Physicochemical and Surface Characteristics Study of Nanoparticles related to ESH Impact of Emerging Nanoparticles and Byproduct in Semiconductor Manufacturing

Hao Wang

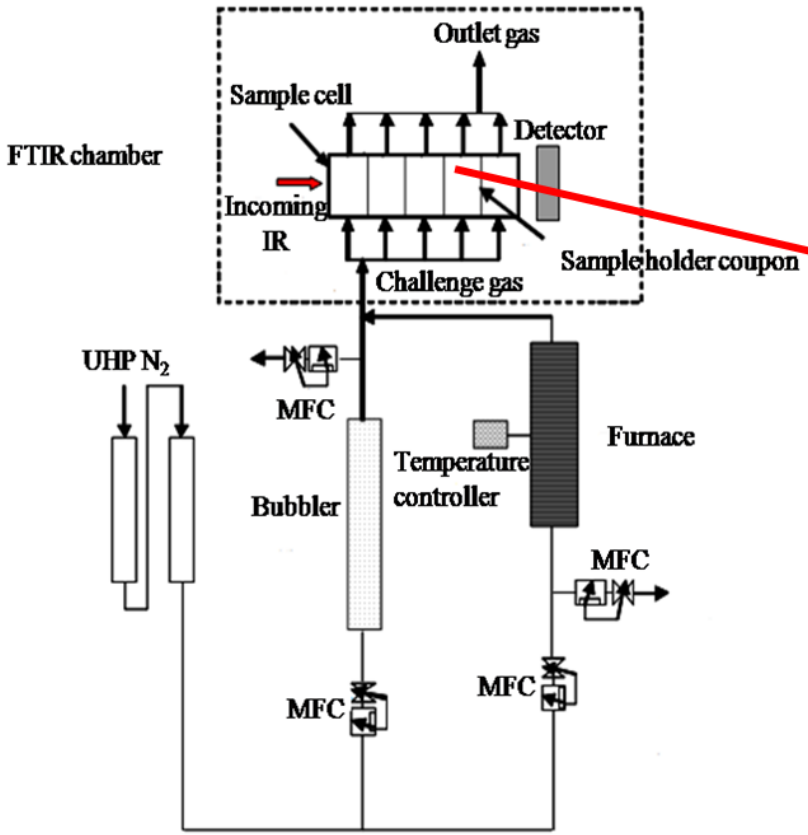
Chemical and Environmental Engineering
University of Arizona

November, 2 0 1 0

Introduction

- Investigation of nanoparticles has indicated that nanoparticles with high specific surface area, reactive surfaces, and absorptive surfaces, will easily absorb other toxic chemicals.
- Surface characteristics of different nanoparticles, such as SiO_2, HfO_2, and CeO_2, have been studied by moisture adsorption and desorption. The result shows species effect and size effect on moisture retention.
- A multilayer transient adsorption and desorption model has been applied to study the surface characteristics of different nanoparticles.

