# SI WAFER MANUFACTURING BY THERMAL SPRAY OF RECYCLED SI POWDERS

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ABSTRACT: The aim of the present work is to demonstrate processing of polycrystalline free-standing Si wafers and thin Si layers on various substrates using thermal spray of relevant Si powders, including recycled ones. Silicon powders were fabricated by milling from two different Si feedstocks: (i) Si kerf produced during sawing of Si wafers from the ingots, and (ii) Si powder from Si scrap (broken wafers). Two different Si powder based structures were produced by thermal spray: (i) free-standing Si-based wafers with thicknesses of about 300-400 micrometres and sizes up to 6 inches, which can be used as supporting parts for "Si wafer equivalent" structures, and, (ii) Si-based layers with thicknesses of about 50-100 micrometres deposited on different supporting substrates, such as aluminium, glass and highly conductive Si powder based sintered substrates. Raman spectroscopy, resistivity, and SEM analyses have been used for characterization of the Si based structures fabricated by thermal spray. It is observed that such layers are poly-crystalline with a low-fraction of the amorphous phase and can be considered as a low-cost alternative for Si PV, which are based on utilization of Si wafers and thin Si layers deposited by conventional methods such as CVD, PECVD, e-beam, etc.

Keywords: Thermal Spray, Silicon, c-Si, Si-Films, Thin Film, Substrates, Grain

## 1 INTRODUCTION

Thermal spraying technology has been employed for many years to synthesize high performance coatings of a wide range of materials, including Si [1-6]. In general, the process of thermal spraying involves feeding a powder based feedstock into a high-energy plasma or flame, in which powder particles are heated, partly or fully melted, and simultaneously accelerated, towards the target surface of a substrate. Silicon particles cool and then solidify onto the substrate, forming a re-crystallized silicon layer. Two commonly used processes for various applications are plasma spray (PS) and flame spray (FS) [7]. It has been shown earlier, that in plasma sprayed silicon conversion efficiencies of thin Si based solar cells of 4.3% can be achieved [4]. However, it should be noted that in flame spraying, relatively low temperatures can be reached in the flame (~3000 °C) compared to common plasma spraying ones, which are quite high (~15000 °C). Therefore, FS has some advantages compared to plasma spray and can be considered as an appropriate method to produce Si coatings on various substrates. In particular, as soon as Si particles are heated to lower temperatures upon FS compared to PS, cooling of such heated/melted particles can be done much faster in case of FS process and a wider range of the supporting substrates for the deposition of Si layers can be used. The aim of the present work is to show the viability of flame spraying for the fabrication of free-standing Si wafers and thin layers on a wide range of supporting substrates, which can be of interest for the low-cost Si based PV.

## 2 EXPERIMENTAL PROCEDURE

### 2.1 Si powders and relevant structures processed by thermal spray

Silicon powders with particle sizes in the range of about 10-50 µm were fabricated by conventional ball milling from two different Si feedstocks: (i) Si kerf produced during sawing of Si wafers from the ingots, and (ii) Si powder from Si scrap (broken wafers). Two different Si powder based structures were produced by the flame based thermal spray: (i) free-standing Si wafers with thicknesses of about 300-400 µm and sizes up to 6 inches, and, (ii) Si-based layers with thicknesses of about 50-100 µm deposited on different supporting substrates, such as aluminium, glass, ceramics and highly conductive sintered Si powder substrates.

### 2.1 Characterization

Raman spectroscopy, resistivity and SEM analyses have been used for the characterization of Si powder based free-standing wafers and thin Si layers deposited on different substrates by flame based spray.

## 3 SILICON POWDER BASED WAFERS AND THIN LAYERS DEPOSITED BY FLAME SPRAYING

### 3.1 Free standing wafers

Optimization of thermal spray parameters resulted in reproducible fabrication of mechanically stable Si wafers with dimensions 50x65 mm$^2$ (**Figure 1**), 156x156mm$^2$ (**Figure 2**) and thicknesses between 300 and 500 microns.

