Light-induced anelastic change in a-Si(H)

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Abstract

The thermal desorption spectra between 400 K and 1100 K and the internal friction spectra between 80 K and 423 K were studied for a-Si(H). The thermal desorption of hydrogen was observed around 650 K (TDH_{650K}) and around 900 K ($TDH_{900K,L}$ and $TDH_{900K,H}$). Both $TDH_{900K,L}$ and $TDH_{900K,H}$ with the activation energy of 1.6 eV were attributed to the desorption of bonded hydrogen. TDH_{650K} was not a diffusion controlled process with the activation energy of 1.0 eV, where one part of TDH_{650K} was attributed to the desorption of isolated hydrogen molecules. The hydrogen-induced internal friction, H-$Q^{-1}_{a\text{-}Si(H)}$, was observed between 80 K and 423 K. Hydrogen responsible for $H\text{-}Q^{-1}_{a\text{-}Si(H)}$ showed the thermal desorption around 650 K (TDH_{650K}), indicating that isolated hydrogen molecules in the amorphous structure may be responsible for H-$Q^{-1}_{a\text{-}Si(H)}$. Light soaking caused changes in H-$Q^{-1}_{a\text{-}Si(H)}$ in the temperature ranges between 80 K and 200 K and between 200 K and 300 K, indicating that light soaking modified the local amorphous structures responsible for these changes in $Q^{-1}_{a\text{-}Si(H)}$.

1. Introduction

Hydrogen plays an important role on the structural and electronic properties of hydrogenated amorphous silicon (a-Si(H)). It is known that light soaking induces conductivity changes in a-Si(H) as known as the Staebler-Wronski effect [1] and causes degradation of the photovoltaic performance of a-Si(H). Although much effort has been devoted to study the light soaking effects, their underlying mechanisms are not clear yet. One of the reasons may be the structural metastability [2-4] inevitable in amorphous materials and the probable high mobility of one part of constituent hydrogen [5, 6]. In a-metal alloys containing an element with a high affinity for hydrogen, hydrogenation brings about a strong increase in the internal friction over the wide temperature range between 5 K and 400 K [7-9]. The hydrogen-induced internal friction in a-metal alloys is due to the stress-induced redistribution of mobile hydrogen atoms which is known as the Snoek relaxation in crystalline metals. Since the solubility of hydrogen in a-metal alloys is much higher than that in the crystalline state and remains unchanged even in the low temperature range, the strong hydrogen-induced internal friction can be observed in the wide temperature range giving insight into the local amorphous

structures [8]. For a-Si(H), the anelastic study is very limited. Liu et al. [10] have reported that the light soaking for several days at room temperature caused an increase in the low temperature internal friction between 0.5 K and 30 K. They claimed that the increase in the low temperature internal friction associated with a change in the density of the two-level tunneling system. In the present work, we studied the hydrogen-induced internal friction in a-Si(H) in the temperature range above 80 K to get insight into the light-soaking-induced structural changes. It is noted that the anelasticity response may detect the structural changes and defects which can interact with elastic strain, e.g., including the electrically inert ones.

2. Experimental

Hydrogenated amorphous silicon (a-Si(H)) films were deposited on crystalline (c-) Si reed-substrates by means of the plasma enhanced chemical vapor deposition (PECVD) method similar to that reported in [11]. The deposition conditions were as follows: The SiH_4 and H_2 flow rates were 20 cc/min and 40 cc/min, respectively, where the total pressure was 80 Pa and the RF power was, typically, 12W. The substrate temperature during deposition, T_{dep}, was 423 K, 523 K and 623 K. The deposition rate, R_{dep}, was 0.1 nm/s for most cases and 0.4 nm/s for the highest rate deposition case. It is known that the concentration of hydrogen in a-Si(H) is a function of both T_{dep} and R_{dep}. In the following, a-Si(H) prepared at T_{dep} and R_{dep}, e.g. at 423 K and 0.1 nm/s, will be referred to a-Si(H)$_{423K,0.1}$. The thickness of a-Si(H) films, $t_{a\text{-Si}}$, was between 0.5 μm and 1 μm for most cases and 3 μm for the thickest case. The concentration of hydrogen, C_H, and the hydrogen effusion characteristics, dC_H/dt $vs.$ T, were measured by means of the thermal desorption spectroscopy which was carried out during heating with a constant rate, α, of, typically, 24, 48 and 96 K/min in a vacuum of 10^{-5} Pa. The specimen setup for the internal friction measurements was similar to that reported in [12], where the resonant frequency and the internal friction, Q^{-1}, of the composite reed, a Si-reed with an a-Si(H) film, were measured between 80 K and 423 K. The strain amplitude in a-Si(H) and the resonant frequency of the reed were 10^{-6} and about 600 Hz, respectively. Light soaking was carried out by using the infrared-radiation-filtered white light from a halogen lamp, where the soaking light was conducted to the a-Si(H) film surface by a quartz rod and its intensity on the specimen surface was 100 mW/cm^2 (1 sun, hereafter).

