing will help us optimize the photo-CVD processing.

Acknowledgments

We wish to thank professor Hiroshi Imagawa and Mr. Takehiko Arai for measuring VUV spectra of the samples.

References

1. J. Y.-T. Chen, R. C. Henderson, J. T. Hall, and J. W. Peters, J. Electrochem. Soc., **131**, 2146 (1984).
2. H. Nonaka, K. Arai, Y. Fujino, and S. Ichimura, J. Appl. Phys. **64**, 4168 (1988).
3. H. Nonaka, K. Arai, and S. Ichimura, Mat. Res. Soc. Symp. Proc., **131**, 507 (1989).
4. D. L. Griscom, J. Non-Cryst. Solids, **73**, 51 (1985).
5. H. Imai, K. Arai, T Saito, S. Ichimura, H. Nonaka, J. P. Vigouroux, H. Hosono, Y. Abe, and H. Imagawa, in <u>the Physics and Technology of Amorphous SiO_2</u>, 1987, edited by R. Devine, (Plenum, New York, 1988).
6. K. Arai, H. Imai, H. Hosono, Y. Abe, H. Imagawa, Appl. Phys. Lett., **53**, 1891 (1988).
7. J. H. Stathis and M. A. Kastner, Phys. Rev. **B29**, 7079 (1984).
8. H. Nisikawa, R. Nakamura, R. Tohmon, and Y. Ohki, Phys. Rev. **B41**, 7828 (1990).
9. H. Imai, K. Arai, H. Imagawa, H. Hosono, and Y. Abe, Phys. Rev. **B38**, 12772 (1988).
10. H. Nonaka, S. Ichimura, K. Arai, and C. Le Gressus, Surf. Interface Analy. **16**, 435 (1990).

Table 1 Characteristics of the films

Film	Si_2H_6	Si_2F_6	thick-ness	growth rate	[OH]	[H]	[F]	880 cm^{-1}
	/sccm	/sccm	/μm	/$Amin^{-1}$	mol.%	at.%	at.%	/cm^{-1}
A	0.5	0	1.0	50	0.7	0.5	---	8
B	0.5	1.9	1.3	100	<0.1	~0	2.2	~0
C	2.4	0	1.3	342	1.1	0.8	---	54
D	2.4	2.4	1.1	629	<0.1	0.5	2.3	33

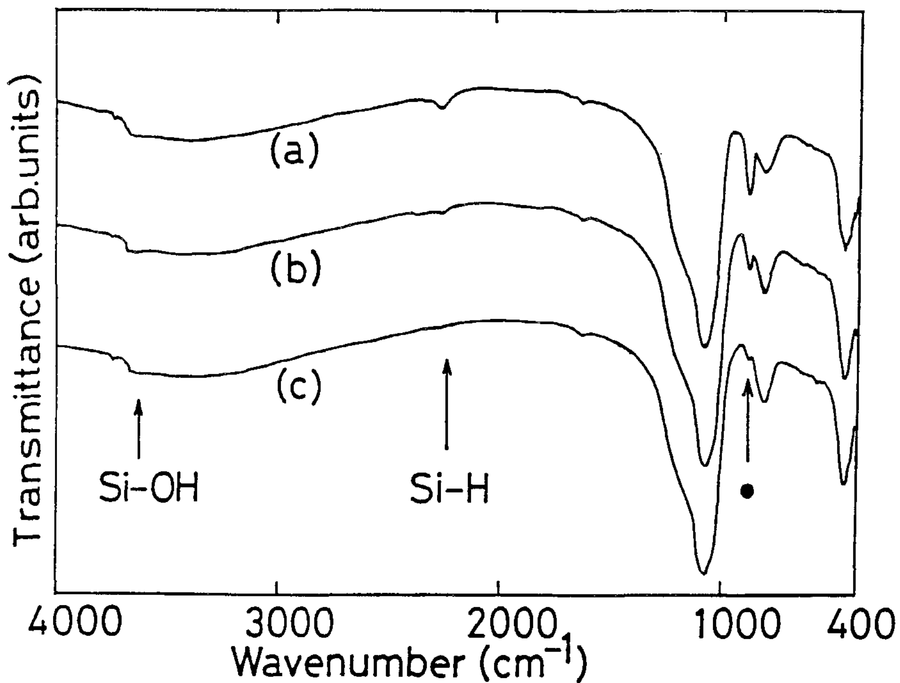

Figure 1. IR spectra of the film C before and after D_2- lamp irradiation; (a) as-deposited, (b) and (c) after 1-hour and 2-hour irradiation, respectively, where ● indicates the 880 cm^{-1} peak.

