Silicon nitride multilayers as permeation barrier for OLEDs on flexible PET substrates. Effect of Ar plasma treatment

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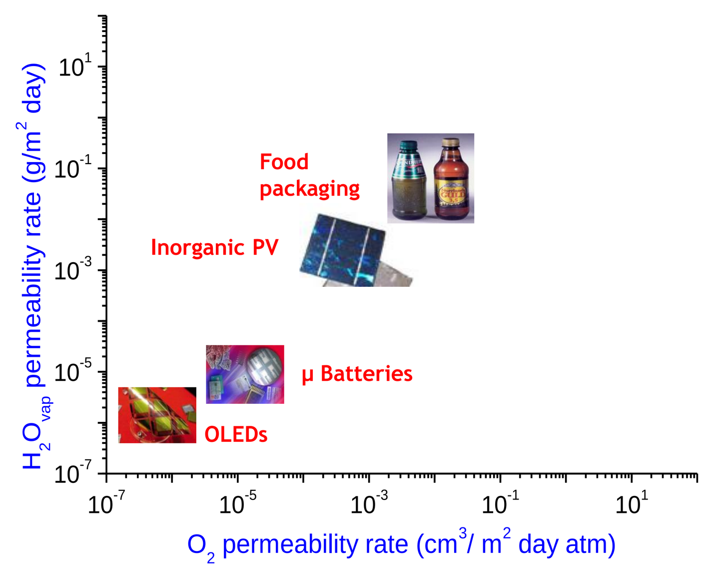
INTRODUCTION

Advantages of organic LEDs deposited on flexible PET:

- Low cost fabrication of large area devices
- Low specific weight
- Mechanical flexibility
- Easy tunability of chemical properties of organic materials
- Increased range of colors
- Better performance in low and indirect light

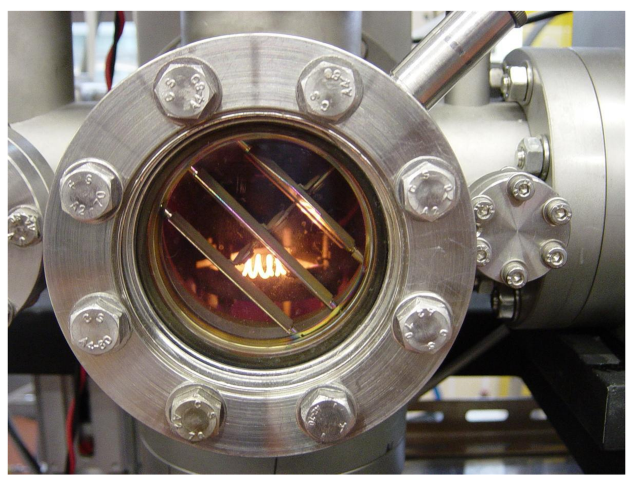
Drawback of organic LEDs: OLEDs are extremely moisture sensitive and so their lifetime is limited.

MOTIVATION (BARRIER REQUIREMENTS)



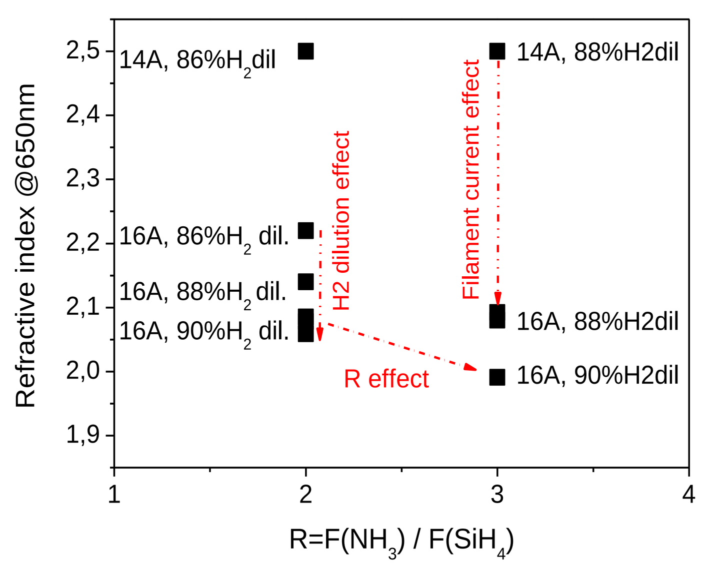
- ✓ Characteristics needed for barrier films :
  - dense
  - without surface defects
  - good adhesion
  - thermal stability
  - constant thickness
- ✓ Requirements for barrier materials:
  - low temperature deposition
  - without stress
  - transparent and insulating