Experimental Setup



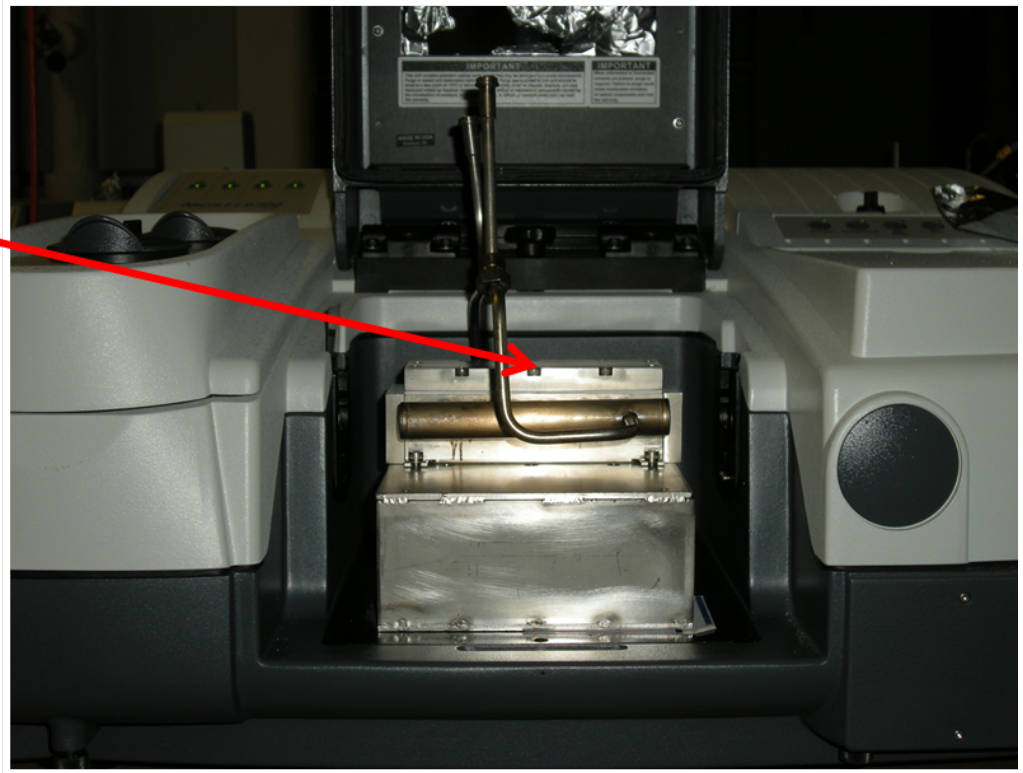


Figure: Schematic of FTIR experimental setup

Mechanism of adsorption and desorption

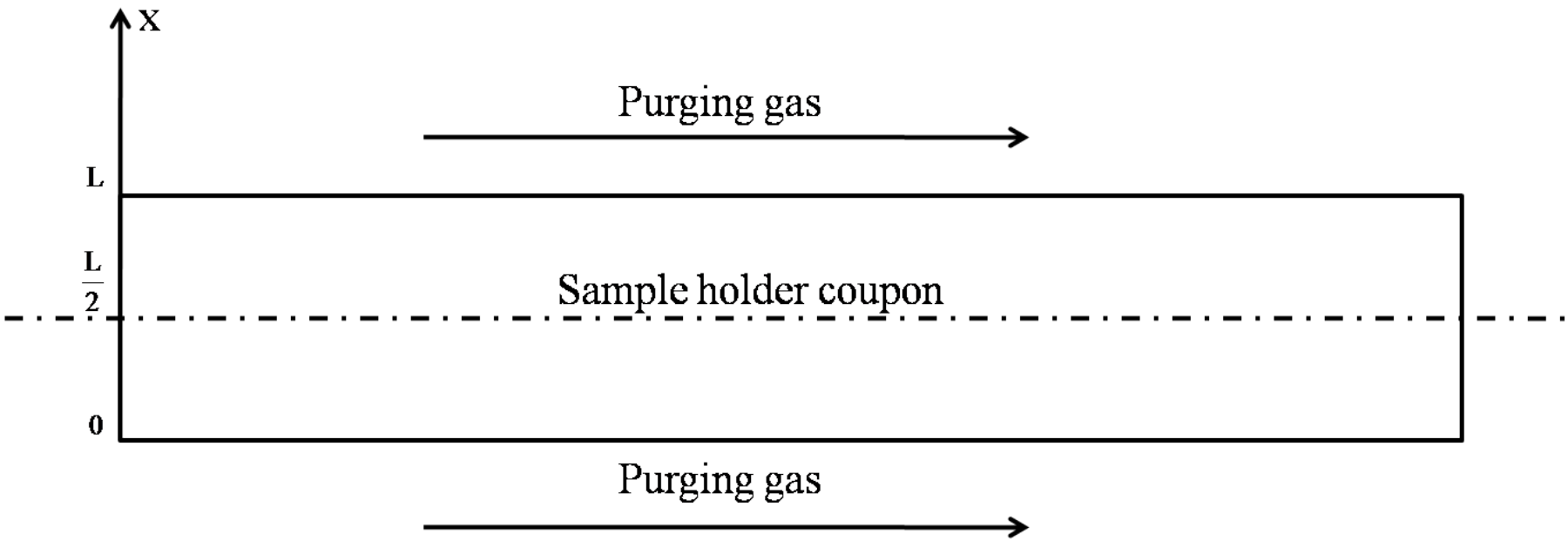


Figure: Schematic of sample holder coupon

Mechanism of adsorption and desorption

The adsorption and desorption rate:

$$r_a = k_a(S_0 - C_s)C_g$$
$$r_d = k_d C_s$$

- k_a adsorption rate coefficient
- k_d desorption rate coefficient
- C_g moisture concentration in the gas phase
- C_s moisture concentration on the surface
- S_0 total concentration of available sites of all the available layers under certain challenge concentration

Mechanism of adsorption and desorption

The rate coefficients:

$$k_a = k_{a_0} \exp(\frac{-E_a}{RT})$$

$$k_d = k_{d_0} \exp(\frac{-E_d}{RT})$$

k_{a_0} adsorption prefactor

k_{d_0} desorption prefactor

E_a total adsorption energy

E_d total desorption energy

R gas constant

T temperature

Mechanism of adsorption and desorption

Total adsorption and desorption energy:

$$E_a = E_{a_1}\frac{C_{s_0} - C_s}{C_{s_0}} + E_{a_2}\frac{C_s}{C_{s_0}}$$

$$E_d = E_{d_1}\frac{C_{s_0} - C_s}{C_{s_0}} + E_{d_2}\frac{C_s}{C_{s_0}}$$

E_{a_1} total chemical adsorption energy

E_{a_2} total physical adsorption energy

E_{d_1} total chemical desorption energy

E_{d_2} total physical desorption energy

Governing Equations

Moisture concentration in gas phase:

$$\frac{\partial C_g}{\partial t} = D_e \frac{\partial^2 C_g}{\partial x^2} + (1-\epsilon)\frac{3}{r}[k_d C_s - k_a C_g (S_0 - C_s)]$$

Moisture concentration on the surface:

$$\frac{\partial C_s}{\partial t} = [k_a C_g (S_0 - C_s) - k_d C_s]$$

- D_e effective diffusivity
- ϵ porosity of coupon
- r radius of nanoparticle
- t time

