Chemical solution deposition of thin films

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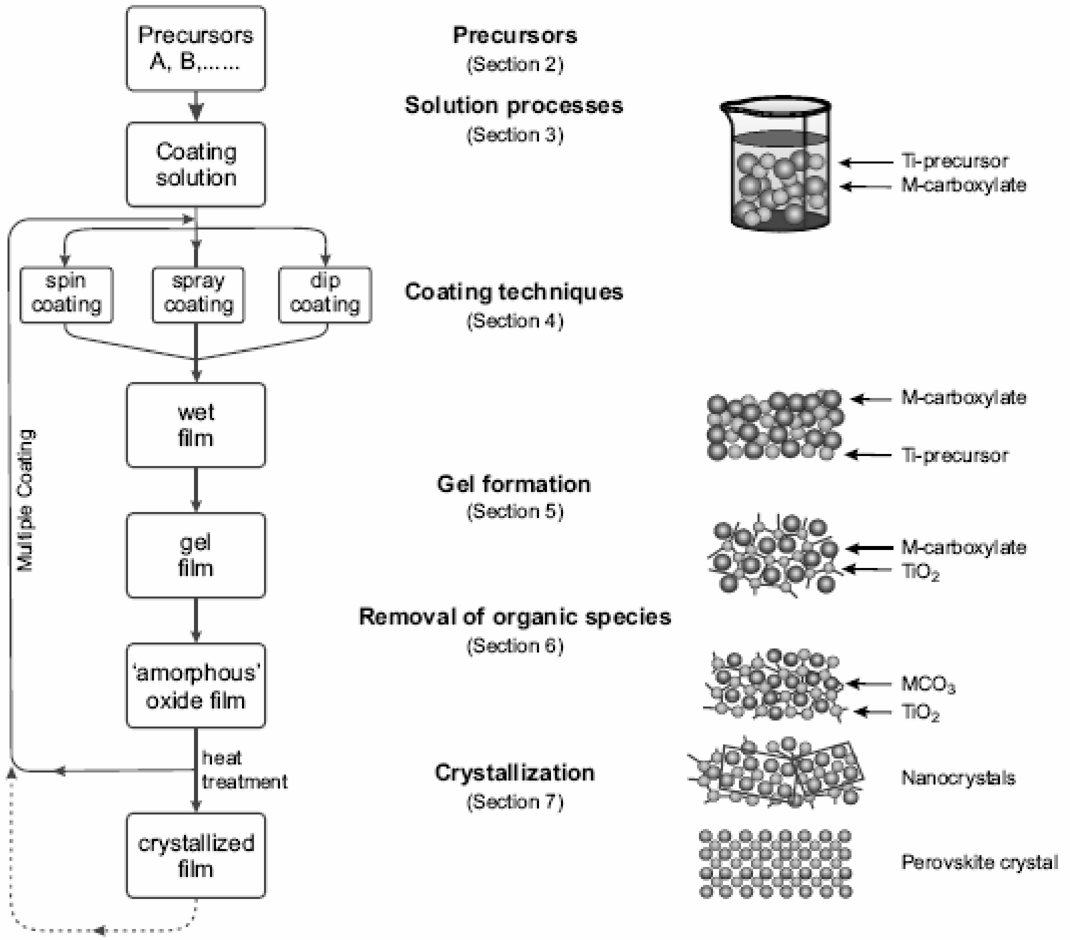
SINTEF

Chemical solution deposition (CSD)

The application of a solution of metalorganic compound(s) in a suitable solvent on to a substrate, in such a way that a film is formed, followed by pyrolysis and crystallization into oxide as a result of heat treatment.

CSD process



Schwartz, R. W.; Schneller, T.; Waser, R. *Comptes Rendus Chimie* **2004**, *7*, 433-461.

Pros of CSD

- Very good stoichiometry control
- Can cover large surfaces
- Large thickness range (<10nm-10µm)
- Requires relatively little equipment

Cons of CSD

- "High" temperatures may be required for crystallization (6-700^{o}C)
- Reactions with substrate (buffer layer must often be used)
- Precursor development can be elaborate

Requirements for CSD

1. Sufficient solubility of precursor in solvent
2. Precursors must not contaminate the final product
3. Precursor must retain homogeneity at atomic scale during pyrolysis/crystallization
4. The solvent must wet the substrate
5. Suitable viscosity for deposition method
6. No crack formation during pyrolysis
7. Limited reaction with the substrate
8. Sufficient sol stability

Precursors

- Metal source compounds
  - Alkoxides
  - Carboxylates
    - Acetates
  - Nitrates
- Solvents
  - Alcohols
  - Organic acids (acetic acid)
- Stabilizers
  - Acetylacetonate (acac)
  - Diethanolamine

Alkoxides

- General formula: $[M(OR)_x]_n$
  - OR can be the deprotonated form of:
    - Simple alcohols as MeOH, EtOH, Pr^nOH, Bu^nOH
    - Steric alcohols: Pr^iOH, Bu^tOH
    - Multidentate alcohols HOEt-X (X=OMe, OEt, OBu^n, NR_2, PR_2)
- Why use alkoxides?
  - Versatility
    - Solubility, vapor pressure and reactivity can be adjusted by choosing different OR-groups
  - Low carbon to metal ratio
  - Heterometallic compounds often possible

Hetrometallic alkoxides

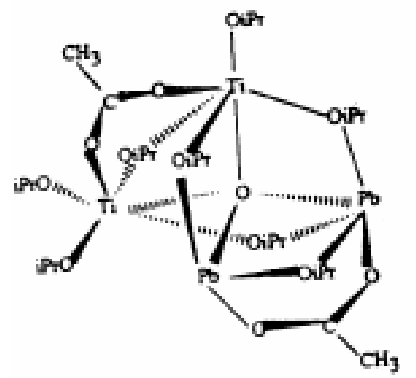
- All metals in correct stoichiometric ratio present in one molecule

⇨ Elemental homogeneity on a molecular level

⇩

Very low crystallization temperatures if framework is maintained

$Pb_2Ti_2(\mu_4\text{-}O)(OAc)_2(O^iPr)_8$



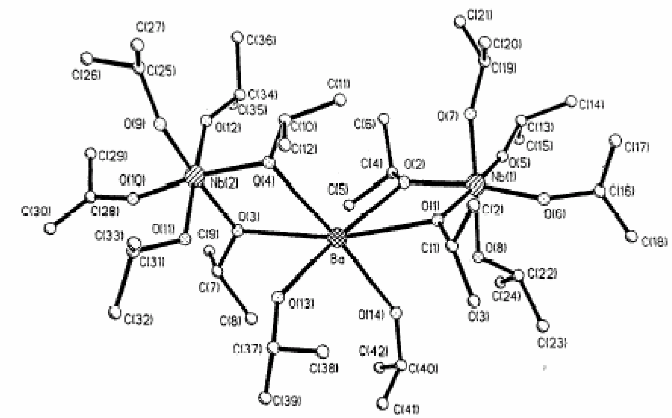


Fig. 14. Molecular structure of [Ba{Nb(OPr^i)_6}_2(Pr^iOH)_2] [22].

L.G. Hubert-Pfalzgraf, S. Daniele, J.M. Decams, *J. Sol–Gel Sci. Tech.* 8 (1997) 49
Turevskaya, E. P. et al. , *Polyhedron,* **1995**, 14, 1531.

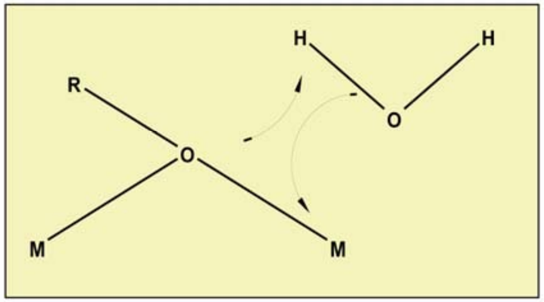
Hydrolysis

- Alkoxides are very reactive towards hydroxyl (e.g. water)
  - A little tricky to handle

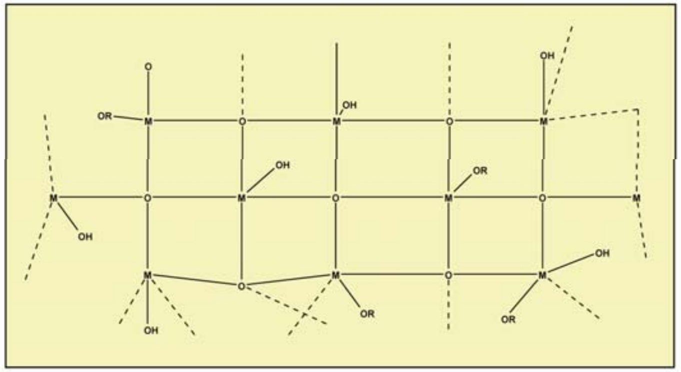
Degree of hydrolysis:

$$h = \frac{[H_2O]}{[M(OR)_x]}$$

Hydrolysis: $M(OR)_x + H_2O \rightarrow M(OR)_{x-1}(OH) + ROH$



Condensation: $2M(OR)_{x-1}(OH) \rightarrow (RO)_{x-1}M\text{-}O\text{-}M(OR)_{x-1} + H_2O$