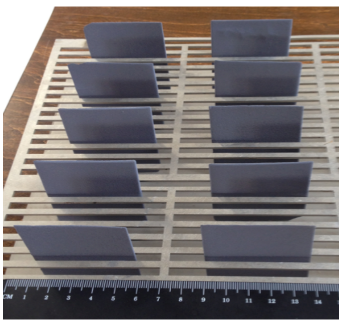


***Figure 1:*** *Free standing 50x65 mm$^2$ Si powder based wafers*

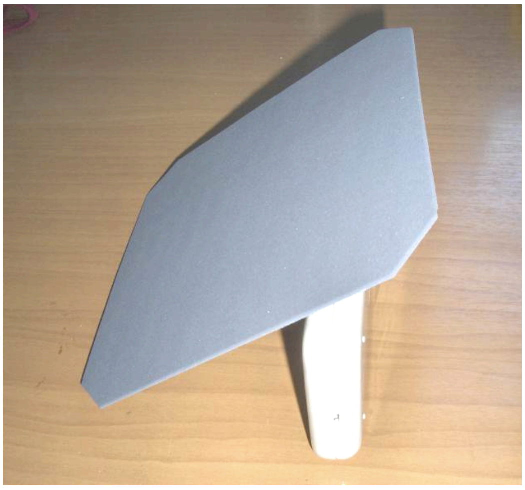
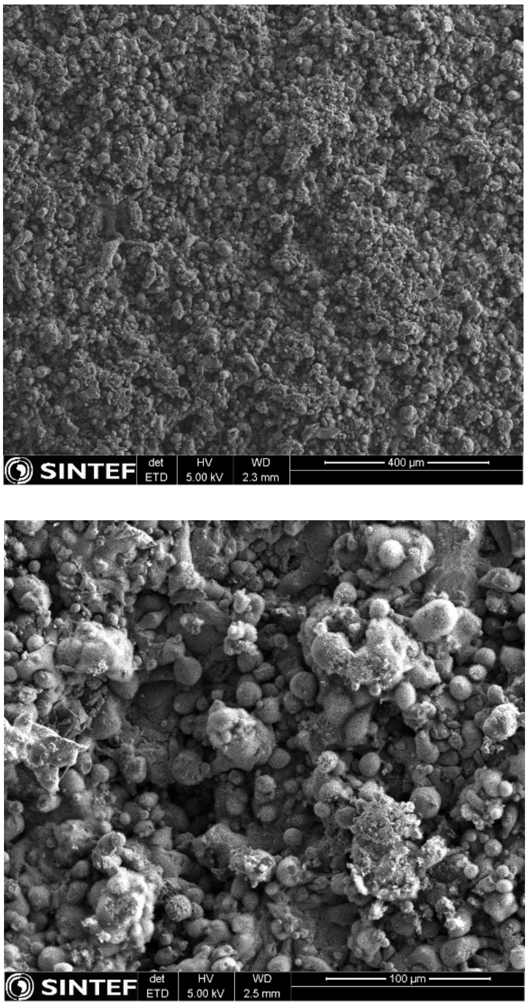


***Figure 2:*** *Free standing 156x156 mm$^2$ Si powder based wafer*

SEM images taken at different magnifications of the surface of a thermal sprayed wafer are shown in **Figure**




**3**.

***Figure 3****: SEM images of the surface of a free standing thermal sprayed wafer*

From **Figure 3** it can be concluded that surface of Si powder based wafers consists of grains with different shapes, which are assembled in a "naturally" textured Si based structure.

**Figure 4** shows results of Si line Raman mapping for the surface area (100x100 µm$^2$) of a free-standing Si powder based substrate.

