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# Status Of Sputtering, CVD And Their Roles In Solar Photovoltaics

Advancements in sputtering and CVD technologies will greatly aid manufacturers in their quest to trim operational and capital costs.

■ Dr. Mark George

Thin-film deposition technologies are used in the manufacture of crystalline-silicon (including multicrystalline silicon and thick-film silicon) and thin-film solar cells. Thin-film photocells include amorphous silicon (a-Si), microcrystalline silicon, copper indium gallium selenide (CIGS), copper indium selenide (CIS) and cadmium telluride.



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Sputtering technologies are used for the deposition of high-quality thin films, such as metals, metal oxides, transparent conductive oxides and even some active layers. Here, a plasma is created over the surface of the target material that will be deposited onto the substrate.

The electrons in the plasma are confined by a magnetic field in close proximity to the target surface. Ions (usually argon) in the plasma sputter the target material, creating a vapor plume that is directed to the surface of the photocell substrate.

Sputtering is used in a large variety of applications, and several CIGS and CIS solar-cell start-ups (Miasole, Daystar, Solyndra, etc.) have recently chosen sputtering to deposit their entire active layers.

The back reflector of thin-film silicon cells is often composed of zinc

oxide, which is deposited by sputtering in the presence of oxygen from a metallic zinc target to produce and deposit a zinc oxide. The molybdenum base layer in CIGS and CIS cells are also deposited via sputtering.

The conductive top layers of some thin-film cells are composed of a transparent conductive oxide (TCO) based on either sputtered indium tin oxide (ITO) or aluminum-doped zinc oxide (Al:ZnO). For crystalline-silicon PV applications, some high-performance cells use sputtered metallic contacts to reduce series resistance or employ an additional layer of metal oxide (TiO<sub>2</sub>, SiO<sub>2</sub> or nitride of silicon) as an index-matching layer to improve optical input.

All of these films can now be manufactured in ways not possible just a few years ago. One enabling factor has been the end of the rotary-magnetron monopoly via the expiration of the rotary magnetron patent (U.S. Patent #4356073).

Open competition has generated substantial advancements in this technology. One of the primary benefits is dramatically improved target material utilization, pushing utilization from 35% (for a conventional high-performance planar magnetron) to greater than 70%.

Rotatable magnetrons give process engineers the ability to increase deposition rates by operating at higher powers, enabled by improved target

cooling. Also, rotatable technology enables longer times between target changes and can reduce the number of sputtering sources required for the same film deposition - improving machine uptime and/or throughput.

## Indium costs

A main driver for achieving higher target utilization has been the skyrocketing cost of indium, which has forced many equipment and material suppliers to consider more economical deposition methods for TCO in the thin-film PV market.

Traditionally, these ceramic layers were deposited by planar magnetrons due to the manufacturing complexity of the ceramic TCO tubes required for rotary magnetrons. Many target manufacturers recognized this opportunity to expand their market share and have recently introduced composite ITO and Al:ZnO ceramic tubes for rotary magnetrons.



*A moving-magnet planar magnetron specializing in high-target utilization. The moving-magnet advancement can achieve over 50% target utilization.*

*Photo courtesy of General Plasma.*

Several magnetron suppliers have also tackled this problem by offering high-utilization, moving-magnet planar magnetrons that can achieve material utilization greater than 50%. However, a trade-off between the cheaper planar target tiles and more expensive composite target tubes must be made on a technological basis for individual production line cost structure.

The magnetron design can be further improved by the magnetic confinement of the electrons in the plasma. One of the most important advancements is the creation of an unbalanced magnetic (UBM) field that directs the electrons and ions in the plasma toward the substrate. The additional ion bombardment from the UBM greatly improves the performance of deposited thin films. The UBM option is available for both rotary and planar magnetrons from several magnetron suppliers.

Power-supply technology has also contributed to the improvement of the sputtering process. Some processes have switched over from using constant DC power supplies to mid-frequency AC and pulsed DC power supplies.

These advanced magnetron power supplies offer excellent arc-handling capabilities, which greatly reduces the number of defects introduced into the deposited thin films. Additionally, plasmas driven at mid-frequencies improve thin-film quality by adding more energy into the sputtering plasma.

The combination of all these technological innovations has resulted in higher-performing devices, greater product yields and increased throughput.

## CVD

Chemical vapor deposition (CVD) technologies are used to deposit thin-film materials with performance not easily matched by sputtering (such as dielectrics and semiconductors).

In this vapor deposition process, a chemical (precursor) containing a portion of the to-be-deposited thin-film material is introduced into the deposition equipment. Heat in the reactor is responsible for dissociating the precursor and reacting it with other gases to form the desired thin film.

