Rotary Bonded Multi-Segment Cast Silicon Targets as a Replacement for Sprayed Silicon

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ABSTRACT

Plasma sprayed non-Al alloyed Si(:B) rotary sputtering targets suffer from strong nodule formation both in SiO_2 (display industry) and SiN_x:H (PV industry) reactive deposition processes using MF-AC technology. Such problems can be resolved with multi-segment, bonded cast-Si rotary targets having a much higher density (> 99.5 % of theoretical density, TD; max. 96 % of TD for sprayed targets) combined with a much better chemical purity (appr. 5N; 3N7 for sprayed equivalents). This paper presents coating results for both SiO_2 and SiN_x deposition using bonded, cast Si rotary targets in MF-AC sputtering processes on a vertical dynamic pilot glass coating line. The sputter stability in a real industrial coating system has also been evaluated. Finally, a detailed coating cost comparison using both cast Si and sprayed Si targets for a typical application in the display industry has been performed. The higher machine up time with cast Si targets (no need for regular nodule removal by mechanical abrasion, fewer target changes), combined with a higher power load potential and increased product yield due to less arcing and with a considerably higher amount of available Si per target (factor of 2.5-3) give rise to a 20 % lower coating cost for cast Si despite higher target costs on a mass basis.

INTRODUCTION

Rotary, plasma sprayed aluminum-alloyed (8-12 wt.%) silicon sputtering targets have been used successfully for more than two decades in the architectural glass industry in order to deposit silicon-nitride coatings in low-emissivity stacks. More recently, non aluminium-alloyed equivalents have been introduced in the display industry, e.g. for depositing silicon-dioxide (SiO_2) coatings as a metal ion barrier/nucleation layer and as low index optical layer for projected capacitive touch sensors or as an etch stop barrier in multiple domain vertical alignment type TFT-LCD's. The deposition of silicon-nitride (SiN_x:H) coatings with high refractive index in crystalline-silicon photovoltaic cells (anti-reflection/passivation layer) is also being performed with such targets. Reactive sputtering processes using MF-AC power generators with twin rotary cathodes are the standard in all those applications.

Unfortunately, due to their low density/high porosity and limited chemical purity, rapid nodule formation giving rise to strong arcing problems generally arises with sprayed silicon targets. This paper introduces a new type of pure silicon sputtering target consisting of multiple cast silicon cylindrical segments, bonded to a backing tube.

TARGET CHARACTERISTICS OF SPRAYED VS. CAST SI TARGETS, NODULE FORMATION

A plasma spray process condenses the sprayed particles on the backing tube in a 'pancake'-like micro-structure with considerable micro- and even macro-porosity. Many sprayed targets have a density less than 90 % of theoretical density. High quality boron-doped sprayed Si targets are being used in the display industry and can be produced with densities up to 96 % of theoretical. An example of the microstructure of such a target is shown in Figure 1.

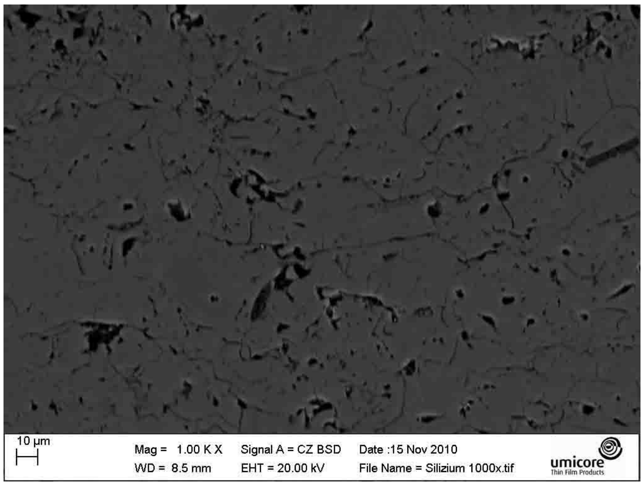

Figure 1: SEM micro-graph of a cross section through a high density sprayed Si target (Density = 96 % of TD), the black areas indicate porosity.