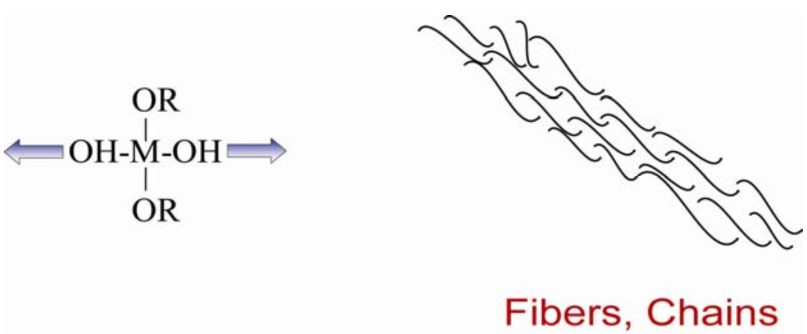


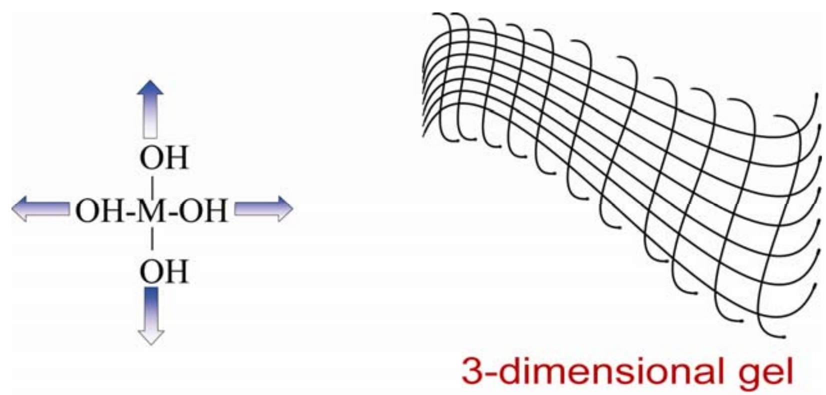
Controlled hydrolysis

- At low water concentrations condensation reactions may begin before hydrolysis is complete. This reaction may be catalyzed by acids.
- High water concentrations favor hydrolysis and retards condensation. Thus the hydrolysis is complete before condensation starts. This reaction may be catalyzed by bases.

$$[H_2O] \prec [M(OR)_x]$$

$$[H_2O] \succ [M(OR)_x]$$





Alkoxides in organic acid

- Example using acetic acid as solvent for $Ti(OR)_4$:

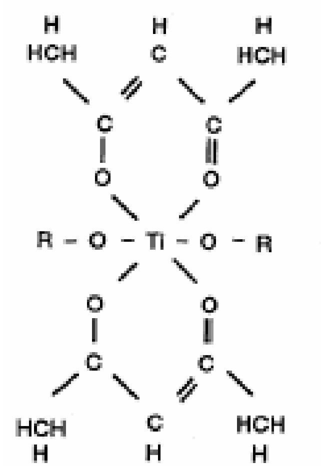
$$Ti(OR)_4 + CH_3COOH \rightarrow Ti(OR)_3(OOCH_3) + ROH$$

Problem!

Hydrolysis

$M(OR)_x + H_2O \rightarrow M(OR)_{x-1}(OH) + ROH$

$$CH_3COOH + ROH \rightarrow CH_3COOR + H_2O$$



Alkoxides must generally be stabilized (i.e. modified) when using organic acids as solvent:

$$Ti(OR)_4 + 2acacH \rightarrow Ti(OR)_2(acac)_2 + 2ROH$$

Yi, G.; Sayer, M. *Journal of Sol-Gel Science and Technology* **1996**, *6*, 65-74.

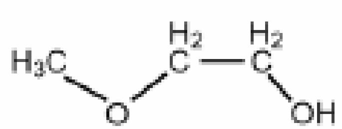
Alcohols as solvent

- Alkoxides:
  - Depending on alcohol acidity group exchange may take place:

$$M(OR)_x + R'OH \rightarrow M(OR')_x + ROH$$

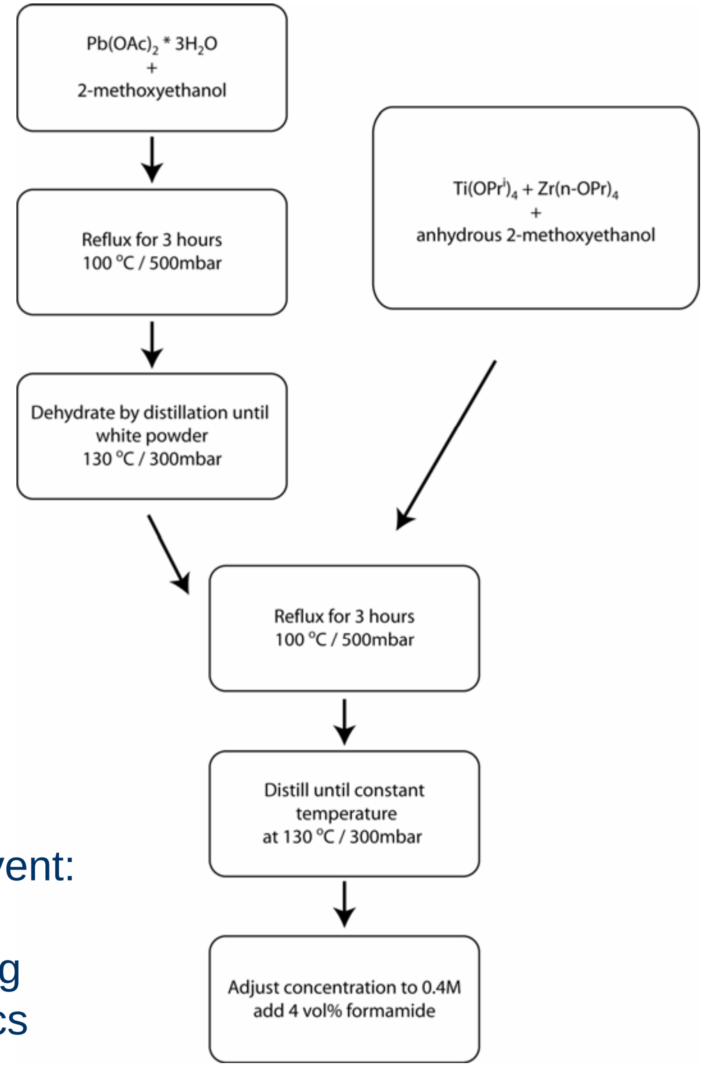
- Acetates:
  - Full or partial group exchange can take place e.g.:

$$Pb(OAc)_2 + MeOEtOH \rightarrow Pb(OAc)(MeOEtO) + AcOH$$



2-methoxyethanol

2-MeOEtOH widely used solvent:
•Stabilizes alkoxides
•Suitable viscosity for spinning
•Suitable drying characteristics



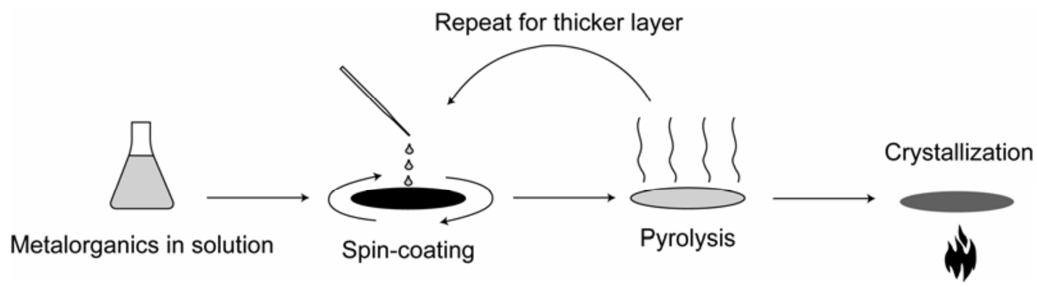
PZT ($Pb(Zr,Ti)O_3$) 2-methoxyethanol route

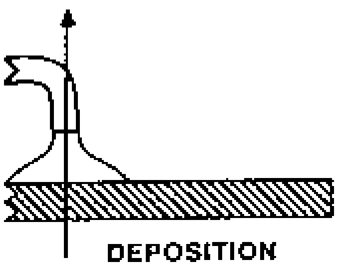
What you need:

- Basics
  - Vacuum manifold for precursor/sol synthesis (2-3000€)
  - Spinner + hotplate in flowbox (5000€)
  - Furnace (2-3000€)

