Title	Passivation quality of a stoichiometric SiN_x single passivation layer on crystalline silicon prepared by catalytic chemical vapor deposition and successive annealing
Author(s)	Thi, Trinh Cham; Koyama, Koichi; Ohdaira, Keisuke; Matsumura, Hideki
Citation	Japanese Journal of Applied Physics, 53(2): 022301-1-022301-6
Issue Date	2014-01-22
Type	Journal Article
Text version	author
URL	http://hdl.handle.net/10119/12140
Rights	This is the author's version of the work. It is posted here by permission of The Japan Society of Applied Physics. Copyright (C) 2014 The Japan Society of Applied Physics. Trinh Cham Thi, Koichi Koyama, Keisuke Ohdaira and Hideki Matsumura, Japanese Journal of Applied Physics, 53(2), 2014, 022301-1-022301-6. http://dx.doi.org/10.7567/JJAP.53.022301
Description	

Passivation quality of a stoichiometric SiN_x single passivation layer on crystalline silicon prepared by catalytic chemical vapor deposition (Cat-CVD) and successive annealing

Trinh Cham Thi[1,2,*], Koichi Koyama[1,2], Keisuke Ohdaira[1,2], and Hideki Matsumura[1,2]

[1]Japan Advanced Institute of Science and Technology (JAIST), Nomi, Ishikawa 923-1292, Japan

[2]CREST, Japan Science and Technology Agency (JST), Kawaguchi, Saitama 332-0012, Japan

*E-mail: s1240009@jaist.ac.jp

Abstract

A silicon nitride (SiN_x) 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 (τ_{eff}) monotonically increases with increase in deposition substrate temperature (T_s) for samples passivated by as-deposited SiN_x films, while more significant increase in τ_{eff} by annealing tends to be seen for the samples with SiN_x films deposited at lower T_s. The τ_{eff} obtained for the sample deposited at T_s of 100 ^{o}C and pressure (P) of 10 Pa, after annealing at 350 ^{o}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 (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 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 SiN_x film instead of a-Si film. The obtained results show that SiN_x/Si-rich SiN_x stacked layers as passivation films on c-Si achieves a SRV of as low as 3 cm/s with 30 % improvement in transparency at a wavelength of 400 nm compared to that of 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 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 ~ 2) SiN_x single layer on c-Si. 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 τ_{eff} is improved significantly by annealing. Samples prepared at lower substrate temperature during deposition (T_s) show more significant improvement in τ_{eff} by annealing, probably due to higher H content. Highest τ_{eff} obtained for the sample deposited at T_s of 100 ^{o}C and pressure (P) of 10 Pa is about 3 ms, corresponding to SRV of 5.0 cm/s. Passivation quality of SiN_x films on c-Si have been investigated by many researchers [6-17]. Most of SiN_x 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_x 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_x films [14]. There are, however, few reports for the passivation of c-Si surface using Cat-CVD SiN_x films [16, 17]. The work of Cat-CVD SiN_x/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_x films were deposited by Cat-CVD. SiN_x films with an approximately same refractive index of ~ 2 were deposited at various T_s

and *P*. SiN_x films were also deposited onto glass substrates for optical transmission measurements. We also formed 100-nm-thick SiN_x films on quartz substrates to measure defect density of the films. The deposition conditions of the SiN_x films are summarized in Table I. To measure H content by Fourier-transform infrared spectroscopy (FTIR), SiN_x films with a thickness of about 100 nm were deposited on c-Si substrates with a high resistivity of 3460 Ωcm [18]. Fixed charge density (Q_f) of 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 Ωcm p-type floating-zone (FZ)-grown c-Si wafers by evaporation. The Al/c-Si structure was annealed at 400 ^oC for 15 min in N_2 atmosphere to obtain Ohmic contact. 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 SiN_x layers through a hard mask. Some samples were annealed at 350 ^oC 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 SiN_x films were deposited on both sides of 290-µm-thick n-type (100) FZ Si wafers with a resistivity of 2.5 Ωcm to measure effective minority carrier lifetime (τ_{eff}). Samples were then annealing in N_2 atmosphere to investigate the effect of annealing on the passivation quality of 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^{TM} spectroscopic ellipsometer, using Cauchy model for data analysis [20].

The film density was measured by X-ray reflectivity [20]. Atomic contents of the SiN_x films were measured by X-ray photoelectron spectroscopy (XPS). The transmission spectra of SiN_x 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_x layers on c-Si, we carried out microwave photo-conductivity decay (μ-PCD) measurement (Kobelco LTA-1510EP) using a 904 nm wavelength pulse laser with a photon density of 5×10^{13} 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_x films on c-Si wafers

The effect of annealing on the passivation quality of various SiN_x films has also been reported by many authors [9, 23, 24]. It is demonstrated that the rearrangement of SiN_x structure and H diffusion during annealing can terminated defects at SiN_x/c-Si interface, thus, which results in improvement in passivation quality. In previous study, we also found that passivation quality of Cat-CVD SiN_x/Si-rich SiN_x 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_x single films on c-Si wafers. In this experiment, stoichiometric SiN_x films were deposited at T_s of 50, 100, and 150 ^oC at a fixed P of 10 Pa. Figure 1(a) shows τ_{eff} of SiN_x films deposited at T_s of 50, 100, and 150 ºC at a fixed P of 10 Pa, and H concentration of those at a T_s of 150 ºC as functions of T_a with a fixed duration of 30 min.

τ_{eff} increases with increase in T_a, reaches maximum value, and then, decreases dramatically. The improvement in τ_{eff} on T_a may be related to the diffusion of H atoms in the films and the termination of defect at SiN_x/c-Si interface by H atoms during annealing. T_a of 350 ^oC might be a proper temperature to support sufficient energy for H diffusion and defect-termination, resulting in the formation of good-quality SiN_x/c-Si interface. Figure 1(b) shows FTIR spectra of SiN_x films deposited at a T_s of 150 ^oC at various T_a for 30 min. Increase in H content after annealing at 350 ^oC, 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 τ_{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 ^oC, which is a clear evidence for H loss to environment.

