Title	Thickness dependence of the passivation quality of Cat-CVD SiN_x films
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Citation	Japanese Journal of Applied Physics, 59(SC): SCCB07-1-SCCB07-4
Issue Date	2019-12-04
Type	Journal Article
Text version	author
URL	http://hdl.handle.net/10119/16970
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Thickness dependence of the passivation quality of Cat-CVD SiN$_x$ Films

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We investigate the thickness dependence of the passivation quality of silicon nitride (SiN$_x$) films formed by catalytic chemical vapor deposition (Cat-CVD). The passivation quality of SiN$_x$ films, evaluated by measuring effective minority carrier lifetime (τ_{eff}), can be enhanced by post annealing, and show a significant thickness dependence. τ_{eff} increases with SiN$_x$ thickness up to 90 nm and shows no more significant improvement with further increase in SiN$_x$ thickness. Interface state density (D_{it}) shows high consistency with thickness dependence of τ_{eff} before and after annealing, whereas fixed charge density (Q_f) rather decreases with increase in SiN$_x$ thickness. We propose a possible mechanism that SiN$_x$ films may release hydrogen (H) atoms during post annealing to terminate dangling bonds on the c-Si surface which leads to decrease in D_{it}. Increase of τ_{eff} with SiN$_x$ thickness before annealing might be caused by annealing effect from a heated catalyzing wire.

1. Introduction

Silicon nitride (SiN$_x$) films, which can be formed by various methods such as sputtering,[1] atomic layer deposition,[2] chemical vapor deposition (CVD),[3–5] and vapor-phase nitridation,[6,7] have been widely used in semiconductor devices.[1,8–13] One of the most important roles for SiN$_x$ films particularly in crystalline silicon (c-Si)-based solar cells is to reduce the recombination of carriers via defect levels within the bandgap of c-Si.[14] SiN$_x$ films formed by CVD generally contain hydrogen (H) atoms, which can terminate Si dangling bonds on c-Si surfaces and inside bulk c-Si especially after post-annealing.[15–18] It is well known that SiN$_x$ films also act as antireflection coatings in the c-Si solar cells,[19–21]

and SiN_x is thus a crucial material to obtain high conversion efficiency.

It has been reported that the formation of SiN_x films by plasma-enhanced CVD induces plasma damage, leading to the deterioration of film/c-Si interfaces.[22–25] Catalytic CVD (Cat-CVD), often also referred to as hot-wire CVD, is a method of depositing thin films by decomposing gas molecules on a heated catalyzing wire such as tungsten and tantalum. One of the advantages of Cat-CVD is that it can realize plasma-damage-less deposition, and high-quality film/c-Si interfaces are therefore expected. We have thus far demonstrated that an outstandingly low surface recombination velocity (SRV) below 5 cm/s can be achieved when mirror-polished n-type floating-zone (FZ) c-Si wafers are passivated with 100-nm-thick Cat-CVD SiN_x films.[18] We have also reported that the passivation quality of Cat-CVD SiN_x films becomes drastically worse by reducing their thickness to 5-40 nm.[26] Since SiN_x films with various thicknesses can be utilized in c-Si cells, it is quite important to know how the passivation quality of Cat-CVD SiN_x films changes depending on SiN_x thickness and to understand the reason for the change of their passivation quality.

In this study, we clarify the relationship between the passivation quality of Cat-CVD SiN_x films and their thicknesses in a wide range. To understand the mechanism of the thickness-dependent passivation quality, we evaluate two factors determining the passivation quality of SiN_x films — interface states density (D_{it}) and fixed charge density (Q_f) — extracted from capacitance–voltage (C–V) curves. We also investigate the effect of radiant heat from a heated catalyzer, which increases substrate temperature during the deposition of SiN_x films and can have annealing effect.

