

Sputtering targets: The advantages of Powder Metallurgy in the production process

Though production of sputtering targets could be considered a niche application, Powder Metallurgy processes are widely used for the manufacture of a significant range of different coating source materials. In this article, Plansee SE's Jörg Winkler and Christian Linke review the major materials and applications of sputtered and arc-deposited thin films, describe important material and product characteristics of a sputtering target to achieve a stable coating process, and highlight the specific advantages of PM.

Sputter deposition and arc evaporation belong to the group of Physical Vapour Deposition (PVD) technologies. PVD coating processes are widely used for the vacuum deposition of functional thin films, ranging from a few nanometers up to several micrometers in thickness, in a multitude of applications. In these processes the source material is provided as a solid plate, disc or tube, called a sputtering target

or arc cathode, which is consumed during the coating process. For ease of comprehension, when referring to the coating source we will only use the terms 'sputtering target', or just 'target' in this article, but most of the discussion also applies to arc cathodes.

Depending on the substrates or parts to be coated, different coating equipment with sputtering targets or arc cathodes in various sizes and

shapes is used. R&D deposition equipment often relies on 50–100 mm disc-shaped targets with a thickness of 4–8 mm (Fig. 1); mass production coaters typically require rectangular targets with 1–3.8 m in length, 150–250 mm in width and 10–20 mm thickness. For high-throughput systems, rotary targets of 1–4 m in length are commonly used. Coating sources are available from almost



Fig. 1 Plansee's PVD application laboratory performs sputtering in near-real life conditions



Large-size Mo planar target for the flat panel display industry (pressing & sintering, hot rolling)



Cr rotary target for architectural glass coating (thermal spraying)



Ultra-high purity W targets for the semiconductor industry (hot pressing or hot isostatic pressing)



AlX arc cathodes for tool coating application (pressing & forging)



TiSi targets for hard coating applications (spark plasma sintering)



Ceramic TiB₂ target bonded on a copper cooling plate (vacuum hot pressing)

Fig. 2 Example of various sputtering target and arc cathode designs, shapes, and sizes for various applications, made by powder metallurgical processes

all inorganic materials, metals, alloys, intermetallics, ceramics and composite materials. Examples of various sputtering target and arc cathode designs can be seen in Fig. 2.

The sputter deposition process

The operating principle of a sputtering process with a planar target is shown in Fig. 3. The sputtering target is generally mounted on a water-cooled backing plate in a vacuum chamber. The substrate to be coated is placed at a distance of 60–120 mm face-to-face with the target. Argon (Ar) gas is introduced into the chamber up to a typical working gas pressure around

5×10^{-3} mbar (0.5 Pa) and a positive voltage of 300–500 V is applied to the target. A plasma discharge ignites in the chamber, consisting of positively charged Ar ions, electrons, and non-ionised Ar. Due to the electric field, the positive Ar ions are accelerated towards the negatively charged cathode, i.e. the sputtering target.

The sputter process can be compared to billiards. The incoming Ar ion hits the surface of the target and its kinetic energy is transferred to other atoms, comparable to the cue ball hitting a rack of coloured balls. Some target atoms gain enough energy to be ejected from the surface (this process is called sputtering), travel some distance

through mostly empty vacuum, and as they condense on the substrate surface, atom by atom, a thin film is formed [1, 2].

The magnetron sputtering process is quite inefficient; depending on the target material, sputtering gas and voltage, only 0.2–2 target atoms are evaporated per impinging Ar ion (with ~400 eV kinetic energy) [3]. More than 90% of the electric power is converted into heat, therefore the target must be cooled efficiently. It is either mechanically clamped, glued (conductive epoxy resin), or soldered with indium ('bonded') on a copper backing plate. A magnetron assembly is located underneath to concentrate the plasma near the target surface and to enhance the sputtering rate.

Sputtering is a very versatile thin film coating process, as almost any material can be deployed. Electrically conductive materials are typically operated with DC (direct current) power, while insulating materials are run in RF (radio frequency alternating current) mode. Using a metal sputtering target, e.g. Ti, and adding oxygen (O₂), nitrogen (N₂), or hydrocarbon gas such as acetylene (C₂H₂) into the working gas will result in the formation of Ti-oxide, Ti-nitride or Ti-carbide thin films, respectively. Besides flat, sheet-type substrates, complex-shaped parts can also be coated efficiently when mounted on a planetary rotatable substrate carrier (e.g. hundreds of cutting tools can be coated in a single batch). Deposition rates (i.e. film growth rates) are typically in the range of 2–200 nm/min, and thickness uniformity can be quite high, depending on the application (± 5 –10%).

While material utilisation for planar targets is limited to about 40% due to the uneven material erosion track in magnetron sputtering, almost 80–85% of the material of a rotary target can be used for coating films. In addition, rotary targets can be operated at a higher power, enabling higher deposition rates and shorter coating cycle times, as cooling is more efficient (cooling water flows in the inside of the tubular target). Rotary targets made from brittle materials or materials

with higher porosity are generally produced by bonding the material to a metallic supporting tube. Materials with enough strength and ductility are made as monolithic types, not requiring a supporting tube.

One major advantage of sputtering is that it allows the operator to tune the thin film properties, especially residual stress, from tensile to compressive, by adjusting the working gas pressure [4], or applying a negative DC bias potential (about 80 V) to the substrate [5]. High compressive stress is often required in wear-resistant tool coatings. In addition, the deposited films are usually very clean and dense, as the process is performed under vacuum. This is especially critical for electronics applications, and high-quality low-resistivity Cu or Al thin films can only be grown by sputtering [6].

However, the vacuum nature is also one of the most commonly mentioned disadvantages of all PVD processes, as vacuum components

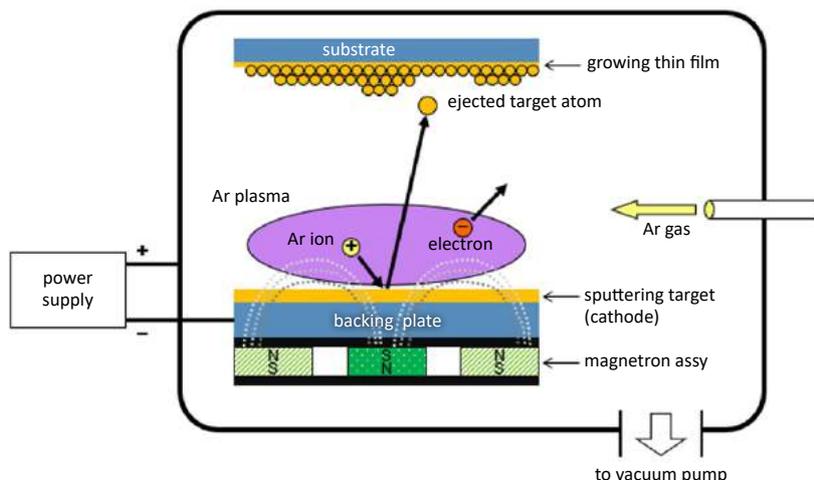


Fig. 3 Operating principle of the sputter deposition process

(chambers, load-locks, pumps, pressure gauges) are expensive and laborious to maintain. From experience, the higher fix-costs of a PVD process can usually be offset by the high throughput of the system, and variable costs are comparable to a non-vacuum process.

