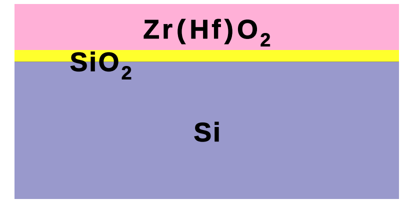
In situ low-angle x-ray scattering study of phase separation at initially mixed HfO_2-SiO_2 thin film interfaces

Paul C. McIntyre
Jeong-hee Ha

Department of Materials Science and Engineering
Stanford University, Stanford CA

Funding: Semiconductor Research Corporation Task 1016.001
Stanford Initiative in Nanoscale Materials and Processes

Motivation



Subsequent high temperature thermal processing causes phase separation
G.Lucovsky et al, Appl.Phys.Lett. 77, 2912 (2000)

Metal oxide/SiO_2 interface structure uncertain due to deposition-induced mixing and thermal instability

Loss of desired dielectric and electrical properties

Need to investigate effects of phase separation upon thermal process

Need to understand abruptness and stability of metal oxide/SiO_2 interfaces

Phase separation of Hf-silicate films forms HfO_2 / SiO_2 interfaces

- Initially intermixed HfO_2-SiO_2 alloy experiences a driving force for phase separation upon annealing

- Form regions of crystalline HfO_2 and amorphous SiO_2

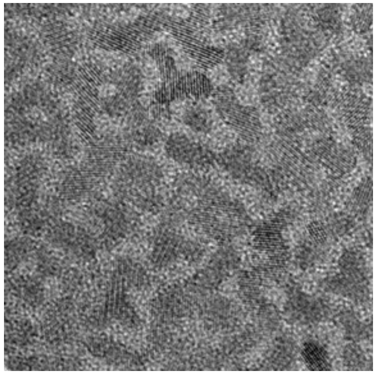
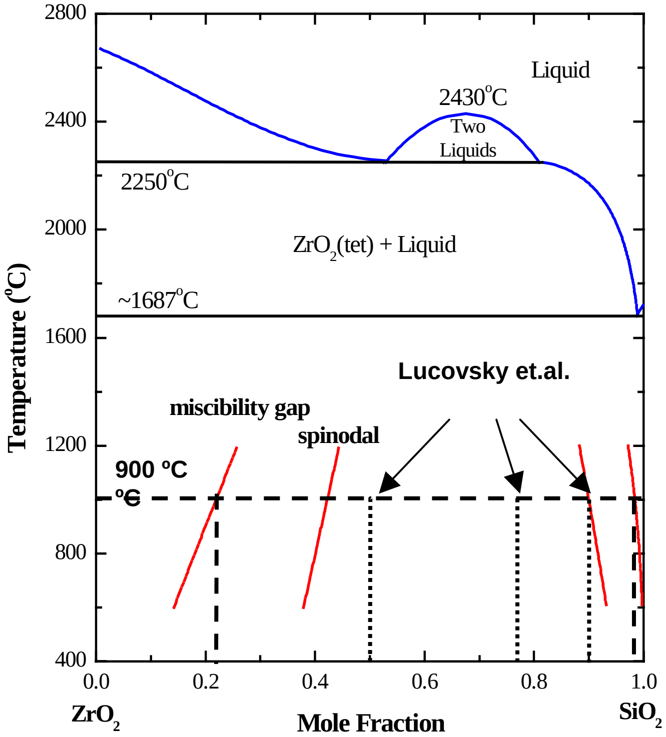
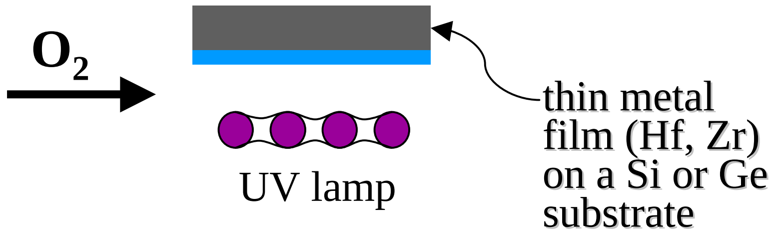