OPTIMIZATION OF SILICON NITRIDE LAYERS USING HW-CVD

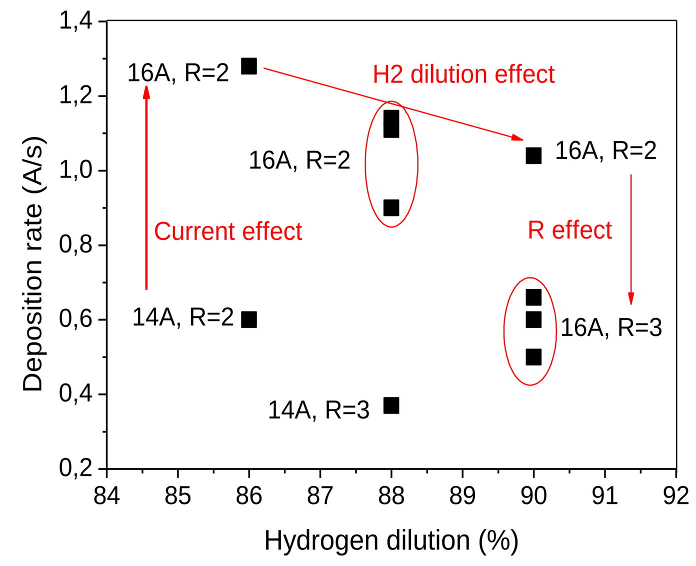


SiNx layers: SiN_x layers were grown by Hot Wire Chemical Vapor Deposition (HWCVD) on PET substrates. Depositions were performed at substrate temperature of 100ºC and working pressure of 25 mTorr. The different series of layers were realized, changing the parameters: the hydrogen dilution (86, 88 and 90%), ammonia-to-silane gas flow ratio R (2 and 3) and Ta filament current (14 and 16A).

$$H_2\ dilution = \frac{F_{H_2}}{F_{H_2}+F_{SiH_4}+F_{NH_3}}$$



The refractive index decreases with filament current, with R and with hydrogen dilution.

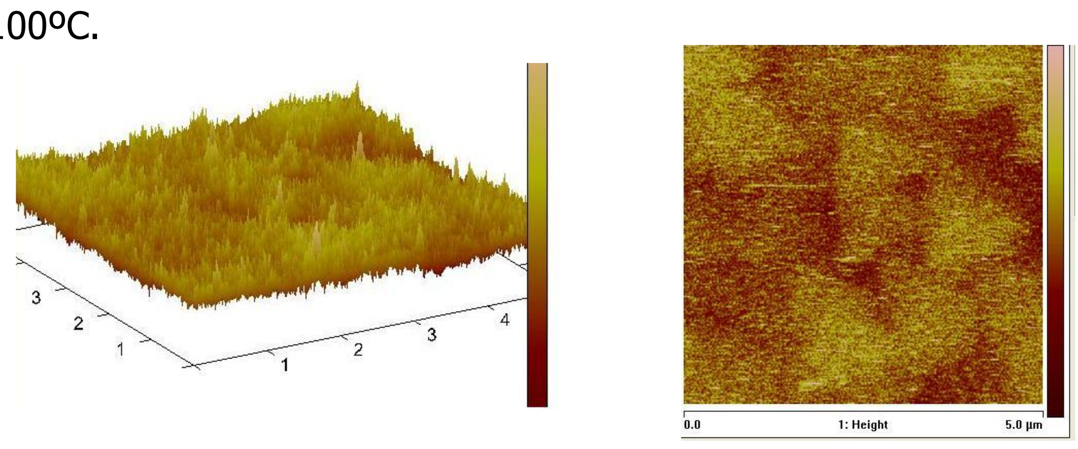


The deposition rate increases with filament current, decreases with R and with hydrogen dilution.

