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NMR AND ESR STUDIES ON ANNEALING EFFECTS IN a-Si:F:H AND a-Si:H

S. Ueda, M. Kumeda and T. Shimizu

Department of Electronics, Kanazawa University, Kanazawa 920, Japan

Abstract.- Measurements of NMR of F in a-Si:F:H and a-Si:F have been carried out and the results are compared with those of H in a-Si:F:H and a-Si:H. Effects of motional narrowing on the linewidth of F NMR in a-Si:F:H show that some fraction of F is incorporated in the form of SiF_4 or $(\text{SiF}_2)_n$ which tends to move easily. When samples are annealed, the increase in the ESR center density is remarkable in a-Si:F:H and a-Si:H corresponding to the decrease in the H content, but the increase in the ESR center density is rather small in hydrogen free a-Si:F.

Introduction.- Investigations of H and/or F incorporation scheme and their distributions in a-Si are important in order to know the mechanism of reducing the density of defects. NMR is a very powerful technique for such investigations in conjunction with IR measurements. NMR measurements of H in a-Si:H have already been carried out by several workers, and interesting informations have been obtained [1 - 3]. Here, we will report for the first time the results of NMR measurements of F in a-Si:F:H and a-Si:F and compare them with the results of H in a-Si:H and a-Si:F:H. In order to study the relation between incorporated H and/or F and defects, we have also measured ESR for the same samples. Especially, we have investigated how the results of NMR and ESR change with annealing. As a result, we have found interesting difference between the effects of H and F. We also found for some cases the narrowing of NMR lines by raising a measurement temperature. To our knowledge this is also the first report of ESR for fluorinated a-Si. A part of the present work was already published [4].

Experimental.- a-Si:H and a-Si:F films were prepared by rf sputtering and a-Si:F:H films were prepared by dc glow discharge. Preparation conditions are briefly summarized in Table 1. All samples were prepared on aluminium foils which were dissolved off before measurements. NMR measurements were performed with a pulse NMR

Table 1. Sample preparation conditions

	a-Si:H	a-Si:F	a-Si:F:H
Preparation method	rf sputtering	rf sputtering	dc glow discharge
Gas	Ar + H ₂	Ar + SiF ₄	SiF ₄ + H ₂
Gas pressure	0.11 Torr	0.04 Torr	1.0 Torr
Gas fraction	40 % H ₂	6 % SiF ₄	12.5 % H ₂
Substrate temperature	water cooled	350°C	300°C

spectrometer at 16 MHz at 4.2 K, 77 K and room temperature. The free induction decay (FID) following a 90° pulse were averaged by computer accumulation and Fourier-transformed. ESR measurements were performed with a JEOL PE 3X spectrometer at room temperature. NMR and ESR measurements were made for the same sample after each step of isochronal annealing for 1 h in a vacuum of $< 10^{-5}$ Torr.

Results.- The NMR spectra of H in either a-Si:H or a-Si:F:H at 77 K can be decomposed into a broad Gaussian line and a narrow Lorentzian line in agreement with the

previous works[1, 2]. The NMR spectra of F at 77 K in a-Si:F are also composed of the two components, but those in a-Si:F:H have no narrow component (less than several % of the broad component in the intensity ratio). The contents of H and F contributing to the component lines are shown in Table 2 together with the NMR linewidths.

Table 2. H and F contents contributing to the broad and narrow NMR lines at 77 K in as-deposited films. Full width half maximum (FWHM) of these lines are shown in parentheses.

	H content (at. %)		F content (at. %)	
	broad (FWHM,kHz)	narrow(FWHM,kHz)	broad (FWHM,kHz)	narrow(FWHM,kHz)
a-Si:H	20.9 (24.0)	1.1 (3.5)	—	—
a-Si:F:H	12.2 (23.4)	2.4 (5.3)	13.6 (23.2)	—
a-Si:F	—	—	12.4 (22.0)	4.4 (8.0)

Changes with annealing of H contents obtained from NMR at 77 K are shown in Fig. 1. The H content contributing to the broad line decreases with annealing temperature faster than that contributing to the narrow line. Changes with annealing of F contents obtained from NMR at 77 K are shown in Fig. 2. A narrow line appears and increases in F spectra of a-Si:F:H by annealing above 450°C, but the total F content does not change with annealing. The F NMR spectra in a-Si:F does not appreciably change with annealing. Figure 3 shows the temperature dependence of NMR linewidths.

