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Description	

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Formation of amorphous silicon passivation films with high stability against postannealing, air exposure, and light soaking using liquid silicon

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We applied liquid-source vapor deposition (LVD), thermal CVD from the vapor of cyclopentasilane (CPS), to form amorphous silicon (a-Si) passivation films on crystalline Si (c-Si) wafers, and investigated the thermal stability of the films against postannealing. LVD a-Si passivation films showed a high initial effective minority carrier lifetime (τ_{eff}) of >300 μs and a higher thermal stability than a reference plasma-enhanced chemical-vapor-deposited (PECVD) sample. The high thermal stability of LVD a-Si passivation films may be attributed to the considerably high deposition temperature of the films at 360 °C or more. LVD a-Si passivation films were sufficiently stable also against air exposure and 1-sun light soaking. We also confirmed that the epitaxial growth of Si films does not occur on c-Si even at such high deposition temperatures, and LVD could realize the simultaneous deposition of a-Si films on both sides of a c-Si wafer.

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1. Introduction

The technologies of the formation of amorphous Si (a-Si) films have become increasingly important along with the growing market for Si heterojunction (SHJ) solar cells.[1-5] Interestingly, a-Si films can be formed not only by vapor deposition in vacuum but also by printing technology at atmospheric pressure using liquid Si, in which Si ink consisting of polydihydrosilane and solvent is used.[6-13] There are many advantages of forming a-Si films by printing such as low equipment cost due to a nonvacuum process, high efficiency of material usage, and the selective formation of a-Si films only on desired positions. The selective formation of a-Si is useful particularly for the fabrication of heterojunction back-contact (HBC) solar cells, in which p-type and n-type a-Si films must be formed interdigitatedly.[14-17] To apply liquid Si to the fabrication of HBC cells, intrinsic a-Si (i-a-Si) passivation films with high thermal stability are required since the formation of p-type and n-type a-Si films from Si ink requires annealing at ~400 °C after the printing.[9] This is probably difficult for a-Si films formed by conventional plasma-enhanced chemical vapor deposition (PECVD) because of a typical deposition temperature of ~200 °C or less for a-Si passivation layers.[18]

We have recently developed a new method to form a-Si films from cyclopentasilane (CPS) vapor.[19-21] Although CPS is used as a precursor of Si ink, we here directly vaporize CPS in a small chamber filled with nitrogen gas, and a-Si films are formed by thermal CVD. We have referred to this novel a-Si formation technique as liquid-source vapor deposition (LVD). Since wafers are heated at 360 °C or more during the deposition, a-Si films formed may have high thermal stability against postannealing at 400 °C.

Furthermore, Mews *et al*. have recently reported that a-Si passivation films formed by the spin coating and successive annealing of Si ink prepared from neopentasilane[23] show the rapid degradation of their passivation ability during exposure to air, although c-Si wafers passivated with a-Si films originally have a high minority carrier lifetime of >1 ms.[23] Thus, we should also examine the stability of LVD a-Si passivation films against air exposure and light soaking as well as their thermal stability. In this paper, we report the stability of a-Si films formed by LVD using CPS vapor against post deposition annealing, air exposure, and 1-sun light soaking.

2. Experimental procedure

Figure 1 shows the schematic of a deposition chamber used for the LVD of a-Si films. The chamber was put in a glove box filled with nitrogen at atmospheric pressure. Oxygen concentration in the glove box was kept to be less than 5 ppm. CPS liquid was stored in two small chambers located on the sides of the main deposition chamber. These chambers have heaters and their temperature can be controlled independently. We prepared floating-zone-grown, n-type, double-side mirror-polished, (100)-oriented c-Si wafers with a resistivity of 1-5 Ωcm, a thickness of 290 μm, and a bulk minority carrier lifetime of >10 ms, and cleaved them into 20×20 mm^2-sized pieces. We set three c-Si pieces in the deposition chamber parallel to each other at an interval of approximately 2 mm after the removal of native oxide in 3% HF diluted with deionized water. The substrates were heated at 360-400 °C during a-Si deposition. CPS was vaporized by heating at 85 °C and introduced into the deposition chamber. 15-20 nm-thick a-Si films were formed on the c-Si substrates after 75 min deposition. We then performed the additional annealing of the substrates in the deposition chamber at 200 °C for 1 h to improve the quality of a-Si/c-Si interfaces.

