Functionalization of Sculptured Thin Films with Atomic Layer Deposition

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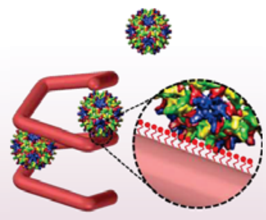
Our Message

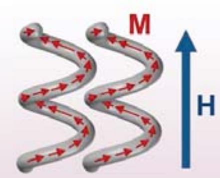
- Glancing angle deposition is utilized to grow metallic sculptured thin films (STFs). Subsequently, a thin conformal Al_2O_3 passivation layer is coated by means of atomic layer deposition (ALD).
- An anisotropic Bruggeman EMA approach is employed to analyze Mueller matrix ellipsometry spectra and to determine monoclinic optical and structural properties as well as fractions of film constituents.
- Core optical constants change upon deposition of a passivation layer, possibly due to the large surface area to volume ratio (SA:V = 190)!
- Al_2O_3 passivated STFs do not show aging effects!
- ALD is an excellent technique to functionalize STFs and modify their physical properties!

Motivation

Selective capsid capturing in hollow-core nanohelices with matched dimensions



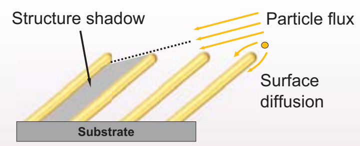
Viral attachment on bio-functionalized (self-assembled monolayers) nanoscaffold surfaces



Chiral magnetic domain alignment in ferromagnetic core-shell helices. Preserve as-deposited physical properties over time.

Experimental Techniques

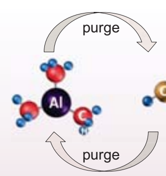
Glancing Angle Deposition



A collimated particle flux, generated by electron beam evaporation impinges at a glancing angle onto the substrate and results in self-organized, randomly distributed but highly coherent slanted nanocolumns (F1-STFs).

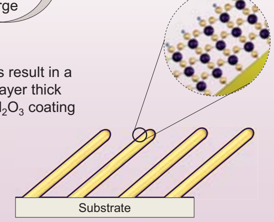
100 nm Co can still be transparent!

Atomic Layer Deposition

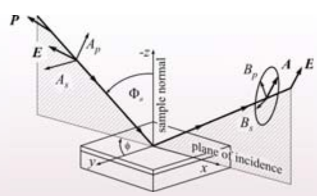


Subsequent cycling of Trimethylaluminum (TMA) and H_2O

Three cycles result in a three monolayer thick conformal Al_2O_3 coating



Mueller Matrix Ellipsometry



Ellipsometry measures the polarization state change of an electromagnetic wave upon reflection off a sample surface.

If the sample is anisotropic, spectroscopic Mueller matrix ellipsometry allows for determination of complete sets of optical constants.

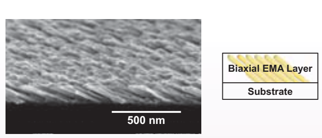
The 4×4 real-valued Mueller matrix connects the incident and emergent Stokes vector components

$$\begin{bmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \end{bmatrix}_{out} = \begin{pmatrix} M_{11} & M_{12} & M_{13} & M_{14} \\ M_{21} & M_{22} & M_{23} & M_{24} \\ M_{31} & M_{32} & M_{33} & M_{34} \\ M_{41} & M_{42} & M_{43} & M_{44} \end{pmatrix} \begin{bmatrix} I_P + I_S \\ I_P - I_S \\ I_{45} - I_{-45} \\ I_{RC} - I_{LC} \end{bmatrix}_{in}$$

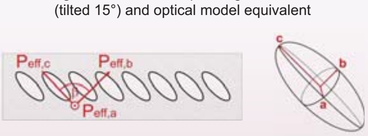
D. Schmidt *et al.* Appl. Phys. Lett. **94**, 011914 (2009).

Results

Optical Model



Scanning electron microscope image of a Co F1-STF (tilted 15°) and optical model equivalent

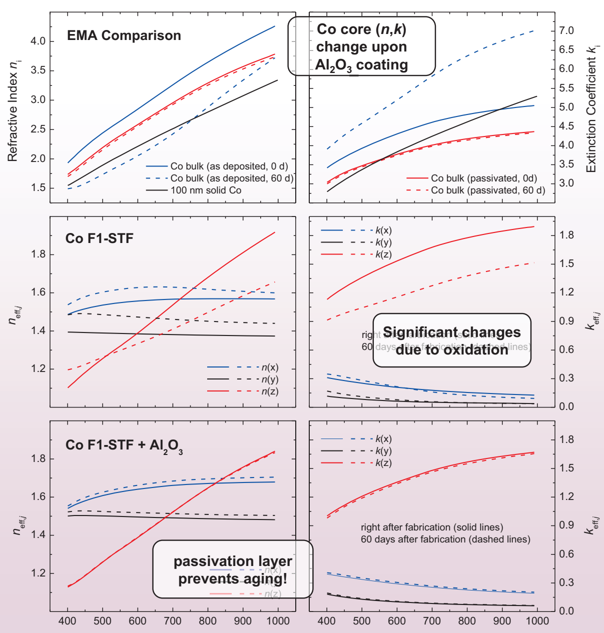


Spatially aligned, anisotropic inclusions with three major effective polarizabilities $P_{eff,j}$ along principal axes j = **a**,**b**,**c** (based on Bruggeman)

$$\sum_{n=1}^{m} f \frac{\varepsilon_n - \varepsilon_{\mathrm{eff},j}}{\varepsilon_{\mathrm{eff},j} + L_j(\varepsilon_n - \varepsilon_{\mathrm{eff},j})} = 0$$

This model accounts for m different constituents with bulk-like optical constants ε_n. Depolarization factors L_j represent the biaxial film geometry. A projection matrix is applied to transform the virtual orthogonal basis into a monoclinic system.

D. Schmidt *et al.* Appl. Phys. Lett. (in submission, 2011).



Best-Match Model Parameters

Parameter	Co F1 (0 d)	Co F1 (after 60 d)	Co F1+Al_2O_3 (0 d)	Co F1+Al_2O_3 (after 60 d)
t (nm)	84.80(3)	84.88(4)	89.46(3)	89.86(3)
Θ (°)	62.52(1)	61.85(1)	62.69(1)	62.80(1)
β (°)	80.91(3)	84.21(2)	82.96(2)	83.39(2)
f_{void} (%)	75.99(1)	77.44(1)	62.03(1)	59.33(6)
f_{Al2O3} (%)	---	---	13.98(8)*	16.74(6)*
L^D_a	0.3983(1)	0.3817(1)	0.4035(2)	0.4030(2)
L^D_b	0.5134(1)	0.4469(1)	0.5267(2)	0.5283(2)
L^D_c	0.0884(3)	0.1714(4)	0.0698(7)	0.0688(6)
MSE	12.45	13.42	8.45	10.82

*marginal changes are attributed to humidity changes
→ very sensitive optical humidity sensor

SEM Estimates

r_{avg} = 11 nm (Co F1)
$n_C \approx$ 360 columns/μm²

Ellipsometry Results

n_C = 302 columns/μm²
surface area SA = 4.9 μm²
surface area to volume ratio SA:V = 190

Al_2O_3 thickness t_{AlO} = 2.80 nm

Al_2O_3 ALD with identical parameters on 100 nm solid Co reference sample results in a layer thickness t_{AlO} = 3.29 nm

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