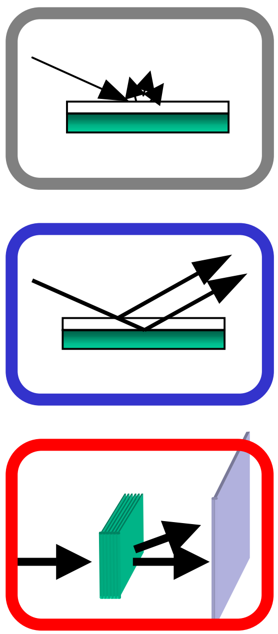
SANS Characterization of Nanoporous Thin Films for the Next Generation of Integrated Circuits



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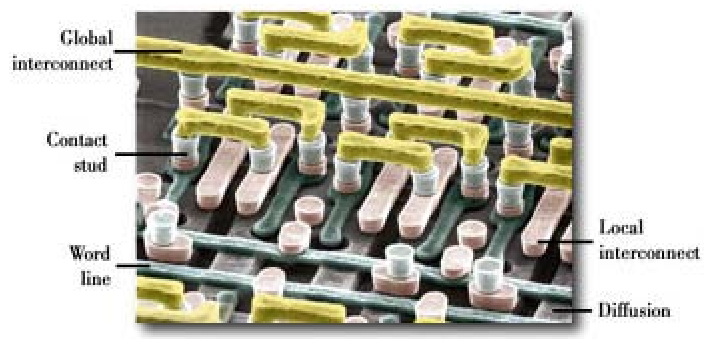
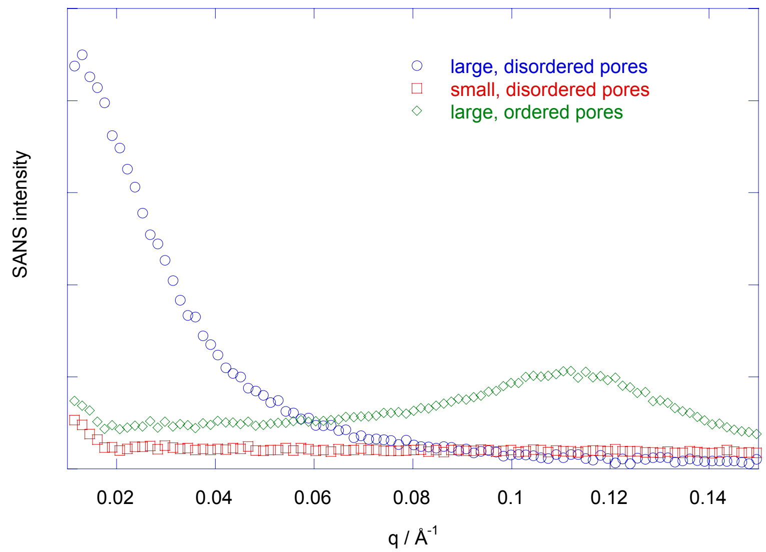
dielectric requirements for new integrated circuits

- the semiconductor industry is driven by miniaturization
  - low dielectric constant interlayer dielectrics are required
    - high switching speed
    - low crosstalk
  - the limits of conventional dielectric materials are being reached
    - k = 2.7 to 2.2 possible
    - lower values of dielectric constants (1.7 by 2007) require porosity
  - nano-porous dielectrics
    - pores can reduce k by reducing matrix volume fraction
    - other important physical properties are also changed
      - strength
      - barrier properties
- SANS characterization of morphology
  - pore volume fraction, P
  - matrix density, ρ
  - pore type and average size
  - pore connectivity
  - pore size distribution (PSD)



SANS measurements of nano-porous films



- NCNR 8m SANS
- 0.01 Å^{-1} < q < 0.15 Å^{-1}
- 6 h / sample
- 100 samples / 4 y

