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Impermeable Thin Film Encapsulation for Lighting, Displays and Solar Cells

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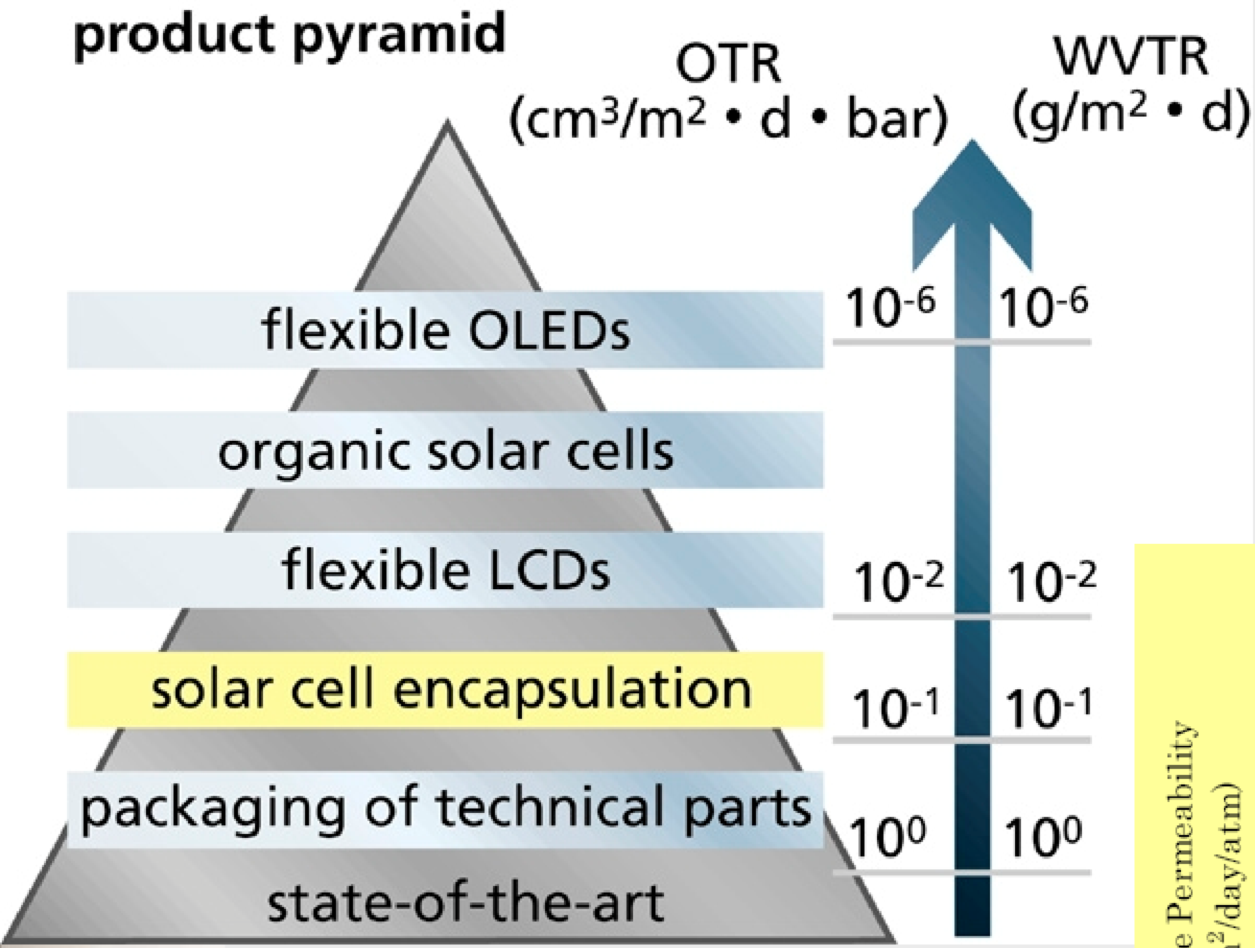
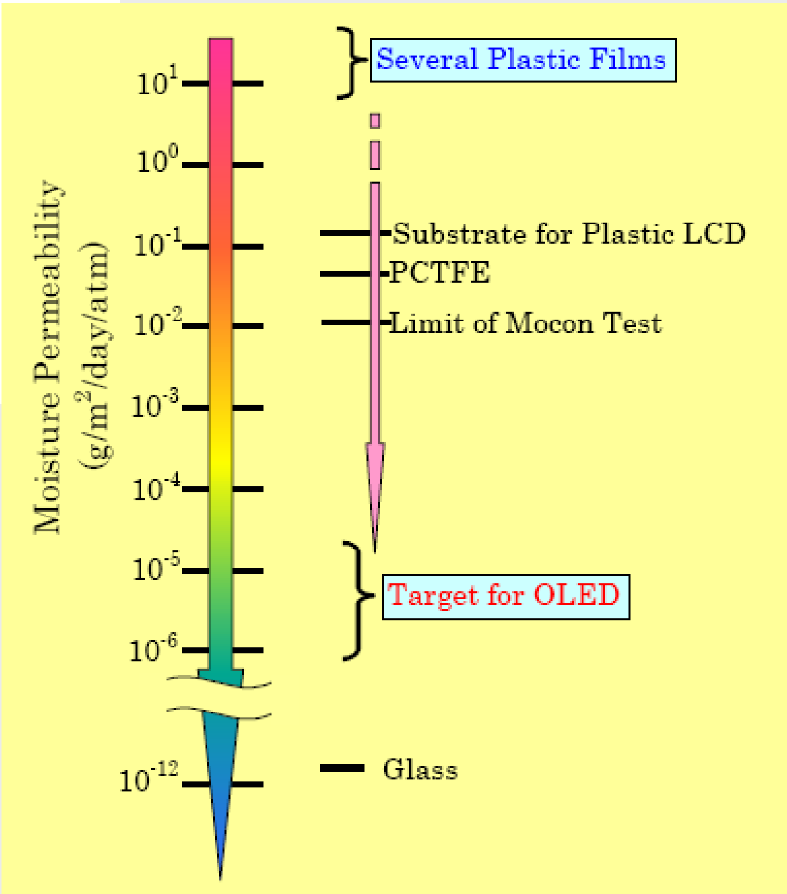
  - Stability under SiN_x deposition conditions
    - Temperature
    - Atomic hydrogen
- Low temperature SiN_x deposition
- Conclusion/Discussion