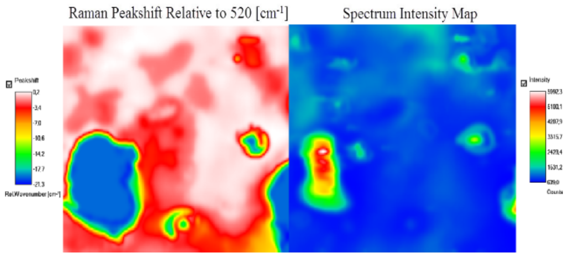



***Figure 4****: Si line Raman mapping: free standing Si powder substrate, surface area 100x100 µm$^2$.*

From **Figure 4** it can be concluded that Si wafer, sintered by thermal spray, consists of mainly poly-Si grains with small portion of the amorphous Si phase inclusions.

As an option, resistivity of such wafers can be regulated by the mixing of Al and/or B powders prior to thermal spray. **Table 1** shows results of the resistivity measurements for Si wafers processed by thermal spray of a mix of Al/Si powders with different proportions of Al and Si.

***Table 1:*** *Resistivity of free standing*

| Al content in Si powder | Resistivity, Ωcm |
|---|---|
| 0% | 10 |
| 1% | 0.6 |
| 3% | 0.47 |
| 5% | 0.024 |
| 10% | 0.018 |
| 15% | 0.002 |

From **Table 1** it can be seen that highly conductive Si based wafers can be sintered by thermal spray of Al/Si powders mixtures.

3.2 Si powder based layers deposited on Al substrates by thermal spraying

**Figure 5** shows SEM images taken at different magnifications of the surface of a thermal sprayed pure Si powder based layer on an Al substrate and **Figure 6** shows results of the Si line Raman mapping for the surface area (100x100 µm$^2$) for the same structure.

From **Figures 5** and **6** it can be concluded that similar to the case of free-standing Si wafers, surface of Si powder based wafers consists of grains with different shapes and different degree of crystallinity. Mainly poly-Si phase is dominating, with a small portion of the a-Si inclusions. It should be noted that grains in this case are quite smooth and grain boundaries are not as pronounced as in case of free-standing Si powder based wafers processed by thermal spraying. It can be speculated that presence of an Al substrate provides specific conditions for the crystallization of partly melted Si particles on the Al surface. More detailed analysis is required to clarify the origin of the observed effect.

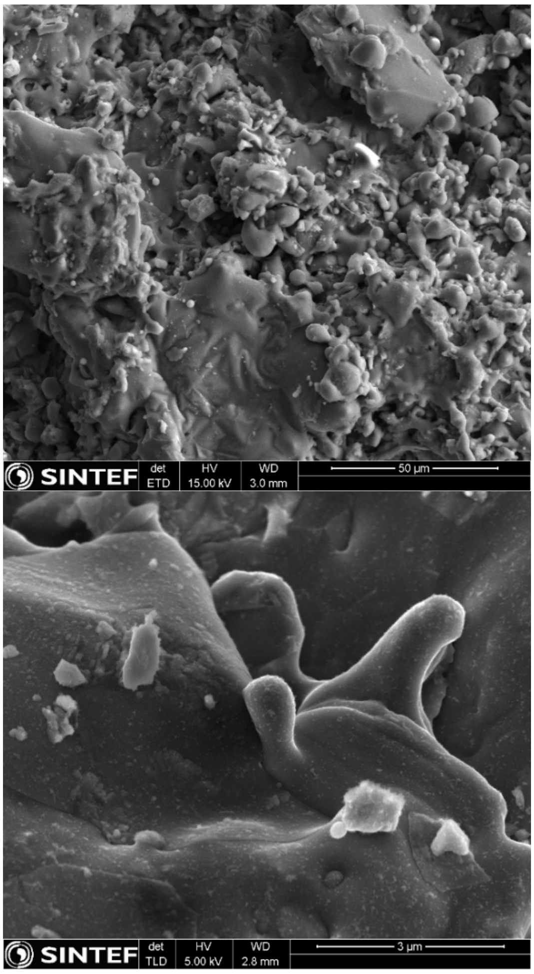



*Figure 5: SEM images of the surface of Si powder based thin layer deposited on an Al substrate.*