3. Results

In order to pursue the type of hydrogen responsible for the hydrogen-induced internal friction in a-Si(H), the thermal desorption spectroscopy was carried out. Fig.1 shows examples of the thermal desorption spectra observed for a-Si(H)$_{423K,0.2}$, a-Si(H)$_{523K,0.4}$ and a-Si(H)$_{623K,0.15}$ films, where C_H was ~27 at% for a-Si(H)$_{423K,0.2}$, 15 at% for a-Si(H)$_{523K,0.4}$ and 9 at% for a-Si(H)$_{623K,0.15}$ films, respectively. After taking into account the specimen preparation conditions, the thermal desorption spectra seen in Fig. 1 and C_H are similar to those reported [13,14]. In Fig. 1, broad peaks of the thermal desorption of hydrogen can be seen at around 650 K (TDH$_{650K}$) and 900 K (TDH$_{900K}$), where TDH$_{900K}$ is composed of two constituent peaks, TDH$_{900K,L}$ and TDH$_{900K,H}$ at the lower and higher temperatures, respectively. The preferential growth of the TDH$_{900K,H}$ with decreasing T_{dep} or increasing C_H indicates that TDH$_{900K,L}$ and TDH$_{900K,H}$ are TDH from Si-H and Si-H$_2$, respectively [15]. Fig. 2 shows the a-Si(H) film thickness dependence of the thermal desorption spectra observed for a 1 μm-thick a-Si(H)$_{423K,0.4}$ film, a 3 μm-thick a-Si(H)$_{423K,0.4}$ film and a 1 μm-thick a-Si(H)$_{423K,0.2}$ film. The thermal desorption spectra for the 1 μm-thick a-Si(H)$_{423K,0.4}$ film were very similar

to those for the 1 μm-thick a-Si(H)$_{423K,0.2}$ film except that the strength of TDH$_{650K}$ was much larger in a-Si(H)$_{423K,0.4}$ because of an increased deposition rate. As seen in Fig. 2, TDH$_{650K}$ showed no thickness dependence and TDH$_{900K}$ showed a shift to the higher temperature side for the thicker specimen, where a change in the profile of TDH$_{900K}$ associated with the crystallization was also observed. Fig. 3(a) shows the heating rate dependence of thermal desorption spectra observed for the 1 μm-thick a-Si(H)$_{423K,0.25}$ films, where both TDH$_{650K}$ and TDH$_{900K}$ showed a shift to the higher temperature side with increasing the heating rate. Fig. 3(b) shows the Kissinger plot [16] for TDH$_{650K}$, TDH$_{900K,L}$ and TDH$_{900K,H}$ where the activation energy found was E_{650K} = 1.0 eV for TDH$_{650K}$, $E_{900K,L}$ = 1.6 eV for TDH$_{900K,L}$ and $E_{900K,H}$ = 1.6 eV for TDH$_{900K,H}$, respectively. $E_{900K,L}$ and $E_{900K,H}$ found in Fig. 3(b) show good agreement with the activation energy of the migration of bonded hydrogen in a-Si(H) whose mechanism reported is, e.g., the floating bond mediated migration [6].

Fig. 4(a) shows examples of Q^{-1} spectra observed for c-Si reeds prior to deposition and those after deposition of the a-Si(H)$_{423K,0.4}$, a-Si(H)$_{523K,0.15}$ and a-Si(H)$_{623K,0.15}$ films 1 μm thick. A monotonous increase in Q^{-1} for T above about 200 K is associated with the thermoelastic relaxation [17]. From Q^{-1} shown in Fig. 4(a), the internal friction of a-Si(H), $Q^{-1}_{a\text{-Si(H)}}$, may be given by,

$$Q^{-1}_{a\text{-Si(H)}} = (t_s/3t_{a\text{-Si(H)}})(M_s/M_{a\text{-Si(H)}})(Q^{-1} - Q^{-1}_s), \qquad (1)$$

