Synthesis and Characterization of Nanoporous Thin Films using Molecular Beams

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Work supported by NNI LDRD Initiative.

Nanoporous Materials are of Great Technological and Scientific Importance

Technological

- High-surface area, chemically-selective catalysts
- Novel separations materials
- Materials with tailored optical / electronic properties
- Novel hydrogen storage materials

Scientific

- Transport and reactivity in restricted geometries
- Environmental chemistry in heterogeneous systems
- Creation and characterization of novel chemically active defects

K. Robbie, M. J. Brett J. Vac. Sci. Technol. **15** (1997) 1460.
J. C. Sit, D. Vick, K. Robbie, M. J. Brett, J. Mater. Res. **14** (1999) 1197

Motivation

- Metal oxides are catalytically and environmentally important materials.
- Surface defects are predicted to strongly affect adsorption and reactivity.
- MgO is a prototypical ionic oxide with a single valence state (+2), a simple structure, and only one thermally stable unreconstructed surface (100).

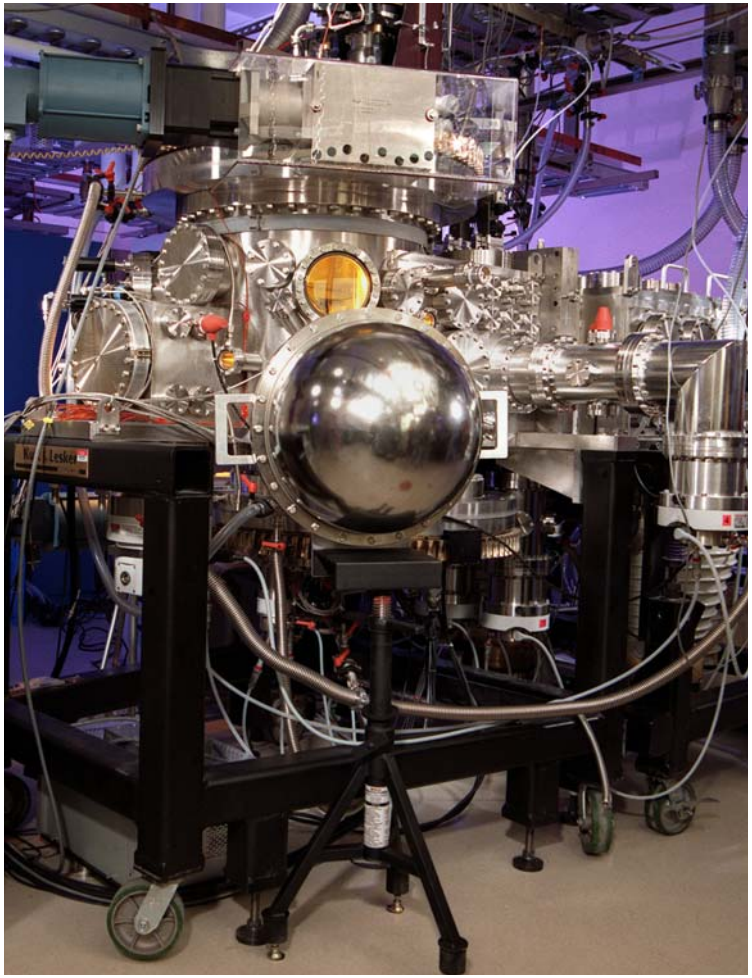
Approach

- Vary the growth conditions of thin MgO films to synthesize samples with desired surface area and defect densities.
- Use physisorption of weakly bound species to characterize the films (surface area, defect density and binding energy).

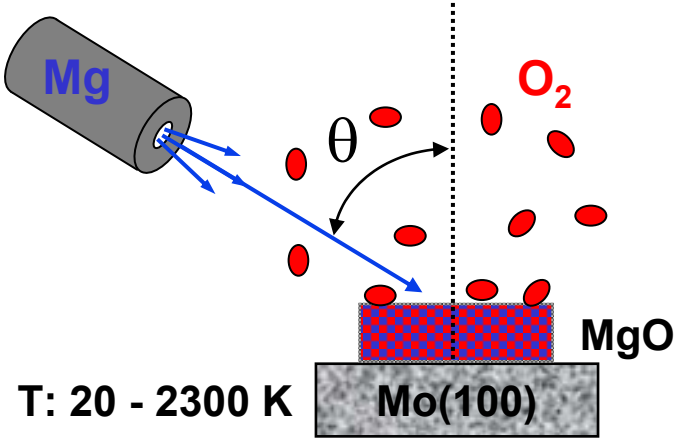
Experimental parameters: Deposition flux, incident angle and substrate temperature

Experimental Setup for MgO Growth

Molecular Beam Surface Dynamics and Kinetics Instrumentation



MgO Thin Films Growth



- The evaporated Mg is deposited on the Mo(100), Silicon, and quartz substrates, and oxidized by ambient O_2 (10^{-6} Torr).

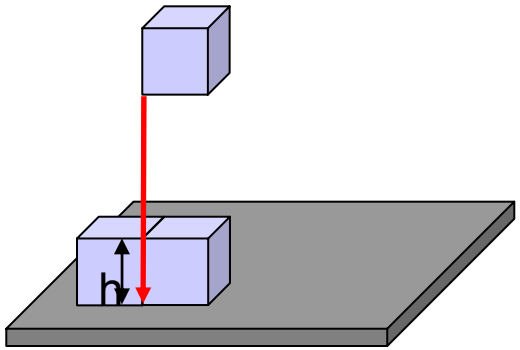
Characterization of Thin MgO Films

- Multiple molecular beams are used for film characterization.
- In situ surface analysis and processing: *TPD, LEED, AES, Ar+*
- Ex situ analysis: *SEM, HRTEM, XRD*

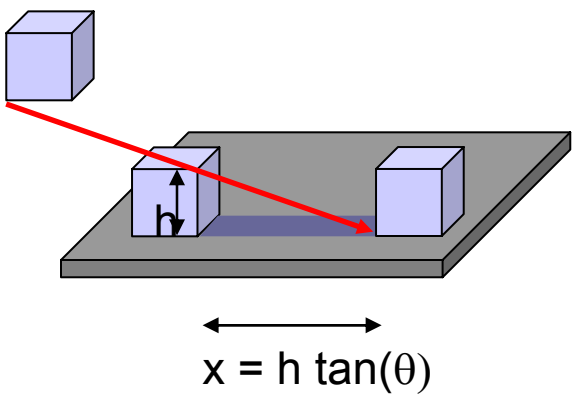
M.-C. Wu, J. S. Corneille, C. A. Estrada, J.-W. He, D. W. Goodman, Chem.Phys. Lett. **182** (1991) 472.