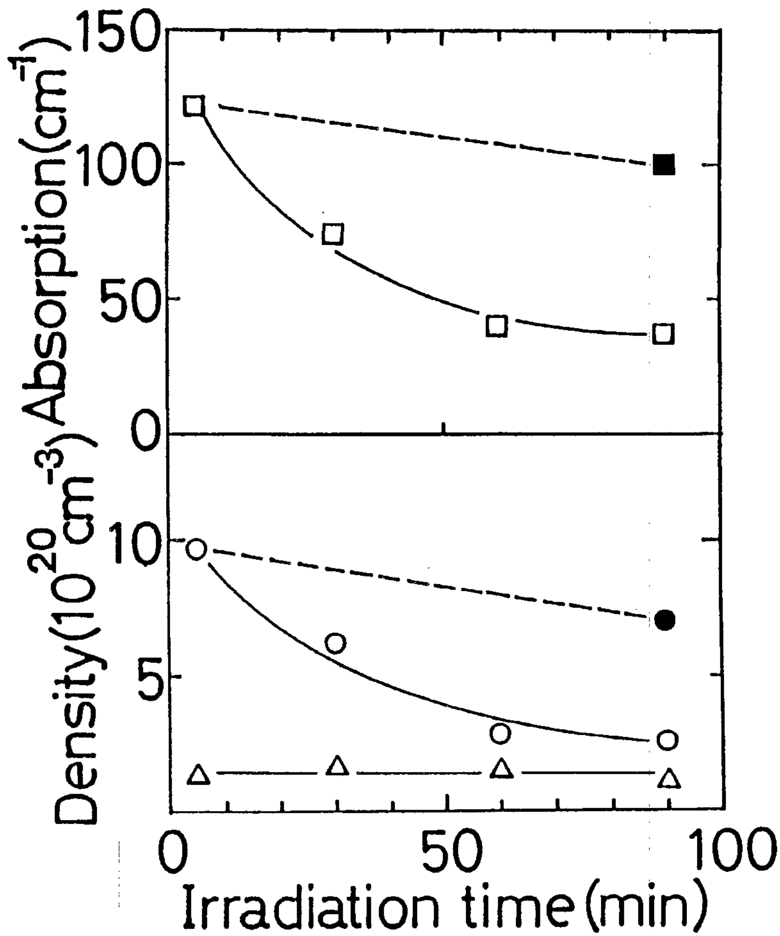

Figure 2. Irradiation-time dependence of the peak height of 880 cm^{-1} band (□) and the defect densities of ≡Si-H (○) and ≡Si-OH (△) for the film C, where filled marks (i.e., ■,●,and ▲) indicate the data for heat treatment without irradiation. Line are only for guides to the eye.

