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Author(s)	J. W. M. Lim, C. S. Chan, L. Xu, T. M. Ong, S. Y. Huang, D. Y. Wei, Y. N. Guo and S. Xu
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**MRS Singapore – ICMAT Symposia Proceedings****8th International Conference on Materials for Advanced Technologies****High quality hydrogenated amorphous silicon thin films with enhanced growth rates for surface passivation in an Al<sub>2</sub>O<sub>3</sub> based ICP reactor**

J.W.M. Lim<sup>a\*</sup>, C.S. Chan<sup>a</sup>, L.Xu<sup>a</sup>, T.M. Ong<sup>a</sup>, S.Y. Huang<sup>a</sup>, D.Y. Wei<sup>a</sup>, Y.N. Guo<sup>a</sup>,  
S.Xu<sup>a</sup>

<sup>a</sup> Plasma Sources and Applications Center (PSAC), NIE, Nanyang Technological University, 1 Nanyang Walk, 637616, Singapore

**Abstract**

Plasma processing of materials in low frequency inductively coupled plasma (LF-ICP) reactors has limitations involving the presence of contaminant species found in the discharge. It was been shown in previous work through optical emission spectroscopy that a main source of contaminants were oxygen related species which were not part of the feedstock recipe. In this work, amorphous silicon thin films were grown on silicon substrates with a LF-ICP reactor. The dielectric top lid plays an important role in the reduction of oxygen species detected in the thin films. It was postulated that the source of the contaminants came from sputtering of the lids. The replacement of the conventional quartz (SiO<sub>2</sub>) lid with that of alumina (Al<sub>2</sub>O<sub>3</sub>) reduced the oxygen species present in the resulting discharge, which is often a source of contamination in the resulting thin films, impinging the passivation grade of the resulting films. The modified reactor configuration also resulted in increased hydrogenation and deposition rate of the thin films. The results show that alumina lids serve as a promising alternative in replacing the conventional quartz lids in LF-ICP reactors for materials processing, resulting in efficient power transfer to the plasma and films which are rid of contaminant species.

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\* Corresponding author. E-mail address: [marklim84th@gmail.com](mailto:marklim84th@gmail.com)

**Keywords:** Plasma ; Materials processing; OES; FTIR; SIMS; Surface passivation; Amorphous silicon

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## 1. Introduction

Applications of plasmas in materials processing has a wide appeal as it has the ability to precisely control and tailor properties whether mechanical, optical or electronic to a great degree of success, through variation of the numerous discharge and processing parameters[1-3]. One of the most popular applications of plasma processing for fabrication of device grade materials would be the growth of thin films[4]. Thin film growth has applications in very diverse fields to suit various functions, ranging from anti-reflection coatings to surface passivation layers most commonly seen in photovoltaic (PV) cells. Plasma processing allows the accurate manipulation of thin film thickness for tight trapping mechanisms fill[5], as well as controlled recipes to ensure optimal and uniform processing conditions to yield superior material properties which offers potential for scaling up for industrial applications[6-9].

In this work, an inductively coupled plasma (ICP) reactor was utilized for the growth of highly hydrogenated amorphous silicon thin films through ICP assisted chemical vapour deposition (CVD). Amorphous silicon thin films are commonly employed for passivation of surfaces in PV cells[10-12]. Crystalline silicon based PV cells are widely employed in solar harvesting grids due to its low cost and high-throughput ease of fabrication. However a huge trade-off in silicon based PV cells is its relatively low power conversion efficiencies (PCE). One of the key contributing factors to the low PCEs of silicon based cells would be the high carrier recombination losses that occur throughout recombination sites throughout the material[13-15]. Dangling bonds which reside on the surface of the silicon also serve as recombination centers, and it is therefore vital to minimize the presence of these sites in order to increase the operational PCE of current PV cells.

In previous work, the optical emission of similar discharges have been studied through OES[16, 17]. It was derived that the peaks corresponding to various atomic and molecular species of contaminants such as carbon and oxygen, which were not part of the feedstock recipe, were detected in the discharge[18]. The intensities of these signals increased with an increase in RF power supplied during processing. These contaminant species pose huge problems since they give rise to additional defect and trap states which has the potential to drastically reduce the minority carrier lifetimes and consequently, the resulting PCE of the PV cells. Since the ICP chambers in this work were evacuated to  $< 10^{-4}$  Pa through the aid of a turbomolecular pump, it is suggested that the source of the oxygen contaminants came about as a result of sputtering from the dielectric lids which line the top of the reactor.

