Structure and dielectric properties of HfO_2 films prepared by sol-gel route

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Outline

1. Introduction:
   - HfO_2 properties and applications
2. Experimental
   - Film preparation *sol-gel*
   - Film characterisation
3. Results and discussion
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   - laser annealing
4. Conclusions

Introduction

HfO_2 properties:

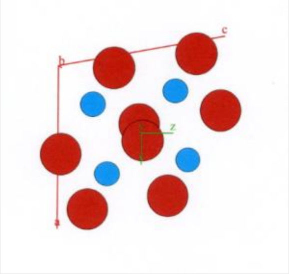
- High density (9.86 g/cm^2)
- High melting point (2800^0C)
- High thermal and chemical stability
- Large heat of formation (271 Kcal/mol)
- Large band gap (5.86 eV)
- High refractive index (~ 2.00)
- **High dielectric constant ($k \approx 15\text{-}25$)**
- Stable bulk structures
  - **monoclinic: symmetry, P121/c1, SGP- (14)**

    (a = 0.51156nm, b= 0.51722 nm, c= 0.52948 nm , β = 99,2)
  - **orthorhombic: symmetry , Pbca , SGP- (61)**

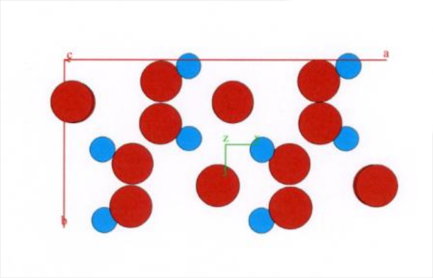
    (a = 1.0017 nm , b= 0.5228 nm, c= 0.506 nm)
- **High temperature structures**

  (1700°C) tetragonal (a = 0.515 nm, c = 0.525 nm), symmetry P42/nmc

  (2600°C) cubic (a = 0.511), symmetry F3m3



Monoclinic
[010] HfO_2



Orthorhombic
[001] HfO_2

Introdution

Applications:

- in micro and optoelectronics,
  - *high k material* (as replacing SiO_2) in electronic and optoelectronic devices
  - optical coatings when high optical damage thresholds are needed
  - waveguide fabrication

- as material for nanofiltration membranes
- films with high pencil hardness (over 9H) and hydophobicity
- protection material against oxidation/corrosion

Introdution

- HfO_2 thin films can be prepared by various methods:
  - Atomic Layer Deposition,
  - Pulsed Laser Deposition,
  - Chemical Vapor Deposition,
  - Radio Frequency Sputtering
  - Plasma oxidation of Hf film

- All mentioned techniques require high temperature treatments that induce a deterioration of the device performance and reliability

- The sol–gel process offers an alternative method to avoid the deterioration of film properties by high thermal treatment

Experimental

- **The reagents:**

- Hf-ethoxide $Hf(OC_2H_5)_4$ (Alfa Aesar), Hf-pentadionate and Hf-chloride, as HfO_2 source,

- acetyl acetone AcAc (Fluka) as chelating agent and

- absolute alcohol p.a. (Merck) as solvent.

- Molar ratio: $Hf(OC_2H_5)_4$/Acac = 1

- **Solution preparation: mixing of the reagents in N_2 atmosphere at 100^0C for two hours when staring with Hf-ethoxide, and ambient atmosphere for the other precursors.**

Experimental

- **Film deposition:**
  - **substrates:** ***[100] silicon wafer***
  - **deposition method:** ***dip-coating, 5 cm/min***

- **Film drying and thermal crystallization:**
  - **drying 10 min at 100 °C**
  - **precursor species elimination and densification 30 min at 400, 600, 800°C**

- **Laser annealing:**
  - **XeCl Lambda Physics excimer laser (l = 308 nm, tFWHM = 10 ns) using a homogenised laser beam spot with an area of about 1cm^2, with:**
    - **fluences between 30 and 120 mJ/cm^2 and**
    - **different number of pulses between 100 and 10000.**

Experimental

Films characterisation

- *High resolution TEM* **imaging using a Topcon 002 B electron microscope**
- **Conventional TEM imaging and SAED pattern using a Jeol 200CX microscope**

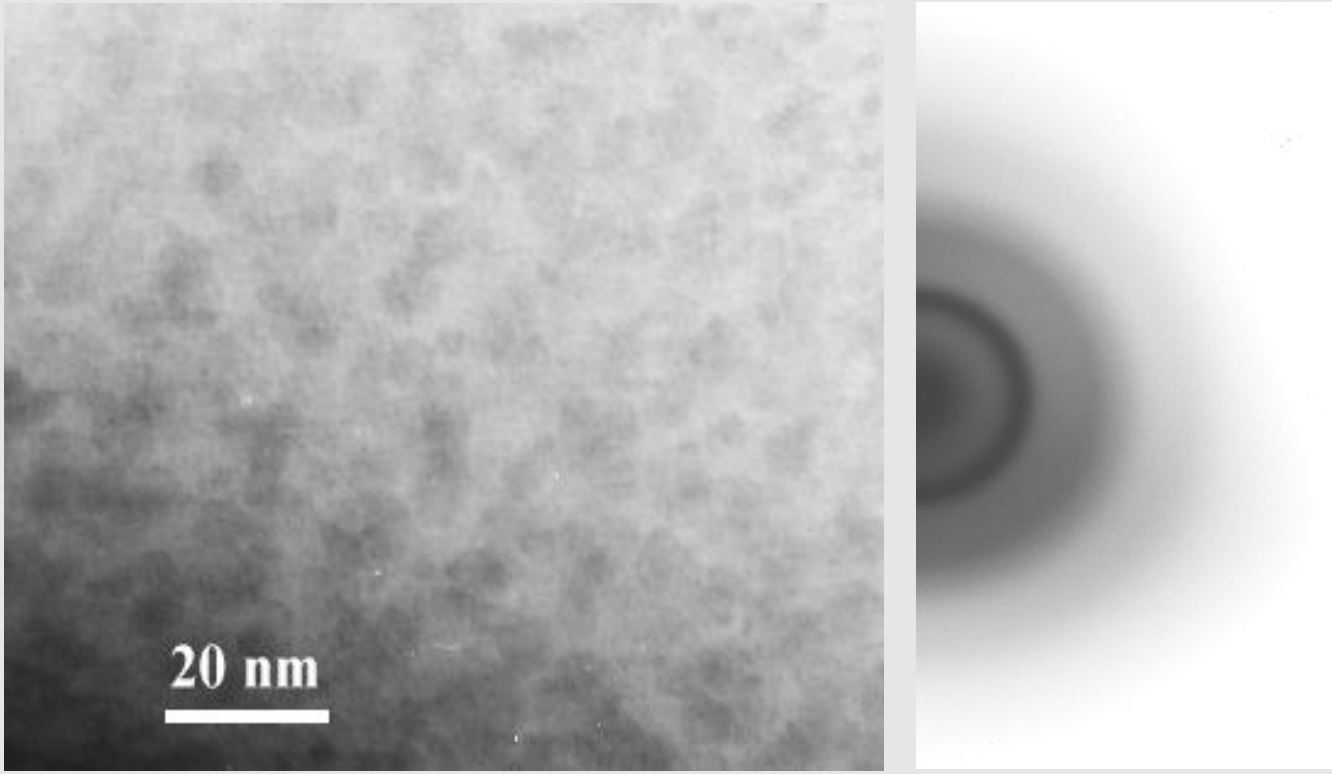
- **TEM specimen preparation by two methods :**
  Cross section (XTEM) preparation using the conventional methods with
  mechanical and ion-milling (Gatan 691A- PIPS)

- ***AFM images***

- ***RBS measurements***

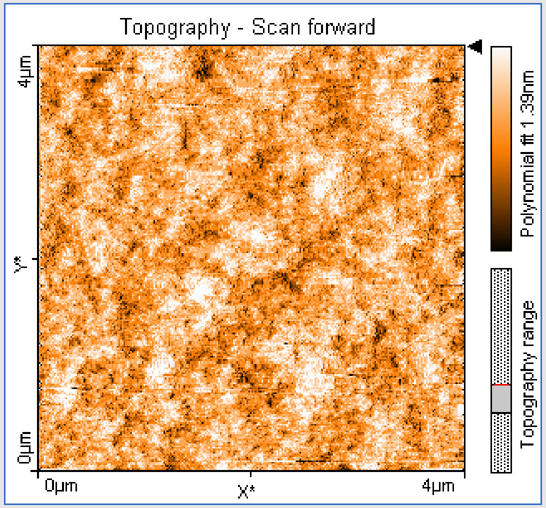
- ***Dielectric constant measuremenst***