Experimental Data

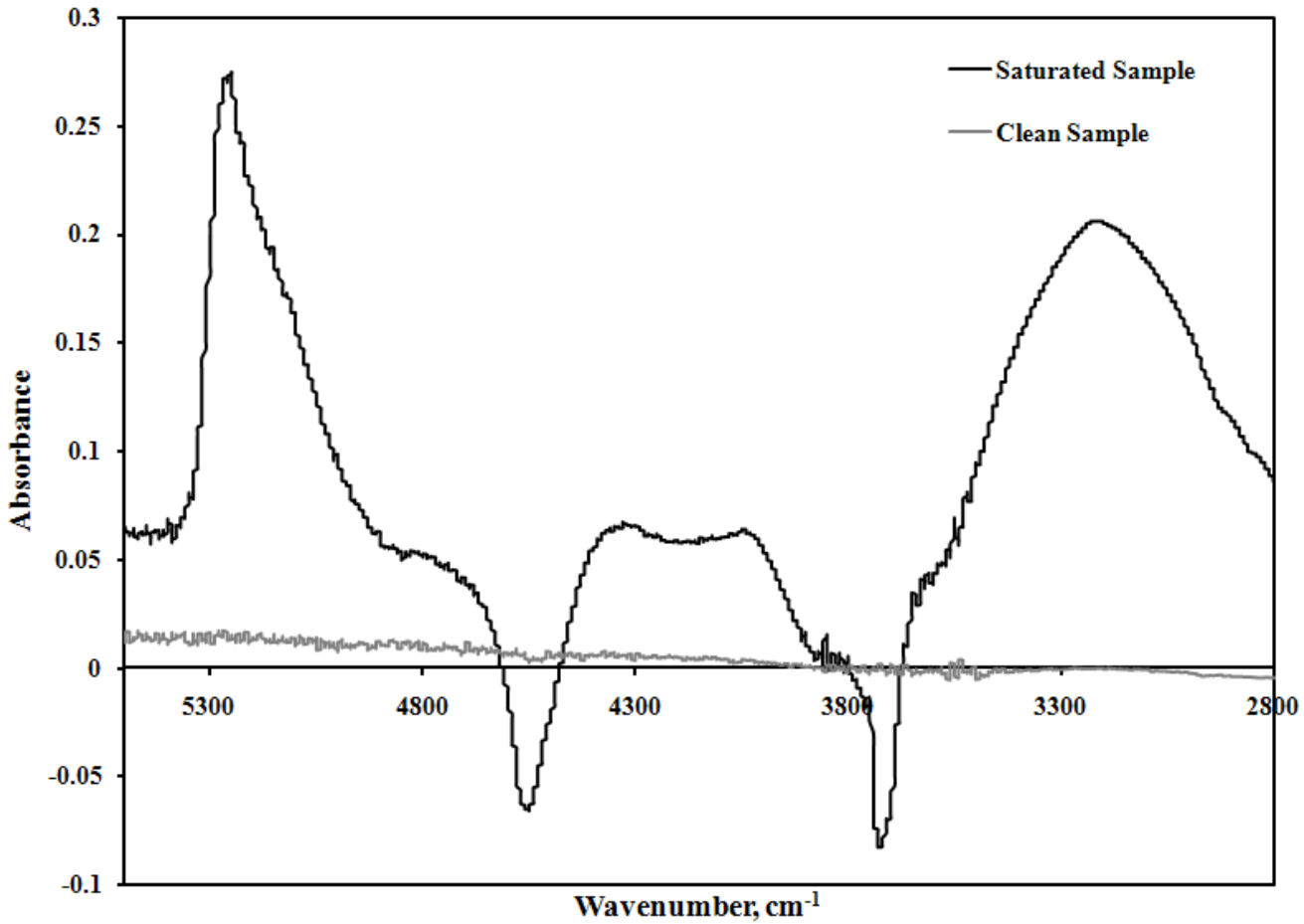


Figure: Moisture absorbance peak on SiO_2 (20nm)