To evaluate the passivation ability of the a-Si films, the effective minority carrier lifetime (τ_{eff}) of the samples was measured by microwave photoconductivity decay (μ-PCD) after taking them out of the chamber. The τ_{eff} values shown below are maximum values in a 20×20 mm^2 sample area. Furthermore, to investigation the thermal stability of the passivation quality of the films, additional post deposition annealing was performed in a tubular furnace at 360-400 °C under nitrogen atmosphere. The τ_{eff} measurement and 30 min furnace annealing were repeated alternately. We also evaluated the thermal stability of a c-Si wafer passivated with PECVD a-Si films deposited at 150 °C under a pressure of 7 Pa and a SiH_4 flow rate of 20 sccm using a plasma power and a frequency of 20 W and 27 MHz, respectively, for comparison.

To confirm the stability of LVD a-Si passivation films against air exposure, c-Si wafers passivated with LVD a-Si films formed at 360-400 °C were exposed to air under 64%RH at 23 °C for up to one week, during which the samples were wrapped in aluminum foils to exclude the effect of degradation by light soaking. We measured the τ_{eff} of these samples for every 12 or 24 h. For the investigation of the light-induced degradation of LVD a-Si films, we laminated c-Si wafers passivated with LVD a-Si films using glass, ethylene-vinyl

acetate (EVA) copolymer[24] and a backsheet, by which we can avoid the effect of air exposure. A laminated sample structure is schematically shown in Fig. 2. 1-sun light was illuminated to the laminated samples for up to 2700 min.

We deposited a-Si films also on glass substrates under the same conditions mentioned above and measured the thickness of the a-Si films by spectroscopic ellipsometry, by which the emergence of the epitaxial growth of Si can be examined.

3. Results and discussion

Figure 3(a) shows the τ_{eff} of a c-Si wafer passivated with PECVD a-Si films as a function of the duration of postannealing at 380 °C. A rapid reduction in τ_{eff} was confirmed after 30 min annealing. This is probably due to the desorption of hydrogen atoms from a-Si films and a-Si/c-Si interfaces and the resulting deterioration of the interface quality. Figures 3(b)-3(d) show the τ_{eff} values of c-Si wafers passivated with LVD a-Si films as a function of the duration of postannealing at 360, 380, and 400 °C, respectively. A markedly high τ_{eff} of up to ~350 μs is obtained for c-Si wafers passivated with LVD i-a-Si films before post deposition annealing. These values are smaller than those reported by Mews *et al*. prepared by using a-Si films formed by the spin coating and annealing of Si ink.[23] However, it should be emphasized that Mews *et al*. have used considerably thick (>50 nm) a-Si films, while our LVD a-Si films of <20 nm are practically thin. In contrast to the case of the c-Si wafer passivated with PECVD a-Si films, the reduction in τ_{eff} is smaller even after postannealing for 60 min or more. We can thus conclude that LVD a-Si passivation films have a higher thermal stability than conventional PECVD ones. The desorption of hydrogen atoms during postannealing is probably the reason for the decreased τ_{eff} in the c-Si wafer passivated with PECVD i-a-Si films. On the other side, since LVD a-Si films are formed at a temperature similar to that of postannealing, Si-H bonds with low thermal stability have already been depleted during film formation. This may be the reason for the suppressed hydrogen desorption during postannealing and the resulting higher thermal stability of LVD a-Si passivation films. The τ_{eff} of c-Si wafers passivated with LVD a-Si films also slightly decreases after post deposition annealing, particularly at a post deposition annealing temperature of 400 °C. Note that the annealing temperature and duration for the doped a-Si film formation by printing and annealing Si

ink are limited to ≤390 °C and ≤30 min, respectively, to prevent the marked diffusion of dopant atoms.[25] This indicates that, based on the experimental results shown in Fig. 3(d), a τ_{eff} of at least 150 μs can be obtained even after post deposition annealing at 390 °C for 30 min. Thus, the high thermal stability of LVD a-Si passivation films will allow us to form p-type and n-type a-Si films on them by Si ink printing and annealing without the marked deterioration of the a-Si/c-Si interface quality.

It should be emphasized that, unlike the case of a-Si deposition by conventional CVD, LVD can form a-Si films on both sides of c-Si wafers simultaneously. We confirmed no significant difference in thickness between the front-side and rear-side a-Si films and no marked areal distribution of the film thickness. This might be related to the low sticking coefficient of CPS molecules. The advantage of simultaneous film deposition is significantly beneficial for a low-cost process because a large number of Si wafers can be installed in the same deposition batch.