Passivation quality of SiN_x films can be stable for long time annealing, as shown in Fig. 1(c). Degradation of τ_{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 ^oC and t_a of 30 min as ideal annealing conditions for all samples for high passivation quality improvement after annealing.

Figure 2 shows τ_{eff} of c-Si wafers with SiN_x films as functions of T_s and P before and after annealing at a T_a of 350 ^oC for 30 min. τ_{eff} of as-deposited film before annealing increases with increase in T_s, while decreases with increase in P. The low τ_{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 SiN_x films can suppress H etching effect. However, films deposited with high deposition rate (at low T_s and high P) might leads to the insufficient coverage of c-Si surface, resulting in decrease in τ_{eff}. The reason of low τ_{eff} at these conditions can also be explained by low Q_f, which will be discussed later. Figure 2 also shows that τ_{eff} is improved significantly after annealing. For annealed samples, τ_{eff} reaches its highest value at T_s of 100 ^{o}C, then it decreases with increase in T_s, while τ_{eff} increases with increase of P and reaches a saturated value at $P \geq 10$ Pa. τ_{eff} obtained for the as-deposited sample at T_s of 100 ^{o}C and P of 10 Pa is about 0.1 ms, corresponding to a SRV of 144 cm/s. τ_{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 SiN_x films deposited at T_s of 150 ^{o}C and P of 10 Pa before and after annealing at a T_a of 350 ^{o}C for 30 min, simulated value of transmission of a 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 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 SiN_x films show sufficiently high optical transmission even in short wavelength region, unlike a-Si or Si-rich 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_x 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_x 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_x film density and H concentration in SiN_x films before and after annealing at a T_a of 350 ^{o}C for 30 min as functions of T_s and P. H concentration of SiN_x films were determined from FTIR spectra, parts of which are shown in Fig. 5. H concentration of SiN_x 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_x films, while Si-H/N-H bond density ratio is kept almost constant. Compared to SiN_x films deposited at higher T_s, the SiN_x film deposited at a T_s of 50 ^{o}C have a Si-H peak shifted to lower wavenumber. This might be related to the lower electro-negativity of backboned Si atoms for SiN_x 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 τ_{eff} by annealing, and H may contribute to improvement in

τ_{eff}. Sample prepared at T_s <100 ^{o}C, exceptionally shows less significant improvement in τ_{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 desorsption slower [16, 28]. Here, SiN_x film density is ~ 2.1 g/cm^3 for the sample deposited at T_s of 50 ^{o}C, while it is more than 2.4 g/cm^3 for sample deposited at $T_s \geq$ 100 ^{o}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 τ_{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 τ_{eff} after annealing samples deposited at various P. Improvement in τ_{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 SiN_x films deposited at high P.

Figure 6 shows N content and Q_f of SiN_x films as functions of T_s and P before and after annealing at a T_a of 350 ^{o}C for 30 min. Q_f increases with increase in T_s, and reaches highest value at a T_s of 250 ^{o}C, then it slightly decreases at 300 ^{o}C. Q_f of 7.5×10^{11} cm^{-2} is quite low for the SiN_x films deposited at T_s of 50 ^{o}C, which can be one of possible reasons to explain low τ_{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 ^{o}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 ^{o}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 SiN_x but also at SiN_x/c-Si interface during annealing, and τ_{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 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 τ_{eff} of Si wafers passivated by SiNx films. The value of Q_f on the order of 10^{12} cm^{-2} is high enough to express field-effect passivation. Fixed charge in SiN_x films can thus partially contribute to suppression in surface recombination. Q_f, however, decreases after annealing, while τ_{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 SiN_x films, which is consistent with our previous results [5].

4. Conclusions

Stoichiometric 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 τ_{eff} by annealing. The possible reasons for this effect are the diffusion of H atoms in the films and the termination of defect at SiN_x/c-Si interface by H atoms during annealing. H content in the films thus plays an important role on improving τ_{eff}. The highest τ_{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_x films as passivation layers for c-Si solar cells.

Acknowledgement

This work is supported by JST CREST program.

References

[1] A. Goetzberger, J. Knobloch and B. Vob, *Crystalline Silicon Solar Cells* (Wiley, Chichester, U. K., 1998) p. 87.

[2] H. Matsumura, J. Appl. Phys. **65** (1989) 4396.

[3] K. Koyama, K. Ohdaira and H. Matsumura, Appl. Phys. Lett. **97** (2010) 0821081.

[4] Trinh Cham Thi, K. Koyama, K. Ohdaira, and H. Matsumura, Sol. Energy Mater. Sol. Cells **100** (2012) 169.

[5] Trinh Cham Thi, K. Koyama, K. Ohdaira, and H. Matsumura, submitted to Thin Solid Films.

[6] A.G. Aberle, Sol. Energy Mater. Sol. Cells **65** (2001) 239.

[7] F. Duerinckx and J. Szulfcik, Sol. Energy Mater. Sol. Cells **72** (2002) 231.

[8] T. Lauinger, A.G. Aberle, R. Hezel, Proc. 14th European Photovoltaic Solar Energy Conf., 1997, p. 853.

[9] V. Yelundur, A. Rohatgi, J.I. Hanoka, R. Reedy, Proc. 19th European Photovoltaic Solar Energy Conf., 2004, p. 951.

[10] Y. Larionova, V. Mertens, N. Harder, and R. Brendel, Appl. Phys. Lett. **101** (2012) 201601.

[11] S. Duttagupta, B.Hoex, A. G. Aberle, presented at 22nd Int. Photovoltaic Science and Engineering Conf., 2012.

[12] J. Schmidt and S. Dauwe, presented at Workshop Fundamentals of a-SiNx:H in Industrial Solar Cell Processing, 2005.

[13] J. Schmidt and M. Kerr, Sol. Energy Mater. Sol. Cells **65** (2001) 585.

[14] J. Schmidt and A.G. Aberle, J. Appl. Phys. **85** (1998) 3626.

