Hybrid poly(vinyl acetal)s / silica nanoparticles thin films for optical sensing of humidity

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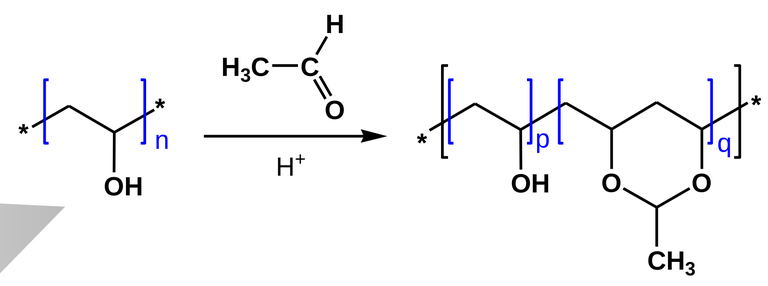
A possible approach for enhancement of PVA humidity sensing performance using hydrophobically modified PVA copolymers is studied. Series of poly(vinylalcohol-*co*-vinylacetal)s (PVA-Ac) of acetal content in the range 18-28 % are synthesized by partial acetalization of hydroxyl groups of PVA with acetaldehyde. Thin films of PVA-Ac and PVA-Ac doped with SiO_2 are deposited by spin-coating using silicon substrates. Sensing properties are probed through reflectance measurements at relative humidity in the range 5-95 %RH. The influence of film thickness and concentration of SiO_2 nanoparticles on hysteresis, sensitivity and accuracy/resolution of humidity sensing is studied for partially acetalyzed PVA copolymer films and comparison with neat PVA is made. Enhancement of sensing behavior through preparation of polymer-silica hybrids is demonstrated.

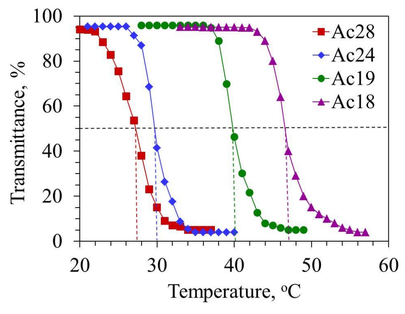
Copolymer synthesis and characterization

Four PVA-Ac copolymers of different composition were synthesized varying PVA-to-acetaldehyde molar ratio. The reaction scheme and chemical structure of the obtained PVA copolymers is shown here



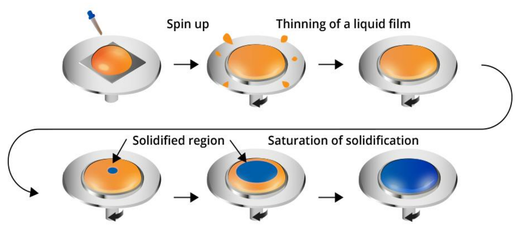
Hydrophobicity	Sample	Acetal content, % (NMR)	T_{CP}, °C (UV-VIS)
↓	PVA	0	-
	Ac18	18	47
	Ac19	19	40
	Ac24	24	30
	Ac28	28	27

Clouding curves of the obtained copolymers registered in transmittance mode at 500 nm



➢ Obtained poly(vinylalcohol-*co*-vinylacetal)s are smart materials exhibiting reversible phase transition in aqueous solution with increasing temperature. The higher the acetal content, the higher the hydrophobicity and the lower the phase transition temperature.