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Due to contamination a.o. introduced in the spraying gun, the chemical purity of sprayed Si targets is considerably lower than that of cast metallurgical Si targets. An LA-ICP-MS analysis summarized in Table 1 includes elements such as Al, Cu, Ti, Fe. Their presence points to contact between the partially liquid precursor powder and the metallic spraying gun. The material also contains a significant level of Ge, a typical contaminant in Si, indicative of the usage of a lower purity precursor powder. Even without considering nitrogen, carbon and oxygen, the total sprayed target chemical purity is only 3N7.

Table 1: Impurity content in a high quality, rotary, sprayed Si target as measured with LA-ICP-MS.

Element	Ge	B	Al	Cu	Ti	Fe	O	N	C
Concentration (ppm)	72	56	25	21	18	11	3657	288	201

Experience in the display industry has shown that targets of this type considerably generate nodules (see Figure 2) during the sputtering process.

Target properties such as low chemical purity and low physical density [1] strongly promote the formation of nodules, as they cause arcing easily. Arcing is known to be one of the main promoters of nodule formation with ITO [2].

Figure 3 shows an optical micrograph of a cross section through one of the nodules on a sprayed Si target. The bulk of the nodule seems to simply consist of original silicon target material, the erosion of which must have been prohibited locally due to re-deposition of matter with much lower sputter rate (a thin layer of such matter might still be distinguishable in Figure 3), in line with observations made on other materials such as ITO [3]. Local re-deposition might have resulted from geometrical inhibition due to pores or pore concentrations. In any case, rapid formation of nodules on sprayed Si targets gives rise to heavy arcing and brings the need for regular cleaning of the targets using highly abrasive tools. Such cleaning creates large dimples in the target and reduces effective target utilization. It also reduces machine up time. The nodules themselves cause reductions in product yield by promoting arcing.

Figure 2: Nodules generated on a sprayed Si target used in a reactive process to sputter SiO_2 - coatings.

Figure 3: Optical micro-graph from a cross section through a nodule on a sprayed silicon target.

Cast, cylindrical metallurgical B-doped silicon segments can be produced with a purity of appr. 5N (if abstraction is made of B, N, O and C) and have a density of appr. 2.32 kg/dm^3 or almost theoretical density (> 99.5 % of TD). Several segments can be bonded to a backing tube to form a rotary sputtering target. The wall thickness is typically 14 mm but can range up to 20 mm whereas sprayed Si targets are usually limited to 9 mm with ends of 12 mm for dog-bone shaped targets, however many companies in the display industry work with 6 mm thickness because target density drops with increases in sprayed Si thickness. Cast targets can also be made in a dog-bone format (e.g. 14/18 mm), and therefore, overall a cast multi-segment Si rotary target has a much longer coater stand-time than a sprayed equivalent (a 2.0 m long cast 14/18 mm dog-bone target has 2.57 times more Si available compared to a sprayed 6/9 mm dog-bone target with a density of 96 % of TD).

The measurements in Table 1 show high oxygen content in sprayed Si targets. This will lead to uncontrollable fluctuations in reactive processes to form SiO_2 (and Si_3N_4) in which either plasma emission monitoring (PEM-control) or voltage control is used to fix the working point away from poisoned mode.

THIN FILM DEPOSITIONS WITH CAST-SI ROTARY TARGETS

Pilot thin film depositions were done on a Leybold Optics A600V7 dynamic vertical glass coating line equipped with a twin rotary magnetron (SCI end-blocks and magnet arrays from Leybold Optics, target length 0.6m each) and two 10 kW Advanced Energy PEII MF-AC (40 kHz) power supplies used in master-slave mode (max. power 20 kW, equivalent to max. 33.33 kW per meter of target length). Non-alkali glass from Schott Glass (B270) was used for the substrates and two B-doped cast multi-segment rotary Si targets from Umicore (target wall thickness 14 mm) were installed for reactive depositions of either optically clear SiO_2 or SiN_x coatings.