2. Experimental procedures

We used 280 μm-thick, 1–5 Ωcm, mirror-polished n-type c-Si(100) wafers with a bulk lifetime >10 ms. The wafers were cleaved into 20×20 mm^2 pieces, and were ultrasonically cleaned in acetone, ethanol, and deionized (DI) water for 5 min, respectively (twice only for DI water). The substrates were then dipped in 5% hydrofluoric acid (HF) to remove native

oxide. After the HF dipping, the substrates were carried into a load lock chamber of a Cat-CVD system immediately. The substrates were then pre-heated up to a target temperature of 100 °C in H_2 atmosphere at 30 Pa for 5 min before the deposition of SiN_x films. The Cat-CVD of SiN_x films were performed using a tungsten catalyzer heated at 1800 °C with a length of ~200 cm and a a a diameter of 0.5 mm placed at a distance of 12 cm from a substrate holder. The samples were set in face-down configuration and four sides of each sample were contacted to the substrate holder. The pressure in the chamber without gas flow was 10^{-6} Pa. The detailed deposition conditions of SiN_x films are summarized in Table I. SiN_x films were deposited symmetrically on the both sides of the Si substrates. To obtain SiN_x films with various thicknesses, the duration of deposition was systematically varied from 30 to 900 s.

To investigate annealing effect caused by radiant heat from the heated catalyzer, we used irreversible temperature-sensitive labels for the measurement of substrate temperature during SiN_x deposition. A 4×5 mm^2-sized temperature-sensitive label was put on the center of a c-Si substrate where an Al film with the same area were evaporated as a reflective coating to avoid the direct absorption of radiant heat in the thermal sheet.

The thickness and refractive index of SiN_x films were measured on J. A. Woollam HS-190[TM] spectroscopic ellipsometer, using Cauchy model for data analysis. All the SiN_x films had an approximately constant refractive index of 2.0. A 30 minutes post annealing at 350 °C in N_2 atmosphere was performed to enhance the passivation ability of SiN_x films.[18] In order to investigate the passivation quality of SiN_x films on c-Si, the effective minority carrier lifetime (τ_{eff}) of the c-Si samples was measured by microwave photoconductivity decay (μ-PCD) (Kobelco LTA-1510EP) using a laser pulse at a wavelength of 904 nm with a photon density of 5×10^{13} cm^{-2} for the generation of excess carriers. τ_{eff} was measured before and after the post annealing for comparison.

D_{it} at SiN_x/c-Si interfaces and Q_f in the SiN_x films were calculated based on the results of $C–V$ measurement for metal-insulator-semiconductor (MIS) structures. We deposited a SiN_x film on one side of c-Si and formed Al by evaporation on the other side, and we prepared the MIS structures with SiN_x films with different thicknesses: 59, 115 and 167 nm. $C–V$

curves were measured with a mercury probe at a frequency of 1 MHz. After a 30-min post annealing at 350 °C in N_2 atmosphere, $C–V$ curves were measured again for comparison. Q_f was calculated based on the shifts of flat band voltage. D_{it} was calculated by Terman method[27–30] with a MATLAB program.

3. Results and discussion

3.1 Thickness dependence of passivation quality

Figure 1 shows the τ_{eff} of c-Si samples passivated with SiN_x films before and after post annealing as a function of the thickness of SiN_x films. τ_{eff} before annealing is comparatively low and increases monotonically with increasing thickness. We consider this tendency is not due to the increase of SiN_x thickness but due to annealing effect by radiant heat from a catalyzer, as will be discussed in detail in section 3.3. τ_{eff} increases significantly by post annealing. τ_{eff} after post annealing increases monotonically with thickness up to ~100 nm, while τ_{eff} saturates with further increase in the film thickness. This means passivation quality cannot be improved simply by increasing SiN_x thickness above the critical thickness of ~100 nm. We should mention the wide fluctuation of τ_{eff} particularly in a large SiN_x thickness region. This may come from many factors such as the wall condition of the Cat-CVD chamber and the position of samples in a holder during SiN_x deposition. An important point here is that τ_{eff} shows a saturation tendency against film thickness.