Where Q^{-1}_s is the internal friction of the c-Si substrate, M_s and $M_{a\text{-Si(H)}}$ is the Young's modulus of the substrate c-Si and the a-Si(H) film, and t_s and $t_{a\text{-Si(H)}}$ denote the thickness of the substrate-reed and the film, respectively [18]. Fig. 4(b) shows $Q^{-1}_{a\text{-Si(H)}}$ determined from the Q^{-1} data shown in Fig. 4(a) and Eq. (1). $Q^{-1}_{a\text{-Si(H)}}$ was observed in the whole temperature range between 80 K and 423 K showing a broad peak between 80 K and 200 K ($Q^{-1}_{a\text{-Si(H)},80\text{-}200K}$, hereafter) and an increase with increasing temperature above 200 K. For most a-Si(H) specimens, in addition to the increase in $Q^{-1}_{a\text{-Si(H)}}$ above 200 K, a broad peak between 200 K and 300 K ($Q^{-1}_{a\text{-Si(H)},200\text{-}300K}$, hereafter) was observed too as seen in Fig. 4(b). It is noted that although the magnitude of $Q^{-1}_{a\text{-Si(H)}}$ showed, in general, an increase in the whole temperature range with decreasing T_{dep} or increasing C_H, the detailed feature and the magnitude of $Q^{-1}_{a\text{-Si(H)},80\text{-}200K}$ and $Q^{-1}_{a\text{-Si(H)},200\text{-}300K}$ varied among a-Si(H) specimens. These features of $Q^{-1}_{a\text{-Si(H)}}$ are very similar to the hydrogen-induced internal friction in a-metal alloys [7-9] except that the magnitude of $Q^{-1}_{a\text{-Si(H)}}$ was lower by more than one digit than that of the hydrogen-induced internal friction in a-metal alloys. Fig. 5 shows the effect of degassing treatment on $Q^{-1}_{a\text{-Si(H)}}$ observed for the a-Si(H)$_{423K,0.1}$ film. The degassing treatment at 550 K for 2 h in a high vacuum modified little both $Q^{-1}_{a\text{-Si(H)}}$ and TDH$_{650K}$ (not shown here). In contrast, the degassing treatment at 580 K for 2 h in a high vacuum brought about a considerable decrease in both $Q^{-1}_{a\text{-Si(H)}}$ and TDH$_{650K}$ (not shown here). These results indicate that the hydrogen-induced internal friction, H-$Q^{-1}_{a\text{-Si(H)}}$, is the major constituent internal friction in $Q^{-1}_{a\text{-Si(H)}}$ and hydrogen responsible for $Q^{-1}_{a\text{-Si(H)}}$ can be degassed during TDH$_{650K}$.

Fig. 6 shows examples of an effect of light soaking at 100 K on $Q^{-1}_{a\text{-Si(H)}}$ observed for the a-Si(H)$_{523K,0.15}$ film. For the a-Si(H)$_{523K,0.15}$ film shown in Fig. 6, light soaking at 100 K caused a decrease in $Q^{-1}_{a\text{-Si(H)},80\text{-}200K}$ and an slight increase in $Q^{-1}_{a\text{-Si(H)},200\text{-}300K}$ and the light-soaking induced changes in $Q^{-1}_{a\text{-Si(H)}}$ were almost recovered after heating to 423 K. It is noted that both the magnitude and the sign of changes of $Q^{-1}_{a\text{-Si(H)}}$ were variable among various a-Si(H) films, however, light soaking always modified $Q^{-1}_{a\text{-Si(H)},80\text{-}200K}$ and $Q^{-1}_{a\text{-Si(H)},200\text{-}300K}$ and annealing at 423 K cancelled the light soaking effects.

Fig. 7 (a) and 7(b) show two typical examples of $Q^{-1}_{a\text{-Si(H)}}$ observed during light soaking for a-Si(H)$_{523K,0.15}$ films, the a-Si(H)$_{523K,0.15}$-1 film and the the a-Si(H)$_{523K,0.15}$-2 film hereafter. For the a-Si(H)$_{523K,0.15}$-1 film shown in Fig. 7(a), the *in situ* light soaking caused a strong

decrease in $Q^{-1}_{a\text{-Si(H)},80\text{-}200K}$ and a slight increase in $Q^{-1}_{a\text{-Si(H)},200\text{-}300K}$. These changes in $Q^{-1}_{a\text{-Si(H)}}$ were recovered after heating to 423 K (not shown here). For the a-Si(H)$_{523K,0.15}$-2 film shown in Fig. 7(b), the *in situ* light soaking caused a slight decrease in $Q^{-1}_{a\text{-Si(H)},80\text{-}200K}$ and a considerable increase in $Q^{-1}_{a\text{-Si(H)},200\text{-}300K}$.