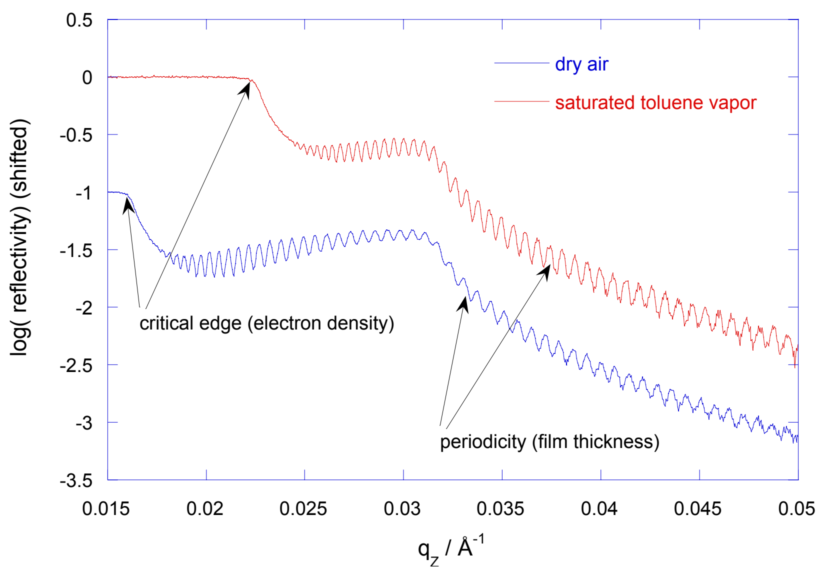
Note: all uncertainties are for one standard deviation. in cases where uncertainties are smaller than plot symbols, they are not shown.

- films are typically 1 μm thick on a 1 mm Silicon substrate
- high transmission of the substrate and high contrast of the film to pore required
- three morphology types
  - spin on film, porogen
    - large, disordered
  - chemical vapor deposition
    - small, disordered
  - surfactant templated
    - large, ordered

SANS data analysis

- invariant analysis: $\int_0^\infty q^2 I(q)dq$ $\quad P(1-P)\sigma^2\rho^2$
- Debye function, random: $I(q) = \dfrac{8\pi P(1-P)\sigma^2\rho^2\xi^3}{(1+q^2\xi^2)^2}$
- Percus – Yevick spheres
  - monodisperse – radius, volume fraction
  - polydisperse - additional PSD type and width
  - ordering – non-overlap radius > pore size
- contrast match
  - absolute intensities not required
  - open pores & uniform matrix – wall density
  - closed pores – closed pore volume fraction and PSD

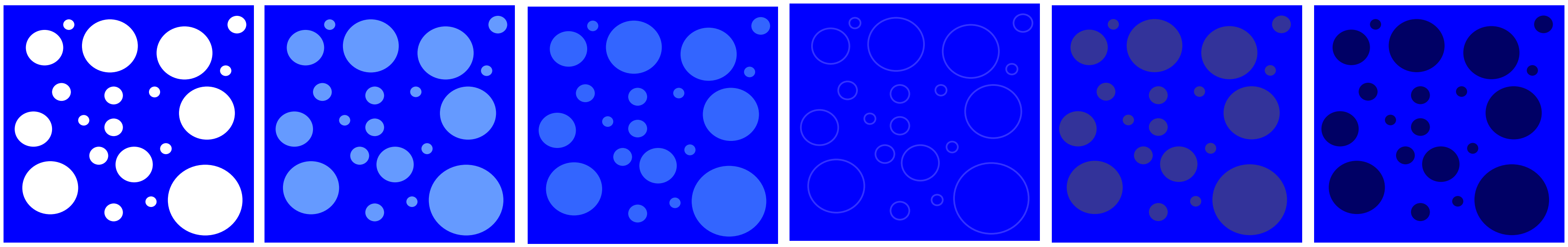
information from x-ray reflectivity (XR) and ion scattering



