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# Effect of reducing impurity concentration of microcrystalline silicon thin films for solar cells using radio frequency hollow electrode enhanced glow plasma

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ABSTRACT

Microcrystalline silicon (μc-Si) thin films with low impurity (oxygen) concentrations were prepared by radio frequency hollow electrode enhanced glow plasma (RF-HEEPT). By using metal gasket seals with the RF-HEEPT system, the oxygen concentration in the thin films was reduced to $3.0 \times 10^{17}$ $cm^{-3}$, which is approximately two orders of magnitude less than that of films fabricated in a system using rubber gasket seals. Under the reduced oxygen conditions, we were able to deposit μc-Si thin films at a maximum deposition rate of 10.0 nm/s. We also investigated the spectral response of μc-Si thin-film solar cells. The spectral response of the solar cells fabricated with a low oxygen concentration was improved, especially in the near-infrared region. However, with increasing deposition rate of the thin films, the peaks of the spectral response shifted toward shorter wavelengths and the magnitudes decreased, especially in the near-infrared region, indicating that grain boundaries or defects in the thin films increased at higher deposition rate.



## 1. Introduction

Currently, the development of environment friendly energy sources has attracted much attention worldwide, and solar cells are one of the most environment friendly power generation sources. Among a variety of materials used for solar cells, silicon solar cells are produced in large quantities and have been thoroughly investigated because silicon is a very abundant and environmentally benign element. The key issues are the reduction of the manufacturing costs of silicon solar cells and improving their performance. Thin-film silicon solar cells use small quantities of silicon material as compared to bulk silicon solar cells, and the performance of these solar cells has improved over the years.

Silicon thin films deposited using plasma-enhanced chemical vapor deposition (PECVD) are considered to be primary candidates for next-generation solar cells because this technique is not only simple but is also capable of relatively high performance as compared to other deposition techniques [1–3]. There are mainly two types of silicon thin films. One is hydrogenated microcrystalline silicon (μc-Si) and the other is hydrogenated amorphous silicon (a-Si). The μc-Si thin films are more stable against light exposure [4]. However, μc-Si solar cells also require a thicker intrinsic film than a-Si films because μc-Si thin films have a lower light absorption coefficient owing to their indirect photo-electron band-gap transition. Thus, high deposition of μc-Si thin films by PECVD is technologically very important in terms of low-cost manufacturing. However, high deposition of high-quality μc-Si thin films has been challenging because the defect density in the thin films usually increases with increasing deposition rate.

Many types of plasma generation systems have been proposed for high deposition of high-quality μc-Si thin films, including hollow plasma [5,6], very-high-frequency (VHF) plasma [7,8], and surface wave-excited plasma [9]. We previously proposed a plasma generation system called radio frequency (13.56 MHz) hollow electrode enhanced glow plasma transportation (RF–HEEPT) [10], and obtained μc-Si thin films at a maximum deposition rate of 6.0 nm/s [11]. We also achieved a rate of 12.5 nm/s by applying a higher plasma excitation frequency of 105 MHz to the HEEPT system (VHF–HEEPT) [12]. The HEEPT system has also been demonstrated to deposit films of a uniform thickness over a large area [13].

In this work, to further enhance both the quality and the deposition rate of μc-Si thin films fabricated by the RF-HEEPT system, we developed a method of reducing the impurity concentration in the thin films. Impurities, in particular oxygen, are known to play a critical role in thin films, affecting their electrical properties

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and grain structure [14–17]. Hence, we regarded oxygen as an impurity in this study. Main impurity sources are air leak and outgassing from the inner wall of the reactor. In order to reduce the air leak and outgassing, we prepared an ultrahigh-vacuum RF-HEEPT apparatus by introducing metal seals and a polished inner wall. The experimental setup and measurement of the thin film properties are presented in the next section. In the results and discussion section, we first demonstrate the contribution of the ultrahigh-vacuum RF-HEEPT system for reducing the oxygen concentration in μc-Si thin films (section 3.1). We then discuss the enhancement of the deposition rate of μc-Si thin films with low oxygen concentration in section 3.2. Finally, the performance of the spectral response of the μc-Si thin film solar cells is presented in section 3.3.

## 2. Experimental

Intrinsic silicon thin films were deposited using the RF-HEEPT system. The basic structure of the RF-HEEPT system and the mechanism of plasma generation are described in our previous publications [10–12,18,19]. In brief, RF-HEEPT system consists of two spaces. One is discharge space, having a RF electrode (cathode electrode), a counter electrode (anode electrode). The other is deposition space, having a substrate holder with heater. The RF electrode has a showerhead structure with holes for uniform distribution of gases, and also has a cave structure. The holes and cave structure operate as a hollow RF electrode discharge space. An orifice is prepared at the center of the counter electrode, and a straight aluminum nozzle is attached to the orifice. The orifice and nozzle operate as a hollow anode discharge space. The original RF-HEEPT system, which is sealed by rubber gaskets and has a rough inner wall surface, will henceforth be referred to as a "conventional RF-HEEPT". A vacuum evacuation system consisting of a compound turbo-molecular pump and a dry vacuum pump was used. In this study, we improved the RF-HEEPT reactor by modifying the vacuum seal structure, while leaving the vacuum pumping system and the gas purification system the same as with the conventional reactor. The other improvement was smoothing out the inner wall of reactor. In order to reduce the background pressure and outgassing rate, the vacuum seal structure was changed into all-metal ultrahigh-vacuum seals and the inside wall of the reactor was polished. In addition, the reactor was baked using tape heaters at 200 °C. As a result, the background pressure and outgassing rate of the RF-HEEPT reactor decreased to $3.2 \times 10^{-8}$ Pa and $2.7 \times 10^{-6}$ Pa L/s, respectively, whereas those of the conventional reactor were $8.0 \times 10^{-5}$ Pa and $1.3 \times 10^{-3}$ Pa L/s.

