Optical Modeling of Nanohybrid Functional Columnar Thin Films

Center for Nanohybrid Functional Materials

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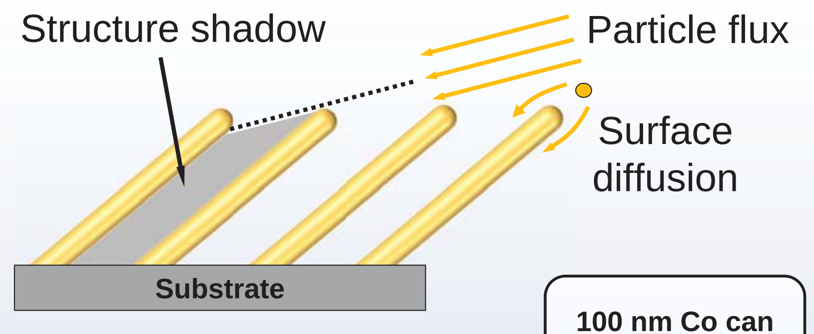
Our Message

- **Glancing angle deposition is utilized to grow metal columnar thin films. Subsequently, a functional conformal metal or dielectric is coated by means of atomic layer deposition (ALD).**
- **Anisotropic Bruggeman EMA (TAB and RAB) approaches are employed to analyze Mueller matrix ellipsometry spectra and to determine biaxial optical and structural properties as well as fractions of all film constituents.**
- **The validity of the AB-EMA models is tested by comparison with an assumption-free homogeneous biaxial layer approach and SEM estimates.**
- **Thin films comprising heterogeneous metal-metal and metal-dielectric nanocolumns require different model approaches.**

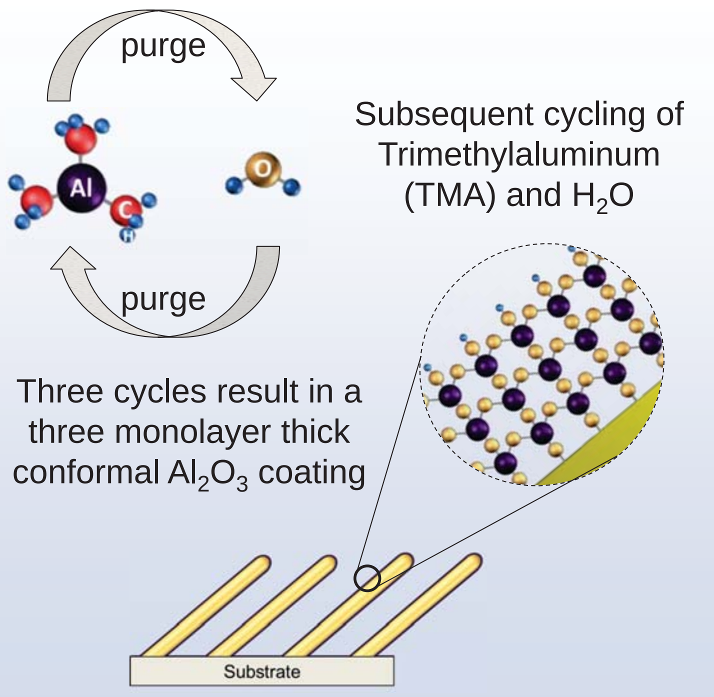
Nanostructure Fabrication

Glancing Angle Deposition



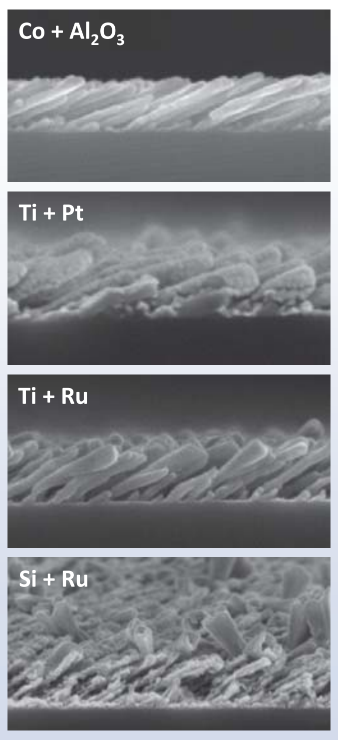
A collimated particle flux, generated by electron beam evaporation impinges at a glancing angle onto the substrate and results in self-organized, randomly distributed but highly coherent slanted nanocolumns (F1-STFs).