Thin-film silicon substrates often start with a glass substrate coated with a TCO of fluorinated tin oxide ( $\text{SnO}_2:\text{F}$ ), which is deposited inline on a float-glass line by an atmospheric CVD process driven by the excess heat of the float line. An alternative approach is to deposit the TCO layers on bare glass substrates in an effort to reduce manufacturing costs.

Several inline, belt-driven atmospheric CVD furnaces are commercially available to deposit either  $\text{Al}:\text{ZnO}$  or  $\text{SnO}_2:\text{F}$  transparent oxides.

Layers that require better optoelectronic properties are often deposited by plasma enhanced chemical vapor deposition (PECVD). In this process, a plasma is created to supply the energy to dissociate the chemical precursor.

Crystalline-silicon cell manufacturers take advantage of PECVD for deposition of silicon nitride ( $\text{SiN}$ ) layers to provide a combination of electronic and optical properties. The  $\text{SiN}$  passivates the silicon surface by supplying a hydrogen source that eliminates defects in the silicon substrate and acts as an optical matching layer to minimize reflection of incident sunlight. This process can improve efficiency of cells by 0.5% to 1%, depending on the cell architecture.

Several plasma source technologies are available for deposition of these layers. One of the strongest technologies is an inline, remote plasma microwave source that operates at 2.45 GHz. The microwave plasma provides a soft source ideal for sensitive surface applications, such as crystalline silicon.

Less frequently used is a low frequency (40 to 100 kHz) parallel-plate source. This low-frequency source



*Rotary magnetrons can achieve greater than 70% utilization, but more complex target materials can be expensive.*

*Photo courtesy of General Plasma.*

operates in a batch mode and can cause surface damage, which affects cell performance.

PECVD may play an even more important role in crystalline silicon cell technologies as manufacturers begin to explore high-efficiency heterojunction architectures.

Later this year, the core SANYO HIT (heterojunction with intrinsic thin layer) patent (U.S. Patent #5066340) expires, with the expectation that crystalline-silicon cell manufacturers will want to explore the addition of heterojunction technology to their product portfolios.

The heterojunction design includes thin films of a-Si and/or microcrystalline silicon on the front surface of the crystalline silicon cell. SANYO has demonstrated efficiencies of these cells to be greater than 21%. Manufacturers will have to consider if the improvements of efficiency can offset the increased manufacturing costs.

## Thin-film PECVD

Thin-film silicon cell manufacturers utilize PECVD processes to provide the active-layer silicon thin films required for their products. Those manufacturing silicon thin-film modules require toxic and hazardous gases, and must have effluent management of these reactive precursors, such as silane, phosphine and trimethylborane or diborane.

Radio frequency plasma reactors operating at 13.56 MHz or 27 MHz are predominately used to deposit a-Si

thin films in inline or batch reactors. These technologies are dependent on good reactor design, pumping schemes and precursor distribution to avoid detrimental particle formation.

Cell efficiency for a well-designed PECVD line for a-Si cells is typically between 5.5% and 6.5%. In order to increase cell efficiency, a second junction (tandem junction), or even a third junction, can be added to the a-Si thin film in a multi-junction cell configuration. Multi-junction cells utilize thin films like microcrystalline silicon (this combination is known as micromorph) and silicon carbide (a-SiC), efficiently absorbing the red portion of the solar spectrum that a-Si does not.

However, in order to provide the necessary plasma chemistry that favors the microcrystalline silicon structure or a-SiC films, new reactor and power supply configurations are required. Currently, new plasma reactors and power supplies operating

at much higher frequencies (between 100 MHz and 700 MHz) are in development for microcrystalline silicon thin-film deposition.

Some believe that for thin-film silicon to compete in the long term against crystalline silicon, thin-film efficiencies must be realized in the 10% range. Increasing the deposition rate of large-area silicon thin films remains the economic hurdle for thin-film silicon solar cells. With deposition rates between one and three angstroms/second, these technologies may not be able to compete with crystalline silicon, especially because crystalline feedstock material costs are expected to fall by as much as 50% when new capacity comes on line over the next year.

Several equipment and solar cell manufacturing companies are working on new plasma sources to overcome the deposition-rate hurdle of silicon thin-film technologies. High-rate (>1,000 angstroms/sec) PECVD

of silicon active layers have been demonstrated by remote plasma downstream sources for semiconductor manufacturing. This shows that there is no fundamental limiting deposition rate - but current plasma sources are not scalable to the size and dimensions required for the large surface areas of thin-film solar cells.

But overall, plasma vapor deposition technologies such as sputtering and PECVD will remain integral manufacturing steps for both crystalline and thin-film solar cells. Recent advancements in sputtering and CVD technologies will greatly aid manufacturers in their quest to trim operational and capital costs. ☞

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