Thin film deposition. Optimization of thickness and post-deposition annealing

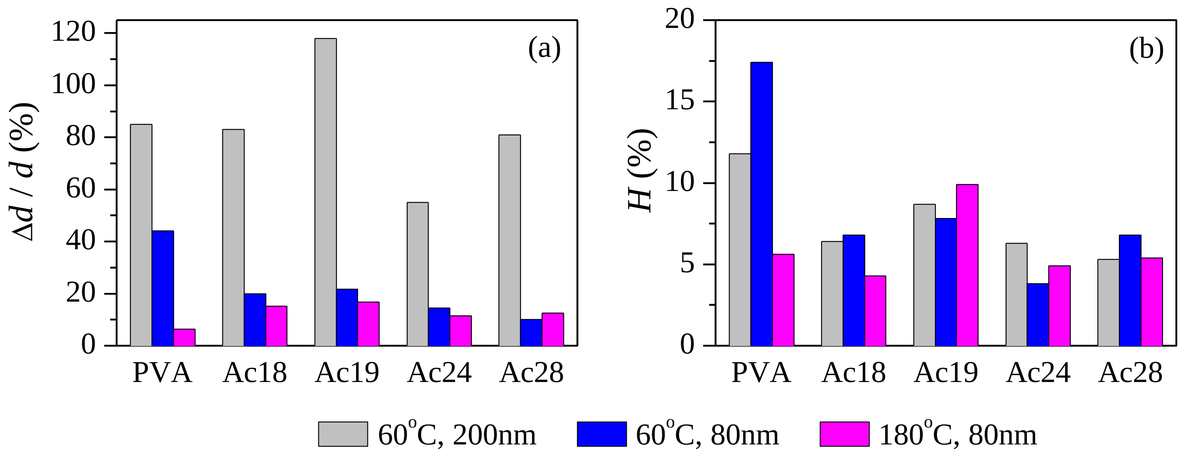


➢ Spin coating: 0.250 ml drop, 4000 rpm, 60s
➢ Postdeposition annealing: 30 min, T = 60°C, 180°C
➢ Substrates: Si-wafer
➢ Thickness: 80 nm / 200 nm

Percentage of hysteresis, *H*

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

Thickness change (a) and Percentage of hysteresis, *H* (b) due to humidity exposure from 5 to 95 %RH of polymer films.

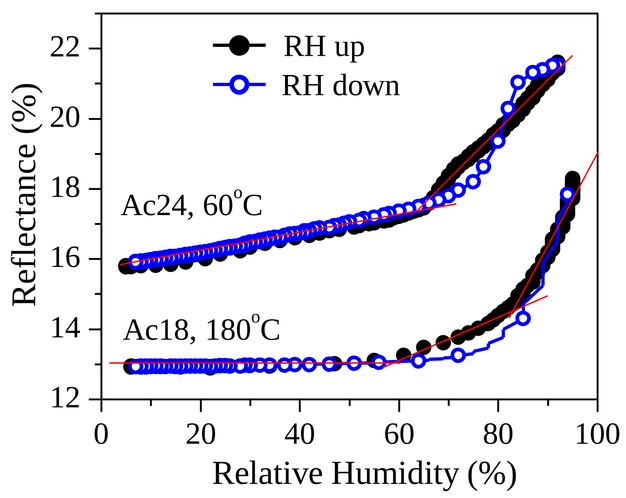


➢ The dimensional changes of films pre-annealed at 180°C are smaller as compared to the case of 60°C especially for the neat PVA films where the decrease of swelling is almost 7 times.
➢ The smallest *H*-values (4.3 % and 3.8 %) are achieved for PVA-modified samples (80 nm) with acetal content of 18 % and 24 %, pre-annealed at 180 °C and 60 °C, respectively.

Humidity sensing

1

Reflectance versus relative humidity curves for films with 24 % and 18 % acetal content (80 nm thick), pre-annealed at 60 °C and 180 °C, respectively, measured for increasing (RH up) and decreasing (RH down) humidity.



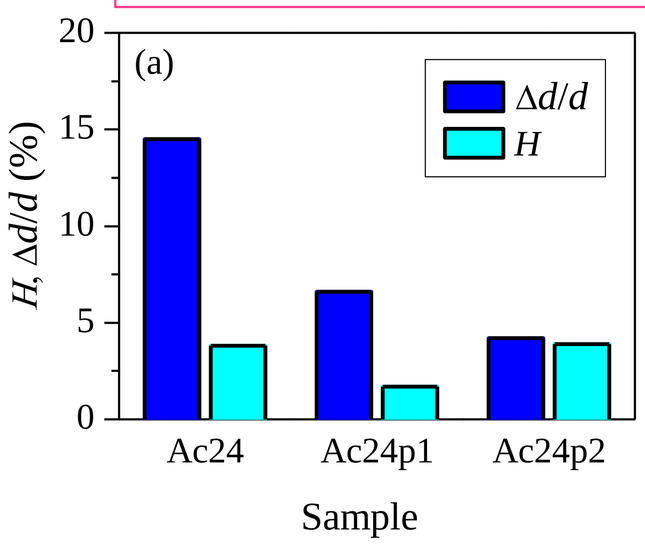
➢ Reflectance for Ac18 is almost the same for wide humidity range (5-60 %RH) and starts to increase exponentially for RH>60%.
➢ For sample Ac24 two linear dependences of R-vs-RH plot with different slopes are well distinguished. The sensitivity is 0.03 for RH = 5-65 % and increases to 0.14 in the range 65-95 %RH.