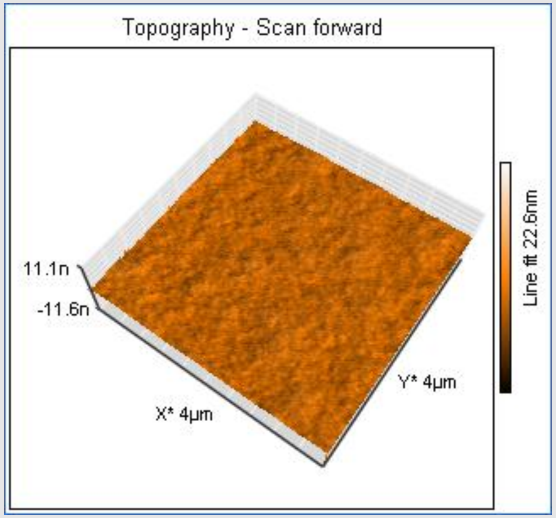
Thermal annealing



Plan view conventional TEM image and SAED pattern from a HfO_2 sol-gel film dried at 100ºC and supplementary annealed at 150ºC for 30 minutes, to increase the stability in the microscope (Hf-etoxide precursor)

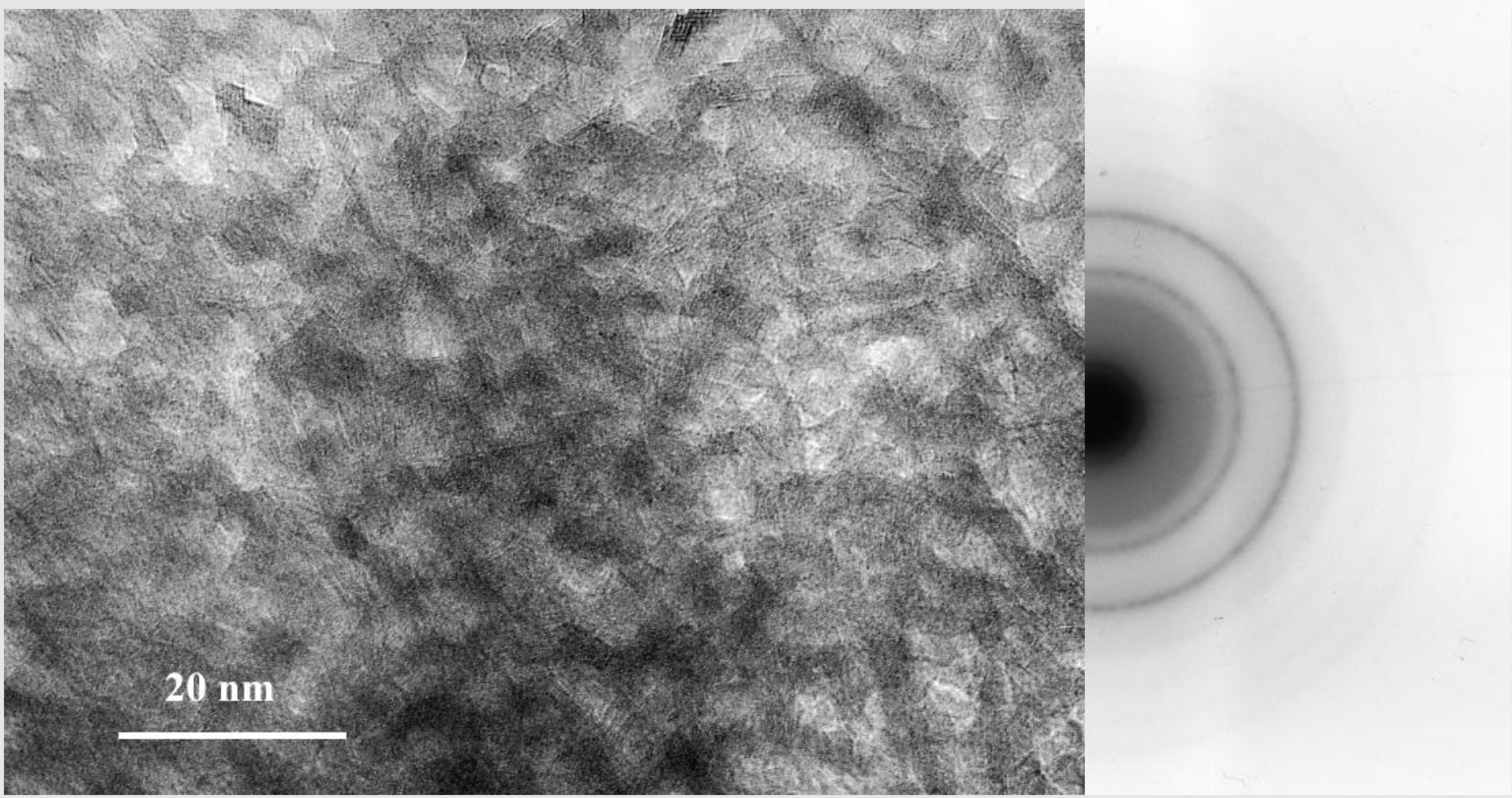
Thermal annealing





- AFM images of the dip coated films – 1 layer dried at 100°C
  - Very low RMS roughness: 0.23 nm

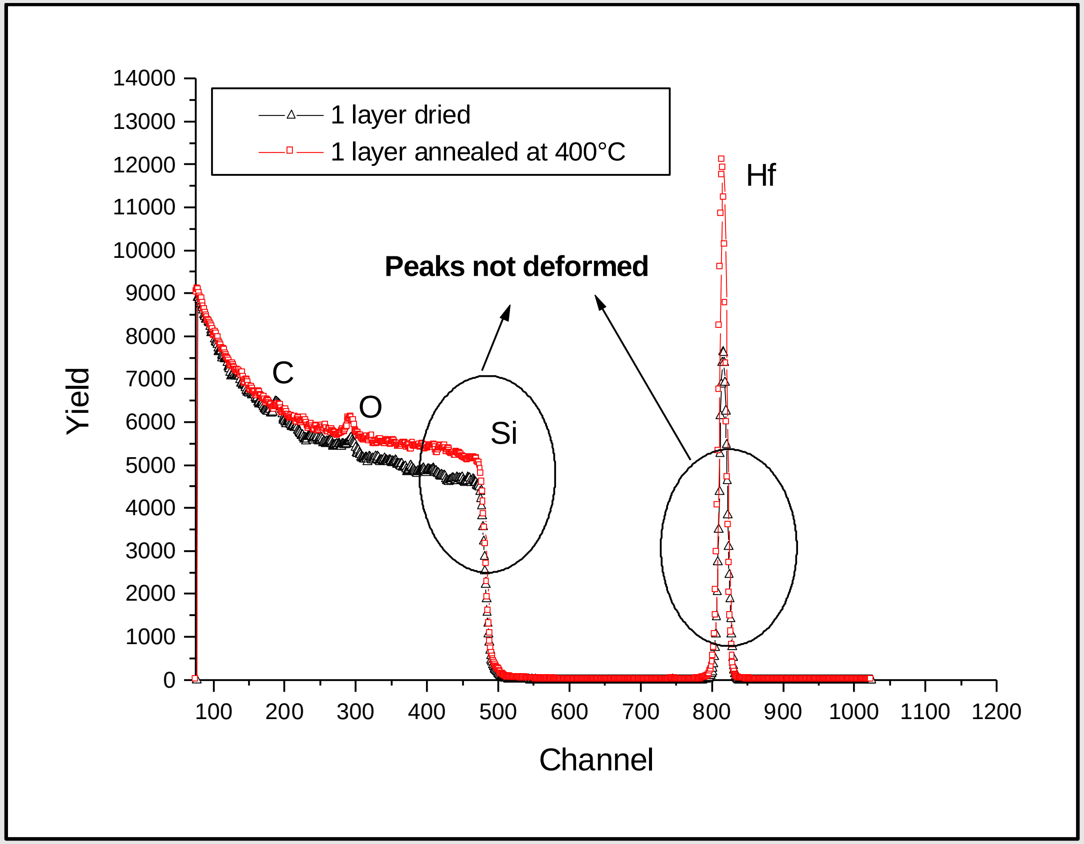
Thermal annealing



Plan view conventional TEM image and SAED pattern from a HfO_2 double layer annealed at 400ºC