To investigate the effect of the dielectric lid on the plasma discharge (and hence the material properties of the thin films), the conventional quartz ( $\text{SiO}_2$ ) lid was compared alongside that of alumina ( $\text{Al}_2\text{O}_3$ ) in the growth of amorphous silicon thin films in a LF-ICP reactor. This work reveals the advantages of a simple modification of the lid to an ICP reactor to that of  $\text{Al}_2\text{O}_3$ . As predicted, the oxygen content detected in the resulting thin films was greatly reduced when an  $\text{Al}_2\text{O}_3$  lid was utilized. It was also observed that the thin films grown with the  $\text{Al}_2\text{O}_3$  lid were thicker which corresponds to an increased deposition rate, and were highly hydrogenated as shown through FTIR and SIMS. These results further substantiates the advantages of utilizing an  $\text{Al}_2\text{O}_3$  lid in processing for high-throughput fabrication of high quality hydrogenated amorphous silicon thin films for passivation of silicon surfaces in PV applications.

## 2. Experimental methods

1.5 cm x 1.5 cm crystalline silicon wafers were used as substrates throughout this work. Prior to processing, the substrates were treated with the standard RCA 1 clean. The substrates were placed in ICP reactors with varied dielectric lids for growth of amorphous silicon thin films as illustrated in Fig. 1.. The cylindrical ICP reactors were constructed out of stainless steel and features doubled walls for the circulation of fluids to remove heat from the

walls during processing. The reactor has an internal diameter of 32 cm and has 4 portholes aligned radially to facilitate the addition of diagnostic probes and visual diagnosis of the discharge. The sample stage is connected to an external high voltage DC bias supply, and has a heating element attached to it for heating of substrates. Feedstock gases are introduced into the reactor through gas inlets at the top of the reactor, and the flow rates are controlled with MKS (1100 series) mass flow controllers. The base pressure of the chamber during processing was varied manually through varying the width of the vacuum outlet. The reactor is topped with a planar RF coil which resides on top of the dielectric lids which were varied. A 460 kHz RF generator supplied the RF power to the reactor through a matching network, and enabled the provision of up to 4000 W of power. Coaxial tubes line the RF coil for circulation of coolants. The air tight seal was made possible with Viton O-rings which separated the lid and the reactor. The chamber was evacuated through a 2 stage rotary and KYKY turbo-molecular pump system which enabled a vacuum of  $> 10^{-4}$  Pa.

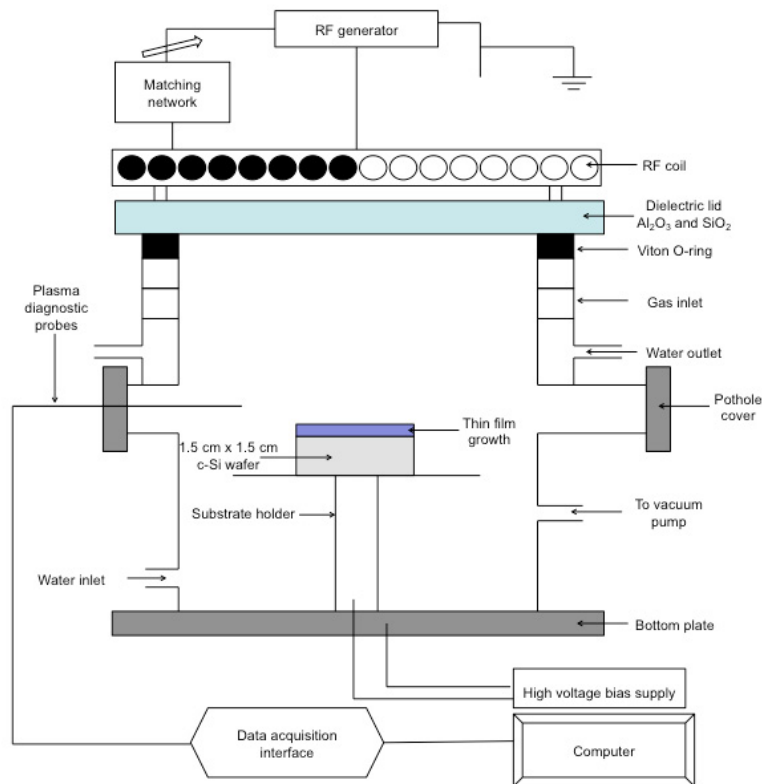


Fig. 1. Schematic set-up of the ICP reactor used for amorphous silicon thin film deposition.