Sample	Sensitivity (%/% RH)	Accuracy (%RH)	Humidity Range
AC18 (180°C)	0.07 0.3	1 4	60-84%RH >84%RH
AC24 (60°C)	0.03 0.14	10 2	5-65%RH >65%RH

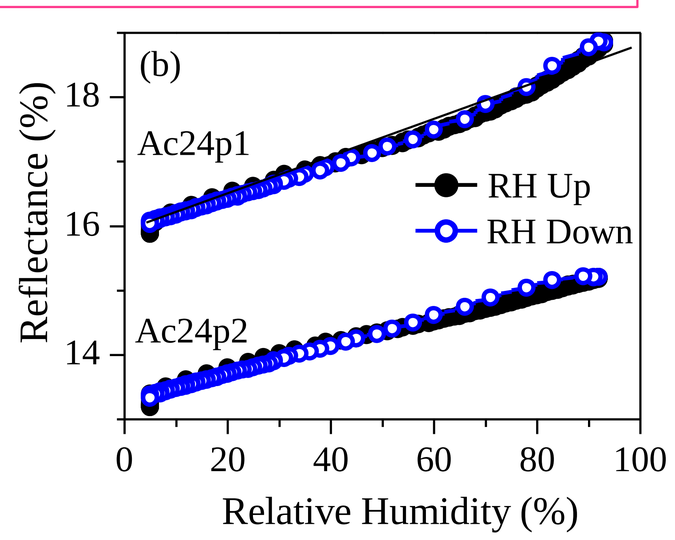
Most appropriate for humidity sensing is Ac24 sample (PVA modified with 24% acetal) with thickness of 80 nm pre-annealed at 60°C.

2

Selected for best performance PVA-Ac modified with 24% acetal is doped with two different concentrations of SiO_2 nanoparticles - 20% and 50%. Thin films are deposited by spin-coating and annealed at 60°C .



Percentage of hysteresis, *H* and relative change of film thickness, $\Delta d/d$ due to humidity exposure from 5 to 95%RH for polymer films (about 80 nm in thickness) with 24 % acetal content (Ac24) doped with 20% (Ac24p1) and 50% (Ac24p2) SiO_2 particles.



Reflectance versus relative humidity curve for films with 24% acetal content doped with 20% and 50% SiO_2 particles measured for increasing (solid black symbols) and decreasing (open blue symbols) humidity.

➢ The swelling decreases with doping.
➢ Percentage of hysteresis, *H* decreases more than twice for 20 % doped sample.
➢ The sample doped with 20 % SiO_2 particles has full dynamic range and linear dependence of the measured signal as a function of relative humidity. The accuracy of measurements is 10 %RH.

Conclusions:

1. The successful humidity sensing application of thin films of hydrophobically modified PVA copolymers, namely poly(vinylalcohol-*co*-vinylacetal)s (PVA-Ac) of acetal content in the range 18-28% is demonstrated.
2. A decrease of hysteresis, increase of sensitivity and widening of dynamic range are observed for modified films as compared to the neat PVA film.
3. The best sensor characteristics are obtained for films modified with acetal content around 24 % with 80 nm thickness and post-deposition annealing temperature of 60°C.
4. A doping of PVA-Ac (24 %) with silica particles (20 % and 50%) is utilized.
5. Humidity sensitive hybrid films have thickness values around 80 nm that guarantees fast sensing.
6. The hybrid thin film samples have full dynamic range and linear dependence of the measured signal in the entire humidity range.

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