4. Discussion

It is reported that the thermal desorption spectra observed for a-Si(H)$_{298K}$ showed a strong and narrow TDH near 670 K which was claimed to be indicative of the presence of an interconnected void network and/or a columnar microstructure [13]. TDH$_{650K}$ observed for a-Si(H)$_{423K}$, a-Si(H)$_{523K}$ and a-Si(H)$_{623K}$ films are broader in width and much lower in strength than the narrow TDH near 670 K, indicating that most of hydrogen responsible for TDH$_{650K}$ is hydrogen other than that trapped by inner surfaces or interfaces assumed for the narrow TDH near 670 K [13]. The observed no thickness dependence of TDH$_{650K}$ indicates that hydrogen responsible for TDH$_{650K}$ was highly mobile near 650 K and TDH$_{650K}$ was governed by the surface recombination process. Since hydrogen trapped by inner surfaces or interfaces is not expected to give rise H-$Q^{-1}_{a\text{-Si(H)}}$, hydrogen responsible for H-$Q^{-1}_{a\text{-Si(H)}}$ should be hydrogen existing in the amorphous structure other than bonded hydrogen which is responsible for TDH$_{900K}$. A recent theoretical work predicts the existence of hydrogen molecules in the amorphous structure of a-Si(H) and its high mobility [19,20]. Experimentally, it is reported that there exist both isolated hydrogen molecules and clustered ones in a-Si(H) and the isolated ones can act as relaxation centers [21]. On the other hand, the $Q^{-1}_{a\text{-Si(H)}}$ data shown in Figs. 4(b) and 5 indicate that the activation energy of the anelastic relaxation for $Q^{-1}_{a\text{-Si(H)}}$ shows a wide distribution. When the anelastic model for the hydrogenated a-metal alloys is valid for H-$Q^{-1}_{a\text{-Si(H)}}$, such a wide distribution is associated with the variation in the local amorphous structures. The observed results shown in Figs. 6 and 7 indicate that light soaking modify the local amorphous structures responsible for $Q^{-1}_{a\text{-Si(H)},80\text{-}200K}$ and $Q^{-1}_{a\text{-Si(H)},200\text{-}300K}$. On the other hand, the magnitude of $Q^{-1}_{a\text{-Si(H)},80\text{-}200K}$ and $Q^{-1}_{a\text{-Si(H)},200\text{-}300K}$ and the magnitude of the light soaking effects on them are variable among a-Si(H) films prepared by almost the same preparation condition. These results indicate that the understanding and the experimental control of the local amorphous structures responsible for $Q^{-1}_{a\text{-Si(H)},80\text{-}200K}$ and $Q^{-1}_{a\text{-Si(H)},200\text{-}300K}$ are important to clarify the light soaking effects in a-Si(H). In order to pursue these issues, the further work is in progress.

5. Conclusion

For a-Si(H), the thermal desorption of hydrogen was observed around 650 K (TDH$_{650K}$) and around 900 K (TDH$_{900K,L}$ and TDH$_{900K,H}$). Both TDH$_{900K,L}$ and TDH$_{900K,H}$ with the activation energy of 1.6 eV were attributed to the desorption of bonded hydrogen. TDH$_{650K}$ is not a diffusion controlled process with the activation energy of 1.0 eV, where one part of TDH$_{650K}$ is attributed to the desorption of isolated hydrogen molecules in the amorphous structure. The hydrogen-induced internal friction, H-$Q^{-1}_{a\text{-Si(H)}}$, is observed between 80 K and 423 K. Isolated hydrogen molecules in the amorphous structure may be responsible for H-$Q^{-1}_{a\text{-Si(H)}}$. Light soaking caused changes in H-$Q^{-1}_{a\text{-Si(H)}}$ in the temperature ranges between 80 K and 200 K and between 200 K and 300K, indicating that light soaking modified the local amorphous structures.

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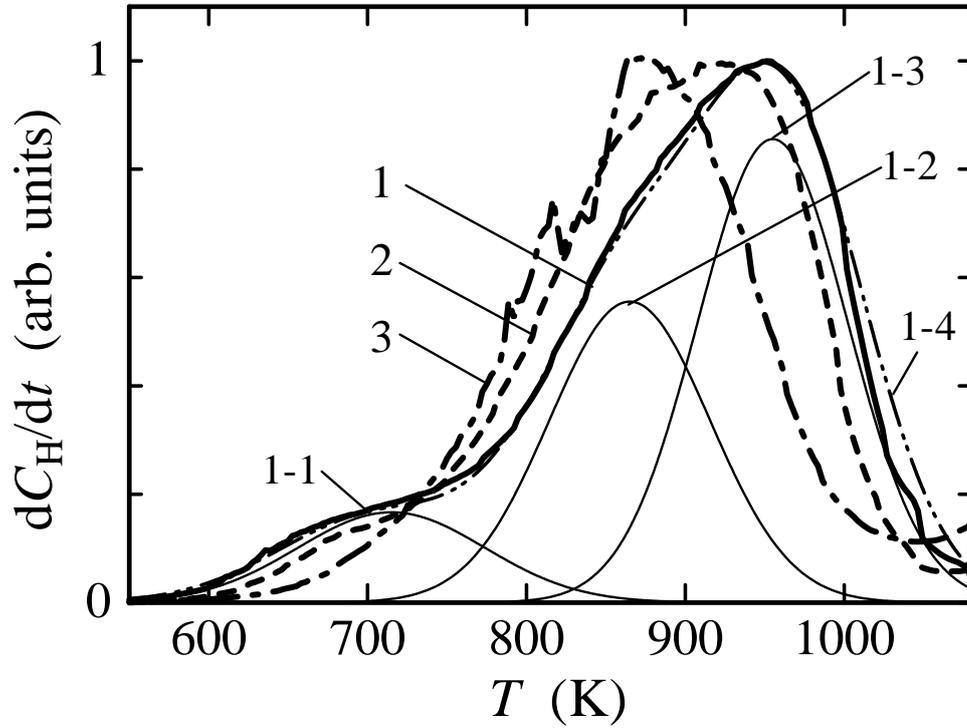
Fig.1.