Figure 4 shows the τ_{eff} of c-Si wafers passivated with LVD a-Si films as a function of air exposure duration. Although a slight reduction in τ_{eff} is seen in the first two days, the value becomes stable from the third day. We have also separately confirmed that the τ_{eff} of samples with LVD a-Si films does not change when the samples are stored in nitrogen atmosphere or vacuum, which indicates that oxygen and/or water vapor degrades the passivation quality. The reduction in τ_{eff} observed in this study is much smaller than that seen in the case of a-Si films formed from Si ink.[23] The higher tolerance to oxygen and water vapor probably originates from the higher density of LVD a-Si films than of a-Si films formed by spin coating and annealing.[19] Figure 5 shows the τ_{eff} of c-Si wafers passivated with LVD a-Si films as a function of light soaking duration. No marked reduction in τ_{eff} can be seen, which indicates the high stability of LVD a-Si passivation films against light soaking, as in the case of a-Si films formed by conventional CVD.[26-29]

To examine the epitaxial growth of Si films during LVD, we measured the thickness of a-Si films on c-Si and glass substrates. Since epitaxially grown Si layers cannot be optically distinguished from c-Si substrates, the thickness of a-Si films on c-Si wafers must be smaller than that on glass substrates when epitaxial growth takes place.[30] According to the ellipsometry measurements shown in Fig. 6, there is no significant difference in thickness between the Si films formed on c-Si and glass substrates (~17 nm). This clearly indicates

that epitaxial growth does not occur in LVD even at considerably high substrate temperatures of 360 °C or more. The epitaxial growth of Si cannot be avoided at such high temperatures in the case of conventional PECVD.[31,32] This may originate from the difference in gas species supplied onto the substrates during the deposition of a-Si films. It is known that active SiH_3 radicals are the major species for the formation of a-Si films in PECVD, which leads to the emergence of epitaxial growth more likely. On the contrary, CPS molecules reach the surface of c-Si wafers in their original form. The contribution of less active species results in the suppression of Si epitaxial growth even at such high temperatures.

4. Conclusions

The a-Si passivation films formed by LVD show high thermal stability against postannealing at temperatures as high as 360 °C or more. The LVD a-Si films also have sufficient stability against exposure to air and light. In addition, in spite of the deposition of a-Si films at high temperatures of 360 °C or more, epitaxial growth does not occur during LVD. The simultaneous deposition of a-Si films on the front and back of a c-Si wafer is also a remarkable benefit to utilize LVD for the formation of a-Si passivation films.

Acknowledgments

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Figure captions

Fig. 1. (Color online) Schematic diagram of a LVD chamber used in this study.

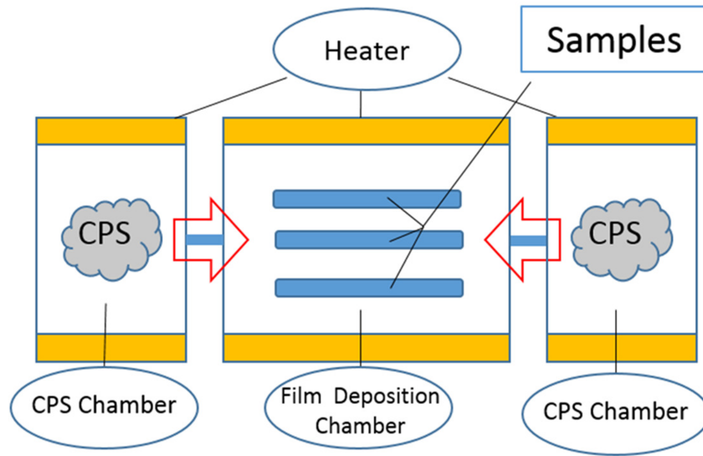
Fig. 2. (Color online) Schematic of a laminated c-Si wafer passivated with LVD a-Si films used for light soaking.

Fig. 3. (Color online) τ_{eff} of c-Si wafers passivated with (a) PECVD a-Si films as a function of the duration of postannealing at 380 °C and with LVD a-Si films as a function of the duration of postannealing at (b) 360, (c) 380, and (d) 400 °C. c-Si wafers with LVD a-Si films formed at 360, 380, and 400 °C were evaluated.

Fig. 4. (Color online) τ_{eff} of c-Si wafers passivated with LVD a-Si films as a function of air exposure duration. c-Si wafers with LVD a-Si films formed at 360, 380, and 400 °C were evaluated.

Fig. 5. (Color online) τ_{eff} of c-Si wafers passivated with LVD a-Si films as a function of light soaking duration. A c-Si wafer with LVD a-Si films formed at 360 °C was evaluated.