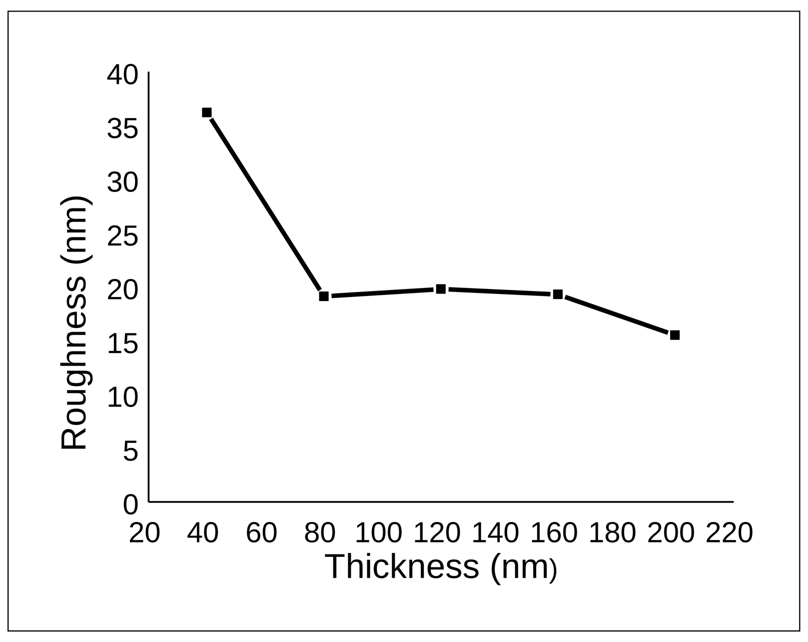
RESULTS (AFM & Ca Tests)

Multilayer structures: *n (1 to 5)* x sequence of 40nm thick SiN_x layer (produced at optimized conditions: 16A; R=2; 90%H_2 dilution).

Ar-plasma surface treatment: The HWCVD SiN_x layers were transferred without breaking the vacuum to a twin chamber and treated for 120s with Ar-plasma at working pressure of 50 mTorr and substrate temperature of 100ºC.



AFM images of surface of the film



❑ **The sample roughness decreases with the number of SiN_x layers, i.e. with the sample thickness.**

Series	Samples	Roughness (nm)
SiN Series	40nm	36.2
	80nm	19.1
	120nm	19.8
	160nm	19.3
	200nm	15.5
SiN + Ar treatment series	40 + Ar + 40	25.9
	40 + Ar + 40 + Ar + 40	26.8
	40 + Ar + 40 + Ar + 40 + Ar + 40	29.8
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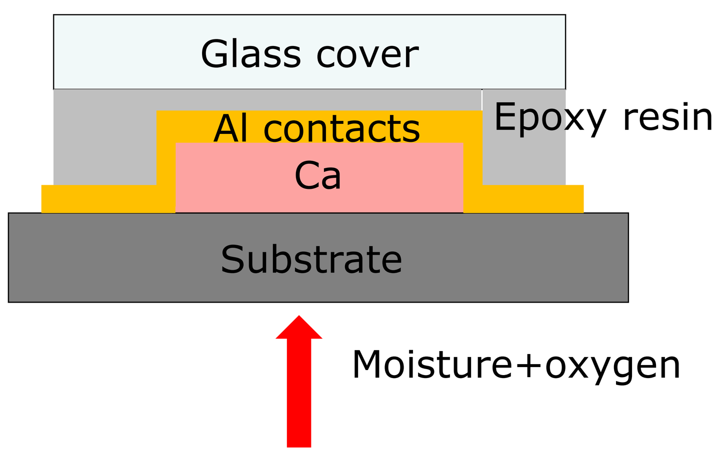
❑ **The sample roughness increases after Ar treatment- reaching almost the same value, independent of the thickness.**