The structure is still amorphous with a beginning of crystallization

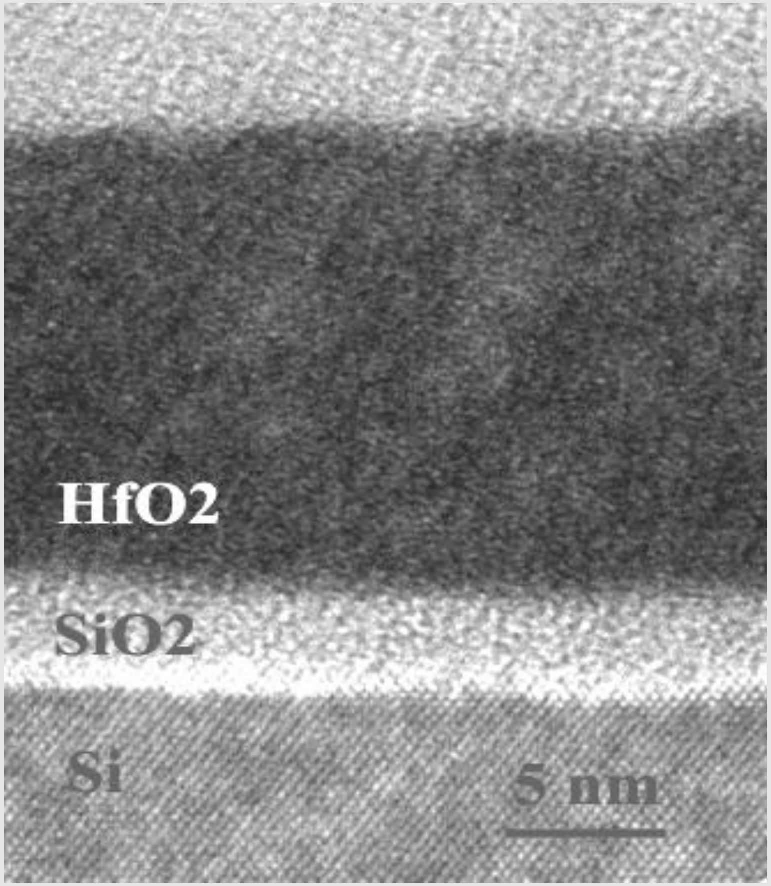
Thermal annealing



RBS spectra of the dried and thermally treated film at 400^{0}C

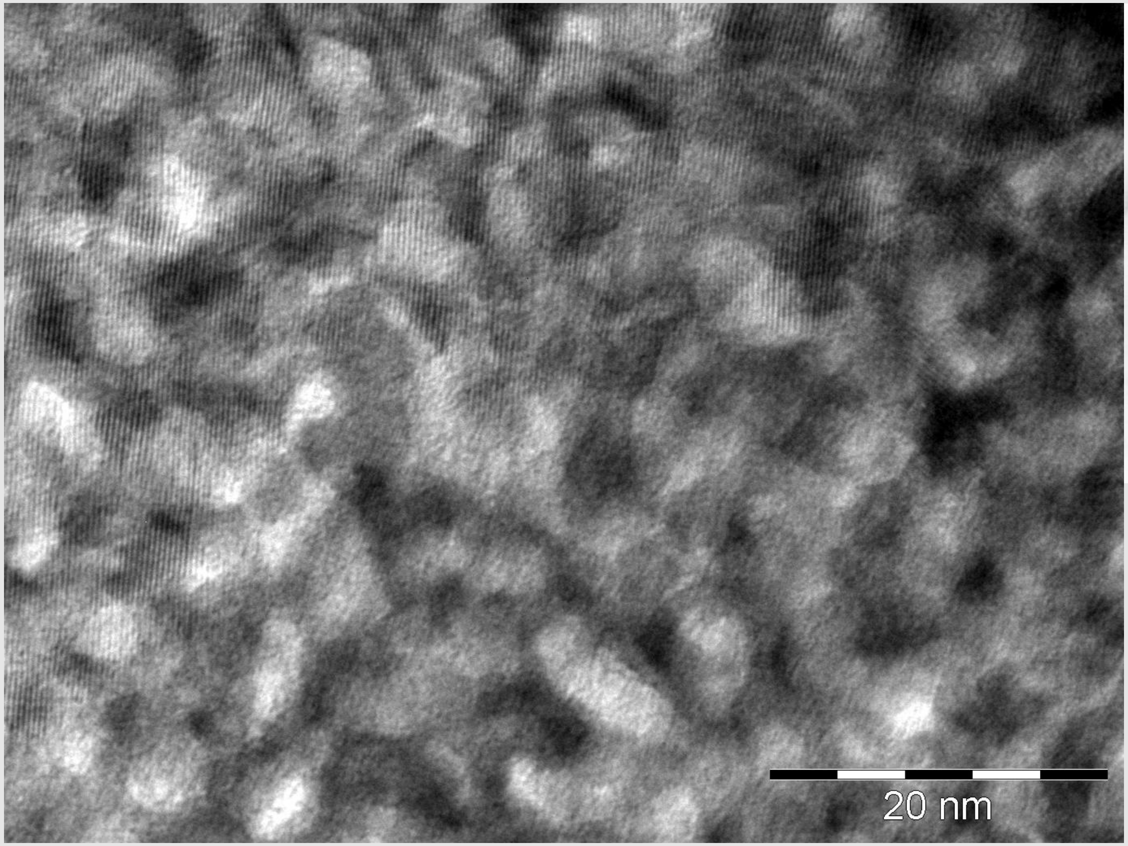
No traces of precursors are revealed by the RBS spectra after the 400^{o}C annealing of the HfO2 films

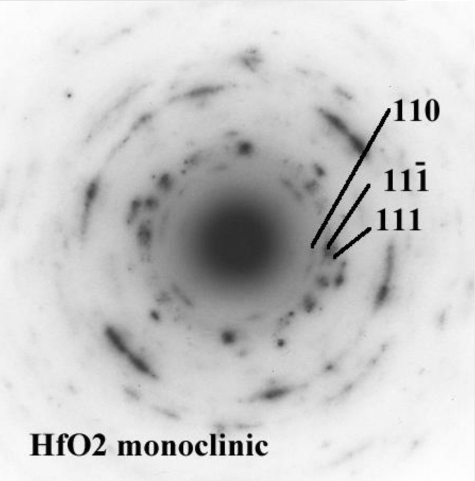
Thermal annealing



XTEM images of an amorphous sol-gel HfO_2 mono-layer film after annealing at 400°C..