Experimental Data

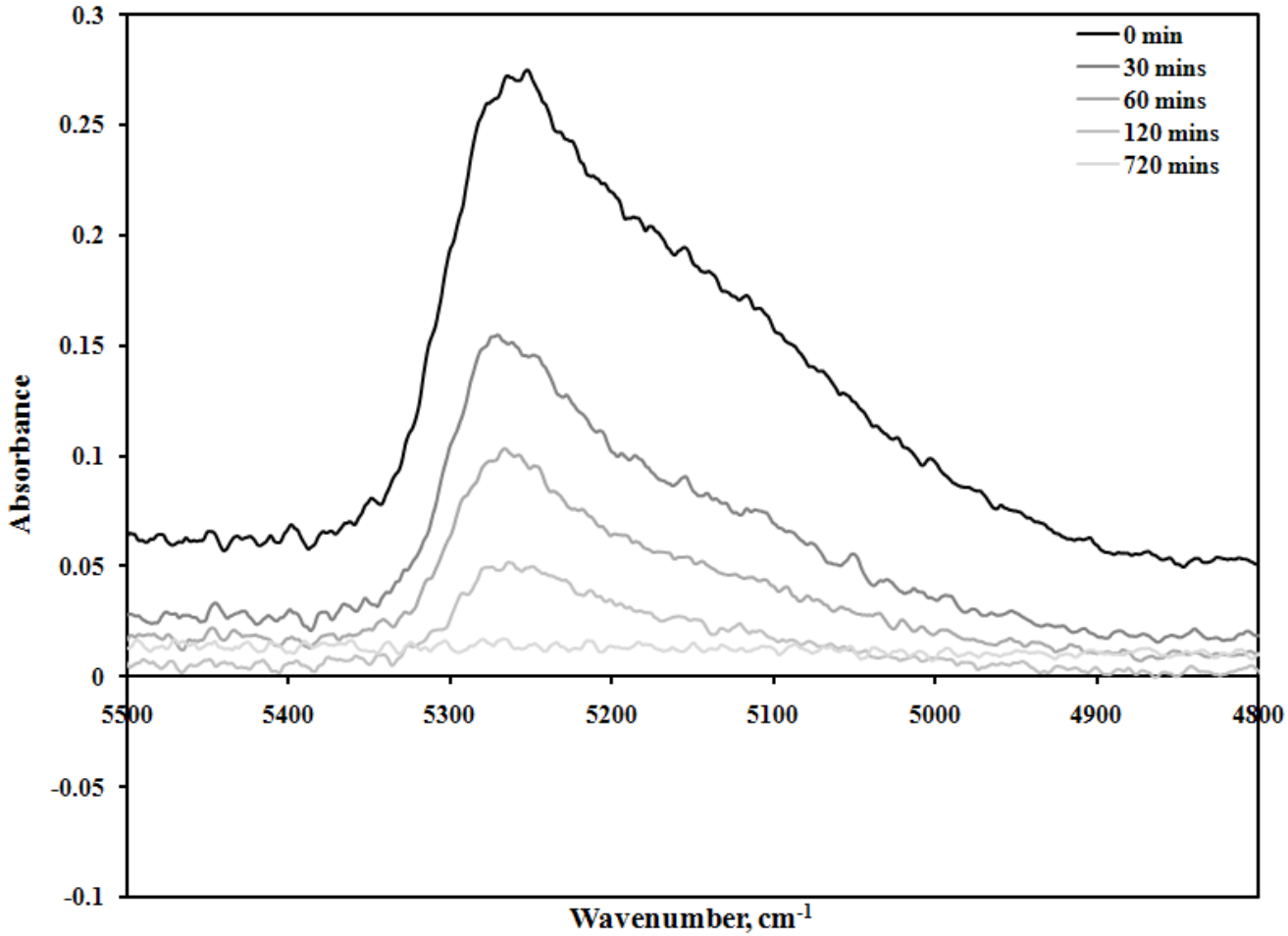


Figure: Spectrum of SiO_2 changes with time during the purge phase

Model verification

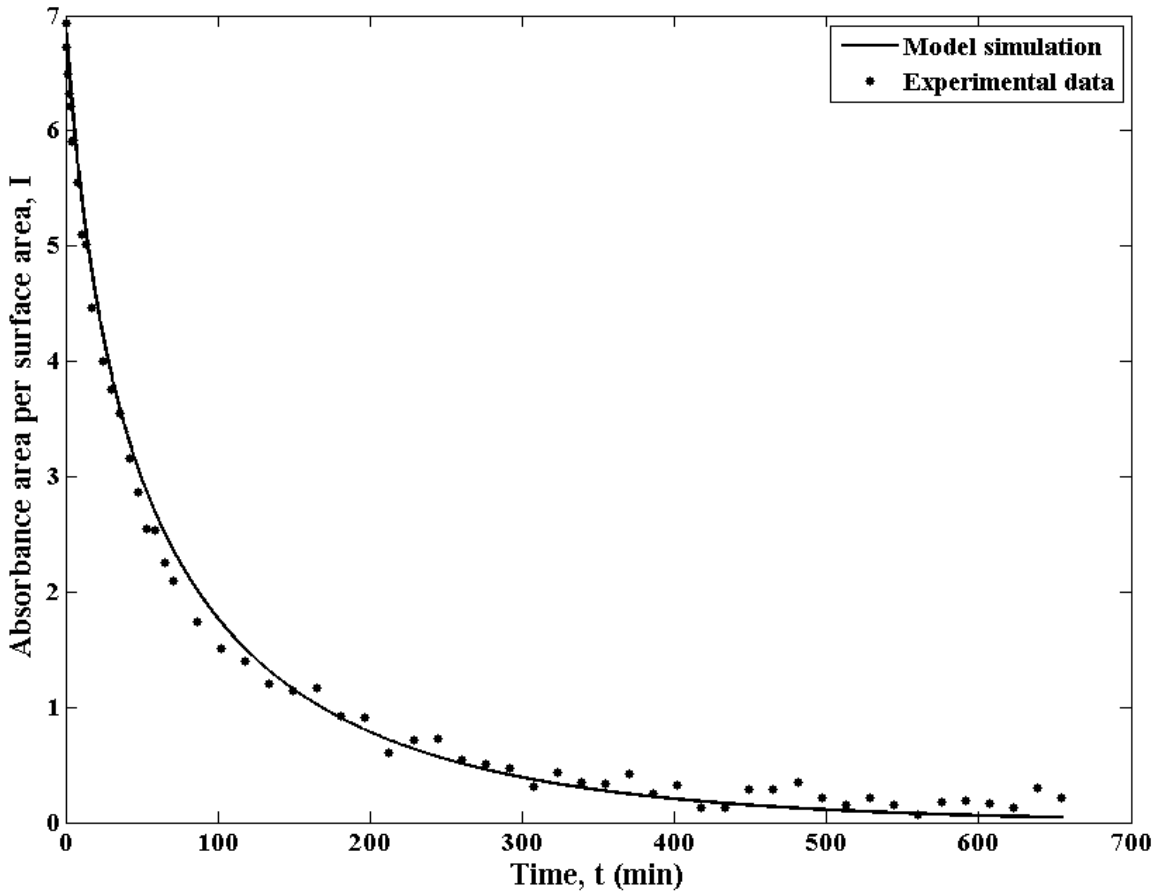


Figure: Model simulation and experimental data for SiO_2 (20nm)