Fig. 6. (Color online) Thickness of LVD a-Si films formed at 400 °C on c-Si and glass substrates.



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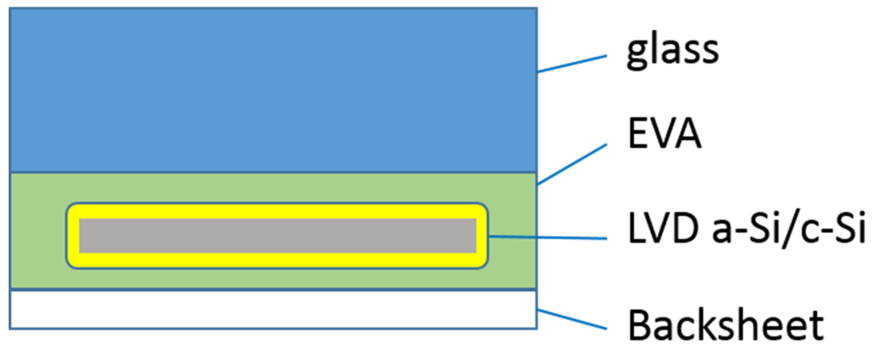

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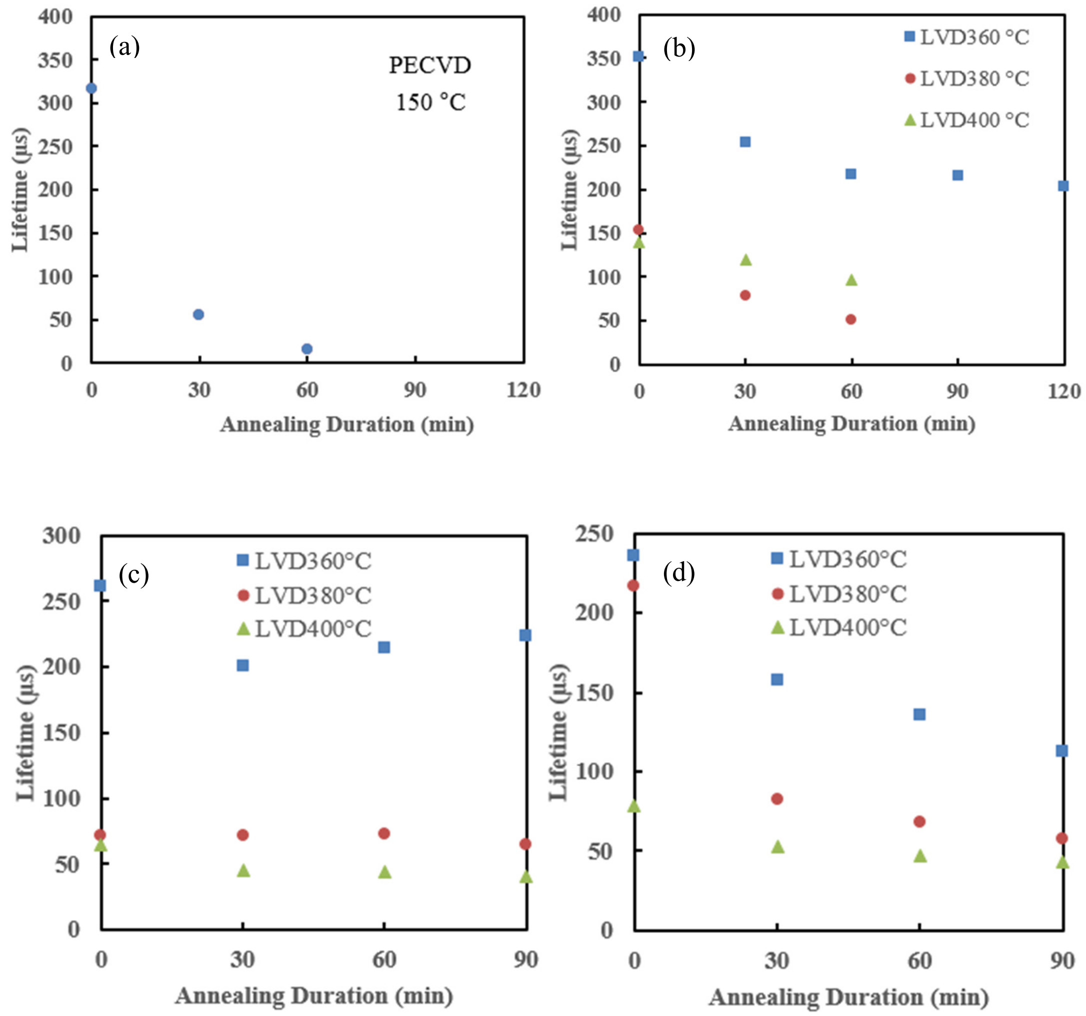

