PVD coating materials for laser coatings

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Agenda

Laser coating applications

Laser coating design types and material functions

Limiting mechanisms in laser coatings

Impact of coating material & coating process

Typical & tailored laser coating materials

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Laser coating applications

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Biggest application segments 2014 w/ annual growth rate 2015-19

• Communications	+ 6.0 %
• kW & micro materials processing & marking	+ 3.5-6.0%
• Photolithography	+ 8.5 %
• Lifescience & Medical	+ 9.0 %
• Sensors & Instrumentation	+ 6.5 %
• Optical data storage	- 30.0 %
• Displays & Light shows	+28.0 %
• Defense / Security	+ 5.1 %
• Energy Conversion	n.a.

The worldwide market for lasers, Market Review and Forecast 2015
Nogee, Pennwell, Strategies Unlimited, 2015

Laser coating applications

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Market segments w/ typically high requirements for total optical loss AND / OR laser damage

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Laser coating design types and material functions

Examples for coating stack design types for optical laser components

- **Mirrors (HR Coatings)**
- **Output Couplers / Beam Splitters (PR Coatings)**
- **Polarizing Beam splitters**
- **AR coatings**
- **Retardation Plates (Waveplates)**
- **Protective windows**
- **Beam-shaping mirrors (Gaussian, Parabolic)**
- **Filters (edge, pass, wide band, narrow band, ...)**
- **...**

Laser coating design types and material functions

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Examples for material functions in laser coating stacks

- **H, M, L-index function for dielectric coatings**
- **Adhesion promotion**
- **Protection of brittle or reactive layers**
- **Prevention of interdiffusion**
- **Mechanical stress compensation**
- **Metallic high reflectance w/ high thermal conductivity**
- **...**

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Limiting mechanisms in laser coatings

- **Light scatter losses**
- **Absorption losses**
- **Laser damage**

Limiting mechanisms in laser coatings

Light scatter losses in coatings

- **surface and interface roughness**
- **phase or crystal grain boundaries**
- **irregularities (defects, voids, ...)**

Limiting mechanisms in laser coatings

Absorption losses in coatings

- **intrinsic absorption of material**
- **extrinsic absorption:**
  - **substoichiometry**
  - **impurities**
  - **defects**

Primary absorption can be amplified by scattering (light trapping)

Limiting mechanisms in laser coatings

Laser-induced damage in coatings

- **Due to absorption**
- **Caused by defects / inhomogeneities**
- **Based on electronic excitation**

Limiting mechanisms in laser coatings

Laser-induced damage in coatings

- **Due to absorption**
- **Caused by defects / inhomogeneities**
- **Based on electronic excitation**

Limitation to dielectric coatings

Limiting mechanisms in laser coatings

Laser-induced damage for dielectric coatings

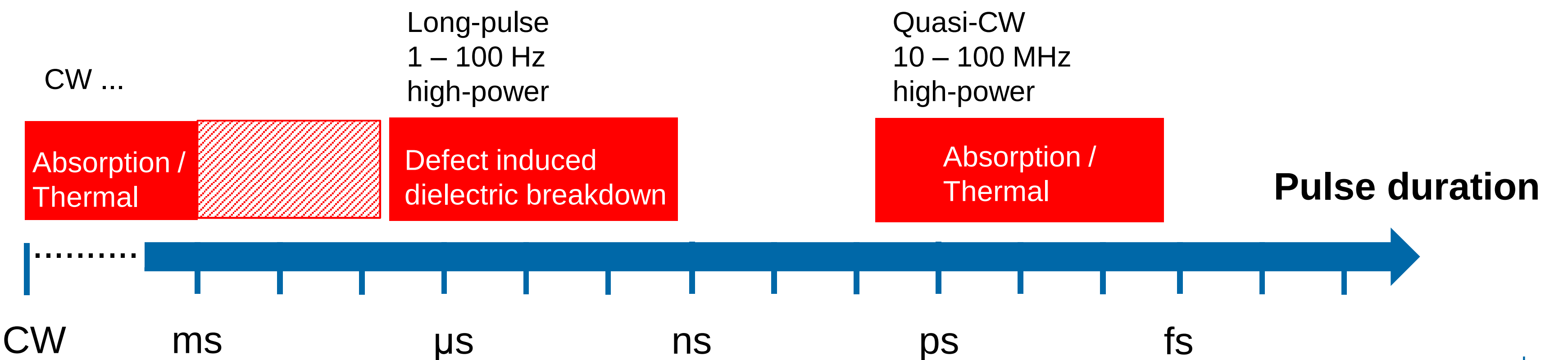
Relevance of laser operation regimes:

Pulse duration

- CW
- Short pulse
- Ultra short pulse

Pulse repetition rates
Pulse power / intensity
Wavelength (range)

