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MATERION ADVANCED CHEMICALS
COATING MATERIALS NEWS
September 2011 Volume 21 Issue 2

TUTORIAL ON SPUTTER DEPOSITION

Among the variety of PVD (Physical Vapor Deposition) processes, deposition by sputtering holds a unique position. Well known advantages over evaporation processes include wide-area uniform coverage, ability to coat temperature-sensitive substrate materials, and the virtually limitless variety of materials that can be deposited. Included in the latter category are metals, compounds, alloys, and mixtures. Oxide, nitride, and fluoride compounds can be reactively sputtered starting from metal targets. Alternatively, the full compound targets can be sputtered when the generally poor target strength and conductivity are accounted for. A large alphabet of process variations exists today, starting with DC sputtering optimum for metals and covering high frequency pulsed power developed for dielectrics and special compositions. We review some of the more widely used processes.

PRIMARY APPLICATIONS

High volume production of film of metals, dielectrics, transparent conductors, and AR coatings is done by sputter deposition because the process is adaptable to large area and roll coating configurations. Thermal control architectural window coatings, automotive windshields, food storage, CD and DVD disks, flat panel display screens, and solar cells are major users of the technology.

BASICS OF THE SPUTTERING PROCESS

As shown in Figure 1, the essential components are a cathode and an anode, between which an electric field is established that produces a specific power density. An electron and ion plasma is established between the electrodes in a working gas such as Argon. The cathode or target is

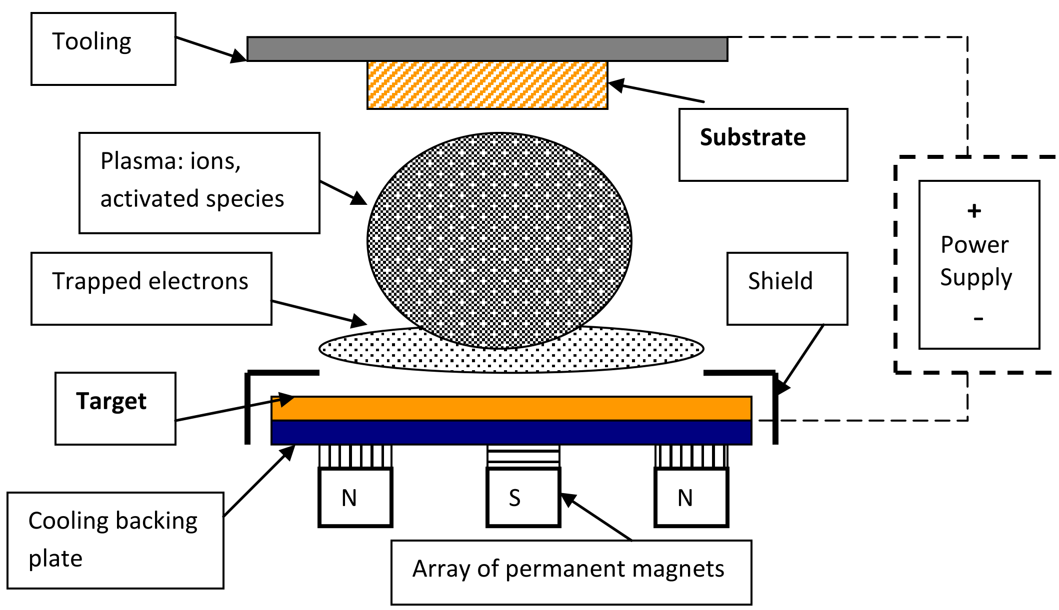

Figure 1. Basic functional components of a planar magnetron sputtering system. The system can be inverted to configure downward directed-sputtering.

NEW ON THE WEB

Non-Silicon Thin-Film PV Materials Progress and Challenges

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View the whole presentation at: www.materion.com/AdvancedChemicals in the Resource Center.

Sputter deposition is playing a large role in the development of non-silicon based thin film solar cells. Materion designs materials for CIGS and CdTe technologies.