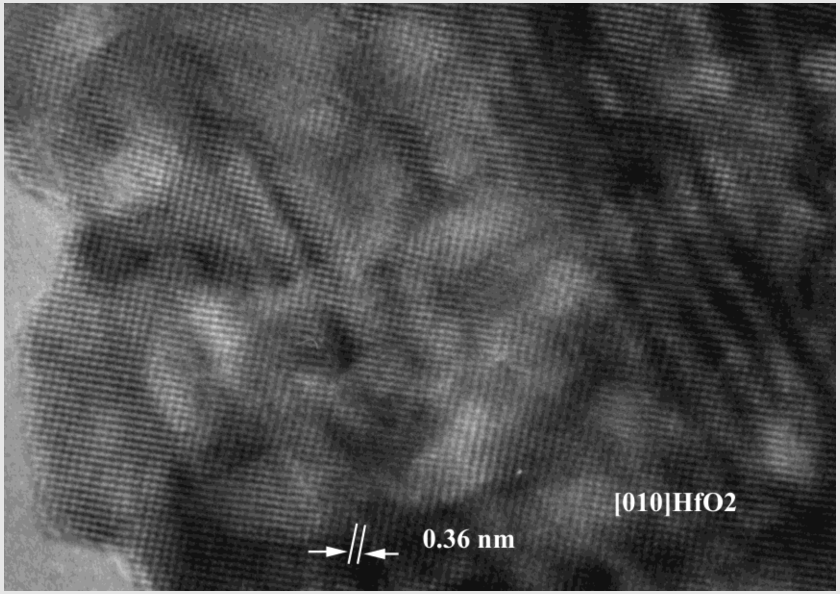
Thermal annealing

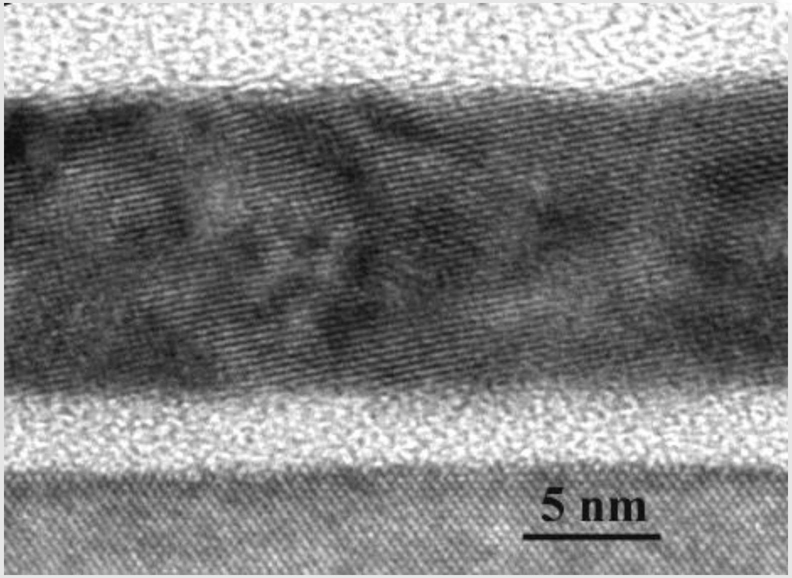




Plan view HRTEM image of a double layer film annealed at 600ºC

Thermal annealing

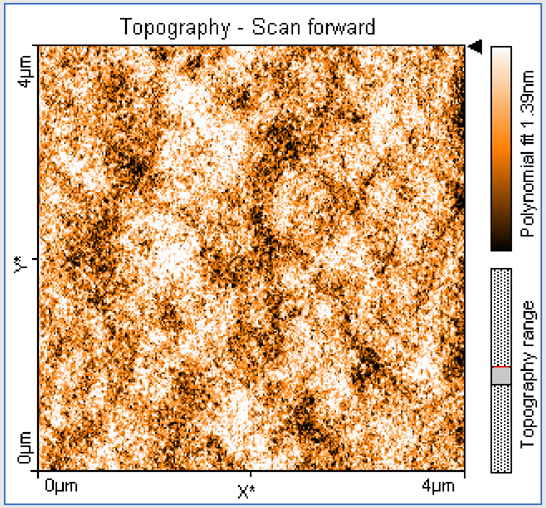


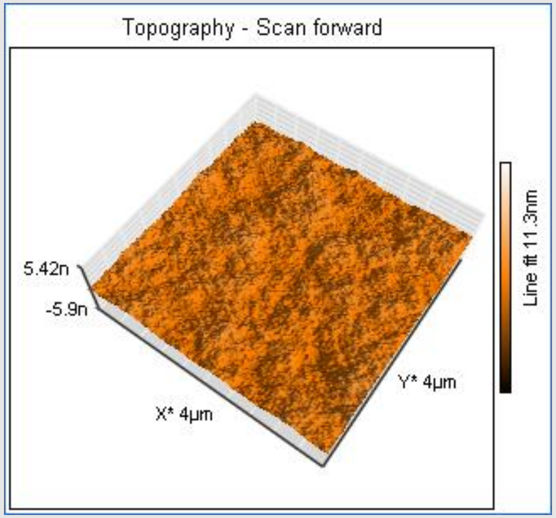


HRTEM plan view of HfO_2 mono-layer film annealed at 600°C

XTEM observation of a monolayer HfO_2 sol-gel film obtained by thermal annealing at 600^oC

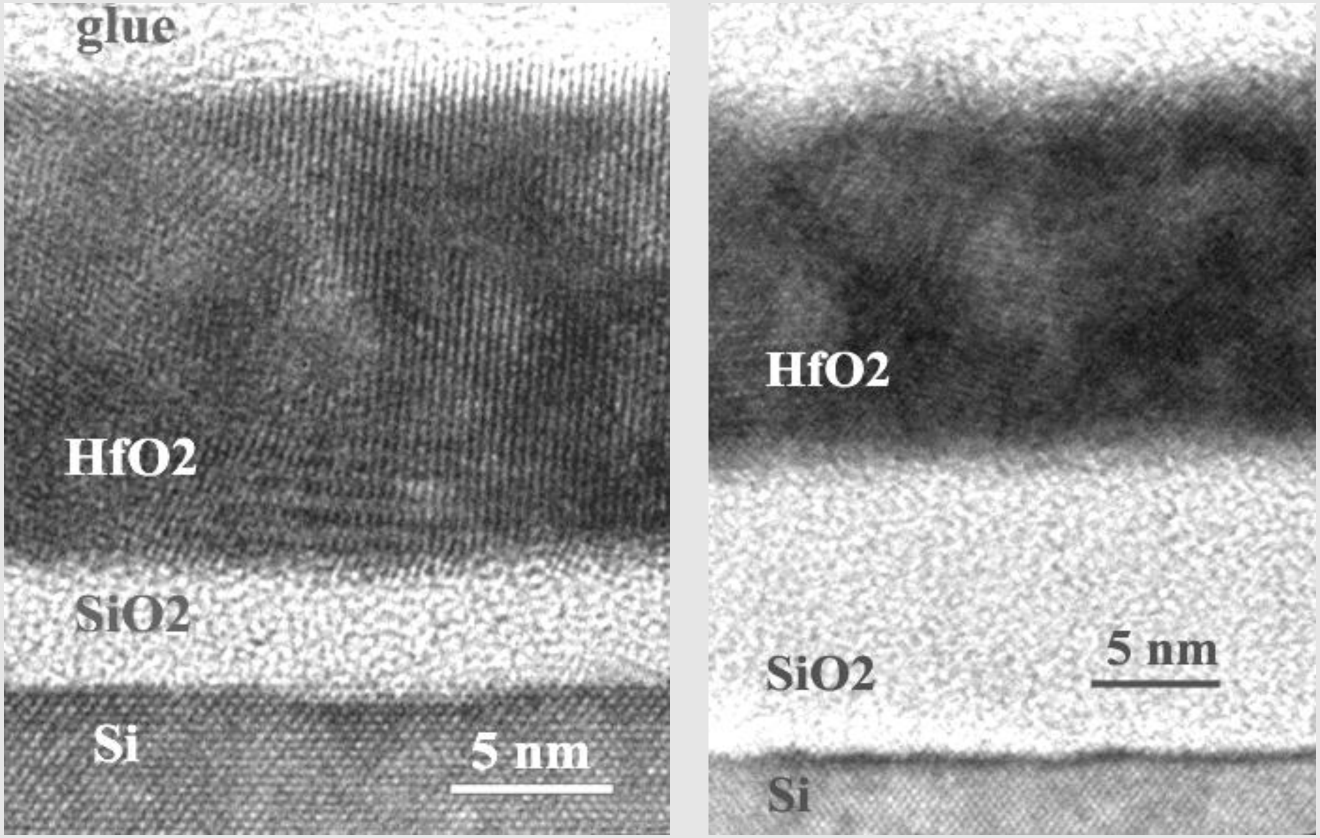
Thermal annealing





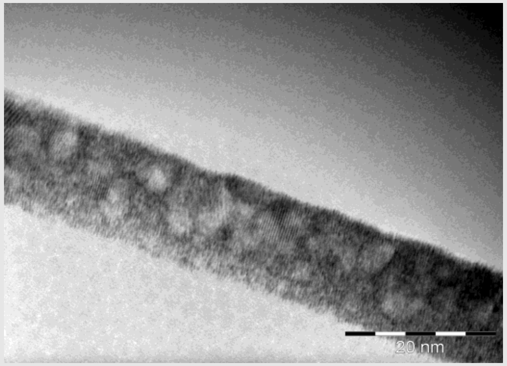
- AFM images of the dip coated films – 1 layer thermally treated at 600 °C
  - Very low RMS roughness: 0.32 nm

Thermal annealing

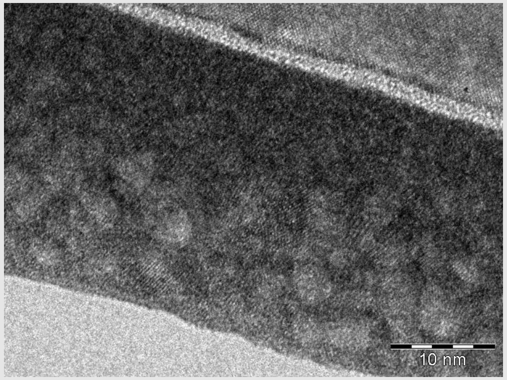


Cross section high resolution XTEM images from a monolayer film annealed at 600°C (left) and 800^{o}C (right)

