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Author(s)	Hayakawa, Taro; Miyamoto, Motoharu; Koyama, Koichi; Ohdaira, Keisuke; Matsumura, Hideki
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# **Extremely Low Recombination Velocity on Crystalline Silicon Surfaces Realized by Low-Temperature Impurity Doping in Cat-CVD Technology**

Taro Hayakawa, Motoharu Miyamoto, Koichi Koyama, Keisuke Ohdaira, and Hideki Matsumura

Japan Advanced Institute of Science and technology (JAIST), 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

s0940153@jaist.ac.jp

## **ABSTRACT:**

To reduce surface recombination velocity (SRV) at the interface between amorphous Si (a-Si) and crystalline silicon (c-Si), we particularly investigated the treatment of c-Si surface prior to a-Si deposition using decomposed radicals of hydrogen (H<sub>2</sub>) and phosphine (PH<sub>3</sub>). The SRV can be reduced dramatically to 1.6 cm/s only for n-type c-Si, while no such reduction is observed in p-type c-Si. Secondary ion mass spectrometry (SIMS) and the Hall effect measurement actually reveal the existence of phosphorus (P) atoms in c-Si near the surface.

**Keywords;** Solar cells, Surface recombination velocity, Impurity doping, Phosphorus, Low temperature, Cat-CVD, Hot-Wire CVD

## 1. Introduction

Surface passivation of crystalline silicon (c-Si) is important to increase the efficiency of solar cells. Heterojunction with Intrinsic Thin layer (HIT) solar cell, consisting of heterojunctions with thin intrinsic amorphous Si (a-Si) layers and c-Si, is known as a high efficiency solar cell [1]. In the case of HIT solar cells, except for the recombination in bulk c-Si, the surface recombination velocity (SRV) at the interfaces between a-Si and c-Si limits minority carrier lifetime. We have reported that the SRV of c-Si is dramatically reduced by the radical treatment of phosphine (PH<sub>3</sub>) and hydrogen (H<sub>2</sub>) [2]. Since the reduction of SRV is found only for n-type c-Si, the reduction of SRV is caused by the downward band bending close to the c-Si surfaces due to the formation of impurity doped n<sup>+</sup> layers. In order to confirm that P atoms are actually doped into c-Si by the radical treatment using PH<sub>3</sub> and H<sub>2</sub>, we have investigated the depth profile of P atoms in c-Si and in-plane electrical properties of P-radical-treated c-Si surfaces. We have also investigated optimum radical treatment conditions such as catalyzer temperature and PH<sub>3</sub> flow rate to reduce SRV by n<sup>+</sup> layer formation without serious etching of c-Si surface by atomic hydrogen.

## 2. Experimental

The radical treatment was performed using a Cat-CVD system shown in Fig.1 [3]. H<sub>2</sub> and PH<sub>3</sub> were decomposed by a tungsten catalyzer with a diameter of 0.5 mm and a length of 210 cm. This catalyzer was folded in twelve times and mounted in the chamber. PH<sub>3</sub> was diluted to 2.25% in helium. In this study, the flow rate of PH<sub>3</sub> was expressed by the net flow rate of PH<sub>3</sub>. Si wafers were exposed to the radicals immediately after washing by deionized water and hydrofluoric acid. All radical

treatment was performed at a substrate temperature of 150 °C and a pressure of 1 Pa. We used double-side mirror-polished, n-type Si wafers for carrier lifetime measurement. Czochralski-grown (CZ) wafers with a resistivity of 1-5 Ωcm were used to investigate the effect of atomic hydrogen, and floating-zone-grown (FZ) wafers with a resistivity of 3.2-3.4 Ωcm a minority carrier lifetime of 10.9 ms were used for radical treatment using PH<sub>3</sub> in order to precisely evaluate SRVs on P-radical-treated c-Si surfaces. The wafers were coated on the both sides with 45-nm-thick Cat-CVD a-Si films for surface passivation after the radical treatment. One of the P-radical-treated and a-Si-passivated FZ Si wafers was also used for secondary ion mass spectrometry (SIMS) to check the depth profile of P atoms. Effective minority carrier lifetimes were measured by microwave photo-conductivity decay (μ-PCD) method using Kobelco LTA-1510EP. Carrier excitation was performed by a 904 nm pulse laser with a photon density of  $5 \times 10^{13} / \text{cm}^2$ .

The sheet carrier concentration of catalyzer temperature and PH<sub>3</sub> flow rate dependence was measured by the Hall effect. The p-type magnetic-Czochralski (MCZ) wafers with a high resistivity of 3000 Ωcm were used as the substrates of Van der Pauw structures for the Hall measurement. In all measurement, the majority carriers were found to be electrons. Thus, the carrier concentration of substrate does not affect the measured carrier concentration of the doped layer, because the depletion layer between substrate and doped layer insulates the substrate from the doped layer.