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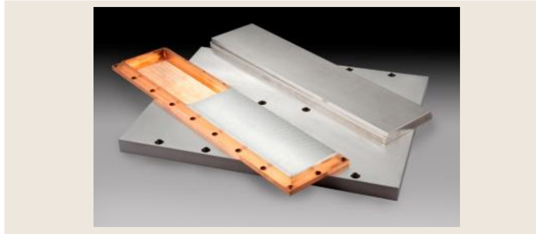


backed by a strong electric field that enhances the density of ionized particles near the target surface. The heavier Argon ions created in the plasma cause cathode material to be mechanically sputtered from the surface by momentum transfer. Depending on the gas pressure (which determines the mean free path), target particles and ions are attracted to the anode where they condense and grow a thin film layer. The composition of that growing layer is determined by the target particle composition, the reactivity and energy of the plasma species between the targets and the anode surfaces. The deposition rate is determined by the energy density at the cathode surface and the reactivity in the plasma. Limits to the sputter rate are imposed by the binding energy of the target material and the tolerable temperature rise permitted for the target and its backing structure.

COMPARISON WITH THERMAL EVAPORATION

Until recently, sputter deposition was limited to the production of semiconductors, metals, tribological surfaces, and decorative and metal coating. Sputtering is currently applied successfully to the coating of optical components for the UV through Visible wavelengths, mostly restricted to oxide and nitride compounds. Fluoride and sulfide compound film layers, normally only grown by thermal evaporation, have been sputter deposited for special applications. Comparison between the advantages and disadvantages of the two processes is made in Table 1.

Table 1. Comparison between sputter and evaporation deposition processes for Oxide compound deposition.

Property	**Sputtering**	**Evaporation**
Materials available	Metal, compounds, alloys, ceramics	Compounds, mixtures, metals
Film Quality	Good stoichiometry	Requires IAD for Complete oxidation
Packing density	Dense	Requires IAD, high temp.
Mechanical stress	Controllable	Compressive
Substrate temperature	<100° C OK for polymers	Can be high: >200°
Deposition rate (Å/s)	2 -5	5 -10
Step / curvature coverage	Good, can shape targets	Difficult
Thickness monitoring	Off-set	Good
Repeatability	Excellent	Difficult
Process variables	Many	Few, but less control
Cost	High for material targets and power supplies	Low

Both deposition processes have their place in production. Sputter deposition is a proven production process, especially for large area coating. Adaptations for new materials and applications are straightforward. The reader is encouraged to review past issues that discuss many aspects of sputter deposition at www.materion.com/AdvancedChemicals under Literature in the Resource Center.

VARIABLES IN THE SPUTTER PROCESS

The presence of a biasing voltage between target and substrate affects the energies of the sputtered species. This variant can result either from self-biasing or from an applied bias voltage achieved by isolating the substrate from the chassis. The higher energies present an increase chemical reactivity and ensure correct film composition, specifically, complete oxidation. The result is a film with more consistent optical, compositional and mechanical properties as compared with the lower energy environment present in evaporation. Figure 2 illustrates film microstructure as produced by different adatom energies associated with deposition processes [Pulker & Schlichtherle, OIC Tucson 2004]. Evaporation processes produce adatom energies in the 0.1's eV, while sputtered energies are 1 to 10 eV. It is necessary with thermal evaporation to heat substrates to high temperatures (200 to 300° C) in order to achieve high packing densities and complete oxidation of oxide compound film layers. Ion assist (IAD) bombardment of the growing film with ions of energies 10 to 100 eV achieves the same function with greater efficiency and lower temperature. The energetic environment of the dense plasma in sputtering accomplishes nearly the same results.