[15] J.-F. Lelièvre, E. Fourmond, A. Kaminski, O. Palais, D. Ballutaud and M. Lemiti, Sol. Energy Mater. Sol. Cells **93** (2009) 1281.

[16] J. K. Holt, D. G. Goodwin, A. M. Gabor, F. Jiang, M. Stavola and H. A. Atwater, Thin Solid Films **430** (2003) 37.

[17] H. Matsumura, A. Kikkawa, T. Tsutsumi, A. Masuda, A. Izumi, M. Takahashi, H. Ohtsuka and J. D. Moschner, Proc. 3rd World Conf. Photovoltaic Energy Conversion, 2003, p. 114.

[18] W. A. Lanford, J. Appl. Phys. **49** (1978) 2473.

[19] E. H. Nicollian, J. A. Brews, *MOS Physics and Technology* (Wiley, New York, 1982) p. 83.

[20] Guide to Using WVASE32^{TM}: Software for Vase and M-44 Ellipsometers (J.A. Woollam, Lincoln, NE, USA, 1989) p. 159.

[21] L. Xiangna, Z. Zhouyin and W. Yong, Chin. Phys. Lett. **7** (1990) 79.

[22] K. Lauer, A. Laades, H. Übensee, H. Metzner and A. L awerenz, J. Appl. Phys. **104** (2008) 104503.

[23] B. Sopori, R. Reedy, K. Jones, Y. Yan and M. Al-Jassim, Proc. 31st Photovoltaic Specialists Conf., 2005, p. 1039.

[24] J. Hong, W. M. M. Kessels, M. J. Soppe, A. W. Weeber, W. M. Arnoldbik and M. C. M. Van de Sanden, J. Vac. Sci. Technol. B **21** (2003) 2123.

[25] H.F.W. Dekkers, G. Beaucarne, M. Hiller, H. Charifi and A. Slaoui, Appl. Phys. Lett. **89** (2006) 211914.

[26] H. Matsumura, K. Kamesaki, A. Masuda and A. Izumi, Jpn. J. Appl. Phys. **40** (2001) L289.

[27] H. Fujiwara, *Spectroscopic Ellipsometry Principles and Application* (Wiley, Chichester, U. K., 2007) p. 22.

[28] G. Lucovsky, Solid State Commun. **29** (1979) 571.

[29] J. Robertson, W.L. Warren, J. Kanicki, J. Non-Cryst. Solids **187** (1995) 297.

[30] W. L. Warren, J. Robertson, and J. Kanicki, Appl. Phys. Lett. **63** (1993) 2685.

Figure captions

Fig. 1. (a) τ_{eff} of SiN_x films deposited at T_s of 50, 100, and 150 ºC at a fixed P of 10 Pa, and H concentration of those at a T_s of 150 ºC as functions of T_a with a fixed duration of 30 min. (b) FTIR spectra of SiN_x films deposited at a T_s of 150 ^{o}C at various T_a for 30 min. (c) τ_{eff} as a function of t_a at a T_a of 350 ^{o}C.

Fig. 2. τ_{eff} as functions of T_s and P before and after annealing at a T_a of 350 ^{o}C for 30 min in N_2 atmosphere.

Fig. 3. Transmission spectra of SiN_x films deposited at T_s of 150 ^{o}C and P of 10 Pa before and after annealing at a T_a of 350 ^{o}C for 30 min, simulated value of transmission of a SiN_x film is also shown.

Fig. 4. Film density and H concentration of SiN_x films before and after annealing at a T_a of 350 ^{o}C for 30 min as functions of T_s and P.

Fig. 5. FTIR spectra of SiN_x films deposited at various T_s and P.

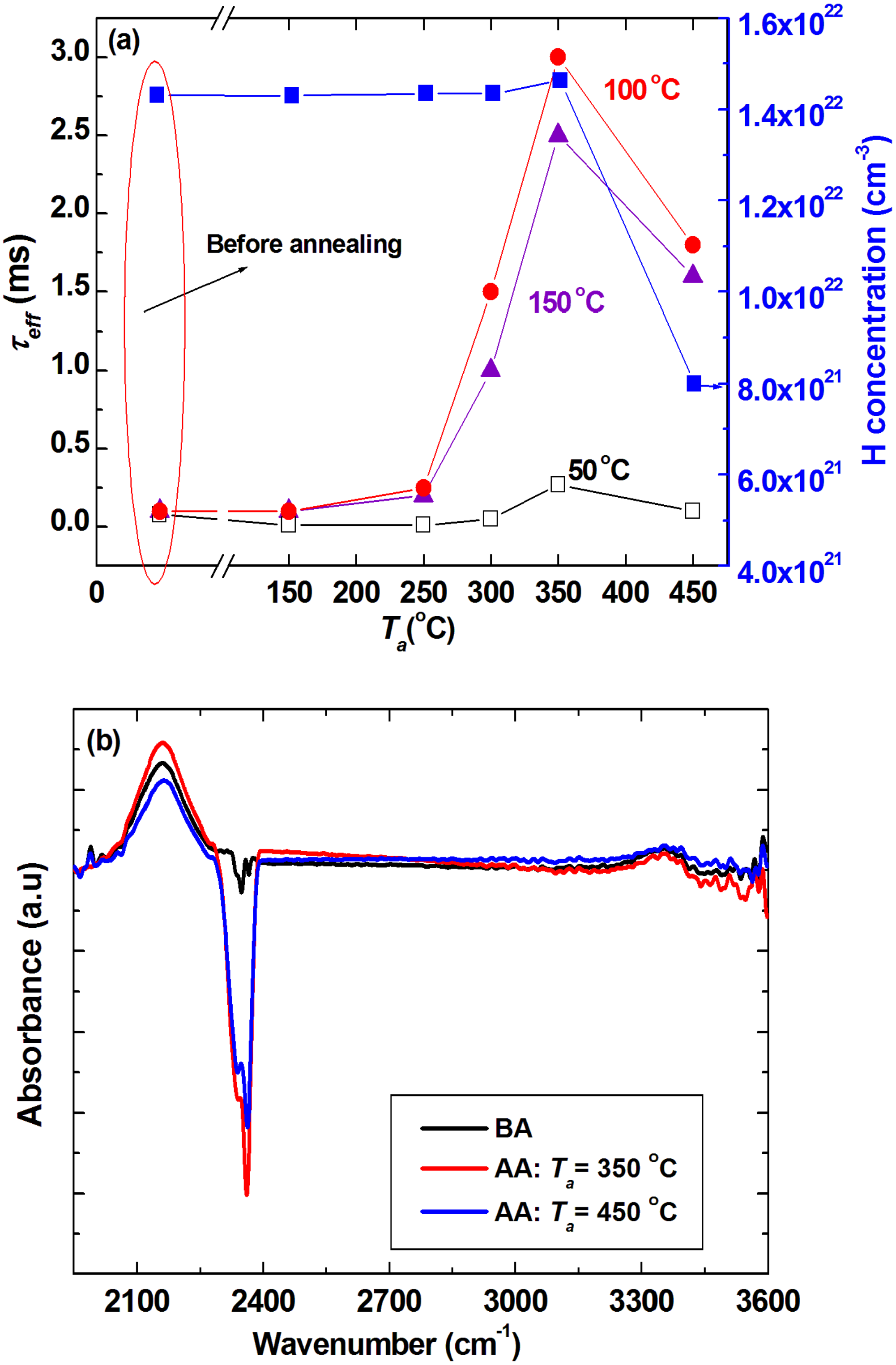
Fig. 6. N content and Q_f of SiN_x films as functions of T_s and P before and after annealing at a T_a of 350 ^{o}C for 30 min.

