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MOISTURE-RESPONSIVE POLYMER FILMS ON FLEXIBLE SUBSTRATES FOR OPTICAL SENSING OF HUMIDITY

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TABLE OF CONTENT

FLEXIBLE SUBSTRATES

- ✓ Development of biosensors with in situ monitoring of biological fluids
- ✓ Wearable electronics
- ✓ Flexible/stretchable sensors for gaseous analytes in the surrounding environment, that affects human health

Developing such sensors faces a multiple challenges:

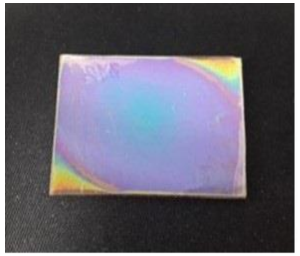
!?

- ✓ Compatible materials
- ✓ Suitable manufacturing techniques
- ✓ Suitable substrates
- ✓ Readout interface

OPTICAL SENSORS

- Work at room temperature
- Low cost
- Do not require power supply

How it works? -> change of color due to different stimuli



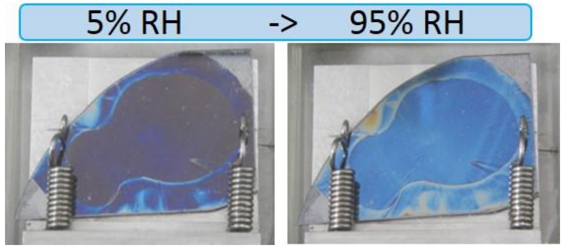
Great variety of materials can be used that can:

- change their refractive index
- change their extinction coefficient and/or thicknesses

OUR IDEA

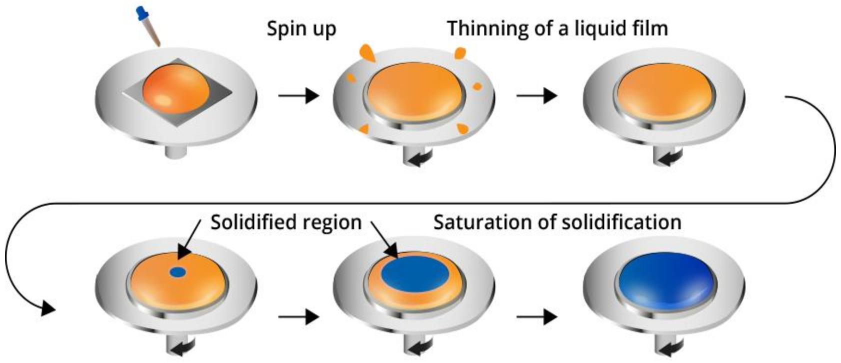
It would be a novelty to make humidity optical sensors:

- ✓ on a flexible substrate
- ✓ do not require power supply
- ✓ have easy production technology
- ✓ rely entirely on optical detection by simple change of the color



- ✓ Development of humidity sensor with *in situ* monitoring of humidity
- ✓ Wearable and flexible/stretchable sensors for humidity in the surrounding environment
- ✓ Use thin films of hydrophobically modified PVA copolymers that are suitable for optical sensing of humidity which change its thickness and refractive index n
- ✓ Find the suitable flexible substrate with best performance!

MATERIALS AND METHODS



- ✓ Spin coating: 0.250 ml drop, 4000 rpm, 60 s
- ✓ Substrates: PET, PLA, Compo-Sil, Glass, Si-wafer
- ✓ Postdeposition annealing: $T = 60^{o}C$ in air for 30 min

- ❑ Hydrophobically modified PVA copolymer, poly(vinyl alcohol-*co*-vinyl acetal) with acetal content of 24% (PVA–Ac24) synthesized by partial acetalization of hydroxyl groups of PVA with acetaldehyde.
- ❑ Copolymer solutions of concentration 1 wt.% in mixed water–methanol solvent (20:80 volume ratio) were prepared for the thin film deposition.
- ❑ Three types of flexible substrates used - poly(ethylene terephthalate) (PET), polylactide (PLA) and composite polysiloxane (Compo-Sil)
- ❑ Substrates coated with single 30 nm thick Au–Pd layer before spin-coating the modified copolymer PVA–Ac24.