The Effect of Shadowing on The Growth Morphology of Thin Films

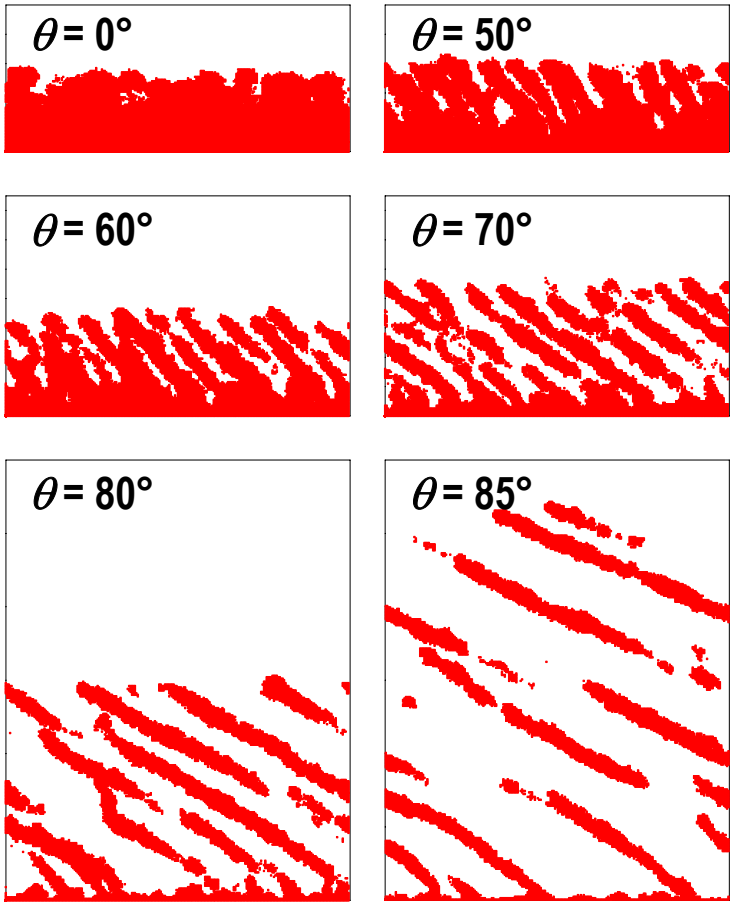
Normal Angle of Incidence



Glancing Angle of Incidence



3-D Ballistic Deposition Simulation

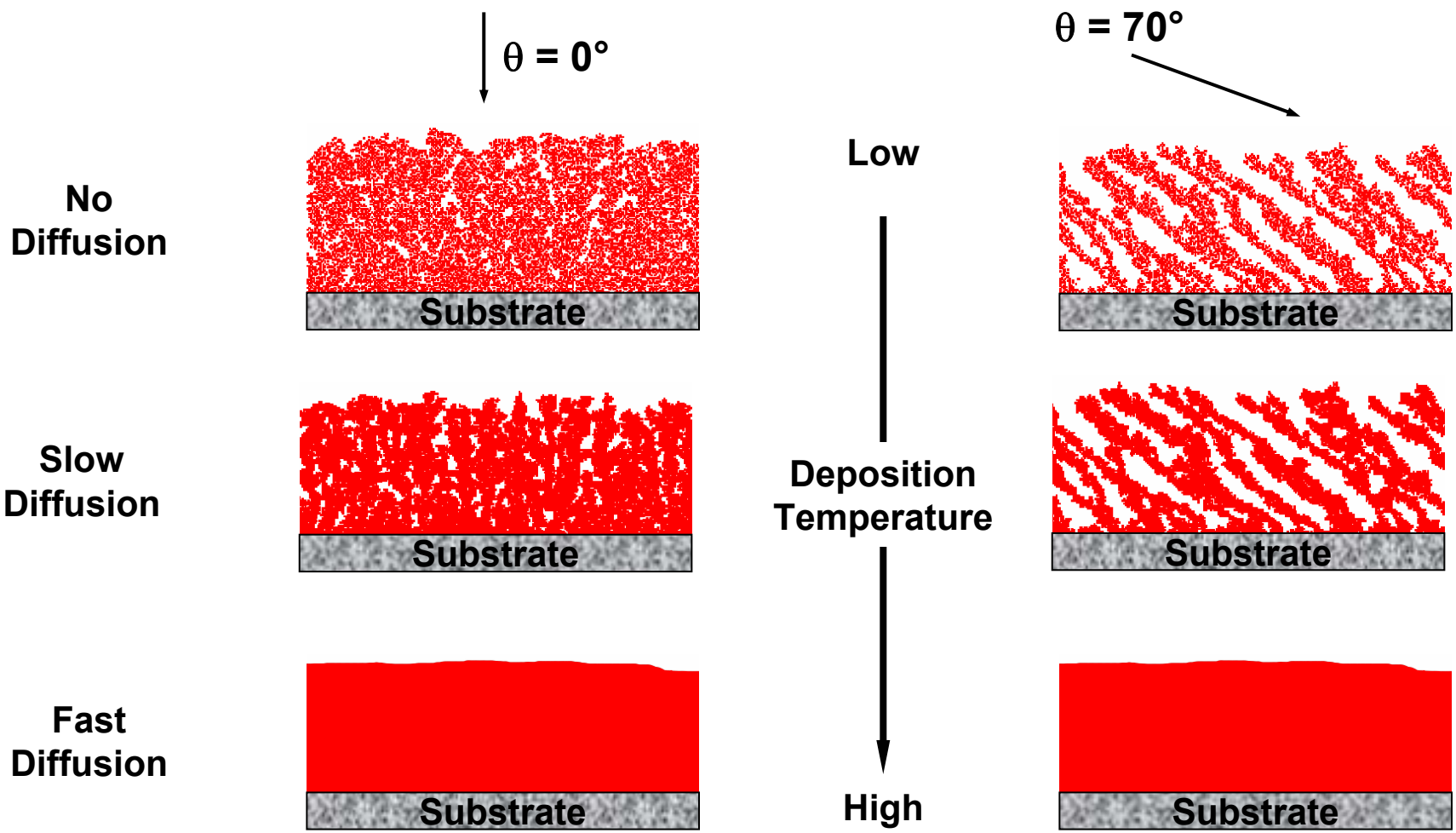


- **The separation of filaments depends strongly on the deposition angle.**

G. A. Kimmel, Z. Dohnálek, K. P. Stevenson, R. Scott Smith, and B. D. Kay, J. Chem. Phys. **114** (2001) 5295.

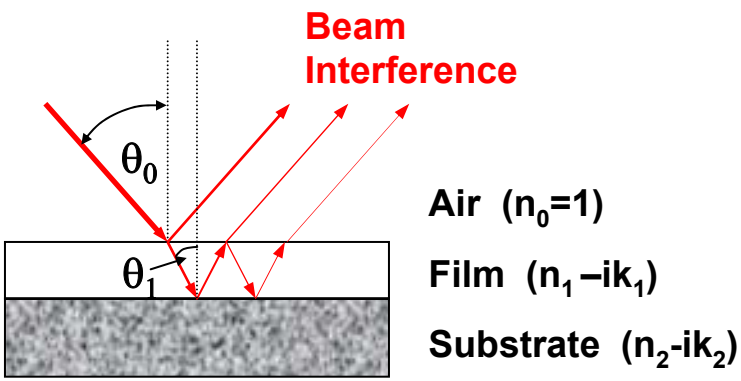
Ballistic Deposition Model for Nanoporous Thin Film Growth

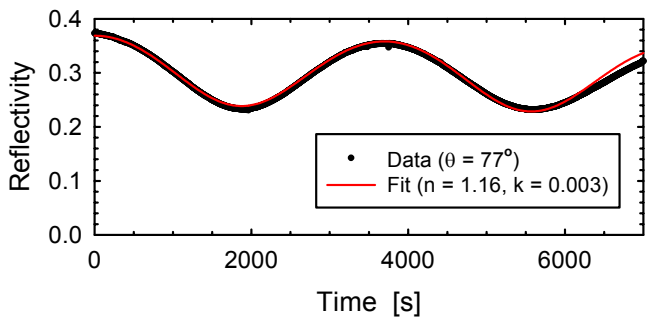
"Hit and Stick" model with limited surface mobility.

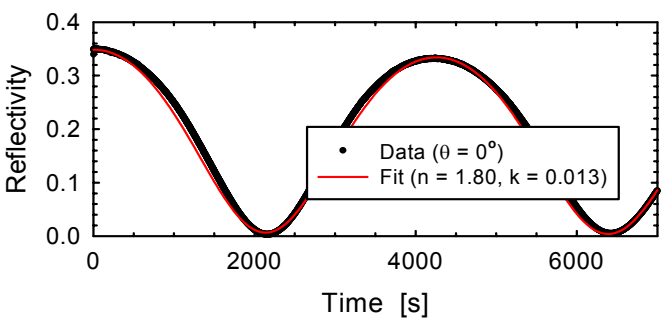


GA Kimmel, Z Dohnálek, KP Stevenson, RS Smith, and BD Kay, J. Chem. Phys. **114** (2001) 5295.