Examples of the thermal desorption spectra observed for the a-Si(H)$_{423K,0.2}$ (1), a-Si(H)$_{523K,0.4}$ (2) and a-Si(H)$_{623K,0.15}$ (3) films with the film thickness, $t_{a\text{-Si}}$, of 1 μm. The desorption rate, dC_H/dt, is plotted against T, where α was 48 K/min. The theoretical curve 1-4 is fitted to the observed spectrum 1, where the theoretical constituent curves 1-1, 1-2 and 1-3 denote the TDH$_{600K}$, TDH$_{900K,L}$ and TDH$_{900K,H}$, respectively. See text for details.
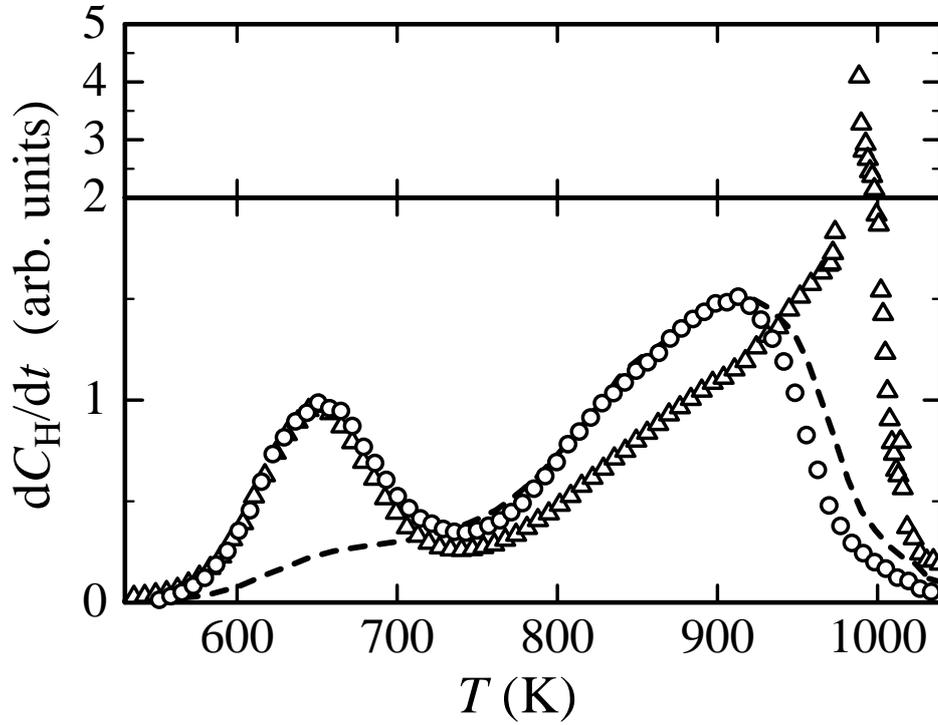
Fig.2.

The thermal desorption spectra observed for the a-Si(H)$_{423K,0.4}$ film 1 μm thick (open circles), the a-Si(H)$_{423K,0.4}$ film 3 μm thick (open triangles) and the a-Si(H)$_{423K,0.2}$ film 1 μm thick (dashed curve), where α was 24 K/min.
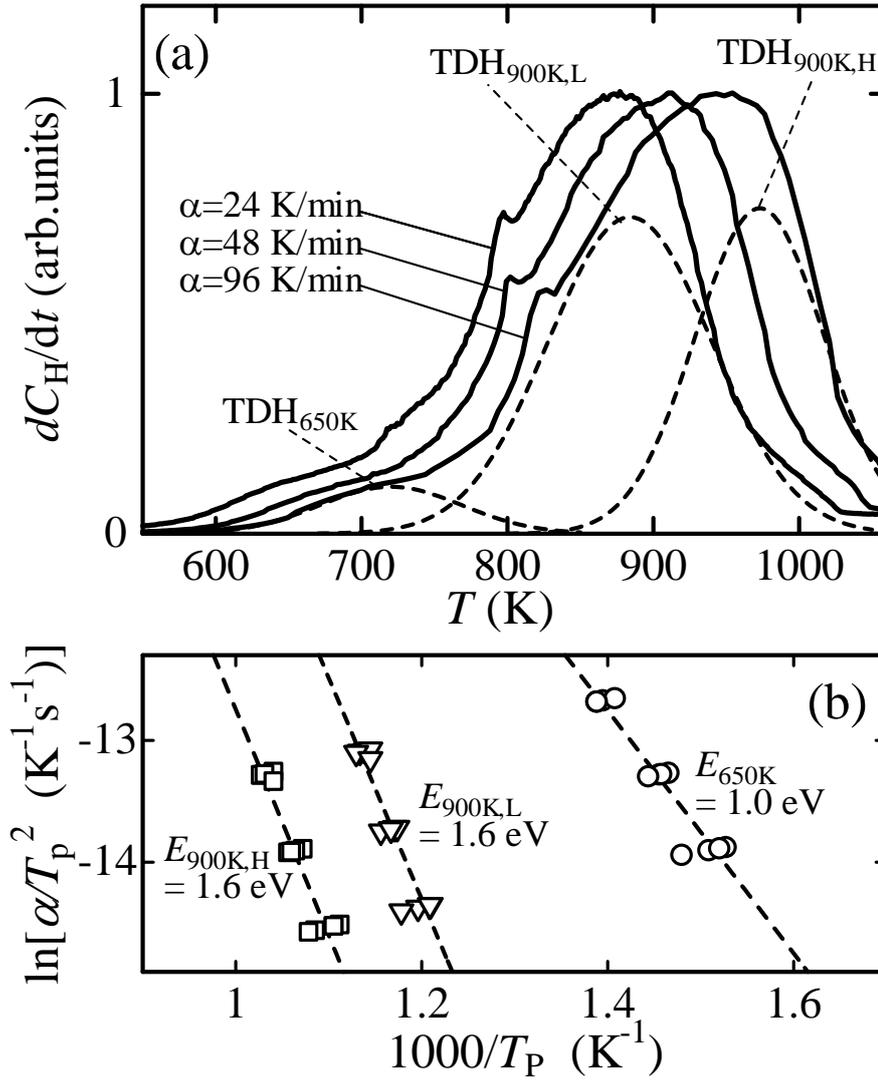
Fig.3.