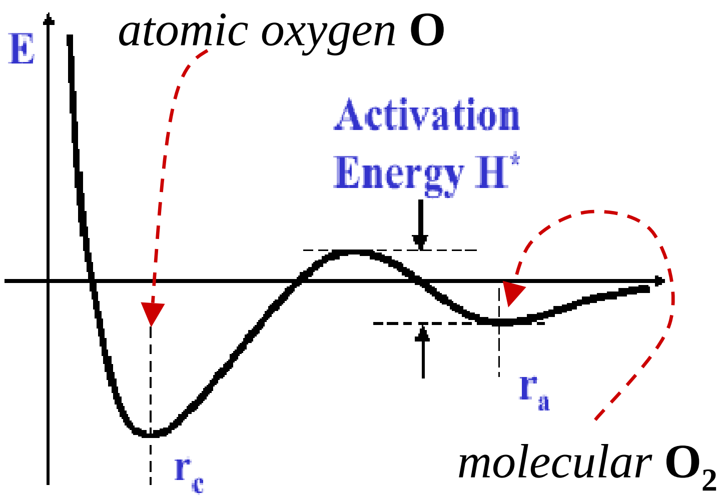
Image courtesy of S. Stemmer



H. Kim et al., J. Appl. Phys. (2002).
S. Stemmer et al., Jpn. J. Appl. Phys. (2003).
Lucovsky et al., Appl. Phys. Lett. (2000).

Growth of Metal Oxide Dielectrics : UV-Ozone Oxidation





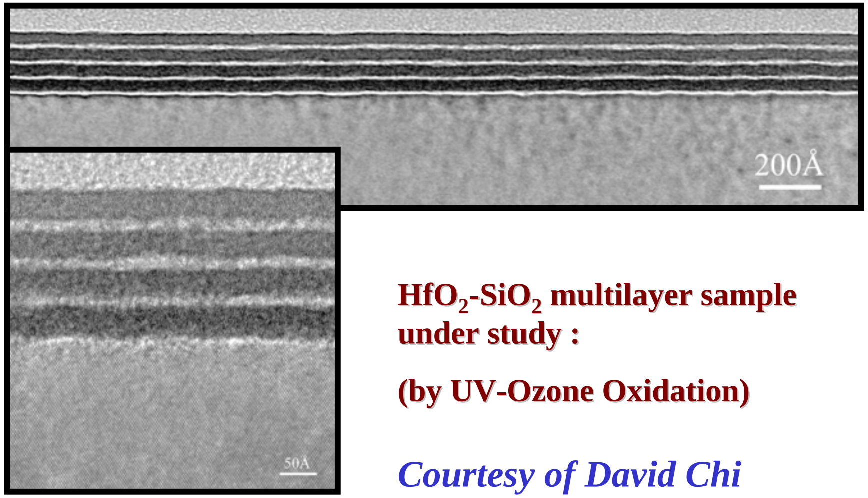
- UV light supplies atomic oxygen and ozone to surface through the following reactions:

$$O_2 + h\nu' \longrightarrow 2O$$
$$O + O_2 \longrightarrow O_3$$
$$O_3 + h\nu'' \longrightarrow O_2 + O$$

- Benefits
  - Low temperature
  - Low contamination
  - Simplicity
  - Can modify substrate surface passivation

S. Ramanathan et al., Appl. Phys. Lett. (2001)

Multilayer test structure for HfO_2 / SiO_2 interfaces



HfO_2-SiO_2 multilayer sample under study :

(by UV-Ozone Oxidation)

Courtesy of David Chi

- **(1.4nm SiO_2 / 4nm HfO_2)$_4$** structure on top of Si (100) substrate
- Grown by **UVO oxidation**
- **Growth conditions**