### **3. Results and discussion**

#### **3-1. The profiles of Phosphorus atoms**

In this radical treatment, the reduction of SRV is considered due to the downward

band bending near c-Si surfaces caused by the formation of  $n^+$  layers. The existence of P atoms is confirmed by SIMS measurement of the lifetime measurement sample using FZ wafer. Figure 2 shows the SIMS profile of P concentration plotted along with secondary ion intensity of elements such as Si, H, and oxygen (O). The profile of P atoms shows a peak at the c-Si surface with a concentration on the order of as high as  $10^{19} /\text{cm}^3$ . This peak corresponds to the diffused P atoms by the radical treatment. The background density of P atoms around  $10^{15} \text{ cm}^{-3}$  corresponds to the wafer resistivity of 3.2-3.4  $\Omega\text{cm}$ .

### **3-2. Optimization of catalyzer temperature**

The atomic hydrogen has two effects, passivation of recombination centers and etching the surface roughly [4]. Figure 3 shows the dependence of catalyzer temperature on the minority carrier lifetimes of pure atomic H treatment. In this experiment, CZ Si wafers were exposed to atomic hydrogen for 60 s at 150 °C under a pressure of 1Pa with 20 sccm flow rate of pure  $\text{H}_2$ .

The minority carrier lifetimes increase below 1300 °C of catalyzer temperatures, and then start to decrease over 1300 °C. The increase below 1300 °C is due to the increase of the density of atomic hydrogen passivating the recombination centers, whereas the decrease over 1300 °C is supposed that the excess atomic hydrogen creates recombination centers by etching the surface.

The sheet carrier concentration of the Hall element samples of  $\text{H}_2$  and  $\text{PH}_3$  radical-treatment is also indicated in Fig. 3. This radical treatment was performed for 60 s at 150 °C and the pressure of 1 Pa on the p-type high resistivity wafer as described in experimental section. The source gas of  $\text{H}_2$  with the flow rate of 20 sccm and  $\text{PH}_3$  of

0.43 sccm were used in this treatment. The sheet carrier concentration increases as the catalyzer temperature increases. The increase is due to the increase of the catalytic cracking ability of the catalyzer. From this experiment, using the catalyzer heated at 1300 °C, it is confirmed that the doping of P atoms into c-Si occurs without forming defects. The P donors are also doped by the radical-treatment at temperatures more than 1300 °C, however the lifetimes are expected to decrease due to the excess atomic H density.

### **3-3. Dependence of PH<sub>3</sub> flow rate**

The flow rate of PH<sub>3</sub> affects the amount of introduced P atoms. In this experiment, all samples were exposed to the radicals generated by 1300 °C heated catalyzer at a substrate temperature of 150 °C at the pressure of 1Pa for 60 s. The source gas is the mixed gas of H<sub>2</sub> with 20 sccm flow rate and various flow rates of PH<sub>3</sub>. Figure 4 indicates that the sheet carrier concentration increases with the flow rate of PH<sub>3</sub>. The minority carrier lifetime increases when the slight amount of diluted PH<sub>3</sub> with flow rate of 0.085 sccm is mixed to H<sub>2</sub> with flow rate of 20 sccm, while the minority carrier lifetime decreases slightly with the more increase of PH<sub>3</sub> flow rate. This decrease appears to imply that the dense doping layer causes to create another recombination centers. The best carrier lifetime obtained is ~5 ms, as shown in Fig. 4. This value corresponds to the SRV of as low as 1.6 cm/s, and thus, this novel process is applicable to the fabrication of high-efficiency solar cells.

## **4. Conclusion**

The SRV of an n-type c-Si wafer is reduced by the radical treatment of H<sub>2</sub> and PH<sub>3</sub>.

In this radical treatment, P atoms are introduced into a c-Si wafer, resulting in the formation of an n<sup>+</sup>-doped layer and the electrical passivation of the c-Si wafer surface. By controlling the catalyzer temperature at 1300 °C, the c-Si wafer is doped by P atoms without defect formation. The slight inclusion of diluted PH<sub>3</sub> with flow rate of 0.085 sccm to H<sub>2</sub> with flow rate of 20 sccm is effective to obtain n<sup>+</sup>-doped passivation layer with low SRV. This method can realize the SRV of as low as 1.6 cm/s for n-type wafers, and could be utilized for bulk c-Si solar cell fabrication.

## **5. Acknowledgement**

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### **Figure captions**

Fig. 1 Schematic of a Cat-CVD system for low temperature doping.

Fig. 2 SIMS profiles of P, H, O, and Si atoms in the a-Si/c-Si heterostructure.

Fig. 3 Catalyzer temperature dependence of the effective minority carrier lifetimes of atomic H treated c-Si and the majority carrier sheet concentration of H<sub>2</sub> and PH<sub>3</sub> radical-treated c-Si.

Fig.4 PH<sub>3</sub> flow rate dependence of the effective minority carrier lifetime and the majority carrier sheet concentration of PH<sub>3</sub> radical-treated c-Si.