Applications of sputtered thin films

Functional thin films deposited by a sputtering process are used in numerous applications, including architectural glass, microelectronics, flat panel displays, tool/wear parts/

Large area coating, spectrally selective glazing (low emissivity coatings, anti-reflection coatings)			
Sputtering target material	Typical target manufacturing method(s)	Thin film material (coating)	Thin film function
Ag, Ag-Alloys	VIM-C-W	Ag	reflector layer
Si	TS, C	Si ₃ N ₄ , SiO ₂	high / low-refractive index layer
SiAl	TS, C	SiAlO _x	low-refractive index layer
TiO _x	TS	TiO ₂ , TiO _x N _y	high-refractive index layer
Ti	C-W	TiO ₂ , TiO _x N _y	high-refractive index layer
Zn	C	ZnO ₂	base coat, transparent conductive oxide
ZnAl-2 wt.%	TS	ZnO _x :AlO _x ("AZO")	transparent conductive layer
ZnO/Al ₂ O ₃ (98/2 wt.%)	P-S, HP, HIP	ZnO _x :AlO _x ("AZO")	transparent conductive layer
NiCr-20 wt.%	VIM-C	NiCrO _x	top coat (chemical, mechanical resistant)
Sn	C-W	SnO ₂	protective layer, optical interference layer
Cr	TS, HIP	Cr ₂ O ₃ , CrO _x N _y	optical interference layer
In ₂ O ₃ /SnO ₂ (90/10 wt.%)	P-S, HIP	InO _x :SnO _x ("ITO")	transparent conductive layer

Table 1 Applications of thin films, target and thin film materials, and functions in large area coating, spectrally selective glazing (low emissivity coatings, anti-reflection coatings)*

*For the sake of completeness, target materials not manufactured by PM are included, as indicated in the second column (VIM: vacuum induction melting; EBM: electron beam melting; C: casting; W: cold or hot working; TS: thermal spraying; HP: hot pressing; SPS: spark plasma sintering; HIP: Hot Isostatic Pressing; P: pressing; S: sintering; SF: spray forming); for most applications, thin films are deposited by magnetron sputtering, except for tool & parts coating applications, where cathodic arc evaporation is more prominent.

Microelectronics (integrated circuits, memory, logic, MEMS)			
Sputtering target material	Typical target manufacturing method(s)	Thin film material (coating)	Thin film function
Al	C-W	Al	interconnect
AlCu-0.5...4 wt.%	C-W	AlCu	interconnect
AlSi-1...2 wt.%	C-W	AlSi	interconnect
AlCuSi	C-W	AlCuSi	interconnect
Cu	C-W	Cu	interconnect
Ti	C-W	Ti, TiN _x	diffusion barrier in Al process
Ta	EBM-W	Ta, TaN _x	diffusion barrier in Cu process
W	HP, HIP	W	gate metal
Ni	C-W	Ni	metallisation (front end)
Co	C-W	Co	metallisation (front end), gate
Au	C-W	Au	bond pad metallisation (back end)
AuSn	C-W	AuSn	bond pad metallisation (back end)
NiV-7 wt.%	C-W	NiV	bond pad metallisation (back end)
WTi-10 wt.%	HIP, HP	WTi	diffusion barrier (packaging)
Pb(Zr _x Ti _{1-x})O ₃	P-S, HP, HIP	Pb(Zr _x Ti _{1-x})O ₃ ("PZT")	piezoelectric film (RF filters)
AlSc	C-W, HP, HIP	AlScN _x	piezoelectric film (RF filters)
Mo, W	P-S-W, HIP	Mo, W	Bragg reflector (RF filters)
Si	C	Si	Bragg reflector (RF filters)

Table 1 contd. Applications of thin films, target and thin film materials, and functions in microelectronics (integrated circuits, memory, logic, MEMS)*

Flat panel displays (thin film transistors; TFTs)			
Sputtering target material	Typical target manufacturing method(s)	Thin film material (coating)	Thin film function
Al	C-W	Al	TFT metallisation
AlNd-1 wt.%	SF-W	AlNd	TFT metallisation, less hillock formation
Cu	C-W	Cu	TFT metallisation
Mo	P-S-W, HIP	Mo	adhesion promotion and diffusion barrier
MoX (X = W, Nb, Ti, Ta)	P-S-W, HIP	MoX	adhesion promotion and diffusion barrier
Ti	C-W	Ti	adhesion promotion and diffusion barrier
W	P-S-W	W	adhesion promotion and diffusion barrier
In ₂ O ₃ /SnO ₂ (90/10 wt.%)	P-S, HIP	In _{0.8} :SnO _{0.2} ("ITO")	transparent conductive layer
InGaZnO _x	P-S	InGaZnO _x ("IGZO")	semiconductor
Ag, AgX	VIM-C-W	Ag, AgX	OLED anode and reflection layer

Table 1 contd. Applications of thin films, target and thin film materials, and functions in flat panel displays*

*For the sake of completeness, target materials not manufactured by PM are included, as indicated in the second column (VIM: vacuum induction melting; EBM: electron beam melting; C: casting; W: cold or hot working; TS: thermal spraying; HP: hot pressing; SPS: spark plasma sintering; HIP: Hot Isostatic Pressing; P: pressing; S: sintering; SF: spray forming); for most applications, thin films are deposited by magnetron sputtering, except for tool & parts coating applications, where cathodic arc evaporation is more prominent.

decorative coatings, optical coatings (e.g. eye glasses, precision optics), solar cells, data storage and others (Table 1) [2, 7, 8, 9].

In terms of area and material consumption, architectural window glass is by far the largest and most widespread application, with an annual coated area of more than 1000 million m². One glass substrate can be up to 3,300 mm wide and 6,100 mm in length ('Jumbo size'). The sputtering target (mostly rotary) is installed straight across the width of the substrate and is typically some 150–300 mm longer on each side, to ensure high film thickness uniformity (< ±5%). The glazing is coated with a multilayer stack of different materials, combining highly optically reflective materials like Ag with transparent dielectric or electrically conductive metal oxides with high and low refractive indices. The thickness of each individual layer is only in the range of 5–50 nm. The film stack either acts

as an anti-reflection coating, or as a so-called spectrally selective coating (low emissivity or 'low-E' coating), being transparent for visible light and reflective for infrared (IR) radiation. Depending on which side of the window glazing this coating is applied to, it will keep a building warm (if

Sputtering targets for microelectronic applications are the largest application by revenue, with a market size of almost \$700 million per annum [11]. Substrate sizes to be coated are the standardised, common sizes of silicon wafers, i.e. 200 or 300 mm diameter, with the 450 mm process in

“In terms of area and material consumption, architectural window glass is by far the largest and most widespread application”

applied to the inside), or cool (if applied to the outside). In large area coating, most of the sputtering target materials are either cast or produced by atmospheric plasma spraying of powder directly onto a supporting tube. In the latter case, used targets can also be refurbished after reaching the end of their lifetime [10].

introduction phase. The diameter of the disc-shaped sputtering target is typically around 1.5 x the wafer diameter. Thin films are only a couple of 10 nm in thickness, and mainly used as interconnects, metallisation or diffusion barriers (Ti- and Ta-Nitride) [7]. The semiconductor industry primarily requires ultra-high purity

Tool, parts, and decorative coatings			
Sputtering target material	Typical target manufacturing method(s)	Thin film material (coating)	Thin film function
TiAl (+ Si, Ta, V, B, Cr, Y,...)	P-W	(TiAl)N _x	wear-resistant coating for cutting tools
AlCr (+ Si, Ta, V, ...)	P-W	(AlCr)N _x	wear-resistant coating for cutting tools
Cr	HIP	Cr/CrN _x	adhesion layer for DLC, decorative coating
Cr	HIP	CrN _x	high-hardness, low-friction coatings for combustion engine components
WC	HP	WC/C	low-friction layer for tribological applications
TiSi	SPS	(TiSi)N _x	wear-resistant coating for cutting tools
C	S	DLC	low-friction, high wear resistant for tribology
CrW	SPS	(CrW)N _x	wear-resistant coating for forming tools
TiB ₂	HP	TiB ₂	cutting tools for aluminium alloys
Ti, Zr	C	TiN _x , ZrN _x	decorative, wear-resistant coatings

Table 1 contd. Applications of thin films, target and thin film materials, and functions in tool, parts, and decorative coatings*

*For the sake of completeness, target materials not manufactured by PM are included, as indicated in the second column (VIM: vacuum induction melting; EBM: electron beam melting; C: casting; W: cold or hot working; TS: thermal spraying; HP: hot pressing; SPS: spark plasma sintering; HIP: Hot Isostatic Pressing; P: pressing; S: sintering; SF: spray forming); for most applications, thin films are deposited by magnetron sputtering, except for tool & parts coating applications, where cathodic arc evaporation is more prominent.