A number of refinements to the general sputter process have evolved. Stable operation is ensured through feedback control techniques such as emission spectroscopy that prevent excessive insulating oxide formation on the target surface. The sputter rate for oxides is much lower than that for the metal. In addition, arcing will occur as charge builds on the insulating oxide layer. Sputtered films have a more densely packed microstructure than evaporated films, and consequently have higher intrinsic stress. Film stress can be dialed between compressive and tensive by changing the bias voltage, since bias voltage controls ion momentum. Film nano-structure can be modified through the structure-zones from tensile and porous at low ion momentum, through zero stress, and transition to compressive stress and a dense structure at high momentum; see Figure 2.

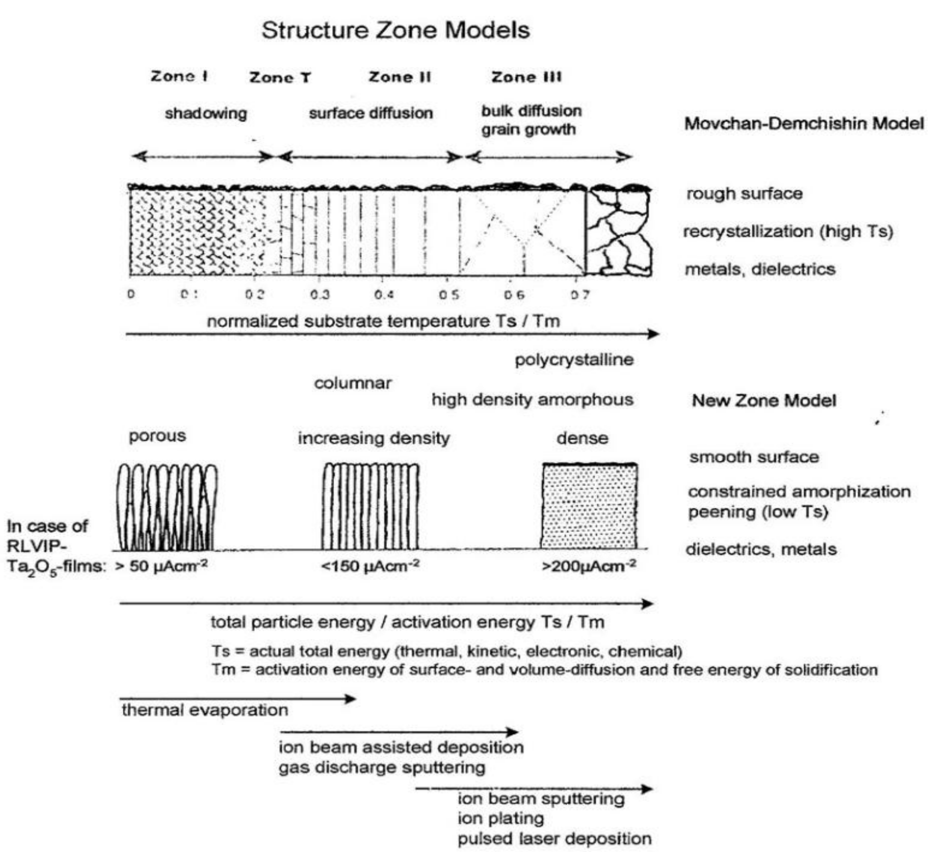


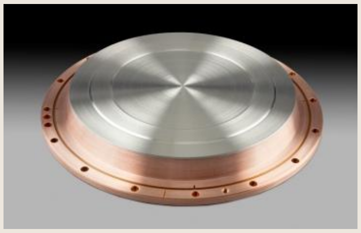
Figure 2. Structure zone model relating film nano-structure to process energy. Sputtering is between thermal evaporation and ion beam sputtering and high energy plasma processes.

CdS Sputtering Targets

- Dense custom microcrystalline CdS powder is consolidated into tiles at high volume for sputtering.
- Tiles with sizes up to 175mm x 200" at densities exceeding 89% are produced for bonding and direct use.
- Indium bonding is the most efficient bonding method when recycling backing plates.
- Target Performance Considerations: management of re-deposition, sputtering power and arc sensitivity, and temperature of target and process.