The 2 dielectric lids used in this work were furnished out of high quality quartz ( $\text{SiO}_2$ ) and alumina ( $\text{Al}_2\text{O}_3$ ). Both were cylindrical in geometry and measured 38 cm in diameter, and 2.5 cm in thickness. The processing conditions were kept constant as shown in table 1, with 3.2 kW of RF power supplied and -750 V of external applied bias over a process time of 30 minutes. The feedstock used for this discharge was purely  $\text{SiH}_4$  and it was held at a base pressure of 2 Pa at a flow rate of 20 sccm throughout processing. Thin films were grown first with an ICP reactor with a  $\text{SiO}_2$  lid, before the lids were swapped to  $\text{Al}_2\text{O}_3$ . To avoid cross contamination, the reactors were cleaned thoroughly and baked before being allowed to be pumped down to high vacuum for the next series of thin film growth experiments with an  $\text{Al}_2\text{O}_3$  lid.

Table 1. Processing conditions for growth of amorphous silicon thin films

RF power (W)	Applied bias (V)	Feedstock gas	Feedstock flow rate (sccm)	Pressure (Pa)	Process time (min)
3200	-750	SiH <sub>4</sub>	20	2.0	30

The resulting samples were characterized through scanning electron microscopy (SEM) with a JEOL JSM 6700F, and ellipsometry with a Gaertner L166 ellipsometer, to determine the thickness of the thin films. From there, the deposition rates of the thin films in the 2 reactor configurations were calculated. Secondary ion mass spectroscopy (SIMS) using a Trift II time of flight secondary ion mass spectrometer was employed to determine the absolute oxygen concentration as well as the hydrogen content in the films. The former gives a representation of the oxygen impurity concentration present in the discharge as a result from sputtering of the dielectric lids. The latter shows the degree of hydrogenation in the films reflecting the effectiveness in serving as passivation grade materials. SIMS was also effective in confirming the thickness of the thin films, and the growth rates of the thin films in both reactor configurations. Finally, Fourier-transform infra-red spectroscopy (FTIR) was employed with a Perkin Elmer FTIR spectrometer to study the chemical composition of the thin film as well as to diagnose the hydrogenation content of the films quantitatively through calculations.

### 3. Results and discussion

Fig. 2. shows the SIMS oxygen content profile of the thin films grown with the different reactor configurations. It is observed that the absolute oxygen concentration detected in the thin films grown with the Al<sub>2</sub>O<sub>3</sub> lid was significantly less pronounced than that of the ones grown with the conventional SiO<sub>2</sub> lid. It is also noted that the thin films that were produced were thicker which would be reconfirmed through SEM and ellipsometry later.

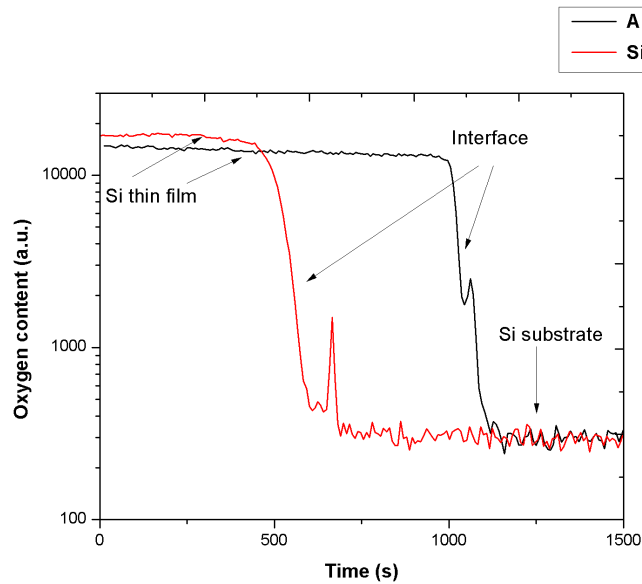


Fig. 2. SIMS oxygen content depth profile of amorphous silicon thin films in different reactor configurations.

From the SIMS oxygen content profile, the absolute oxygen concentration could be derived through mathematical calculation[19, 20]. Since the silicon wafers used were industrial 7.5 – 12.5  $\Omega\text{cm}$  Cz wafers, the known values of the oxygen content ( $C_O < 1 \times 10^{18} \text{ cm}^{-3}$ ) was used as the upper limit for the calculation.

$$C_{O_{Thin\ film}} = \frac{I_{O_{Thin\ film}}}{I_{O_{Substrate}}} \times C_O \quad (1)$$