Precision optical coatings (filters, anti-reflection coatings, mirrors)			
Sputtering target material	Typical target manufacturing method(s)	Thin film material (coating)	Thin film function
Nb	EBM-C-W, HP	Nb ₂ O ₅	anti-reflection coating (high index)
Nb ₂ O _{5-x}	HP, HIP	Nb ₂ O ₅	anti-reflection coating (high index)
Ti	C-W	TiO ₂ , TiN	anti-reflection coating (high index)
TiO _x	TS	TiO ₂	anti-reflection coating (high index)
Hf	EBM-C-W	HfO ₂	anti-reflection coating (high index)
CeO ₂	P-S	CeO ₂	anti-reflection coating (high index)
Si	C	SiO ₂ , Si ₃ N ₄	anti-reflection coating (low, high index)
Al	C-W	Al	reflective layer
		Al ₂ O ₃	anti-reflection coating (low index)
ZnO	P-S	ZnO	anti-reflection coating
SnO ₂	P-S, HIP	SnO ₂	anti-reflection coating
In ₂ O ₃ /SnO ₂ (90/10 wt.%)	P-S, HIP	InO _x :SnO _x ("ITO")	anti-reflection coating

Table 1 contd. Applications of thin films, target and thin film materials, and functions in precision optical coatings*

Switchable glass (electrochromic glass, smart glass)			
Sputtering target material	Typical target manufacturing method(s)	Thin film material (coating)	Thin film function
W	TS, P-S	WO _x	electrode layer
W _{Ni}	TS, P-S-W	W _{Ni} O _x	electrode layer
Ni(V)	VIM-C-W	Ni(V)O _x	electrode layer
Ta	EBM-W	Ta ₂ O ₅	electrolyte (Li ion conductor)
Li ₃ PO ₄	HP, HIP	LiPON	electrolyte (Li ion conductor)
In ₂ O ₃ /SnO ₂ (90/10 wt.%)	P-S, HIP	InO _x :SnO _x ("ITO")	transparent conductive layer

Table 1 contd. Applications of thin films, target and thin film materials, and functions in electrochromic and smart glass*

Thin film batteries (all-solid state, Li-ion)			
Sputtering target material	Typical target manufacturing method(s)	Thin film material (coating)	Thin film function
LiCoO ₂ (and similar oxides)	HP, HIP, S	LiCoO ₂	cathode layer
Li ₃ PO ₄ , Li ₃ PO ₄ :graphite	HP, HIP	LiPON	electrolyte layer
Li	C-W	Li	anode layer

Table 1 contd. Applications of thin films, target and thin film materials, and functions in thin film batteries*

*For the sake of completeness, target materials not manufactured by PM are included, as indicated in the second column (VIM: vacuum induction melting; EBM: electron beam melting; C: casting; W: cold or hot working; TS: thermal spraying; HP: hot pressing; SPS: spark plasma sintering; HIP: Hot Isostatic Pressing; P: pressing; S: sintering; SF: spray forming); for most applications, thin films are deposited by magnetron sputtering, except for tool & parts coating applications, where cathodic arc evaporation is more prominent.

metal targets like Ta (4N), Ti (5N), Cu (>6N) or AlCu (>5N), all of which are produced by casting; the most prominent PM materials are WTi (5N) and W (>4N), typically produced by vacuum hot pressing and/or Hot Isostatic Pressing at temperatures well above 1400°C and dwell times of up to ten hours, to achieve high density but avoid excessive grain growth [12].

In terms of the number of parts being coated, tribological and oxidation resistant coatings are the most

important category. Most of the coatings are ceramic materials, including nitrides, oxides, carbides and borides of transition metals, and diamond-like carbon (DLC) in a thickness range of some hundreds of nanometers up to some micrometers. Typically, the thin films are used to increase the hardness, thermal stability, oxidation/corrosion resistance and chemical inertness of a component or part. Millions of high-speed steel

or cemented carbide-based cutting tools (indexable inserts, end mills, drill bits, etc) are coated annually to improve their cutting performance and to prolong their lifetime [13]. With rising customer awareness and policy regulations calling for emission reduction and to reduce fuel consumption in passenger cars, the need for low-friction, wear-resistant tribological coatings and thermal barrier coatings in the automotive industry is increasing; parts to be

Photovoltaics (thin film solar cells)			
Sputtering target material	Typical target manufacturing method(s)	Thin film material (coating)	Thin film function
CuGa 20...30 wt.%	C-W, HIP	Cu(In,Ga)Se ₂	absorber layer in CIGS solar cell
CuInGa	HIP	Cu(In,Ga)Se ₂	absorber layer in CIGS solar cell
Mo	P-S-W	Mo	back electrode layer in CIGS
Mo:Na ₂ MoO ₄	HP, HIP	Mo:Na	sodium doping layer
ZnAl-2 wt.%	TS	ZnO _x :AlO _x	transparent conductive layer ("AZO")
ZnO/Al ₂ O ₃ (98/2 wt.%)	HP, HIP	ZnO _x :AlO _x	transparent conductive layer ("AZO")
Sn	C-W	SnO ₂	transparent conductive layer in CdTe
NiV-7 wt.%	C-W	NiV	back contact in CdTe solar cell
Cr	HIP	Cr	barrier coating on metallic substrates
ZnTe, ZnS	HP, HIP	ZnTe, ZnS	window layer in CdTe solar cell
Si	TS, C	Si ₃ N ₄	barrier coating (on glass substrates)

Table 1 contd. Applications of thin films, target and thin film materials, and functions in photovoltaics (thin film solar cells)*

Data storage (hard disc drives, optical recording media)			
Sputtering target material	Typical target manufacturing method(s)	Thin film material (coating)	Thin film function
Co-Fe, Co-Ni, Co-Ni-Cr	VIM-C-W, HIP, HP	Co-Fe, Co-Ni, Co-Ni-Cr	magnetic recording media
Fe-Ni, Fe-Tb		Fe-Ni, Fe-Tb	magnetic recording media
Co-Cr, Co-Cr-Ta, Co-Cr-Ta-Pt		Co-Cr, Co-Cr-Ta, Co-Cr-Ta-Pt	ferromagnetic film (recording media)
Tb-Fe-Co, Tb-Fe-Co-Cr		Tb-Fe-Co, Tb-Fe-Co-Cr	magneto-optical recording media
Gd-Fe-Co, Dy-Fe-Co		Gd-Fe-Co, Dy-Fe-Co	magneto-optical recording media

Table 1 concluded. Applications of thin films, target and thin film materials, and functions in hard disc drives, optical recording media*

*For the sake of completeness, target materials not manufactured by PM are included, as indicated in the second column (VIM: vacuum induction melting; EBM: electron beam melting; C: casting; W: cold or hot working; TS: thermal spraying; HP: hot pressing; SPS: spark plasma sintering; HIP: Hot Isostatic Pressing; P: pressing; S: sintering; SF: spray forming); for most applications, thin films are deposited by magnetron sputtering, except for tool & parts coating applications, where cathodic arc evaporation is more prominent.