Selected laser damaging types by operation regimes (schematic):



Limiting mechanisms in laser coatings

Laser-induced damage for dielectric coatings

Mechanism for «Absorption / thermal» type of laser damage:

- Excitation of electrons from valence band into the conduction band
- Further excitation of conduction band electrons
- Heating of material by electron-phonon collisions
- Structural changes, film delamination, film cracking, melting

Material impact

- Optical bandgap
- Mechanical properties
- Melting point
- Thermal conductivity

Limiting mechanisms in laser coatings

Laser-induced damage for dielectric coatings

Mechanism for «Dielectric breakdown» type of laser damage:

- Local absorption at any irregularities
  - intrinsic / extrinsic absorption centers
  - particles
  - vacancies, pores, voids, cracks, film interface roughness, phase and crystal grain boundaries
- Due to bad thermal conductivity / short interaction time local heat up
- Plasma formation → breakdown
- Melting, eruptive ejection of defects, film stress induced cracking / delamination

Material impact

- Stoichiometry, purity, density, microstructure, mechanical properties, melting point, thermal conductivity, miscibility, recrystallization temperature, ...

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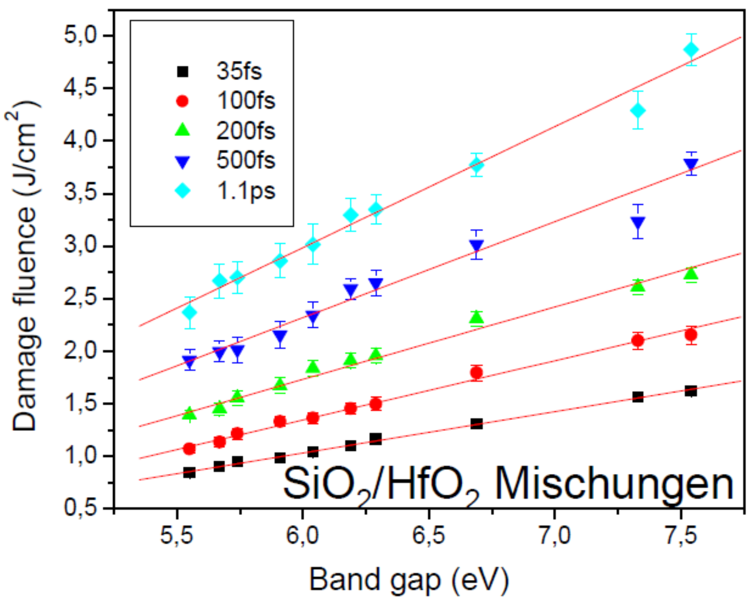
Impact of coating material & coating process

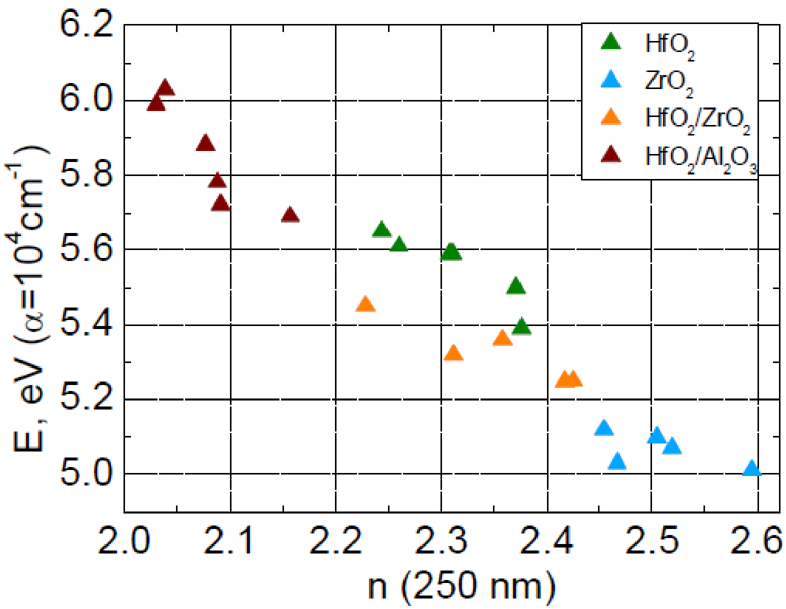
Typical & tailored laser coating materials

Impact of coating material & coating process

- For absorptive / thermal damage type LIDT for dielectric materials increasing with increasing optical bandgap, i.e. decreasing refractive index



Investigations on SiO2/HfO2 mixtures for ns and fs pulses, Jensen et al., SPIE 7842:78207, 2010