Optical Interference can be used to Determine Index of Refraction and Film Density







- **Reflected fraction of the incident beam during the film growth can be calculated by evaluating the following expression:**

$$R = \frac{r_1 + r_2 \exp(-i2\delta_1)}{1 + r_1 r_2 \exp(-i2\delta_1)}$$

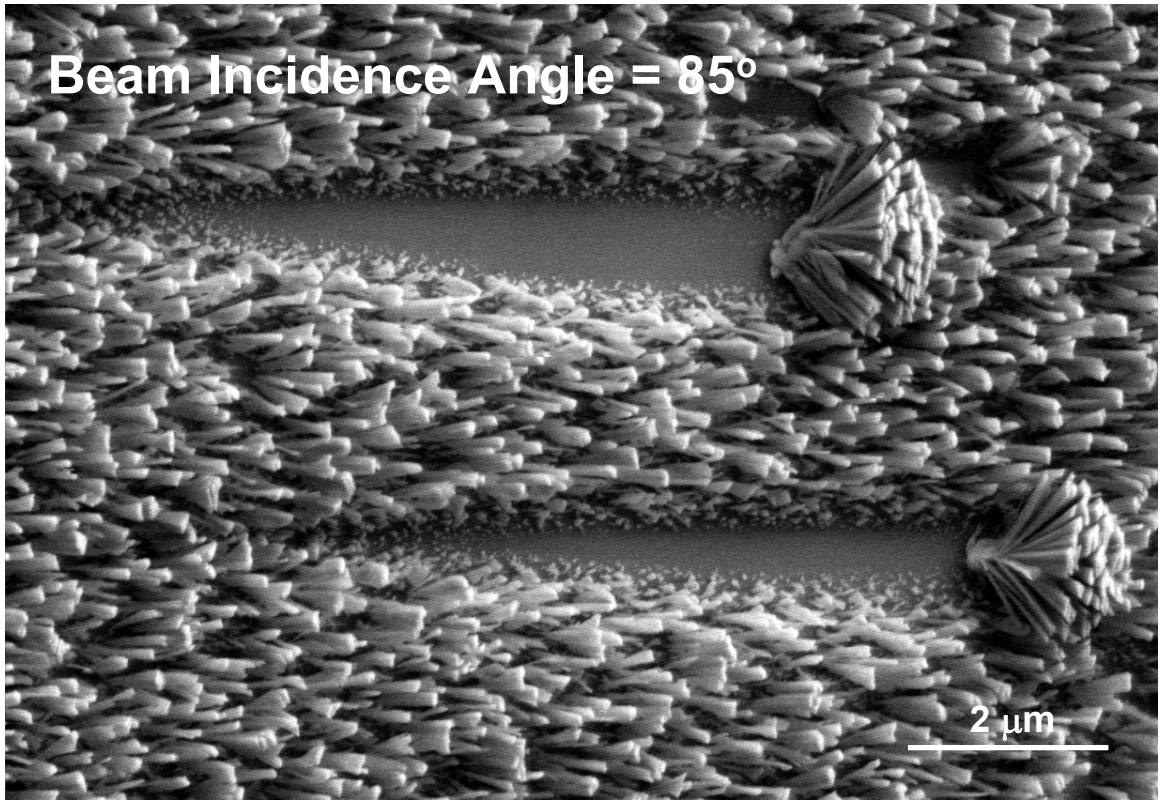
where r_1 and r_2 are Fresnel coefficients and δ_1 is optical phase thickness of the film.

- **Lorentz-Lorenz Equation relates film density and index of refraction:**

$$\frac{\rho}{\rho_i} = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{n_i^2 + 2}{n_i^2 - 1}$$

- **Densities as low as 1/10 of the bulk MgO (3.6 g/cm^3) are measured by optical interference.**
- **This corresponds to porosities as high as 90 %.**

Structured Nanoporous MgO Films Grown via Ballistic Molecular Beam Deposition



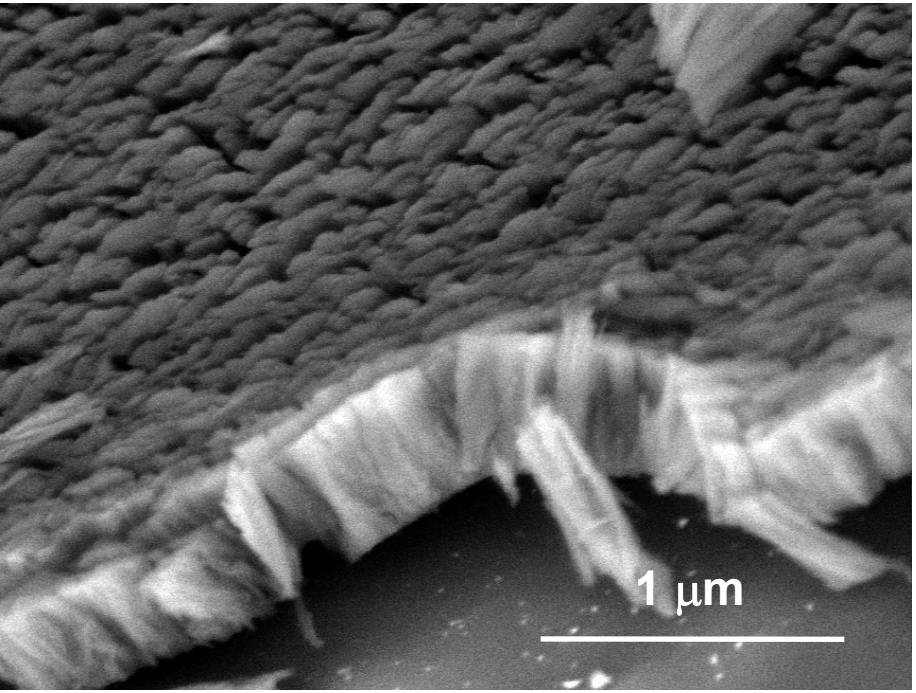
Deposition Direction

- **SEM micrograph reveals nanoscale structures rigidly attached to a macroscopic substrate.**
- **Substrate dust gives rise to long shadowed regions.**

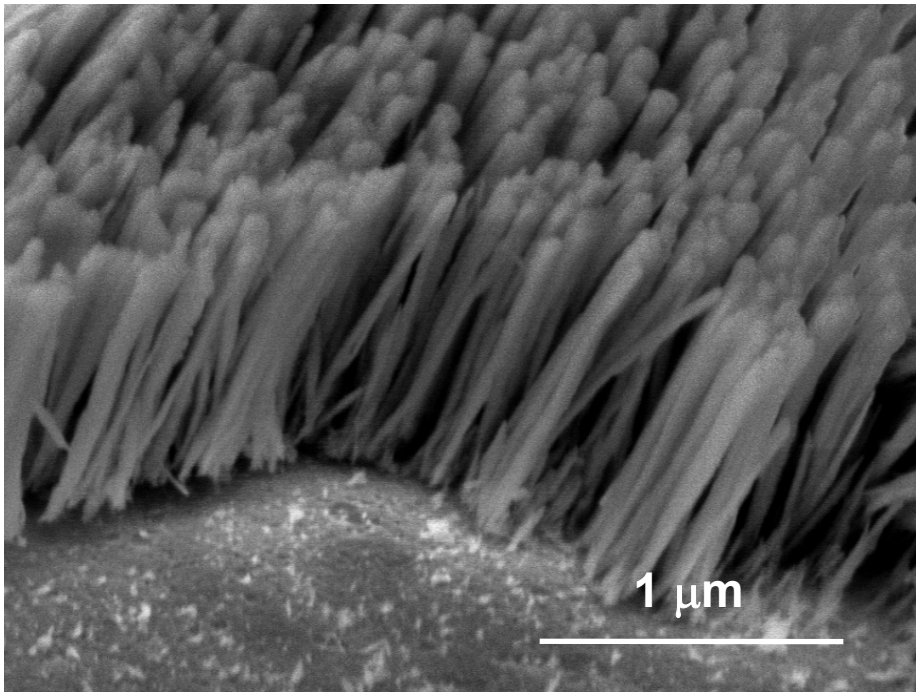
Z. Dohnálek, G.A. Kimmel, D.E. McCready, J.S. Young, A. Dohnálková, R.S. Smith, and B.D. Kay, J. Phys. Chem. B (on the web - articles ASAP).