Fig. 7. Defect density of SiN_x films as functions of T_s and P before and after annealing at a T_a of 350 ^{o}C for 30 min.

Table I. Deposition conditions of SiN_x films. Refractive index and thickness of deposited films are also summarized.

Film	SiH_4 (sccm)	NH_3 (sccm)	Gas pressure (Pa)	T_s (^oC)	T_{cat} (^oC)	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


(a)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
τ_{eff} (ms)
Before annealing
100 °C
150 °C
50 °C
0
150
200
250
300
350
400
450
T_a(°C)
1.6x10^22
1.4x10^22
1.2x10^22
1.0x10^22
8.0x10^21
6.0x10^21
4.0x10^21
H concentration (cm^-3)
(b)
Absorbance (a.u)
BA
AA: T_a = 350 °C
AA: T_a = 450 °C
2100
2400
2700
3000
3300
3600
Wavenumber (cm^-1)

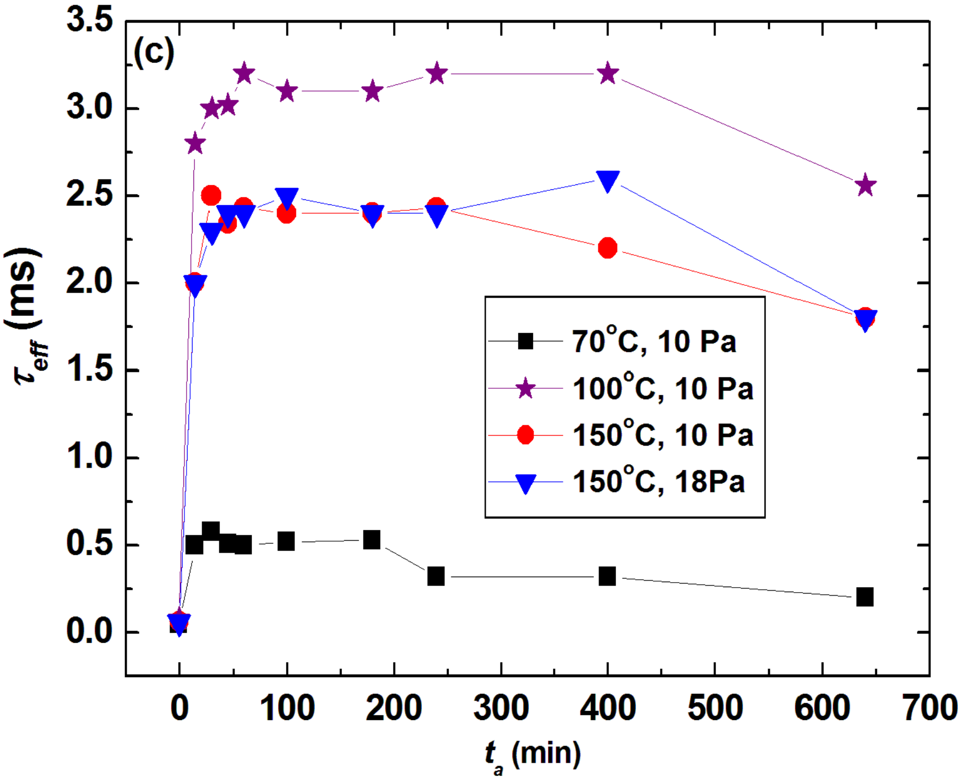

(c)
τ_{eff} (ms)
t_a (min)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
70°C, 10 Pa
100°C, 10 Pa
150°C, 10 Pa
150°C, 18Pa

