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Study of CO_2 Adsorption on Amorphous HfO_2 using PTA on the Netzsch 449

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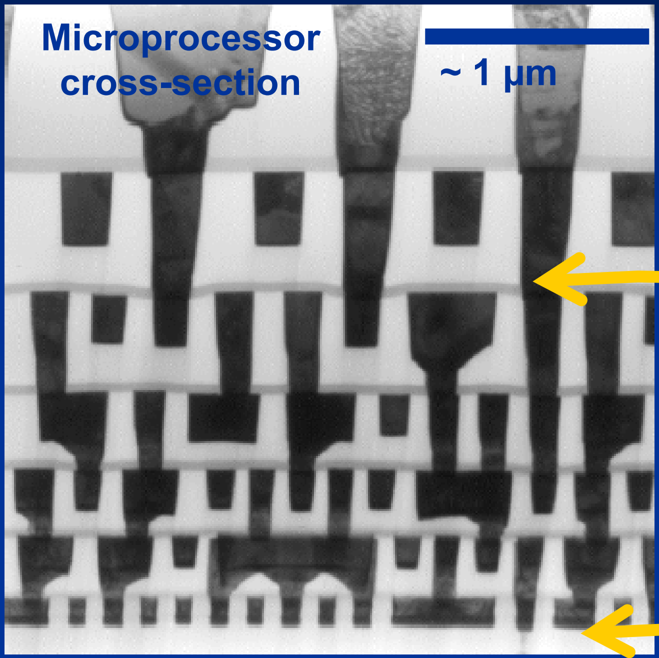
This work is part of the project on themochemistry of alternative gate dielectrics funded by Motorola and UC-SMART program.

MOTOROLA LABS
Physical Sciences Research Labs

Quest for SiO_2 replacement in the next generations of the microprocessors:



by “low-K” oxide
- to prevent cross-talk between back-side interconnects

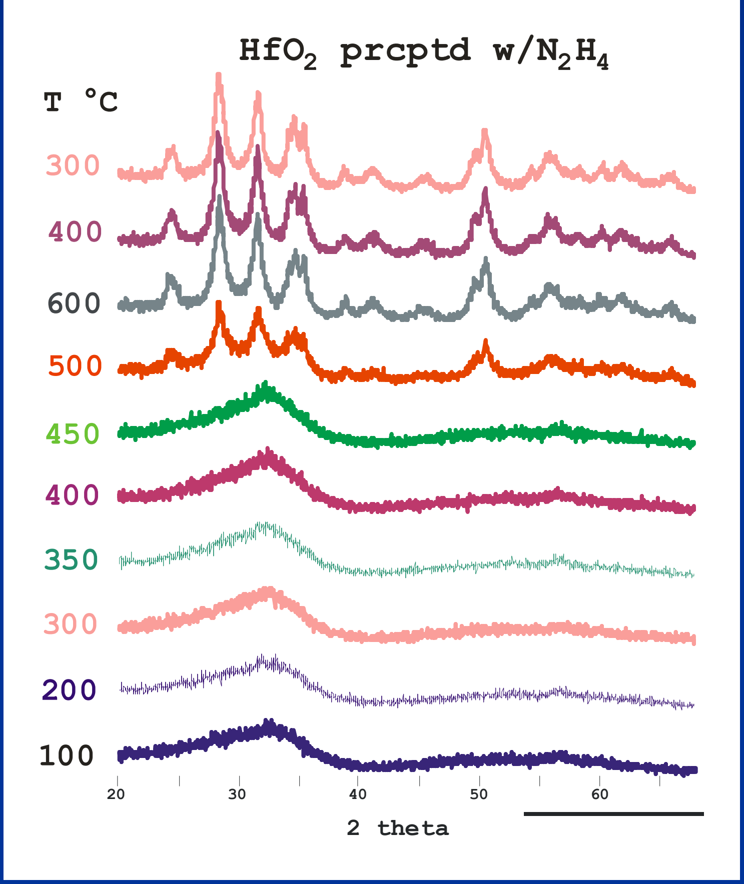
by “high-K” gate oxide
- to switch transistors faster

HfO_2 is a prospective high-*k* replacement for SiO_2 for future integrated circuits. We study energetic of amorphous and nanocrystalline hafnium oxide by high temperature oxide melt solution calorimetry to establish critical sizes where phase stability switches by surface energy terms.