Atomic Layer Deposition



Subsequent cycling of Trimethylaluminum (TMA) and H_2O

Three cycles result in a three monolayer thick conformal Al_2O_3 coating



Ellipsometry Models for Nanohybrid Functional Columnar Thin Films

Homogeneous Biaxial Layer

F1-STFs can be described as single homogeneous biaxial layers with thickness *d* and complex functions $\varepsilon_{\text{eff},j}$ are individually determined

other model parameters are

- Euler angles φ, θ of rotation matrix **A**
- internal angle β of projection matrix **U**

Dielectric Tensor

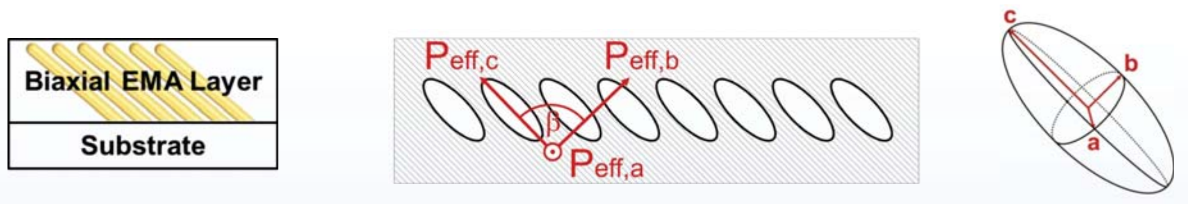
$$\varepsilon = \mathbf{AU}\begin{pmatrix} \varepsilon_{\text{eff},a} & 0 & 0 \\ 0 & \varepsilon_{\text{eff},b} & 0 \\ 0 & 0 & \varepsilon_{\text{eff},c} \end{pmatrix}\mathbf{U}^{\mathrm{T}}\mathbf{A}^{-1}$$

A: rotation matrix (Euler angle rotation)
U: projection matrix (if triclinic or monoclinic)

assumption-free model approach

D. Schmidt *et al.* Opt. Lett. **34**, 992 (2009); Appl. Phys. Lett. **94**, 011914 (2009).

Traditional Anisotropic Bruggeman EMA (TAB-EMA)

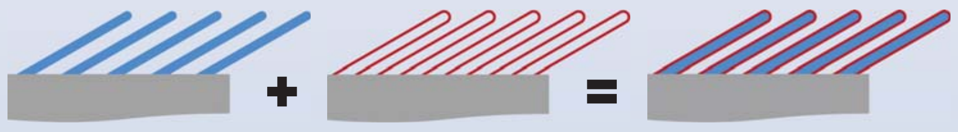


Slanted columns are represented by spatially aligned, anisotropic inclusions with three major effective polarizabilities $\mathbf{P}_{\text{eff},j}$ along principal axes j = **a**,**b**,**c**

The model accounts for *m* different constituents ε_n and volume fractions *f*. Real-valued depolarization factors L_j render the biaxial film geometry (electrostatic approach). $\sum f_n = 1; \sum L_j = 1$

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

$$L_j = \frac{U_x U_y U_z}{2}\int_0^\infty \frac{(s+U_j^2)^{-1}}{[(s+U_x^2)(s+U_y^2)(s+U_z^2)]^{1/2}}\mathrm{d}s$$



Schematic of a coated columnar thin film with *m*=3 constituents: solid columns and hollow coating in host medium air