Data for the reactive process to form SiO_2 coatings were collected at power loads ranging from 6 kW (10 kW/m) to 10 kW (16.67 kW/m) with Ar flow fixed and variable O_2 flow yielding sputtering pressures of 2.3 µbar and higher. The results shown in Figure 4 demonstrate a strong hysteresis. Additionally, the transition from metallic to poisoned sputtering mode is very steep, regardless of power level. As a consequence, the process cannot be fixed in the intermediate mode without a means of active control such as negative feed-back coupling as is used with a PEM-control system.

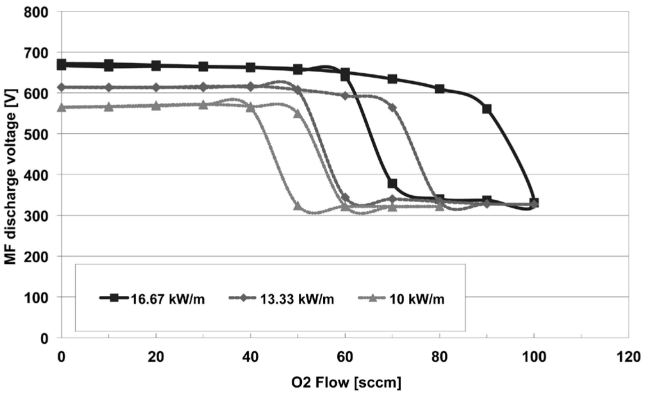

Figure 4: Hysteresis curves for the reactive process with O_2 and B-doped Silicon cast rotary targets. Curves were recorded with a fixed Ar flow of 125 sccm, variable O_2 flow (variable sputter pressure from 2.3 µbar and up) for various power loads.

Because the indicated sputter system had no feed-back control system, all depositions of SiO_2 were done in poisoned mode.

On the other hand, the reactive process with N_2 to form SiN_x coatings exhibits no hysteresis (see Figure 5) and a fairly broad reactive partial pressure range in which the process changes from metallic mode into poisoned mode sputtering. Even without active control, the sputtering process can be fixed in a point in the intermediate mode, as has been demonstrated for sputtering runs with duration up to one hour.

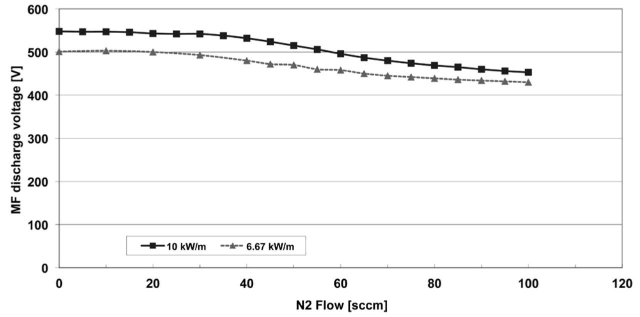

Figure 5: Discharge voltage vs. nitrogen concentration in the plasma for the reactive process with N_2 and B-doped Silicon cast rotary targets. Curves were recorded with a fixed Ar flow of 150 sccm, variable N_2 flow, both increasing and decreasing, (variable sputter pressure from 3.2 µbar and up) for two power loads.

Both processes, i.e. the one to form SiO_2 coatings operating in poisoned mode and the one to form SiN_x coatings in the intermediate mode, are stable (i.e. no visible arcs in the plasma) up to at least 10 kW (i.e. 16.67 kW/m) of power load.