MgO Film Morphology Depends Critically on Incident Beam Growth Angle

Beam Incidence Angle = 75°



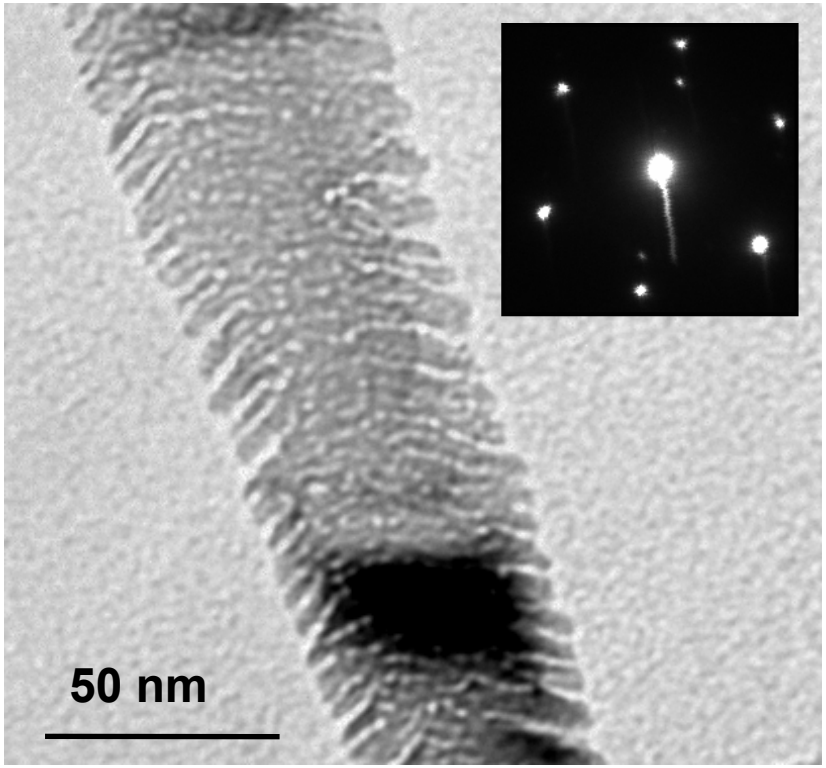
Beam Incidence Angle = 85°

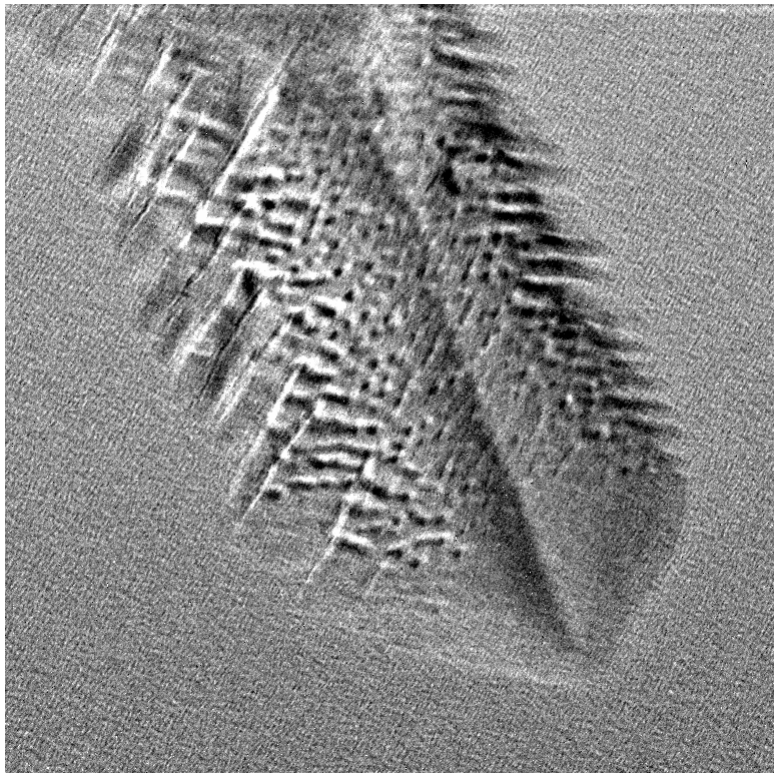


- **The structure of the film can be fine-tuned by variation of incident beam conditions.**

TEM Analysis is Used to Analyze Internal Structure of The Individual MgO Columns

TEM Image of Individual MgO Columns

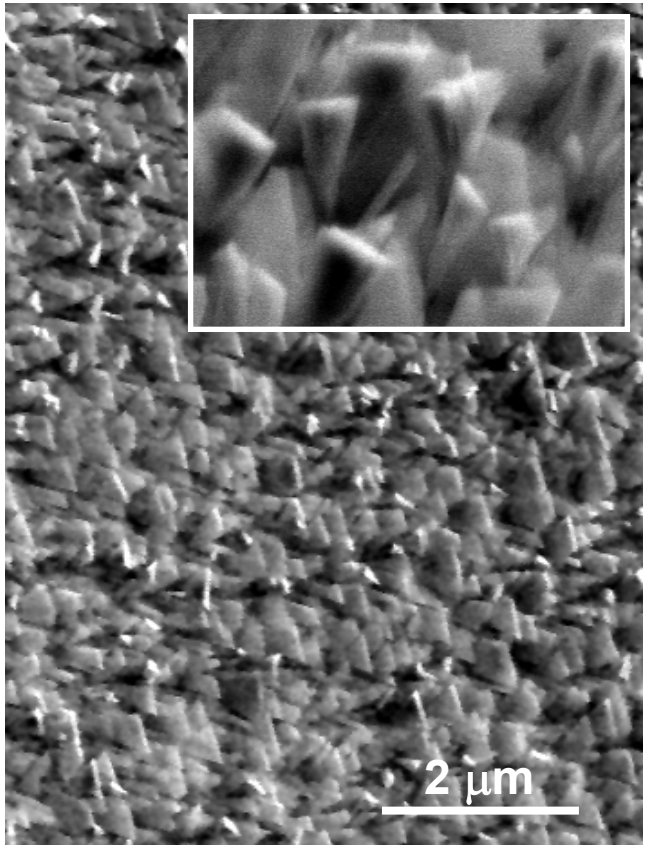




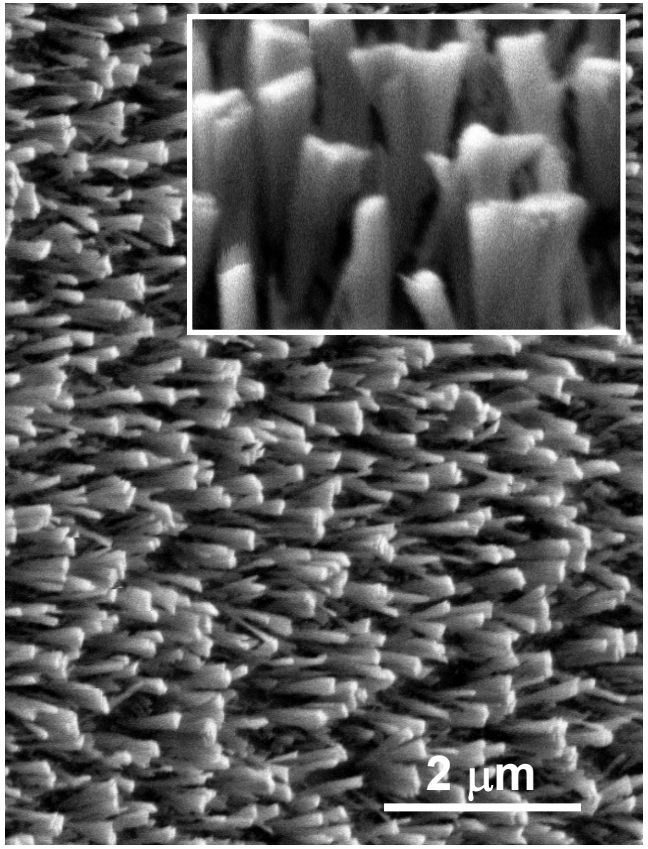
- TEM images reveal an internal fractal-like surface structure within an individual MgO column.
- TEM diffraction shows crystalline nature of the MgO columns.