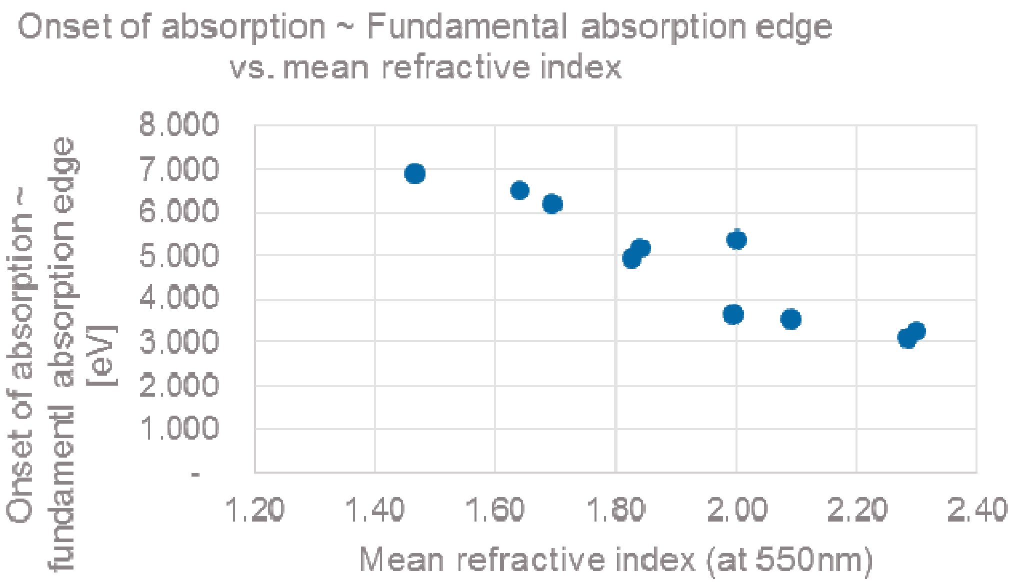


Tailored Nanocomposite Coatings for Optics, Stenzel et al., OIC 2010 Poster PMD2 (Project TAILOR)

→ search materal w/ highest opt. bandgap E_0 w/ still reasonable refractive index n for intended interference coating stack

Impact of coating material & coating process

- LIDT increasing with increasing optical bandgap, i.e. decreasing index

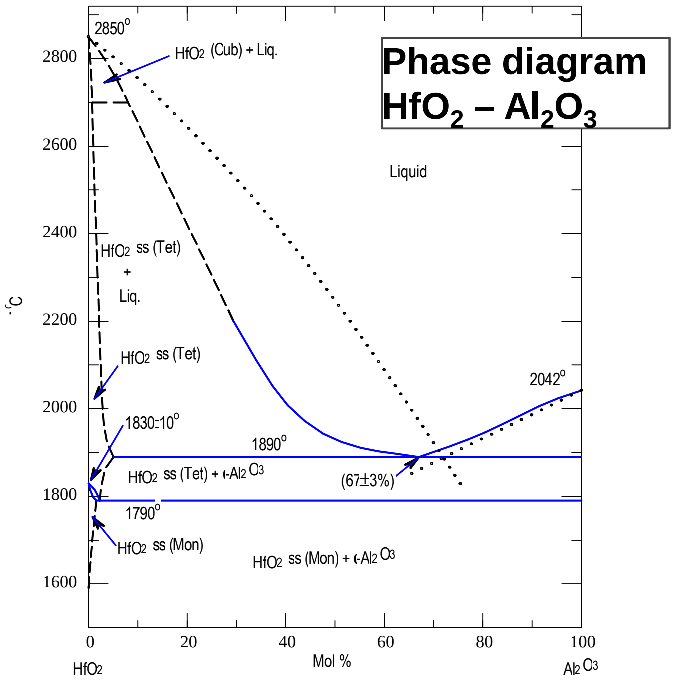


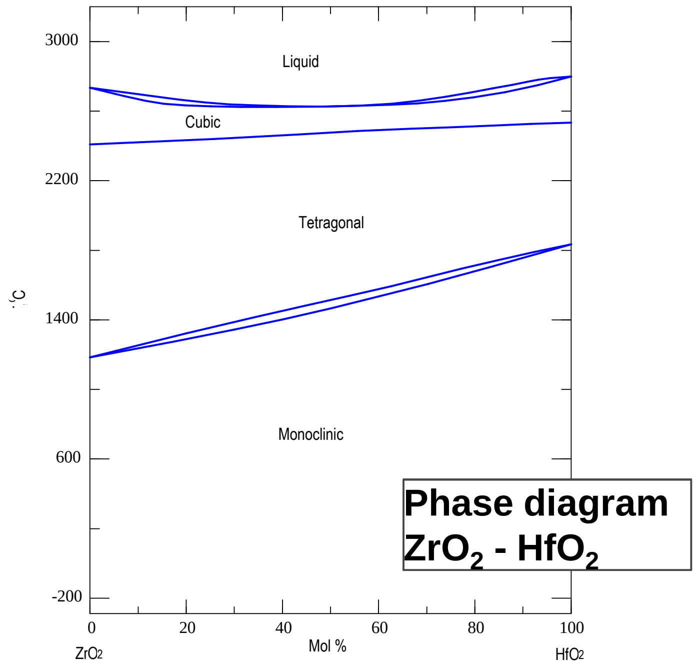
Umicore Thin Film Products,
Consumables for PVD applications, Evaporation materials, Oxides