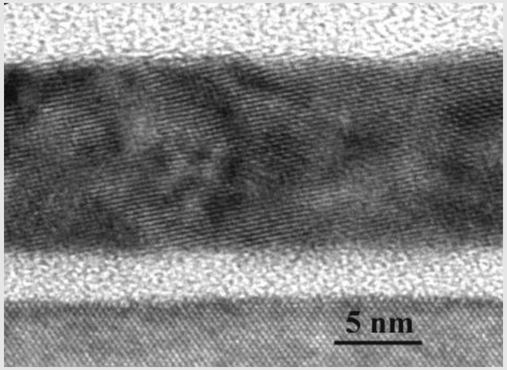
Thermal annealing



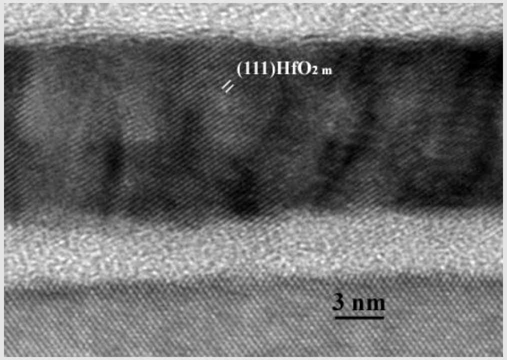
TEM image of a mono-layer film annealed at 450^{o}C, obtained from Hf-ethoxide precursor.



TEM image of a monolayer film annealed at 450^{0}C, obtained from Hf-chloride precursor



TEM image of a mono-layer film annealed at 600^{o}C, obtained from Hf-ethoxide precursor.



TEM image of a mono-layer film annealed at 600^{o}C, obtained from Hf-pentadionate precursor

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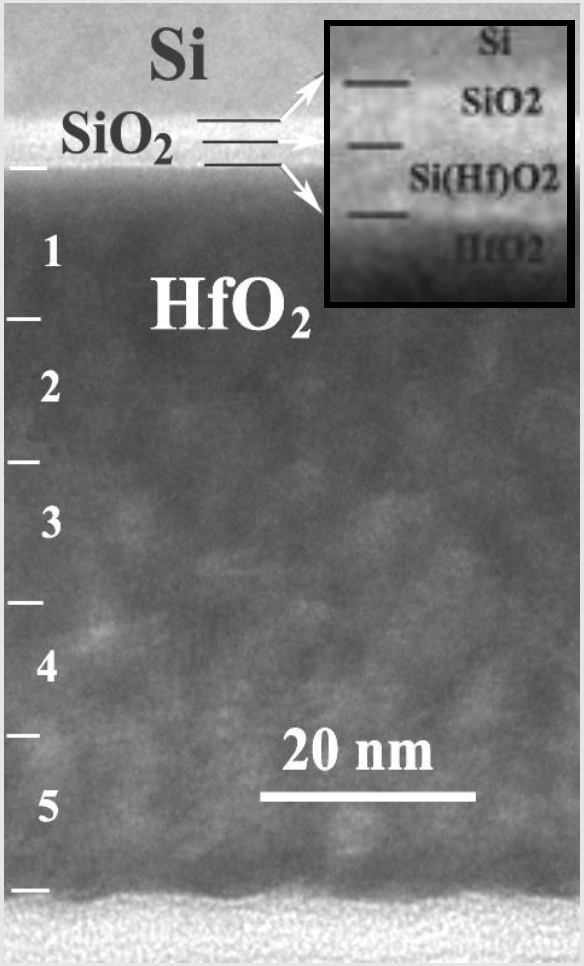
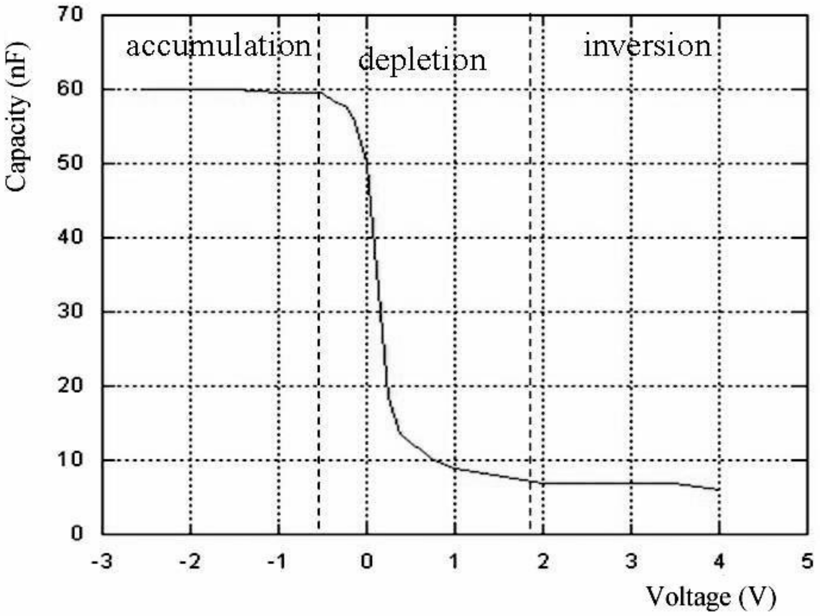
- M.Zaharescu, V.S. Teodorescu, M.Gartner, M.G.Blanchin, A.Barau, M.Anastasescu, J. Non-Cryst. Solids, 354, 409-415 (2008)

Thermal annealing



Low resolution XTEM image of a 5 ayers HfO_2 film, taken in a thick area of the XTEM specimen

Thermal annealing



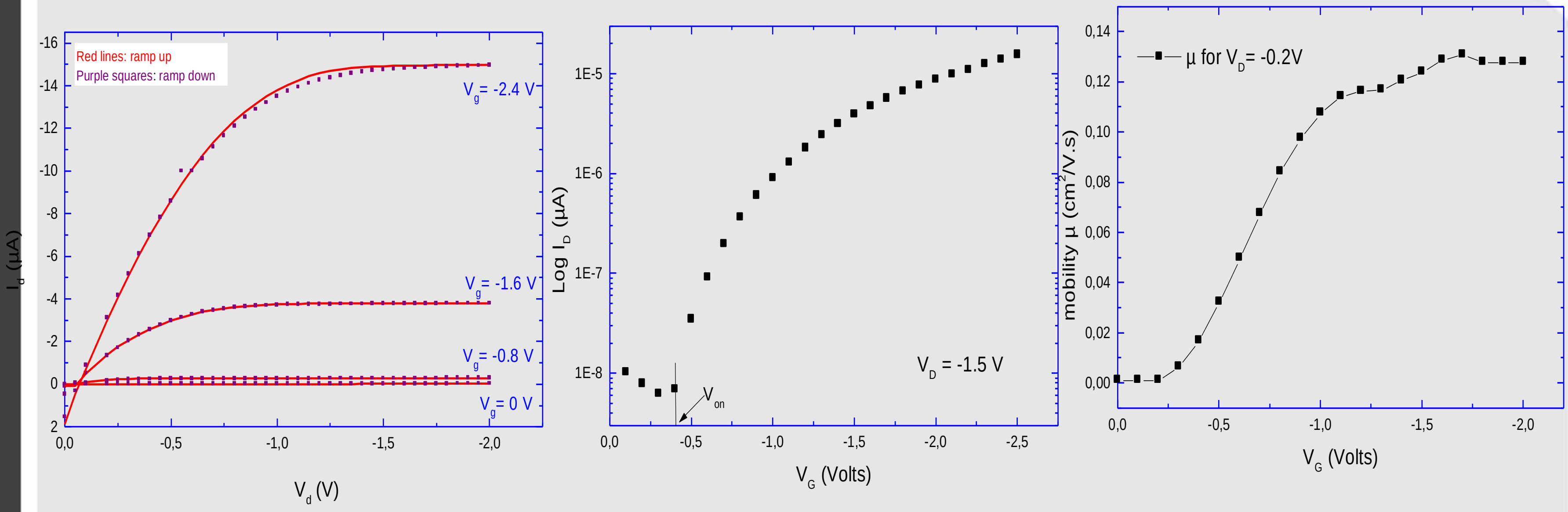
Typical C-V curve for a MOS structure including a four layer HfO_2 film annealed at 600ºC

k = 25

M.G.Blanchin, B.Canut, Y.Lambert, V.S.Teodorescu, A.Barău, M.Zaharescu, J.Sol-Gel Sci.Technol., 47, 165-172, (2008)