Element	Target 1 µg/g	Target 2 µg/g	Ratio
Si	4	2	2
P	2	0.7	2.9
S	0.5	0.4	1.3
Cr	24	12	2
K	26	11	2.4
Ca	13	8	1.6
Fe	21	18	1.2
Al	3	7	0.4
Ni	7.5	4.6	1.6
Cu	4.9	5.9	0.8

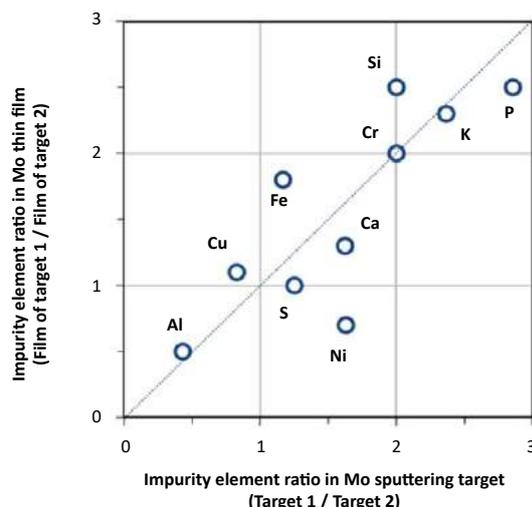


Fig. 4 Comparison of chemical impurities in two molybdenum targets, as measured by GDMS (glow discharge mass spectrometry), and impurity element ratios of respective thin films, as measured by SIMS (secondary ion mass spectrometry). Only elements well above the detection limits of both analysis methods are shown

coated include engine components (piston pins, piston rings), valve train components (valves, camshafts), transmission components (bevel and sun gears, etc.) and fuel system components (plungers, solenoids, needles) [14, 15].

generally necessary to achieve the specified flatness and surface roughness (often Ra < 10 µm). So why use Powder Metallurgy at all?

For most applications, homogeneous coating thickness is essential; within a coating run, large substrate areas must be coated with minimum

casting, where materials are always heated above the melting point, PM enables the tuning of material characteristics like phase composition, segregations, grain size and physical properties (density) in a wide range. An as-cast microstructure, with its different solidification zones, or complex phases in the case of alloys, is unsuitable for a sputtering process; castings are usually subjected to subsequent thermomechanical processing (cold or hot working, annealing) for grain refinement and homogenisation.

Material compositions specific to certain applications or customers can be readily produced by mixing various powders, for example, complex multi-element compositions (alloys, composites) with stoichiometries not accessible by traditional (liquid) metallurgical processes at all. In addition, PM process equipment such as blenders or sintering and hot-pressing furnaces are available in various sizes, and thus even low-volume batches with customer-specific material compositions can be produced cost-effectively.

Ceramic coatings are versatile and required in many applications, as shown in Table 1. A fully-reactive PVD process (using Ar working gas in combination with O₂, N₂, or C-containing gases such as acetylene) is often not desirable, due to complex

“PM processes offer the crucial advantage of the parts produced exhibiting consistent, predictable and homogeneous microstructure...”

Powder Metallurgy processes

Most of the well-known advantages and characteristics of Powder Metallurgy are not fully utilised in the manufacture of sputtering targets or arc cathodes. As shown in Fig. 2, the shape of the coating source is far from complex. Only for materials with high hardness or brittleness (intermetallics, ceramics), being difficult to machine, is the near-net shape capability of PM embraced. In addition, the compacted parts do not require great precision, narrow tolerances or a high-quality surface finish, as some final machining operations (milling, grinding and polishing) are

thickness tolerances; from run to run, the thin film thickness is not allowed to drift, throughout the entire target lifetime. To attain high thickness uniformity, a homogeneous microstructure of the target material is of paramount importance. The plates or tubes should be free from through-thickness gradients of chemical composition, phase composition or crystallographic texture; these features should also be consistent across different material lots.

Powder Metallurgy processes offer the crucial advantage of the parts produced exhibiting consistent, predictable and homogeneous microstructure. In contrast to melting and

process control and hysteresis effects [2]. Consequently, powder metallurgically produced ceramic targets or arc cathodes (oxides, nitrides, carbides, borides) are sought more frequently.

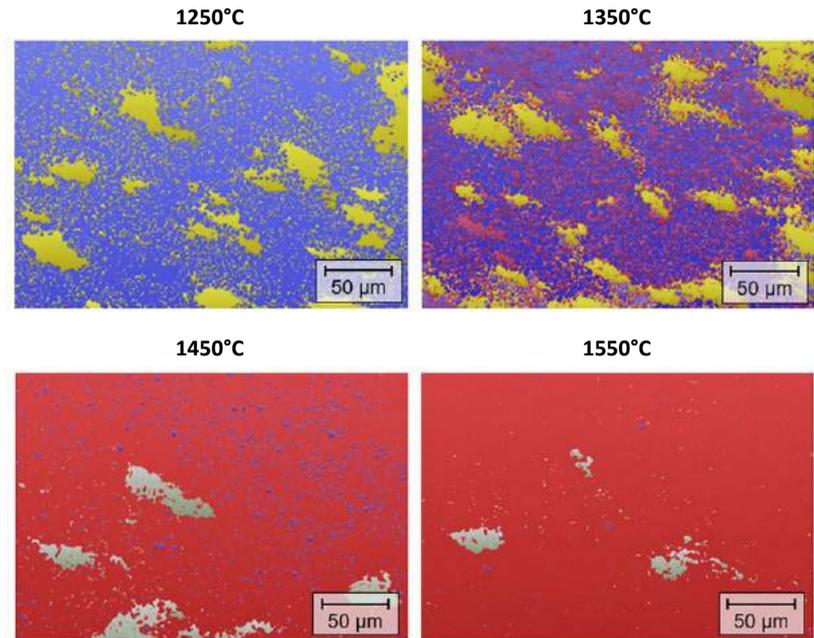
More detailed application examples highlighting the advantages of Powder Metallurgy are included in the following section.

Sputtering target material properties and performance

While in the early days of sputtering the target was perceived as a simple plate of metal, this has changed. The target design and its metallurgical properties can significantly influence the stability, reproducibility and performance of a PVD coating process, as well as the properties of the deposited thin films. In this section the most important properties of a target will be described, i.e. chemical purity, microstructure (phase composition, grain size, texture) and density.

Chemical purity

The required chemical purity of the sputtering target material heavily depends on the application, with microelectronics demanding the highest purity levels of up to 99.9999% (6N). In general, impurity elements stemming from the target will also be incorporated in the thin film. In Fig. 4 this is shown for two molybdenum targets exhibiting different concentrations of trace elements. Thin films were deposited from both targets and the chemical composition of the coatings was analysed by SIMS (secondary ion mass spectrometry). Due to the lack of an appropriate calibration standard, it was not possible to obtain absolute concentration values. Therefore, relative concentration ratios of selected chemical elements in the coatings are compared. For example, if the Cr impurity level of Target 1 is double the Cr impurity level of Target 2, a similar concentration ratio was also found in the thin films deposited from these targets. This relationship is approximately linear, but additional effects like



Hot press temp.	Phase composition (area fraction in BSE image)			
	Ti	Ti-rich (β Ti, W)	W-rich (β Ti, W)	W
1250°C	0%	31%	0%	69%
1350°C	0%	22%	30%	48%
1450°C	3%	0%	92%	5%
1550°C	2%	0%	98%	0%

Fig. 5 Microstructure of multiple-phase WTi-10 wt.% alloy as a function of hot-pressing temperature at constant dwell time. Four phases were observed: Ti (green), a Ti-rich (β Ti, W) phase (yellow), a W-rich (β Ti, W) phase (red) and a W (blue). The area fractions of the individual phases were obtained by image analysis of BSE (backscattered electrons) images.

impurity element-specific sputtering yield [3] and angular emission profile [16, 17] will lead to deviations for some chemical elements.