→ search materal w/ highest opt. bandgap E_0 w/ still reasonable refractive index n for intended interference coating stack

Impact of coating material & coating process

- Mixtures w/ better compromise between opt. bandgap and refractive index





→ thermodynamical limitations as evaporation material

→ full miscibility (example right) only for a few mixtures, miscibility gap and potentially different vapour pressures for same T lead to composite layers and uncontrollable inhomogeneity

→ full miscible Hf-Zr-oxide → additionally better homogeneity than HfO_2

Impact of coating material & coating process

- Mixtures w/ better compromise between opt. bandgap and refractive index

→ co-evaporation from pure components difficult to control and not feasible in most production coater configurations

  - Hf-Al-oxide from HfO_2 and Al_2O_3 in TAILOR project by Fraunhofer IOF Jena

→ sputtering from mixed targets possible

  - Hf-Si-oxide by Laserzentrum Hannover
  - Hf-Al-oxide

Impact of coating material & coating process

- LIDT ~ Opt. bandgap: larger for amorphous vs. crystalline state
- Scatter losses: smaller for amorphous vs. nano / micro-crystalline state

→ combination of starting material & deposition process needs to lead to amorphous, low absorbing, dense films

- for Magnetron Sputtering (MS) of suboxide target for deposition of fully oxidized layer:
  by optimal choice of O_2 reactive gas pressure, substrate temperature and deposition rate

- for Ion Beam sputtering (IBS) of HfO_2:
  use optimal composition of the starting material: Hf metal

- for Plasma/ion assisted evaporation of oxides
  balancing effect from substrate temperature and plasma / ion assistance

- for Conventional evaporation process → ....

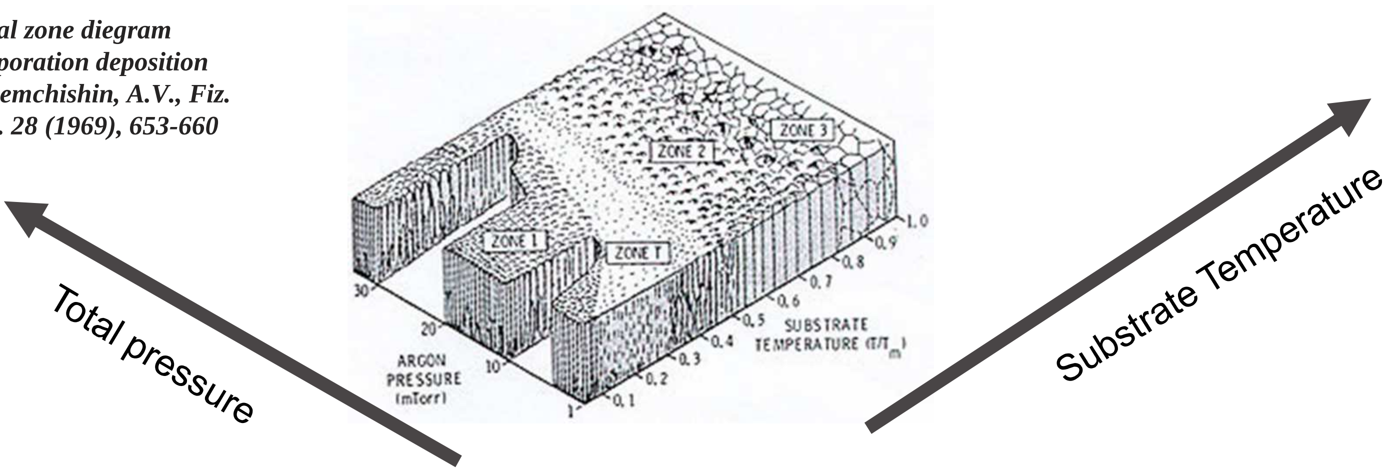
Impact of coating material & coating process

- ... cont'd: prevention of crystallization

Conventional evaporation of many dielectrics (oxides, fluorides):

- general: stay below critical substrate temperature → avoid zone 3 → prevent recrystallization
- oxides:
  - → selection of optimal starting material composition + reactive pressure + temperature
  - → balancing coating material oxygen content and reactive pressure (increased reactive pressure suppresses recrystallization)