Thermal annealing

Electric characteristics of Organic Field Effect Transistor based on pentacene prepared with HfO_2 high k gate dielectric



- Low operation voltage
- Almost no hysteresis
- Very limited gate leakage
- Good mobility

J.Tardy, M.Erouel, A.L.Deman, A.Gagnaire, V.S.Teodorescu, M.G.Blanchin, B.Canut, A.Barau, M.Zaharescu, Micoelectronics and Reliability, 47, 372 (2007)

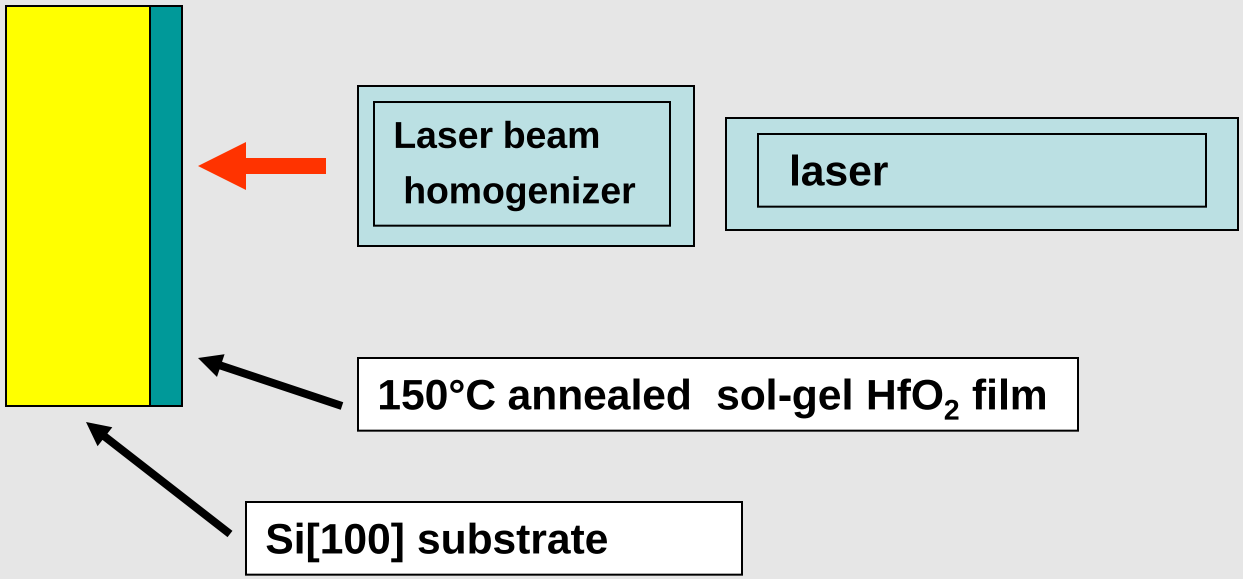
Conclusion – thermal annealing

- The as-deposited HfO_2 film is amorphous and start to crystallize at 400^0C, leading to a very homogeneous morphology and very low roughness
- . Thermal annealing at 600°C leads to crystallization of the HfO_2 sol-gel film in monoclinic phase
- An intermediate SiO_2 layer of about 5 nm was formed assigned to Si wafer oxidation, that increases by subsequent thermal treatment
- Dens films could be obtained by multi-layer deposition.
- Such films present a dielectric constant close to that of the bulk material.

➢ Pulse laser annealing can provide a method to limit the growth of the SiO_2 layer due to the limited time of oxygen diffusion from the film surface to the substrate interface

Laser annealing

- **XeCl Lambda Physics excimer laser (l = 308 nm, tFWHM = 10 ns) using a homogenised laser beam spot with an area of about 1cm^2, with:**
  - **fluences between 30 and 120 mJ/cm2 and**
  - **different number of pulses between 100 and 10000.**



Laser beam homogenizer

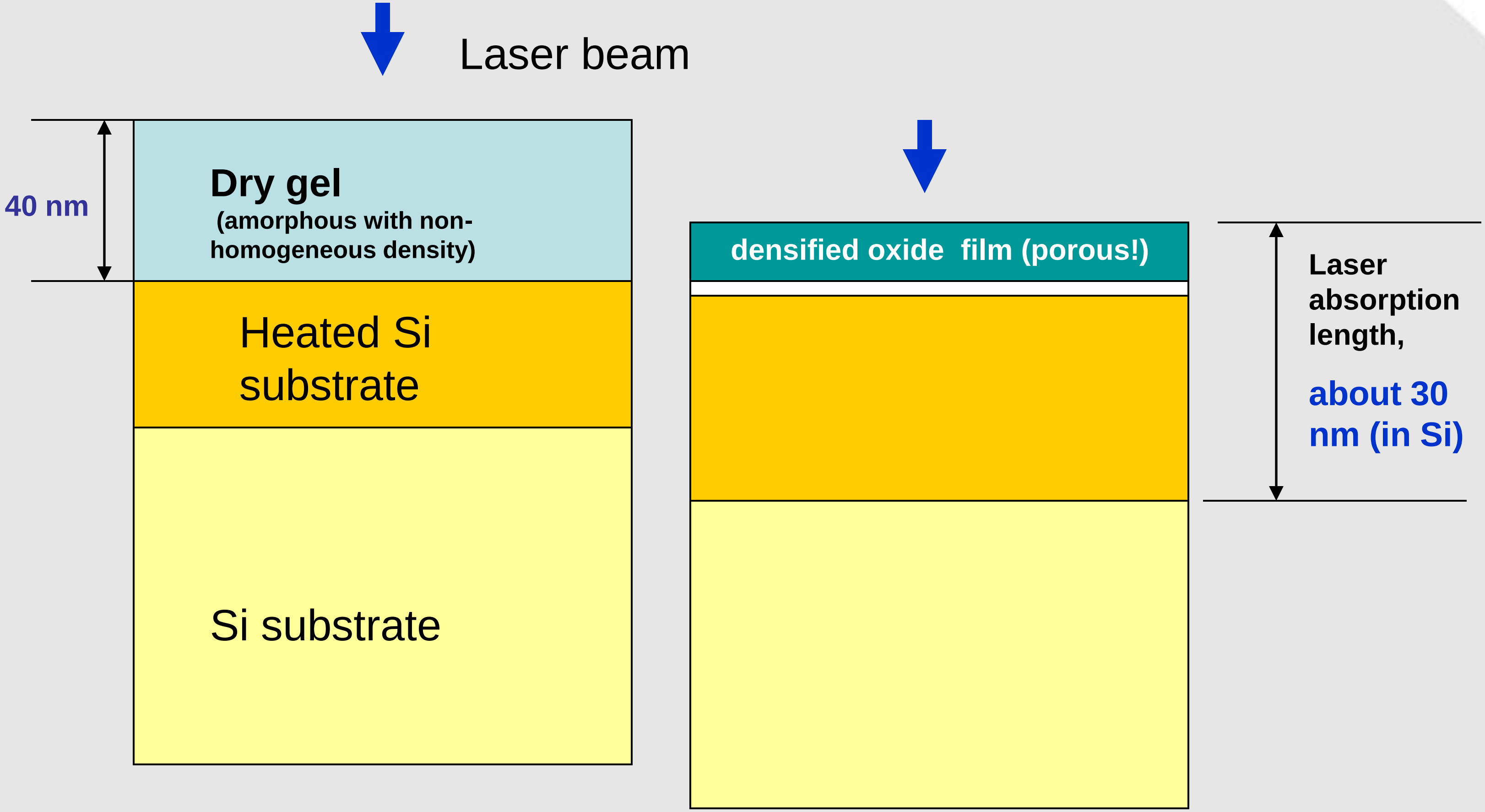
laser

150°C annealed sol-gel HfO$_2$ film

Si[100] substrate

Laser irradiation set-up

Laser annealing


Laser beam

40 nm

Dry gel

(amorphous with non-homogeneous density)