- Hf, Si sputtered in 2 mTorr Ar pressure (~0.2 Å/sec) with base pressure 5E-9 Torr
- Oxidized for 1 hr at 600 Torr O_2 pressure in UV light

* Advantage of using multilayers :

- Deliberate exaggeration of particular interface effects
- Separation of interface effects on electrical properties by comparing multi- and single layers

X-ray diffraction: probe of local electron density

The scattered amplitude of the x-ray diffraction from the given system is just proportional to the Fourier transform of the local electron density :

$$\varepsilon_c = \frac{E_0 r_e}{R} \exp\left[i(wt - kR)\right] \int e^{iq\cdot r} \rho_c(r)\, dV$$

so that $$I \propto \left(\int e^{iq\cdot r} \rho_c(r)\, dV\right)^2$$

E_0 : electric field magnitude

r_e : electron radius

R : distance from the sample to the detector

q : scattering vector

$\rho_c(r)$: spatial electron density distribution

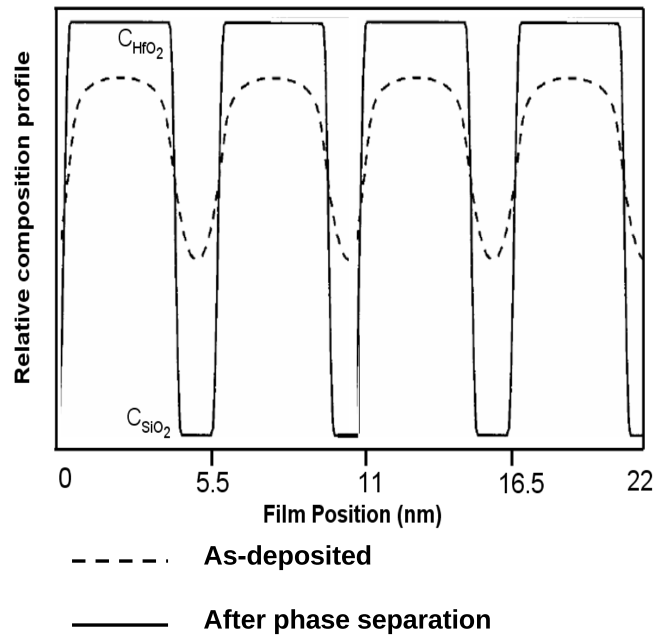
So, we can deduce information about changes in the electron density distribution (e.g. a composition profile) by observing XRD data.

Multilayer structure and its XRD pattern

- Electron density distribution in the multilayer sample can be modeled as a square wave.

- The scattered amplitude is proportional to the Fourier series of the square wave given.

- The weighting of the n=1 (first order) harmonic wave reflects the degree of the interdiffusion.