Demands for barrier layers





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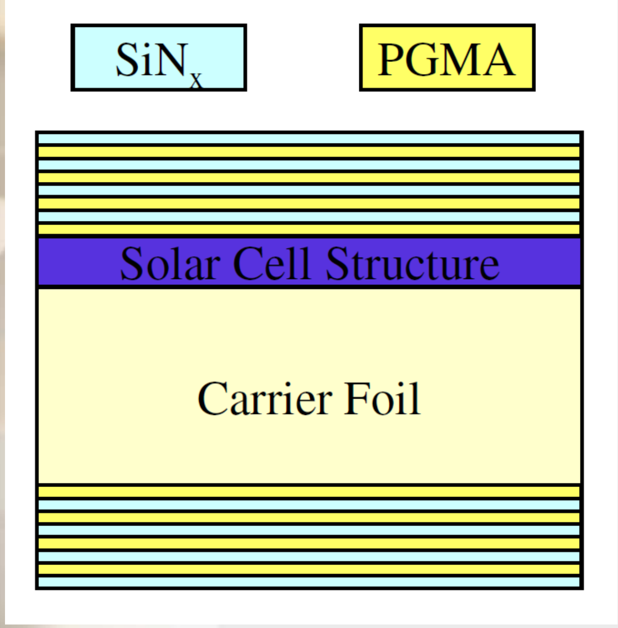
Introduction