Low oxygen impurity levels are typically required for deposition of metal films and are particularly critical for metal targets which are strong oxide formers (Ti, Al, Nb, Ta, Cr, Mo). High oxygen content leads to particle and droplet formation during the PVD process, resulting in in-film defects and significant yield loss intolerable for semiconductor or flat panel display applications. Similarly, high oxygen impurity content in $Ti_{0.5}Al_{0.5}$ targets causes a remarkable decrease in hardness from 35 to 20 GPa in reactively deposited

$TiAlN_x$ hardcoatings, by altering the growth orientation and morphology of these coatings [18]. Limiting the oxygen concentration to an acceptably low level can present a certain challenge for PM processes. For example, oxygen levels in PM-grade hot pressed Nb or Ta are typically higher by two orders of magnitude, compared to e-beam melted material. On the other hand, sintering in high vacuum or reducing atmosphere (dry hydrogen), or addition of oxygen getters (Ca, Mg), can effectively reduce the oxygen content in sintered material. For instance, the oxygen content of Mo, hydrogen sintered at a temperature above 1800°C, is below 12 ppm [19].

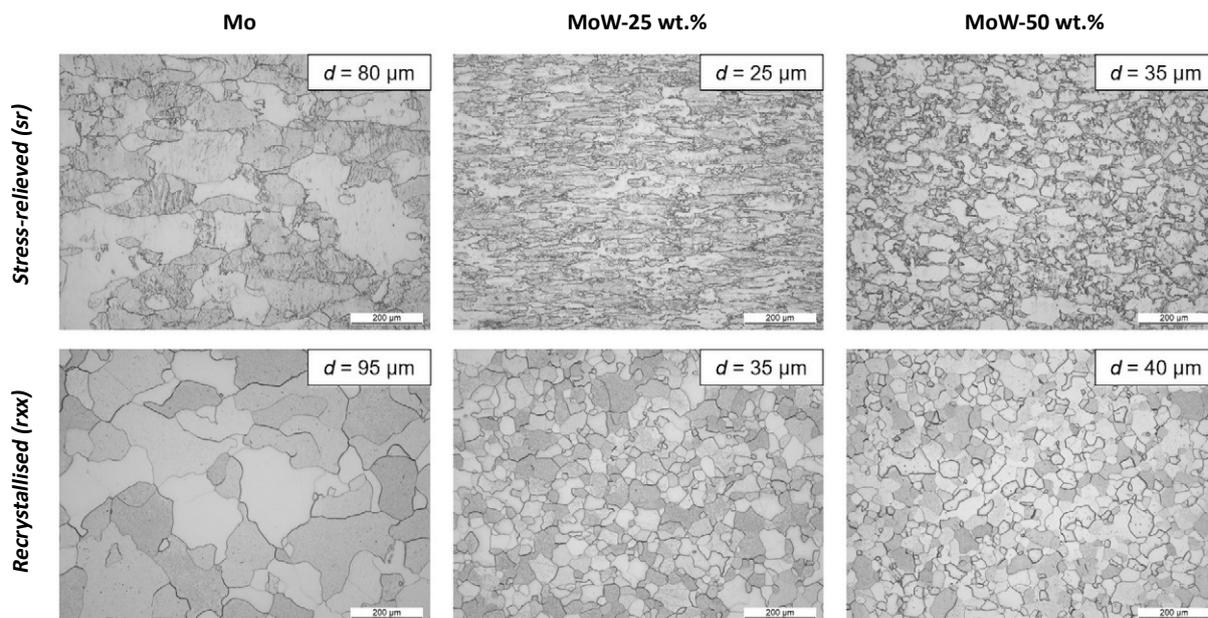


Fig. 6 Microstructures of Mo, MoW25, and MoW50 sputtering targets in stress-relieved (upper row) and recrystallised (lower row) condition. The samples represent the plane section (parallel to sheet plane) of the rolled material. Rolling direction is the same for all samples (left-right). Magnification is 100:1 for all samples, inset gives the mean grain size d , as measured by ASTM E112.

Microstructure: Phase composition

In multi-element sputtering targets the chemical composition and phase distribution within the material are key parameters and PM processes enable extensive freedom of design in tailoring the target microstructure. Firstly, PM enables chemical compositions which may not be accessible by casting processes at all, for example due to large differences in melting temperatures of the constituting elements (e.g. TiAl, AlCr, WTi, CuGa, CuIn). Additionally, in PM processes like sintering, hot pressing, or HIPing, the process temperature can be lower than the melting points of all, or only selected elements or compounds. Consequently, it is possible to customise the phase composition of the target by deliberately limiting the process temperature (in combination with the time at temperature) and to control the formation of intermetallic compounds, precipitates or segregations.

The phase composition of multi-element materials is known to affect the particle performance of the

target. For example, WTi-10 wt.% alloy, a commonly used diffusion barrier material, can be prepared by mixing Ti and W powders with appropriate particle sizes and size distributions, and compaction by hot-pressing. Adjusting the hot pressing temperature allows tuning of the phase composition in a wide range (Fig. 5).

At the lowest hot pressing temperature (1250°C) the material consists of a W matrix (blue) with a Ti-rich (β Ti, W) second phase (yellow), formed by interdiffusion. At 1350°C an additional W-rich (β Ti, W) phase is detected (red) and poor particle performance of such multiple phase target material was reported [20]. A further increase in hot pressing temperature to 1450°C results in a remarkable change in phase composition, with a W-rich (β Ti, W) matrix (red), some residual W (blue) and Ti precipitates (green); an additional increase in temperature to 1550°C leads to a further increase of the W-rich (β Ti, W) phase, approaching a single-phase structure, which was reported to be least prone to particle formation during the sputtering process.

Microstructure: Texture

The importance of the sputtering target's crystallographic texture, i.e. the grain orientation distribution, cannot be overstated, though this is often overlooked or neglected in practice. Therefore, we want to elaborate on this microstructural feature in more detail.

Metal and ceramic sputtering targets are predominantly polycrystalline. The sputtering rate of a material is strongly dependent on the orientation distribution function of the individual crystallites. For planar Tantalum targets, Wickersham *et al.* found the sputtering yield to increase by a factor of two as the predominant grain orientation changed from (111) to (011) planes parallel to the sputtering surface. The sputtering yield correlates with the atomic packing density in the uppermost atomic layer of the target surface and is proportional to the thin film deposition rate [21]. Consequently, to ensure a stable deposition rate and minimise coating thickness variations during the target lifetime, the target plate's through-thickness uniformity of the crystallographic texture is of paramount importance.