3.2 Mechanism of thickness dependence

There are two possible mechanisms for the improvement of τ_{eff} depending on SiN_x thickness: termination of interface traps on a c-Si surface and band bending induced by positive fixed charges in SiN_x. To clarify the dominant factor for the variation of τ_{eff}, we evaluated D_{it} and Q_f based on the results of $C–V$ measurements. Figure 2 shows the $C–V$ curves of the MIS structures with different SiN_x thicknesses. All the $C–V$ curves are stretched out in the applied voltage direction, and the samples without annealing shows more

significant stretching compared to the samples after annealing. This qualitatively indicates that D_{it} decreases by post annealing. The C–V curves show a shift toward a minus voltage, indicating the existence of positive charges in SiN_x. The other noticeable phenomenon is hysteresis, which may be caused by traps in SiN_x deeper than interface traps. When C–V curve sweep is from depletion to accumulation, those deep traps will be charged, whereas they will be discharged by sweep in the opposite direction. In this study, we thus determined Q_f from C–V curves obtained by accumulation-to-depletion sweep. It should be noted that the hysteresis of the C–V curves becomes smaller after post annealing in all the samples, indicating a decrease in the number of traps in SiN_x by the annealing.

Figure 3 shows D_{it} as a function of SiN_x thickness. D_{it} significantly decreases after annealing. It is noticeable that D_{it} after annealing decreases with an increase in SiN_x thickness from 59 to 115 nm, whereas D_{it} almost unchanged by further increase in SiN_x thickness from 115 to 167 nm. This is consistent with the thickness dependence of τ_{eff} showing monotonical increase in thin SiN_x region and saturation in thick SiN_x region, respectively. Figure 4 shows Q_f as a function of SiN_x thickness. In contrast to the thickness dependence of D_{it}, Q_f is not affected by post annealing. Furthermore, Q_f rather decreases with an increase in SiN_x thickness. These indicate that not an increase in Q_f but a decrease in D_{it} is the primary cause for the thickness dependence of the passivation quality of Cat-CVD SiN_x films.

We propose a possible model which can explain the change of D_{it} depending on SiN_x thickness. A thicker SiN_x film contain a larger number of hydrogen (H) atoms. The H atoms can diffuse in SiN_x during annealing, some of which reaches c-Si surface and terminates dangling bonds there. However, the dangling bonds cannot be terminated completely by the diffused H atoms even if the amount of arriving H atoms are sufficient, because the dissociation of Si–H also occurs simultaneously on the c-Si surface. This may lead to the saturation of D_{it} and τ_{eff} against SiN_x thickness. On the contrary, thin SiN_x does not contain sufficient amount of H, resulting in the insufficient termination of dangling bonds on the c-Si surfaces and higher D_{it} and lower τ_{eff} compared to the case of thicker SiN_x samples.

3.3 Effects of radiant heat from a catalyzer

We finally discuss the effect of radiant heat from a heated catalyzer during SiN_x deposition. It is unavoidable to completely prevent c-Si substrates and a holder from absorbing the radiant heat in a Cat-CVD chamber, and c-Si substrates cannot be maintained at a setting temperature. Figure 5 shows the temperature of c-Si substrates as a function of the duration of exposure to radiant heat from a catalyzer. We see an almost linear increase in the c-Si temperature. Due to the specification of the temperature-sensitive labels used in this study, the measurement was stopped at 260 °C, and the c-Si substrates are heated up to 260 °C within 120 s. We estimate that the temperature of the c-Si substrates may reach 350 °C within 3 minutes, at which effective improvement of τ_{eff} is expected. As shown in Figs. 1 and 3, τ_{eff} of the samples before annealing shows a monotonic increase, corresponding to a monotonic decrease of D_{it}. Figure 6 shows τ_{eff} of the samples only before annealing, with the same data points as those in Fig. 1 and different magnification of the vertical axis. τ_{eff} before annealing increases slowly with SiN_x thickness when the thickness is less than 100 nm, corresponding a deposited duration of ~3 min. The increasing rate of τ_{eff} significantly changes at 100 nm, which suggests that the diffusion of H atoms and resulting termination of dangling bonds are activated. The τ_{eff} increase and D_{it} decrease with SiN_x thickness before annealing are thus considered to be caused by annealing effect of radiant heat rather than thickness increase. Note that the annealing effect of the radiant heat does not affect the τ_{eff} of the samples after post annealing, as shown in Fig. 1.