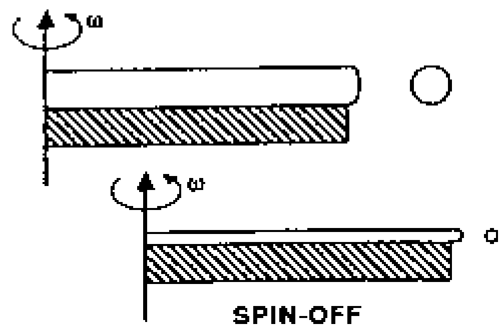
- In addition for state of the art setup
  - RTA furnace (60000€)
  - Cleanroom with flowboxes (☹€)

Spinning



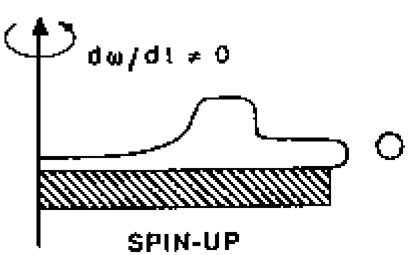


1



3

Viscous forces dominate



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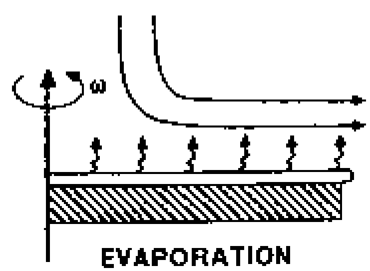
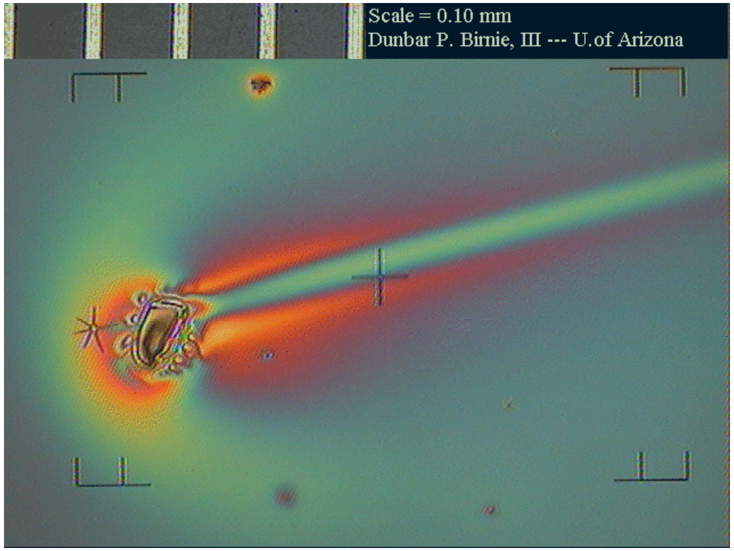


4

Evaporation dominates

Spinning defects

- Dust free environment required for spinning
- Very stringent procedures necessary
  - Cleanroom + flowbox
  - Spinner with suction
  - Filtration of solution
  - Cleaning of substrate



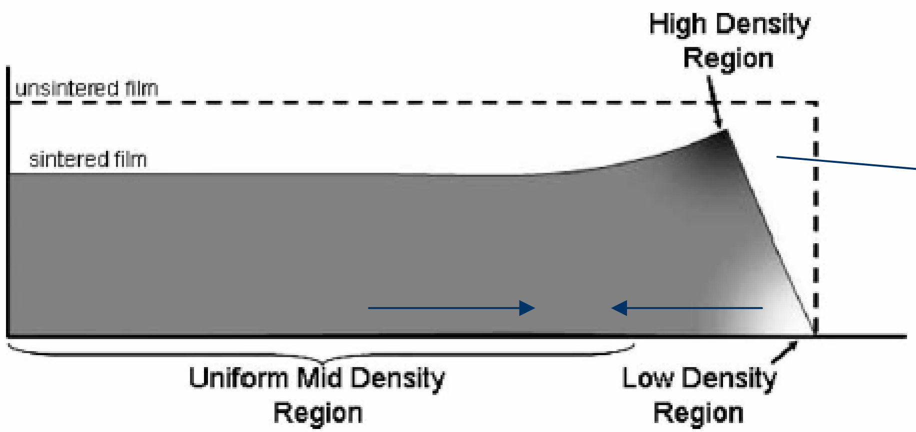
Example of spinning defect due to particle (comet)

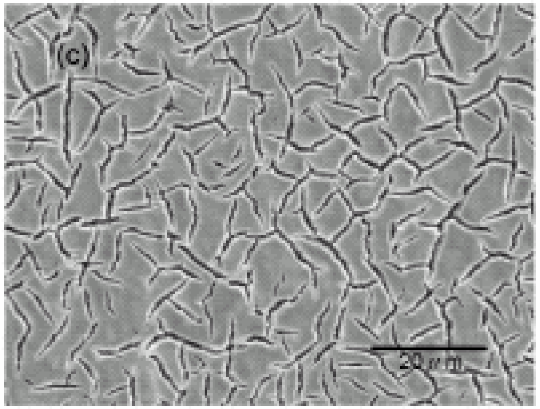
Shrinkage

- Shrinkage during drying/pyrolysis (50-70%) is the main problem when thicker films are targeted
  - Precursors with a low amount of organics should be used
  - Suitable sol concentration
  - Pyrolysis temperature should be high enough
  - Multiple coatings
  - Intermediate crystallizations must be used

CSD thickness range <10nm-8µm (!)

⇨ CSD films normally have significant amounts of residual stress

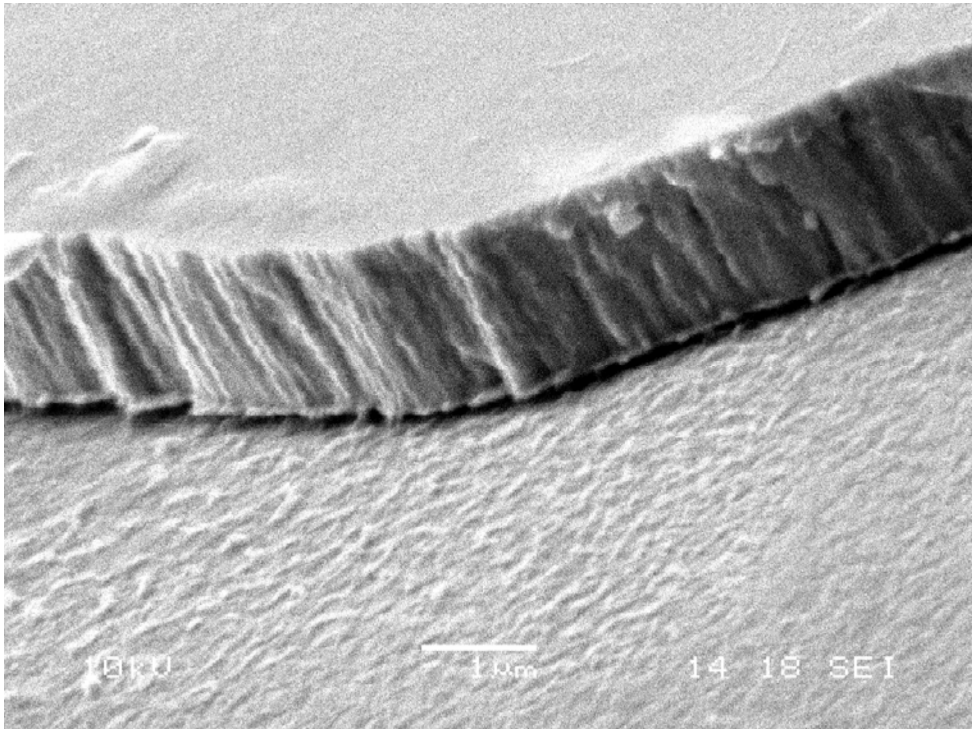




Dorey, R. A.; Whatmore, R. W. *Journal of Electroceramics* **2004**, *12*, 19.