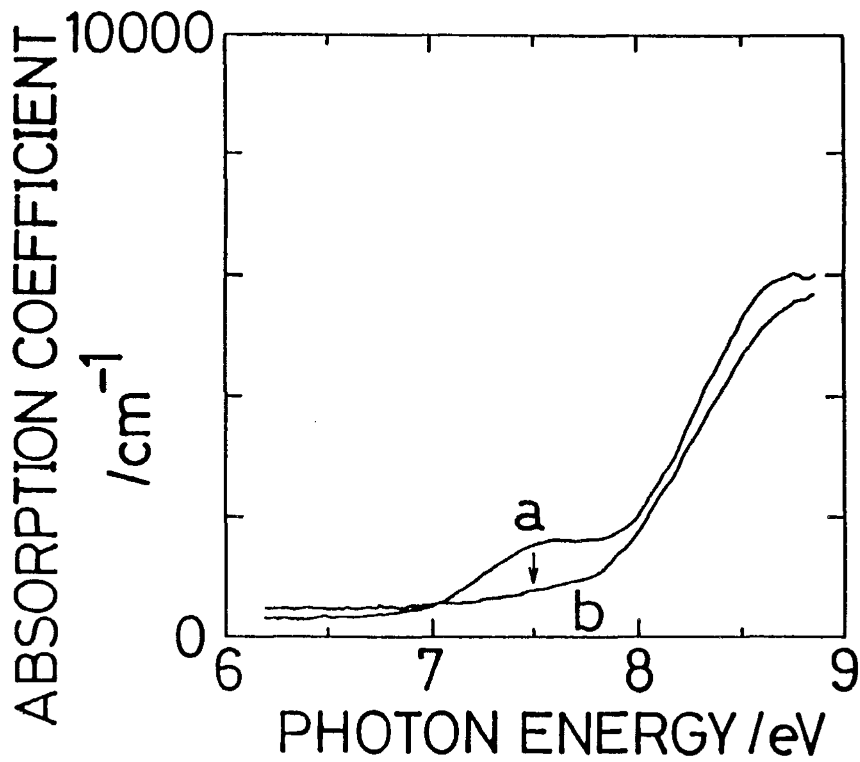

Figure 3. VUV absorption spectra of the film C before and after 1-hour D_2-lamp irradiation.

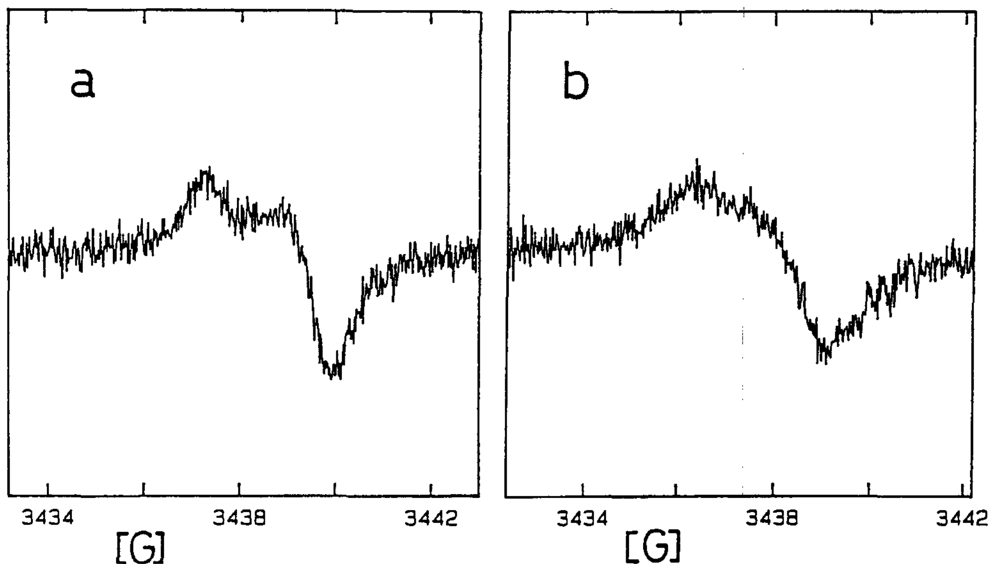

Figure 4. ESR derivative spectra of E' centers in as-deposited films of the films A (a) and C (c); densities of E' centers were estimated to be $\sim 1\times 10^{18}$ cm^{-3} and 2×10^{18} cm^{-3}, respectively.

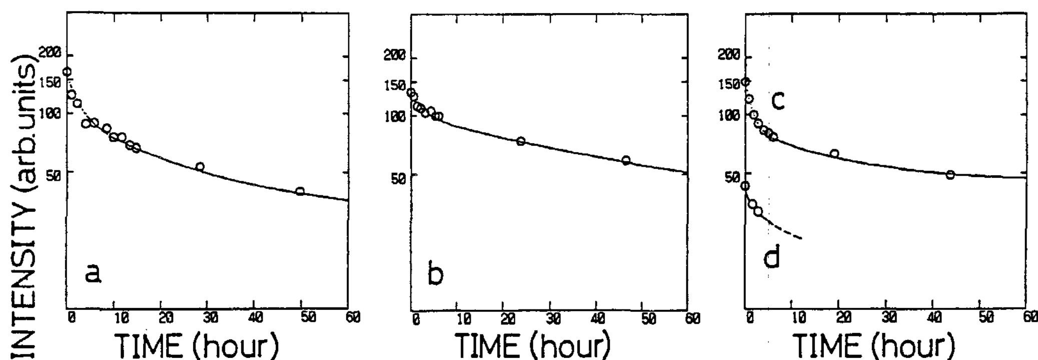

Figure 5. The decay curves for the density of E' centers as a function of time at room temperature for the film C; (a) as-deposited, (b), (c), and (d) after 1-hour, 2-hour, and 3-hour D_2-lamp irradiation, respectively.