Where,

$C_{O_{Thin\ film}}$  = absolute oxygen concentration in films

$I_{O_{Thin\ film}}$  = upper limit of oxygen signal in thin film

$I_{O_{Substrate}}$  = upper limit of oxygen signal in silicon substrate

$C_O = 1 \times 10^{18} \text{ cm}^{-3}$

From the calculations, it was found that the absolute oxygen content of thin films deposited with the  $\text{SiO}_2$  lid was  $6.0 \times 10^{19} \text{ atoms/cm}^3$  whereas those which were deposited with an  $\text{Al}_2\text{O}_3$  lid was found to have values of  $4.5 \times 10^{19} \text{ atoms/cm}^3$ . This shows a dramatic 25 % reduction in detected oxygen present in the thin films for the modified reactor configuration. This is coherent with initial postulates which suggest that the source of the oxygen species came as a result of sputtering from the dielectric lid. The bond energy of Si-O is known to be approximately 452 kJ/mol whereas that of Al-O is approximately 511 kJ/mol[21]. This implies that the oxygen species from the  $\text{SiO}_2$  lid are more prone to plasma etching during discharge, hence contributing to the contaminant species in the discharge as compared to that if a more thermally stable  $\text{Al}_2\text{O}_3$  lid was used.

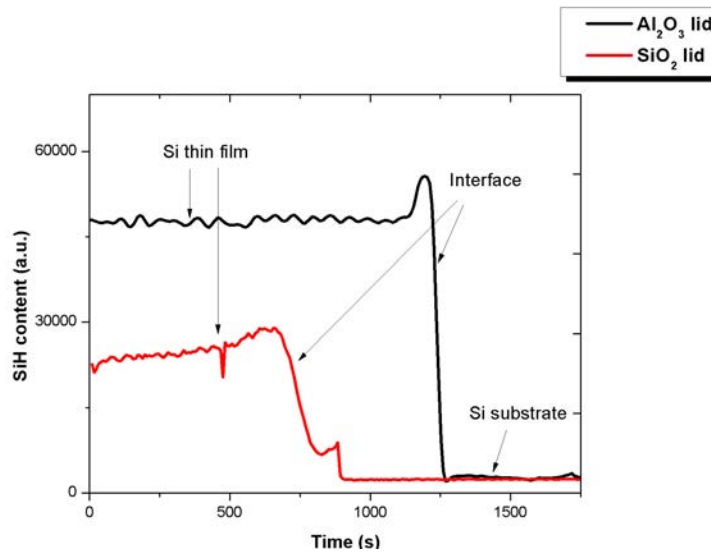


Fig. 3. SIMS SiH content depth profile of amorphous silicon thin films in different reactor configurations.

Fig. 3. and Fig. 4. shows the SIMS SiH content profile and the FTIR absorbance spectra of the thin films deposited with different reactor configurations. It can be observed through the SIMS profile that the thin films grown with the  $\text{Al}_2\text{O}_3$  lid are highly hydrogenated as compared to the thin film grown with the conventional  $\text{SiO}_2$  lid. To quantify the degree of hydrogenation, the hydrogen content,  $C_H$  was determined through calculation from data extracted from the FTIR absorbance spectra[22-24].

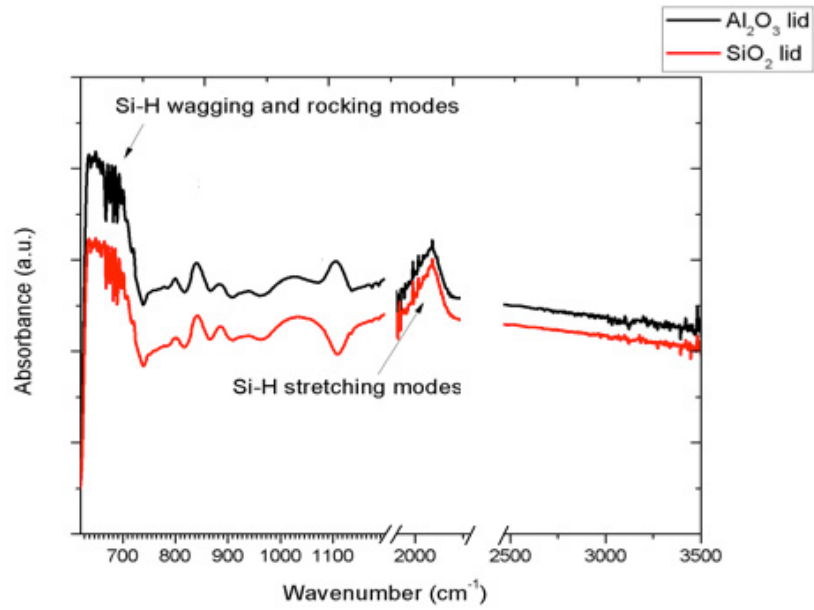


Fig. 4. FTIR absorbance spectra of amorphous silicon thin films deposited in different reactor configurations.