Fig.1 Hayakawa *et al.*,

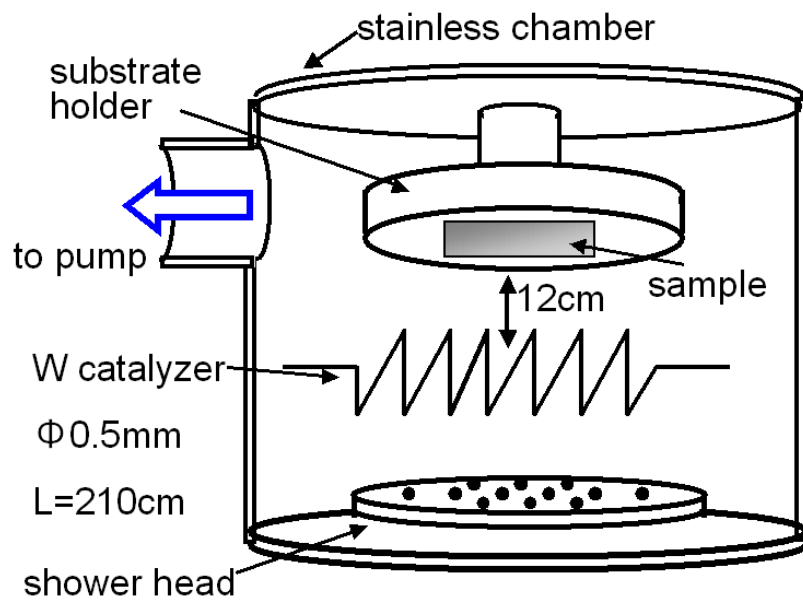


Fig.2 Hayakawa *et al.*,

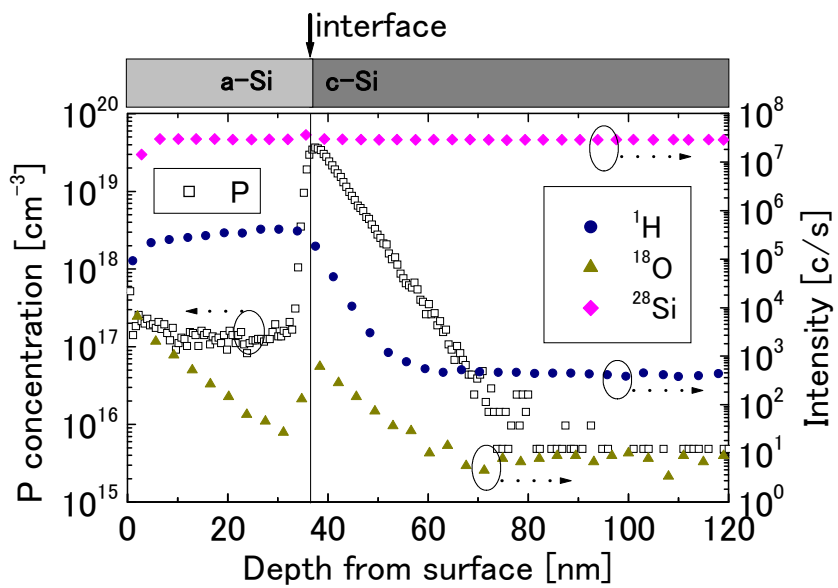


Fig.3 Hayakawa *et al.*,

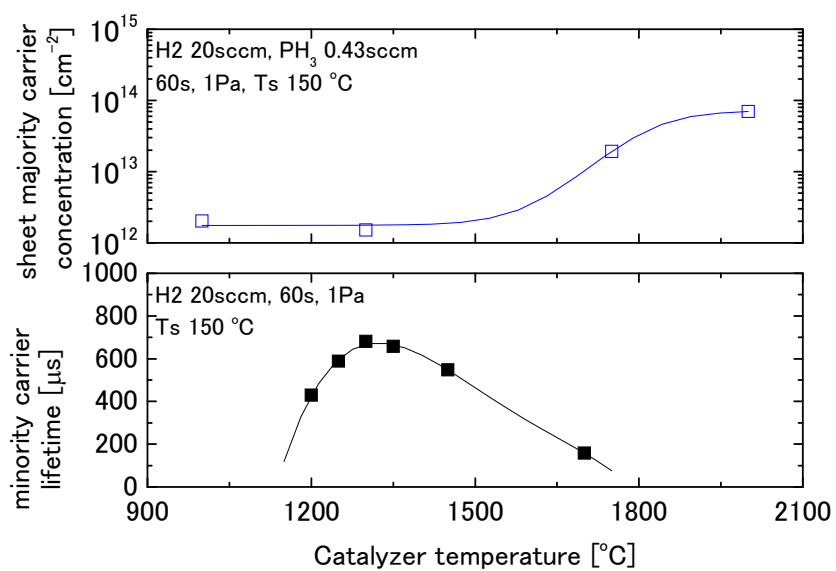


Fig.4 Hayakawa *et al.*,