D. Schmidt *et al.* Appl. Phys. Lett. **100**, 011912 (2012).

Rigorous AB-EMA

$$\sum_{n=1}^{m} f_n \frac{\varepsilon_n - \varepsilon_{\text{eff},j}}{1 + D_j(\varepsilon_n - \varepsilon_{\text{eff},j})} = 0$$

$$D_j = \frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi} \frac{\Gamma_j}{\rho}\, d\theta\, d\phi$$

$$\rho = \frac{\sin^2\theta\cos^2\phi}{U_x^2\varepsilon_{\text{eff},x}^{-1}} + \frac{\sin^2\theta\sin^2\phi}{U_y^2\varepsilon_{\text{eff},y}^{-1}} + \frac{\cos^2\theta}{U_z^2\varepsilon_{\text{eff},z}^{-1}}$$

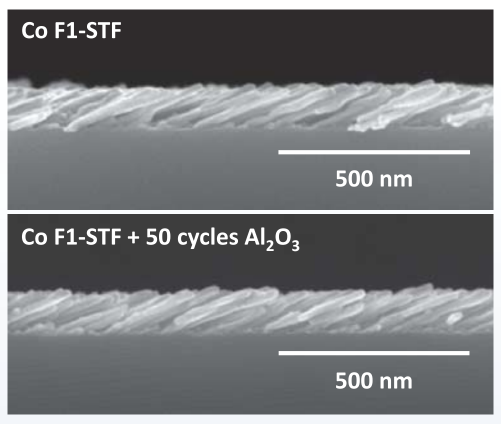
$$\Gamma_{x,y,z} = \frac{\sin^3\theta\cos^2\phi}{U_x^2}, \frac{\sin^3\theta\sin^2\phi}{U_y^2}, \frac{\sin\theta\cos^2\theta}{U_z^2}$$

A more rigorous approach considers the depolarization dyadic to be a function of the inclusions' shape U_j, *and* effective permittivity tensor (electrodynamic approach). D_j are generally complex.

Mackay and Lakhtakia, J. Nanophoton. **6**, 069501 (2012).

