IMPROVEMENT OF SILICON NITRIDE GAS-DIFFUSION BARRIERS BY A LOW ENERGY ARGON PLASMA TREATMENT

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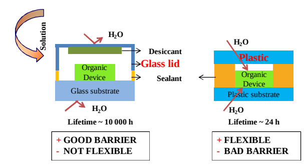
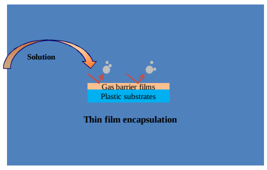
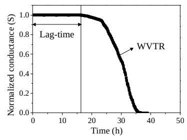
Electrodes and organic layers are very sensitive to water vapor and oxygen
→ **Thin film encapsulation is mandatory for organic electronic devices**:

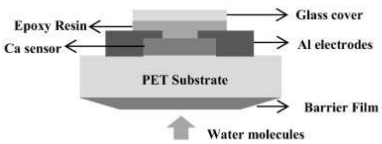


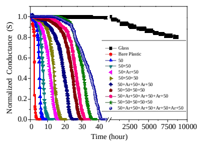


Choice of multilayer barrier material and deposition method:
1. Silicon nitride as compared with silicon dioxide and aluminum oxide
2. hot-wire CVD as compared with plasma-enhanced CVD (lower density material) and atomic layer deposition (very low deposition rate)

Choice of analysis techniques for SiN_x:H films:
X-ray diffraction: structure of layers
UV-visible ellipsometry: refractive index and absorption coefficient
Integrating sphere: transmittance and reflectance
X-ray reflectometry: mass density
Electrical Ca test method: water vapor transmission rate

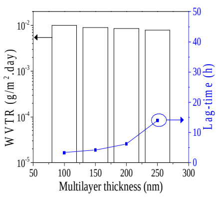






Tentative conclusion for SiN_x:H multilayers grown by HWCVD without any further treatment

Variations of lag-time and WVTR:



✓ Increase of lag-time

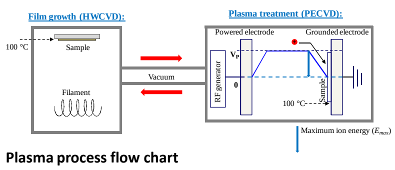
✓ Slight decrease (10%) of WVTR for each successive single-layer

✓ **Minimum WVTR= 8 × 10^{-3} g/ m².day** for 5 x 50 nm multilayer thickness

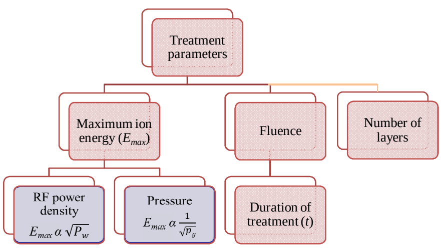
× **Insufficient results for organic devices**

Fabrication of SiN_x:H multilayer barriers grown by HWCVD, each single-layer being separated from the previous one by a plasma treatment

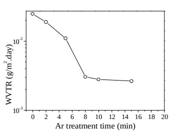
Choice of plasma species: in the case of elastic collision between the incoming ion (M_1) and an atom at rest in the target (M_2), the energy transfer is equal to $4M_1M_2/(M_1 + M_2)^2$ times the maximum kinetic energy of the incoming ion Atoms in the target: Si and N → **Ar^+** chosen as ion species

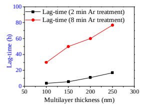


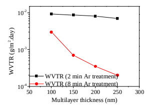
Plasma process flow chart



Effect of treatment duration for low energy E_{max}= 20 eV
Maximum ion bombardment energy is fixed at low value: **20 eV** (P_w = 350 mW/cm² and p_g = 50 mTorr)
Number of layers is fixed at 2 (total thickness = **100 nm**)
→ **Stabilized minimum WVTR obtained for Ar treatment time > 8 min**



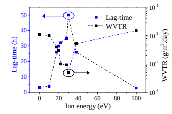


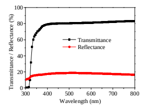


Effect of optimized treatment time on number of SiN_x:H multilayers:
Maximum ion bombardment energy is fixed at low value **20 eV**
Treatment duration is fixed at **8 min**
→ **Increase of lag-time with number of layers**
→ **Decrease of WVTR with number of layers**
→ **Minimum WVTR = 2 × 10^{-4} g/m².day for a total thickness = 250 nm**