Sol-gel PZT

- ~2µm PZT 53/47 by sol-gel
  - Si(100)/SiO_2/TiO_2/Pt"(111)" substrate
- Columnar grains (100-200nm in diam.)
  - {100}-textured
  - Dense microstructure
  - Seed layer used



~2µm {100} textured PZT 53/47 film (SINTEF)

Growth control

Heterogeneous nucleation generally preferred in CSD films. Especially when using high heating rates

⇩

RTA

Nucleation barriers:

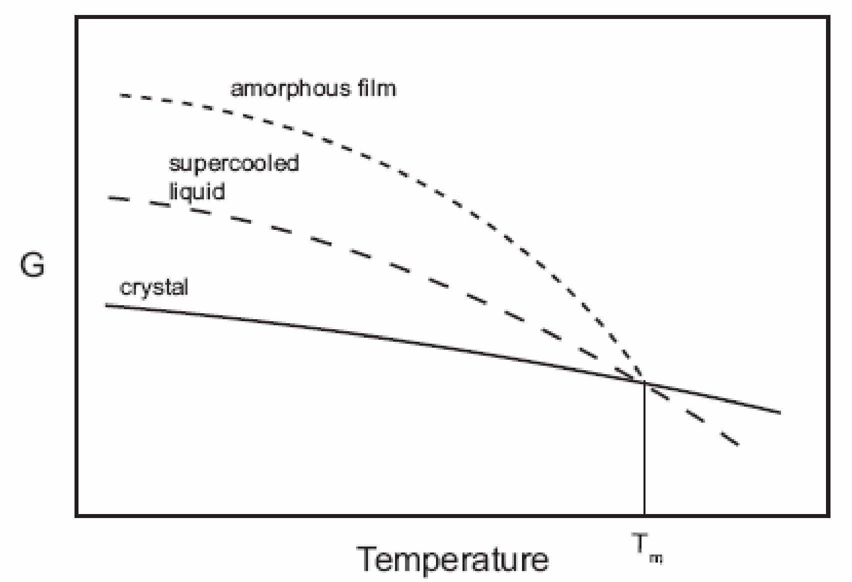
$$\Delta G^*_{\text{homo}} = \frac{16\pi\gamma^3}{3(\Delta G_v)^2}$$

$$\Delta G^*_{\text{hetero}} = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} f(\theta)$$

ΔG_v is the driving force, γ is the interfacial energy and $f(\theta)$ is a function related to the contact angle, θ.

For a hemispherical nucleus $f(\theta)$ can be expressed as:

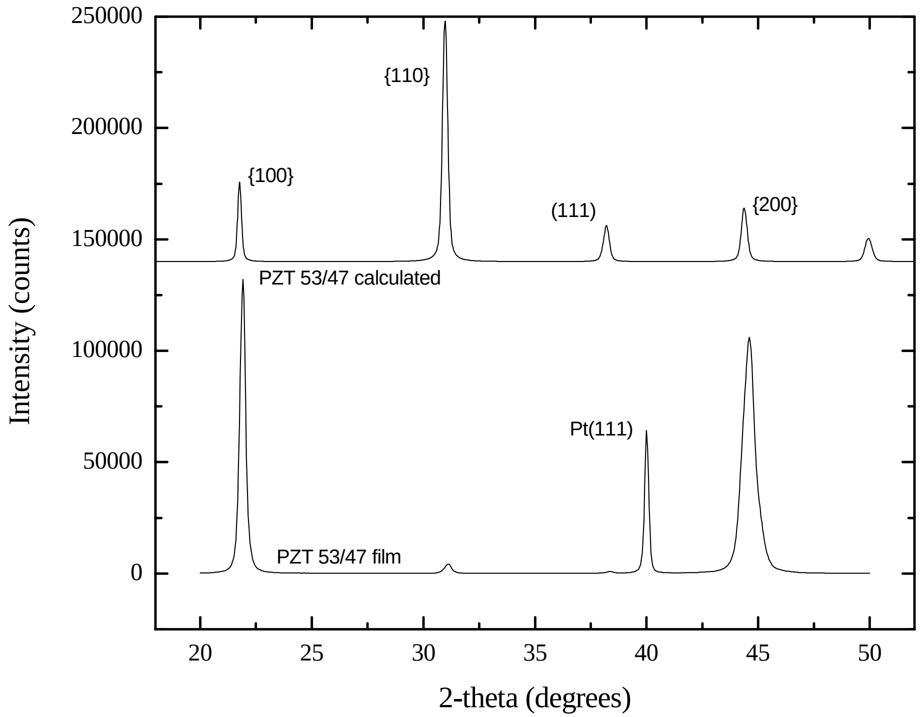
$$f(\theta) = \frac{(2 - 3\cos\theta + \cos^3\theta)}{4}$$



Schwartz, R. W. et al. *Journal of Materials Research* **1997**, *12*, 444-456.

Seeding for {100} texture

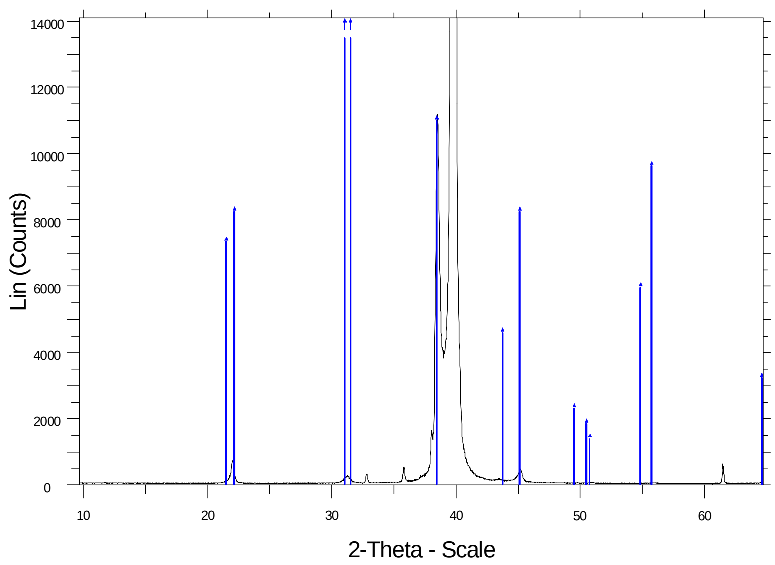
- Sputtered seed layer of $PbTiO_3$ results in {100} textured PZT



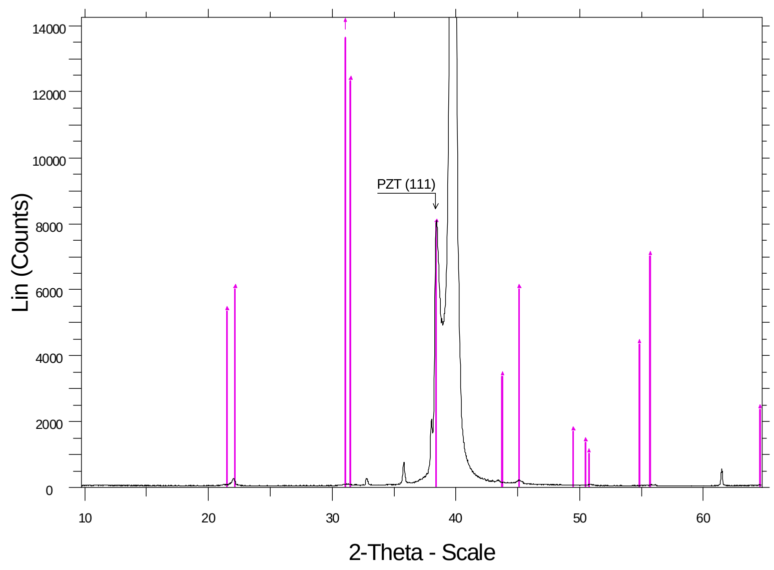
Diffractogram of ~2µm {100} textured PZT 53/47 film (SINTEF)

Seeding for (111) texture

- Two methods for obtaining (111)-textured PZT on Pt(111):
  - Formation of transient Pt_3Pb-phase
  - Use thin layer of TiO_2



Diffractogram of oriented PZT 30/70 on Si/SiO2/Ti/Pt(111) substrate TiO_2-method

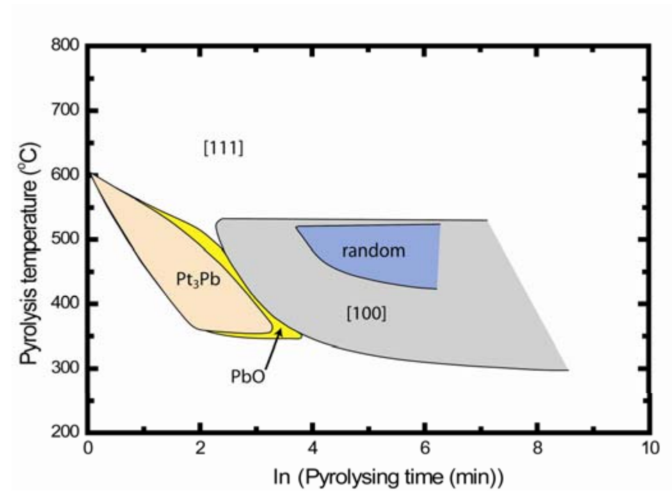


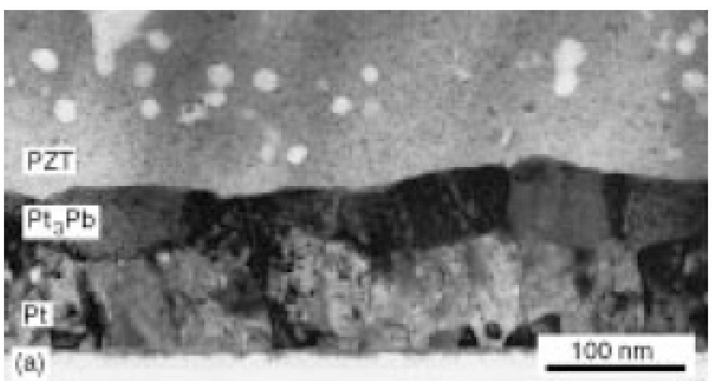
Diffractogram of oriented PZT 30/70 on Si/SiO2/Ti/Pt(111) substrate Pt_3Pb-method