4.   Conclusions

We investigated the thickness dependence of the passivation quality of Cat-CVD SiN_x films. We found that the passivation quality of SiN_x after post annealing improves with an increase in SiN_x thickness up to ~100 nm, while no further increase in τ_{eff} is observed in the samples with thicker SiN_x. The thickness dependence of D_{it} corresponds to that of τ_{eff},

whereas no remarkable relationship between Q_f and τ_{eff} is confirmed. Based on these results, we speculate the reason for the thickness dependence of the passivation quality of SiN$_x$ films that a thicker SiN$_x$ may release more H atoms during annealing to terminate dangling bonds on the c-Si surface. The thickness dependence of τ_{eff} before annealing is considered as a result of annealing effect during SiN$_x$ deposition caused by radiant heat from a catalyzer.

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Figure Captions

Fig. 1. τ_{eff} of the samples passivated with SiN_x films as a function of SiN_x thickness.

Fig. 2. *C–V* curves of the MIS samples with SiN_x films with thicknesses of (a) 59 nm, (b) 115 nm, and (c) 167 nm.

Fig. 3. D_{it} as a function of SiN_x thickness.

Fig. 4. Q_{f} as a function of SiN_x thickness.

Fig. 5. Substrate temperature during SiN_x deposition as a function of the duration of exposure to radiant heat from a catalyzer.

Fig. 6. τ_{eff} of the samples before annealing passivated with SiN_x films as a function of SiN_x thickness.

Table I. Deposition conditions of SiN$_x$ films

Gas sources	SiH$_4$ 8 sccm NH$_3$ 150 sccm
Substrate temperature	100 ℃
Pressure	10 Pa
Catalyzer temperature	1800 ℃
Duration	30–900 s