The most critical process for SiO_2 deposition was run at high power (9 kW, i.e. 15 kW/m) in poisoned mode – discharge voltage 325V - during 6 hours without interruption (deposition pressure 5.6 µbar). A low and steady arc rate occurred under the following arc handling conditions: V_{trip} = 155 V with T_{off} = 240 µs. The target surfaces still looked perfectly clean after the test, i.e. no traces of nodules could be seen (Figure 6), even at the cross-corner regions of the targets.

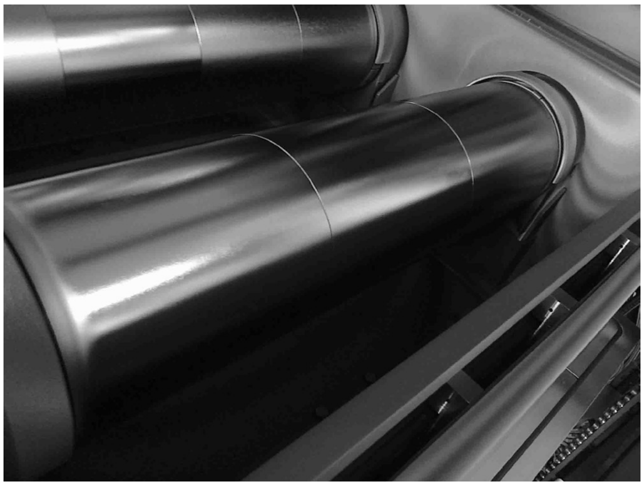

Figure 6: The twin set of cast Si targets after the 6 hour oxide-deposition test.

The SiO_2 thin films deposited at room temperature on a 70 nm AZO layer (as a contrast layer to enable thin film thickness measurements by reflectometry) were essentially absorption free. The dynamic deposition rate at the reference power of 6 kW (i.e. 10 kW/m and poisoned mode) and 6.0 µbar of working pressure was appr. 22.5 nm.m/min, rising to 38.6 nm.m/min at 16.67 kW/m. Results such as these must be seen as lower limit values as sputtering with the necessary control means in the intermediate mode on an industrial coater should yield a considerably higher deposition rate. Proprietary work on other coaters using voltage control has shown DDRs in intermediate mode (discharge voltage around 420 V) of up to 54 nm.m/min at an MF-AC power load of appr. 13.5 kW/m.

INDUSTRIAL APPLICATION EXAMPLE: SiNx:H AS AR/PASSIVATION LAYER IN CRYSTALLINE SILICON SOLAR CELLS

In order to assess the potential of cast Si targets in an industrial process, large size (length 1.987m) cast Si targets were evaluated on an Applied Materials' ATON PVD line with two horizontal drop-in twin rotary magnetrons from Bekaert Advanced Coatings in a classical SiNx:H reactive deposition process for front side passivation layers on crystalline-Si solar cells (p-type substrate) [4]. The sputtering gas consisted of a classical mixture of Ar, NH_3 and H_2 and Hüttinger TruPlasma MF MF-AC power supplies were used at power loads from 27.0 – 34.5 kW. Typical carrier speed was 1 m/min and the chamber was heated to avoid any influence of water in the process. A direct comparison on the same coating line was conducted with sprayed Si targets. About 1 million wafer cells were coated with SiNx:H using 4 sprayed Si targets after which the equipment was opened, cleaned and 4 cast-Si targets were mounted on the same magnetrons. More than 0.8 million wafer cells were then coated with the cast-Si targets. The two campaigns were undertaken on cells produced with the same silicon wafer feedstock material. The total of the two campaigns (including maintenance) took place over a period of more than 100 days in the plant (> 4.6 MWp produced) and therefore has considerable industrial relevance.

Table 2 summarizes the results from both coating campaigns. There was only a marginal difference in average solar cell conversion efficiency between the two technologies with a minor, non meaningful advantage for cast-Si. However, the distribution of the individual efficiencies around the average point was narrower in the case of cast-Si technology (see Figure 7). In other words, the latter technology yielded fewer low and high efficiency cells.

Table 2: Cell characteristics for campaigns done with either sprayed-Si or cast-Si targets.