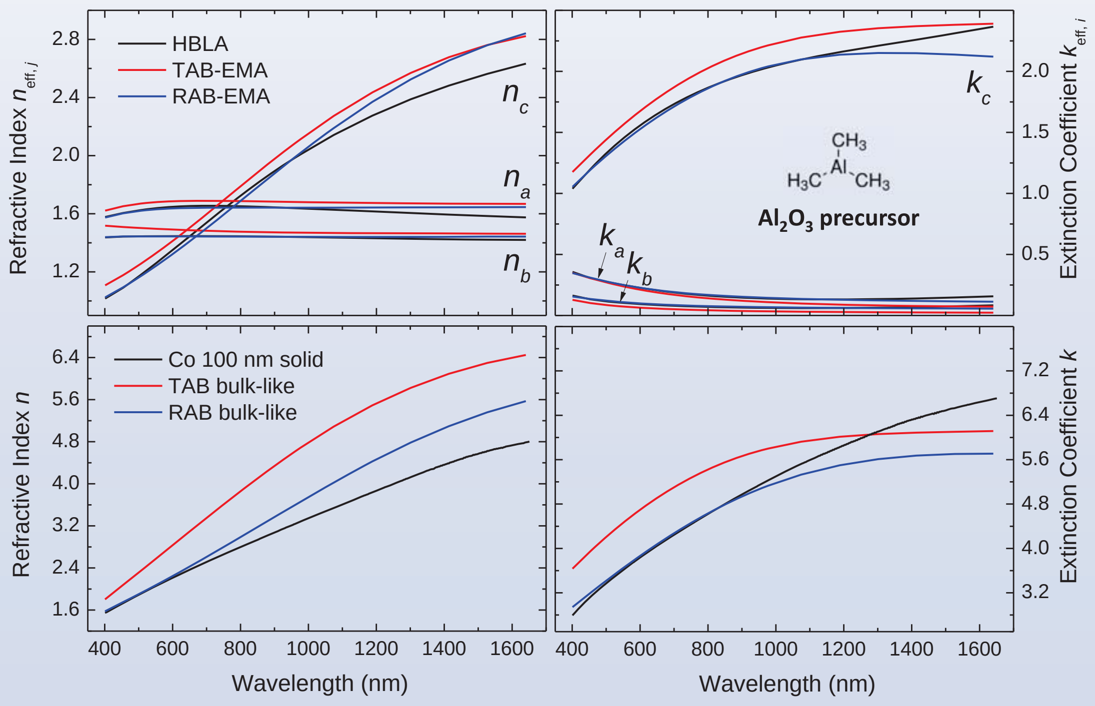
Results and Applications

Conformal Dielectric ALD Coating

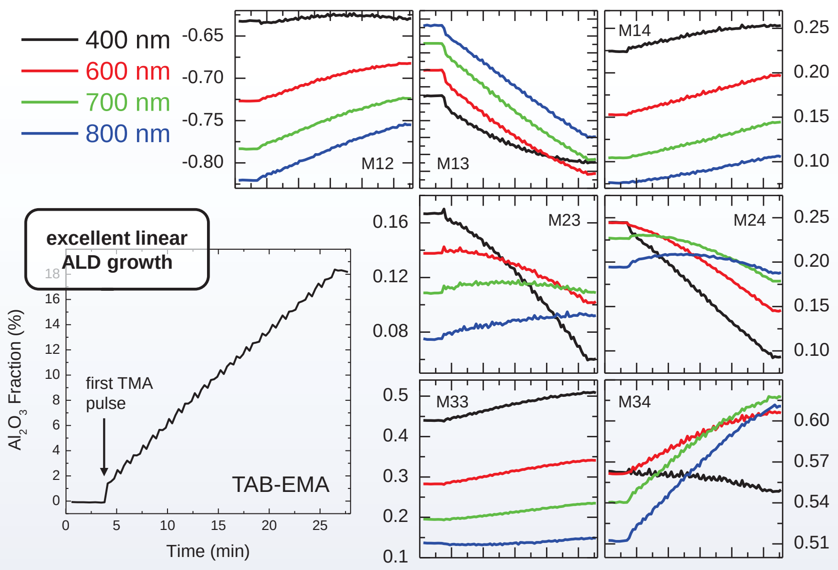


Parameter	HBLA	TAB-EMA	RAB-EMA
t (nm)	95.9(2)	92.34(7)	96.20(9)
Θ (°)	58.38(3)	57.63(3)	58.33(2)
β (°)	89.1(2)	81.40(7)	89.73(8)
f_{Co} (%)		22.9(2)	21.78(5)
f_{Al2O3} (%)		14.9(2)	19.40(7)
U_x		0.23(3)	0.118(3)
U_y		0.19(3)	0.078(2)
MSE	10.66	15.13	11.42

SEM estimates yield a conformal Al_2O_3 thickness of 2.5 nm
TAB(14.9%) = 2.74 nm; RAB(19.4%) = 3.74 nm; (flat control: 2.75 nm)



In-situ ALD Growth Monitoring



45 cycles of Al_2O_3 onto a FeNi F1-STF
(ellipsometry not synchronized with growth cycles)

Metal - Dielectric

optically modeled with a single set of depolarization factors
TAB and RAB are in fair agreement