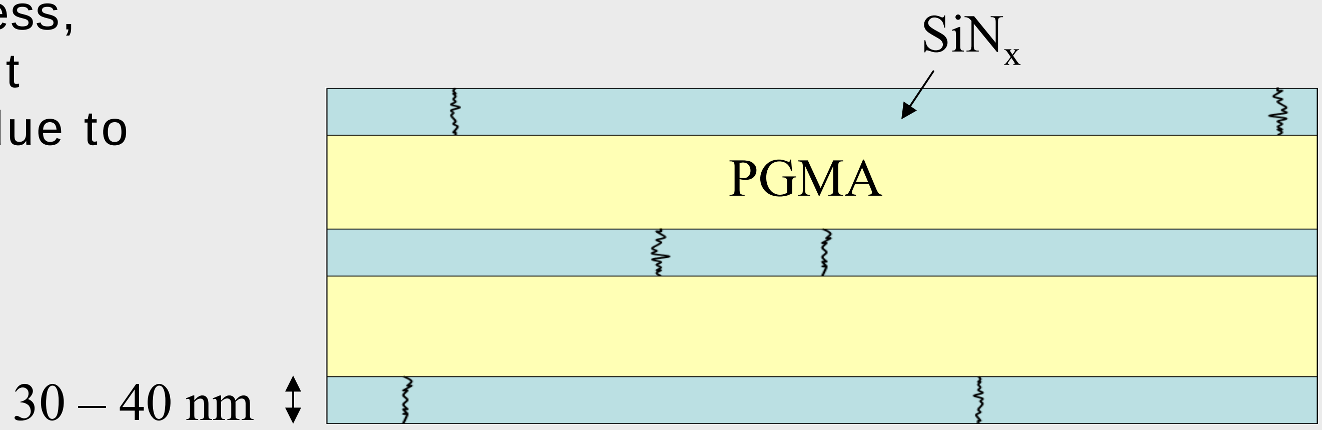


- A combination of high density SiN_x and polymer layers is very suitable as a thin film water and oxygen barrier layer.
- Both materials can be deposited using hot wire chemical vapor deposition (HWCVD), allowing for delicate substrates and sensitive devices, such as Organic LEDs.
- Multilayer should be neutrally transparent and robust

Introduction

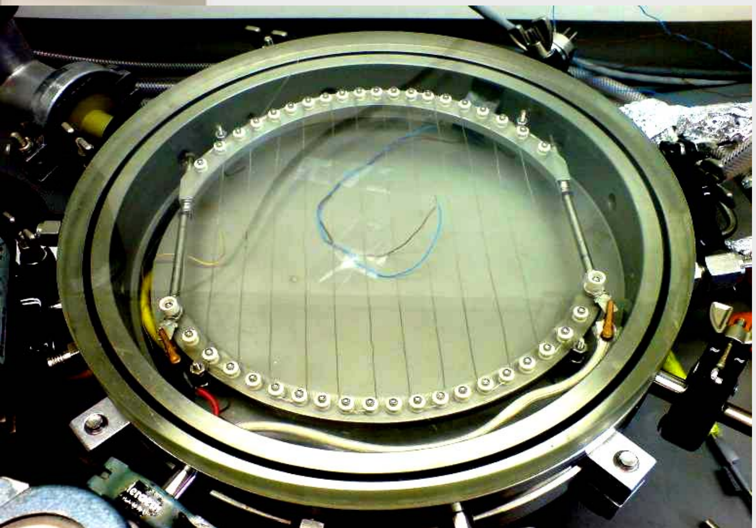
Dense silicon nitride is a very impermeable material.

Above 40 nm thickness, permeability does not decrease anymore, due to pinholes[1].



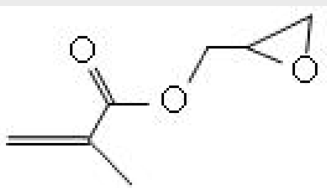
1 N.Cordero et al., Applied Physics Letters 90, 111910 (2007)

Introduction: iCVD of PGMA



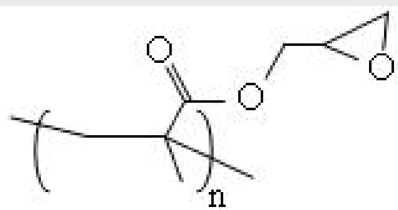
Initiation at the wire	$i\text{–}i \rightarrow 2\, i^{\cdot}$
Propagation at substrate	$i^{\cdot} + n\,M \rightarrow i\text{–}(M)_n^{\cdot}$
Termination at substrate	$i\text{–}(M)n^{\cdot} + i^{\cdot} \rightarrow i\text{–}(M)_n\text{-}i$

monomer



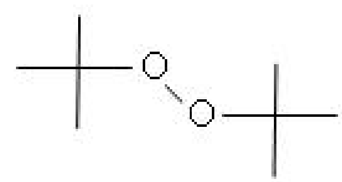
glycidyl methacrylate (GMA)

polymer



poly-glycidyl methacrylate (PGMA)