	Sprayed Si (competition)	Cast Si (Umicore)
Average cell conversion efficiency (all cells, incl. loss) [%]	16.36	16.37
Lost cells (low shunt resistance) [%]	0.80	0.59
Wavelength of min. reflection, target value 616 +/- 15, [nm]	596-632	606-624

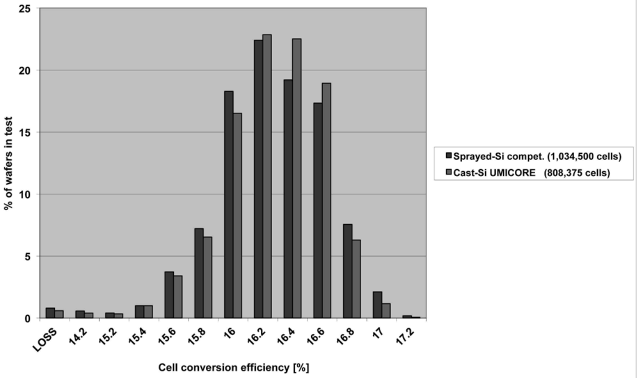

Figure 7: Distribution of cell conversion efficiencies for the two campaigns.

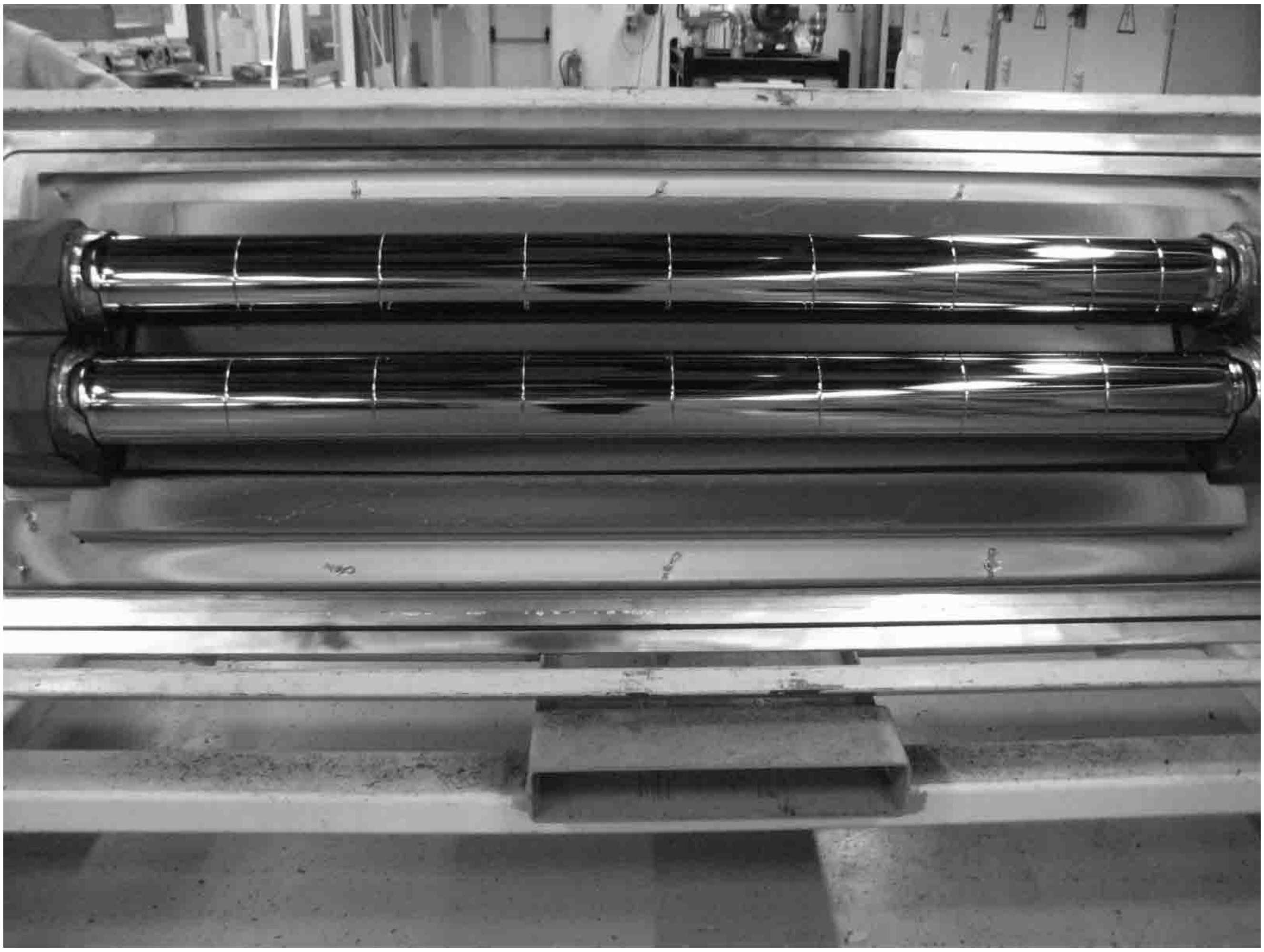

Figure 8: Target surface aspect for one of the two cast-Si target sets after 25,000 kWh into the campaign.

The fraction of cells lost due to low shunt resistance in each campaign is important as a measure of process yield. This amount was 0.21 % higher in the case of sprayed Si. Hence, using cast Si yields a clear direct gain in product yield for the cell manufacturer.

Finally, Table 2 indicates that the wavelength of minimum reflection, a measure for the effectiveness of anti-reflection performance, showed a much broader variation around the target value of 616 nm with the sprayed targets. This is probably the reason for the wider distribution in cell efficiency and comes mainly from thin film thickness fluctuations. Most probably, a higher arcing frequency with the sprayed targets is causing this. Such arcing events are triggered by nodule formation (see Figure 7).

The cast Si targets accumulated a total energy load of appr. 35,000 kWh on each set during the campaign, including some initial explorative sputtering. Extrapolating using the measured target erosion, a total target lifetime of 65,000 – 70,000 kWh is estimated for each set (14 mm cast-Si wall thickness, no dogbone) on these specific magnetrons. Figure 8 shows a picture of one of the two sets after 25,000 kWh of accumulated