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Thermal Spray Applications in the Solar Industry

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Thermal spray is viewed as mature technology in aerospace, petroleum and power generation industries, but is not as well accepted as a viable processing technique in the semiconductor and solar cell manufacturing sectors. An exception is semiconductor processing where materials such as aluminum, alumina, yttria, and silicon are used to reduce particulate contamination. This industrial perspective may be due to higher expectations concerning material purity and density based on manufacturing techniques such as vacuum casting, hot isostatic pressing (HIPing) or hot pressing, traditionally used in these industries.

Solar cells can be categorized into two main divisions; a) crystalline silicon and b) thin film. This article discusses only the latter. Proponents of thin film solar cell technologies tout lower manufacturing costs over crystalline silicon as the primary driving force for continued growth in this area. There are four main types of thin film solar cells manufactured for large scale applications:

- Amorphous silicon (a-Si)
- Cadmium tellurium (CdTe)
- Copper indium selenium (CIS)
- Copper indium gallium selenium (CIGS)

The distinction between CIS and CIGS is that the addition of gallium increases absorption band-gap. The 2008 Solar Technologies Market Report published by the U.S. Department of Energy, January 2010[1], shows an increase of 80% in revenues from 2007 to 2008 worldwide for photovoltaic (PV) cells/modules to $20 billion. A compound annual growth rate of 86% from 1998 to 2008 globally is stated for thin film technologies. In 2003 the total market share for thin film cells was 5% compared to crystalline cells. In 2008, market share grew to 14% globally for thin films. Forecasts of 16 to 34% have been proposed for 2012. CIGS may grow at the expense of CdTe since higher laboratory cell efficiencies have been achieved and this technology uses more benign materials. The essential solar cell architecture usually consists of a back contact, absorber layers (P-N junction), and a transparent conductive layer. Additional layers may be employed to increase the cell efficiency and adherence to the substrate.

Materials research and cell design in the U.S. was initially conducted by physicists at NREL (National Renewable Energy Laboratory). NREL still plays a significant role in research and validation studies. Commercial thin film solar cell manufacturing can be considered an offshoot of both the semiconductor and glass industries. In the past few years, large scale manufacturing techniques for thin film deposition, such as those utilized in the architectural glass industry, are being optimized and implemented as cost-effective methods to form solar cell arrays. In fact, many glass coaters are now providing sputtered back contacts on glass to solar cell manufacturers who further process the sheet into cell arrays.

Roll-to-roll coating is the optimum thin film deposition method for economic production of thin film solar cells. The roll-to-roll process involves traversing continuous sheets of glass, foil or polymer below or above coating sources. Roll-to-roll magnetron sputtering utilizes rotary targets, consisting of the source material, to sequentially build up the solar cell. In certain cases where alternate processes such as plasma enhanced chemical vapor deposition (PECVD) or wet chemistry must be used, sputtering may still be integrated into the process line.

Fabrication of these rotary targets offers the greatest opportunity for thermal spray. The target consists of a water cooled steel, aluminum or copper tube bonded with the coating (source) material. Magnets within the tube optimize the plasma during sputtering. Cylindrical tiles of the source material can be fabricated by HIPing and bonded to the tube using solder material, or material can be directly cast onto the tube in the case of tin and zinc alloys. Rotary targets fabricated via thermal spray have been widely used in the architectural glass applications. However, direct application of the base technology in solar-cell manufacturing has been impeded by higher requirements for material purity and density. Thermal spray does offer certain advantages over casting or press and sinter techniques; including fine grain size, minimum segregation, no length constraints, and ability to reapply some source material without the need to strip entire tube.

Another key advantage is the ability to synthesize complex composites (metal-metalloid, metal-ceramic) using hybrid processing. Table 1 shows some materials currently fabricated into sputtering targets using thermal spray or are being researched as possible candidates for thermal spray.

Table 1 — Thermal sprayed targets for thin film solar applications

	a-Silicon	CdTe	CIS and CIGS
Back contact	Al, Ag		Mo, MoNa
Absorber layer	Si, doped Si		CIG, CI, CIGS, Cu, InSn
Transparent conductive oxide	ITO, AZO(a)	SnO_2(b), Sn, and Zn-based oxides	SnO_2, ITO, AZO, ZnAl

(a) ITO = indium tin oxide; AZO = aluminum doped zinc oxide. (b) SnO_2 and ZnO can be formed by reactive sputtering of tin and zinc targets.

