

Title	Passivation quality of a stoichiometric SiN <sub>x</sub> single passivation layer on crystalline silicon prepared by catalytic chemical vapor deposition and successive annealing
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Citation	Japanese Journal of Applied Physics, 53(2): 022301-1-022301-6
Issue Date	2014-01-22
Type	Journal Article
Text version	author
URL	<a href="http://hdl.handle.net/10119/12140">http://hdl.handle.net/10119/12140</a>
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Description	

**Passivation quality of a stoichiometric SiN<sub>x</sub> single passivation layer on  
crystalline silicon prepared by catalytic chemical vapor deposition  
(Cat-CVD) and successive annealing**

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**Abstract**

A silicon nitride (SiN<sub>x</sub>) single passivation layer, prepared by catalytic chemical vapor deposition (Cat-CVD) and successive annealing, shows high passivation quality on crystalline silicon (c-Si) wafers. Effective minority carrier lifetime ( $\tau_{eff}$ ) monotonically increases with increase in deposition substrate temperature ( $T_s$ ) for samples passivated by as-deposited SiN<sub>x</sub> films, while more significant increase in  $\tau_{eff}$  by annealing tends to be seen for the samples with SiN<sub>x</sub> films deposited at lower  $T_s$ . The  $\tau_{eff}$  obtained for the sample deposited at  $T_s$  of 100 °C and pressure ( $P$ ) of 10 Pa, after annealing at 350 °C for 30 min in

$N_2$ , is about 3.0 ms, corresponding to a surface recombination velocity (SRV) of 5.0 cm/s. According to measured H content and fixed charge density ( $Q_f$ ) in the  $SiN_x$  films,  $Q_f$  partly contributes to the passivation quality of the films particularly before annealing, while H content plays an important role on improving passivation quality of the films after annealing.

## 1. Introduction

An excellent coating layer on a single crystalline silicon (c-Si) surface is essential for producing high-efficiency c-Si solar cells. Such a coating layer needs high optical transparent property and high passivation quality for reducing the recombination of photo-generated carriers at c-Si surface [1]. Catalytic chemical vapor deposition (Cat-CVD), often also referred to as hot-wire CVD [2], is a method of depositing thin films by decomposing gas molecules on a heated catalyzing wire. Cat-CVD can realize plasma-damage-less deposition, and high-quality film/c-Si interface property is thus expected. We have so far demonstrated that silicon nitride ( $\text{SiN}_x$ )/amorphous silicon (a-Si) stacked passivation layers prepared by Cat-CVD on c-Si realize an extremely low surface recombination velocity (SRV) of  $< 1.5 \text{ cm/s}$  [3]. However, parasitic absorption in the a-Si film may result in reducing c-Si solar cell efficiency. In order to overcome this problem, in previous study, we inserted Si-rich  $\text{SiN}_x$  film instead of a-Si film. The obtained results show that  $\text{SiN}_x$ /Si-rich  $\text{SiN}_x$  stacked layers as passivation films on c-Si achieves a SRV of as low as  $3 \text{ cm/s}$  with 30 % improvement in transparency at a wavelength of 400 nm compared to that of  $\text{SiN}_x$ /a-Si films [4]. We have also found that annealing process and H content play important roles in improving the passivation quality of the stacked layers [5]. Ideally, further improvement in transparency should be achieved, because the Si-rich  $\text{SiN}_x$  films still have considerable light absorption. Therefore, in this study, we study on the passivation quality of a Cat-CVD stoichiometric (refractive index of  $\sim 2$ )  $\text{SiN}_x$  single layer on c-Si.  $\text{SiN}_x$  films have

sufficiently high transparency and have been widely used as passivation and anti-reflective coating layers on c-Si [6-7]. The obtained results demonstrate that  $\tau_{eff}$  is improved significantly by annealing. Samples prepared at lower substrate temperature during deposition ( $T_s$ ) show more significant improvement in  $\tau_{eff}$  by annealing, probably due to higher H content. Highest  $\tau_{eff}$  obtained for the sample deposited at  $T_s$  of 100 °C and pressure ( $P$ ) of 10 Pa is about 3 ms, corresponding to SRV of 5.0 cm/s. Passivation quality of SiN<sub>x</sub> films on c-Si have been investigated by many researchers [6-17]. Most of SiN<sub>x</sub> films were prepared by plasma-enhanced CVD (PECVD) and low surface recombination velocities have been achieved. It has been reported that a low SRV of 2 cm/s can be achieved when PECVD SiN<sub>x</sub> films are deposited on 3-5 Ωcm n-type Si wafer [11]. Schmidt *et al.* have achieved SRV lower than 10 cm/s for 1.5 Ωcm p-type Si wafers passivated by stoichiometric SiN<sub>x</sub> films [14]. There are, however, few reports for the passivation of c-Si surface using Cat-CVD SiN<sub>x</sub> films [16, 17]. The work of Cat-CVD SiN<sub>x</sub>/c-Si was already published by our group in 2003 [17]. However, at that time, the effect of annealing and the role of H content in the films were not noticed, and the results obtained are not as good as those shown in this paper.

## **2. Experimental procedure**

### **2.1. Sample preparation**

After cleaning c-Si wafers in diluted (5%) hydro-fluoric acid (HF) solution to remove native oxide on c-Si surface, 100-nm-thick SiN<sub>x</sub> films were deposited by Cat-CVD. SiN<sub>x</sub> films with an approximately same refractive index of  $\sim 2$  were deposited at various  $T_s$

and  $P$ .  $\text{SiN}_x$  films were also deposited onto glass substrates for optical transmission measurements. We also formed 100-nm-thick  $\text{SiN}_x$  films on quartz substrates to measure defect density of the films. The deposition conditions of the  $\text{SiN}_x$  films are summarized in Table I. To measure H content by Fourier-transform infrared spectroscopy (FTIR),  $\text{SiN}_x$  films with a thickness of about 100 nm were deposited on c-Si substrates with a high resistivity of 3460  $\Omega\text{cm}$  [18]. Fixed charge density ( $Q_f$ ) of  $\text{SiN}_x$  films was calculated based on the results of capacitance–voltage measurement for metal-insulator-semiconductor (MIS) structures [5, 19]. Firstly, a 100-nm-thick Aluminum (Al) layer was deposited on one side of 2  $\Omega\text{cm}$  p-type floating-zone (FZ)-grown c-Si wafers by evaporation. The Al/c-Si structure was annealed at 400 °C for 15 min in  $\text{N}_2$  atmosphere to obtain Ohmic contact.  $\text{SiN}_x$  films were then deposited on the other surface of the c-Si wafers. Finally, 2-mm-diameter Al electrodes were evaporated on the  $\text{SiN}_x$  layers through a hard mask. Some samples were annealed at 350 °C for 30 min before the evaporation of the circular Al electrodes in order to investigate the effect of annealing on  $Q_f$ . 100-nm-thick  $\text{SiN}_x$  films were deposited on both sides of 290- $\mu\text{m}$ -thick n-type (100) FZ Si wafers with a resistivity of 2.5  $\Omega\text{cm}$  to measure effective minority carrier lifetime ( $\tau_{eff}$ ). Samples were then annealing in  $\text{N}_2$  atmosphere to investigate the effect of annealing on the passivation quality of  $\text{SiN}_x$  films.