CIGS Sputtering Targets

- Standard single phase: $Cu(In_xGa_{1-x})Se_2$ powder is produced from a range of Copper, Indium and Gallium levels.
- Standard or Custom CIGS powders are manufactured and then consolidated into dense tiles for sputtering.
- Standard $Cu(In_{0.7}Ga_{0.3})Se_2$ tiles exceeding 88% density are available up to 125mm x 125mm or targets of 200mm in diameter.
- The machined tiles/targets are fit for elastomer or indium bonding to rigid backing plates.
- Target Usability Contributors include: sputtering approach, low melting sub-phases, and free metals.



Highly refined processes have been developed by Materion to address bonding target materials to backing plates which have a high degree of difference in their thermal properties (such as CTE), to allow for a broad range of operating temperatures and ease of target recycling.

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The following is a list of the targets commonly used in solar application that are available from Materion Advanced Chemicals. For additional information on these or other products, please contact us at 414-289-9800.

Material	Type	Purity (%)
Cu-In-Ga-Se	target	99.99
	6 mm pcs. & less	99.99
	-200 mesh	99.99
$CuInSe_2$	6 mm pcs. & less	99.999
Cu-In-Ga	target	99.99
Cu-In	powder	99.99
Cu-Ga	target	99.99+
Cu_2Se	target	99.5
	6 mm pcs. & less	99.5
CuSe	6 mm pcs. & less	99.5
In_2Se_3	target	99.9
	6 mm pcs. & less	99.999
Ga_2Se_3	6 mm pcs. & less	99.999
Cu	6 x 6 mm pellets	99.99*
	3 x 3 mm pellets	99.99*
	2-6 mm shot	99.99-99.999*
	-20, +50 mesh	99.95*
In	target	99.99, 99.999
	3mm shot	99.99 - 99.9999*
Ga	3 mm shot	99.99 - 99.9999
Se	3 mm shot	99.99, 99.999*

Pre-deposition cleaning of the substrate by a high density of high-energy Ar ions is often used to insure adhesion. Substrate surface conditioning generates nucleation sites on the substrate surface, thereby affecting the growth microstructure. Similarly, bombardment of the target surface by Ar ions before deposition improves the consistency and repeatability of the sputtered films.

Sputtering power supply can be one of several varieties - depending on target electrical conductivity, DC or RF or pulsed DC sputtering is used. Metals are DC sputtered; insulators require RF or pulsed processes.

SPUTTER TARGETS

Targets are manufactured from pure metals, pressed powders, from castings, alloys, or dual-compound compositions. Metallic and ceramic targets are formed from fine powders, cold pressed, and then sintered. Metal alloy powders are consolidated with some heat; ceramics are consolidated with heat and sometimes additionally sintered. Metal targets are also cast to shape with machining or cast and hot rolled to facilitate coating complex geometries. Other materials are vacuum-melted and pressed into target shapes. Depending on composition, targets can be monolithic, or constructed of closely assembled tiles. During the formation of a sputter target, efforts are made to ensure the composition purity of the material. For example, in casting metal targets, inclusions such as oxygen can create microscopic oxide domains that have a different sputter rate than the bulk metal. Nodules can form on the target surface that can arc and broadcast particulates. Particulate emanation and arrival at the substrate can lead to the growth of nodules in the film layer. For some applications, particulates and nodules and consequent pinholes can render the film unusable.

Materials and Services for Solar Energy Devices

High bulk density is required for the target. Porosity can trap moisture and foreign gases that will affect rate and purity. Bulk densities are >90% and ideally would be near 99%.