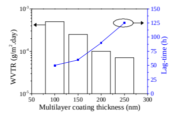
Variation of maximum ion energy with power density and pressure
Maximum ion energy is proportional to $\sqrt{\text{power density}}$
Maximum ion energy is inversely proportional to $\sqrt{\text{pressure}}$

Effect of maximum ion energy for a fixed treatment time = 8 min
Number of layers is fixed at **2** (total thickness = **100 nm**)
Maximum ion energy is increased from **10** to **100 eV**
→ **From 0 to 10 eV: no significant effect on WVTR**
→ **At around 30 eV: minimum WVTR = 5 × 10^{-4} g/m².day**
→ **> 40 eV: increase of WVTR at same level as < 10 eV**
→ **Inverse effect on lag-time**

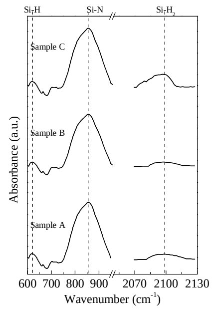




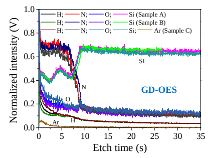
Effect of previously optimized plasma parameters on number of multilayers
Maximum Ar ion bombardment energy is fixed at **30 eV**
Treatment duration is fixed at **8 min**
Number of layers is increased from **2** to **5**
→ **Optical transmittance (~ 80%)**
→ **Maximum lag-time = 125 h**
→ **Minimum WVTR = 7 × 10^{-5} g/m².day measured at RT**



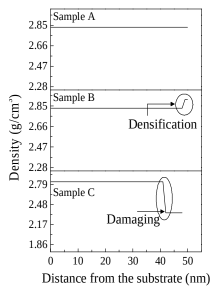
Analysis of results based on FTIR measurements
3 samples (50 nm thick) SiN_x:H layers deposited on crystalline silicon
1) Sample A: as deposited
2) Sample B: maximum Ar ion energy = 30 eV
3) Sample C: maximum Ar ion energy = 100 eV
→ **No significant change between samples A and B**
→ **Increase of Si-H_2 absorbance for sample C compared with A**



Analysis of results based on GD-OES and XPS measurements
For sample B compared with sample A: decrease of H (FTIR and GD-OES) and O (GD-OES and XPS) → decrease of nanovoids
For sample C: increase of H (FTIR and GD-OES) and O (GD-OES and XPS) → increase of nanovoids; detection of Ar signal (< 0.1 at%) by GD-OES while no Ar signal detected by XPS (below detection limit)



Analysis of results based on XRR measurements
For sample A: density = 2.83 g/cm³ in the whole thickness (50 nm)
For sample B: density = 2.83 g/cm³ in the bulk region (48 nm) and higher density (2.91 g/cm³) in the surface region (2 nm)
For sample C: density = 2.83 g/cm³ in the bulk region (43 nm) and lower density (2.35 g/cm³) in the surface region (7 nm)



Interpretation of GD-OES, XPS and XRR analysis results
Surface atomic threshold displacement energy for Si atoms: 15 - 18 eV (much higher than surface binding energy of Si = 4.7 eV/atom)
Sputtering threshold energy for Si: ~ 50 eV
Implantation threshold energy of Ar^+ in Si: > 60 eV
→ **During the Ar plasma treatment, low temperature (100°C) and low maximum ion energy (< 40 eV) are acting simultaneously. There is analogy with ion energy effects observed in silicon ion beam epitaxy: number of defects in the film is very sensitive to both substrate temperature (at low temperature) and ion energy (at low energy)**
An optimum energy window for average transferred ion energy to target atoms (~ 20 eV) at low temperature (100°C) has been found (sample A) for achieving defect free films. This optimum has been associated with surface atomic threshold displacement leading to rearrangement of atoms at the interfaces and thus to an improved permeation barrier
For sample C, implantation of argon has been observed at the surface of SiN_x:H layer (3 nm), associated with a decrease of density, leading to a degraded permeation barrier

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