## 2.2. Characterization of prepared samples

The thickness and refractive index of all the samples were measured on J. A. Woollam, HS-190<sup>TM</sup> spectroscopic ellipsometer, using Cauchy model for data analysis [20].

The film density was measured by X-ray reflectivity [20]. Atomic contents of the SiN<sub>x</sub> films were measured by X-ray photoelectron spectroscopy (XPS). The transmission spectra of SiN<sub>x</sub> films were measured in a Shimadzu, UV-3150 ultraviolet-visible-near infrared spectrophotometer. Defect density was calculated by using electron spin resonance (ESR) [21]. In order to investigate the passivation quality of the SiN<sub>x</sub> layers on c-Si, we carried out microwave photo-conductivity decay ( $\mu$ -PCD) measurement (Kobelco LTA-1510EP) using a 904 nm wavelength pulse laser with a photon density of  $5 \times 10^{13} \text{ cm}^{-2}$  [22]. The method to determine SRV has been described in a previous paper [4].

### 3. Results and discussion

#### 3.1. Passivation quality of SiN<sub>x</sub> films on c-Si wafers

The effect of annealing on the passivation quality of various SiN<sub>x</sub> films has also been reported by many authors [9, 23, 24]. It is demonstrated that the rearrangement of SiN<sub>x</sub> structure and H diffusion during annealing can terminated defects at SiN<sub>x</sub>/c-Si interface, thus, which results in improvement in passivation quality. In previous study, we also found that passivation quality of Cat-CVD SiN<sub>x</sub>/Si-rich SiN<sub>x</sub> films on c-Si wafer is enhanced significantly after annealing [4, 5]. In this study, we thus firstly investigate the effect of annealing temperature ( $T_a$ ) and annealing time ( $t_a$ ) on passivation quality of stoichiometric SiN<sub>x</sub> single films on c-Si wafers. In this experiment, stoichiometric SiN<sub>x</sub> films were deposited at  $T_s$  of 50, 100, and 150 °C at a fixed  $P$  of 10 Pa. Figure 1(a) shows  $\tau_{eff}$  of SiN<sub>x</sub> films deposited at  $T_s$  of 50, 100, and 150 °C at a fixed  $P$  of 10 Pa, and H concentration of those at a  $T_s$  of 150 °C as functions of  $T_a$  with a fixed duration of 30 min.

$\tau_{eff}$  increases with increase in  $T_a$ , reaches maximum value, and then, decreases dramatically. The improvement in  $\tau_{eff}$  on  $T_a$  may be related to the diffusion of H atoms in the films and the termination of defect at SiN<sub>x</sub>/c-Si interface by H atoms during annealing.  $T_a$  of 350 °C might be a proper temperature to support sufficient energy for H diffusion and defect-termination, resulting in the formation of good-quality SiN<sub>x</sub>/c-Si interface. Figure 1(b) shows FTIR spectra of SiN<sub>x</sub> films deposited at a  $T_s$  of 150 °C at various  $T_a$  for 30 min. Increase in H content after annealing at 350 °C, shown in the FTIR spectra, is due to increase in the number of Si-H bonds. This suggests that H atoms diffuse to a c-Si substrate and recombine with dangling bonds on c-Si surface, resulting in increase in Si-H bonds. However, at excessively high  $T_a$ , H atoms can be released to environment and do not terminate defects, and  $\tau_{eff}$  is low [15-25]. As shown in Figs. 1(a) and 1(b), H concentration and Si-H bonding density decrease dramatically at  $T_a$  of 450 °C, which is a clear evidence for H loss to environment.

Passivation quality of SiN<sub>x</sub> films can be stable for long time annealing, as shown in Fig. 1(c). Degradation of  $\tau_{eff}$  at very long  $t_a$  may be due to H desorption caused by breaking of Si-H bonds and N-H bonds, when sample was annealed for very long time. In next steps, we used  $T_a$  of 350 °C and  $t_a$  of 30 min as ideal annealing conditions for all samples for high passivation quality improvement after annealing.

Figure 2 shows  $\tau_{eff}$  of c-Si wafers with SiN<sub>x</sub> films as functions of  $T_s$  and  $P$  before and after annealing at a  $T_a$  of 350 °C for 30 min.  $\tau_{eff}$  of as-deposited film before annealing increases with increase in  $T_s$ , while decreases with increase in  $P$ . The low  $\tau_{eff}$  obtained at



low  $T_s$  is considered to be due to low film quality or the effect of etching by atomic H, which is known to occur more significantly at low  $T_s$  [26]. The effect of etching may be negligible, because at low  $T_s$  with high deposition rate, rapid covering of c-Si surface with  $\text{SiN}_x$  films can suppress H etching effect. However, films deposited with high deposition rate (at low  $T_s$  and high  $P$ ) might lead to the insufficient coverage of c-Si surface, resulting in decrease in  $\tau_{eff}$ . The reason of low  $\tau_{eff}$  at these conditions can also be explained by low  $Q_f$ , which will be discussed later. Figure 2 also shows that  $\tau_{eff}$  is improved significantly after annealing. For annealed samples,  $\tau_{eff}$  reaches its highest value at  $T_s$  of 100 °C, then it decreases with increase in  $T_s$ , while  $\tau_{eff}$  increases with increase of  $P$  and reaches a saturated value at  $P \geq 10$  Pa.  $\tau_{eff}$  obtained for the as-deposited sample at  $T_s$  of 100 °C and  $P$  of 10 Pa is about 0.1 ms, corresponding to a SRV of 144 cm/s.  $\tau_{eff}$  of the same samples increases up to 3 ms after annealing, which corresponds to a SVR of 5.0 cm/s.