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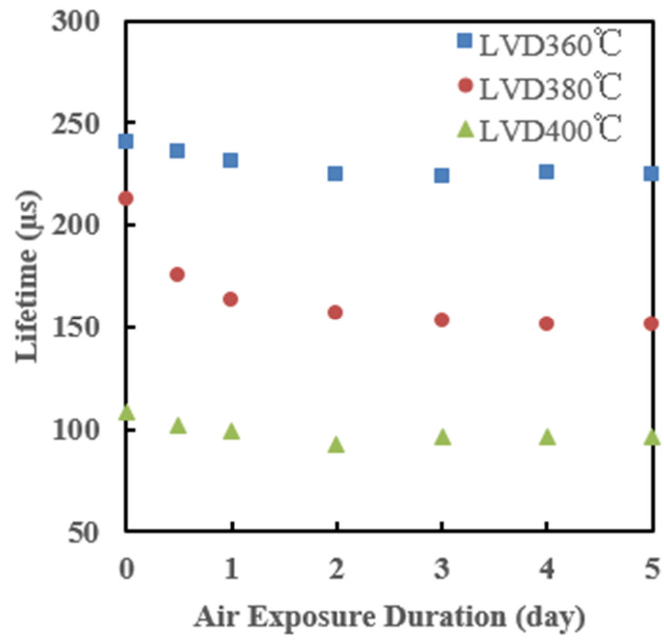

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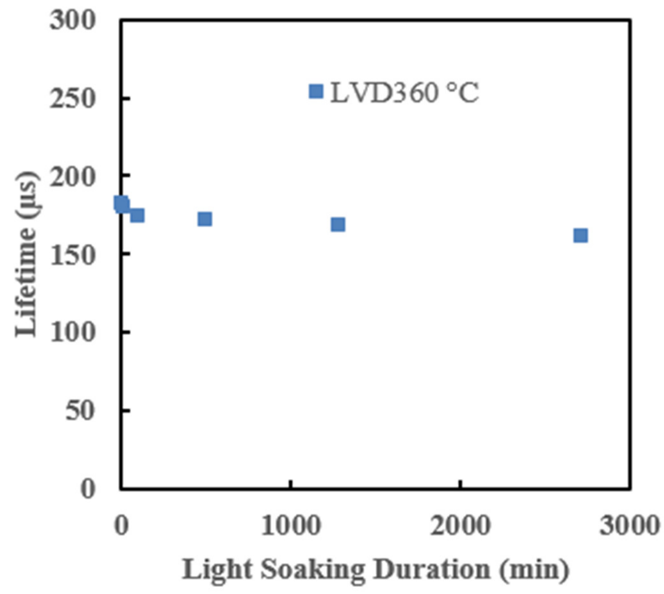

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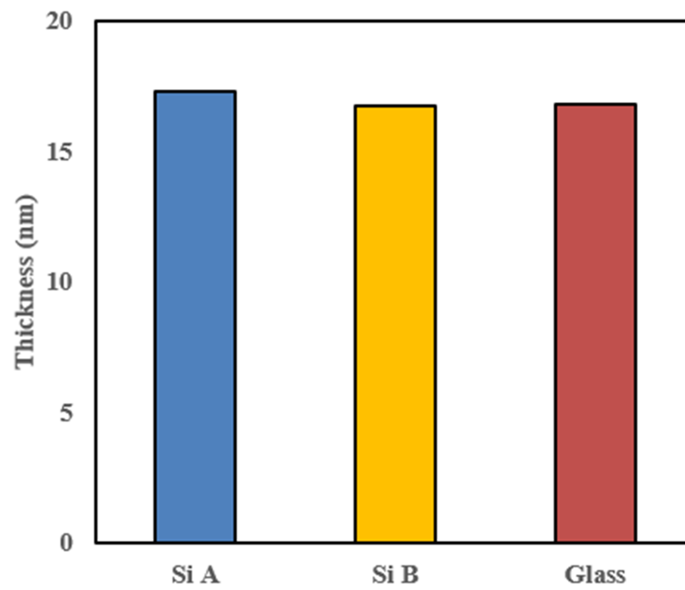

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