Morphology of Thin Nanoporous MgO Films on Epitaxial and Disordered Substrates

Epitaxial Surface: Mo(100)



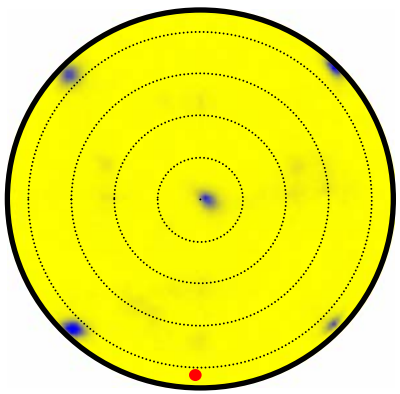
Disordered Surface: Oxidized Si(111)



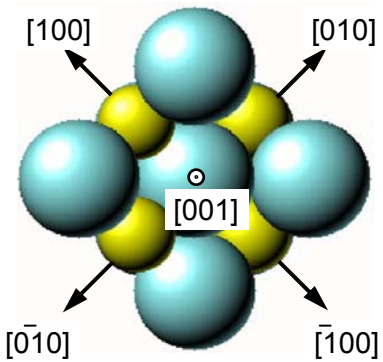
- **The films exhibit similar micron-scale morphology on epitaxial Mo(100) and other disordered substrates (oxidized Si(111) and Si(100), fused silica).**

Structure and Orientation of Thin Nanoporous MgO Films Deposited on Mo(100) and Oxidized Si(111) Substrates

MgO [200] Pole Figure on Mo(100)

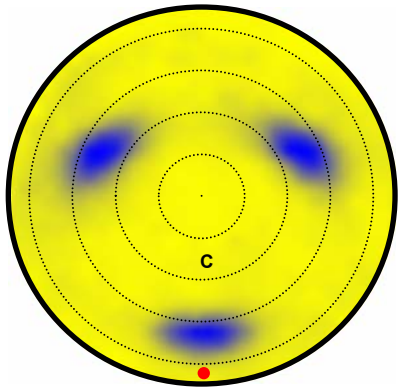


Crystallographic Orientation

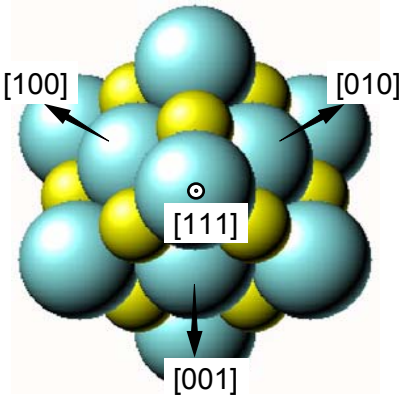


- The films deposited on Mo(100) are crystallographically oriented in registry with the Mo(100) substrate.

MgO [200] Pole Figure on Oxidized Si(111)

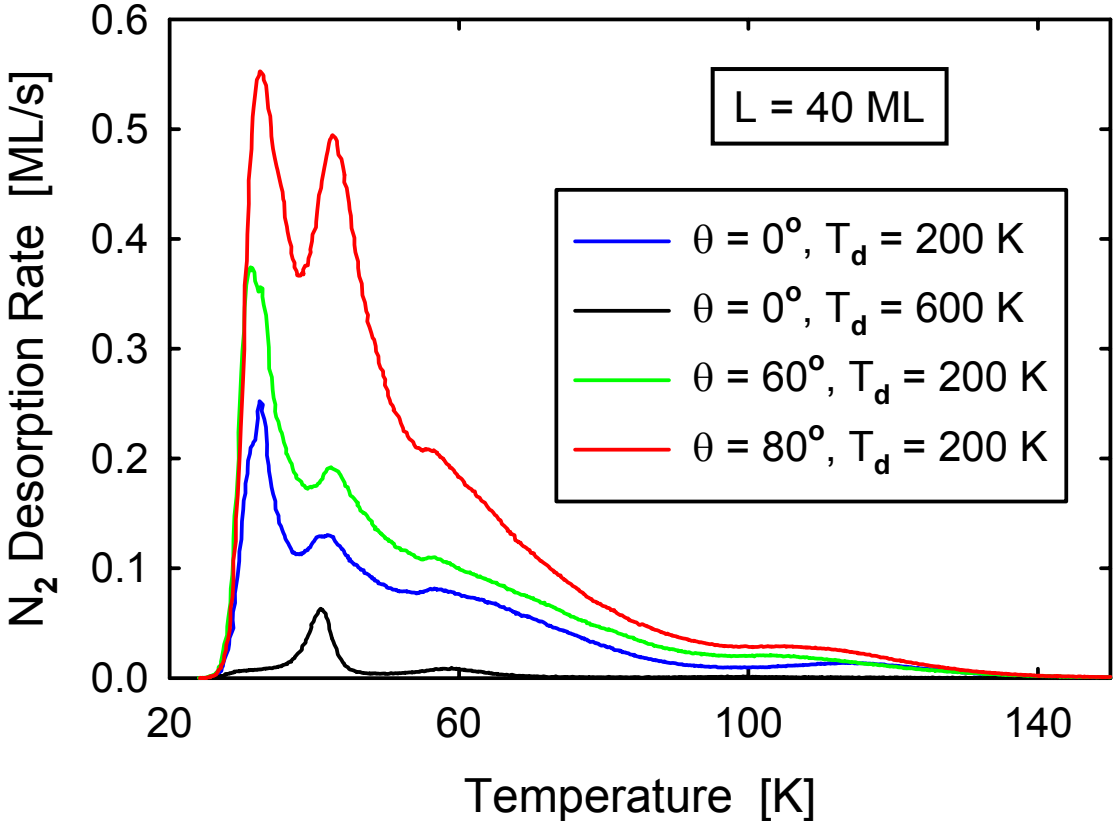


Crystallographic Orientation



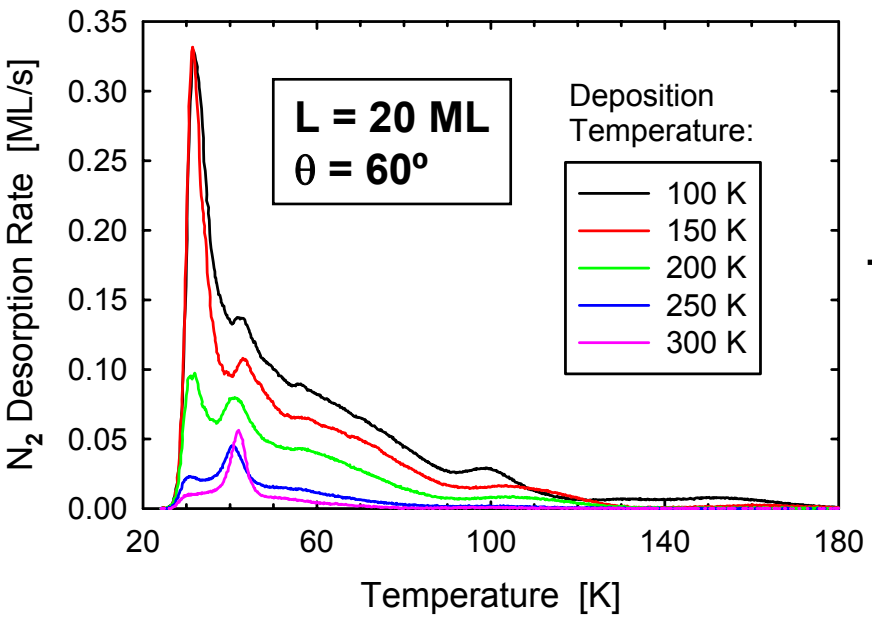
- The films deposited on non-epitaxial, disordered surfaces are crystalline and highly textured.
- Crystallographic orientation of the film is dictated by the overlap of the fastest growing [111] directions with the direction of the film growth and the incoming Mg flux.