Changes with annealing of the center densities of the ESR signal due to dangling bonds are shown in Fig. 4. In a-Si:H and a-Si:F:H, the ESR center density increases by two orders of magnitude by annealing. In a-Si:F, however, the increase is not so prominent.

Discussion.— The origin of the broad and narrow lines of H NMR spectra in a-Si:H has been discussed by several authors, and the narrow line is considered to originate from H dispersed in the form of silicon monohydride (SiH) and the broad line from closely gathered H[3, 5, 6]. The consideration is based on the fact that motional narrowing is not a major factor in the linewidth determination and temperature independent linewidth is dominated by dipolar interaction.

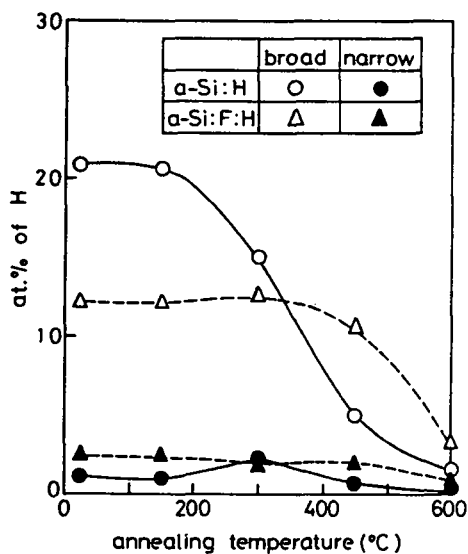


Fig. 1. Changes with annealing of H contents in a-Si:H and a-Si:F:H obtained from NMR at 77 K.

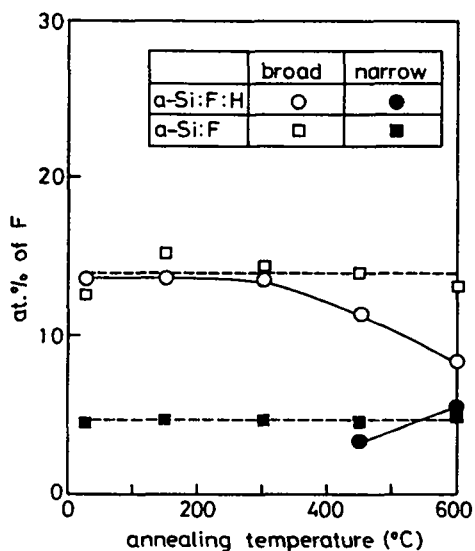


Fig. 2. Changes with annealing of F contents in a-Si:F and a-Si:F:H obtained from NMR at 77 K.

In the present case, however, the linewidths of H and F NMR were found to change in some cases with temperature as shown in Fig. 3. Especially, F NMR spectra in a-Si:F:H annealed at 600°C exhibit the prominent temperature dependence: The spectrum at 4.2 K is a single broad line, that at 77 K is a superposition of a broad and a narrow lines and that at room temperature is a single narrow line. Hence, the narrow line in this case should be motional narrowed one, and is considered to originate from F which is easy to move and not from dispersed F. F NMR spectrum in as-deposited a-Si:F:H also exhibits the effect of motional narrowing although the effect is not so prominent. These facts suggest that F in a-Si:F:H takes movable forms with different degrees of feasibility for movement. The infrared absorption peak at 1010 cm^{-1} in fluorinated a-Si is attributed to SiF_4 [7] or $(\text{SiF}_2)_n$ [8] groups. These groups may be easy to move to cause the motional narrowing. Since the annealing is known to increase the infrared absorption peak at 1010 cm^{-1} for a-Si:F:H[7], it is reasonable that the narrowing effect is more prominent in the annealed films. The linewidths of F NMR at 4.2 K, which will be free from motional narrowing, coincide for as-deposited and annealed a-Si:F:H. The fact shows that the dipolar interaction remains unchanged after H evolves by annealing, which indicates that the dipolar interaction between F and H does not contribute to the linewidth of F NMR. Therefore, F and H are considered not to be located closely in a-Si:F:H.