energy load. The target surface is extremely clean, shiny, and entirely free of nodules. In the gaps shown in Figure 9, some dust has accumulated however. In certain processes, such dust can induce arcing. A preventive gap cleaning is recommended, although during the indicated campaign, none was performed since no process instabilities were observed.

COATING COST COMPARISON.

A coating cost comparison for the two Si materials discussed above was run for the deposition of 50 nm SiO_2 as used in 'invisible-ITO' applications [5] on a Gen6.5 vertical dynamic glass coating line (substrate size H: 1.5 m X L: 2.0 m) equipped with 3 twin rotary cathodes of 1.656 m target length. It is estimated that this coating system costs 14 M$ and 50 % of this investment is attributable to the SiO_2 thin film under study. The coater is used in a 24h/7d regime with 330 working days. Depreciation over 5 years and yearly maintenance hardware costs of 5 % of the original coater value are taken into account. Fully loaded labour rate was assumed at 30 $/hr and electricity cost is 0.1 $/kWh. Dogbone sprayed (9/12 mm) Si targets are compared with dogbone cast and bonded (14/18 mm) targets. It is assumed that the target utilization (TU) for the cast targets is slightly less (80 %) than for the sprayed targets (82.5 %). However, due to grinding away nodules, the effective TU of the sprayed target is only 61.875 %. For both processes, a collection efficiency of 55 % is assumed. Cast Si targets are run at 15.0 kW/m (with corresponding DDR of 51.15 nm.m/min) in intermediate mode whereas for sprayed targets, power was limited to 13.5 kW/m (DDR of 46.03 nm.m/min) in order to keep arcing rates within acceptable limits.