initiator

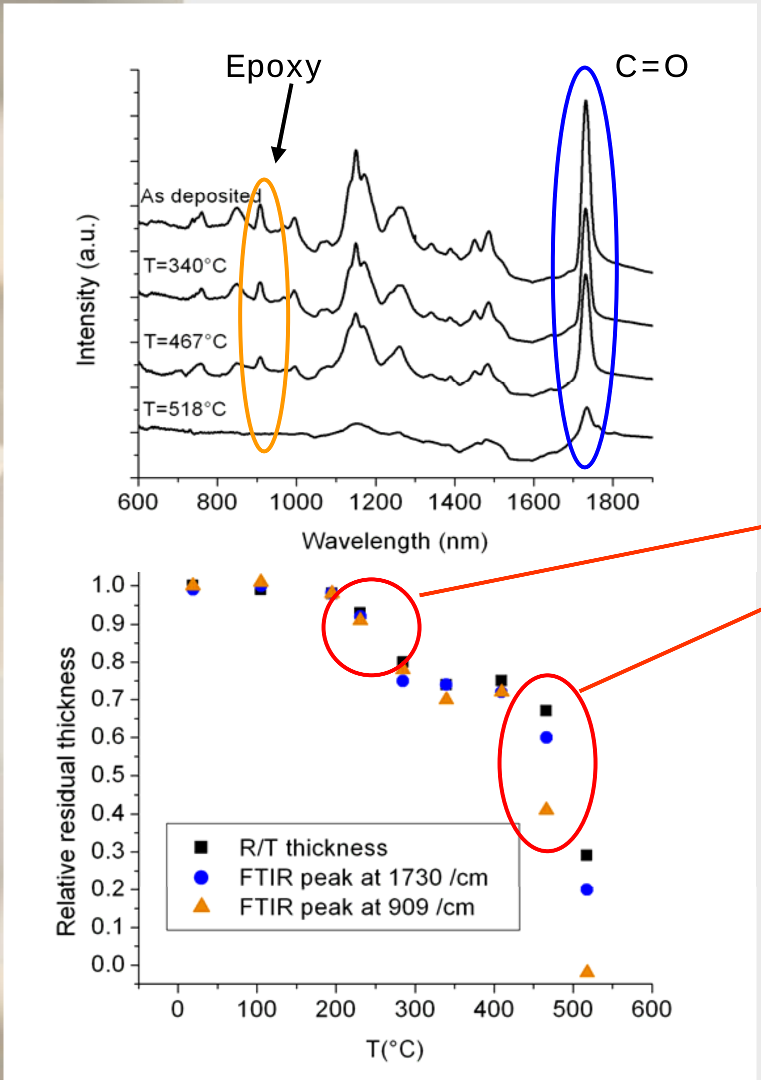


tert-butyl peroxide (TBPO)

Introduction

- At the moment the most important issue in creating Multilayers is to make polymer layers that can withstand HWCVD SiN_x deposition.
- This challenge can be approached in 2 ways:
  - Increasing polymer stability.
  - Decreasing SiN_x deposition temperatures.