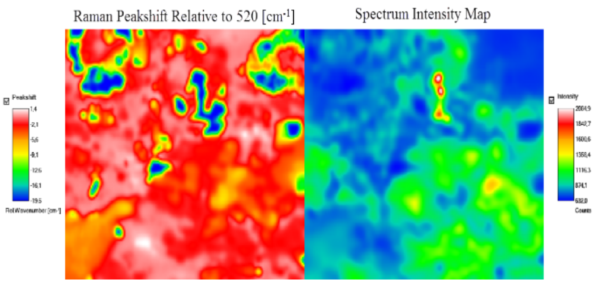



*Figure 6: Si line Raman mapping: Si powder based layer (~100 µm thick) deposited on an Al substrate, surface area 100x100 $\mu m^2$.*

3.3 Si powder based layers deposited on glass substrates by thermal spray

**Figure 7** shows surface and cross section SEM images of a thin Si layer deposited on a glass substrate by thermal spray. Quite dense Si layer with a "naturally" textured Si surface can be formed, as can be seen from **Figure 7**. Several thermal spray scanning velocities were tested in this case and crystallinity of Si layers obtained at different conditions were monitored by micro-Raman. Upon Raman measurements, laser beam was focused on a central part of the largest grains, observed in an optical microscope.

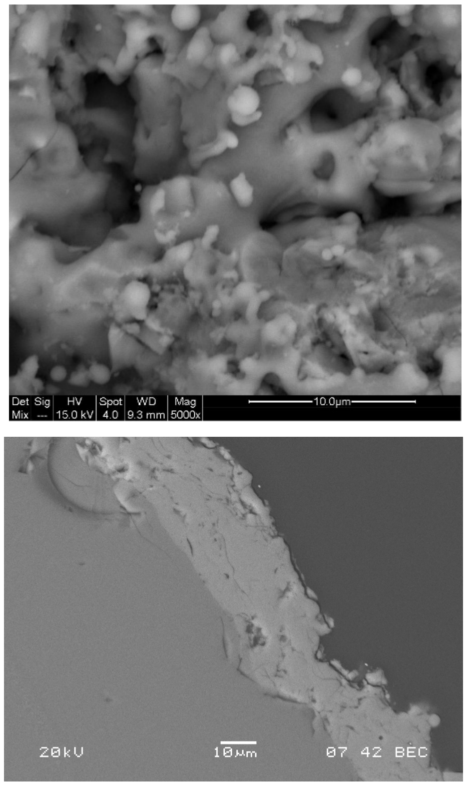



***Figure 7:** Surface and cross section SEM images of a thin Si layer deposited on a glass substrate by thermal spray.*

**Figure 8** shows results of Raman measurements for the optimized thermal spray process (scanning velocity 5). Raman spectra were taken from the centre of 2 different grains and are indicated in **Figure 8** as Si peak (1) and Si peak (2).

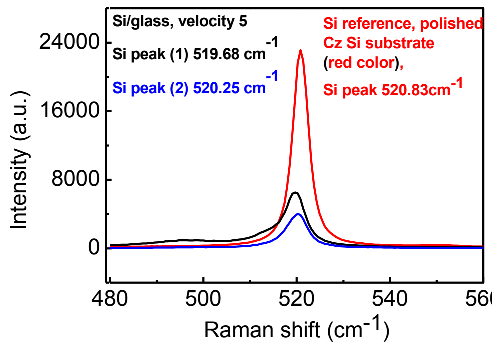



***Figure 8:** Raman spectra of Si lines taken from 2 different grains of Si powder based layer deposited on a glass substrate with an optimized scanning velocity.*

From **Figure 8,** it can be seen that Si grains are crystalline, in contrast to similar Raman measurements for Si powder layers deposited on a glass substrate with the not optimized scanning velocity (velocity 3) upon the thermal spray process (**Figure 9**).