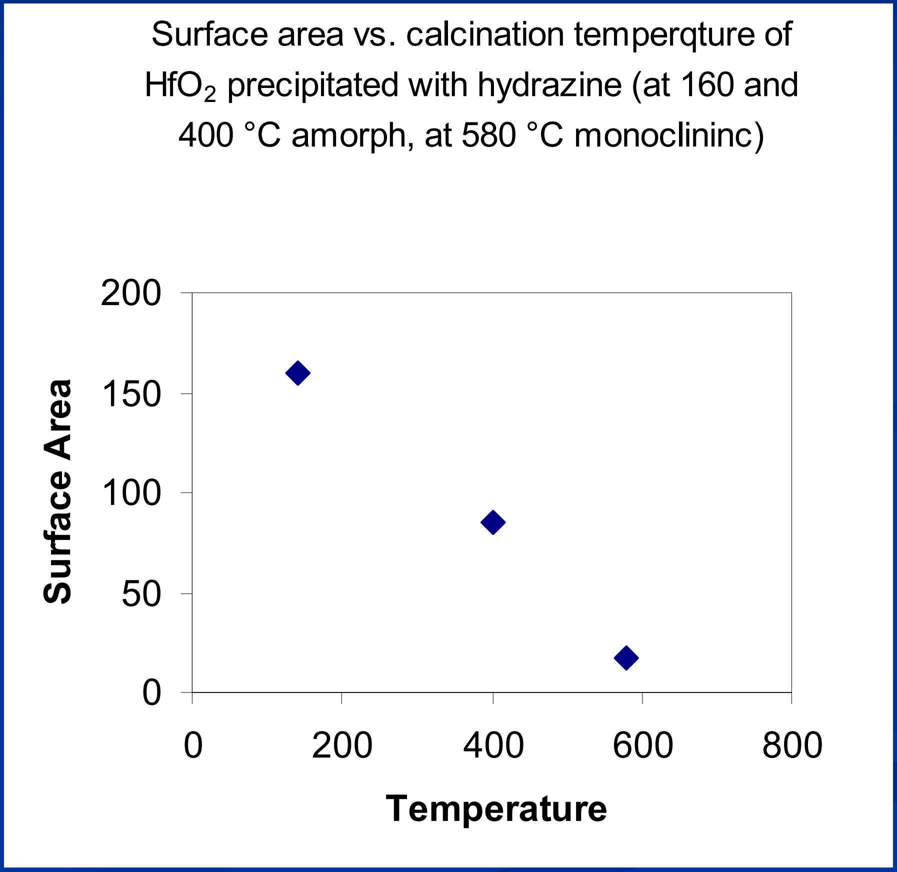
Experimental

Amorphous and crystalline HfO_2 with different surface area can be synthesized by precipitation following by controlled annealing.