Model verification

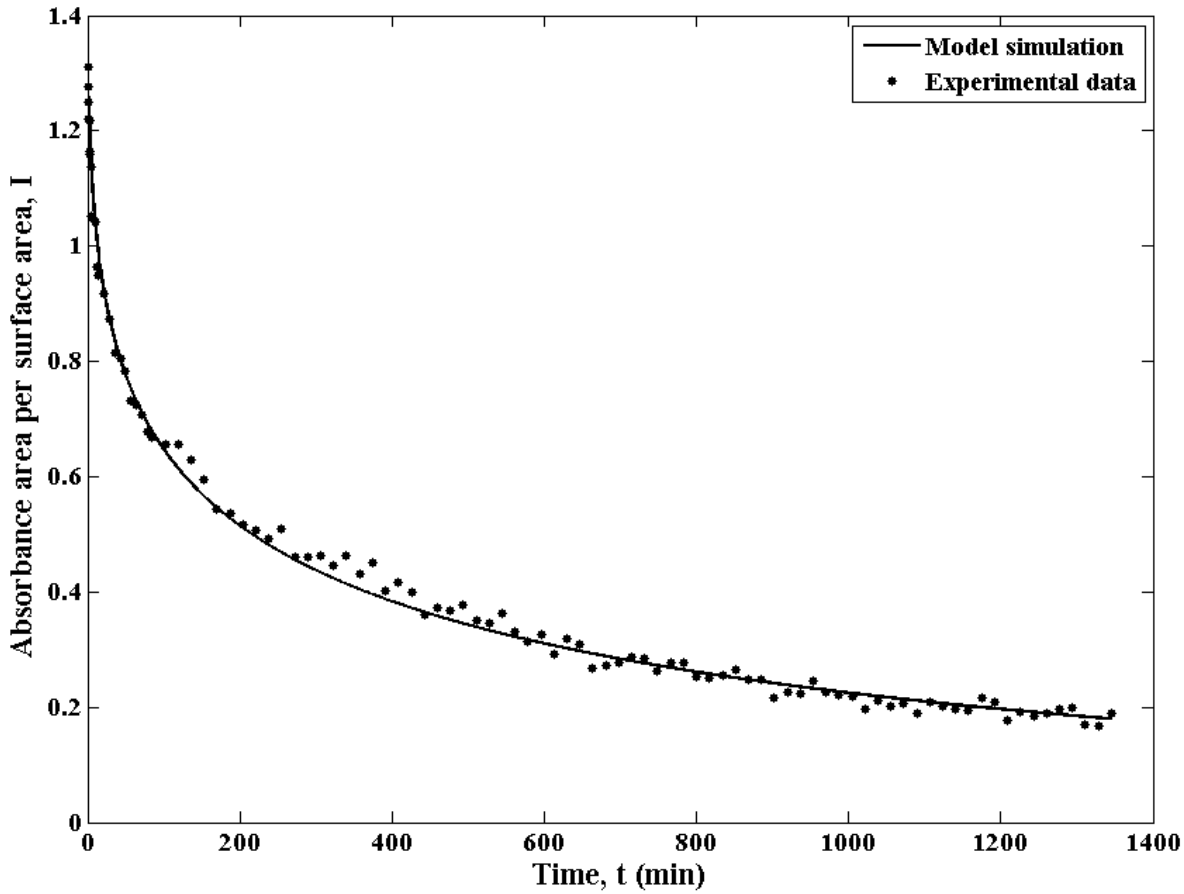


Figure: Model simulation and experimental data for CeO_2 (20nm)