Deposition Angle Dependence of Film Surface Area

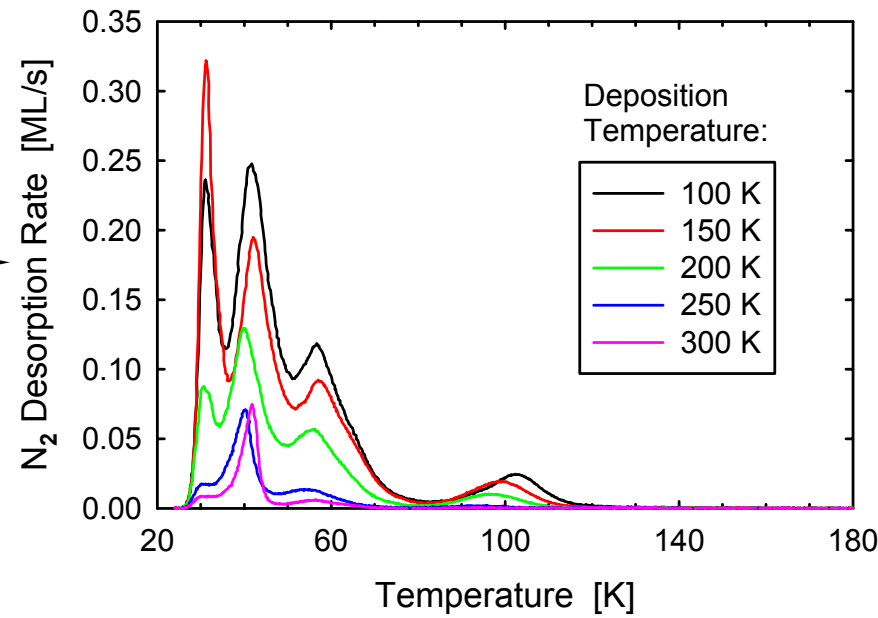


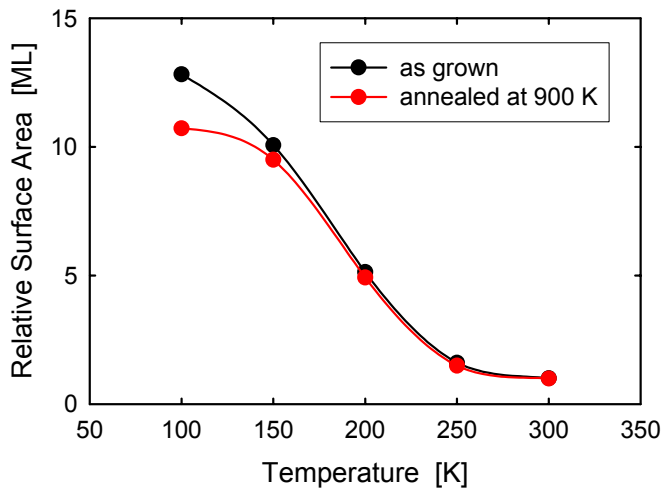
- **Surface area of the films increases with increasing deposition angle.**
- **At highest deposition angle of 80° the surface area reaches 1000 m^2/g.**

Growth Temperature Dependence of The Film Surface Area and



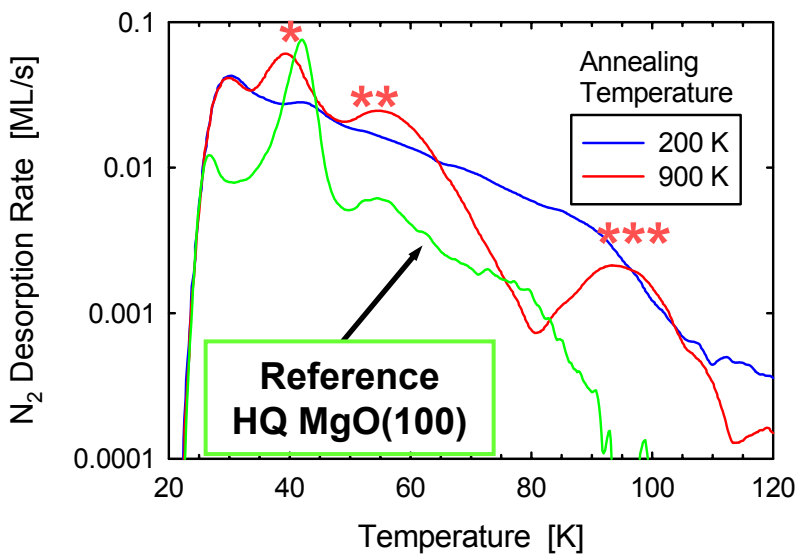
900 K

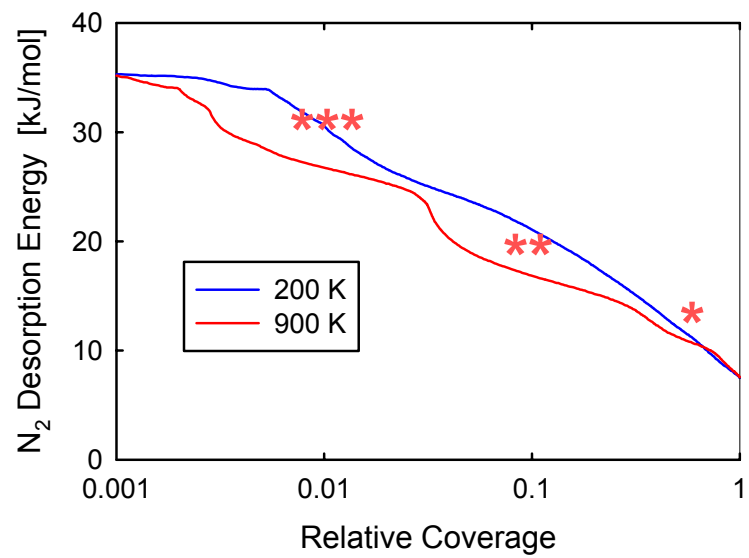




- **The growth temperature increase from 100 to 300 K results in the growth of fully densified films.**
- **Surface area is retained upon 900 K annealing for all growth temperatures.**