Fig. 2

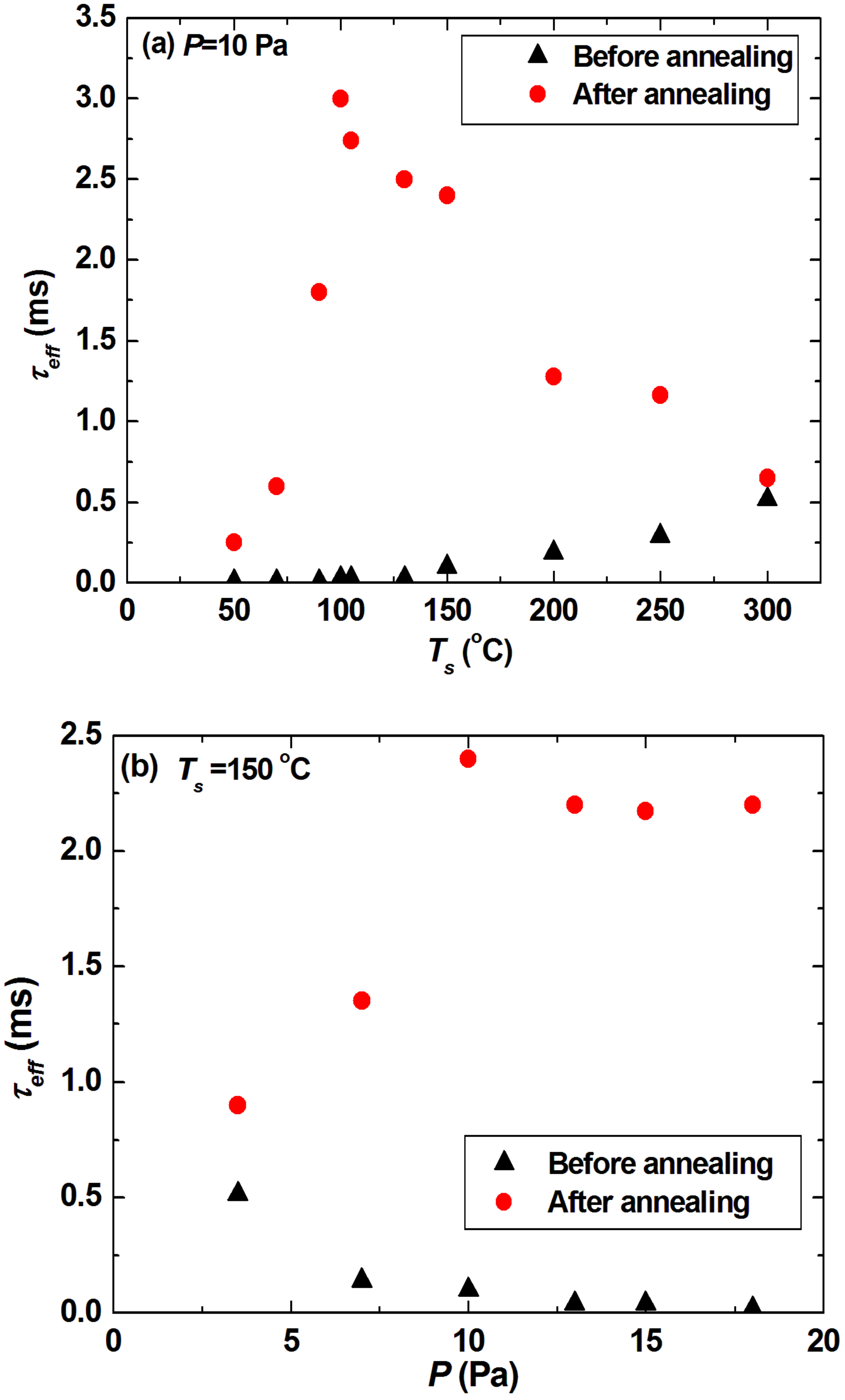
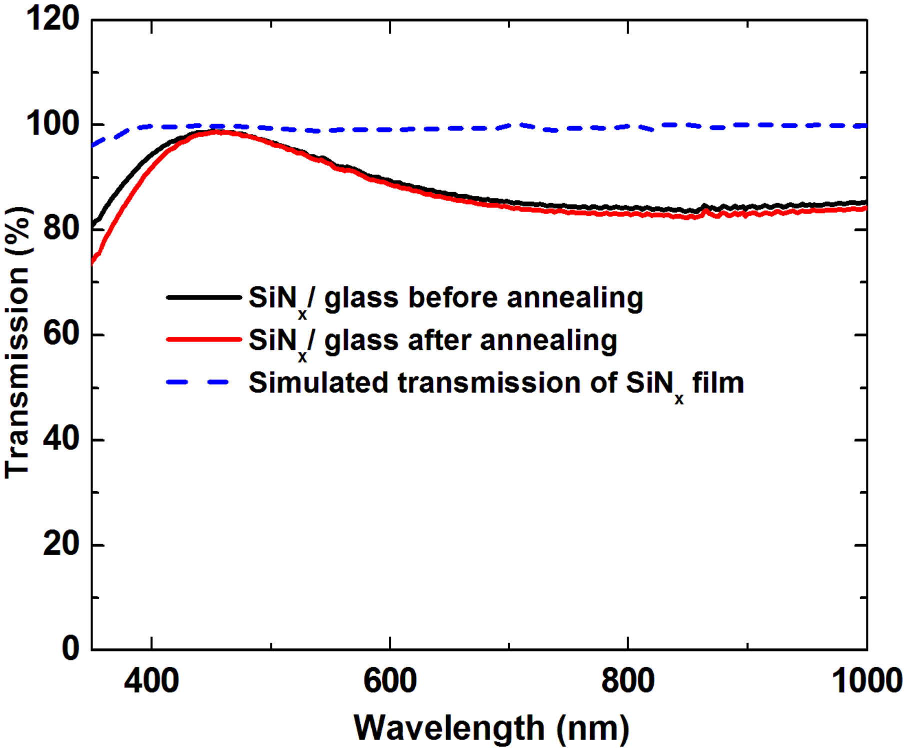

(a) P=10 Pa
Before annealing
After annealing
τ_{eff} (ms)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
50
100
150
200
250
300
T_s (°C)
(b) T_s =150 °C
Before annealing
After annealing
τ_{eff} (ms)
2.5
2.0
1.5
1.0
0.5
0.0
0
5
10
15
20
P (Pa)

Fig. 3



120
100
80
60
40
20
0
400
600
800
1000
Transmission (%)
Wavelength (nm)
SiN$_x$/ glass before annealing
SiN$_x$/ glass after annealing
Simulated transmission of SiN$_x$ film