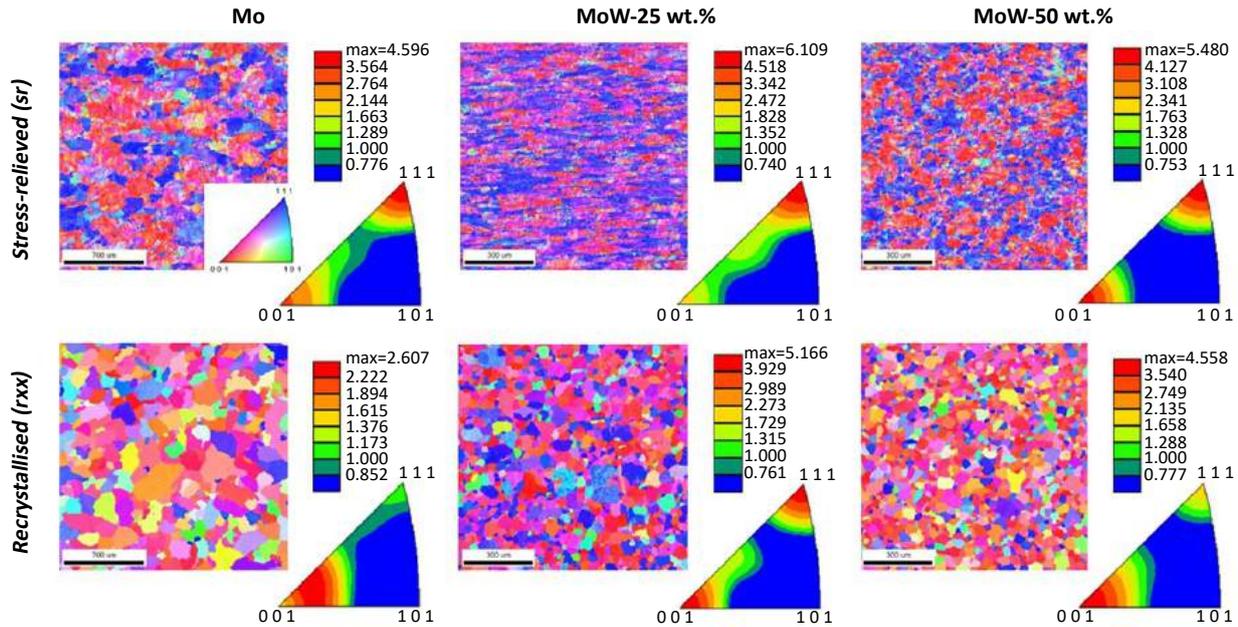


Fig. 7 Grain orientation mapping (colour code map only shown of stress-relieved Mo, same for all samples) and inverse pole figures for the normal direction (i.e. the sputtering surface) of Mo, MoW25, and MoW50 targets in stress-relieved (upper row) and recrystallised (lower row) condition. The strength of texture is indicated by the colour bar graph; a higher max value indicates a more pronounced texture

In addition, the target texture has to be consistent from batch to batch, after a material has been qualified and released for a certain coating process by the customer. Usually no changes of the thermomechanical processes can be made by the manufacturer without prior notice to the end-user. If deviation from a locked-in process of record (POR) is required, the target material usually has to be requalified. Even a supposedly minor process change may have a significant influence.

For example, a variation of the process conditions during the final annealing step of cold isostatically pressed, hydrogen-sintered, hot-rolled Mo and molybdenum-tungsten alloys (MoW-25 wt.% and MoW-50 wt.%) results in a different grain size and grain orientation (texture) of the plates [22], altering the deposition rate of the sputtering targets and consequently the film thickness of the deposited coatings [23]. The microstructures of the three materials are shown in Fig. 6. The as-deformed (hot rolled and stress-relieved) condition is shown in the upper row, while the lower row shows the samples after an additional

recrystallisation annealing treatment.

Molybdenum and tungsten form a solid solution. In the stress-relieved condition all samples exhibit slightly elongated grains in the longitudinal direction resultant from hot rolling. After recrystallisation, the microstructure changes to a more equiaxed grain structure for all materials. The mean grain size of both MoW

amount of {100} orientated grains increases, those of {111} decreases, and the overall intensity of the grain orientation weakens.

The {111} oriented grains exhibit the lowest atomic packing density in bcc molybdenum; their sputtering yield is only 0.98 atoms/ion. In contrast, {100} grains have a higher packing density and higher sput-

“If deviation from a locked-in process of record (POR) is required, the target material usually has to be requalified...”

alloys is smaller than for pure Mo by almost a factor of two. Electron backscatter diffraction (EBSD) analyses of the target samples also reveal a change in crystal orientation distribution due to recrystallisation (Fig. 7).

All three stress-relieved materials exhibit a preferential orientation of {111} planes in normal direction to the surface, whereas a smaller number of grains show a {100} orientation. Upon recrystallisation the

tering yield of 1.29 atoms/ion. {101} oriented grains would be the fastest sputtering ones (1.68 atoms/ion) [24], but are almost non-existent in all samples. Consequently, differences in deposition rate are to be expected in the polycrystalline Mo and Mo alloy materials with different texture.

The sputtering performance and deposition rate of all six materials was assessed at Plansee in the

Target material	Deposition rate (nm/min)		
	400 W	600 W	800 W
Mo, <i>sr</i>	96	142	192
Mo, <i>rxx</i>	98	145	197
Delta (<i>rxx-sr</i>)	1.6%	1.8%	2.4%
MoW25, <i>sr</i>	97	143	192
MoW25, <i>rxx</i>	100	148	199
Delta (<i>rxx-sr</i>)	2.8%	3.5%	3.4%
MoW50, <i>sr</i>	88	131	175
MoW50, <i>rxx</i>	95	141	188
Delta (<i>rxx-sr</i>)	6.8%	7.1%	7.4%

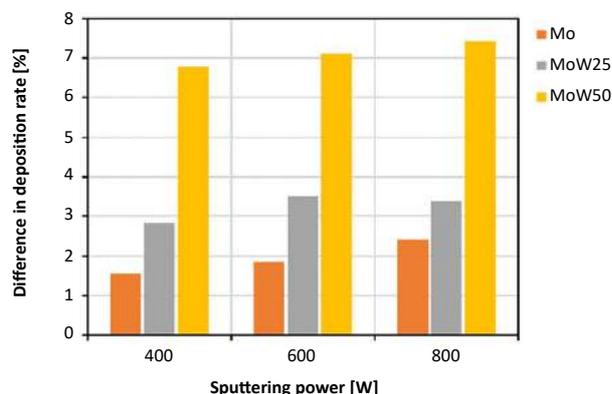


Fig. 8 Comparison deposition rate and relative difference of deposition rate for Mo, MoW25 and MoW50 sputtering targets when changing the microstructure from the stress-relieved (*sr*) to the recrystallised (*rxx*) condition.

in-house R&D sputtering deposition system, using planar sputtering targets (100 mm in diameter and 8 mm in thickness). The deposition rate at three different DC power levels is shown in Fig. 8.

All recrystallised target materials exhibit significantly higher deposition rates than the stress-relieved ones. The largest variation (> 7%) was observed for MoW50 at the highest power setting. As discussed above, this is mainly due to the different texture. For the recrystallised material the share of faster sputtering (100) oriented

grains increases at the expense of slow-sputtering (111) crystallites. The difference in deposition rate also increases with increasing W content. This may be attributed to two effects:

1. Both MoW alloys exhibit a more pronounced texture than Mo (their max values in the inverse pole figure mappings are almost doubled);
2. Recrystallised MoW50 has a higher share of fast-sputtering (111) oriented grains than MoW25.

For applications such as semiconductors, flat panel displays and large area coatings, the film thickness uniformity has to be precisely controlled, and deviations must typically be kept below ±5-10%. In these applications, thickness differences of 10 nm and less have a significant impact and, as shown above, such differences can be caused by seemingly minor manufacturing process modifications, affecting the sputtering target's microstructure.