MATERIALS AND METHODS

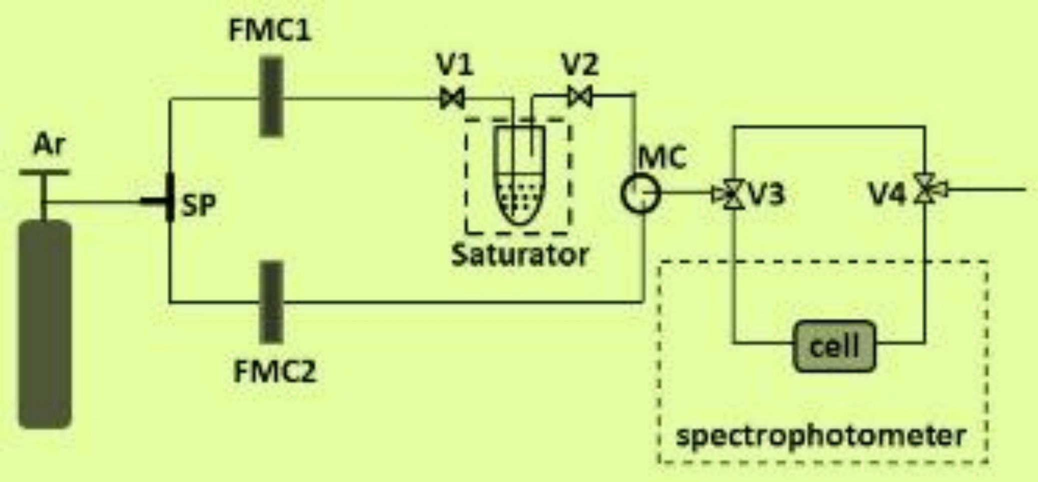
Calculation of the highest humidity responses ΔT (transmittance change) :

$$\Delta T_{max} = |T_{95RH} - T_{5RH}|$$

The percentage of hysteresis (H) defined by:

$$H(\%) = \frac{max|T_{up}-T_{down}|}{\Delta T_{max}} \cdot \frac{\Delta RH_{hyst}}{\Delta RH} \cdot 100$$

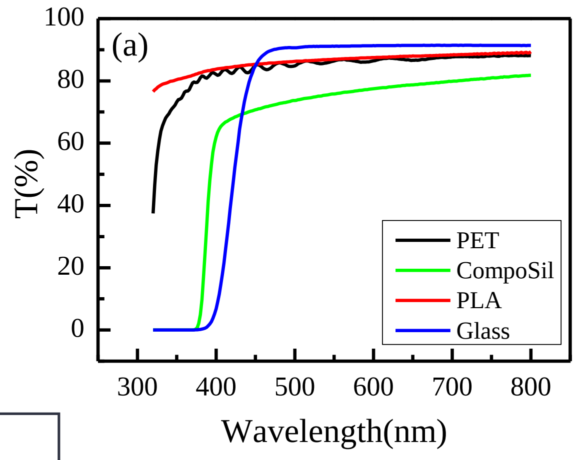
- Thickness of polymer films - 80 nm
- Thickness d, refractive index *n* and extinction coefficient *k* of the PVA–Ac24 film calculated from measured reflectance spectra with UV-VIS-NIR spectrophotometer by using previously developed two-stage nonlinear curve fitting method.
- To conduct humidity sensing experiments was used a homemade bubbler system that generated vapors from liquids and cell with a humidity sensor integrated in it.

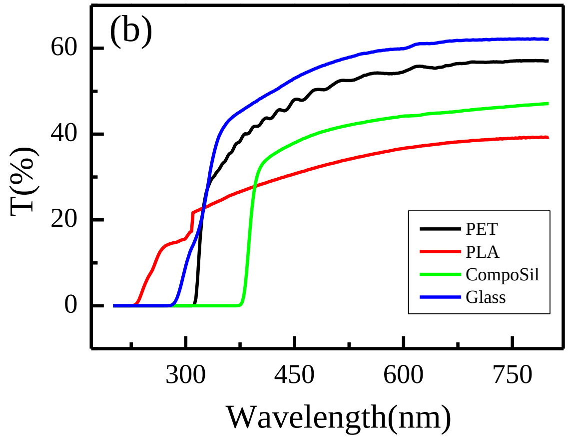


All values of the transmittance T are taken at a wavelength of 600 nm !!!