Stability under SiN_x deposition conditions: Temperature

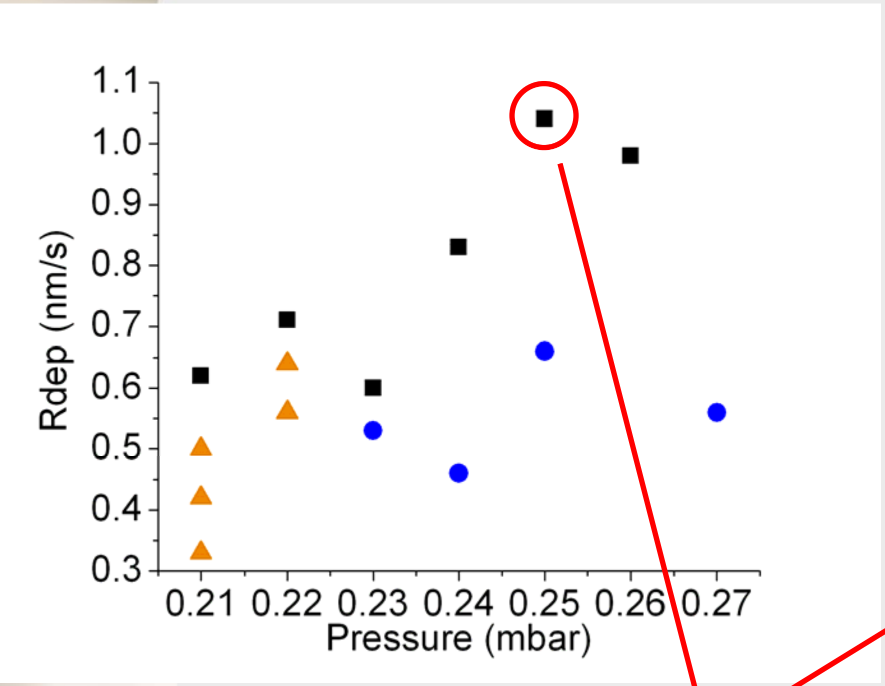


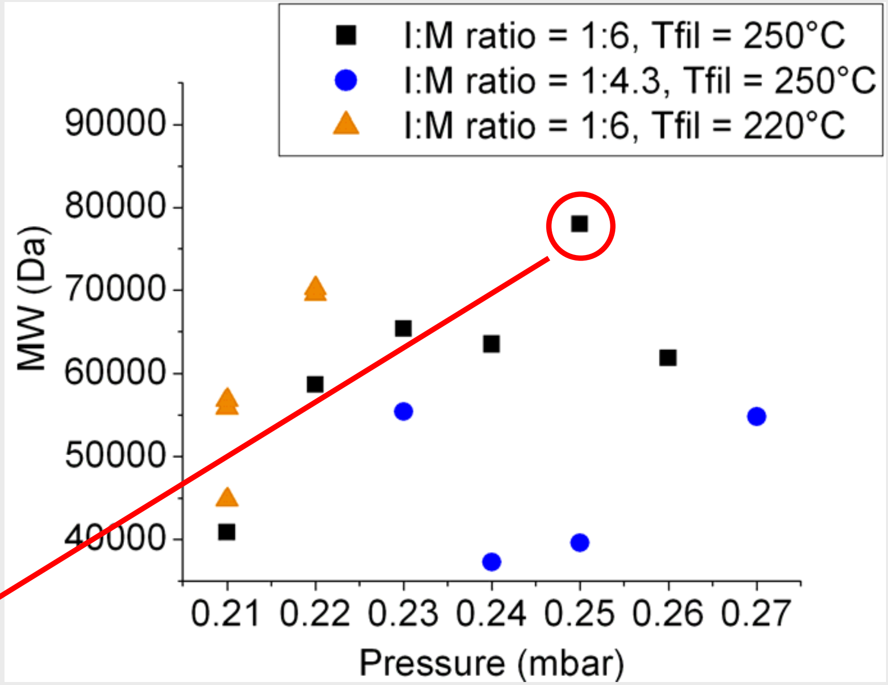
R. Bakker et al., Surface & Coatings technology 201 (2007) 9422-9425

Thermal stability:

- Degradation in two steps:
  - First step at 200˚C: unsaturated chain ends
  - At 450˚C: Random chain cuts
- Large molecules → amount of unsaturated chain ends becomes insignificant: stability increases

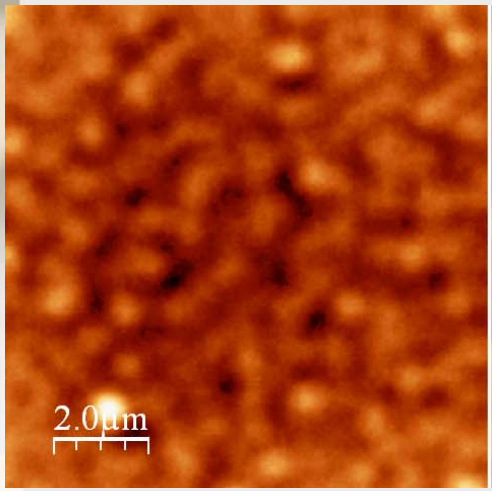
PGMA: Deposition rate and molecular weight



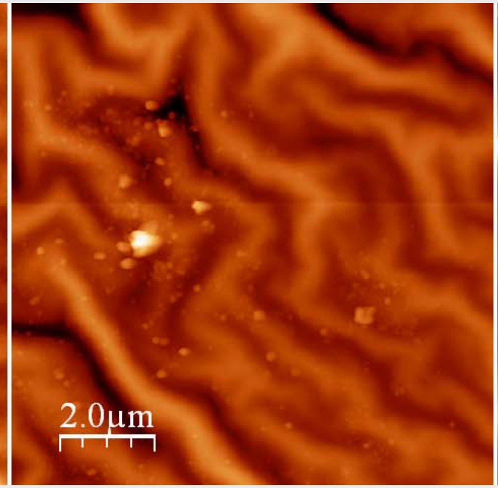


PGMA with an weight-average molecular weight of 78000 Dalton (548 monomers) was deposited at a deposition rate of 1.04 nm/s.