Tyholdt, F.; Fjellvåg H. UiO

Pt_3Pb seed

- Temporary reducing conditions:
  - Formation of intermetallic phase (Pt_3Pb a=4.05Å) at electrode
  - Better lattice than Pt (a=3.923Å) for PZT 30/70 (a=4.035Å)





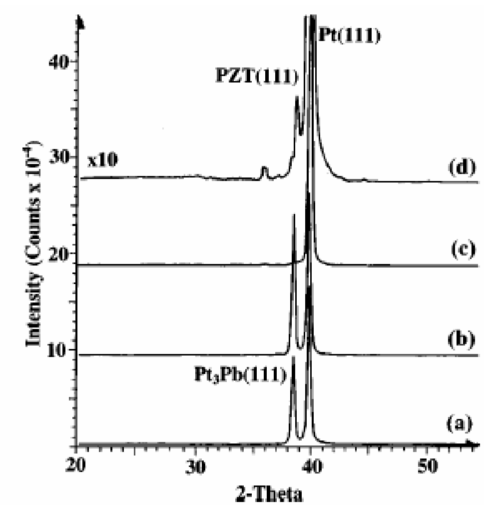
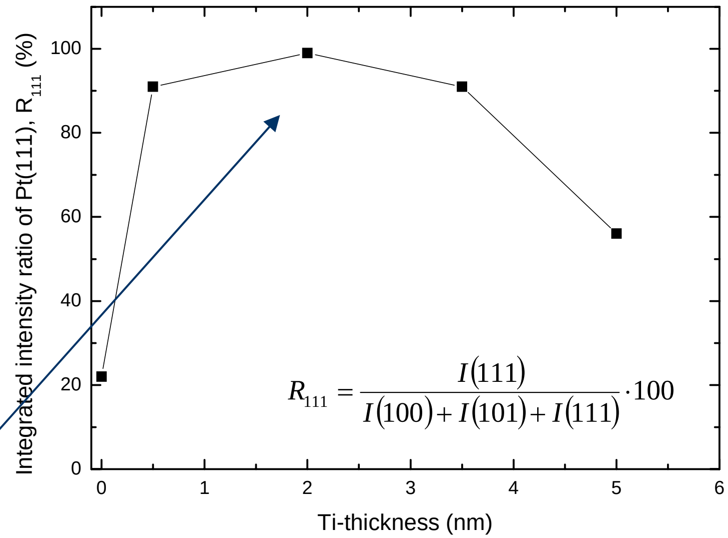


FIG. 1. XRD spectra for PZT films which were dried at 200 °C and annealed at 460 °C after (a) 10; (b) 150; (c) 780; and (d) 5400 s.

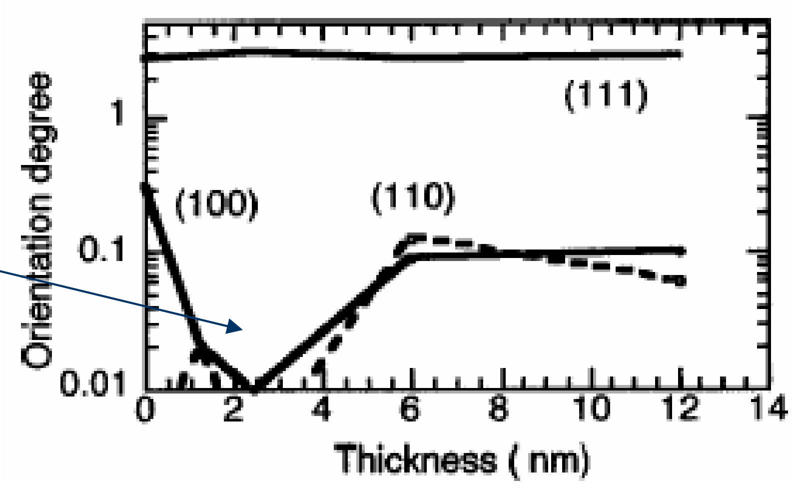
Huang, Z.; Zhang, Q.; Whatmore, R. W. *Journal of Materials Science Letters* **1998**, *17*, 1157.
Chen, S. Y.; Chen, I. W. *Journal of the American Ceramic Society* **1994**, *77*, 2332-2336.
Chen, S. Y.; Chen, I. W. *Journal of the American Ceramic Society* **1994**, *77*, 2337-2344.

Ti/TiO_2 seed

- Epitaxial growth of sputtered TiO_2(110) on Pt(111) grains
- Epitaxial relationship between TiO_2(110) and PZT(111)



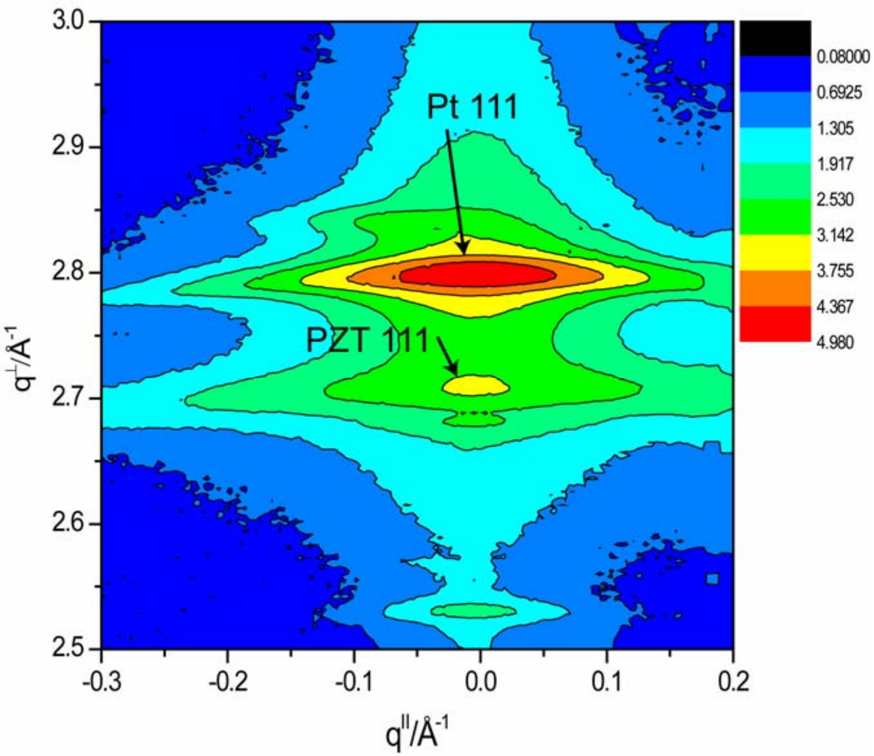
A (110) surface has the lowest surface energy



Assink, R. A.; Schwartz, R. W. *Chemistry of Materials* **1993**, *5*, 511-517.
Muralt, P et al. *Journal of Applied Physics* **1998**, *83*, 3835-3841.

PZT

- 500nm (111) textured PZT (30/70)
  - FWHM of Pt (111) rocking curve 1.8°
  - FWHM of PZT (111) rocking curve 2.7°



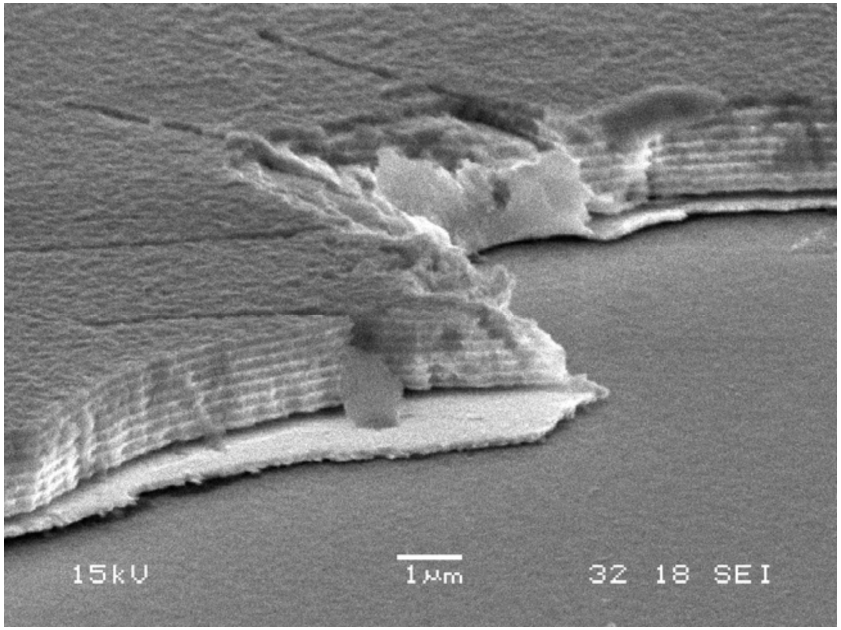
Reciprocal space map of the Pt(111) and PZT(111) reflection