Model verification

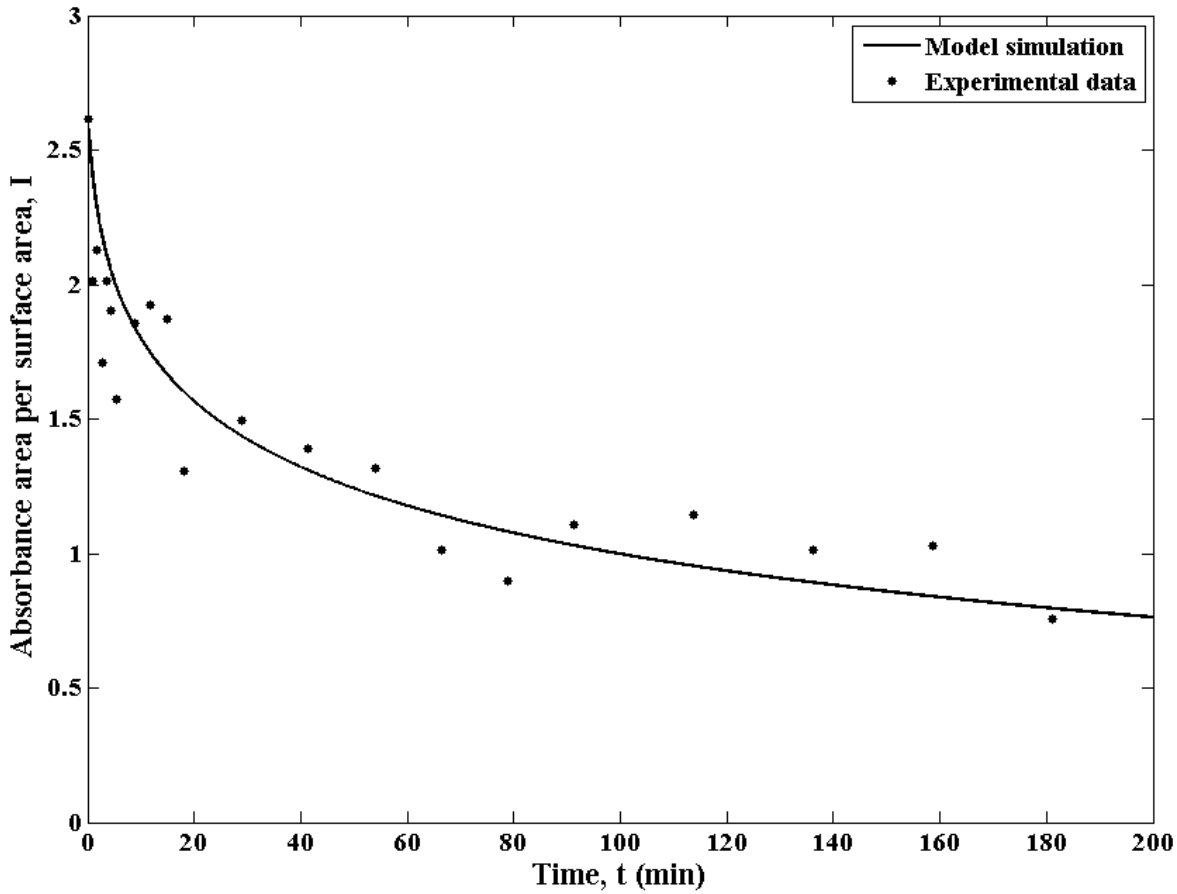


Figure: Model simulation and experimental data for HfO_2 (20nm)

Model verification

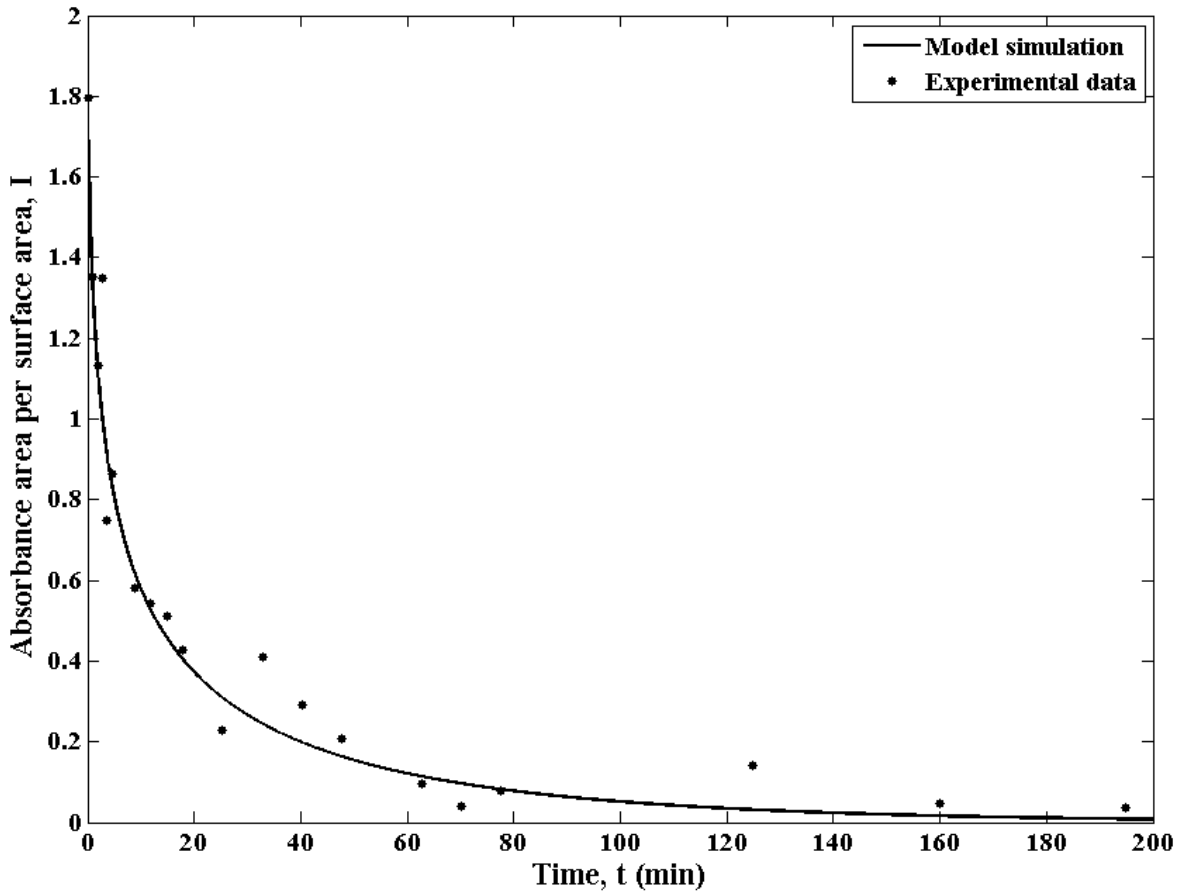


Figure: Model simulation and experimental data for HfO_2 (100nm)