Figure 3 shows the optical transmission spectra of  $\text{SiN}_x$  films deposited at  $T_s$  of 150 °C and  $P$  of 10 Pa before and after annealing at a  $T_a$  of 350 °C for 30 min, simulated value of transmission of a  $\text{SiN}_x$  film is also shown. The appearance of fringe in transmission spectra is probably due to the effect of interference. We also plotted a simulated transmission spectrum of a  $\text{SiN}_x$  film evaluated by using Beer's equation [27], in which absorption coefficient and film thickness obtained by analyzing spectroscopic ellipsometry data using by the Cauchy mode are used. The stoichiometric  $\text{SiN}_x$  films show sufficiently high optical transmission even in short wavelength region, unlike a-Si or Si-rich  $\text{SiN}_x$  films [3, 4]. Furthermore, the transparency of the films does not significantly change by annealing. The very small difference in the transparency in a short wavelength region

might be related to the slight change of network structures such as Si-H bonds by annealing. The improvement in the passivation quality of stoichiometric SiN<sub>x</sub> films without decreasing transparency after annealing is of great advantage for the application of the films in c-Si solar cell fabrication.

### 3.2. Role of H content and fixed charge density on passivation quality of films

In order to investigate the origin of the high passivation quality of SiN<sub>x</sub> films, we evaluated H content and  $Q_f$  in the films [6, 12, 15]. Positive fixed charges send minority carriers (holes) far away from an n-type c-Si surface. They can therefore reduce the trapping probability of minority carriers (holes) at defects near c-Si surface. Another way to reduce recombination is the termination of defects by H atoms. Figure 4 shows SiN<sub>x</sub> film density and H concentration in SiN<sub>x</sub> films before and after annealing at a  $T_a$  of 350 °C for 30 min as functions of  $T_s$  and  $P$ . H concentration of SiN<sub>x</sub> films were determined from FTIR spectra, parts of which are shown in Fig. 5. H concentration of SiN<sub>x</sub> films decreases with increase in  $T_s$ , which is properly due to more enhanced H desorption during deposition at higher  $T_s$ . Higher  $P$  leads to larger amount of H in SiN<sub>x</sub> films, while Si-H/N-H bond density ratio is kept almost constant. Compared to SiN<sub>x</sub> films deposited at higher  $T_s$ , the SiN<sub>x</sub> film deposited at a  $T_s$  of 50 °C have a Si-H peak shifted to lower wavenumber. This might be related to the lower electro-negativity of backbone Si atoms for SiN<sub>x</sub> films with lower N content [28]. Si-H bonding increases much with decrease in  $T_s$  and increase in  $P$ , while N-H bonding slightly tends to increase with increase in  $T_s$  and  $P$ . Samples with high H content show more effective increase in  $\tau_{eff}$  by annealing, and H may contribute to improvement in

$\tau_{eff}$ . Sample prepared at  $T_s < 100$  °C, exceptionally shows less significant improvement in  $\tau_{eff}$  even with high H content. This may be due to low film density. During annealing, low-density materials would release H in the molecular form, while denser films would make H desorption slower [16, 28]. Here,  $\text{SiN}_x$  film density is  $\sim 2.1 \text{ g/cm}^3$  for the sample deposited at  $T_s$  of 50 °C, while it is more than  $2.4 \text{ g/cm}^3$  for sample deposited at  $T_s \geq 100$  °C, as shown in Fig. 4. H atoms might thus be released to atmosphere during annealing and not contribute to passivation, resulting in a low  $\tau_{eff}$ . Samples formed at higher  $T_s$  with much higher film density can suppress H desorption, and H atoms can significantly contribute to passivating defects on the c-Si surface. We also similarly explain improvement in  $\tau_{eff}$  after annealing samples deposited at various  $P$ . Improvement in  $\tau_{eff}$  may be related to H concentration and density of the films. Most of films deposited at various  $P$  have sufficiently high film density and samples deposited at higher  $P$  have higher H concentration, and passivation quality is improved more significantly after annealing for  $\text{SiN}_x$  films deposited at high  $P$ .

Figure 6 shows N content and  $Q_f$  of  $\text{SiN}_x$  films as functions of  $T_s$  and  $P$  before and after annealing at a  $T_a$  of 350 °C for 30 min.  $Q_f$  increases with increase in  $T_s$ , and reaches highest value at a  $T_s$  of 250 °C, then it slightly decreases at 300 °C.  $Q_f$  of  $7.5 \times 10^{11} \text{ cm}^{-2}$  is quite low for the  $\text{SiN}_x$  films deposited at  $T_s$  of 50 °C, which can be one of possible reasons to explain low  $\tau_{eff}$  for sample deposited at low  $T_s$  and high  $P$ , as shown in Fig. 2. N content increases with increasing  $T_s$  or decreasing  $P$ . It may be correlative to film density, which is related to the migration of radicals on c-Si surface during deposition. The origin of fixed

charges is known to be Si-dangling bond defects whose configuration is  $N_3 \equiv Si^+$  in  $SiN_x$  films, generally called  $K^+$  centers [15, 21, 29, 30]. From Fig. 6, we can also see that  $Q_f$  is proportional to N content in films. It is in good agreement with the suggestion of the origin of fixed charges as mentioned above. Decrease in  $Q_f$  at  $T_s$  of 300 °C might be related to decrease in Si-dangling bonds in  $SiN_x$  films when they were deposited at sufficiently high  $T_s$ .

Figure 7 shows the defect density of  $SiN_x$  films as functions of  $T_s$  and  $P$  before and after annealing at a  $T_a$  of 350 °C for 30 min. One can see lower defect density at higher  $T_s$ . One possible reason for this tendency is more enhanced migration of radicals on c-Si substrate during deposition at higher  $T_s$ . Dangling bonds in  $SiN_x$  films is related to Si-dangling bonds back bonded to three N atoms,  $N_3 \equiv Si\cdot$ , generally called  $K^0$  centers, which consist of an unpaired electron and are observable by ESR [12, 13]. The defect density of  $SiN_x$  films deposited at low  $T_s$  may thus be related to N content in the films. Defect density of the  $SiN_x$  film deposited at low  $T_s$  is relatively low, and higher  $P$  leads to lower defect density, as shown in Fig. 7. These trends are same as those of N content in  $SiN_x$  films. It has been reported, by Lelièvre *et al.*, that H atoms can combine with Si-dangling bond defects ( $K^+$  centers) during annealing, resulting in the formation of neutralized dangling bonds (K centers) [15]. Other group has also reported that  $K^0$  centers will be converted to  $K^+$  and  $K^-$  centers by annealing [30]. In this study, defect density ( $K^0$  centers) and fixed charge  $K^+$  decreases significantly by annealing, as shown in Figs. 6 and 7. These are clear evidences of defect termination by H in  $SiN_x$  films during annealing. We can guess that H

