

## Functional Coatings Prepared by Magnetron Sputtering for Innovative Applications

A. Fernández Instituto de Ciencia de Materiales de Sevilla, CSIC-Univ. Sevilla



asuncion@icmse.csic.es www.al-nanofunc.eu





FP7-REGPOT- 285895



- 1.- Plasma spraying
- 2.-Electrolytic and chemical deposition; 3.-Phosphating
- 4.- Nitriding; 5.- Boronising
- 6.- CVD; 7.- PVD, PACVD
- 8.- P3e M

PVD = Physical Vapour Deposition. Magnetron Sputtering.

PACVD = Plasma Assisted Chemical Vapour Deposition

P3e<sup>TM</sup> = Based on arc evaporation using pulse technology (Balzers)

## Broad fields of applications – Broad fields of expertise

Coatings for mechanical parts applications: Hard & Superhard, tribological and wear resistant. Protective coatings (corrosion)



Generic Concept for the Design of Superhald Remotionposites
energy and the strong thermodynamically driven, spinodal segregation
All phases strong materials, Si is not in the metallic phase.







Interference colour

Cermet-based selective surfaces





Porous a-Silicon

Optical coatings: Decorative, refraction index and reflectivity control. Cermet-based selective surfaces

Functional: Electrical and optical

Thin film

**Photovoltaic** 



vertically aligned Zn Nanowires. Transparent & conductive coatings



Biocompatible & Biofunctional coatings







TiO2 based self-cleaning coating



TiN, DLC, multi-component TiC, (Ti,Ta)C-based coatings

## Coatings for mechanical parts applications: Hard & Superhard, tribological and wear resistant. Protective coatings (corrosion)

#### Nanocomposite Structure; (nc-Ti <sub>1-x</sub>Al <sub>x</sub>N)/(a-Si <sub>3</sub>N <sub>4</sub>)



Generic Concept for the Design of Supernard Nanocomposites
Binary (ternary....) system with a strong thermodynamically driven, spinodal segregation
All phases strong materials, Si is not in the metallic phase.

Nanocomposites nc-TiN/a-Si3N4



Nanocrystalline materials. Bulk materials obtained for example by consolidation of nanometric powders or by ball milling. They contain nanocrystalline grains and a big amount of grain boundaries.





Hardness measurements for nanocrystalline copper as a function of grain size (6-50 nm). Comparison to a conventional Cu sample (50 µm grain sice).

Increase of hardness by reduction of grain size.



Hardness ( $\sigma$ ) increases as grain size (d) decreases. Dislocations are not propagated at grain boundaries. Deformation (i.e. indentation) produces dislocations that are stopped at the grain boundaries. The decrease in grain size produces an increase in the number of grain boundaries.

## **Reverse Hall-Petch effect.**

The grain boundaries sliding produces propagation of dislocations J. Schiotx, F.D. Di Tolla, K.W. Jacobsen, Nature, 391 (1998) 561

## BUT: If $d\downarrow\downarrow\Rightarrow\downarrow s_c$

Sliding of grain boundaries appears

## "Nanocomposite" hard coatings



**Amorphous matrix** (ceramic, carbon, metal)



Nanocrystals (hard phase) (nitrides, carbides, borides)



The amorphous phase avoid the grain boundaries sliding and hardness increases overcoming the reverse Hall-Pecht effect. S. Vepřek, J. Vac. Sci. Technol. A 17 (1999) 2041 P. Nesládek & S. Vepřek, Phys. Stat. Sol. 177 (2000) 53

## i.e. System: nc-TiN/a-Si<sub>3</sub>N<sub>4</sub>

S. Vepřek, J. Vac. Sci. Technol. A 17 (1999) 2041 P. Nesládek & S. Vepřek, Phys. Stat. Sol. 177 (2000) 53



## Hardness 40-90 GPa

Spinoidal phase segregation two immiscible materials completely segregate with sharp interfaces.