Transparent conductive oxides are an important class of ceramics having low electrical resistivity combined with transparency in the visible range of the electromagnetic (EM) spectrum. These properties allow use as electrodes where photon movement should not be impeded. Indium tin oxide (ITO) offers excellent performance but is very expensive. Therefore, less expensive alternatives to ITO are being aggressively researched. Many of these materials are based on binary oxides where one material is tin or zinc based. This class of materials offers development opportunities for thermal spray because segregation can be a problem in these systems.

Conventional thermal spray methods at times cannot lead to the desired material properties. An example is plasma sprayed Mo, where air plasma spraying (APS) will lead to an excess of 4,500 ppm oxygen in production targets. When fabricated in an inert chamber at 650 torr, the source material will have 690 ppm oxygen, which is in the same regime as the starting powder (590 ppm)[2]. Chamber pressures below 350 torr will reduce the oxides in the starting powder, and oxygen contents as low as 300 ppm can be achieved. A beneficial consequence of reduced oxygen levels is the increased density of the deposit; (93-95% of theoretical versus 90% for APS), due to increased fluidity of the particles (Fig. 1).

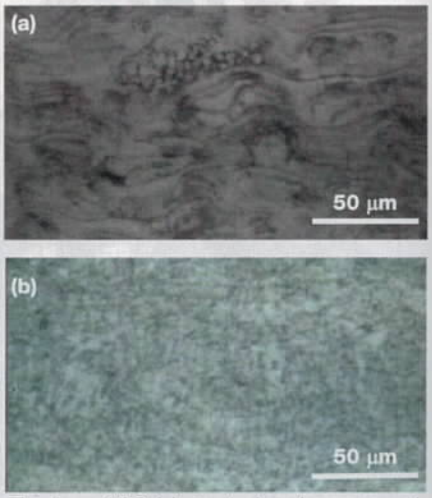

Fig. 1 — *APS (a); inert chamber sprayed Mo (b)*

The resistivity of the deposit, measured using a 4-point probe measured 50 µΩ·cm for the APS deposit versus 15 µΩ·cm for the 650 torr chamber sprayed deposit. For applications in CIGS production, 500 ppm oxygen at 93% density is deemed practical. It must be emphasized that fabrication of such targets involves careful chamber design, with allowances for tube temperature control and dust reduction. Inert chamber spraying can also be used to deposit pure chromium, copper-indium alloys and the like.

Deposition of ITO and AZO via thermal spray is very difficult because both tin oxide and zinc oxide sublime above 1900°C. However, special powder manufacturing and processing techniques now enable formation of these compositions. This overcomes some of the problems observed in using sintered tiles bonded using indium solder, where the solder would melt under the high powers used to sputter these oxides. ITO is widely used as throughout industry from flat panel displays to solar cells.

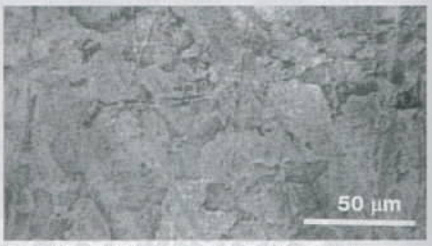

Fig. 2 — *High-rate deposition of tin*

Advanced thermal spray techniques are being investigated and developed to allow spray rates of over 20 kg/min for zinc and tin alloys. Figure 2 shows a tin deposit. The structure in terms of density is comparable to that cast material; however, with a more refined grain size.

To summarize, thermal spray fabrication of targets offers many opportunities in the photovoltaic market. Many of these applications however, will require significant process and equipment development to meet specifications for purity and density. **iTSSe**

References

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2. R. Bamola and L. Gilpin, Development of Low Gas Content Reactive Metal Rotary Plasma Sprayed Targets, 51st Annual Technical Conference Proceedings, SVC, Chicago, Ill., USA, April 19-24, 2008.

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