Annealing Dependent Distribution of Defects on Nanoporous MgO Surfaces

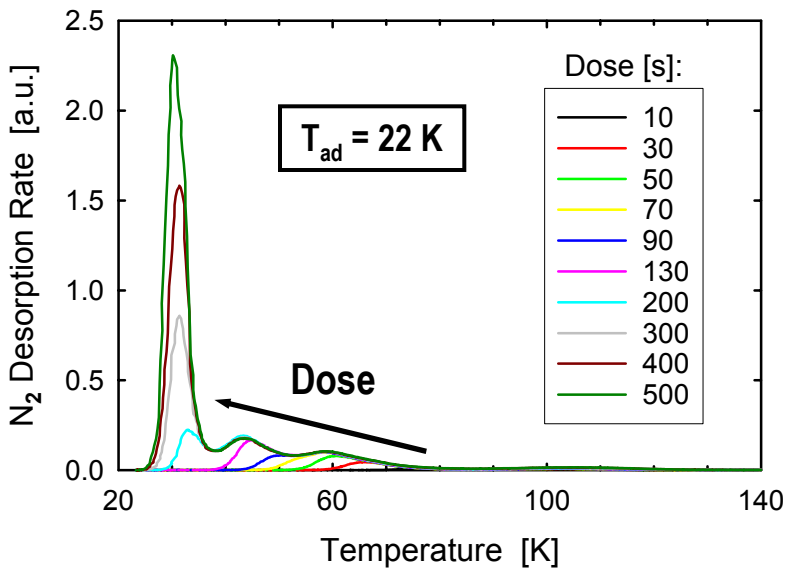


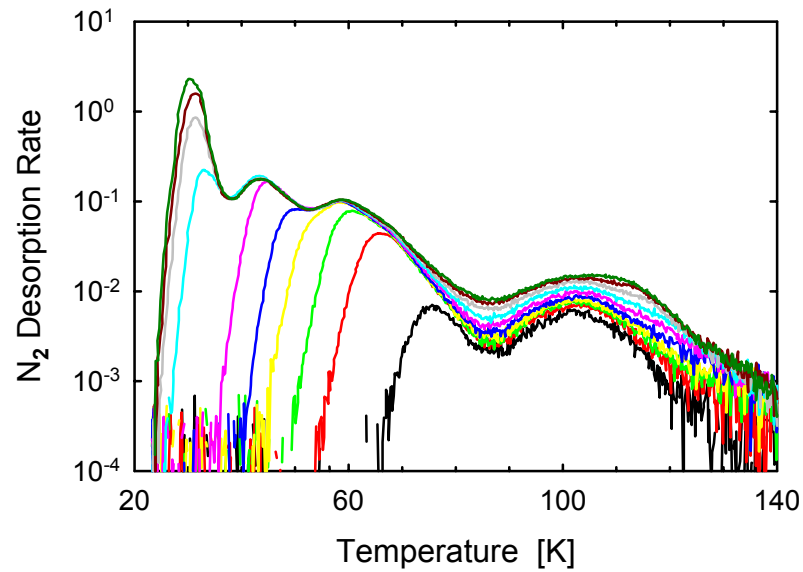


$$-\frac{d\theta}{dt} = \nu \exp\left(-\frac{E_d(\theta)}{RT}\right)\theta$$

- **A distribution of binding energies on nanoporous MgO is obtained by mathematical inversion of the TPD spectra.**
- **High fraction of defects with binding energies up to 3 times higher than that of terrace MgO(100) sites is found on nanoporous MgO.**

Reagent Transport in the Porous Films is Facile

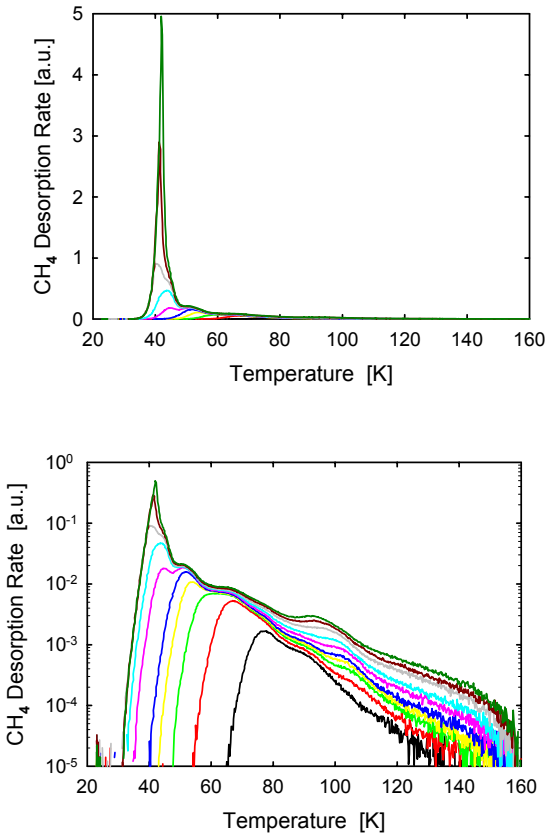




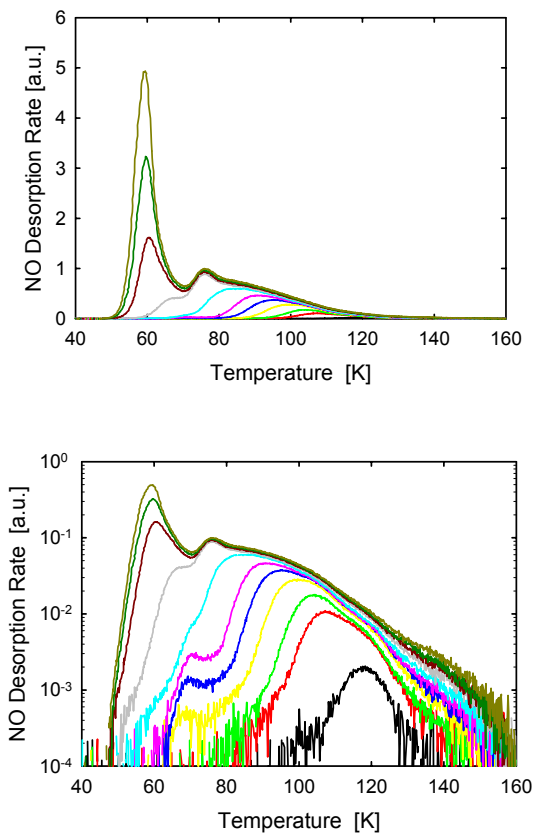
- **The N_2 preferentially finds the high energy binding sites throughout the entire thickness of the film.**
- **The N_2 mobility through the porous MgO is high even at very low temperatures (20 K).**

Adsorption of Weakly Bound Molecules on Nanoporous MgO

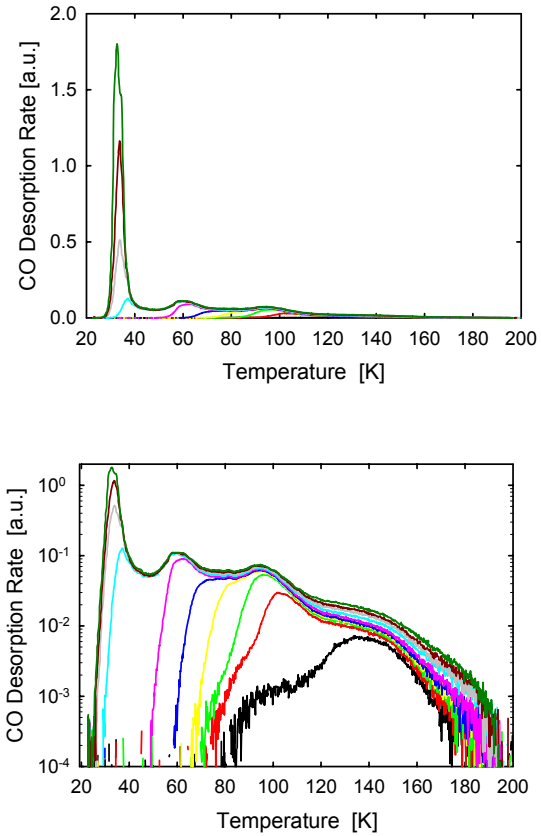
Methane (CH_4)



Nitric Oxide (NO)