To avoid lattice misfit one of the phases should be amorphous

Nanocrystals ( $\emptyset$  =3-10 nm) Amorphous matrix (t = 1-3 nm)

Superhard n-c:TiN/Si<sub>3</sub>N<sub>4</sub> Coatings



J. Patscheider et al. MRS Bulletin 28/3, 180 (2003), APL 96, 071908 (2010)



## Multifunctional coatings.

"Nanocomposite" material which combine hardness with corrosion resistance. High speed machining. High temperatures working operation

•Coatings with a **nanocomposite microstructure:** nc-TiAlN/a-Si<sub>3</sub>N<sub>4</sub> or nc-CrAlN/a-Si<sub>3</sub>N<sub>4</sub>





**Our approach:** Magnetron sputtering with Ti-Al and Si tarjets. N<sub>2</sub> reactive plasma.

S. Veprek: Mainly vacuum arc approach.

## The deposition chamber



DC power supply: Up-to 1000W RF power supply: Up-to 300W Sample holder: Rotable, heatable, bias option.

Ti<sub>3</sub>Al: 100-600 W DC; Si: 250 W RF Bias: 0.25W in RF Substrated temperature: 90°C and 300°C Working pressure: 1.33 Pa N<sub>2</sub> TiAlSiN(O)/600-250/b-300°C Bias and high T improve reduction of oxygen cotent and favour spinoidal segregation

## 2-10 nm crystals

## amorphous matrix 0.5-1.2 nm

{200}, {111}, {202} fcc TiN-based

2.1, 2.4, 1.5 Å

Al if incorporated is occupying Ti positions in a non-ordered way

30 GPa. Substrate T 300°C. Not a complete spinoidal phase segregation . Still too much amorphous phase



V.Godinho, T.C. Rojas, A. Fernández et al, Microscopy & Microanalysis 18, 2012, pp 568-581

TiAlSiN(O)/600-250 No bias and no high T Columnar structure and higher Oxygen content

#### Electron Microscopy. Energy Filtered TEM

White zones higher intensity of that element

Colunms are rich in: Ti, Al, N

> Interface area: Si, O

Inner core rich in Si-O surrounded by Si-O-N

V.Godinho, T.C. Rojas, A. Fernández et al, Microscopy & Microanalysis <u>18</u>, 2012, pp 568-581





N-rich:  $\beta$ -like Si<sub>2</sub>N<sub>3</sub>



○ titanium ○ silicon ● nitrogen ● oxygen



## HAADF/STEM



TiAlSiN(O)/600-250

V.Godinho, T.C. Rojas, A. Fernández et al, Microscopy & Microanalysis <u>18</u>, 2012, pp 568-581



## Multifunctional coatings.

"Nanocomposite" material in which the amorphous phase is a lubricant.

• Coatings with a **nanocomposite microstructure:** nc-TiC/a-C or nc-TiCN/a-CN<sub>x</sub> a combination of hardness and low friction.

## Nanocomposite



5 nm

D.Martínez, A.Fernández, J.C.Sánchez-López et al., J.Vac.Sci.Tech.A, <u>23</u>, 2005

# Optical coatings: Decorative, refraction index and reflectivity control. Cermet-based selective surfaces



Interference colour





Porous a-Silicon

Interference coloured. When the thickness of a coating is of the order of the wavelengths of the incident light, the coating /substrate system can have remarkable reflective properties due to light wave interference and the difference in refractive index between the layer, the air, and the substrate. This effect, known as thin-film interference, can be used either on a single coatings or also in multilayered coatings.

More general periodic structures, not limited to planar layers, are known as **photonic crystals**.

When light moves from a medium of a given refractive index  $n_1$  into a second medium with refractive index  $n_2$ , both reflection and refraction of the light may occur. **The Fresnel equations** describe what fraction of the light is reflected and what fraction is refracted (i.e., transmitted). They also describe the phase shift of the reflected light.

The light reflected from the upper and lower surfaces will interfere. The degree of constructive or destructive interference between the two light waves is dependent upon the difference in their phase. This difference is dependent upon **the thickness** of the film layer, **the refractive index** of the film, and **the angle of incidence** of the original wave on the film.

Structural colour







Magnetron sputtering provides a versatile method with a large selection of materials and excellent adhesion. Plastic covers with PVD coated with optical coating making optical, interference color effect. (CenCorp Corporation)

Optical interference filter coatings produced by **Dual Magnetron Reactive Sputtering (DMRS) technology.** 

(Omega Optical Inc.)