Fig. 1   Y. Wen *et al.*,

(a) 59 nm

— w/o annealing
— After annealing

(b) 115 nm

— w/o annealing
— After annealing
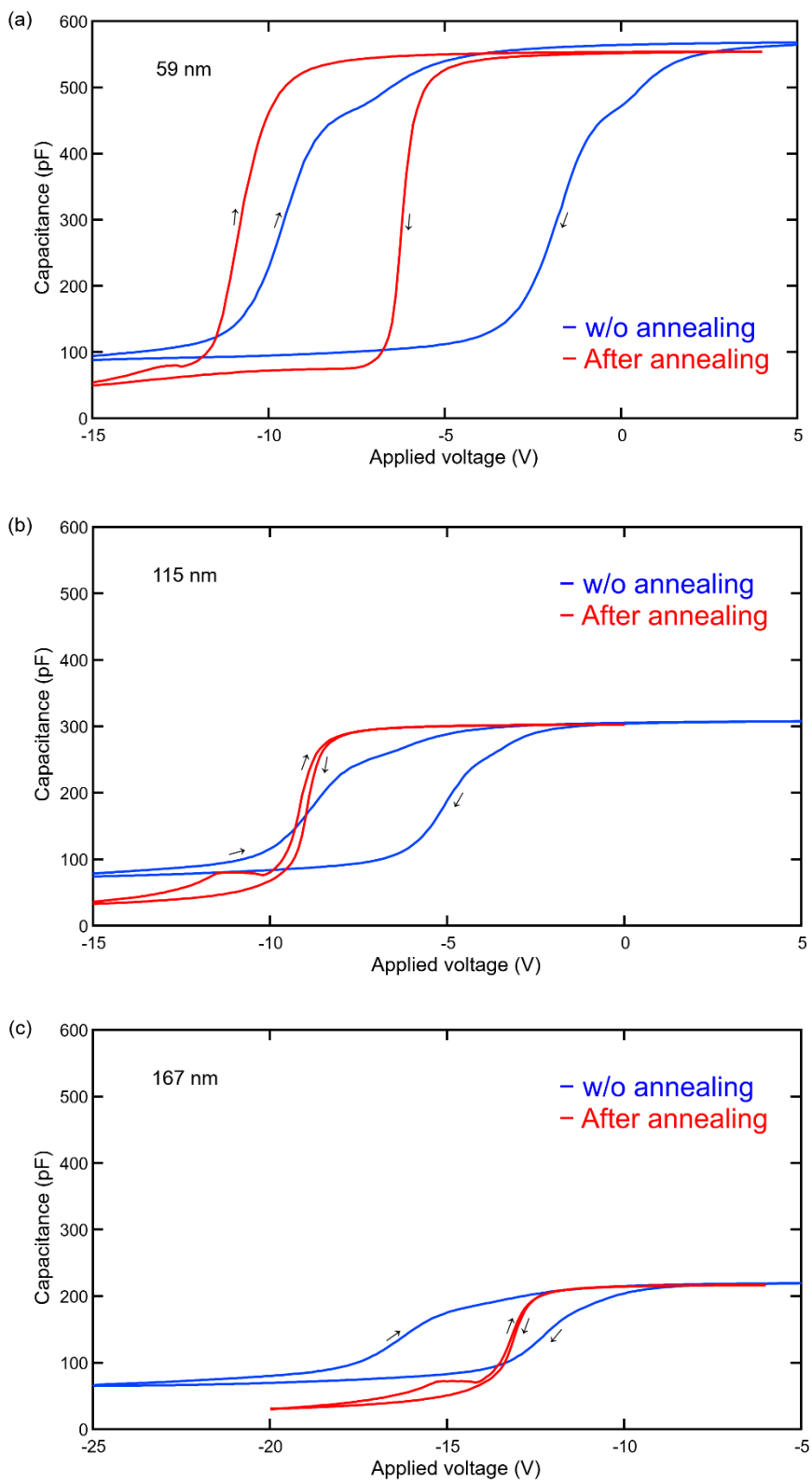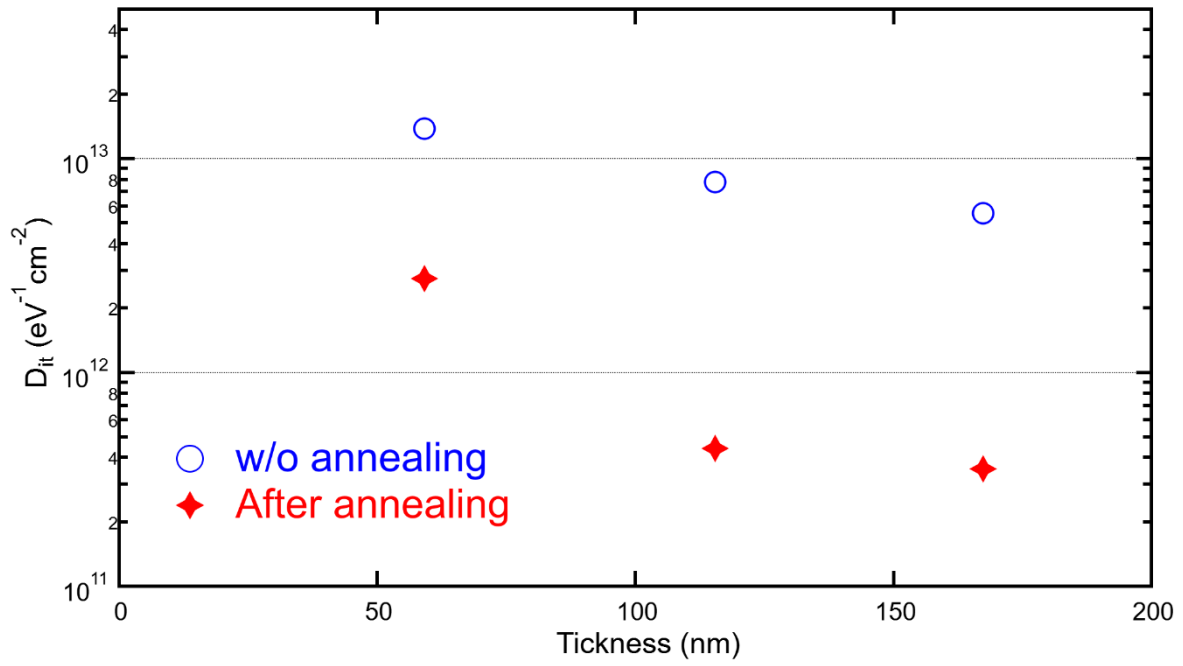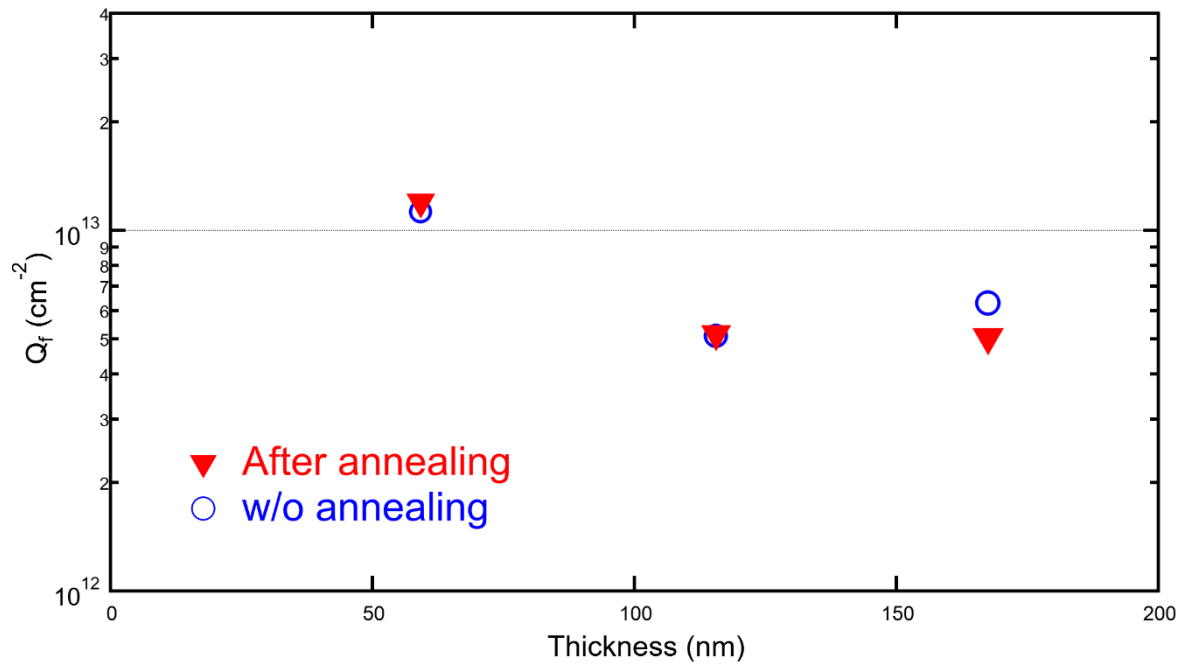
(c) 167 nm