can terminate defects not only inside  $\text{SiN}_x$  but also at  $\text{SiN}_x/\text{c-Si}$  interface during annealing, and  $\tau_{eff}$  is improved significantly by annealing. The samples with lower film density and higher H content show small change in  $Q_f$  and defect density by annealing, as shown in Figs. 6 and 7. This may be because denser films can prevent more hydrogen atoms from releasing to atmosphere during annealing, which results in more H atoms combine with Si-dangling bonds in  $\text{SiN}_x$  films, and more decrease in  $Q_f$  and defect density. This consideration cannot explain the change of defect density and  $Q_f$  by annealing for samples deposited at high  $T_s$ . The difference of H content in the films might be related to this phenomenon.

Finally, we discuss the origin of remarkable high  $\tau_{eff}$  of Si wafers passivated by  $\text{SiN}_x$  films. The value of  $Q_f$  on the order of  $10^{12} \text{ cm}^{-2}$  is high enough to express field-effect passivation. Fixed charge in  $\text{SiN}_x$  films can thus partially contribute to suppression in surface recombination.  $Q_f$ , however, decreases after annealing, while  $\tau_{eff}$  is significantly improved by annealing. This fact indicates that not  $Q_f$  but defect termination by H atoms mainly contributes to improvement in the passivation quality of  $\text{SiN}_x$  films, which is consistent with our previous results [5].

#### 4. Conclusions

Stoichiometric  $\text{SiN}_x$  single films prepared by Cat-CVD have good passivation quality on c-Si wafers. Samples prepared at lower  $T_s$  and high  $P$  show more significant improvement in  $\tau_{eff}$  by annealing. The possible reasons for this effect are the diffusion of H atoms in the films and the termination of defect at  $\text{SiN}_x/\text{c-Si}$  interface by H atoms during

annealing. H content in the films thus plays an important role on improving  $\tau_{eff}$ . The highest  $\tau_{eff}$  obtained is 3 ms, corresponding to SRV of as low as of 5.0 cm/s. This study highlights the application of the Cat-CVD stoichiometric SiN<sub>x</sub> films as passivation layers for c-Si solar cells.

### Acknowledgement

This work is supported by JST CREST program.

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## Figure captions

Fig. 1. (a)  $\tau_{eff}$  of SiN<sub>x</sub> films deposited at  $T_s$  of 50, 100, and 150 °C at a fixed  $P$  of 10 Pa, and H concentration of those at a  $T_s$  of 150 °C as functions of  $T_a$  with a fixed duration of 30 min. (b) FTIR spectra of SiN<sub>x</sub> films deposited at a  $T_s$  of 150 °C at various  $T_a$  for 30 min. (c)  $\tau_{eff}$  as a function of  $t_a$  at a  $T_a$  of 350 °C.

Fig. 2.  $\tau_{eff}$  as functions of  $T_s$  and  $P$  before and after annealing at a  $T_a$  of 350 °C for 30 min in N<sub>2</sub> atmosphere.

Fig. 3. Transmission spectra of SiN<sub>x</sub> films deposited at  $T_s$  of 150 °C and  $P$  of 10 Pa before and after annealing at a  $T_a$  of 350 °C for 30 min, simulated value of transmission of a SiN<sub>x</sub> film is also shown.

Fig. 4. Film density and H concentration of SiN<sub>x</sub> films before and after annealing at a  $T_a$  of 350 °C for 30 min as functions of  $T_s$  and  $P$ .

Fig. 5. FTIR spectra of SiN<sub>x</sub> films deposited at various  $T_s$  and  $P$ .

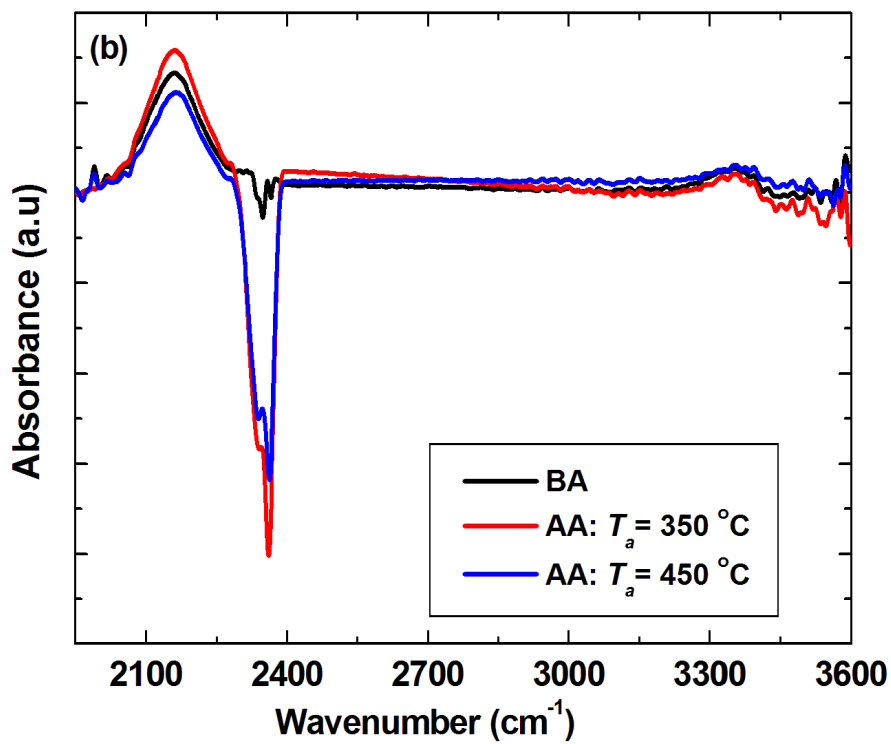
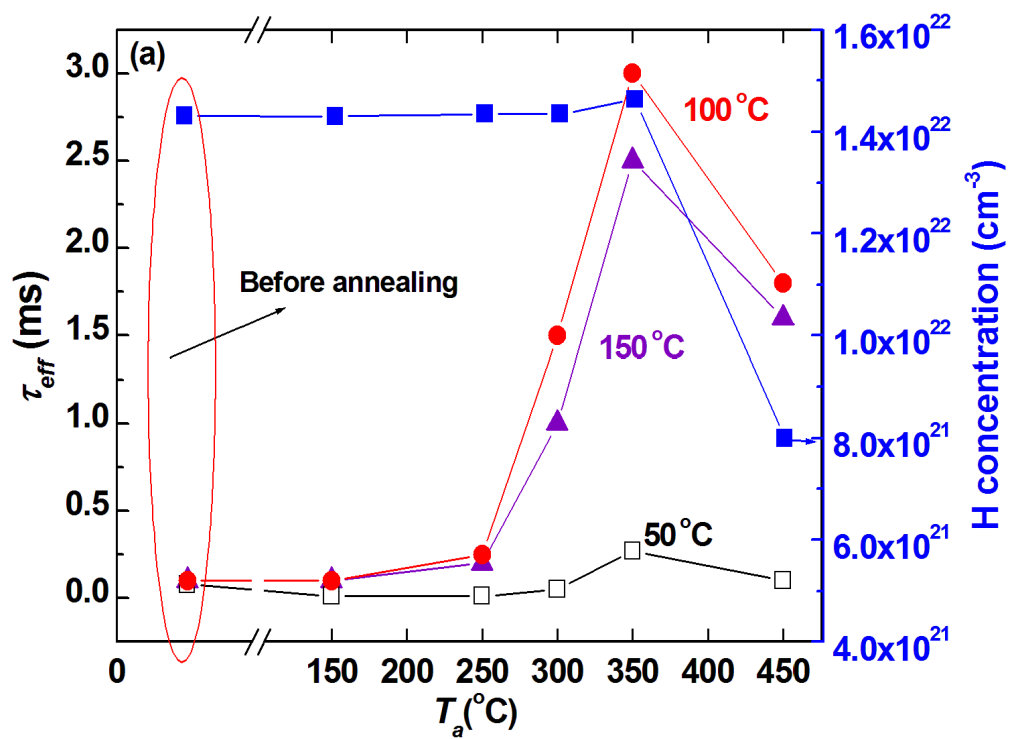
Fig. 6. N content and  $Q_f$  of SiN<sub>x</sub> films as functions of  $T_s$  and  $P$  before and after annealing at a  $T_a$  of 350 °C for 30 min.