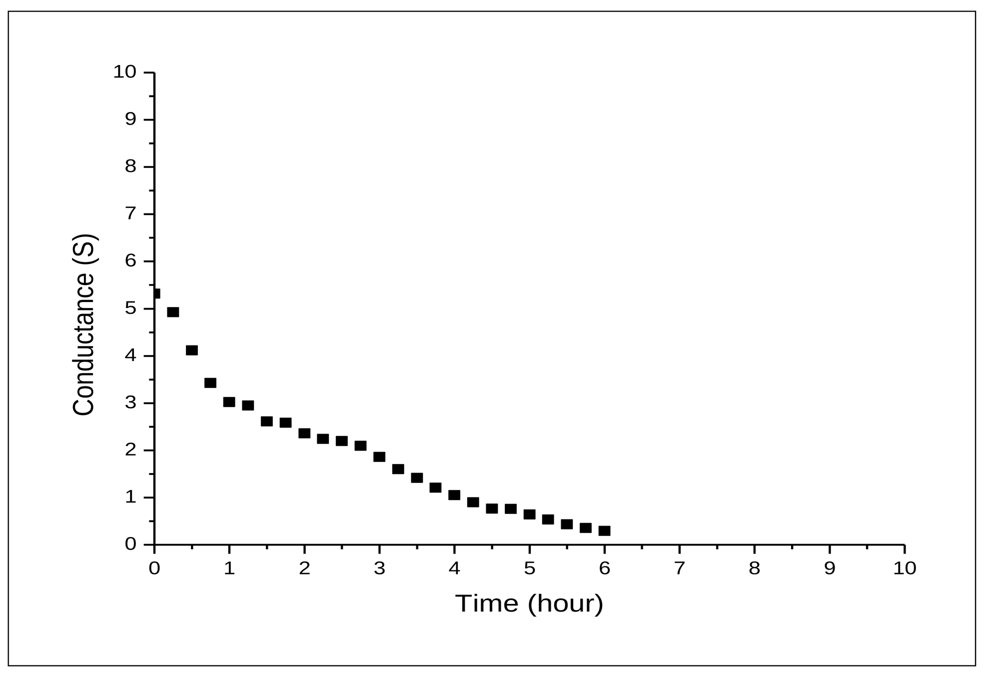


Calcium degradation test set-up

The calcium sensor reacts with water vapour and oxygen which diffuses through the substrate and the sensor oxidizes. Due to this oxidation, the conductance (G) decreases.

$$WVTR\ [g/m^2.day] = -n.\delta_{Ca}.\rho_{Ca}.\frac{dG}{dt}.\frac{l}{w}.\frac{M[water]}{M[calcium]}$$

δ_{Ca}= density of calcium
ρ_{Ca}= resistivity of calcium
$\frac{l}{w}$=length to width ratio of the sensor
M= molar mass
n= molar equivalent of reaction



❑ **Evolution of conductance of 60nm Ca sensor on bare PET substrate. From the slope of this evolution, the WVTR is deduced. WVTR= 0,72 g/m².day**

CONCLUSIONS AND FUTURE WORK

Two series of deposition are performed on bare PET: 1) Multilayer of 40nm thick silicon nitride films, deposited sequencially; 2) Multilayers of 40 nm thick silicon nitride films, deposited sequencially and two subsequent layers are separated by Ar plasma treatment.

From the AFM images, we can conclude that the roughness of the films decreases with thickness. The objective of Ar plasma treatment is to make diffusion of water vapour and oxygen more complex, by disturbing each interface. From the calcium degradation test, we assess the water vapour permeation rate of bare PET substrate.

As a future work, spectroscopic polarimetry measurement will be performed to estimate the density and thickness of SiNx. Organic LEDs will be realized on barrier coated PET substrates and their shelf-lifetime will be measured.

REFERENCES

R.Paetzold, A.Winnacker, D.Henseler, V.Cesari, K.Heuser, "Permeation rate measurements by electrical analysis of calcium corrosion," Rev.Sci.Instrum. **74**, 5147 (2003).

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