Tyholdt, F.; Fjellvåg H. UiO

Inhomogeneities

- Typical crystallization temperatures used in CSD too low for significant diffusion (500-700^{o}C).
  - The interfaces between spin-on layers can be retained in the final film due to:

-Chemical composition variations
(40/60 > 60/40 in a 53/47 film)
-No grain growth through interface



Etched ~2μm {100} textured PZT 53/47 film (SINTEF)

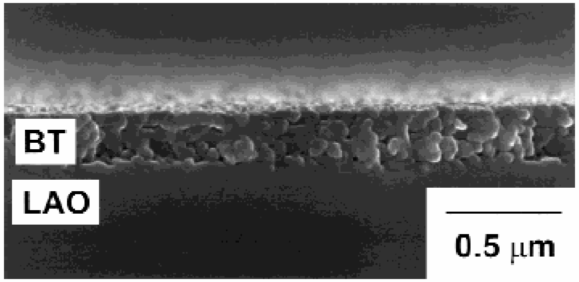
Sol-gel Ba(Sr)TiO_3

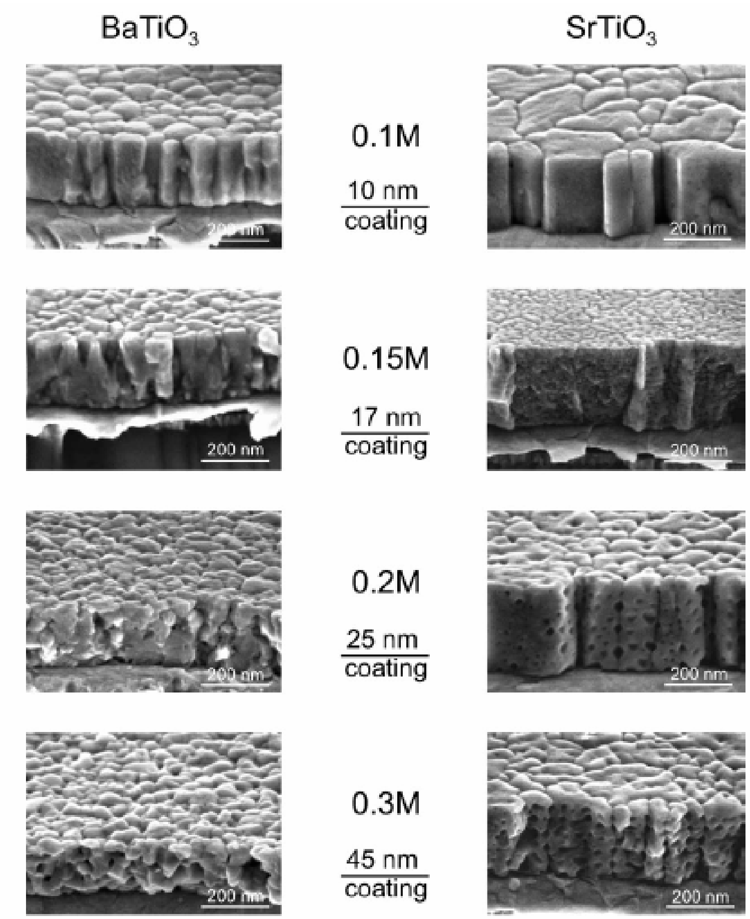
- Homogenous nucleation preferred

Reduction of thickness > reduction of bulk nucleation events

Transformation from homogeneous to heterogeneous nucleation

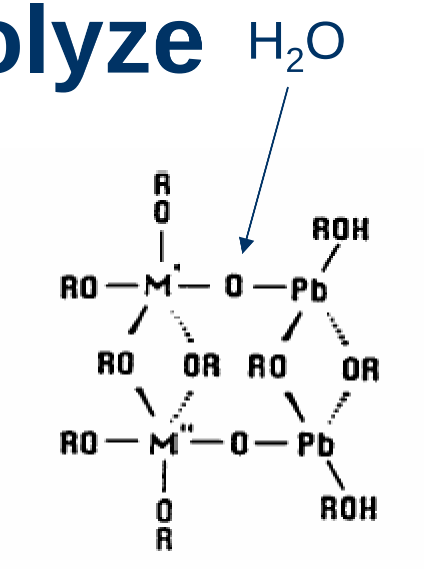
No heterogeneous crystallization even on lattice matched substrate





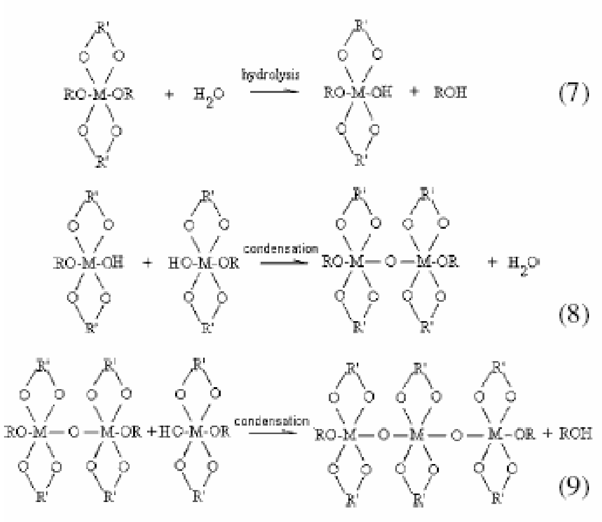
Schwartz, R. W. *Journal of the American Ceramic Society* **1999**, *82*, 2359-2367.
Hoffmann, S.; Waser, R. *Journal of the European Ceramic Society* **1999**, 19, 1339-1343.

To hydrolyze or not to hydrolyze



(a)

- Situation 1:
  - Hydrolyzation can break up multimetallic species
- Situation 2:
  - Can retain elemental homogeneity in a mixture of different alkoxides



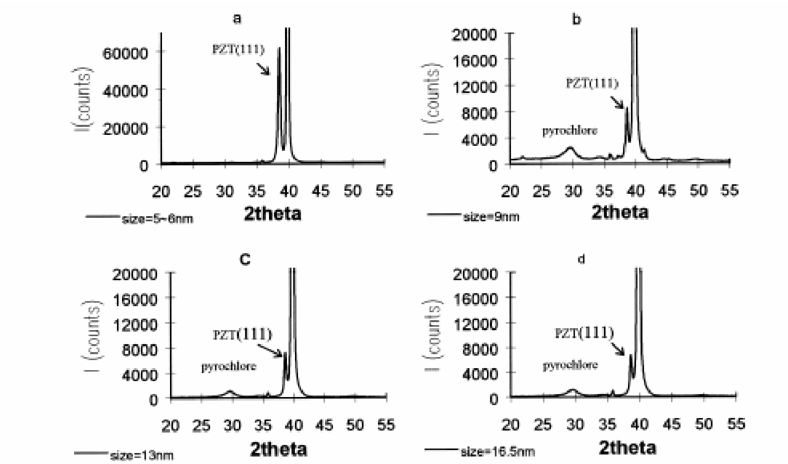


Fig. 3. Effect of particle size in sol–gel precursors on crystallisation and orientation of PZT thin films.

Zhang, Q. et al. *Journal of the European Ceramic Society* **1999**, *19*, 1417-1421.

$BiFeO_3$ films by CSD

- Precursor
  - Mixture of Bi and $Fe(t\text{-}OBu)_3$ in 2-MeOEtOH
  - Hydrolyzed ($M:H_2O=1$)
  - Bi-excess used

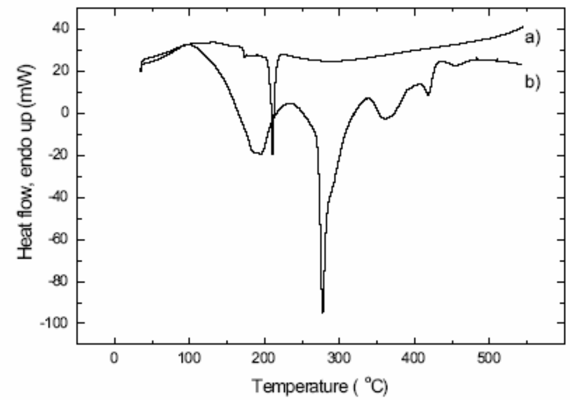


Figure 3: Decomposition of gel as monitored by DSC. a): N_2 purge, b): O_2 purge

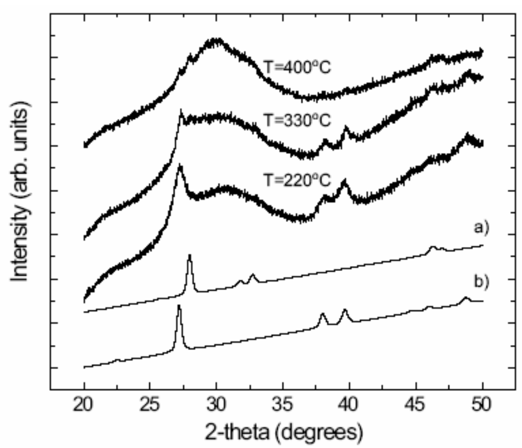


Figure 4: XRD patterns of gels heated inside the DSC instrument in O_2 atmosphere to selected temperatures. Included for comparison patterns of a) Bi_2O_3 (ICSD #62979), b) Bi (ICSD #64703).