Thin film structural zone diegram for unassisted evaporation deposition Movchan, B.A.; Demchishin, A.V., Fiz. Metal. Metalloved. 28 (1969), 653-660



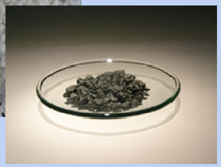
Impact of coating material & coating process

- Overview material & process selection options: example HfO_2 film

Evaporation

E-beam

HfO_2, HfO_{2-x} sintered Granules, tablets, discs


HfO_{2-x} molten Slug, premelt


Hf metal Granules Shavings

Hf metal Discs Pieces

Sputtering

Magnetron

DC,MF — Hf metal Targets

MF — HfO_{2-x} sintered Targets

RF — HfO_2 sintered Targets

IBS

Hf metal Targets

HfO_2 sintered Targets

Impact of coating material & coating process

- Overview material & process selection options: example HfO_2 film

Evaporation: Conventional & IAD

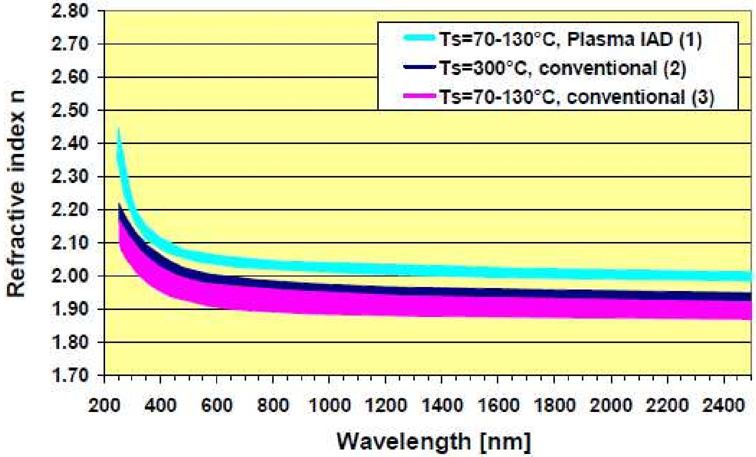


Figure 1: Ranges of the refractive index as a function of wavelength obtained for conventional deposition and for plasma-ion-assisted deposition (plasma IAD).

Evaporation conditions

Region (1)	SyrusPro with HPE6 e-gun, Mo-liner, Advanced Plasma Source (APS), O_2 flow 30 sccm, Ar auxiliary gas inlet, BIAS voltage 120 V, deposition rate 0.5 nm/s.
Regions (2) and (3)	BAK640 coater with ESQ110 e-gun, Mo-liner, O_2 pressure $0.8–8.0 \times 10^{-4}$ mbar, deposition rate 0.2–0.5 nm/s.

Table 2: Technical data of starting material

Chemical formula	HfO_{2-x} with small amounts of ZrO_{2-x}
Color	Black metallic, grey, or white (depending on oxygen deficiency)
Density	9.7 g/cm^3
Melting point	2812 °C
Delivery form	Granulate, tablets

Recommended Process Parameters

Table 3: Conventional deposition

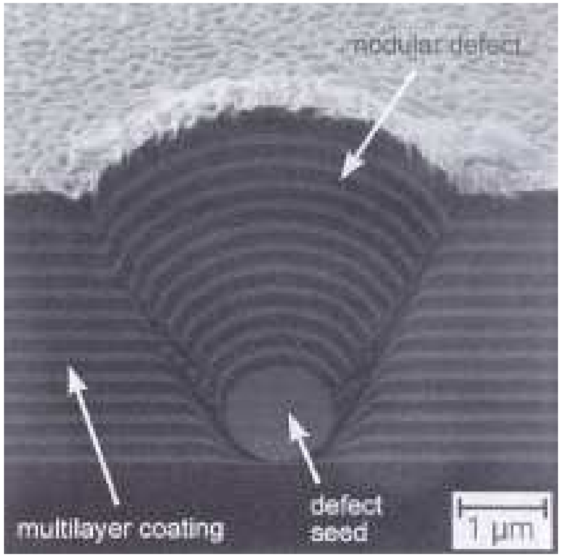
Method	E-beam evaporation
Crucible	Mo-liner, preferably rotating
Substrate temperature	Preferably high (≥ 300 °C)
Rate	0.2–0.5 nm/s
O_2 pressure	$0.8–6.0 \times 10^{-4}$ mbar, to be adjusted depending on the deposition rate

Table 4: Plasma ion assisted deposition (plasma IAD) in a Leybold Optics SyrusPro or 1104 coater with APS source