(a) An example of the heating rate dependence of the TDH spectra observed for a-Si(H)$_{423K,0.25}$ films 1 μm thick. The dashed Gaussian curves are drawn to guide eyes. (b) The Kissinger plots for TDH$_{650K}$, and TDH$_{900K,L}$ and TDH$_{900K,H}$. See text for details.
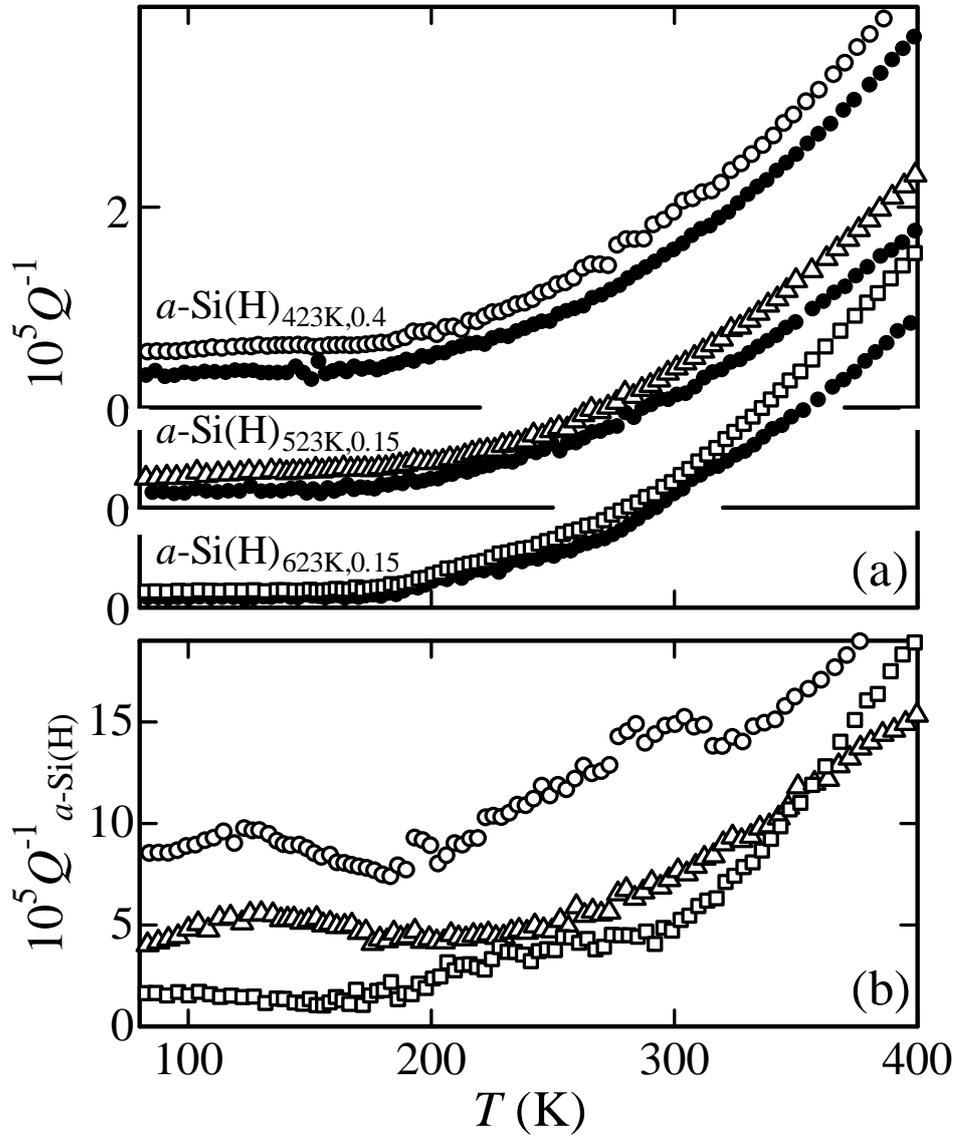
Fig.4.