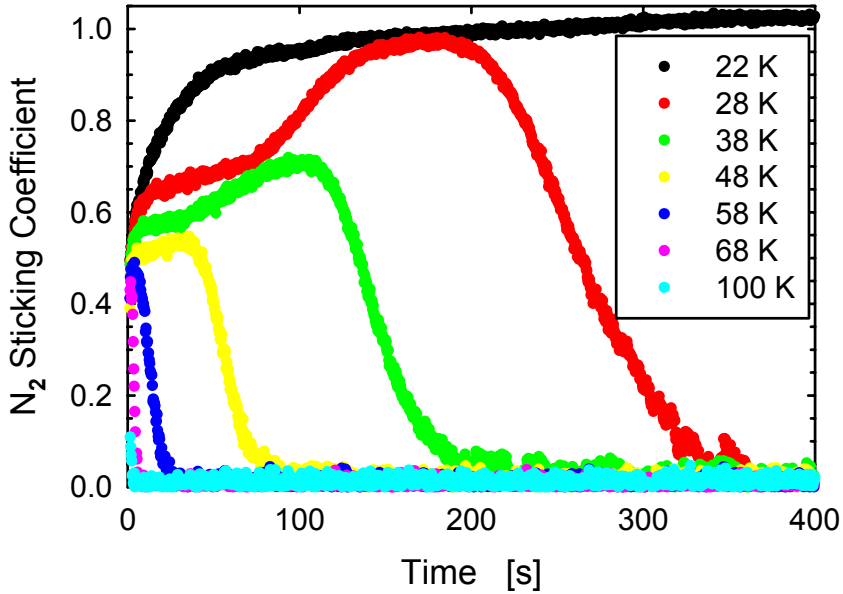


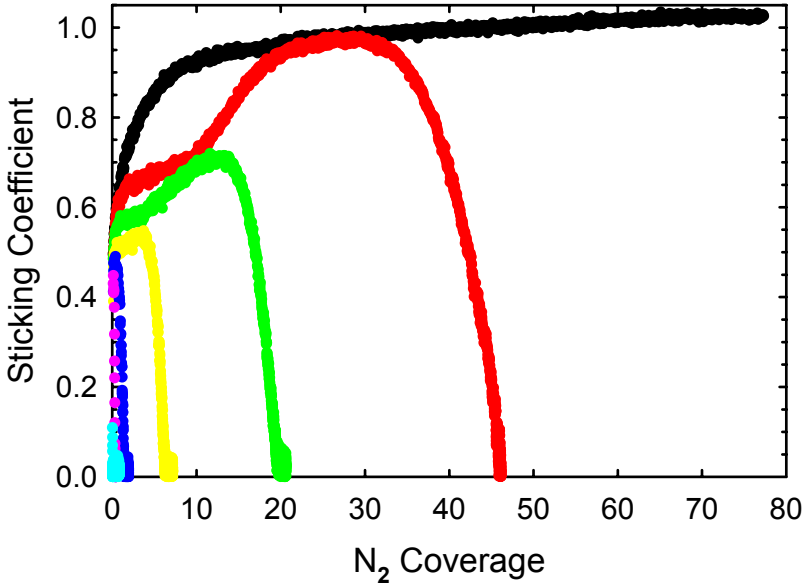
Carbon Monoxide (CO)



- **High resolution TPD shows that adsorbates find the strongest binding sites within the entire film (transport is facile).**

Gas Uptake by Porous Films is Strongly Dependent on Temperature



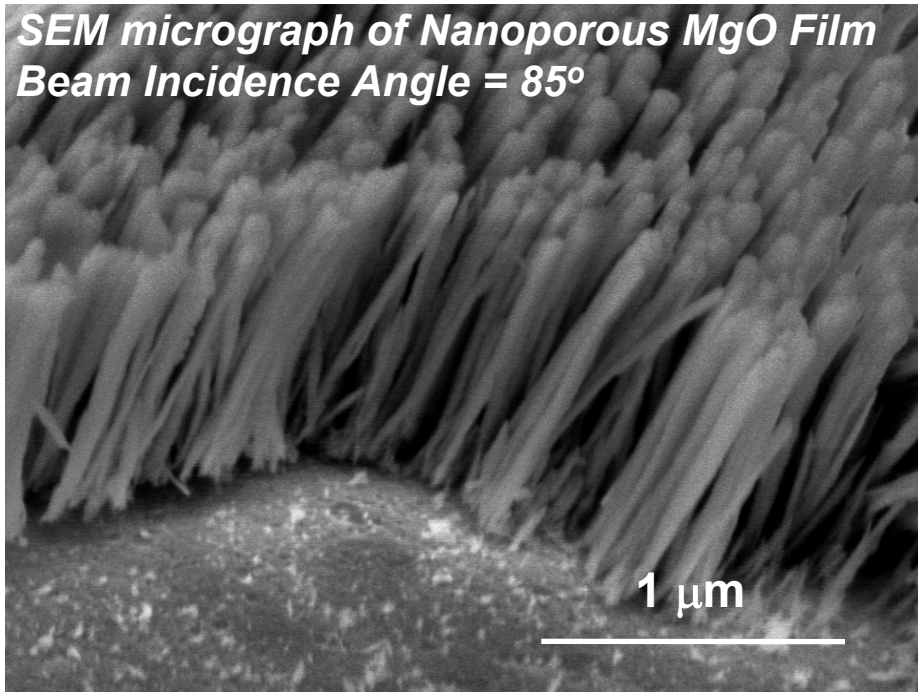


- **The initial sticking is low due to poor energy transfer to the MgO lattice.**
- **Sticking increases with coverage due to adsorbate-projectile interactions.**
- **Strong temperature dependence is due to kinetic coupling between adsorption, diffusion, pore condensation, and desorption.**

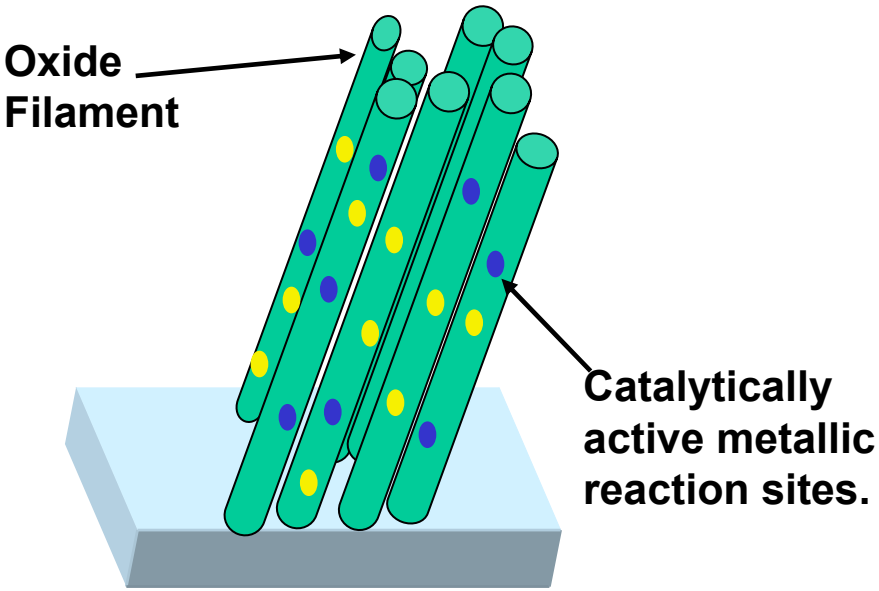
Summary

- Very large (>1000 m^2/g), readily accessible surface area with high porosity (> 90%).
- The films are composed of highly-porous, crystalline filaments exhibiting a high degree of alignment with respect to each other (crystallographic texture).
- High thermal conductivity and stability due to rigid attachment to substrate and largely independent nature of the filaments.
- Relatively large inter-filament spacing gives rise to facile transport of reagents to intra-filament binding sites.
- Reactive Ballistic Deposition (RBD) should be broadly applicable to a wide-range of pure and chemically-tailored materials.
- Ideal platforms for studying strongly coupled transport and reaction kinetics in restricted geometries.

Synthesis and Characterization of Chemically Tailored Nanoporous Materials



Model Nanoporous Catalyst



- **A broad spectrum of nanoporous materials can be grown via ballistic deposition. (metals, oxides, semiconductors, molecular solids)**
- **Chemically active materials will be synthesized by co-depositing reactive metals within the porous oxide. (catalysts, sensors, hydrogen storage)**
- **Transport and reactivity in these novel materials will be examined using in-situ modulated molecular beam scattering and surface techniques.**
- **Nanoporous film structure can be studied with SEM, TEM, XRD, AFM, STM, LEED, and TPD.**