Method	E-beam evaporation with plasma IAD using APS
Crucible	Cu-crucible/Mo-liner, preferably permanently rotating
Substrate temperature	No substrate heating required
Rate	≤ 0.5 nm/s (limited by allowed O_2 flow)
O_2 flow	< 30 sccm, to be adjusted depending on the deposition rate
Auxiliary Ar flows	
Ar 1	typically 3–5 sccm
Ar 2	typically 8–12 sccm
Control	BIAS, via coil current
BIAS	120 V, for very low light scattering up to 160 V

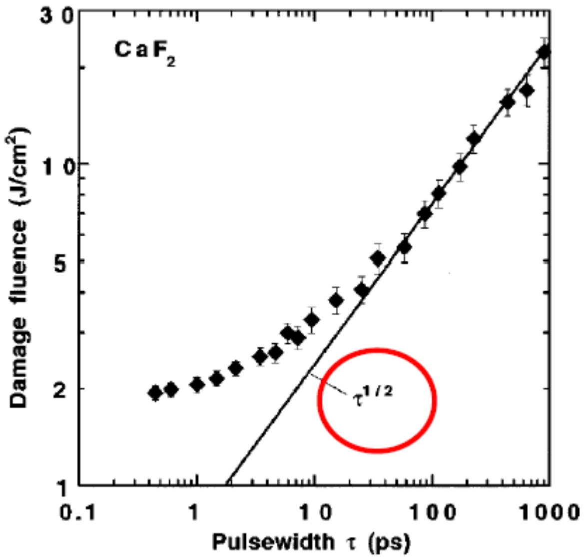
Impact of coating material & coating process

- LIDT dependence on defects & other irregularities



Primary defect («seed») impacting layer stack growth TiO_2/ SiO_2
→ nodules

Tench et al. SPIE 2114, 1993



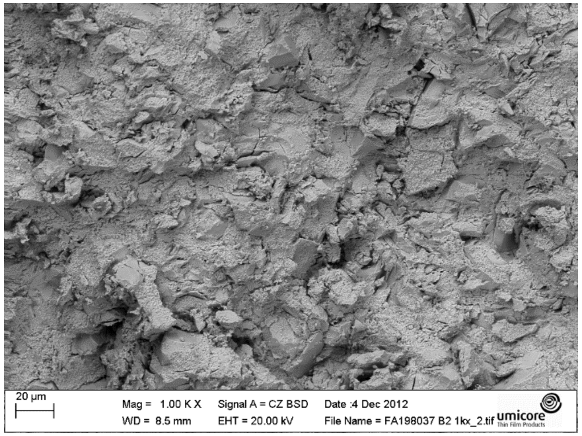
Primary defect («seed») impacting layer stack growth → nodules

Stuart et al. Phys. Rev. B, 2224, 1996

Impact of coating material & coating process

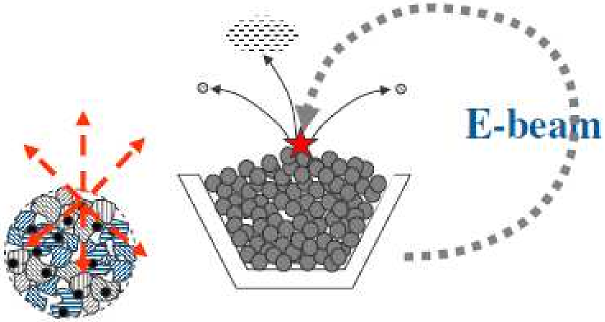
- Prevention of defects and other irregularities: Evaporation

Suboptimal microstructure



Microscopic view of suboptimal HfO_2 tablet / granulate microstructure

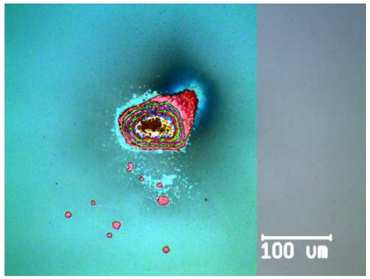
Impact on EB evaporation process

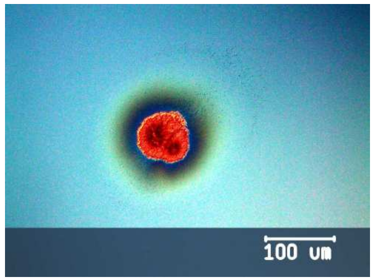


Microstructure

Deposition behaviour: spitting & outgassing

Laser damage





Laser damage for HfO_2 single layer at implanted defects
1064nm, 8ns, 10 Hz, S-on-1, beam spot ~ 250 µm

Impact of coating material & coating process

- Prevention of defects and other irregularities: Evaporation

Adjustment of microstructure during production of sintered evaporation material

Process Steps
Controlled quality parameters

Raw powder
- Purity, PSD, BET, crystallinity, morphology, ...