Fig. 7. Defect density of SiN<sub>x</sub> films as functions of  $T_s$  and  $P$  before and after annealing at a  $T_a$  of 350 °C for 30 min.

**Table I.** Deposition conditions of SiN<sub>x</sub> films. Refractive index and thickness of deposited films are also summarized.

Film	SiH <sub>4</sub> (sccm)	NH <sub>3</sub> (sccm)	Gas pressure (Pa)	T <sub>s</sub> (°C)	T <sub>cat</sub> (°C)	Time deposition (s)	Refractive index	Thickness (nm)
1	8.7	150	10	50	1800	144	2.01	103
2	8.4	150	10	70	1800	160	2.04	103
3	8.2	150	10	90	1800	180	2.02	103
4	8	150	10	100	1800	190	1.99	103
5	7	150	10	150	1800	220	2.01	98
6	6	150	10	200	1800	240	1.99	100
7	5.6	150	10	250	1800	250	2.06	102
8	5.3	150	10	300	1800	300	2.02	96
9	3	60	3.5	150	1800	520	2.01	102
10	5.5	150	7	150	1800	300	1.99	102
11	8.5	150	13	150	1800	180	2.02	101
12	9.5	150	15	150	1800	170	2.01	98
13	11.5	150	18	150	1800	130	2.01	105