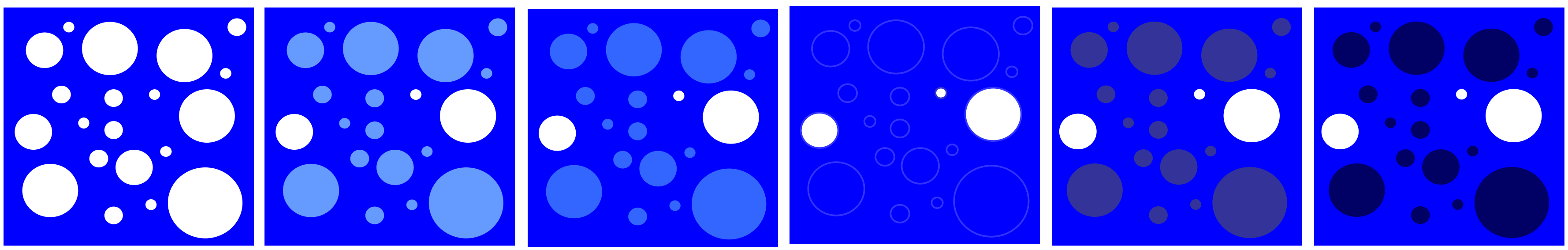
- routinely measured quantities
  - pore volume fraction
  - pore type and average size
  - matrix density
- techniques used
  - SANS, XR, ion scattering

- ion scattering (Rutherford back-scattering and forward recoil elastic scattering)
  - *in situ* measurements
  - atomic (H, C, O, Si) content for neutron and x-ray contrast
- x-ray reflectivity
  - I µm film thickness to ± 1 nm
  - electron density gives average mass density, ρ_{AVE}
    - Average mass density is a combination of pore volume fraction, P, and matrix density, ρ
    - $\rho_{AVE} = (1-P)\rho$

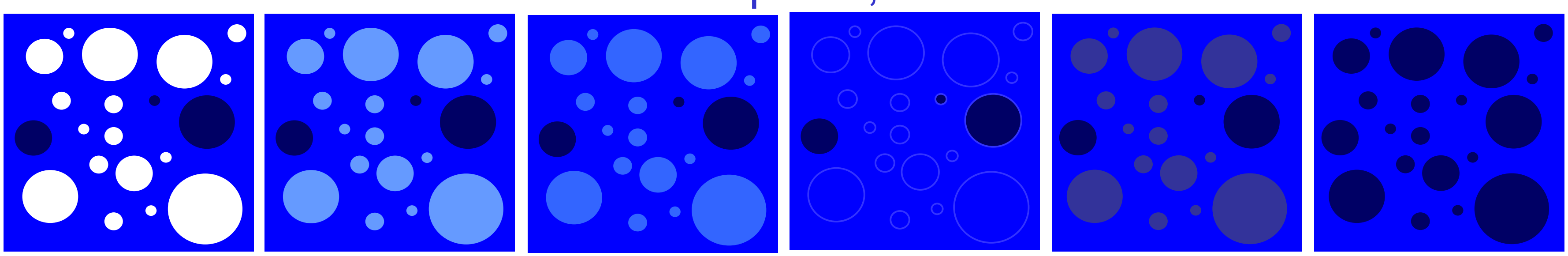
SANS contrast match – possible morphologies