OPTICAL CHARACTERIZATION

Transmittance spectra of bare (a) and covered with Au:Pd/PVA-Ac24 film (b) substrates: PET, PLA ad Compo-Sil and borosilicate glass

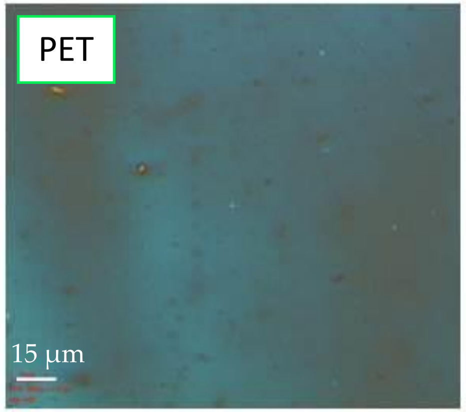


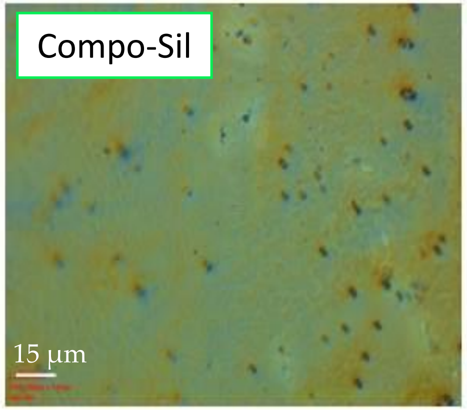


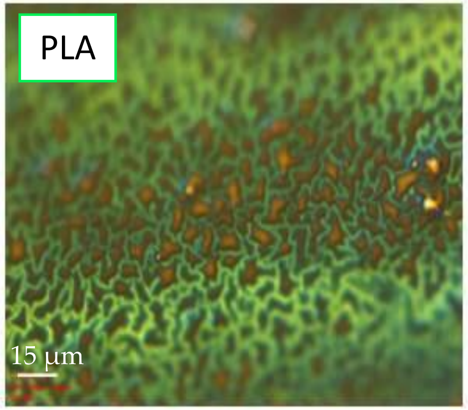
- ✓ PET and PLA samples have almost identical T spectra and transmittance values of 87%.
- ✓ Compo-Sil substrate have lower transparency level and transmission coefficient - 77%.

- ➢ The spectrum of PET sample covered with Au:Pd/PVA-Ac24 is very close to the spectrum of the same structure deposited on glass.
- ➢ The transmission coefficient is 55 % for PET and 59 % for glass.
- ➢ Compo-Sil and PLA have lower transparency level and transmission coefficients 44 % and 36 %, respectively.

SURFACE MORPHOLOGY





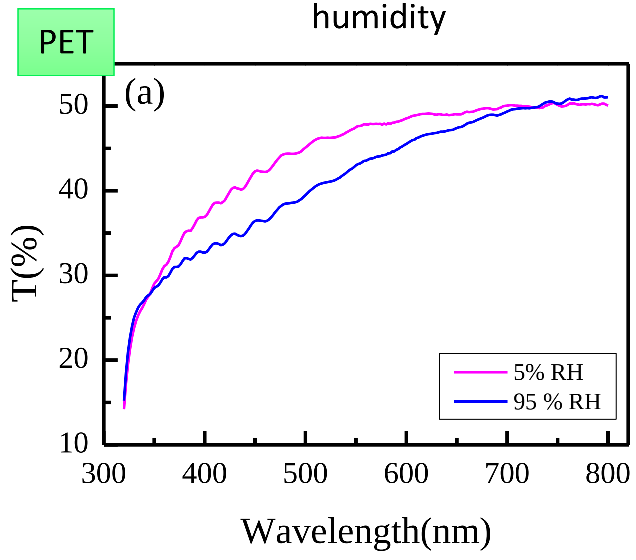


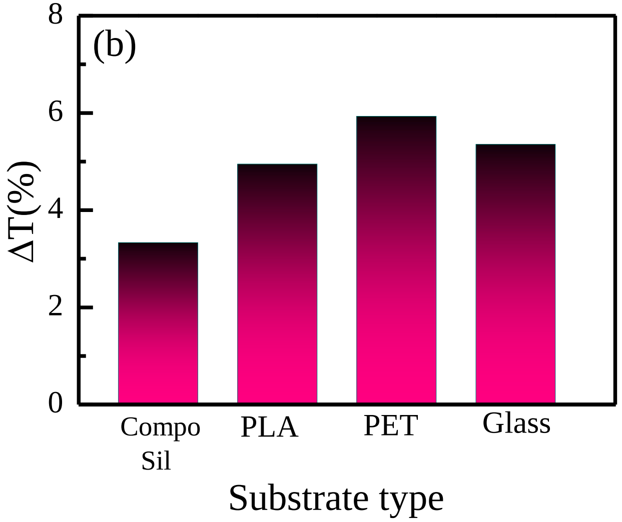
- ✓ PET substrate with Au:Pd/polymer deposited on top has the smoothest surface and even distribution of the thickness, followed by the Compo-Sil sample.
- ✓ PLA sample is inhomogeneous and with different thickness sections (different colors on the picture), which is a prerequisite for the stronger scattering and lower light transmission.