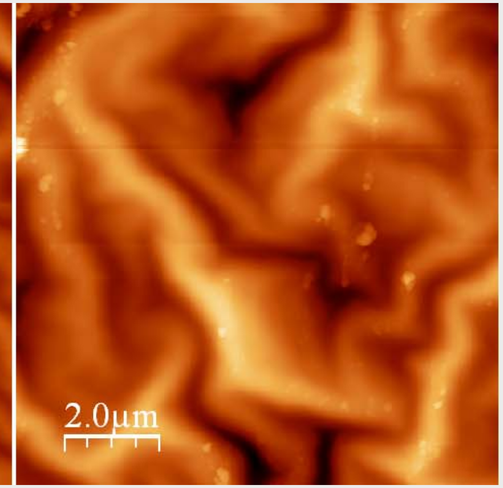
PGMA: Stability under HWCVD SiN_x deposition conditions: atomic hydrogen



As deposited
RMS roughness 2.7 nm



190 seconds
RMS roughness 26.1 nm

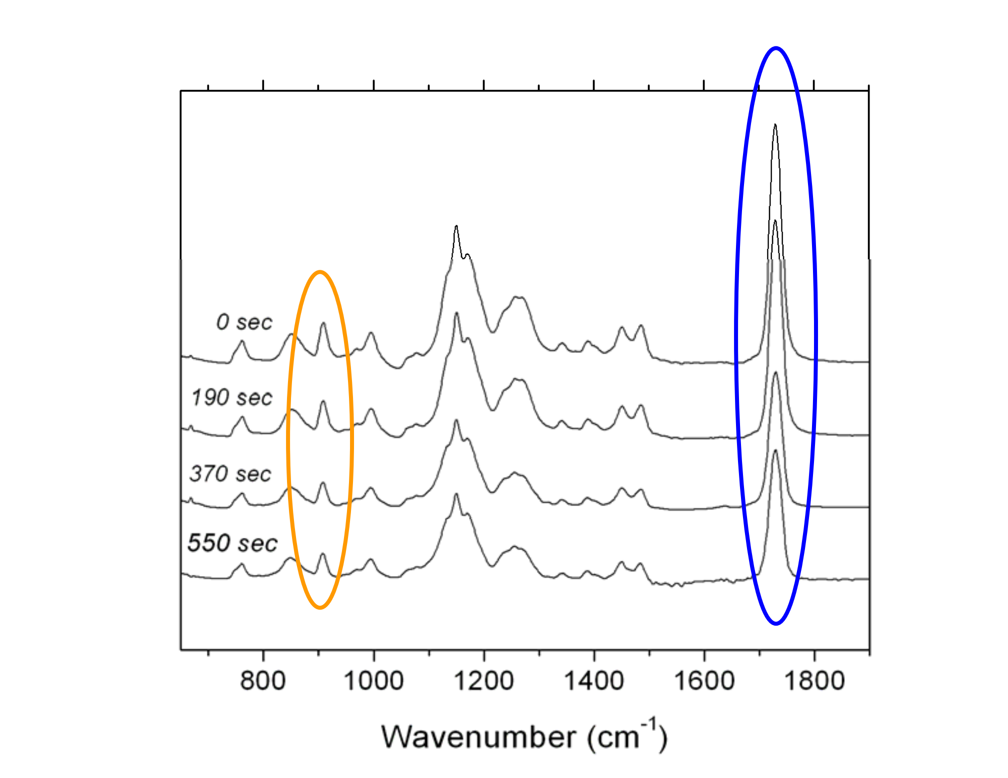


370 seconds
RMS roughness 66.3 nm

Samples were exposed to atomic hydrogen made by HWCVD for, 190, 370 and 550 sec.

Surface roughness becomes high and refractive index is not exactly known after layers are degraded → impossible to determine the thickness with RT measurements.

PGMA: Stability under HWCVD SiN_x deposition conditions: atomic hydrogen



Heights of FTIR peaks were used as a measure for degradation.

C=O peak vanishes faster than epoxy peak, contrary to thermal degradation.

Thickness derived from FTIR peak height

Since degradation takes place at the surface one should use absolute decrease in thickness.

$t_{initial}$ = R/T thickness
h = FTIR peak height

$$Thickness \;\; decrease \; = \; t_{initial} - \left(\frac{t_{initial}}{h_{initial}} h_{after}\right) = t_{initial}\left(1 - \frac{h_{after}}{h_{initial}}\right)$$