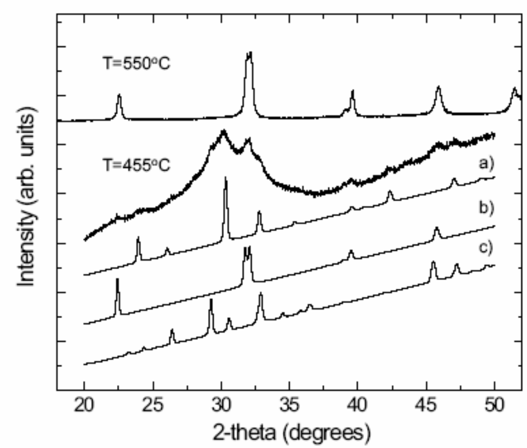
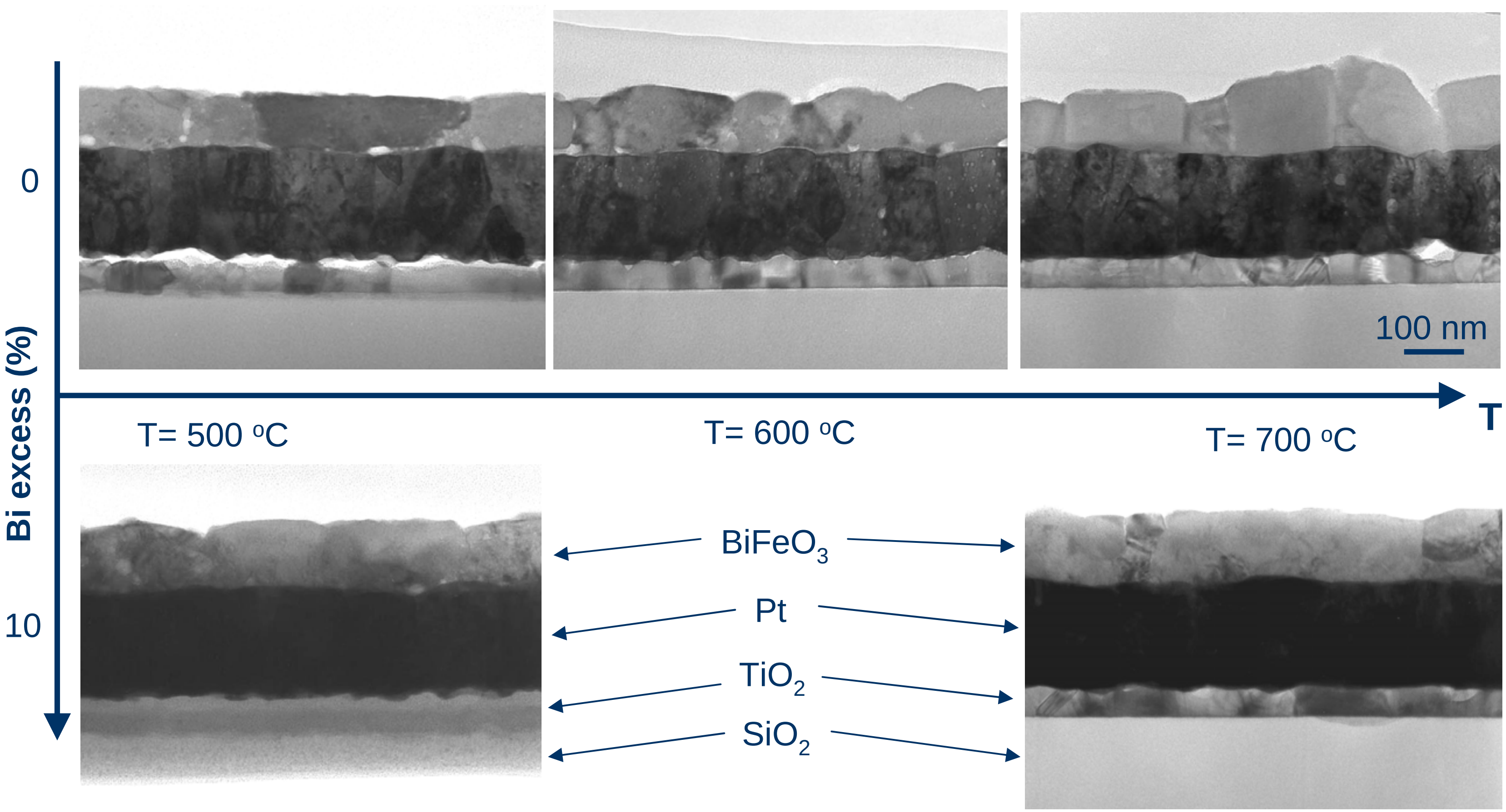


Figure 5: XRD patterns of gels heated inside the DSC instrument in O_2 atmosphere to 455°C and 550°C. Included for comparison patterns of a) $Bi_2O_2CO_3$ (ICSD #94740), b) $BiFeO_3$ (ICSD #82614), c) $Bi_2O_{2.3}$ (ICSD #37366).

Tyholdt, F.; Gunnæs, E. A.; Jørgensen, S.; Fjellvåg, F. *Journal of Materials Research* **2005**, *in press (aug. -05)*.

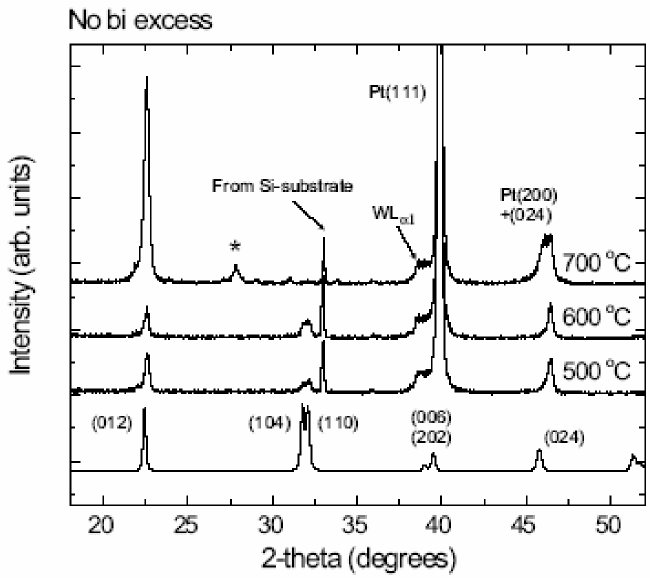
Microstructure

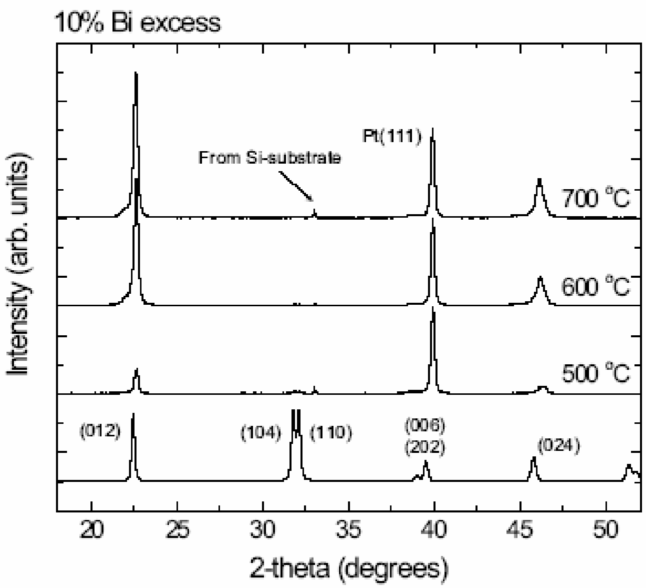


Tyholdt, F.; Gunnæs, E. A.; Jørgensen, S.; Fjellvåg, F. *Journal of Materials Research* **2005**, *in press (aug. -05)*.