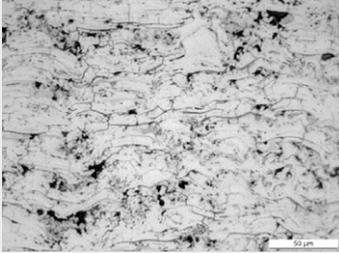
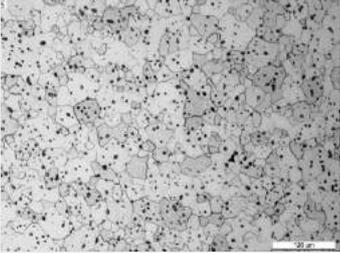
Properties	Manufacturing process		
	Thermal spraying (APS)	Hot Isostatic Pressing (HIP)	Pressing, H ₂ sintering, hot working
Relative density	87%	97%	99.5%
Oxygen content	0.25 wt. %	0.03 wt. %	0.005 wt. %
Microstructure	layered grains, voids and oxides	equiaxed grains, residual pores	deformed grains, no pores or voids
Light optical micrograph			

Table 2 Properties and metallographic cross sections of Mo rotary sputtering targets manufactured by different powder metallurgical processes (APS: atmospheric plasma spraying).

Microstructure: Density

Sputtering target density (residual porosity) also has a significant influence on its performance. Voids are known to be potential particle sources [25]. During sputtering, continuous erosion along the grain boundaries will eventually separate individual grains from the bulk material, which may potentially drop onto the substrate. In addition, lower target density might cause poor thin film performance. Chi-Fung Lo et al observed an increase in electrical resistivity of sputtered W films from 14 to 26 $\mu\Omega\text{cm}$ (+86%) when the relative density of the W target decreased from 99.5% to 82.5% [20].

In general, the relative density of a target should be as high as possible, at least > 95%, and obviously the manufacturing process has a major influence. In Table 2 some physical and microstructural properties of molybdenum rotary targets, made by three different PM process routes, are compared.

Pressed, sintered and hot worked molybdenum is characterised by a dense microstructure with low oxygen content; HIPed Mo exhibits some residual porosity with an oxygen content an order of magnitude higher, compared to pressed & sintered material. The lowest density and purity is obtained with thermal spraying (APS).

Droplet formation is associated with occurrence of an electrical discharge (arc) in the deposition system. Sputtering tests were performed with all three materials by continually ramping up the specific power (8 → 33 kW/m at constant rate) and counting the arcs. The lower density thermally sprayed and HIPed targets were prone to arcing and particle formation at specific power levels of 21 and 16 kW/m, respectively, while arcing was only observed at 33 kW/m for sintered & hot worked Mo (note: 33 kW/m is a very high power level). In addition, the sintered and hot worked Mo produced very few arcs during the total test period of

2.5 hours (arc frequency: 3.8 Arcs/hour), while the less dense targets showed a much higher frequency of electrical discharges.

Pronounced differences were observed in the deposited coatings as well. Thin films sputtered from the sintered & hot worked target had a homogeneous, defect-free surface with low electrical resistivity (15.1 $\mu\Omega\text{cm}$; Fig. 10) and the typical rice grain shape microstructure. In contrast, the thin films deposited from the APS target had a higher number of in-film defects and particles, as well as higher electrical resistivity (25.5 $\mu\Omega\text{cm}$), probably a direct result of the higher impurity content and lower density of the sprayed target material [26].

Technology trends

Sputter and arc deposition processes have been in commercial use for decades; in fact, the universal genius Thomas Edison applied for a patent as far back as 1900, claiming the deposition process of a gold seed layer on his phonograph wax master cylinders [27]. The thin film coatings market is steadily growing, and consequently, this is attracting many new suppliers to the market, leading to enhanced competition. Usually, target manufacturers seek to protect their intellectual property by applying for patents for either the target material (composition or microstructure), its manufacturing process, its application in a deposi-

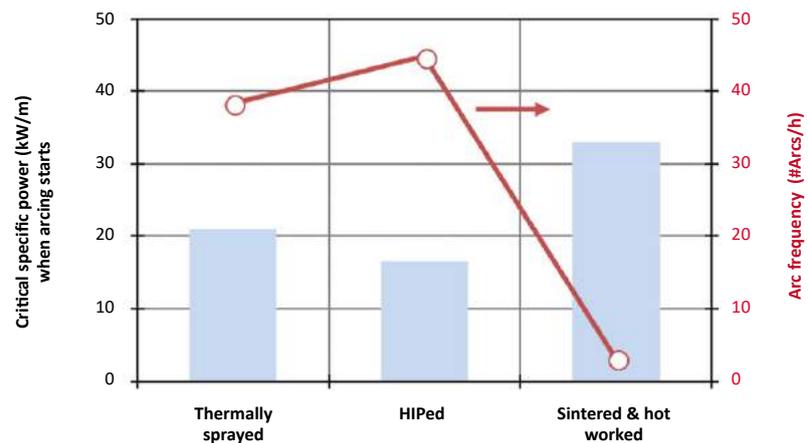


Fig. 9 Comparison of arc frequency and critical specific power levels for initiating arcs during DC sputtering of different molybdenum rotary sputtering targets (Ø152 x 600 mm).

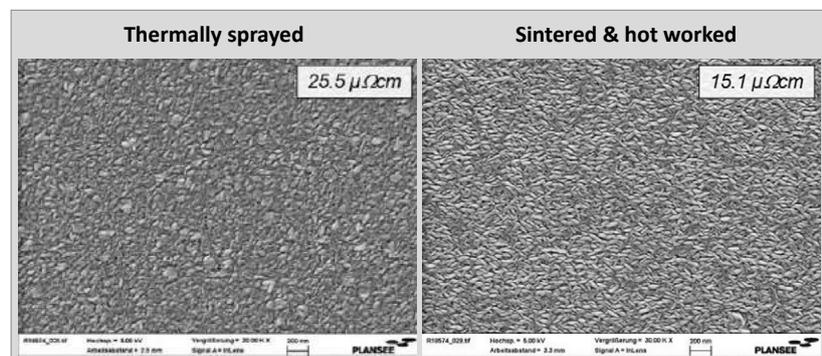


Fig. 10 SEM pictures (30.000 X) of the surface of sputtered thin films sputtered from thermally sprayed (left) and sintered & hot worked (right) Mo targets. Substrate: soda-lime glass; film thickness: ~500 nm; electrical resistivity measured by four-point probe.

Trends in thin film and PVD technologies	Trends in PM processing of sputtering targets
<ul style="list-style-type: none"> • technologies to increase target utilisation (planar → rotary; magnetron retrofits) • increase deposition rate (efficient target cooling and bonding technologies) • tightening particle performance requirements • novel driving modes (e.g. high-power impulse magnetron sputtering, HIPIMS) • deposition at room temperature, avoidance of substrate damage from plasma (flexible electronics) • deepening understanding of plasma-target interactions through advanced numerical simulation and analysis tools • increasing competitive pressure from atmospheric deposition processes (ink-jet printing; screen printing) 	<ul style="list-style-type: none"> • growing demand for (low-volume) customer-specific material compositions, with ever increasing complexity • increased utilisation of SPS, HP and HIP processes • microstructure tailored to application requirements (design to cost) • ceramics replacing respective metals • materials or microstructures with improved thermal-shock resistance, low CTE, and high thermal conductivity • refurbishing, recycling

Table 3 Technological trends in thin film and PVD process technologies (left) and Powder Metallurgy materials and processes (right)

tion process, or the derived thin film coatings and device structures. The number and complexity of such patents is increasing, and suppliers must allocate considerable resources to ensure freedom-to-operate. Some key technology trends are summarised in Table 3.