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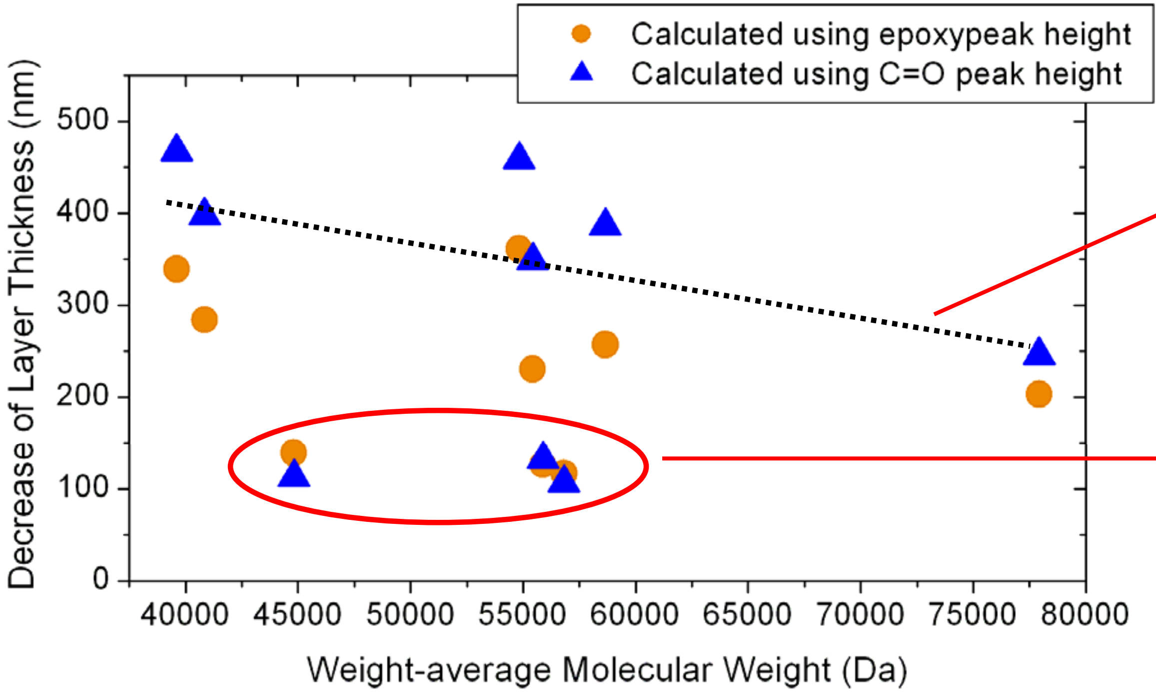
PGMA: Stability under HWCVD SiN_x deposition conditions: atomic hydrogen



A trend could be seen for samples made at a wire temperature of 250˚C.

Samples made at a wire temperature of 220˚C are clearly more stable.

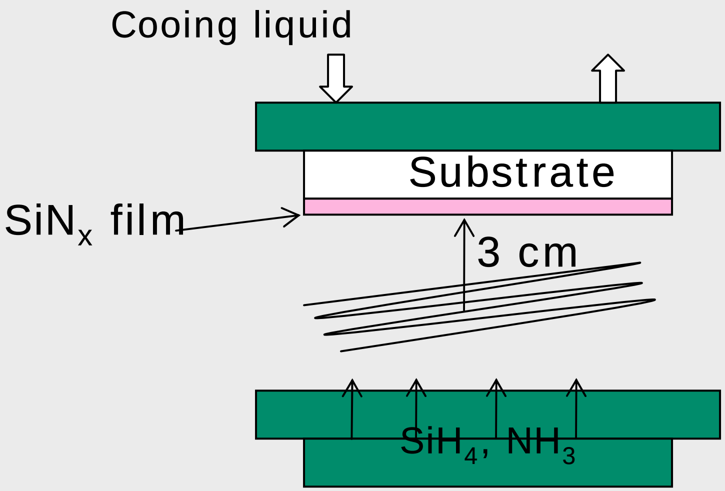
PGMA: Stability under HWCVD SiN_x deposition conditions: atomic hydrogen

- For stability the wire temperature used for deposition is the most important parameter, rather than M_W or surface roughness.
- No difference in deposited layers could be found using FTIR with wire temperature.
- Possibly the structure of the layer varies with wire temperature.
  - Higher wire temperatures results in higher substrate temperature.
  - Higher temperatures cause gas phase monomer reactions (above 222˚C)[1].
  - Higher temperatures make the initiator dissociate into different radicals[2].