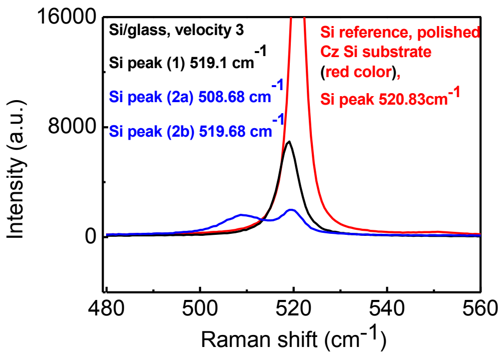



***Figure 9:*** *Raman spectra of Si lines taken from 2 different grains of Si powder based layer deposited on a glass substrate with the non-optimized scanning velocity*

In this case, Si peak (1) (519.1cm$^{-1}$) is shifted from the standard peak position of crystalline Si (520 cm$^{-1}$), and Si peak (2) consists of 2 well pronounced lines – 508.68 cm$^{-1}$, which can be attributed to a poly-Si and 519.68 cm-1 line, which can be attributed to a stressed crystalline Si grain. From **Figures 8** and **9** it can be concluded that scanning velocity in Si powder thermal spray process is an important parameter, which should be taken into account for the process optimization. In an optimized case, substrate is heated by flame to the most suitable temperatures, which can provide proper crystallization of Si powders and relevant Si layers.

3.4 Si powder based layers deposited on Si powder sintered substrates by thermal spray

It has been established, that sintering of Si powder based substrates, including highly conductive ones, can dramatically reduce the thermal budget required [8-11]. Such sintered wafers can be used as the low cost supporting substrates, on which high quality Si layers (solar cell base) can be deposited to fabricate "Si wafer equivalent" [12]. **Figure 10** shows results of the Si line Raman mapping for the surface area (100x100 µm$^2$) of a thin Si layer deposited on top of the hot pressed and sintered Si powder based substrate [9, 11].

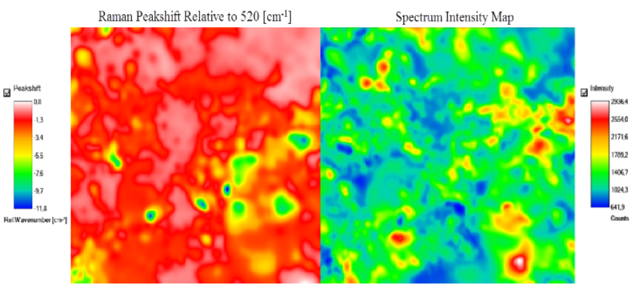



***Figure 10****: Si line Raman mapping: Si powder based layer (~100 µm thick) deposited on a sintered Si powder based substrate.*

From **Figure 10** it can be seen, that only poly-Si and crystalline Si phases are present in this case, without any traces of amorphous silicon, which was observed in previous cases (free-standing wafers, Al and glass substrates). It can be concluded that the origin of a supporting substrate plays an important role for the resulting crystallinity of Si layers deposited on supporting substrates by thermal spray of Si powders.

## 5 CONCLUSION AND OUTLOOK

It was demonstrated that Si powder based structures – free-standing Si wafers or thin Si films can be processed by the flame based thermal spray. Important to note that thin Si layers can be deposited on several types of low-cost substrates (Al, glass, Si) with the low temperature melting points. It is shown, that thermal spray processing conditions and the origin of the supporting substrates play an important role for the crystallinity of the thermal spray deposited Si layers.

It is established that fabricated at appropriate thermal spray processing conditions, such layers are poly-crystalline with a low fraction of the amorphous phase and can be considered as a low-cost alternative for Si PV, which is based on utilization of Si wafers and thin Si layers deposited by conventional methods such as CVD, PECVD, e-beam, etc.

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