Affinity for water molecules

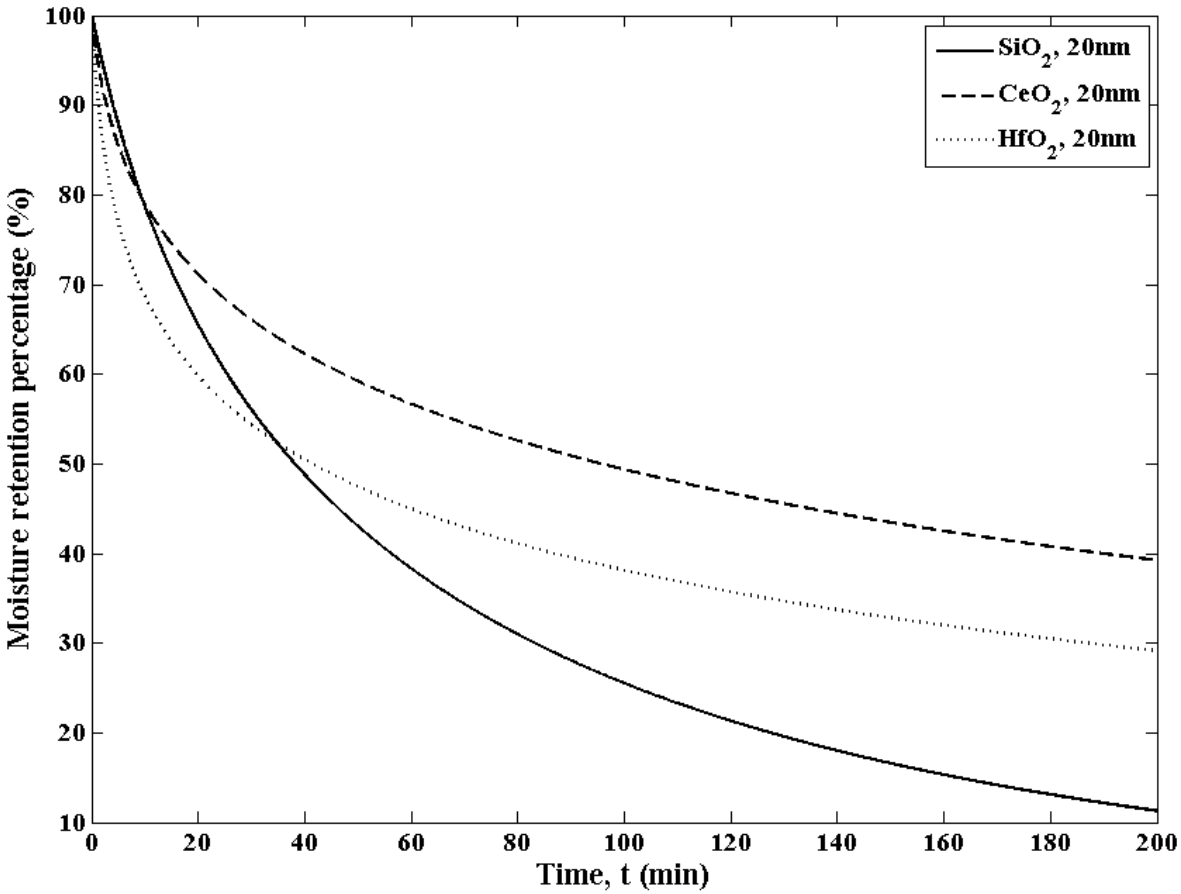


Figure: Moisture retention percentage of different nanoparticle species with the same size