No closed pores, uniform wall



Some closed pores, uniform wall

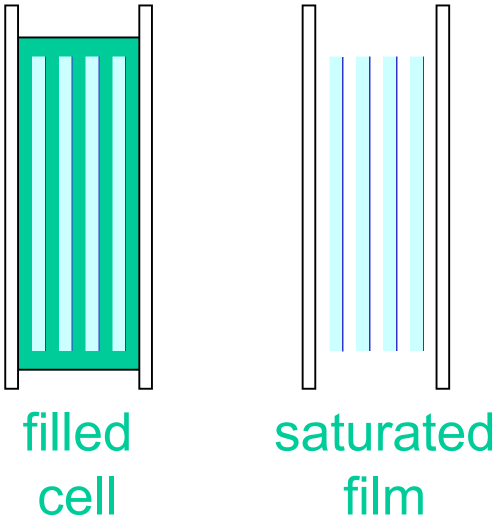


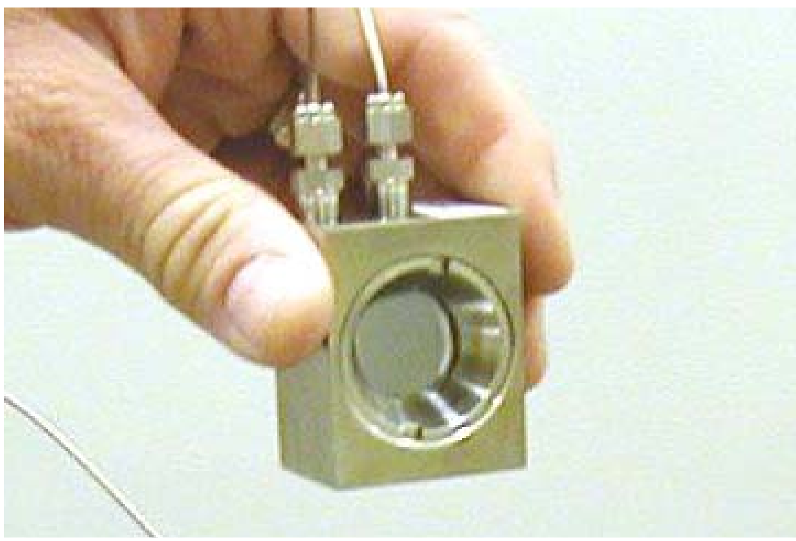
No closed pores, 2 phase wall

SANS measurements using probe molecules

- SANS contrast match
  - fill pores with mixtures of proton and deuterium solvents
  - not dependent on morphology type
  - closed pore porosity measured directly
  - matrix swelling monitored by XR thickness
- SANS porosimetry
  - fill pores with match mixture at controlled vapor pressure
  - pores are filled by capillary action
  - pores are filled according to the Kelvin equation
  - $r = -2\gamma V/(RT)/\ln(P/P_0)$
  - SANS from unfilled pores – pore size distribution