— w/o annealing
— After annealing

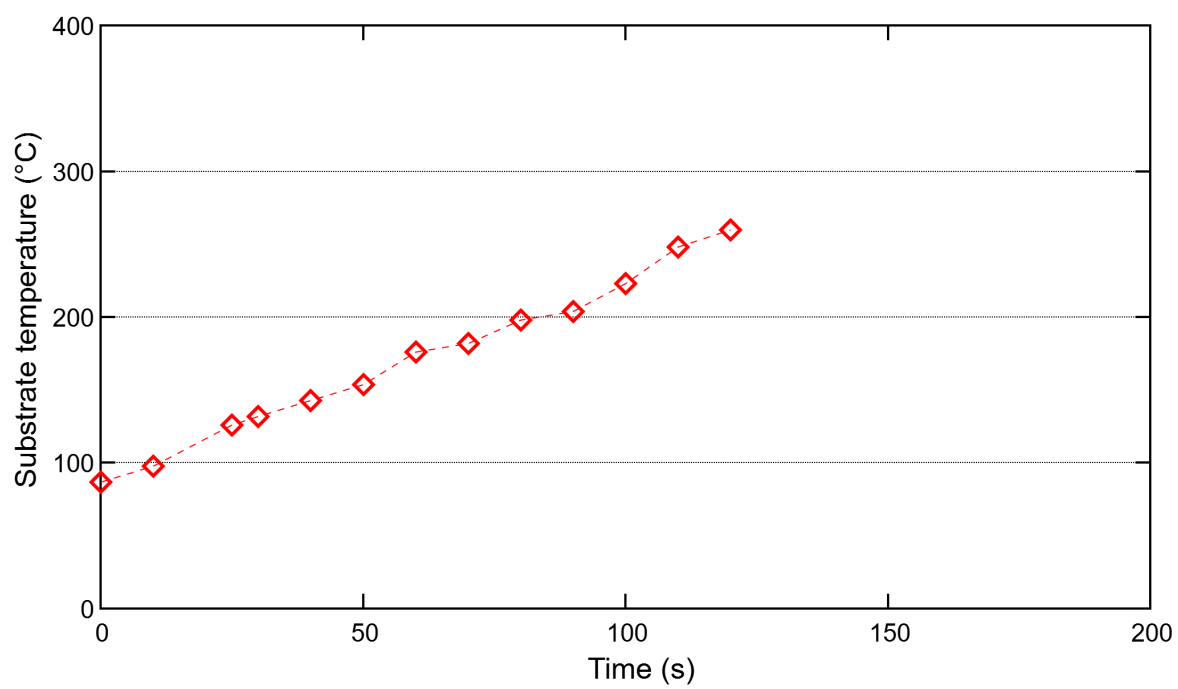Figure 2   Y. Wen *et al.*,

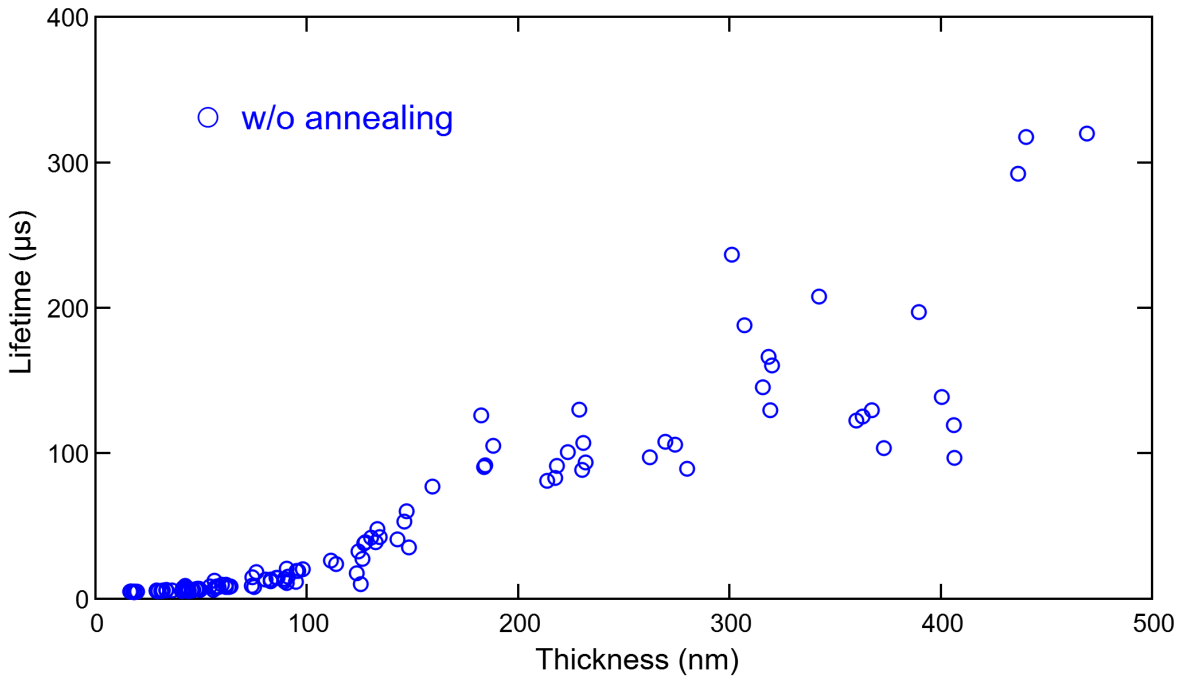12