Affinity for water molecules

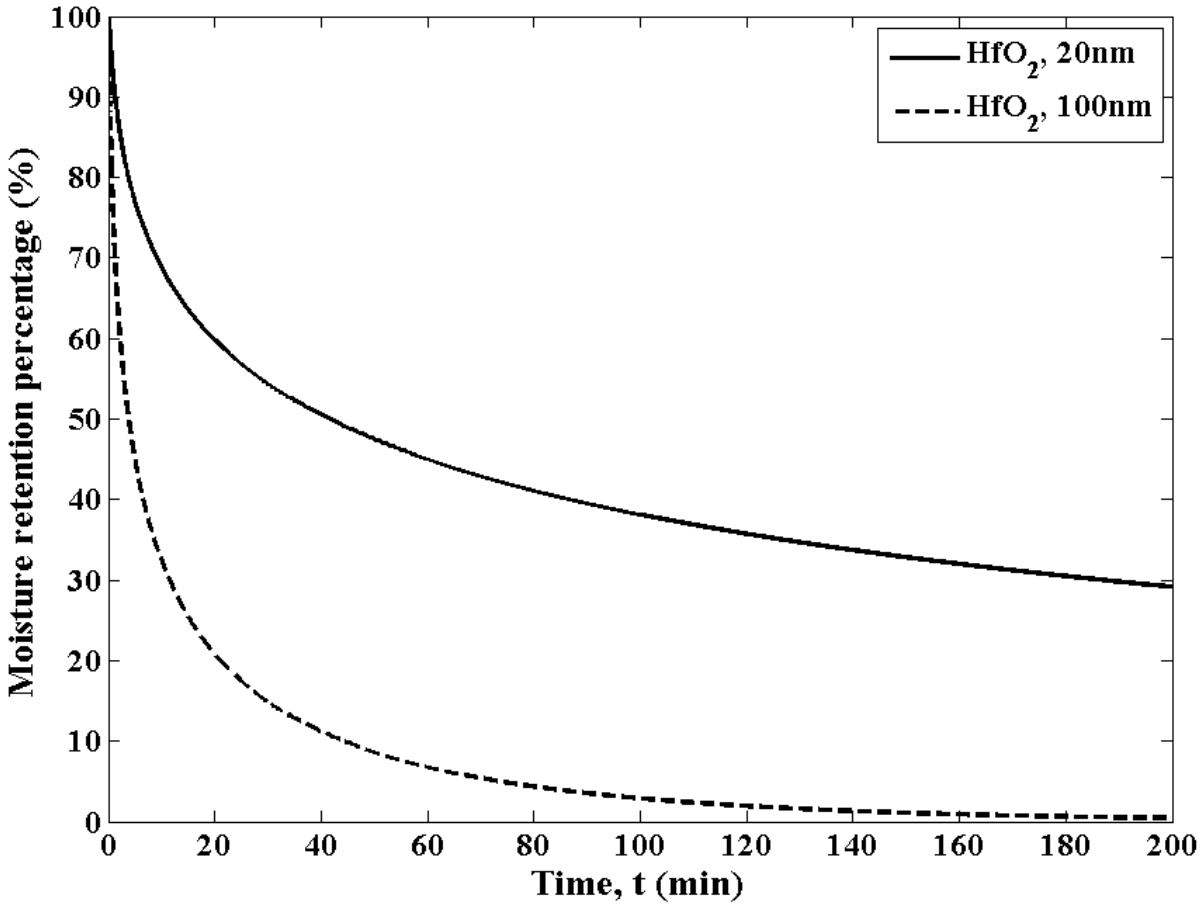


Figure: Moisture retention percentage of the same nanoparticle species with different sizes

Parametric study

Table: Saturated surface concentration and total surface available sites for different NPs

Sample 20nm	Surface available sites S_0 (mol/m^2)	Saturated surface concentration C_{s_0} (mol/m^2)	Surface available site coverage $\theta(\%)$
SiO_2	7.1×10^{-6}	2.8×10^{-6}	39
CeO_2	5.5×10^{-7}	5.4×10^{-7}	98
HfO_2	1.5×10^{-6}	1.1×10^{-6}	73

Table: Parameters of adsorption and desorption coefficient functions for different NPs

Sample (20nm)	k_{a_0} (m^2/mole/s)	k_{d_0} (/s)	E_{a_1} (J/mol)	E_{a_2} (J/mol)	E_{d_1} (J/mol)	E_{d_2} (J/mol)
SiO_2	0.028	0.003	4500	4000	6000	3000
CeO_2	0.800	0.005	1200	1000	9000	2000
HfO_2	0.200	0.010	800	300	12000	1000

Parametric study

Table: Saturated surface concentration and total surface available sites for different sizes of NPs

Sample	Surface available sites S_0 (mol/m^2)	Saturated surface concentration C_{s_0} (mol/m^2)	Surface available site coverage $\theta(\%)$
HfO_2 (20nm)	1.5×10^{-6}	1.1×10^{-6}	73
HfO_2 (100nm)	8.7×10^{-7}	7.3×10^{-7}	84

Table: Parameters of adsorption and desorption coefficient functions for different sizes of NPs

Sample	k_{a_0} (m^2/mole/s)	k_{d_0} (/s)	E_{a_1} (J/mol)	E_{a_2} (J/mol)	E_{d_1} (J/mol)	E_{d_2} (J/mol)
HfO_2 (20nm)	0.20	0.010	800	300	12000	1000
HfO_2 (100nm)	1.29	0.035	600	400	6000	1200

Summary

- Surface characteristics study of nanoparticles has species effect and size effect.
- The affinity of nanoparticles for H_2O retention decreases in the order: $CeO_2 > HfO_2 > SiO_2$. The surface available sites under certain concentration decreases in the order: $SiO_2 > HfO_2 > CeO_2$.
- Nanoparticles with smaller size will have larger surface available sites and larger saturated surface concentration under certain challenge concentration. They also have higher affinity for moisture retention.

Future Work

- Study the temperature effect on moisture adsorption and desorption
- Improve the transient adsorption and desorption model to calculate number of layers in each time step
- Introduce a distribution function to indicate the moisture distribution on the surface

Acknowledgments

- Farhang Shadman, Regents' Professor, Dept. of Chemical & Environmental Engineering, University of Arizona.
- Reyes Sierra, Associate Professor, Dept. Chemical & Environmental Engineering, University of Arizona.
- SRC/SEMATECH Engineering Research Center

Thank you!