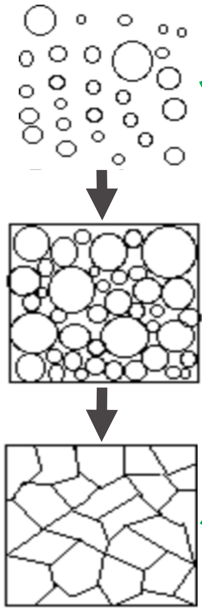
Powder pretreatment
- Flowability, ...

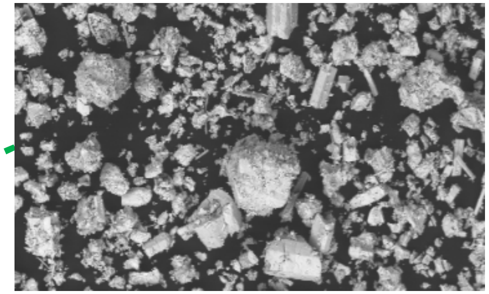
↓

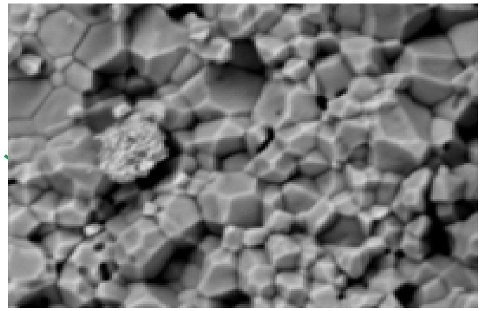
Pressing
- Green geometry, green density, ...

↓

Sintering
- Density, crystallinity, integrity, ...



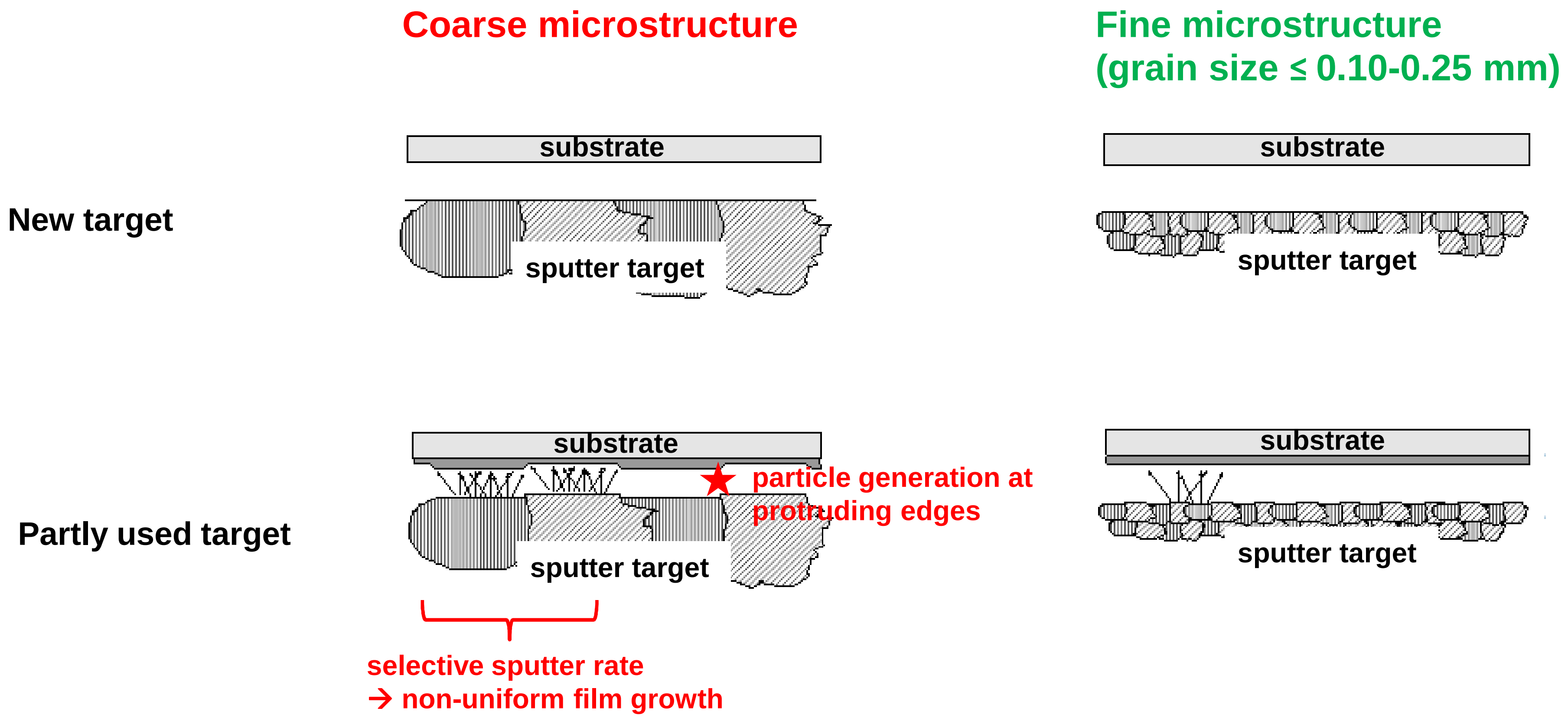




Optimal microstructure
→ suppressed cracking
→ strongly reduced spitting
→ absent outgassing