Relative concentration profile in HfO_2/SiO_2 multilayer structure

$$\tilde{D} = \frac{-L^2}{8\pi^2}\frac{d}{dt}\ln\left[\frac{I(t)}{I(0)}\right]$$

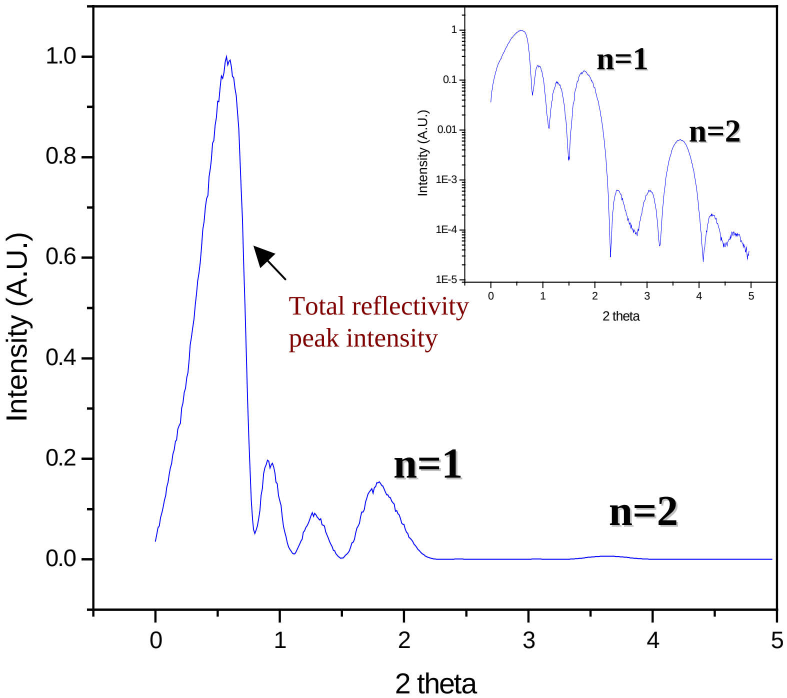
$\tilde{D}$: effective interdiffusivity

L : bilayer period

I : the first-order low-angle x-ray modulation peak

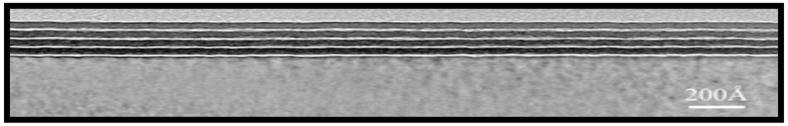
Stanford University
Dept of Materials Science and Engineering.

In-situ Low-angle XRD Studies



Low angle XRD data

for (SiO$_2$ /HfO$_2$)$_4$ multilayer structure



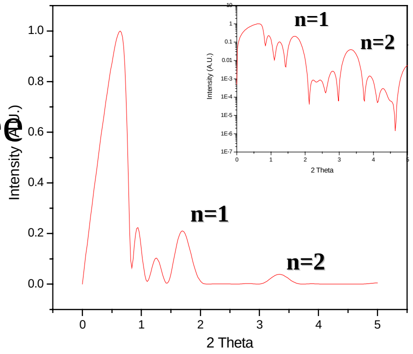
HfO_2-SiO_2 multilayer sample under study :

(by UV-Ozone Oxidation) ***Courtesy of David Chi***

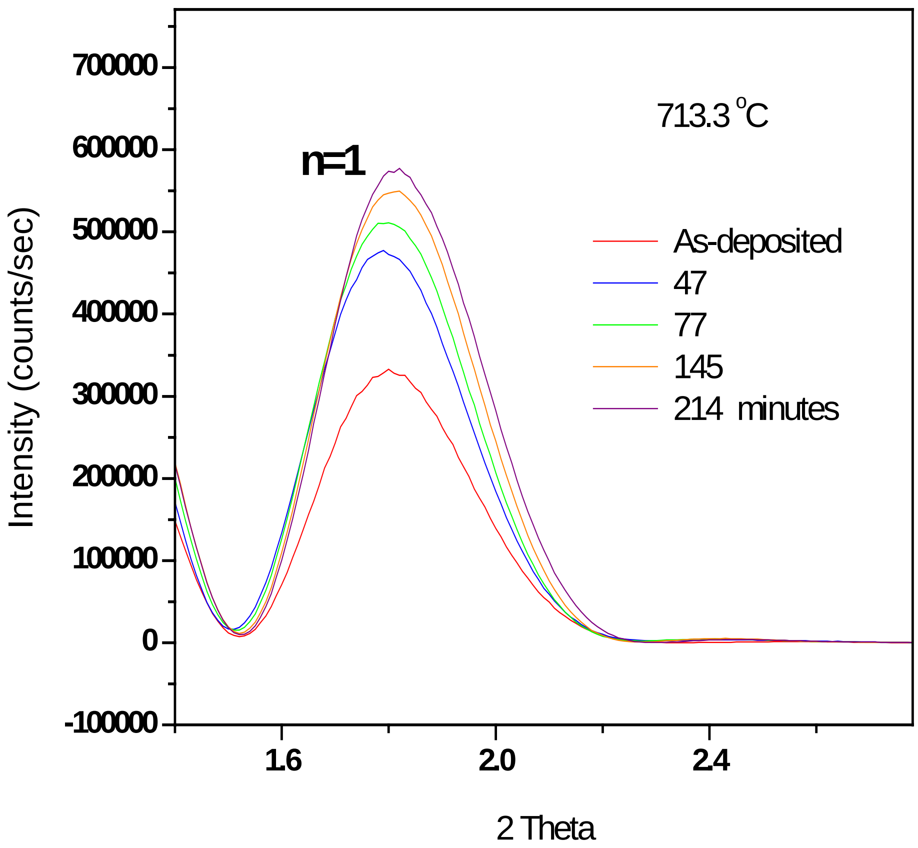
- The scattered intensity for N layers is given by:

$$I \propto \left(\sum_{n=0}^{N-1} f_n(q) e^{iq\cdot R_n}\right)^2 = f^2(q) \frac{\sin^2(Nq_z L/2)}{\sin^2(q_z L/2)}$$

Measured data agree well with the simulated result :



$(HfO_2/SiO_2)*4$ structure, N_2 anneal

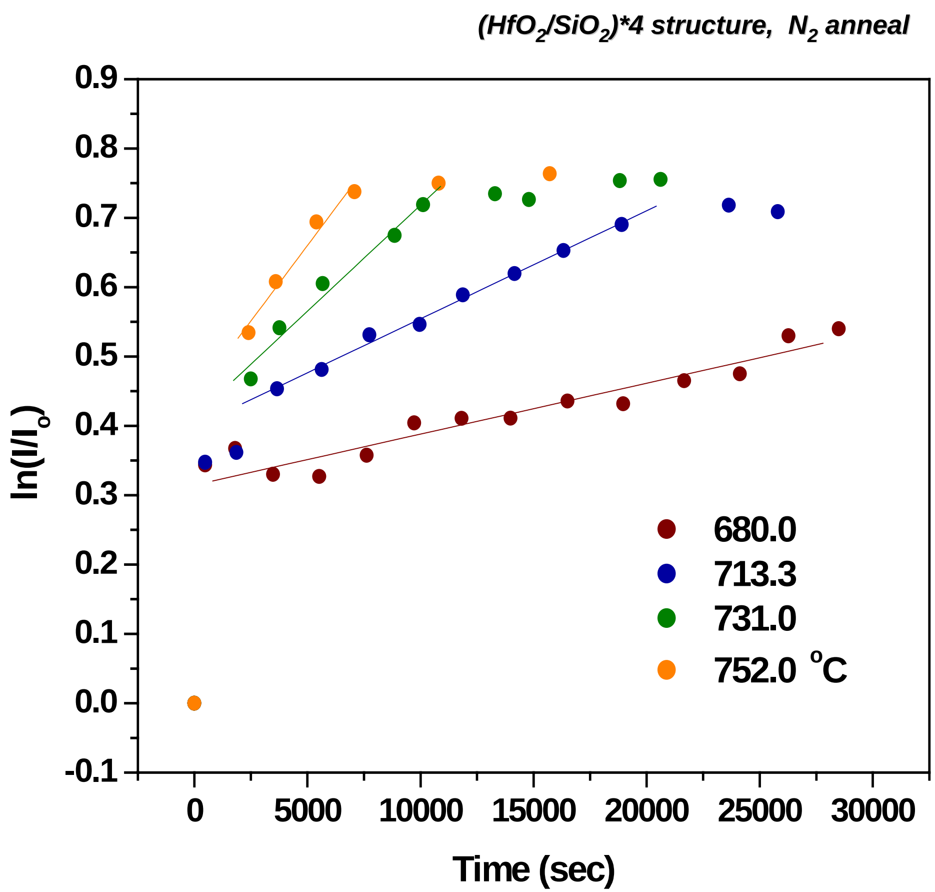


The intensity of n = 1 satellite peak ***increases*** as annealing proceeds

Evidence of phase separation at the initially-intermixed as-deposited HfO_2/SiO_2 interfaces

Stanford University
Dept of Materials Science and Engineering.