During the sputter process, the energetic plasma in contact with target surface generates high temperatures. Insulating targets are bonded to a backing plate that is cooled to keep the target temperature within acceptable limits. Indium or an elastomer, depending on target composition, is used for bonding targets to the backing plate. Formation technique and target thickness are adjusted to prevent de-bonding from the cooling plate or fracturing due to thermal mismatch or poor conductive heat removal. Target useful life is limited by the extent of erosion. Erosion patterns on planar targets are generally oval in shape ('racetrack'), and the target can be used only to a predetermined eroded depth. Extended life is achieved by forming targets into cylinders that are rotated to uniformly spread the erosion over a large area. This approach is used in large-area coating with applications to producing low-e thermal control architectural glass and thin-film solar cells. Targets and magnet arrangements that rotate are also techniques that distribute exposure to the eroding plasma.

CURRENT RELEVANCE: PV SOLAR CELL PRODUCTION

Sputter deposition is playing a large role in the development of non-silicon based thin-film solar cells. Materion's Coating Materials News of Dec 2009 (Volume 19, Issue 4), introduced the subject. CIGS and CdTe solar films include a layer of CdS, and process sputtering of CdS is now developed to production status. Tiles with sizes up to 175mm x 200mm at densities exceeding 89% are produced for Indium bonding to copper backs or for direct use. A mosaic tiles format is used to assemble larger targets. Kilo-Ohm resistances permit RF sputtering, but pulsed DC has been tried. CIGS sputter targets are available. Single phase: $Cu(In_xGa_{1-x})Se_2$ powder is produced from a range of Copper, Indium and Gallium levels. Standard $Cu(In_{0.7}Ga_{0.3})Se_2$ tiles exceeding 88% density with tile size up to 125 mm x 125 mm or targets of 200mm diameter are in use. The machined tiles/targets are bonded using elastomer or indium to rigid backing plates.

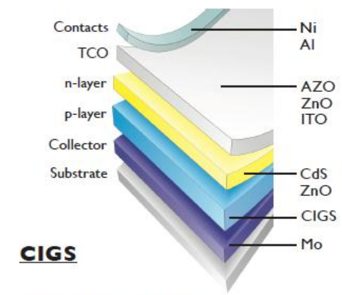
Issues encountered with controlling important In / (In + Ga) and Ga / (In + Ga) ratios in the CIGS layer led to requests for stable binary compounds. As is the case for the full CIGS target, -Se retention and control remains a key factor for the binary targets.

The presence of Selenium in the compound limits target conductivity and makes use of pulsed DC or DC sputtering difficult. In_2Se_3 and Cu_2Se targets seem to have an even more dramatic conductivity vs. temperature relationship. With less sub-phases possible, the onset of melting and poisoning of the target surface remain key hurdles for process development. Process approach and conditions are less advanced than CIGS. Cu-In-Ga target development is in process.

We'll report advances in these areas as they are developed in ongoing R & D.

REFERENCE

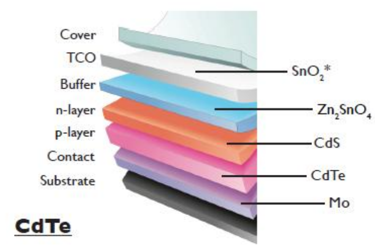
Non-Silicon Thin-Film PV Materials Progress and Challenges. David A. Sanchez. SolarCon Republic of Korea, April 8, 2011



CIGS/CIS Solar Cell Options

- CuInGaSe*
- AZO
- CuGa Alloys
- CuInGa Alloys
- Mo
- (ZnMg)O
- In_2Se_3
- ZnS
- ITO
- CdS
- NaF
- ZnO
- In_2S_3
- $CuInSe_2$
- CuSe
- Cu_2Se

*Materion provides four element CIGS compositions.



CdTe Solar Cell Options

- ZTO
- Ni Alloys
- NiV
- Zn_2SnO_4
- Ti
- Cu….
- CdTe
- ZnSn
- Cd_2SnO_4
- Sb_2Te_3
- Al
- CdSn
- CdS
- ZnTe
- Mo
- Cr
- *SnO_2 also acts as Ar Coating

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COATING MATERIALS NEWS is a quarterly publication published by Materion Advanced Chemicals.

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