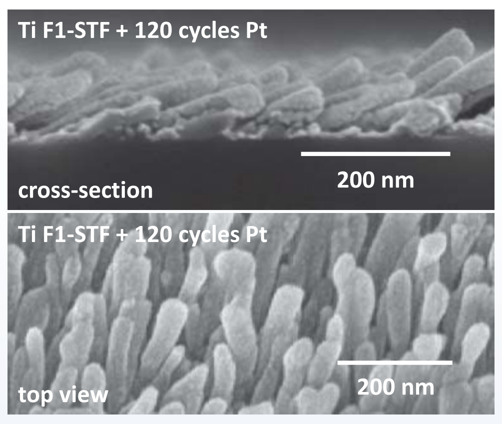
Metal - Metal

set of depolarization factors for each constituent required possibly reveals limitations of AB-EMA models

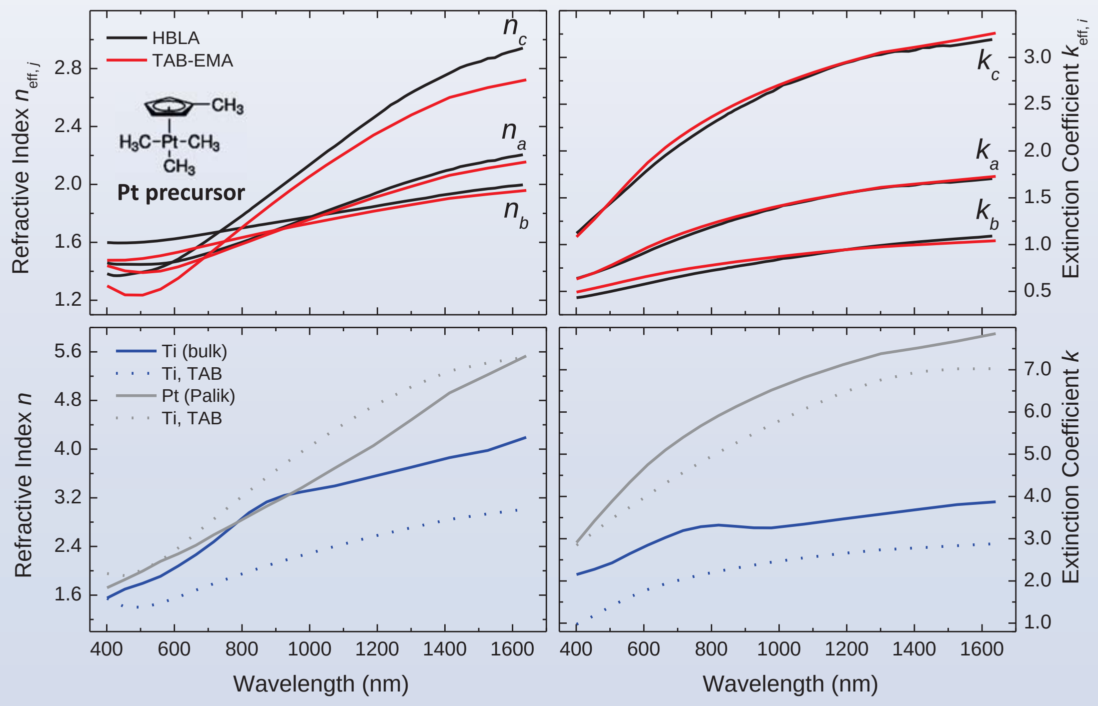
→ AB-EMA approach yields excellent fraction estimates for thin films with heterogeneous nanocolumns

Conformal Metal ALD Coating

Parameter	HBLA	TAB-EMA
t (nm)	83.5(2)	81.1(4)
Θ (°)	67.84(4)	66.0(1)
β (°)	79.18(7)	85.82(9)
f_{Ti} (%)		20(2)
f_{Pt} (%)		24.7(4)
L^D_a Ti, Pt		0.000(1), 0.472(5)
L^D_b Ti, Pt		0.000(1), 0.391(5)
L^D_c Ti, Pt		1.000(1), 0.137(5)
MSE	2.59	3.61



with film surface area estimates the TAB-EMA result of f_{Pt} = 24.7%
yields a Pt thickness of 4.9 nm (flat control: ~5.0 nm)



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