$(HfO_2 / SiO_2)*4$ structure, N_2 anneal

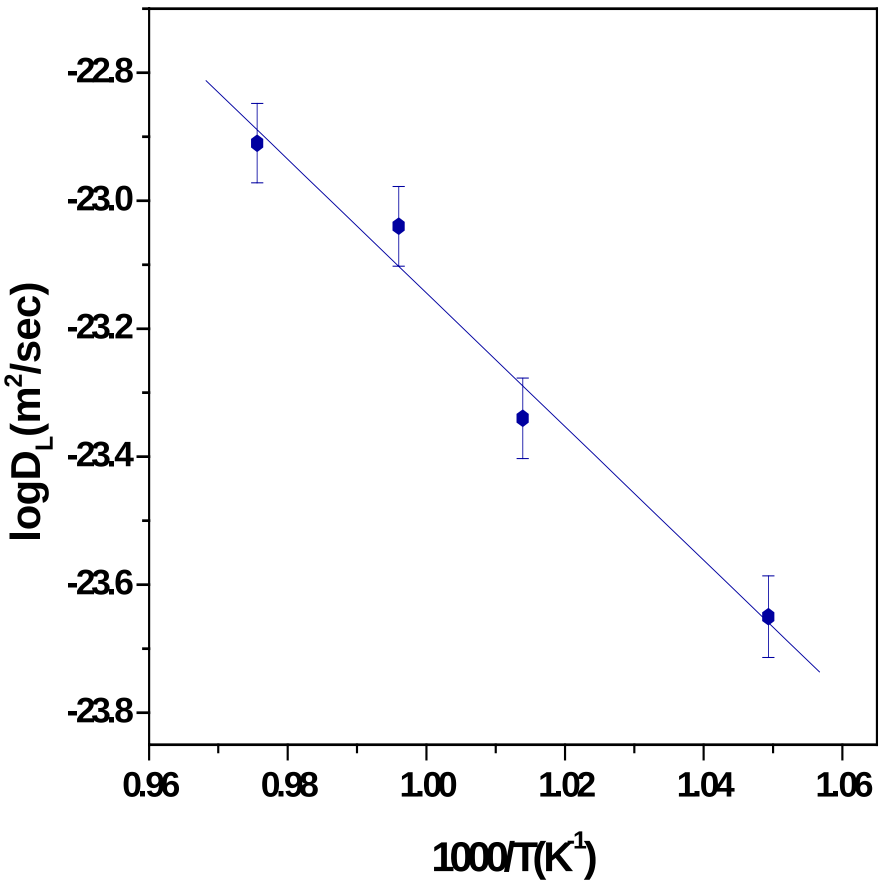


$$\tilde{D} = \frac{-L^2}{8\pi^2} \frac{d}{dt} \ln\left[\frac{I(t)}{I(0)}\right]$$

Temperature (℃)	Interdiffusivity(m^2/sec)
680.0	$2.34*10^{-24}$
713.3	$5.65*10^{-24}$
731.0	$9.11*10^{-24}$
752.0	$25.18*10^{-24}$

Stanford University
Dept of Materials Science
and Engineering.

Activation energy for the phase separation



- The activation energy ΔH for phase separation can be obtained from the Arrhenius rate law :

$$D_e = D_o \exp(-\frac{\Delta H}{k_B T})$$

- The obtained ΔH for the phase separation is 2.06 ± 0.15 eV.

Stanford University
Dept of Materials Science
and Engineering.

Summary

- **Accomplishments**
  - Used multilayer x-ray scattering to probe the kinetics of phase separation at as-deposited mixed HfO_2/SiO_2 interfaces
  - Obtained the activation energy of 2.06 ± 0.15 eV for phase separation in HfO_2/SiO_2 interface system
  - Determined temperature range for phase separation at initially-intermixed HfO_2/SiO_2 interface: T > 650°C