Intrinsically coloured. Amorphous mixed oxide M<sub>x</sub>Si<sub>y</sub>O<sub>2</sub> thin films (M: Fe, Ni, Co, Mo, W, Cu) for optical, coloring, and aesthetic applications. Specific colors can be selected by adjusting the plasma gas composition and the Si-M ratio in the magnetron target. M cations are randomly distributed within the SiO<sub>2</sub> amorphous matrix and that both the M concentration and its chemical state are the key parameters to control the final color of the films.

#### $M_xSi_yO_7$ thin films have been prepared by reactive MS using a silicon target on which a series of metal strips have been arranged axially.

Geometry: Substrates placed parallel to the magnetron. Power: 100–300 W and pulsed DC voltage of 250-500 V at a frequency of 80 kHz.

Deposition pressure:  $5.0 \times 10^{-3}$ mbar.

Process gas:  $O_2/Ar$  mixtures with mass flow ratios from 0.05 to 2.5 depending on the type of thin film.

#### **Coloured ceramic plates**



lenses

dx.doi.org/10.1021/am302778h | ACS Appl. Mater. Interfaces 2013, 5, 1967–1976 J. Gil-Rostra, J. Chaboy, F. Yubero, A. Vilajoana, and A.R. Gonzalez-Elipe

#### Light Absorbance / Reflection



**Solar absorptance**. Solar radiation-absorption (*a*). The ratio of absorbed to incident radiation in the solar spectrum region.

**Emittance**, thermal infrared radiation-emission ( $\varepsilon$ ). The energy radiated by the surface of a body per second per unit area

**Kirchhoff's law** recognized the experimental observation that a good absorber is a good emitter, and a poor absorber is a poor emitter. Naturally, a good reflector must be a poor absorber.

Black body,  $\lambda$  for which the intensity is maximal at a given T:

#### Dielectric Constant, Refractive Index. Reflectivity.

There is also a relation between optical and electrical properties in a material. For most naturally occurring materials at optical frequencies **the dielectric constant** ( $\varepsilon$ ) is approximately the square of **the refractive index** (n<sup>2</sup>).

High refractive index materials have in general high reflectivity in air.



**S**: solar constant =  $1353 \text{ W/m}^2$ 

Duffie & Beckmann, Solar Engineering of Thermal Processes, 1980

#### Selective surfaces

In solar thermal collectors, a selective surface or selective absorber is a means to increase its operation temperature and/or efficiency.

**The selectivity** is defined as the ratio of solar radiation-absorption (a) - to thermal infrared radiation-emission ( $\varepsilon$ ).

Selective surfaces take advantage of the **different wavelengths range** of incident solar radiation and the emissive radiation from the absorbing surface:

**Solar radiation** covers approximately the wavelengths 350 nm - 4.000 nm (UV-A, visible and near infrared (NIR) or IRA+IRB).

**Thermal infrared radiation**, from materials with temperatures approximately in the interval -40 - 100°C, covers approximately the wavelengths 4.000 nm-40.000 nm = 4 um-.40 um. The thermal infrared radiation interval being named or covered by: MIR, LWIR or IR-C.



Maximize solar absorptance & Minimize thermal emission http://www.physics.usyd.edu.au/app/solar/research/sputtering.html The Solar Energy Group. University of Sydney

#### Selective surfaces

Anodic Solar absorbers. Magnetron sputtering based coatings (less environmental polluting than electrochemical coatings) based on DC reactive sputtering. Graded Al-N or  $Mo-Al_2O_3$  cermet coatings based on conventional magnetron sputtering.



Fig.1. Schematic diagram of a solar selective absorber with double cermet layers, a low metal volume fraction (LMVF) cermet layer on a high metal volume fraction (HMVF) layer on a metal infrared reflector with a ceramic anti-reflection layer.