Fig. 1



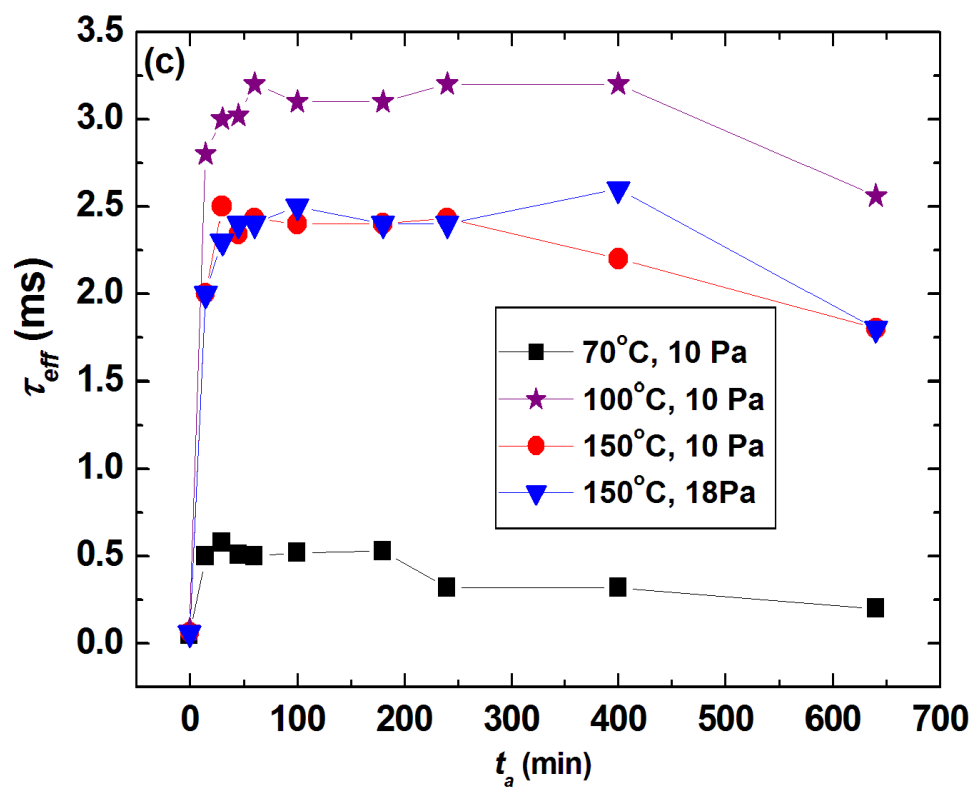
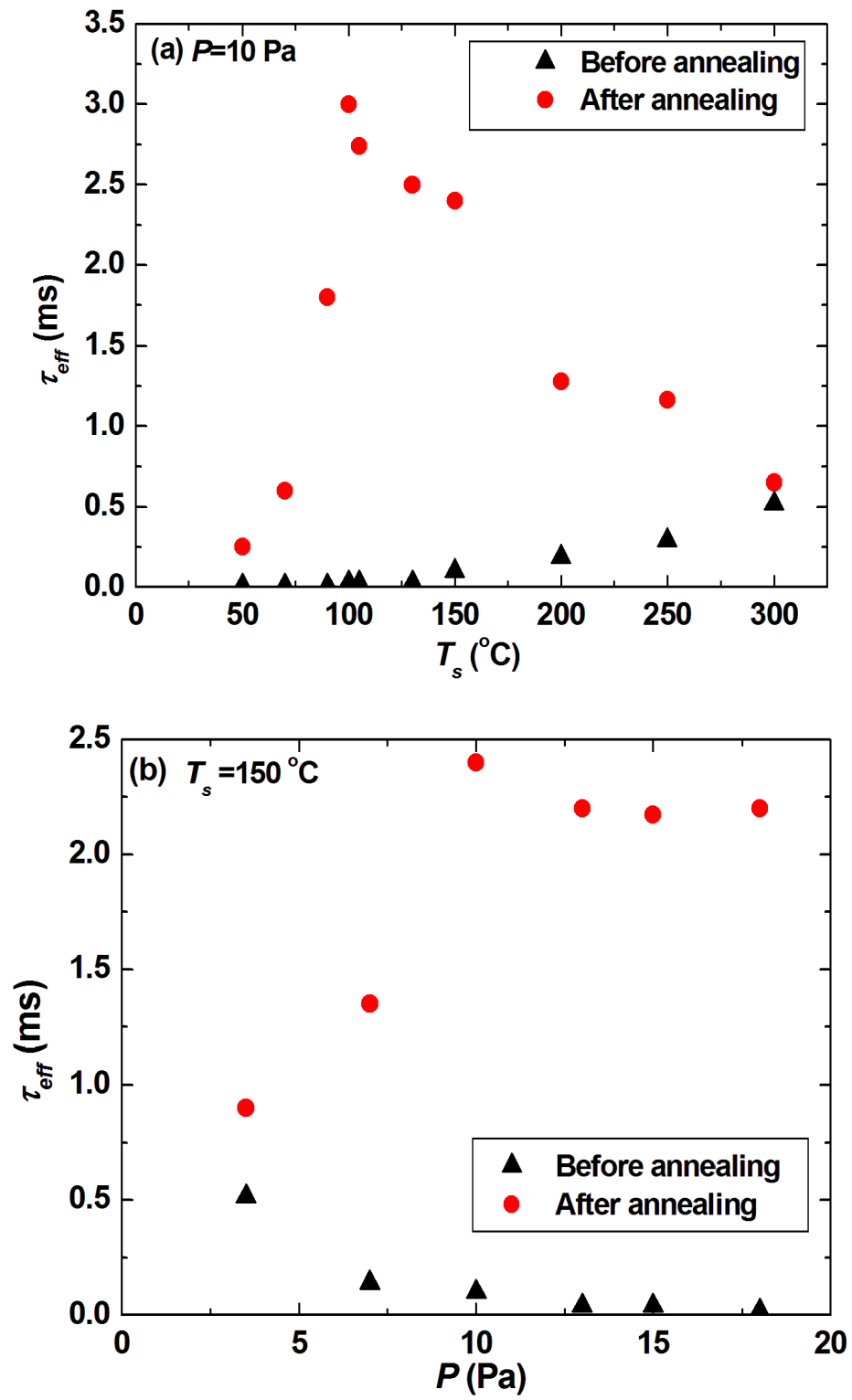