Heated Si substrate

Si substrate

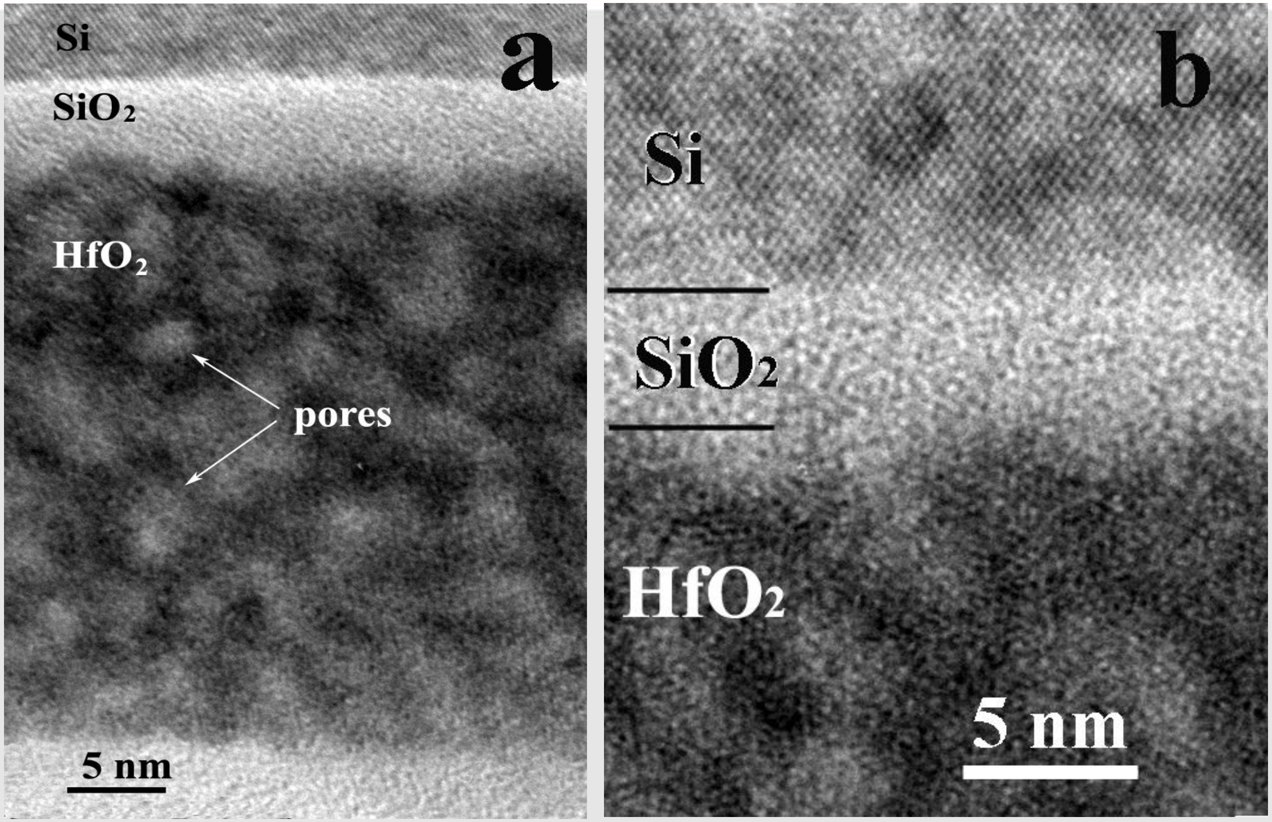
densified oxide film (porous!)

Laser absorption length,

about 30 nm (in Si)

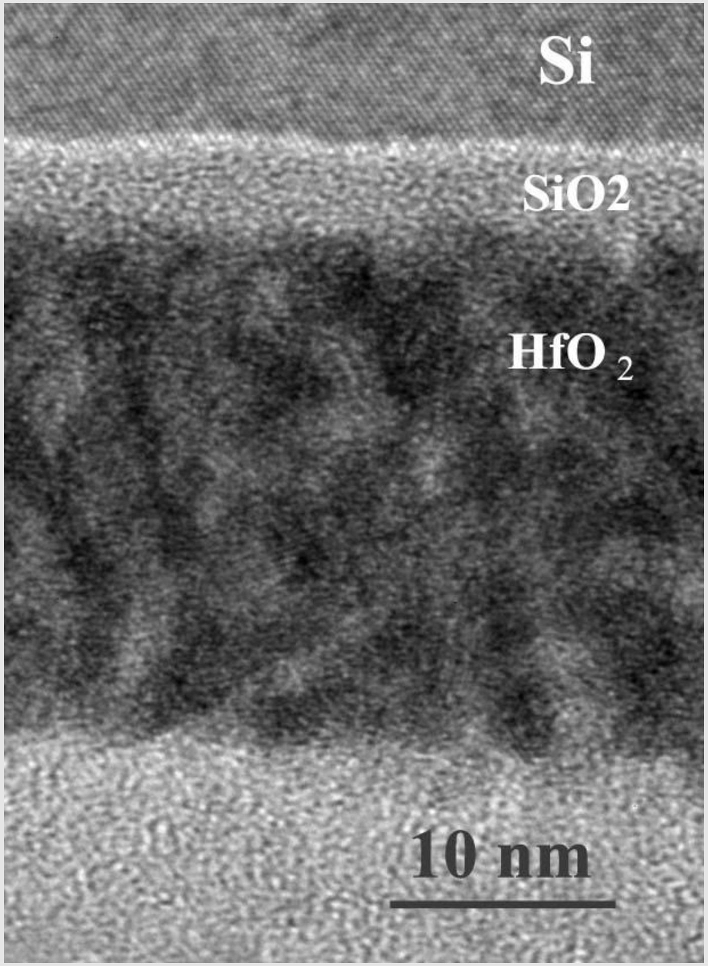
Schematic mechanism of the laser heating and densification of the HfO_2 sol-gel films

Laser annealing



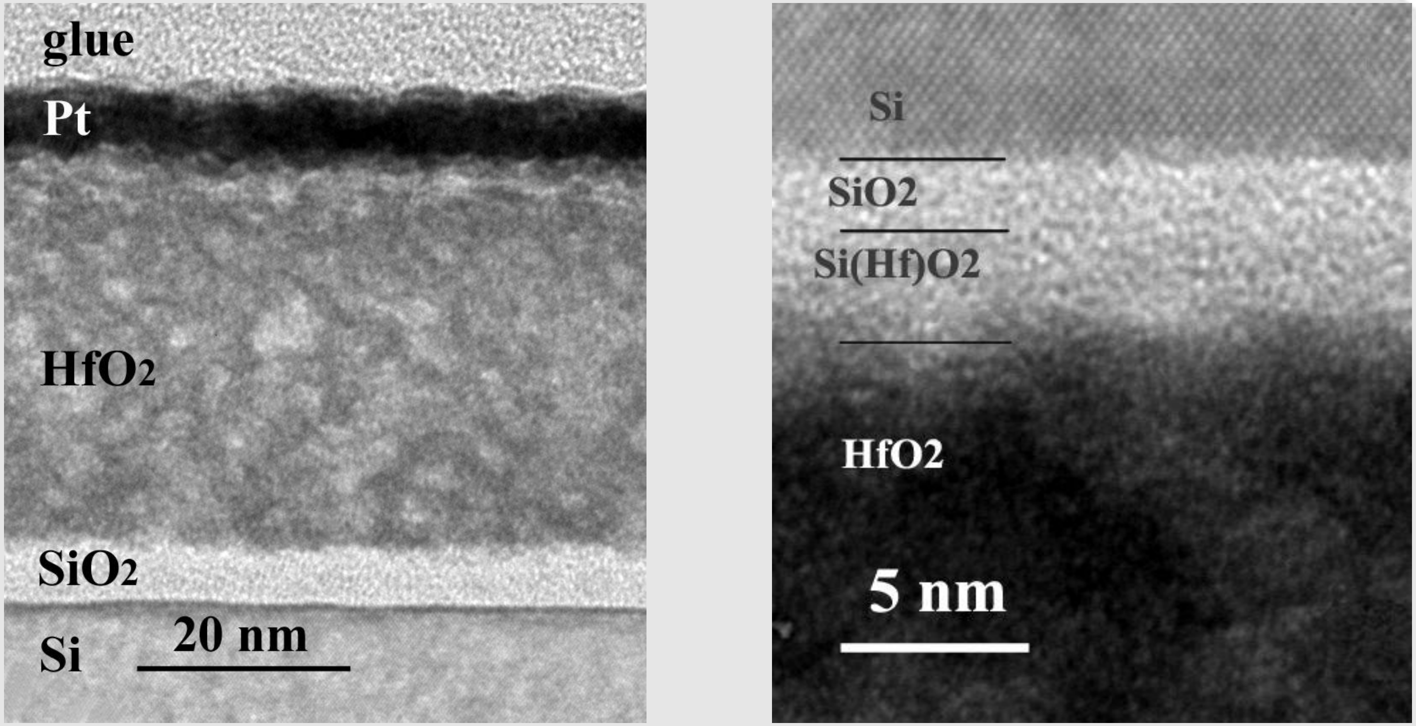
XTEM images of a HfO_2 sol-gel double layer film (a) and detail of the interface with the silicon substrate (b). The film was laser irradiated with 100 laser pulses at the fluence of 30 mJ/cm^2 . The thickness of the SiO_2 interface layer is about 4 nm