Impact of coating material & coating process

- Prevention of defects and other irregularities: Sputtering



Impact of coating material & coating process

- Prevention of defects and other irregularities: Sputtering

Adjustment of microstructure during production of metal sputter targets

Selection of right purity raw material

↓

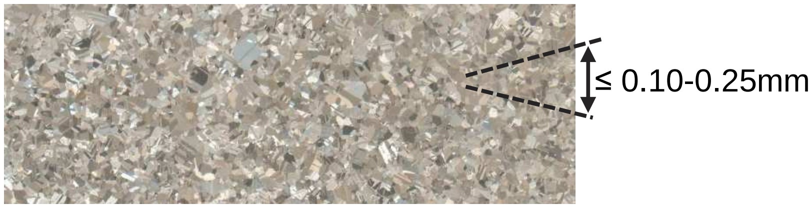
Vacuum induction, e-beam or zone melting

↓

Transformation by rolling, forging

↓

Heat treatment



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Typical & tailored laser coating materials

Typical & tailored laser coating materials

- Overview of typical thin film coating materials for laser coatings, applicable by PVD

	Spectral range						
	EUV	**DUV**	**NUV**	**VIS**	**NIR**	**MWIR**	**LWIR**
Typical PVD coating technology	MS	EVAP	EVAP,MS,IBS	EVAP,MS,IBS	EVAP,MS,IBS	EVAP,(MS)	EVAP
Typical PVD film materials							
Metals, Elemental	Ru, Si	Al, Mg	Au,Ag,Al	Au,Ag,Al	Au,Ag,Al	Au,Ag,Al	Au,Ag,Al
Oxides		SiO_2, Al_2O_3	SiO_2, Al_2O_3, HfO_2, ZrO_2, Ta_2O_5, TiO_2	SiO_2, Al_2O_3, HfO_2, ZrO_2, Ta_2O_5, TiO_2	SiO_2, Al_2O_3, HfO_2, ZrO_2, Ta_2O_5, TiO_2	Y_2O_3, MgO, Sc_2O_3, (SiO_2, Al_2O_3, HfO_2, Ta_2O_5, TiO_2)	Y_2O_3, MgO, Sc_2O_3
Fluorides		LaF_3,MgF_2, GdF_3,NdF_3	YF_3,MgF_2	YF_3,MgF_2	YF_3,MgF_2	ThF_3, DyF_3, YbF_3, YF_3, Mixtures	ThF_3, DyF_3, YbF_3, YF_3, Mixtures
Chalcogenides				(ZnS, ZnSe)	(ZnS, ZnSe)	ZnS, ZnSe	ZnS, ZnSe
Other	$MoSi_2$, BN						

Typical & tailored laser coating materials

- Requirements for tailored laser coating materials formulations

  - **Lowest possible UV absorption edge (material selection & purity)**
  - **Capable of low-defect deposition (no spitting, no arcing, no nodal growth) and reduced outgassing**
  - **Pure or mixed w/o miscibility gap (evaporation w/o composite films)**
  - **Congruent or controlled incongruent evaporation**
  - **Intrinsic low film stress (mixtures, oxidation state)**
  - **Suppressed recrystallization for growing film**
  - **Capable of microscopically uniform deposition / low roughness**

Typical & tailored laser coating materials

- Tailored laser coating materials formulations Umicore

Evaporation materials:

- NUV – VIS – NIR: Lasergrade oxides: HfO_2, Sc_2O_3, Ta_2O_5, Al_2O_3, SiO_2, ...
  Hf-Zr-ox, HfO_2:Al, Ta-Al-ox
  Lasergrade metals: Hf, Al, Si, ...
- LWIR: High-pure fluorides: DyF_3, YbF_3, YF_3, IRF-625, IRF-900, ...
- General: High-pure metals: Au, Rh, AgCu, Al, ...

Sputtering materials:

- NUV – VIS – NIR: Lasergrade metals: Hf, Al, Si, ...
- General: High-pure metals: Au, Rh, AgCu, Al, Ta, Nb, ...

Thank you for your attention !

For further questions & interest please visit our booth or contact us:

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