X-ray diffraction

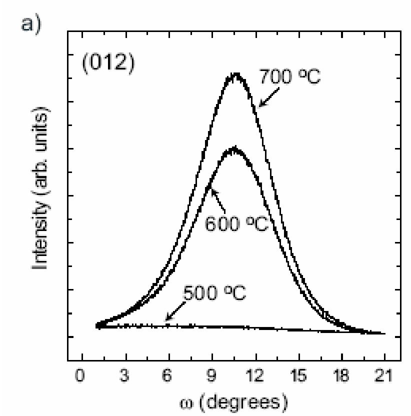
- Films fully crystallized at 500^{o}C
- All films display texturing
  - Increases with crystallization temperature and by Bi-excess



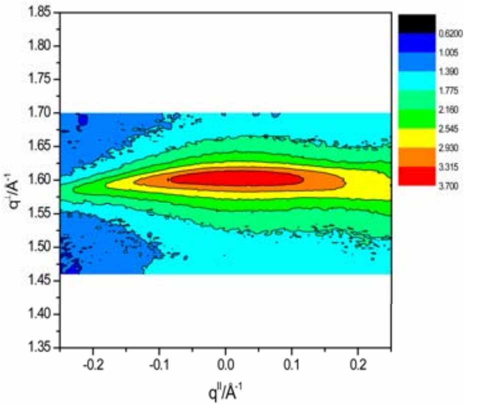


Texture

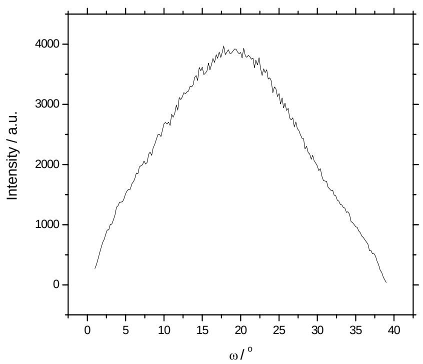
- Substrate has low degree of texture
  - Rocking curve FWHM 23.2º
- FWHM of rocking curve for $BiFeO_3$ 012-peak: 6.4º (T_{cryst}= 600ºC)
- Phi-scan of $BiFeO_3$ (214) shows no in-plane orientation



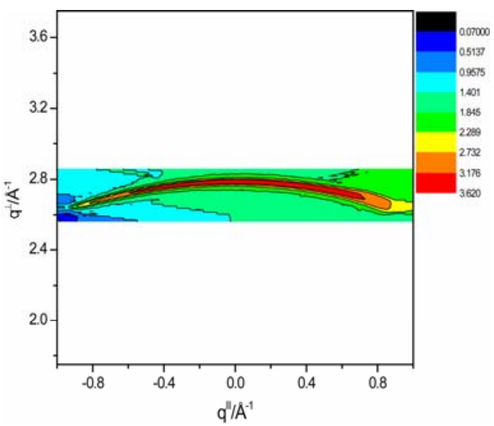
Rocking curves of $BiFeO_3$ 012-peak



Reciprocal space map of $BiFeO_3$ 012-peak



Rocking curve of Pt 111-peak



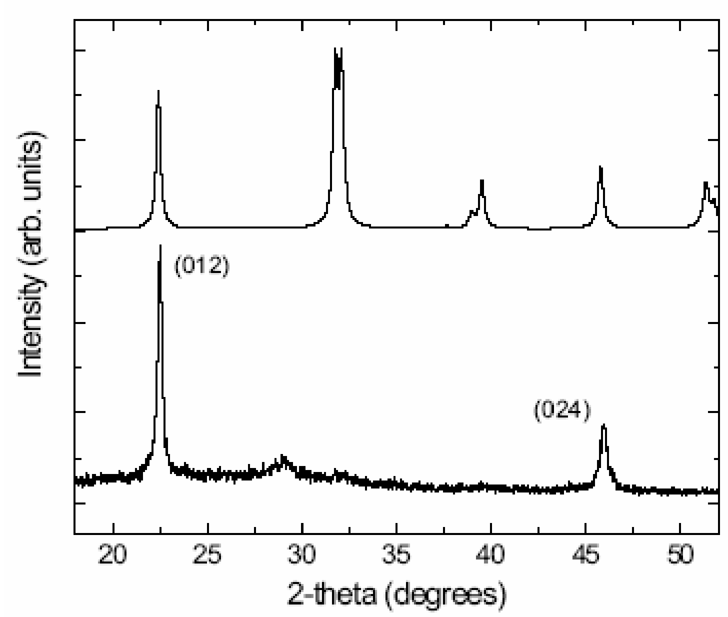
Reciprocal space map of Pt 111-peak

Tyholdt, F.; Gunnæs, E. A.; Jørgensen, S.; Fjellvåg, F. *Journal of Materials Research* **2005**, *in press (aug. -05)*.

Texture on glass

- $BiFeO_3$ displays high degree of texture even on amorphous substrate

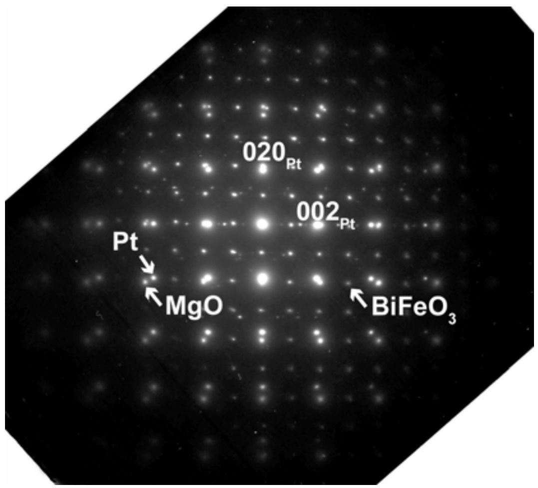
1. Nucleation of randomly oriented grains at glass-film interface
2. The slower growing planes will develop and lead to columnar growth
3. High heating rate is used to minimize crystallization driving force

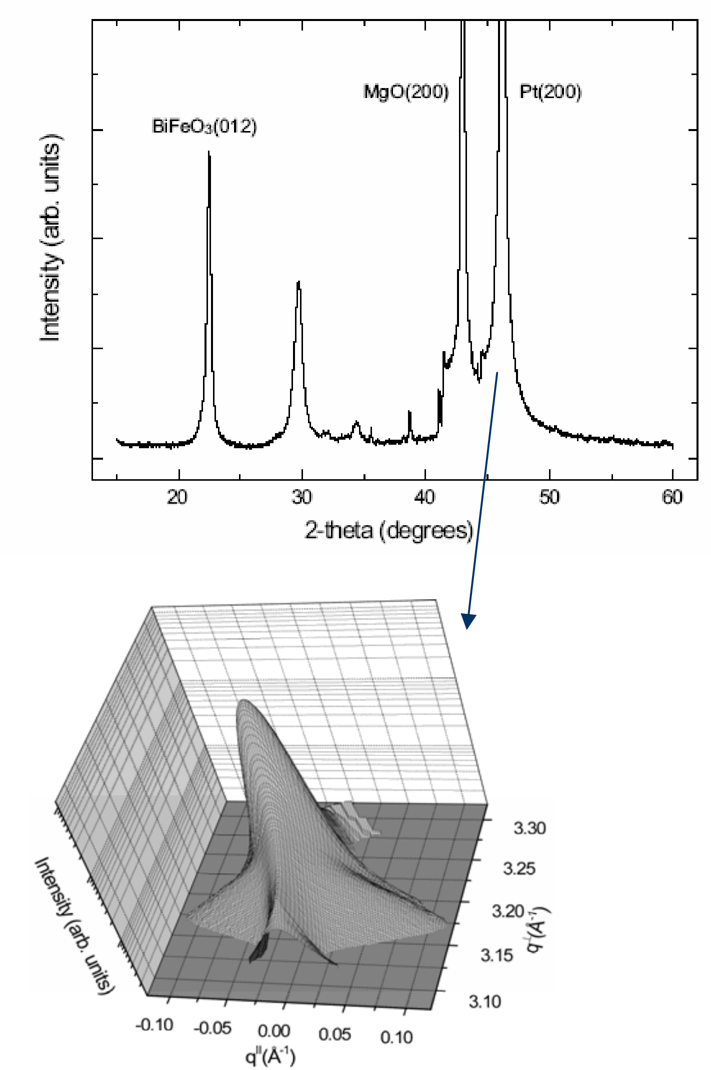


120nm $BiFeO_3$ film on glass substrate crystallized at 600°C

Epitaxial $BiFeO_3$ by CSD

- Epitaxial $BiFeO_3$ film on MgO(100)/Pt(200) substrate (120nm)





Tyholdt, F.; Gunnæs, A.E.; Leclerc, G.; Fjellvåg, H. *unpublished results* **2005**.

Summary

- High quality multicomponent oxide films can be fabricated by CSD
- Large thickness range possible by adjusting sol concentration/multiple coating
- Control (and knowledge) of precursor chemistry is essential
- Textured and epitaxial films can be obtained by use of seeding layer/matching substrate

Have a nice Sunday!