Fig. 4

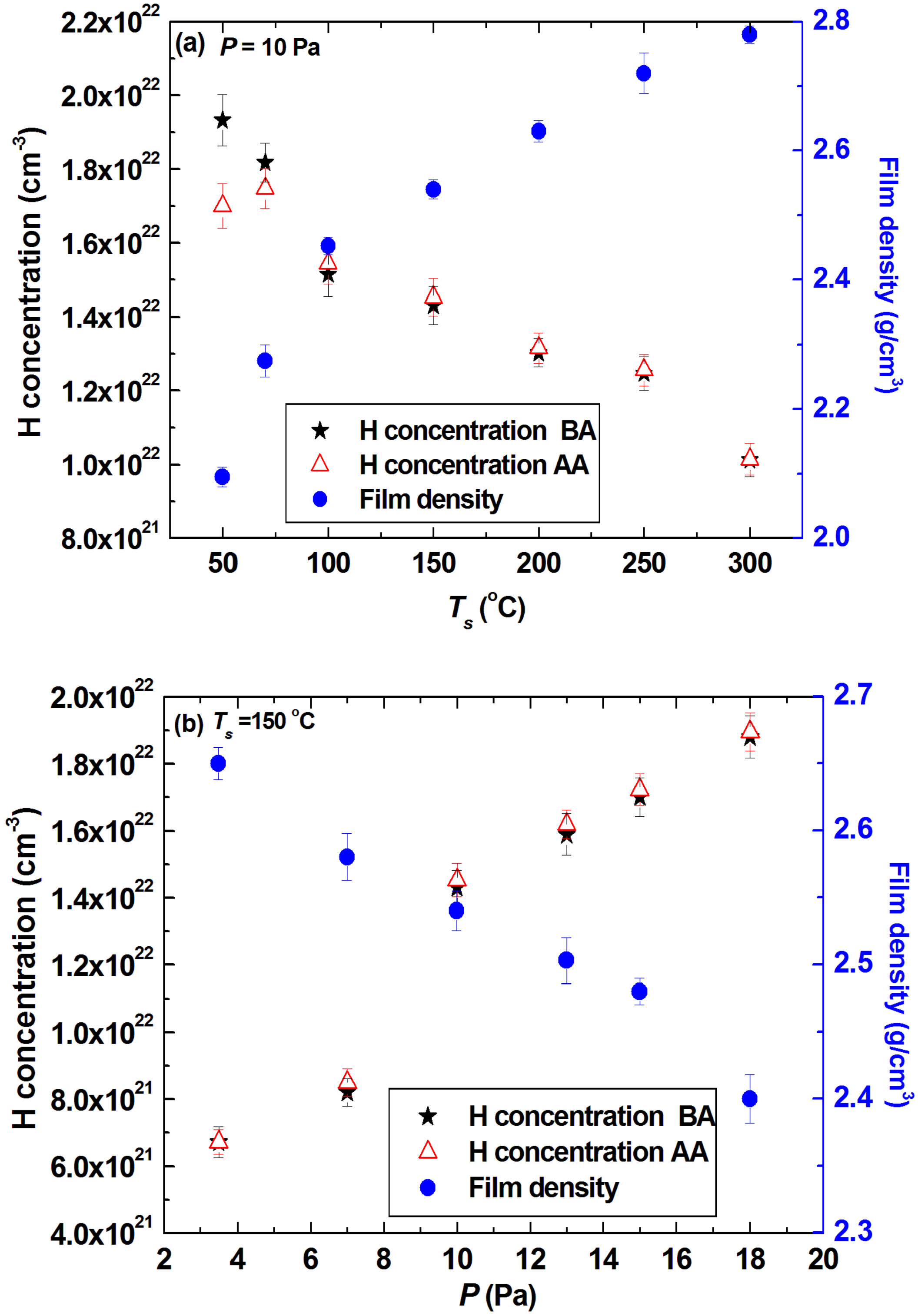

(a) P = 10 Pa
H concentration (cm^{-3})
2.2x10^{22}
2.0x10^{22}
1.8x10^{22}
1.6x10^{22}
1.4x10^{22}
1.2x10^{22}
1.0x10^{22}
8.0x10^{21}
Film density (g/cm^{3})
2.8
2.6
2.4
2.2
2.0
50
100
150
200
250
300
T_s (°C)
★ H concentration BA
△ H concentration AA
● Film density
(b) T_s =150 °C
H concentration (cm^{-3})
2.0x10^{22}
1.8x10^{22}
1.6x10^{22}
1.4x10^{22}
1.2x10^{22}
1.0x10^{22}
8.0x10^{21}
6.0x10^{21}
4.0x10^{21}
Film density (g/cm^{3})
2.7
2.6
2.5
2.4
2.3
2
4
6
8
10
12
14
16
18
20
P (Pa)
★ H concentration BA
△ H concentration AA
● Film density