These differences may be due to:

- ❑ the adhesion of every substrate itself
- ❑ the different film formation during the spin-coating process
- ❑ heat treatment after the deposition of the thin films that could decrease the mechanical strength of the substrates, especially those of PLA, that is the thinnest one

The change of the measured spectra of PET substrate with deposited Au:Pd/PVA-Ac24, when exposed to low and high relative humidity





Calculated values of transmittance change ΔT_{max} of all samples

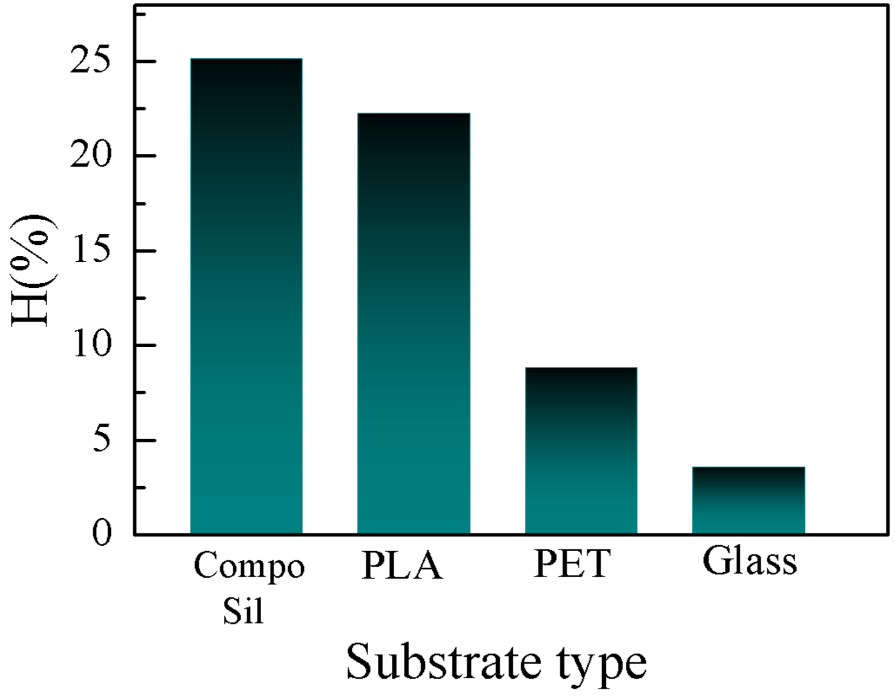
SENSING PROPERTIES

- The highest humidity response (spectra change) ΔT_{max} of 5.9 % is achieved for PET sample at wavelength of 476 nm.

Results can be explained with surface roughness and transparency of the substrates as well as with different adhesion of film to different substrates

- The value of transmittance change ΔT_{max} for Compo-Sil sample is the smallest (3.3%) compared to other substrates and the strongest response is achieved for PET sample (5.9%).

SENSING PROPERTIES



Percentage of hysteresis, H calculated for Compo-Sil, PLA, PET and glass substrates with deposited Au:Pd/PVA-Ac24 at low and high relative humidity.

Percentage of hysteresis, H - parameter that determines the suitability of the material for sensing applications

!!!

For flexible substrates the smallest H-value of 8.9 % is achieved for PVA-Ac24 deposited on PET, which is almost three times smaller compared to samples PLA (22.3%) and Compo-Sil (25.2%).

Our main goal:
to keep H value as low as possible

Conclusions

- ✓ The successful humidity sensing application of thin films of poly(vinyl alcohol-*co*-vinyl acetal) with acetal content 24% deposited on PET, PLA and Compo-Sil flexible substrates is demonstrated.
- ✓ All types of substrates used are shown to be suitable for deposition of metal (Au:Pd) sublayer and for polymers deposition via spin-coating.
- ✓ PET substrate with Au:Pd/polymer deposited on top has the smoothest surface and even distribution of the thickness with no visible cracks and defects.
- ✓ The best sensor characteristics are obtained for PVA-Ac24 films deposited on PET substrate – highest transmittance change (5.9 %) and smallest hysteresis value (8.9 %).
- ✓ Results obtained for PET substrate are similar to the results for glass sample with Au:Pd/polymer thus taking advantage of the flexibility of the substrate but retaining the excellent optical properties of the glass which gives new opportunities for their potential feature use as *in situ* optical flexible/wearable sensors for humidity in the surrounding environment.

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THANK YOU

For your kind attention!