Figure 9: Detail of a few of the gaps between cast-Si cylinders after 25,000 kWh of accumulated energy load on the set.

Under these assumptions, the coating costs are summarized in Figure 10. On a unit basis, cast Si targets are more expensive than sprayed targets. Even when calculated per kg of available Si, cast targets are about 32 % more expensive. However, the higher effective TU with cast Si compensates for this almost entirely. Materials cost with cast Si is only 7 % higher. The higher coater up-time, together with a higher substrate speed and a marginally higher product yield with cast Si, generates a much higher yearly line output (393,900 units) compared to sprayed Si (190,000 units). Hence, machine and labour costs are distributed over a much larger output. By consequence, total coating costs with cast Si are almost 20 % lower in the indicated application.

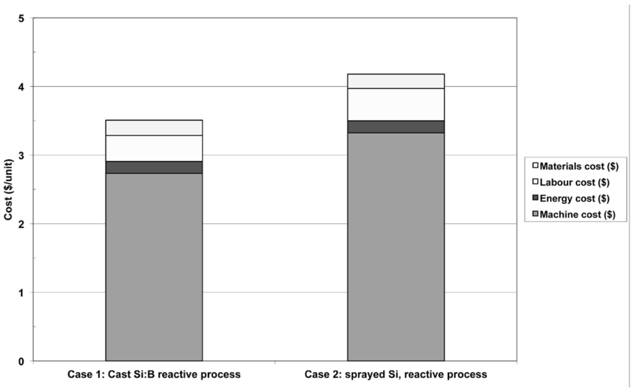

Figure 10: Result of the coating cost comparison for the touch sensor application in the display industry (details in the text). The substrate unit is 1.5 X 2.0 m.

CONCLUSIONS

Cast Si targets are a viable alternative for sprayed, non-aluminium alloyed Si targets. They behave like the latter targets in reactive processes and hence require either voltage control or PEM control when sputtering SiO_2, a process with strong hysteresis. The higher target density combined with the better chemical purity leads to much less nodule generation. The reactive process for SiNx:H deposition in the c-Si PV industry has been demonstrated to run nodule free with high target lifetimes. The cast-Si yielded cells with a narrower property distribution at a higher product yield. Although cast Si targets are more expensive than sprayed equivalents, total coating costs have been demonstrated to be approximately 20 % lower for cast targets.

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REFERENCES

1. Takahisa Omata, Masao Kita, Hideya Okada, Shinya Otsuka-Yao-Matsuo, Naoki Ono, Hiroyuki Ikawa: “Characterization of indium-tin oxide sputtering targets showing various densities of nodule formation”, Thin Solid Films 503 (2006) pp. 22-28. http://dx.doi.org/10.1016/j.tsf.2005.09.200

2. K. Nakashima and Y. Kumahara, “Effect of tin oxide dispersion on nodule formation in ITO sputtering”, Vacuum 66 (2002) pp. 221-226.
http://dx.doi.org/10.1016/S0042-207X(02)00145-8

3. M. Schlott, M. Kutzner, B. L. Gehman, N. Reger and F. J. Stadermann, “Nodule Formation on Indium-Oxide Tin-Oxide Sputtering Targets”, SID 96 DIGEST, P-31.

4. W. Wolke, J. Catoir, G. Emanuel, J. Liu, M. Ruske and R. Preu, “Surface Passivation for Solar Cells by Large Scale Inline Sputtering of Silicon Nitride”, Proc. 20th EU-PVSEC, June 6-10, 2005, pp. 733-736.

5. P. Sauer, A. Reus, “ITO Layer Systems with Enhanced Functionality for Touch Panel Applications on PET Film”, Proc. AIMCAL Fall Techn. Conf. 2010.