It is known that the peak corresponding to the Si-H wagging mode can be found at  $630\text{ cm}^{-1}$  in the absorbance spectra. The integral of the absorption due to the Si-H bond ( $I_{630}$ ) was determined with equation 2.

$$I_{630} = \int \frac{\alpha_{630}(\omega)}{\omega} d\omega \quad (2)$$

Where,

$\alpha_{630}$  = absorption coefficient of the  $630\text{ cm}^{-1}$  band

$\omega$  = frequency of light

The hydrogen density ( $N_H$ ) was then determined with equation 3.

$$N_H = I_{630} \times A \quad (3)$$

Where,

$A$  = Proportionality constant =  $1.6 \times 10^{19}\text{ cm}^{-2}$  [24, 25]

The hydrogen content can then be computed by applying equation 4.

$$C_H = \frac{N_H}{N_H + N_{Si}} \quad (4)$$

Where,

$$N_{Si} = 5 \times 10^{22} \text{ cm}^{-3}$$

From the calculations, it was found that the hydrogen content of the amorphous silicon films deposited in a reactor with an SiO<sub>2</sub> lid was 3.9 %, whereas films which were deposited with an Al<sub>2</sub>O<sub>3</sub> lid were found to be highly hydrogenated at 5.1 %. This result is exceptionally significant in utilizing deposition of amorphous thin films for surface passivation of PV materials. The increased hydrogenation reaps a benefit of reducing surface recombination through the passivation of dangling bonds. This increased in hydrogen content is explained by the increased power transfer to the reactor mitigated by the change in the dielectric lid. The increased power transfer to the reactor causes the production of more reactive hydrogen species in the discharge, leading to thin films which have higher hydrogen content.

The thin film thickness and deposition rates were determined through SEM and ellipsometry. The results of the characterization can be found in table 2.

Table 2. Summary of results for film thickness, deposition rate, hydrogen content and absolute oxygen concentration.

Reactor lid	Dielectric constant of lid	Thin film thickness (nm)	Deposition rate (nm/min)	Hydrogen content (%)	Absolute oxygen concentration ( atoms/cm <sup>3</sup> )
SiO <sub>2</sub>	4.41	429	14.3	3.9	6.0 x 10 <sup>19</sup>
Al <sub>2</sub> O <sub>3</sub>	9.34	1005	33.5	5.1	4.5 x 10 <sup>19</sup>

The thin film thickness of the films grown with an Al<sub>2</sub>O<sub>3</sub> lid was found to be 1005 nm whereas the films grown with an SiO<sub>2</sub> lid was found to be only 429 nm even though the process time was kept constant. The calculated thin film deposition rate shows a 33.5 nm/min growth rate for an Al<sub>2</sub>O<sub>3</sub> lid reactor while the growth rate for an SiO<sub>2</sub> reactor was 14.3 nm/min. This is well explained by the power transfer mechanism from the RF coil to the ICP discharge as reported in previous work[7, 17, 26]. Most notably, the dielectric constant ( $\epsilon_d$ ) of the material which makes up the lid influences the power absorbed by the plasma. With an increase in  $\epsilon_d$ , the power transferred to the plasma increases accordingly[27]. The  $\epsilon_d$  values of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are 4.41 and 9.34 respectively[28]. Hence, the power absorbed by the discharge in an Al<sub>2</sub>O<sub>3</sub> topped reactor would be greater than that of SiO<sub>2</sub>, giving rise to the increased ability for dissociation of the SiH<sub>4</sub> feedstock in the discharge to reactive species which were eventually deposited on the substrate[4, 29-32]. This accounts for the higher deposition rates and increased hydrogenation in the resulting thin films when the samples were processed with an Al<sub>2</sub>O<sub>3</sub> lid.

#### 4. Conclusion

In this work, it was shown that a simple modification of the lid of a conventional ICP reactor commonly used in materials processing has several advantages. A thermally stable Al<sub>2</sub>O<sub>3</sub> lid prevented the sputtering of oxygen species which would serve as a contaminant source in the discharge. This is most important especially when fabricating high performance device grade materials, where a clean environment rid of impurities is desired. The material properties of the Al<sub>2</sub>O<sub>3</sub> lid, including its known dielectric constant, enabled the increased power transfer to the discharge which resulted in enhanced deposition rates and higher hydrogenation contents of the deposited amorphous silicon thin films. This is exceptionally noteworthy to industries fabricating PV materials, as the higher hydrogenation fraction terminates the dangling bonds more significantly, increasing the minority carrier lifetimes and the PCE of resulting



cells. More importantly, the increased growth rates would also enable higher throughput fabrication of materials with a reduced energy footprint during processing.

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