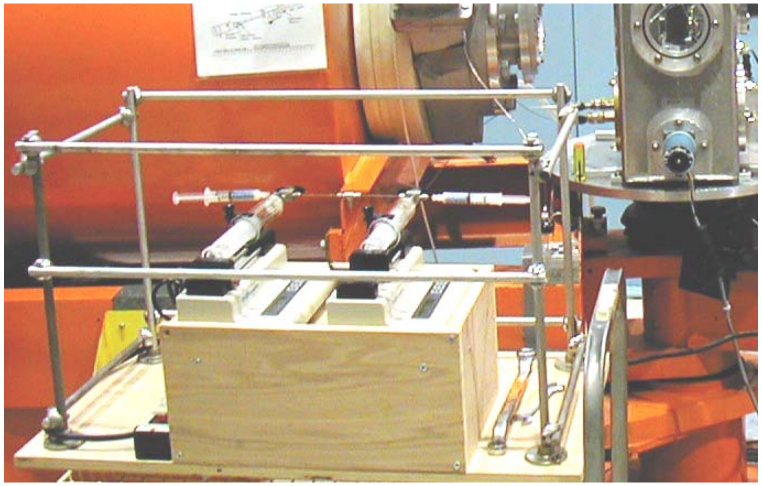
SANS contrast match – vapor adsorption

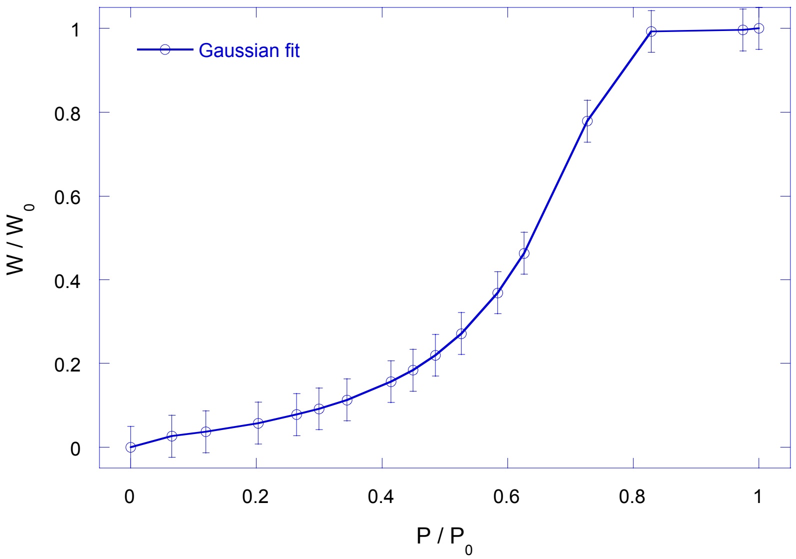




- film thickness is hundreds of times less than space between substrates
- a solvent filled SANS cell produces a large incoherent background
- use a saturated solvent vapor to fill the pores by capillary action
- incoherent scattering background is reduced to acceptable level
- a vacuum tight flow-through cell constructed

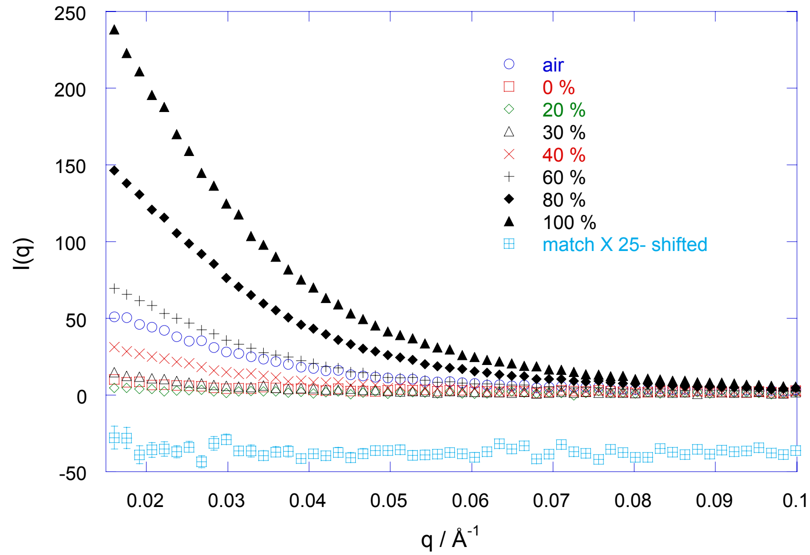
SANS contrast match – vapor adsorption

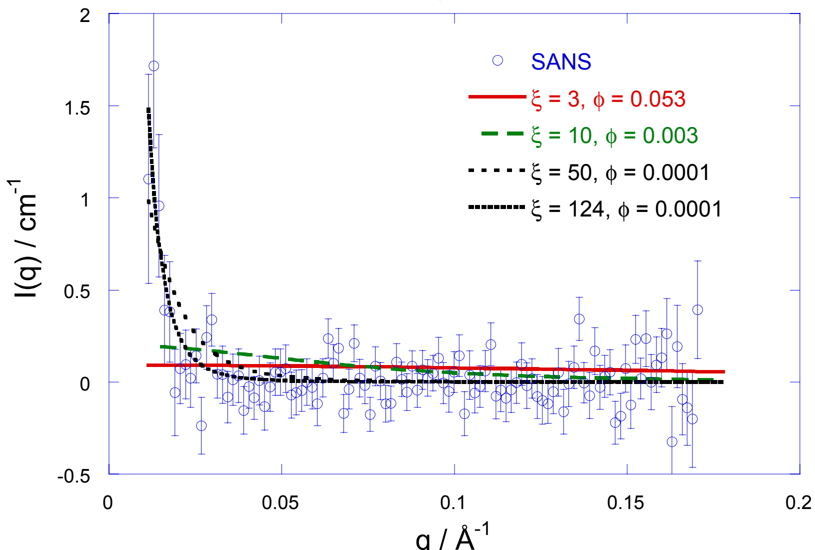




- syringe pumps deliver mixtures of saturated toluene-h_8 and toluene-d_8
- equilibrium is reached in < 30 min
- match point can be calculated from $I(q) \propto (\sigma\rho - (\sigma\rho)_{MATCH})^2$
- next, syringe pumps deliver mixtures of saturated match mixture and dry air
- pressures less than saturation fill pores described by Kelvin equation
- $r = -2\gamma V/(RT)/\ln(P/P_0)$