(a) Examples of the Q^{-1} measurements for a c-Si reed-substrate (filled circles) and that after deposition of the a-Si(H)$_{423K,0.4}$ (open circles), a-Si(H)$_{523K,0.15}$ (open triangles) and a-Si(H)$_{623K,0.15}$ (open squares) films 1 μm thick. (b) $Q^{-1}{}_{a\text{-Si(H)}}$ determined from the Q^{-1} data shown in (a). See text for details.
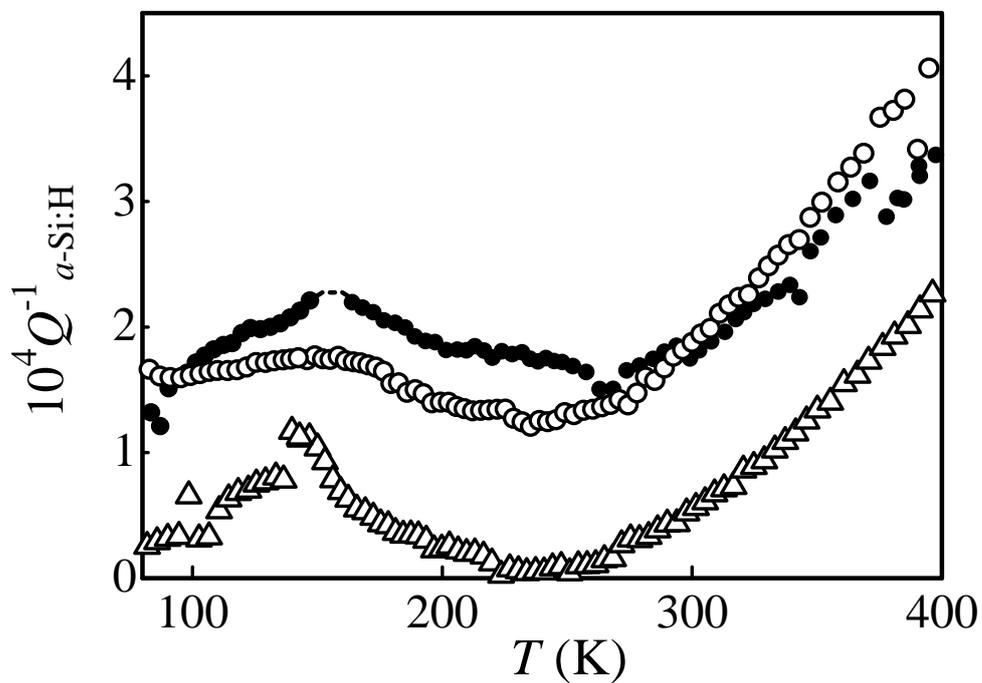
Fig.5.

The $Q^{-1}_{a\text{-Si(H)}}$ observed in an a-Si(H)$_{423\text{K},0.1}$ film 1 μm thick after hydrogen degassing treatments in a vacuum. ●; as-deposited, ○; at 550 K for 2 h, △; at 580 K for 2 h. For the as-deposited data, the data between 150 K and 162 K were missing (dashed curve) because of accidental noises. See text for details.
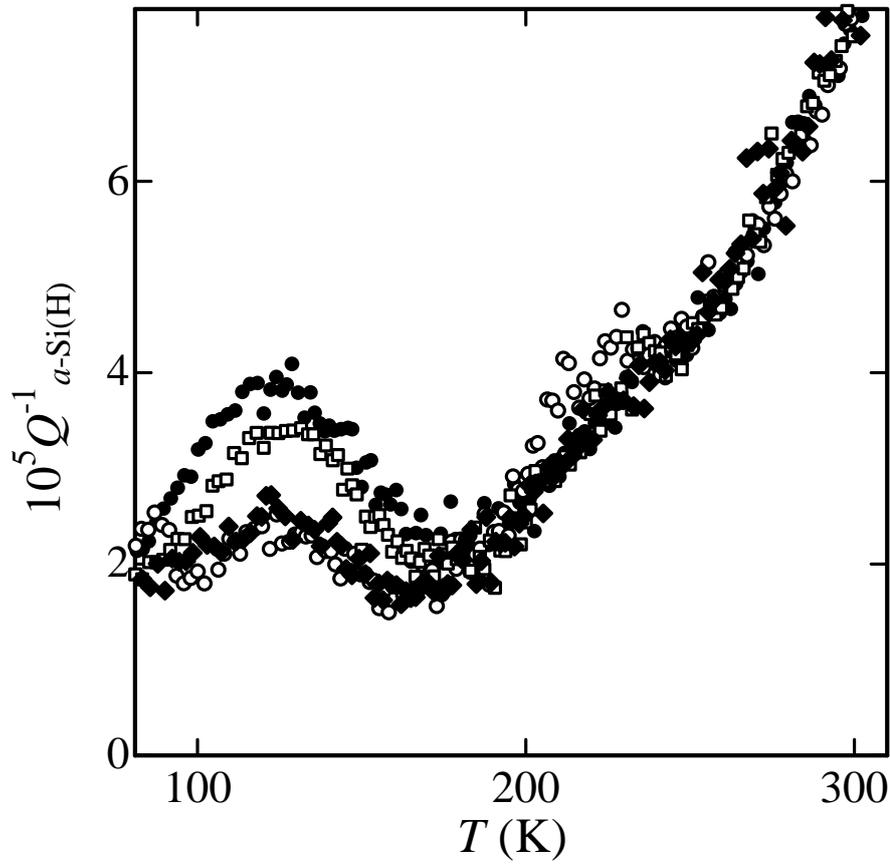
Fig.6.