HTXRD



BET

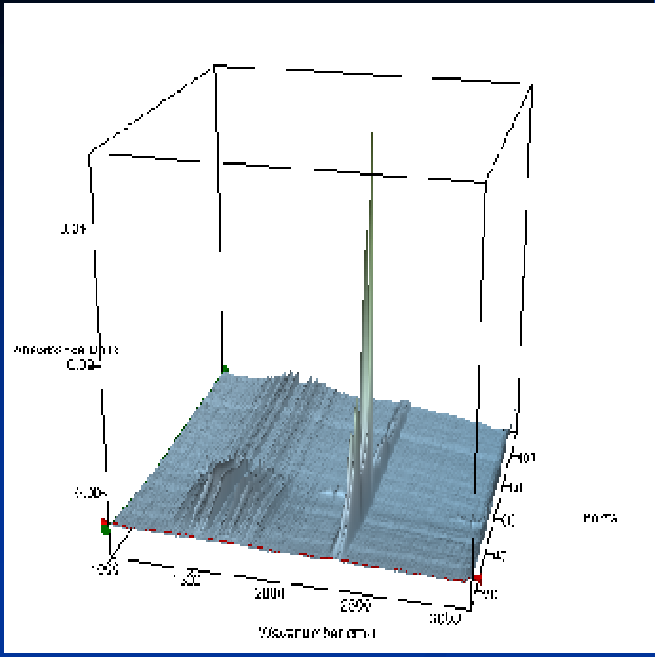


High-temperature XRD and BET on precipitated HfO_2

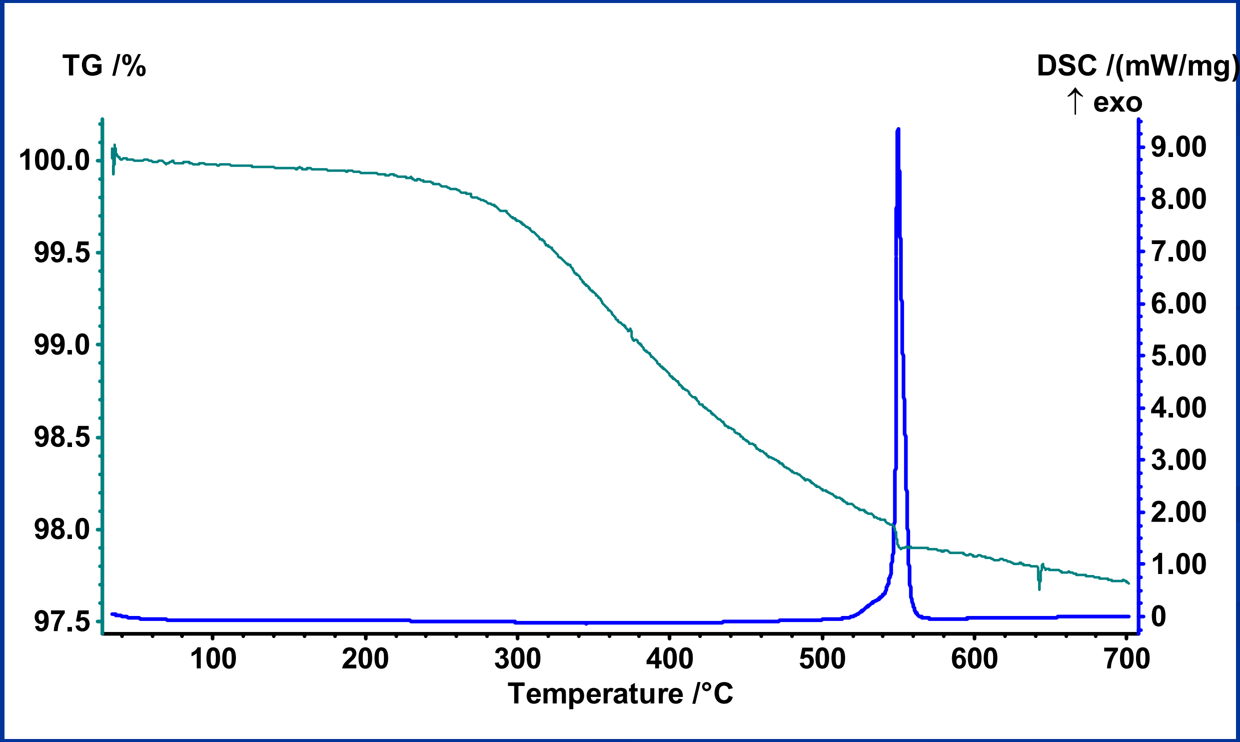
Thermal analysis of precipitated HfO_2 - water and CO_2 evolution detected by FTIR.