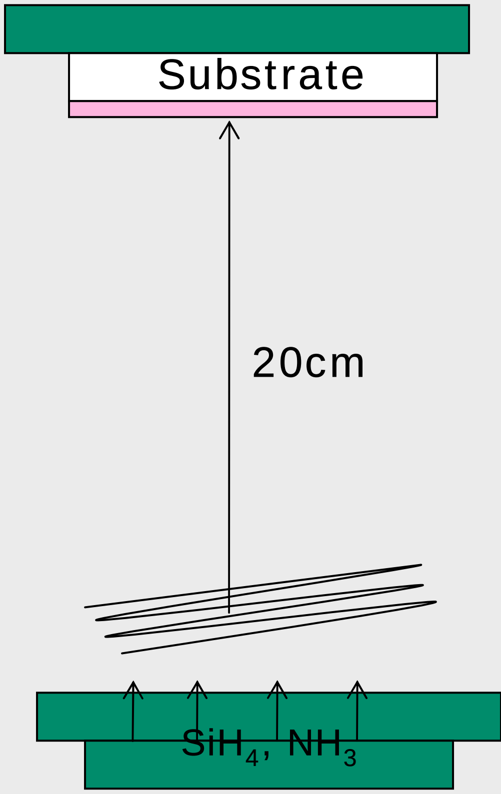
1 Y. Mao and K.K.Gleason, Langmuir 20 (2004) 2484-2488

2 G. Ozaydin-Ince and K.K. Gleason, J. Vac. Sci. Technol. A 27(5) (2009) 1135-1143

HWCVD SiN_x deposition



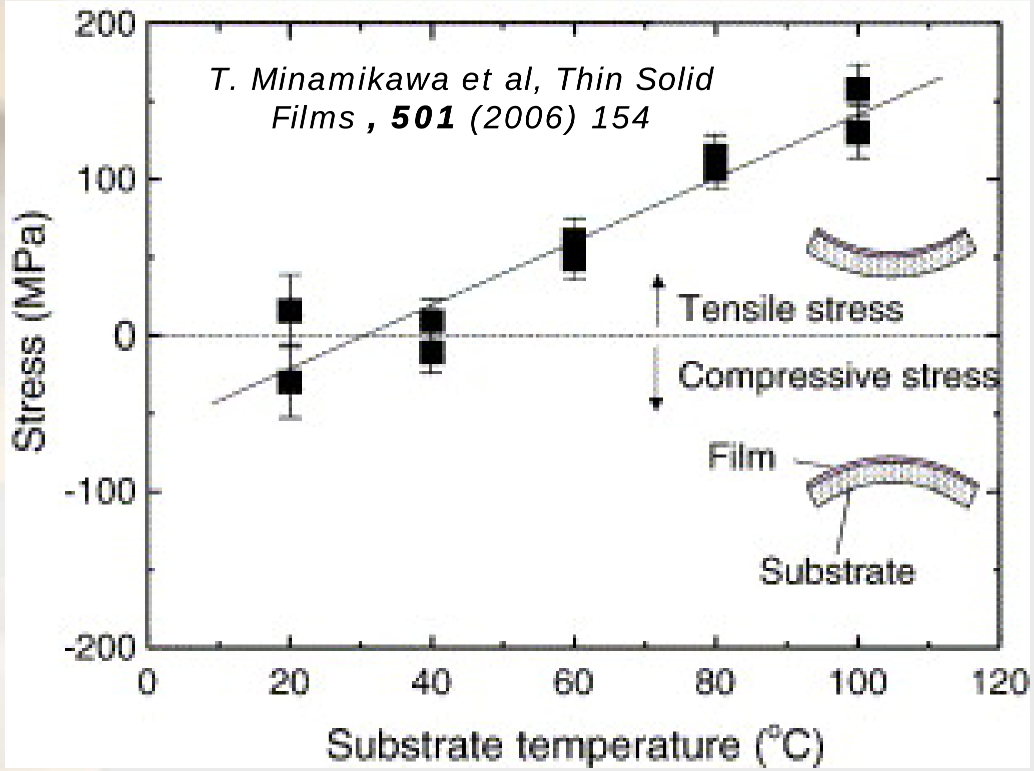
Old config.



New config.

Temperature of 100C or below is possible to reach by the new config.

HWCVD SiN_x deposition



It possible to make a very low stress SiNx material by HWCVD by lowering substrate temperature

Conclusions / Discussion

- PGMA with a M_w of 78000 Dalton was deposited at a r_{dep} of 63nm/min.
- Higher M_w PGMA is thermally more stable.
- For stability under atomic hydrogen exposure, the wire temperature used for deposition (an indirect parameter) is the most important parameter.
- PGMA made at low wire temperatures, should be stable enough to deposit SiN_x on it.

Acknowledgements

Caspar van Bommel

Martin Huijzer

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Thank you for your attention.

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