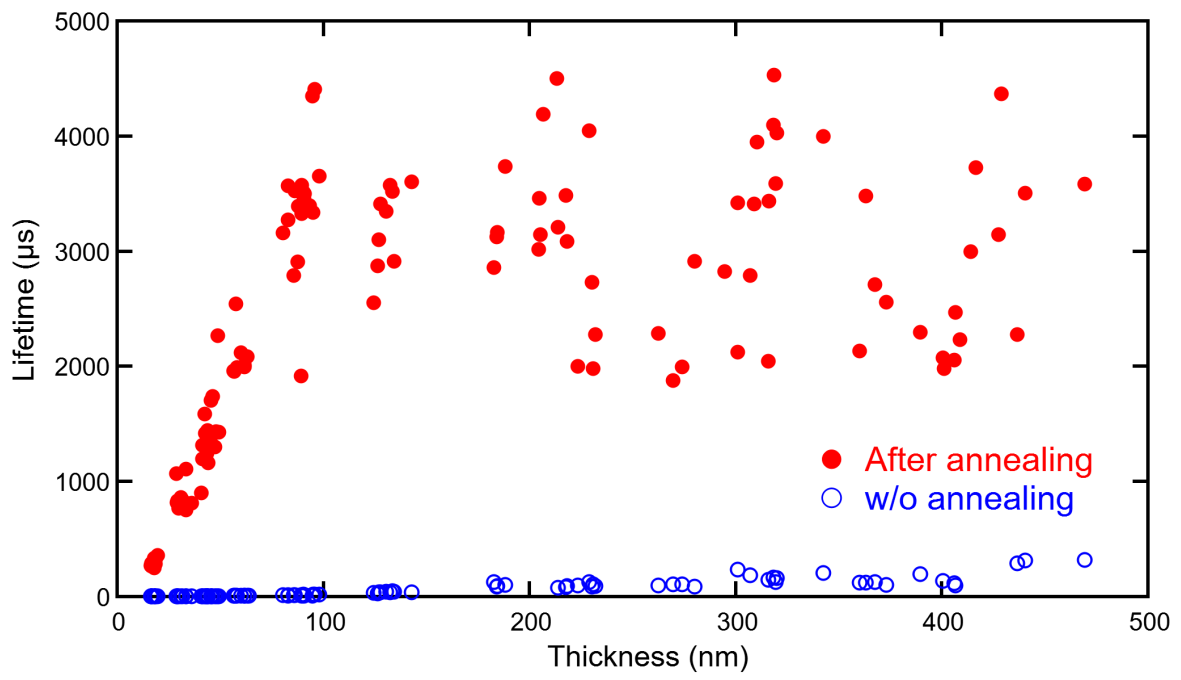
Figure 3　Y. Wen *et al.*,

Figure 4   Y. Wen *et al.*,

Figure 5   Y. Wen *et al.*,

Figure 6   Y. Wen *et al.*,