Fig. 5

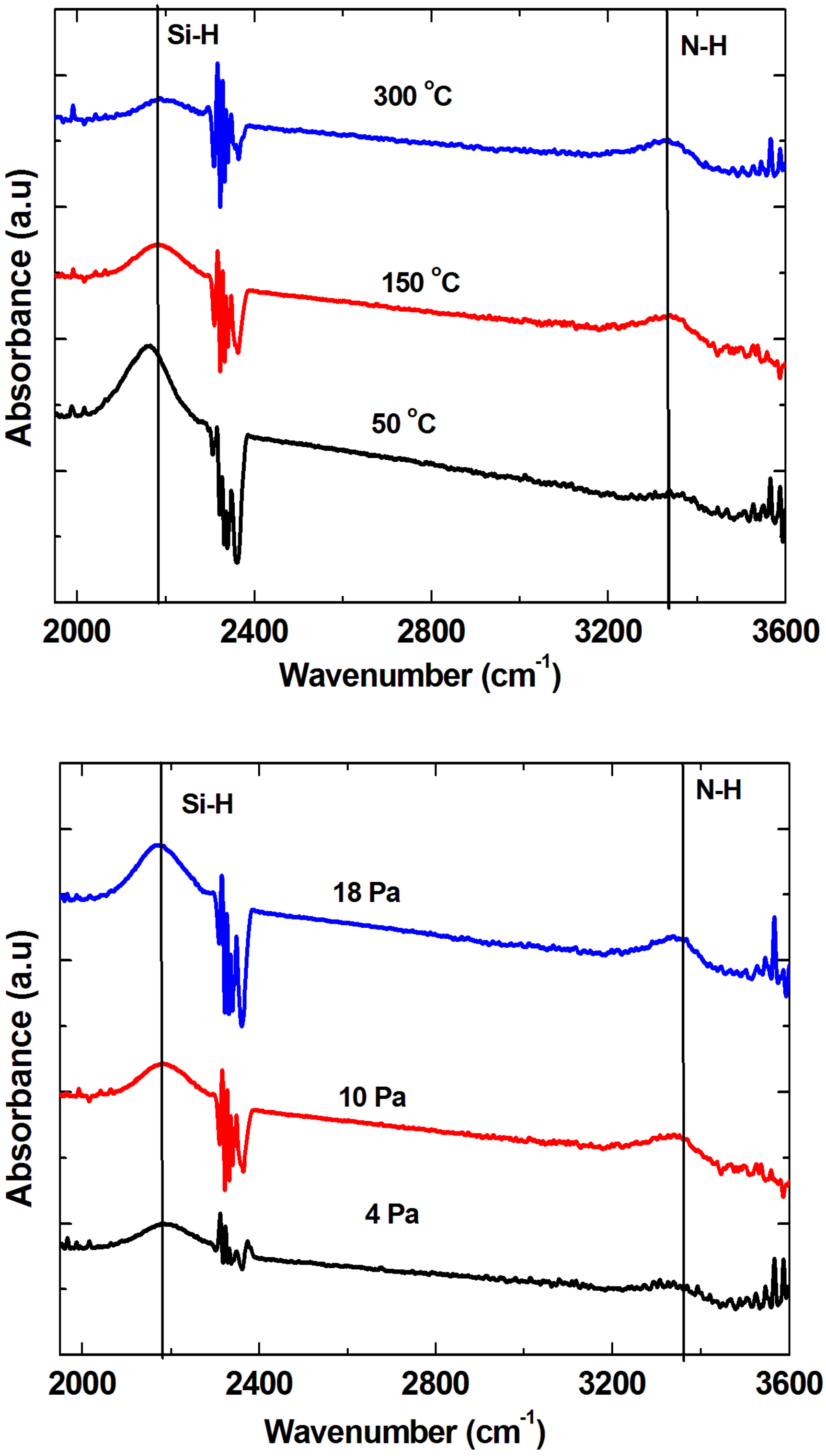
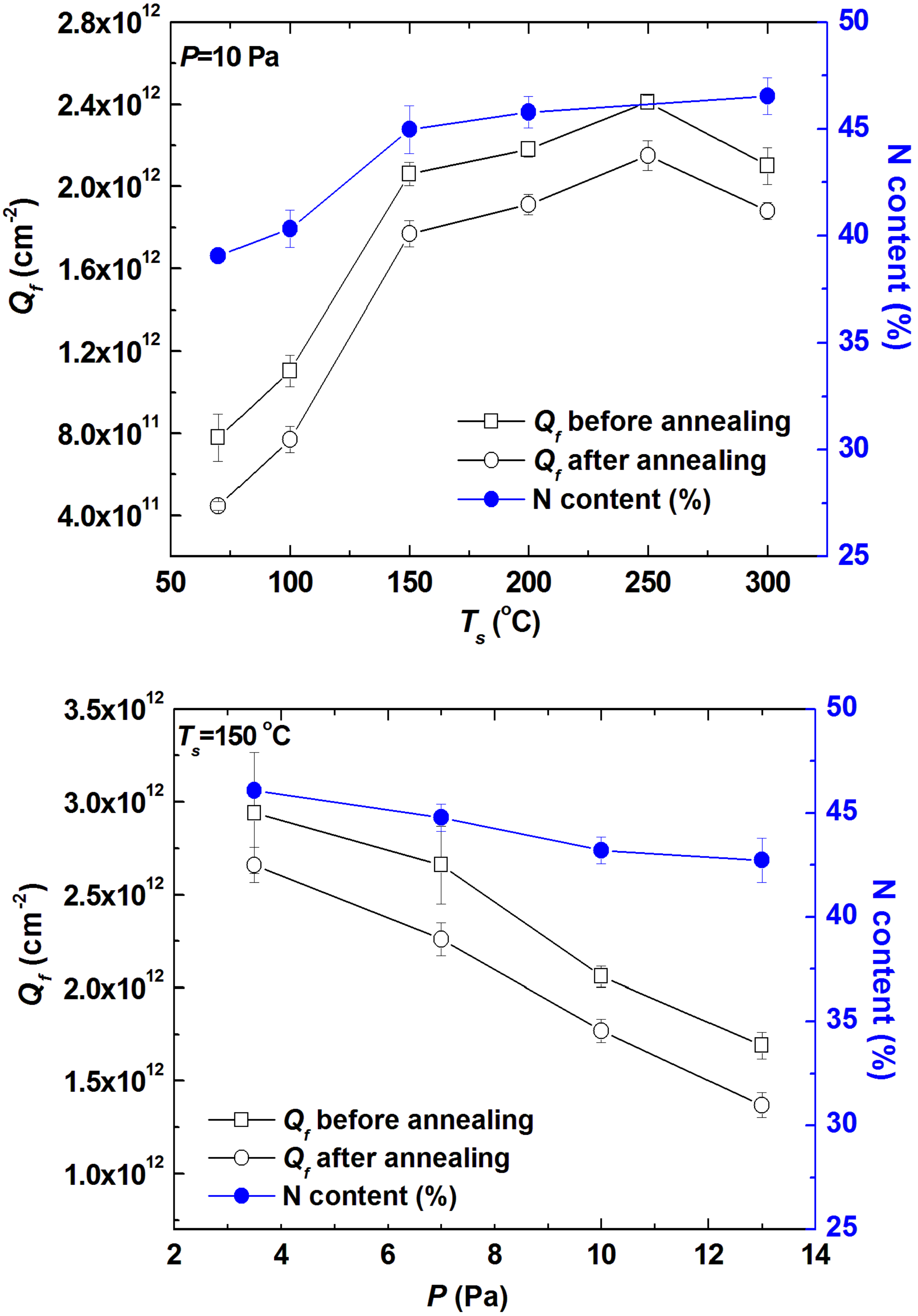
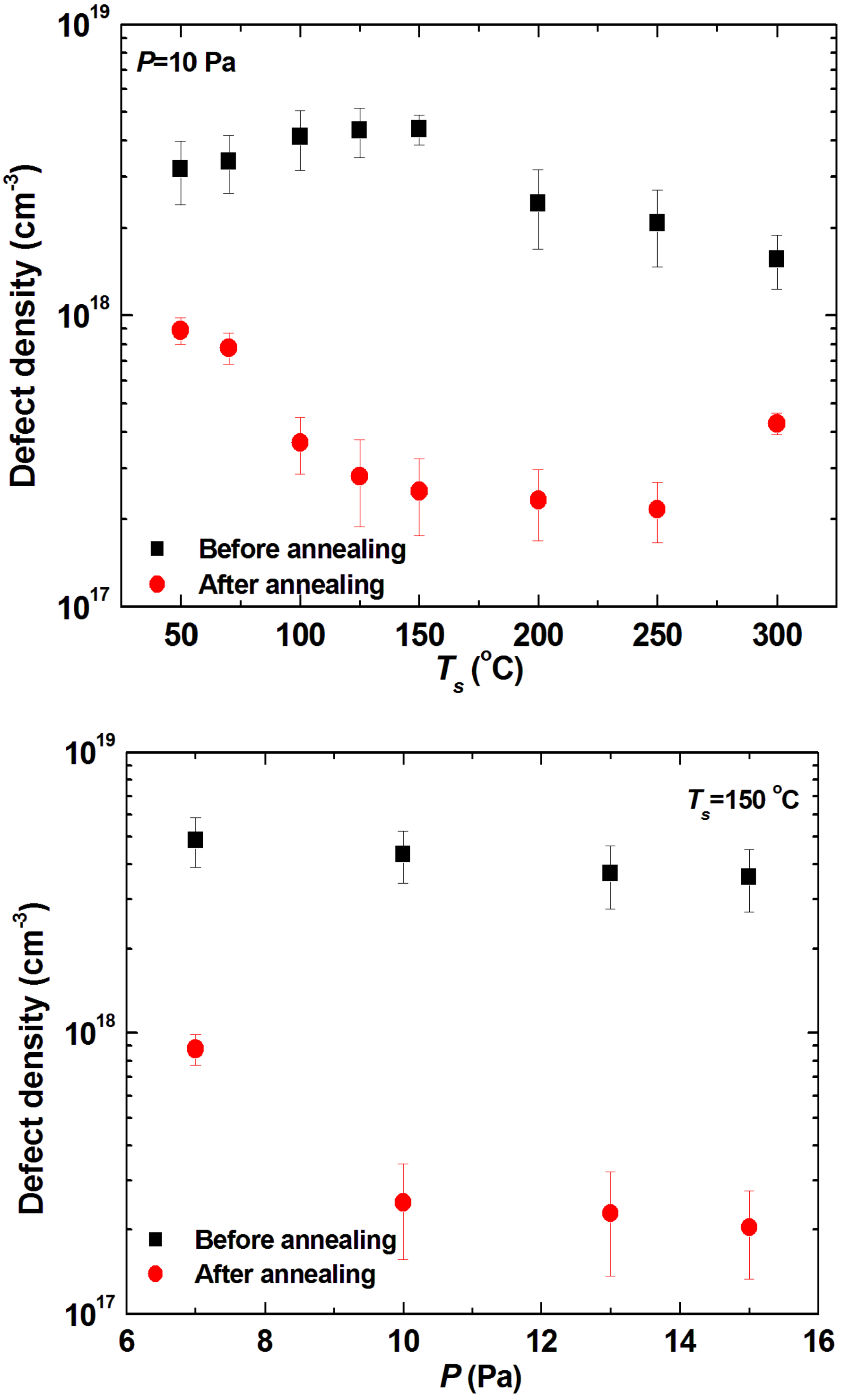