An example of changes in $Q^{-1}_{a\text{-Si(H)}}$ after light soaking at ~100 K observed in an a-Si(H)$_{523K,0.15}$ film 1 μm thick. ●; after warmed up to 423 K, ○; after 1 sun soaking for 1 day following ●, □; after warmed up to 423 K following ○, ◆; after 1 sun soaking for 3 day following □.
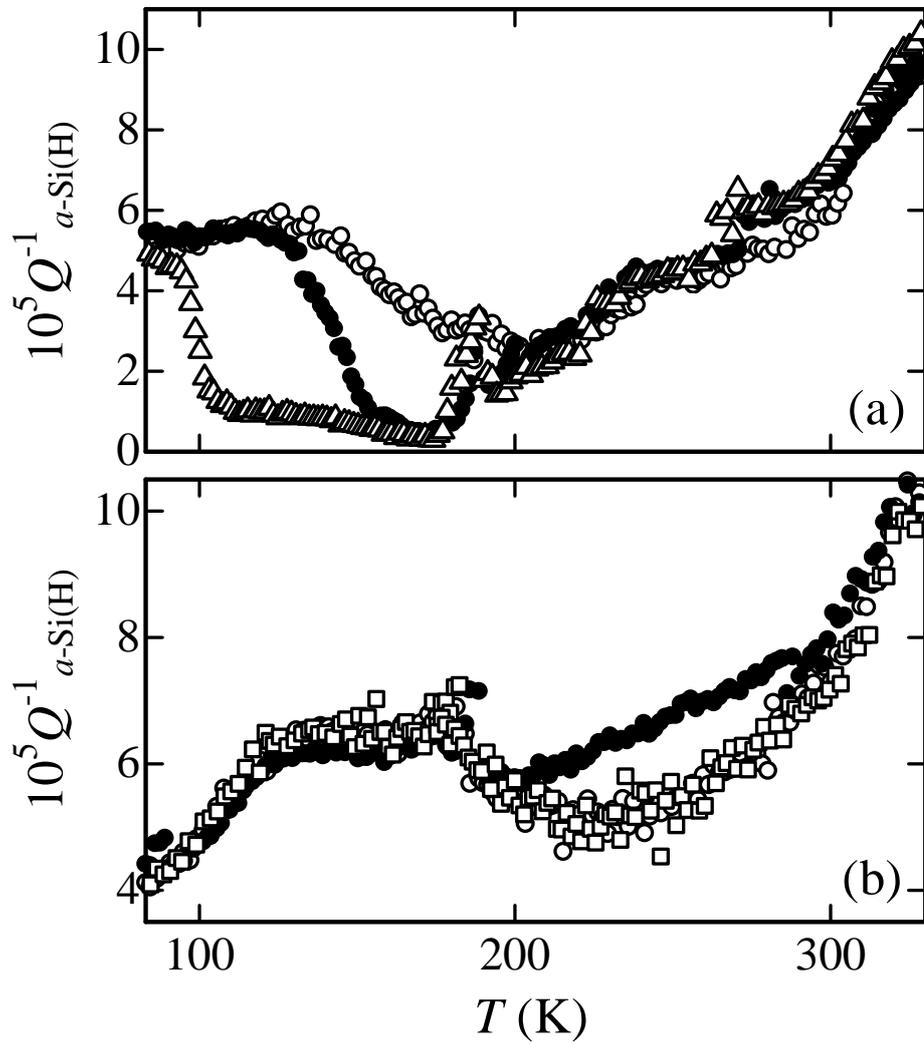
Fig. 7.

Two typical examples of $Q^{-1}_{a\text{-Si(H)}}$ observed during light soaking for a-Si(H)$_{523K,0.15}$ films, (a) and (b), where $t_{a\text{-Si}} = 1$ μm. (a) for an a-Si(H)$_{523K,0.15}$ film, ○; after warm up to 423 K, ●; during 1 sun soaking following ○ and △; during 0.5 sun soaking after warm up to 423 K following ●. (b) for the other a-Si(H)$_{523K,0.15}$ film, ○; after warm up to 423 K, ●; during 1 sun soaking and □; after warm up to 423 K following ●.