<u>Problem</u> :

Bulk amorphous HfO_2 can not be completely dehydrated and decarbonated without crystallizing it.



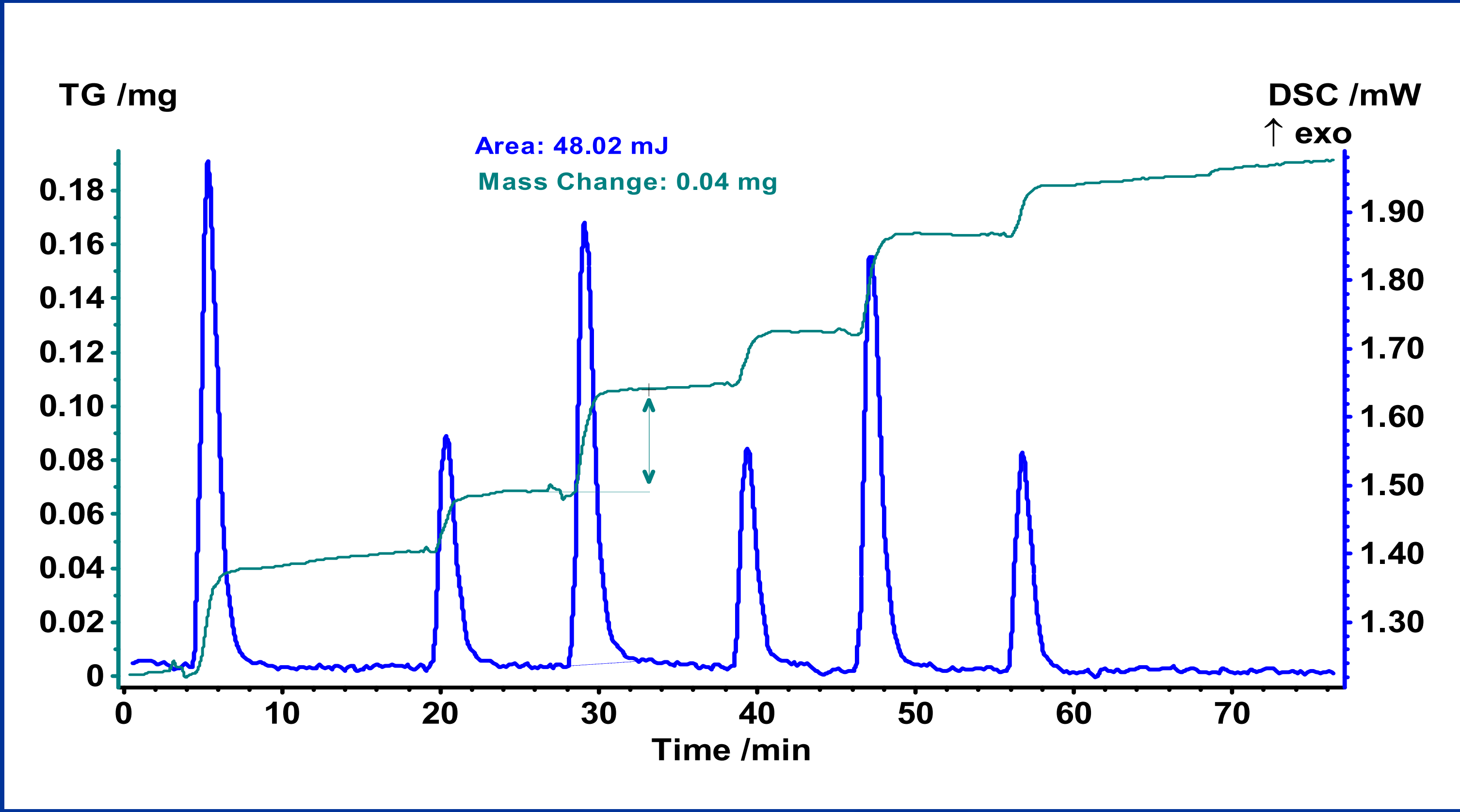
FTIR



Experimental details on CO_2 adsorption on amorphous HfO_2

- amorphous HfO_2 sample was heated in STA 449 up to 400 °C and surface area was detremined by BET to be 84.5 m^2/g