Laser annealing



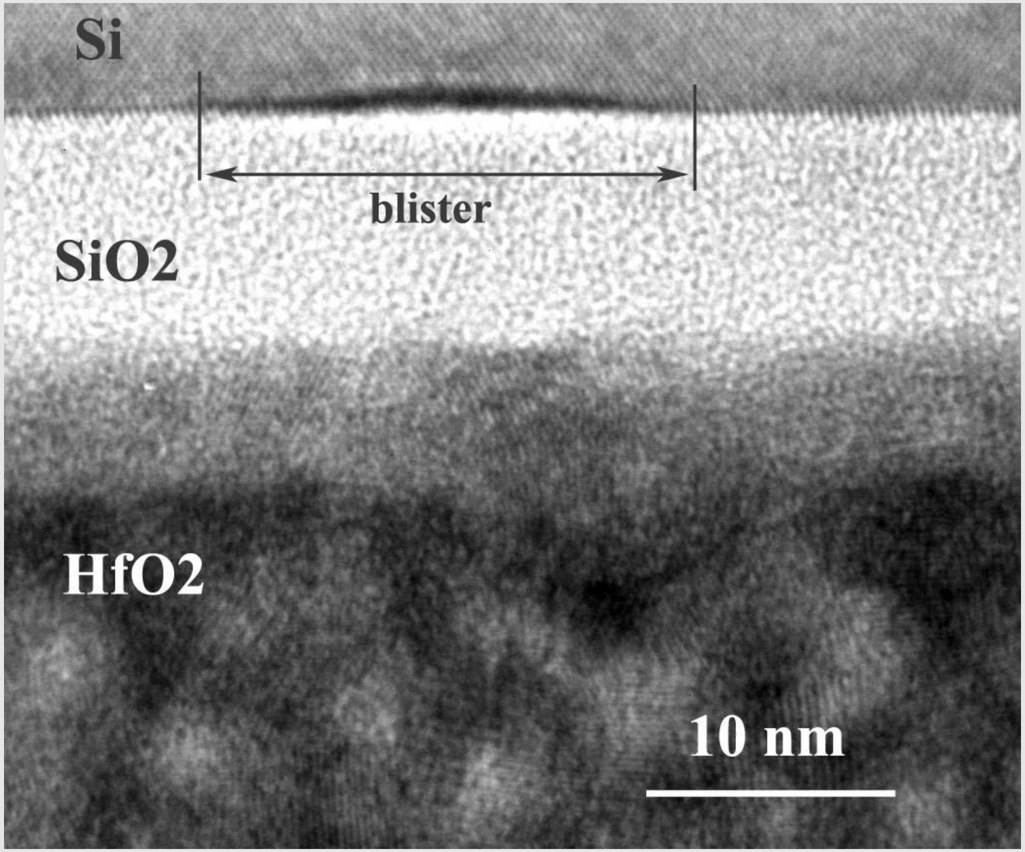
XTEM image of a HfO_2 film after laser irradiation with 100 pulses at the fluence of 65 mJ/cm^2. The HfO_2 thickness is about 24 nm and the SiO_2 interface layer is about 4 nm

Laser annealing



XTEM structure of the HfO_2 film irradiated with 10000 pulses at 80 mJ/cm^2 fluence.
The structure remains amorphous and the SiO_2 interface layer is about 6 nm (left)
Details showing the Si(Hf)O_2 amorphous structure formation (right)

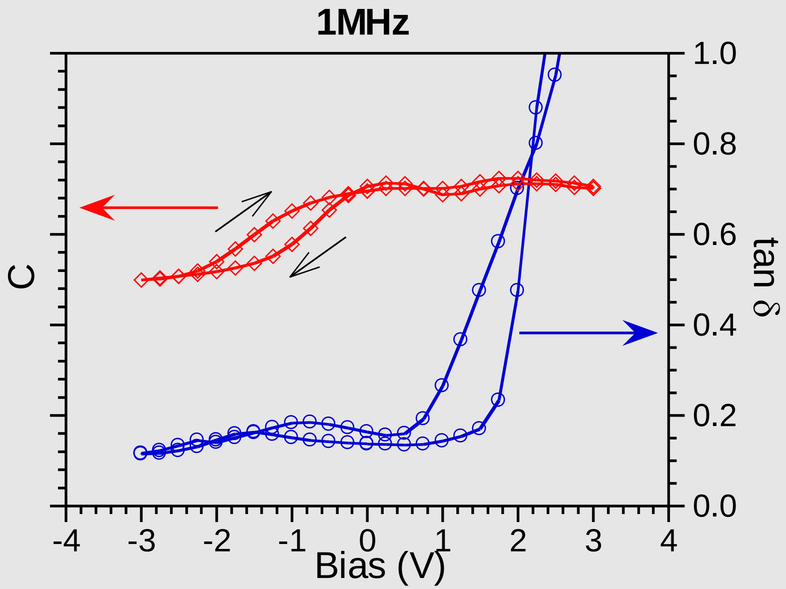
Laser annealing



Blister nucleation at the fluence of 100 mJ/cm^2, after 5000 pulses.

The SiO$_2$ layer arrives at the thickness of about 8 nm.

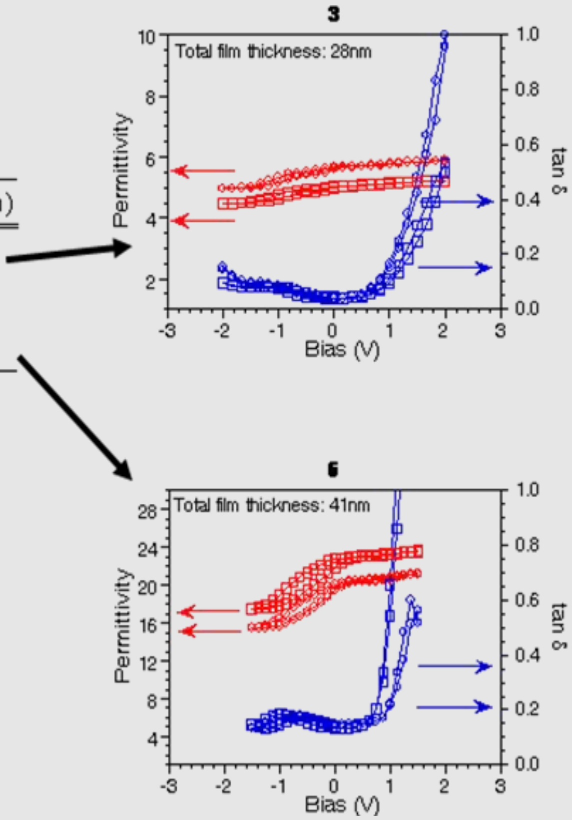
Laser annealing



C-V curves recorded for dielectric measurements in the case of HfO_2 film sample irradiated with 80nJ/cm^2 and 10000 laser pulses.

Laser annealing

No.	Laser condition	HfO_2 (nm)	Amor. (nm)	εeff @100kHz	EOT(nm)
3	65mJ-100p	24	4	5-6	19
10	80mJ-10000p	36	4	30? (very leaky)	5
6	100mJ-5000p	36	5	20-24	7



C-V curves records for dielectric measurements realized at 100Hz and table with calculated dielectric constant values

Conclusions

- Crystallization of amorphous sol-gel HfO_2 thin films has been studied both by thermal annealing and by pulsed laser annealing (at fluences between 30 and 120 mJ/ cm^2 and different number of pulses between 100and 10000 fluence)

- By thermal annealing monoclinic phase is obtained at 600^0C

- By laser annealing at low fluences (under 80 mJ/cm^2) the films did not crystallize and at high fluences (120 mJ/ cm^2) the film crystallize but blistering of the film occur

- In both cases the formation of the intermediate SiO_2 film could not be avoided

- High dielectric constant values could be obtained in both cases (~ 25). The value is strongly influenced by the structure and morphology of the film.

- Thermal treated films present a better structure and morphology for further applications

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Thank you for your attention !