F NMR spectra in a-Si:F do not exhibit the motional narrowing effect as shown in Fig. 3 in spite of the presence of a large amount of SiF_4 or $(\text{SiF}_2)_n$ judging from the infrared absorption spectra[9]. Therefore, it is speculated that there exist SiF_4 or $(\text{SiF}_2)_n$ groups which are easy to move and those which are not easy to move depending on the environment. The invariance of the F NMR spectrum for a-Si:F with annealing is consistent with the fact that the infrared absorption spectrum does not appreciably change with annealing[10]. Since both the F NMR and infrared absorption spectra for a-Si:F:H change at temperature at which H evolves, the movement of H atoms is considered to stimulate the change of F incorporation scheme.

H NMR linewidth for a-Si:F:H has only a small effect of narrowing even at room temperature presumably because the film does not contain an appreciable amount of H

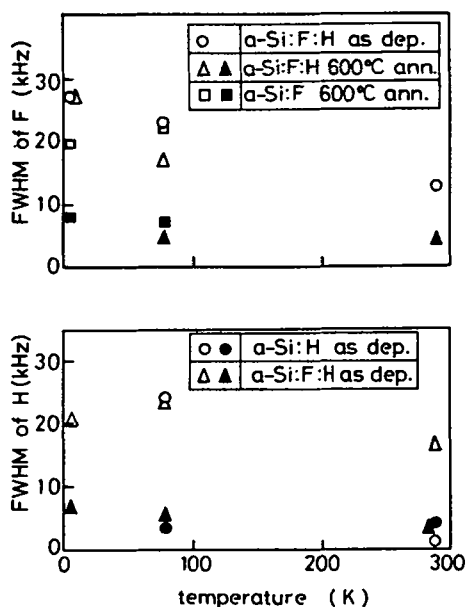


Fig. 3. Temperature dependence of the linewidth of H and F NMR in a-Si:H, a-Si:F:H and a-Si:F as-deposited and annealed at 600°C.

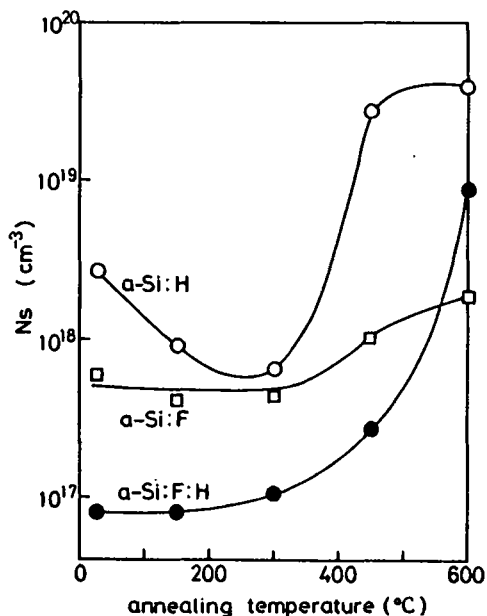


Fig. 4. Changes with annealing of the center density N_s of the ESR signal due to dangling bonds in a-Si:H, a-Si:F:H and a-Si:F.

in the form of movable $(\text{SiH}_2)_n$. The fact is consistent with the fact that for this film the infrared absorption peak is mainly at 2000 cm^{-1} indicating the form of SiH . Thus, the linewidth at 77 K is considered to be one which is free from motional narrowing.

In contrast, H NMR linewidth for as-deposited a-Si:H exhibits a prominent effect of narrowing at room temperature, indicating that the film contains a large amount of H in the form of $(\text{SiH}_2)_n$ in agreement with the fact that the infrared absorption peak is mainly at around 2100 cm^{-1} for this film. The presence of the large amount of H in the form of $(\text{SiH}_2)_n$ may explain the large ESR center density in this film as shown in Fig. 4[11].

It is found from Figs. 1 and 4 that the increase in the ESR center density by annealing corresponds to the decrease in the content of H in a-Si:H and a-Si:F:H. As expected, the increase in the ESR center density by annealing is small for hydrogen free a-Si:F. The origin of the small increase in the ESR center density is not clear, but it might be caused during the cooling process after annealing because a special care was not taken to avoid a rapid cooling.

In conclusion, we measured how the NMR of F and H and the ESR change by annealing in a-Si:F, a-Si:F:H and a-Si:H. The temperature dependence of the NMR linewidth was measured, and the motional narrowing was seen in some cases. The results are correlated with the presence of $(\text{SiF}_2)_n$ or SiF_4 and $(\text{SiH}_2)_n$ which are easy to move. We also found that hydrogen free a-Si:F is much more stable against heating than a-Si:H and a-Si:F:H.

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