

**OPTICAL CHARACTERIZATION OF
ACETONE-SENSITIVE THIN FILMS
OF POLY(VINYL ALCOHOL)-*g*-
POLY(METHYL ACRYLATE)**

Katerina Lazarova^a, Silvia Bozhilova^b, Sijka Ivanova^b, Darinka
Christova^b and Tsvetanka Babeva^a

^a Institute of Optical Materials and Technologies “Acad. J. Malinowski”, Bulgarian Academy of Sciences, Sofia, Bulgaria.

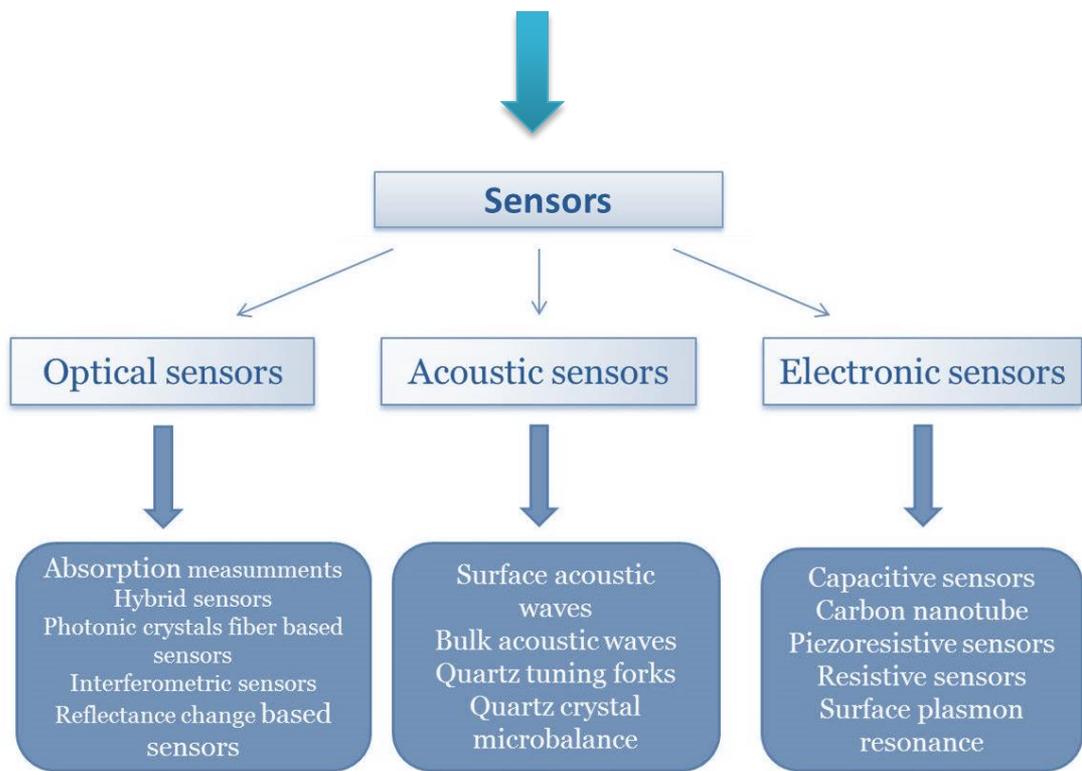
^b Institute of Polymers, Bulgarian Academy of Sciences, Sofia, Bulgaria.



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Different types of volatile organic compounds (VOCs) sensors



Optical sensing is based on perceptual change of color, transmittance, reflectance etc. in response to particular analyte of interest and offers simplicity, convenience and power saving!!!

Optical sensing gains increasing interest due to :

- room temperature operation
- high accuracy
- resistance to electromagnetic interference
- lack of explosion danger.

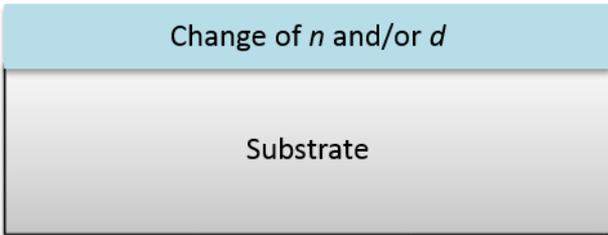
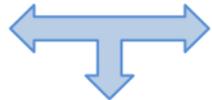
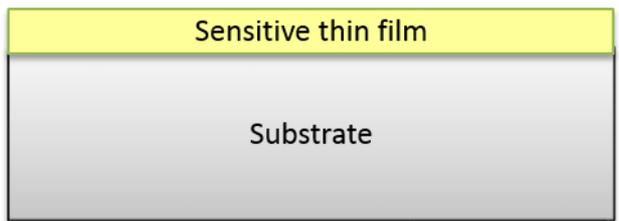


How does optical sensing work?