## Highly absorbing coating in the VIS (black) and transparent in the IR



# $Ti_{1-x}Al_xN(O)$ coatings with selective IR reflectivity



## PVD by reactive magnetron sputtering

Substrates:

AISI 316-R steel, ALUSI steel, Silicon (100), NaCl, Quartz and Glass





Pure Ti target, 99.995% Pure Al target 99,995% N<sub>2</sub>+Ar reactive gas

variable film composition

## TiAIN coatings thickness

Sample	Ti	AI	%N2	t (min)	Profilometry	SEM fractography	Dep. rate (SEM)
TiAIN20	200	400	30	5	45 nm	60 nm	12 nm/min
TiAIN21	400	400	30	4	35 nm	80 nm	20 nm/min
TiAIN22	400	200	30	5	50-100 nm	75 nm	15 nm/min
TiAIN23	400	400	70	4	-	45 nm	11 nm/min
TiAIN24	400	400	15	4	100-140 nm	170 nm	42 nm/min
TiAIN25	200	400	15	5	80-120 nm	150 nm	30 nm/min
TiAIN26	600	400	15	4	140 nm	260 nm	65 nm/min
TiAIN27	400	600	15	5	135-230 nm	271 nm	54 nm/min
TiAIN28	200	600	15	5	105-170 nm	180 nm	36 nm/min
TiAIN29	400	200	15	5	-	235 nm	47 nm/min
TiAIN30	600	200	15	4	-	205 nm	51 nm/min
TiAIN31	600	600	15	3,5	-	202 nm	58 nm/min
TiAIN32	200	200	15	5	-	52 nm	10 nm/min

The deposition rate increases:

➤ by increasing the power supplied

> by decreasing the N2% ratio, the thickness decrease (TiAIN21, 23 and 24)

## TiAIN coatings color



> grey-brown is the intrin<u>sical colour</u>







V.Godinho, A.Fernández, et al. Solar Energy., <u>84,</u> 2010, 1397-1401.

## **Porous silicon**

#### **Photonic devices**

**Microelectronics** 

#### Solar energy conversion

## Up to now

1 Commonly produced by electrochemical methods



Changing electrolyte concentration and current, different structures are obtained



G.Korotcenkov, B.K. Cho Silicon porosification:State of the Art Critical Reviews in Solid State Materials Sciences, 35(2010)153-260

C.S. Solanki, R.R. Bilyalov, J. Poortmans, J. Nijsw, R. Mertens Porous silicon layer transfer processes for solar cells, Solar Energy Materials & Solar Cells 83 (2004) 101–113



(a)







Epitaxial layer



(d)

## New method Control of the micostructure in the Nanoscale



500nm

150W rf

He atmosphere

OPEN ACCESS IOP PUBLISHING

Nanotechnology 24 (2013) 275604 (10pp)

A new bottom-up methodology to produce silicon layers with a closed porosity nanostructure and reduced refractive index

V Godinho<sup>1</sup>, J Caballero-Hernández<sup>1</sup>, D Jamon<sup>2,3</sup>, T C Rojas<sup>1</sup>, R Shierholz<sup>1</sup>, J García-López<sup>4</sup>, F J Ferrer<sup>4</sup> and A Fernández<sup>1</sup>



NANOTECHNOLOGY doi:10.1088/0957-4484/24/27/275604

# Porous Si coatings deposited by magnetron sputtering



material	n <sub>500nm</sub>
c-Si	3.49
a-Si	4.90
PSi	3.5-1

- Handbook of Optics, 3rd edition, Vol. 4. McGraw-Hill 2009



# **p-RBS measurements** were performed with 1.7 MeV protons and a solid state detector located at 165° scattering angle



Sample	thickness (10 <sup>15</sup> at/cm²)	Si (%at)	He (%at)	Ar (%at)
porous	11000	78.7	21.3	
dense	9500	92.0		6.0



## He insolubility in metals is well known



High power and high pressure to increase pore size

4.8Pa He



## Need of **spatially resolved** analytical tools to be abble to measure He signal inside and outside the pores

## **STEM-EELS**

EELS spectra at various (i, j) positions of the sample. STEM-EELS spectrum images were recorded in the low loss range with a pixel size of 1 nm





See more details at poster nº75

"Characterization of amorphous and porous silicon coatings by (S)TEM and EELS"

## **New bottom up method** for the production of amorphous **porous silicon** coatings with **closed porosity** by magnetron sputtering

#### 1<sup>st</sup> bottom up method with closed porosity

- Versatility of magnetron sputtering technique allows to produce coatings with **closed porosity** by depositing directly on large areas
- Depositing on different kinds of substrates like glass or even sensible and flexible substrates like polymers
- The closed porosity **avoids** the **aging drawbacks** due to exposition to air
- The **refractive index** of the coatings can be easily **changed** by controlling porosity
- Direct deposition of **multilayers** alternating **dense** and **porous** materials just by changing the deposition gas
- Deposition of intrinsic or doped silicon









## Functional: Electrical and optical



vertically aligned ZnO Nanowires. Transparent & conductive coatings



## **Transparent Conductive Electrodes**





#### Applications of transparent conductive oxides (TCOs)

#### New applications: High flexible electronics (Prototypes of flexible computers (2013))



..... requires a replacement of TCOs.  $\rightarrow$  Graphene is an excellent candidate!