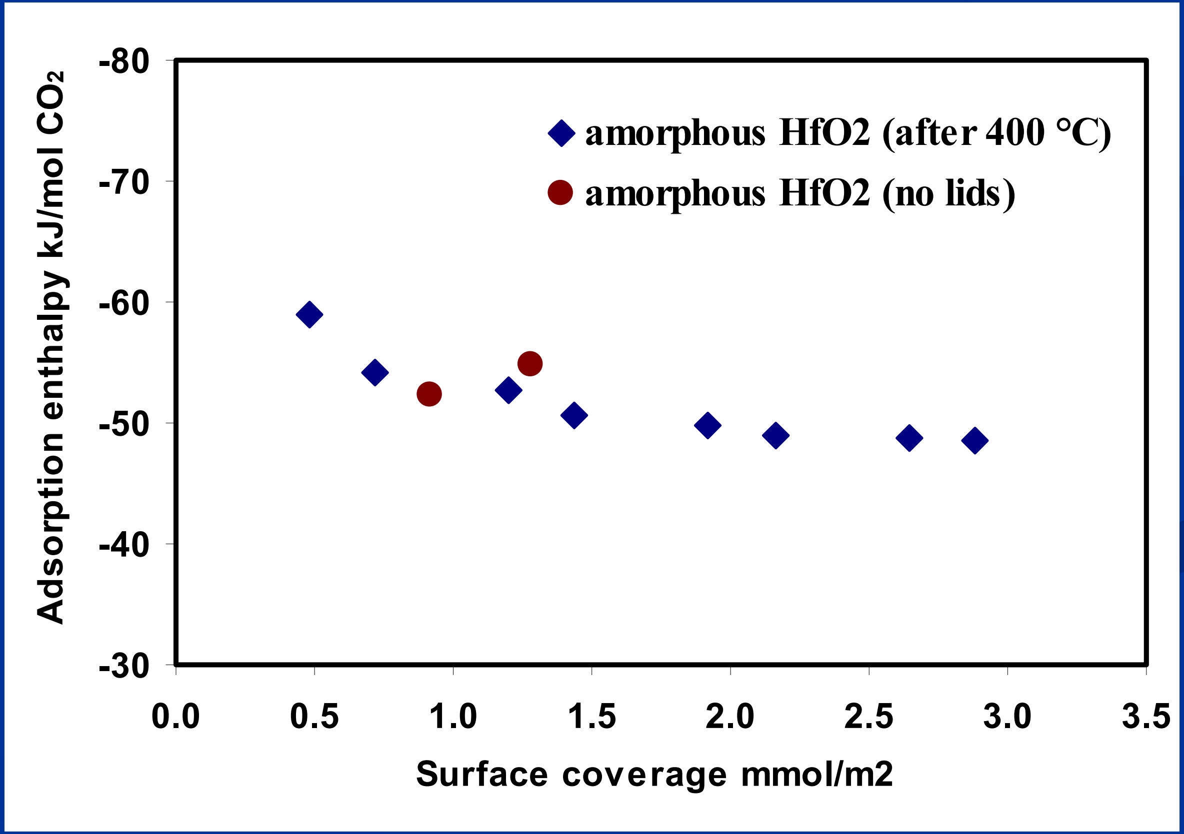
- the new portion of the sample was annealed in STA 449 and exposed to CO_2 pulses (0.25 and 1 ml volumes) injected into 40 ml/min Oxygen flow through the cell at 33 °C



