# Formation of thermally stable a-Si passivation films using liquid Si

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### Abstract

We applied liquid-source vapor deposition (LVD) to form amorphous silicon (a-Si) passivation films on crystalline Si (c-Si) using the vapor of cyclopentasilane (CPS), and investigated their thermal stability against post-annealing. LVD a-Si passivation films showed high initial effective minority carrier lifetime ( $\tau_{eff}$ ) of >300 µs and had better thermal stability than a reference plasma-enhanced chemical-vapor-deposited (PECVD) sample. The high thermal stability of LVD a-Si films may attribute considerably high deposition temperature at 360 °C or more. We also confirmed that the epitaxial growth of Si films does not occur on crystalline Si (c-Si) even at such high deposition temperatures and LVD could realize the simultaneous deposition of a-Si films on both the sides of a c-Si wafer.

## 1. Introduction

a-Si films can be formed not only by vapor deposition but by printing technology using liquid Si, in which Si ink consisting of polydihydrosilane and solvent is used [1]. There are many advantages of printing method for the Si film formation by printing such as low equipment cost due to non-vacuum process, high efficiency of material usage, and selective formation 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 [2]. In order to apply liquid Si for the fabrication of HBC cells, intrinsic 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 needs annealing at ~400 °C after printing. This is probably difficult for a-Si films formed by conventional PECVD because of its deposition temperature of ~200  $\,^{\circ}$ C or less.

We have recently developed a new method to form a-Si films from CPS vapor [3]. 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. Since wafers are heated at 400  $\,^{\circ}$ C during the deposition, a-Si films formed may have high thermal stability against post-annealing at 400  $\,^{\circ}$ C. In this paper, we report the thermal stability of a-Si films formed by LVD using CPS vapor.

#### 2. Experimental procedure



Fig. 1 Schematic diagram of a LVD chamber used in this study.

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. 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. Three  $20 \times 20$  mm<sup>2</sup>-sized (100) c-Si substrates were set in the deposition chamber parallel to each other at intervals of approximately 2 mm after the removal of native oxide in 5% HF diluted with deionized water. The wafers are 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.

In order to evaluate the passivation ability of the a-Si films, the effective minority carrier lifetime ( $\tau_{eff}$ ) of the samples was measured by microwave photo-conductivity decay ( $\mu$ -PCD) after taking out of the chamber. Furthermore, in order to investigate the thermal stability of the passivation quality, additional annealing was performed in a tubular furnace at 380 °C under nitrogen atmosphere. The  $\tau_{eff}$  measurement and 30-min furnace annealing were repeated alternatively. A c-Si wafer passivated with PECVD a-Si films deposited at 150 °C was also evaluated for comparison. We also deposited a-Si on glass substrates under the same condition 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 checked.

#### 3. Results

Figure 2 shows  $\tau_{eff}$  of a c-Si wafer passivated with PECVD a-Si films as a function of post-annealing duration. Rapid reduction in  $\tau_{eff}$  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 interface and resulting deterioration of the interface quality. Figure 3 shows  $\tau_{eff}$  of c-Si wafers passivated with LVD a-Si films as a function of post-annealing duration. The c-Si samples originally have  $\tau_{eff}$  of 150-350  $\mu s,$  and in contrast to the case of the c-Si passivated with PECVD a-Si films, reduction in  $\tau_{eff}$  is less serious even after post-annealing for 60 min or more. We can thus conclude that LVD a-Si passivation films have higher thermal stability than conventional PECVD ones. This phenomenon may be related to the fact that LVD a-Si films have been already heated at similar temperatures  $(360-400 \ \text{C})$  during deposition. 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 an-



Fig. 2  $\tau_{eff}$  of a c-Si wafer passivated with PECVD a-Si films as a function of post-annealing duration.



Fig. 3  $\tau_{eff}$  of c-Si wafers passivated with LVD a-Si films as a function of post-annealing duration.

nealing with keeping a-Si/c-Si interface quality. It should be emphasized that, unlike the case of the 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 the film thickness of the front-side and the rear-side a-Si films. This feature is beneficial for low-cost process because a large number of Si wafers can be installed in the same deposition batch.

In order to check the epitaxial growth of Si films, we measured the thickness of a-Si films on c-Si and glass substrates. Since epitaxially grown Si layer cannot be distinguished from Si substrate, the thickness of a-Si films on c-Si wafers must be smaller than that on glass substrates when epitaxial growth takes place. According to ellipsometry measurement shown in Fig. 3, there is no significant difference in the thickness of 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.



Fig. 3 Thickness of LVD a-Si films on Si and glass substrates.

# 4. Conclusions

a-Si passivation films formed by LVD show high thermal stability against post-annealing at as high as 380 °C. In addition, in spite of the deposition of a-Si films at high temperatures more than 360 °C, epitaxial growth does not occur during LVD. Simultaneous deposition of a-Si films on the front and the back of a c-Si wafer is also a remarkable benefit to utilize LVD for the formation of a-Si passivation films.

#### References

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