Copper indium gallium selenide ( $Culn_xGa_{1-x}Se_2$  or CIGS) is a direct band-gap semiconductor useful for the manufacture of solar cells. Because the material has a high absorption coefficient and strongly absorbs sunlight, a much thinner film is required than of other semiconductor materials. Devices made with CIGS belong to the **thin-film** category of photovoltaic's (PV).

CIGS films can be manufactured by different methods:

The most common vacuum-based process is to **co-evaporate or cosputter copper, gallium, and indium** 

onto a substrate at room temperature, then anneal the resulting film with a selenide vapor to form the final CIGS structure. An alternative process is to co-evaporate copper, gallium, indium and selenium onto a heated substrate.



## Catalytic coatings, self-cleaning

# Co catalysts for H<sub>2</sub> generation



TiO2 based selfcleaning coating

## **Photoatalytic thin Films**



Heterogeneous photocatalysis Oxidative reactions due to photocatalytic effect:  $UV + MO \rightarrow MO (h + e^{-})$ Here MO stands for metal oxide --- $h^{+} + H_2O \rightarrow H^{+} + \bullet OH$  $2 h^{+} + 2 H_2O \rightarrow 2 H^{+} + H_2O_2$  $H_2O_2 \rightarrow HO^{\bullet} + \bullet OH$ The reductive reaction due to photocatalytic effect:  $e^{-} + O_2 \rightarrow \bullet O_2^{-}$  $\bullet O_2^{-} + HO^{\bullet}2 + H^{+} \rightarrow H_2O_2 + O_2$  $HOOH \rightarrow HO^{\bullet} + \bullet OH$ 

## How self-cleaning glass works

# Innovative photo-catalytic and hydrophilic coatings based on TiO<sub>2</sub> work in two stages

The unique dual-action self-cleaning coating is located on the external glass panel.

It has got photo-catalytic and hydrophilic properties, and works in two stages:

 (Stage 1)The coating reacts with natural daylight to break down and loosen organic dirt

• (Stage 2) When it rains, instead of forming droplets, the water spreads evenly over the surface of the glass, forming a thin film and helping to wash away any dirt and reduce streaks.



During long dry spells the glass can be cleaned by simply hosing it down with clean water.

 $TiO_2$  can be deposited by reactive magnetron sputtering from Ti target. But also from dip-coatings methodologies from the hydrolysis of Ti-isopropoxide precursors.

## Hydrogen storage by NaBH<sub>4</sub>

 $NaBH_4 + 2 H_2O \longrightarrow 4 H_2 + NaBO_2, \quad \Delta H < 0$ Catalyst

It is a safe hydrolysis reaction for hydrogen production in portable applications. The process is controled by a catalysts.

Development of **catalytic membranes** depositing Co-based catalysts by magnetron sputtering





### "Magnetron Sputtering" operated at high pressure

The process leads to more granulated or even powdered like materials. Magnetron coupled to a screaper device. Powder is collected below and compacted. Gas phase condensation. Formation of particles in the plasma gas phase by nucleation and growth

![](_page_46_Figure_2.jpeg)

![](_page_46_Picture_3.jpeg)

### "Cluster source" A sputtering source for "evaporating" the material from the target

![](_page_47_Figure_1.jpeg)

"Terminated cluster growth" is a physical vapor deposition technique that allows fabrication of metallic and conducting oxide nanoparticles with a very narrow size distribution. This type of source operates on the principle of quenching a hot metal vapor in a flowing stream of cool inert gas. The supersaturated vapor cools down due to frequent collisions with inert gas atoms, which leads to condensation and formation of clusters and nanoparticles.

![](_page_48_Picture_0.jpeg)