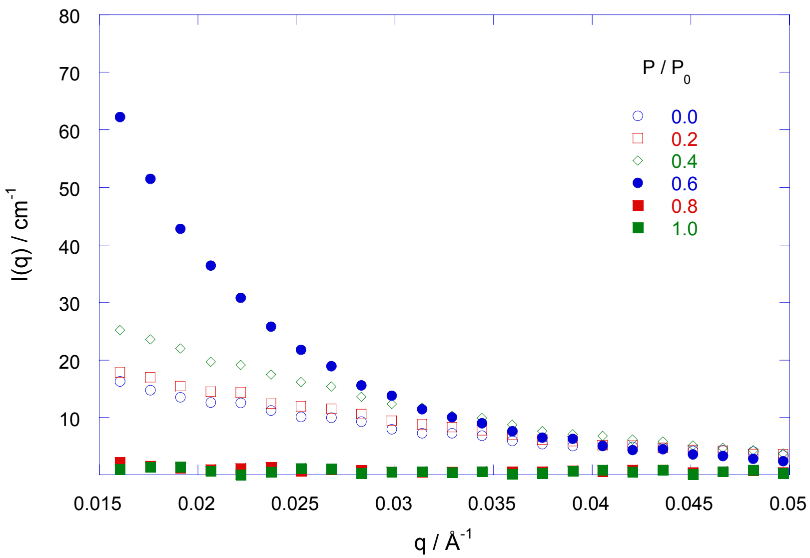
SANS contrast match – xerogel

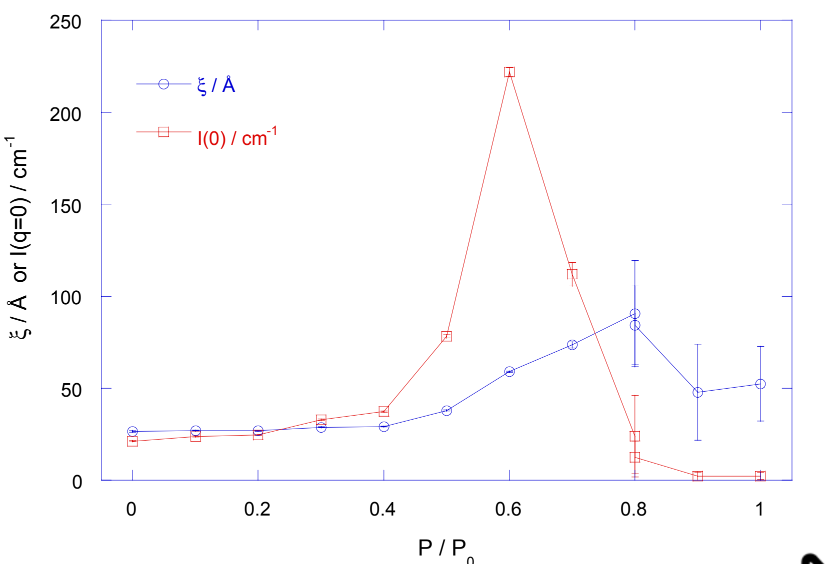




- SANS measurements are made pores filled with toluene-h_8 and $–d_8$
- total scattering goes through a minimum
- there is negligible scattering at the match point
- maximum closed pore porosity can be determined
- the match point is used to calculate wall density and porosity

SANS porosimetry – xerogel





- once match point has been determined, a mixture is prepared
- one syringe has saturated match mixture, the other has dry air
- various partial pressures are applied
- scattering comes from unfilled pores only
- SANS sizes can be compared to XR porosimetry values

summary

- SANS can be used to measure 1 μm thick nanoporous films *in situ* on 1 mm Silicon substrate.

- various models can be applies to extract morphological information on technologically important films.
  - porosity, wall density, pore type and size

- contrast match can provide additional information
  - wall density without absolute intensities for any pore type
  - close pore porosity measured directly

- SANS porosimetry probes PSD

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