Conclusion

PVD processes such as magnetron sputtering or cathodic arc evaporation are widely used for the vacuum deposition of functional thin films in a multitude of applications, including architectural glass, microelectronics, flat panel displays, tools, wear parts, decorative coatings, optical coatings, solar cells and data storage, among others. The quality of the coating source makes a significant contribution to the stability and reproducibility of the coating process and the performance of the thin films itself.

The most important sputtering target properties are high chemical purity, uniform fine-grained microstructure (phase composition, crystallographic texture), and high density. These features can be attained more easily by powder metallurgical processing: PM materials exhibit homogeneous

microstructures, and PM permits the tuning of material characteristics such as phase composition, segregations, grain size and physical properties (density) in a wide range. Similarly, PM enables chemical compositions which may be not accessible by casting processes at all, for example due to large differences in melting temperatures of the constituting elements. It also offers high material utilisation and near-net-shape capability; particularly important for materials which are difficult to machine; and allows for cost-efficient manufacture of low-volume batches with customer-specific material compositions.

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Plansee SE

Plansee is one of the global leaders in the field of Powder Metallurgy. The privately-owned company manufactures refractory metals and composites from metal powders. Plansee covers all aspects of the production process: the company reduces metal oxide to pure metal powder, which is then compacted, sintered, and processed in various additional forming steps to produce highly resistant materials and products. Plansee is at home in electronics, medical technology, or high-temperature furnaces - wherever traditional materials are stretched beyond their limits.

For the coating industry, Plansee has been a valued, reliable supplier of sputtering targets and arc cathodes for many years. Depending

on the customers coating system, the company offers rotary and planar targets in all common sizes. For this, Plansee performs every stage of the production process in-house.

References

- [1] K. S. Harsha, Principles of Physical Vapour Deposition of Thin Films, Oxford: Elsevier Ltd., 2006.
- [2] D. M. Mattox, Handbook of Physical Vapour Deposition (PVD) Processing, Park Ridge: Noyes Publications, 1998.
- [3] N. Laegreid and G. K. Wehner, Sputtering Yields of Metals for Ar+ and Ne+ Ions with Energies from 50 to 600 eV, *J. Appl. Phys.*, Nr. 32, p. 365, 1961.
- [4] J. A. Thornton, J. Tabock and D. W. Hoffman, Internal stresses in metallic films deposited by cylindrical magnetron sputtering, *Thin Solid Films*, Bd. 64, pp. 111-119, 1979.
- [5] J. Soldán, J. Neidhardt, B. Sartory, R. Kaindl, R. Cerstvy, P. H. Mayrhofer, R. Tessadri, P. Polcik, M. Lechthaler and C. Mitterer, Structure-property relations of arc-evaporated Al-Cr-Si-N coatings, *Surf. Coat. Technol.*, Nr. 15, pp. 3555-3562, 2008.
- [6] P. J. Ding, W. A. Lanford, S. Hymes and S. P. Murarka, Oxidation resistant high conductivity copper films, *Appl. Phys. Lett.*, Bd. 64, Nr. 21, p. 2897, 1994.
- [7] J. Sarkar, *Sputtering Materials for VLSI and Thin Film Devices*, Oxford: Elsevier, 2014.
- [8] K. Pulker, *Coatings on Glass*, Oxford: Elsevier, 1984.
- [9] F. W. M. Friz, Coating Materials, in *Optical Interference Coatings*, Berlin, Springer, 2003, pp. 105-130.
- [10] C. Michaluk, Spray Rejuvenation of Sputtering Targets. Patent US2013156967.
- [11] *It's a Materials World-with Positive Forecast*, [Online]. Available: <http://www.semi.org/en/node/56701>. [Accessed on 13 July, 2018].
- [12] C.-F. Lo, „Method of making high-density, high-purity tungsten sputter targets“. Patent US6328927.
- [13] A. Inspektor and P. A. Salvador, Architecture of PVD coatings for metalcutting applications: A review, *Surf. & Coat. Technol.*, Bd. 257, pp. 138-153, 2014.
- [14] Q. M. Mehran, M. A. Fazal, A. R. Bushroa and S. Rubaiee, A Critical Review on Physical Vapour Deposition Coatings Applied on Different Engine Components, *Crit. Rev. Solid State and Mat. Sci.*, Bd. 43, Nr. 2, pp. 125-175, 2018.
- [15] J. Vetter, 60 years of DLC coatings: Historical highlights and technical review of cathodic arc process to synthesize various DLC types, and their evolution for industrial applications, *Surf. Coat. Technol.*, Bd. 257, pp. 213-240, 2014.
- [16] J. Neidhardt, S. Mraz, J. M. Schneider, E. Strub, W. Bohne, B. Liedke, W. Möller and C. Mitterer, Experiment and simulation of the compositional evolution of Ti-B thin films deposited by sputtering of a compound target, *J. Appl. Phys.*, Bd. 104, p. 063304, 2008.
- [17] M. Rausch, M. Pavlovic, P. Kreiml, M. J. Cordill, J. Winkler and C. Mitterer, Sputter deposition of Mo-based multicomponent thin films from rotatable targets: Experiment and simulation, *Appl. Surf. Sci.*, Bd. 455, pp. 1029-1036, 2018.
- [18] H. Riedl, C. M. Koller, F. Munnik, H. Hutter, F. M. Martin, R. Rachbauer, S. Kolozsvári, M. Bartosik and P. H. Mayrhofer, Influence of oxygen impurities on growth morphology, structure and mechanical properties of Ti-Al-N thin films, *Thin Solid Films*, Bd. 603, pp. 39-49, 2016.
- [19] K. Babinsky, J. Weidow, W. Knabl, A. Lorich, K. Leitner and S. Primig, Atom probe study of grain boundary segregation in technically pure molybdenum, *Mat. Characterisation*, Bd. 87, pp. 95-103, 2014.
- [20] C. F. Lo, P. McDonald, D. Draper and P. Gilman, Influence of Tungsten Sputtering Target Density on Physical Vapour Deposition Thin Film Properties, *J. Electron. Mater.*, Bd. 34, Nr. 12, pp. 1468-1473, 2005.
- [21] Z. Zhang, L. Kho and C. E. Wickersham, Effect of grain orientation on tantalum magnetron sputtering yield, *J. Vac. Sci. Technol. A*, Bd. 24, p. 1107, 2006.
- [22] S. Priemig, H. Leitner, W. Knabl, A. Lorich, H. Clemens and R. Stickler, Textural Evolution during Dynamic Recovery and Static Recrystallization of molybdenum, *Metall. Mater. Trans. A*, Bd. 43A, pp. 4794-4805, 2012.
- [23] C. Linke, M. Eidenberger-Schober, H. Köstenbauer, D. Lorenz and J. Winkler, Linking Target Microstructure with its Sputter Performance, in *SVC Tech. Conf. Proceedings*, Providence, RI, USA, 2017.
- [24] H. S. Huang, C. H. Chiu, I. T. Hong, H. C. Tung and F. S. Chien, Determining the sputter yields of molybdenum in low-index crystal planes via electron backscattered diffraction, focused ion beam and atomic force microscope, *Mat. Characteriz.*, Bd. 83, pp. 68-73, 2013.
- [25] C. F. Lo and P. Gilman, Particle generation in W-Ti deposition, *J. Vac. Sci. Technol. A*, Bd. 17, Nr. 2, pp. 608-610, 1999.
- [26] D. Rafaja, H. Köstenbauer, U. Mühle, C. Löffler, M. Schreiber, M. Kathrein and J. Winkler, Effect of the deposition process and substrate temperature on the microstructure defects and electrical conductivity of molybdenum thin films, *Thin Solid Films*, Bd. 528, pp. 42-48, 2012.
- [27] T. A. Edison, Process of coating phonograph-records. US Patent 713863, 18 Nov. 1902.