Fig. 2



**Fig. 3**

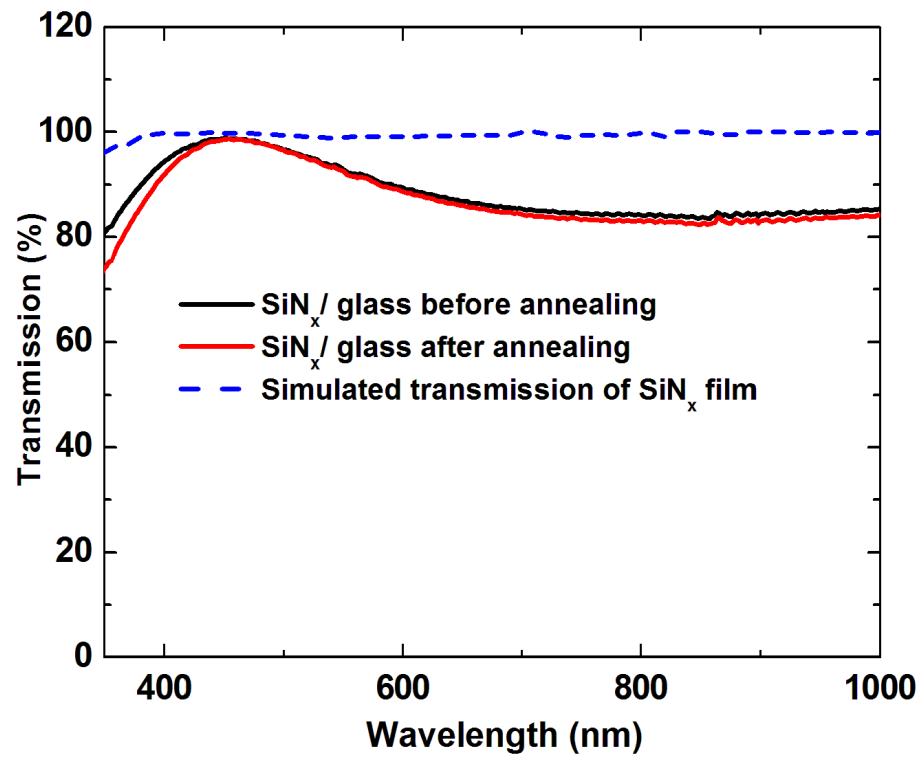
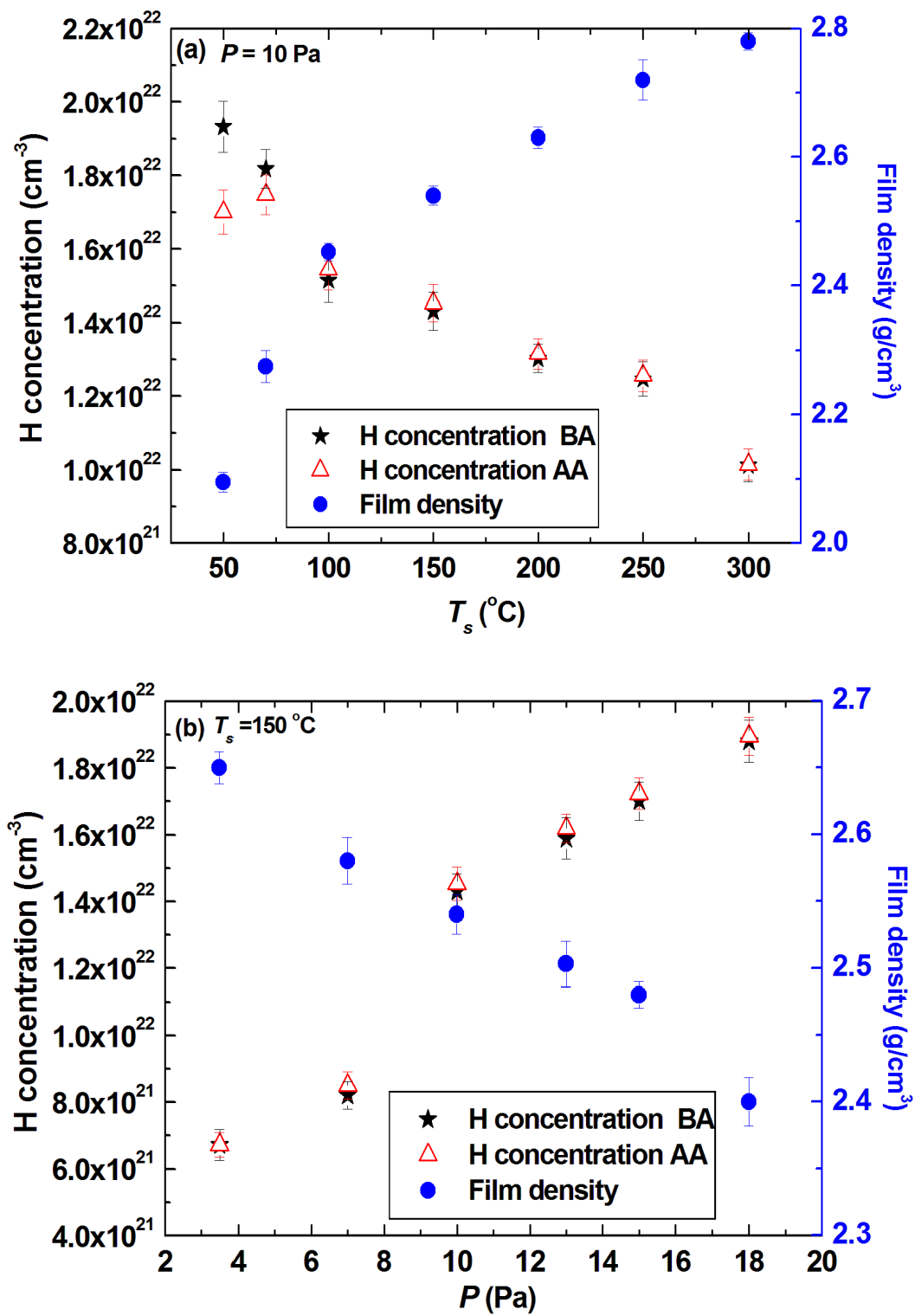


Fig. 4



**Fig. 5**

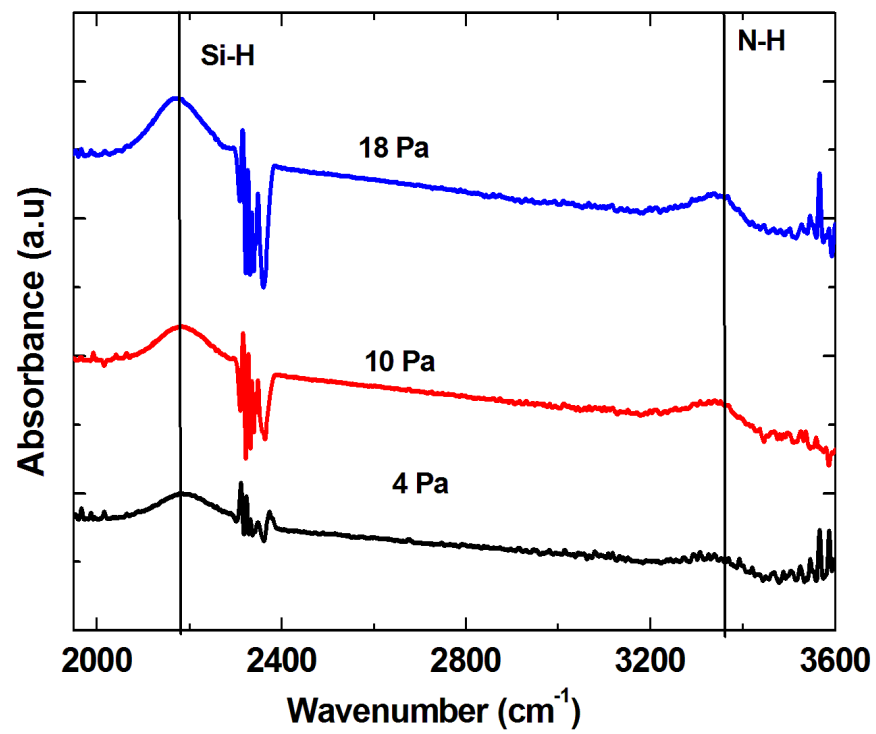
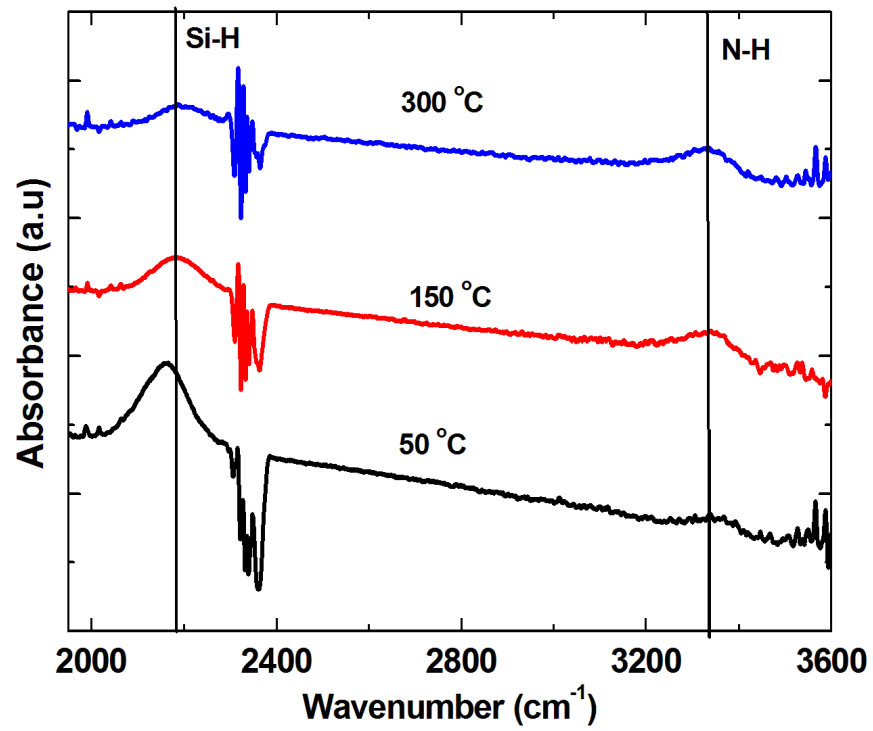