Intrinsic silicon films with a thickness of approximately 2 μm were deposited on glass (Corning 7059) substrates at a substrate temperature of 300 °C. The excitation frequency was kept constant at 13.56 MHz at an RF power ranging from 5 to 45 W. The flow rate of $SiH_4$ varied from 3 to 12 sccm. The flow rate ratio of $SiH_4$ and $H_2$ ($[SiH_4]/([SiH_4]+[H_2])$) was 2% throughout this work. The deposition pressures were fixed at 80 Pa.

The deposition rate was calculated from the thickness of the area just below the nozzle. The oxygen concentrations of the films were analyzed using secondary ion mass spectrometry (SIMS). Crystallinity and crystal orientation were evaluated using micro-Raman spectroscopy and X-ray diffraction, respectively. Dark conductivity and photoconductivity under an illumination of air mass 1.5 (AM1.5, 100 mW/cm$^2$) were measured at room temperature. For the estimation of the photovoltaic performance, we measured the spectral response of the solar cells using band-pass filters. We incorporated identical layers into n-i (intrinsic)-p solar cells on a glass coated with aluminum, and the surface contact layers were made of indium tin oxide (ITO). The intrinsic μc-Si film layers 2 μm thick were deposited using both the RF-HEEPT system. The n-type μc-Si layers 0.5 μm thick and p-type hydrogenated amorphous silicon carbide (a-SiC) layers 10 nm thick were deposited using normal capacitively coupled RF glow plasma CVD. The active area of the solar cells was 1.3 cm$^2$. The light was introduced from the direction of the p-type layer.

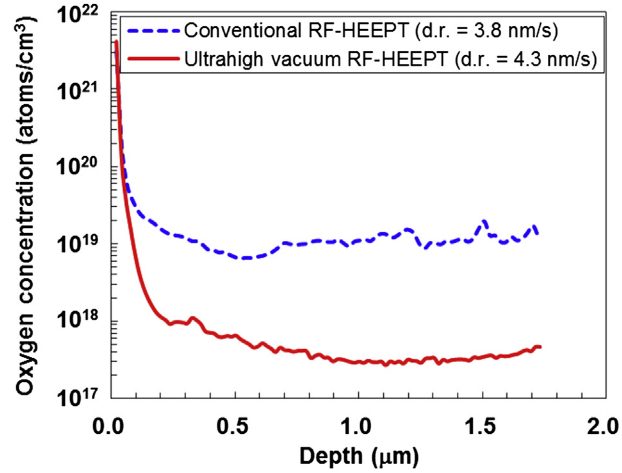


**Fig. 1.** Depth profile of oxygen in μc-Si thin films measured by SIMS. The deposition conditions of both thin films were the same as those of $SiH_4$: 3 sccm, $[SiH_4]/([SiH_4]+[H_2])$: 2%, gas pressure: 80 Pa, RF power: 15 W, substrate temperature: 300 °C, and a deposition rate of approximately 4.0 nm/s.

## 3. Results and discussion

### 3.1. Comparison of thin film properties prepared using ultrahigh-vacuum RF-HEEPT system and conventional system

In order to examine the effect of impurity concentration in the μc-Si thin films, we compared thin films with low oxygen concentration deposited using the ultrahigh-vacuum RF-HEEPT reactor with medium-purity thin films deposited using the conventional reactor. The depth profile of the oxygen concentration in the thin films as measured by SIMS is shown in Fig. 1. When we compare the oxygen concentrations of the two samples with approximately the same deposition rate (4 nm/s) but deposited using different systems, i.e., the conventional RF-HEEPT and the ultrahigh-vacuum RF-HEEPT, the oxygen concentration of the thin film fabricated with the ultrahigh-vacuum RF-HEEPT system decreased to $3.0 \times 10^{17}$ cm$^{-3}$, whereas the thin film deposited using the conventional reactor remained at $1.0 \times 10^{19}$ cm$^{-3}$. Hence, we succeeded in reducing the oxygen concentration in the thin films by two orders of magnitude by using the ultrahigh-vacuum RF-HEEPT system.

Table 1 presents the structural and electrical properties of the silicon thin films deposited using the ultrahigh-vacuum RF-HEEPT system and the conventional system. The deposition conditions of the thin films were the same as those of the films presented in Fig. 1. Employing the Si–TO phonon Raman spectra, the crystallinity is roughly estimated as $I_c/I_a$, where $I_c$ and $I_a$ denote the integrated

**Table 1**
Structural and electrical properties of the silicon thin films deposited using the ultrahigh vacuum RF-HEEPT system and the conventional system.

| RF-HEEPT | Oxygen conc. (cm$^{-3}$) | Raman ratio $I_c/I_a$ | XRD ratio $I_{220}/I_{111}$ | Dark cond. $\sigma_d$ (S/cm) | Photo cond. $\sigma_p$ (S/cm) | $\sigma_p/\sigma_d$ |
|---|---|---|---|---|---|---|
| Ultrahigh vacuum | $3.0 \times 10^{17}$ | 5.0 | 2.5 | $3.6 \times 10^{-6}$ | $2.6 \times 10^{-5}$ | 7.1 |
| Conventional | $1.0 \times 10^{19}$ | 3.7 | 0.4 | $2.6 \times 10^{-6}$ | $8.8 \times 10^{-6}$ | 3.5 |