Si-H
N-H
300 °C
150 °C
50 °C
Absorbance (a.u)
2000
2400
2800
3200
3600
Wavenumber (cm-1)
Si-H
N-H
18 Pa
10 Pa
4 Pa
Absorbance (a.u)
2000
2400
2800
3200
3600
Wavenumber (cm-1)

Fig. 6



P=10 Pa
2.8x10^12
2.4x10^12
2.0x10^12
1.6x10^12
1.2x10^12
8.0x10^11
4.0x10^11
Q_f (cm^-2)
50
45
40
35
30
25
N content (%)
50
100
150
200
250
300
T_s (°C)
Q_f before annealing
Q_f after annealing
N content (%)
T_s=150 °C
3.5x10^12
3.0x10^12
2.5x10^12
2.0x10^12
1.5x10^12
1.0x10^12
Q_f (cm^-2)
50
45
40
35
30
25
N content (%)
2
4
6
8
10
12
14
P (Pa)
Q_f before annealing
Q_f after annealing
N content (%)

Fig. 7


10^{19}
10^{18}
10^{17}
Defect density (cm^{-3})
P=10 Pa
■ Before annealing
● After annealing
50
100
150
200
250
300
T_s (°C)
10^{19}
10^{18}
10^{17}
Defect density (cm^{-3})
T_s=150 °C
■ Before annealing
● After annealing
6
8
10
12
14
16
P (Pa)