Fig. 6

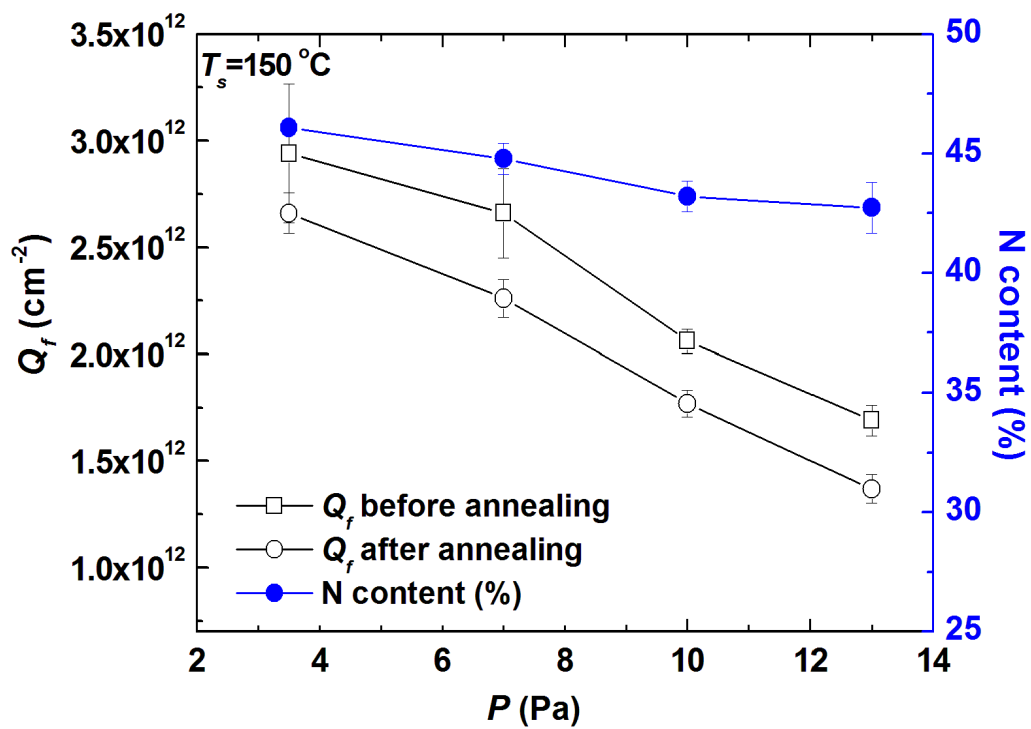
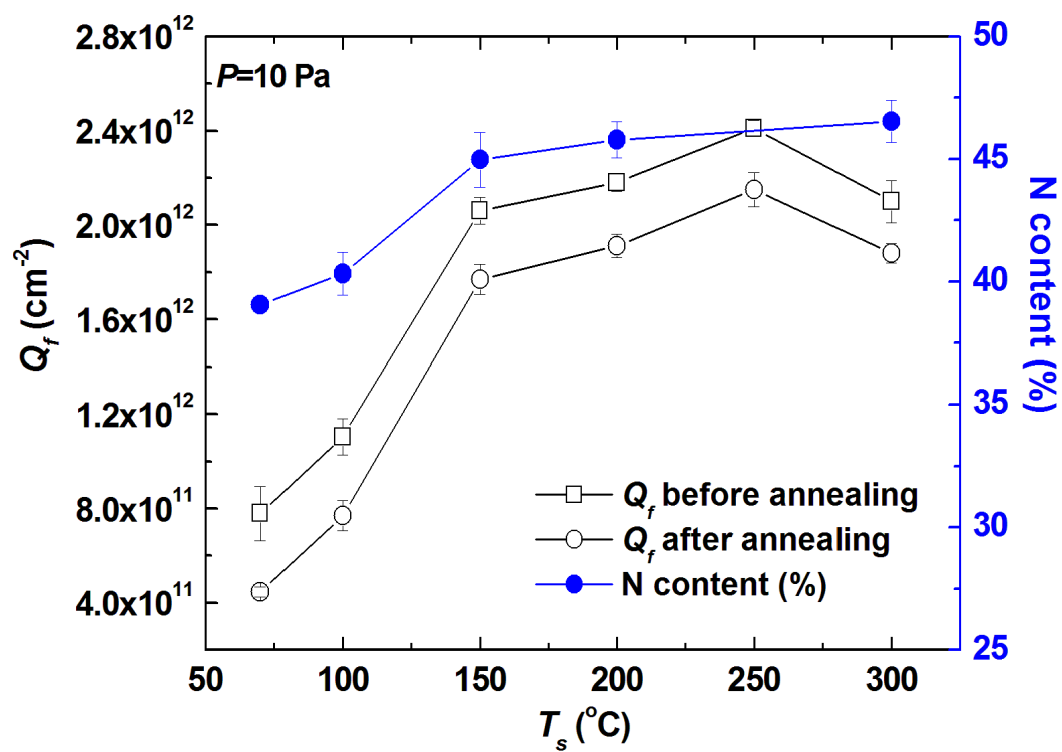


Fig. 7