Adsorption enthalpy of CO_2 on amorphous HfO_2

Sample mass: 43.38 mg
Surface area: 84.5 m^2/g (~3.7 nm particle size)
Sample surface: 3.67 m^2

exo mJ	mass gain mg	J/g CO_2	surf. cover. mmol/m^2	ΔH_{ads} kJ per mole CO_2
-53.55	0.04	-1338.8	0.48	-58.92
-24.59	0.02	-1229.5	0.72	-54.11
-47.85	0.04	-1196.3	1.20	-52.65
-23.04	0.02	-1152.0	1.44	-50.70
-45.23	0.04	-1130.8	1.92	-49.76
-22.24	0.02	-1112.0	2.16	-48.94
-44.23	0.04	-1105.8	2.64	-48.66
-22.08	0.02	-1104.0	2.88	-48.59



Corrections for drop solution calorimetry (for HfO_2)

Assuming weight loss from H_2O and zero hydration enthalpy

$H_2O_{(sorbed,\ 298)} = H_2O_{(l,298)}$	(1) ΔH_{adsH2O}	**0** kJ/mol
$H_2O_{(l,\ 298)} = H_2O_{(g,\ 975)}$	(2) $\Delta H_{(298-\ 975)}H_2O$	**69.01 kJ/mol**

$H_2O_{(sorbed,\ 298)} = H_2O_{(g,\ 975)}$

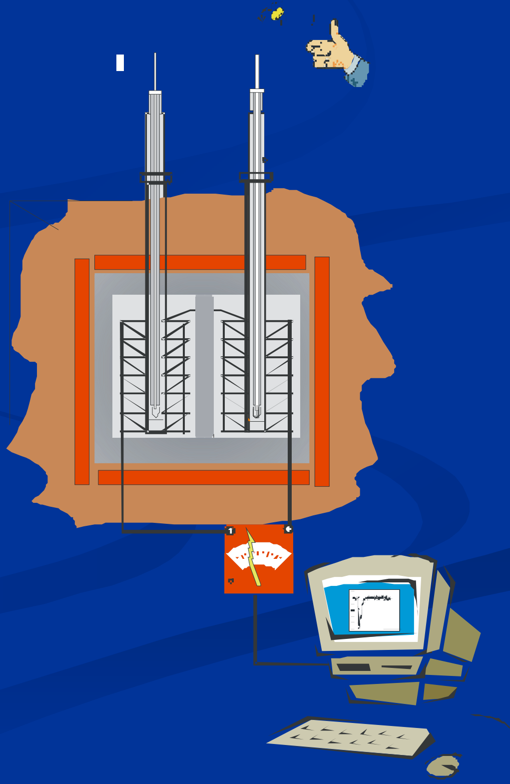
$\Delta H(3) = \Delta H(1) + \Delta H(2) = 69.01$ kJ/mol = 3.8 kJ/gram

Assuming weight loss from CO_2

$CO_{2\ (sorbed,\ 298)} = CO_{2(g,\ 298)}$	(1) ΔH_{adsCO2}	**60 kJ/mol**
$CO_{2(g,\ 298)} = CO_{2(g,\ 975)}$	(2) $\Delta H_{(298-\ 975)}CO_2$	**32.05 kJ/mol**

$CO_{2(sorbed,\ 298)} = CO_{2\ (g,\ 975)}$

$\Delta H(3) = \Delta H(1) + \Delta H(2) = 92.05$ kJ/mol = 2.1 kJ/gram



DSC/TG vs. Calvet-type calorimeter for adsorption studies:

Pros

1. Allows for annealing the sample in-situ before experiment - preparing the surface, repeating adsorption-desorption cycles without opening the cell, etc.

2. Additional information on desorption from EGA and TG.

Cons

1. Sensitivity limited vs. Calvet type.

1. Limited to constant gas-flow conditions.

3. Limited to high surface area samples with large adsorption enthalpies.