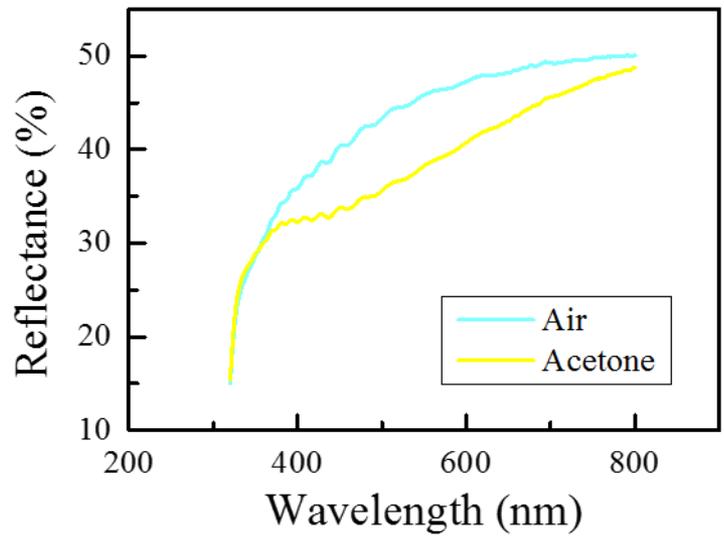
The sensor consists of sensitive thin film deposited on Si substrate. The thin film changes its refractive index n and/or thickness d when exposed to specific analyte.

Air

Acetone



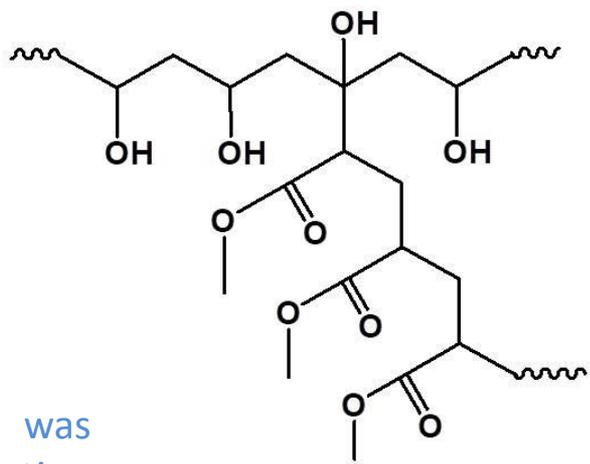
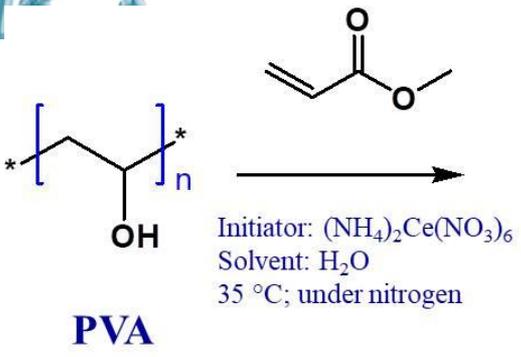
Shift of the reflectance spectrum



Due to changes of n and d , a change of color and shift of reflectance spectrum is observed upon exposure to vapors.



Copolymer synthesis



PVA-g-PMA

As an acetone-sensitive material, new amphiphilic copolymers were synthesized by grafting poly(methyl acrylate) (**PMA**) side chains onto poly(vinyl alcohol) (**PVA**) precursor.

Polymerization reaction was carried out in aqueous solution leading to *in situ* nanoparticles formation. Two copolymers of different grafting density were obtained by varying the initiator's concentration in the reaction mixture. Grafting density of copolymer CP2 is much higher than those of CP1. The size of both CP1 and CP2 nanoparticles, however, was found to be 72 nm independently of the grafting density..



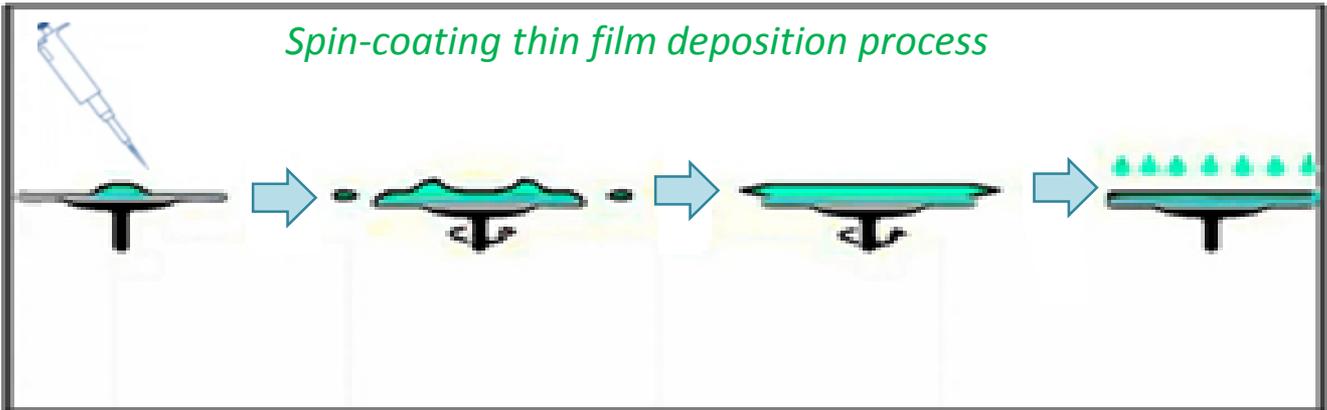
Obtained copolymer aqueous dispersions were purified from reagents residues by dialysis and used for thin films deposition.



Thin polymer film deposition method



- Aqueous dispersions of two different copolymers – CP1 and CP2, were used for film deposition
- Spin coating: 0.250 ml drop, rotation 4000 rpm for 60 s
- Postdeposition annealing time 30 min at $T = 60^{\circ}\text{C}$
- Substrates: Si-wafer



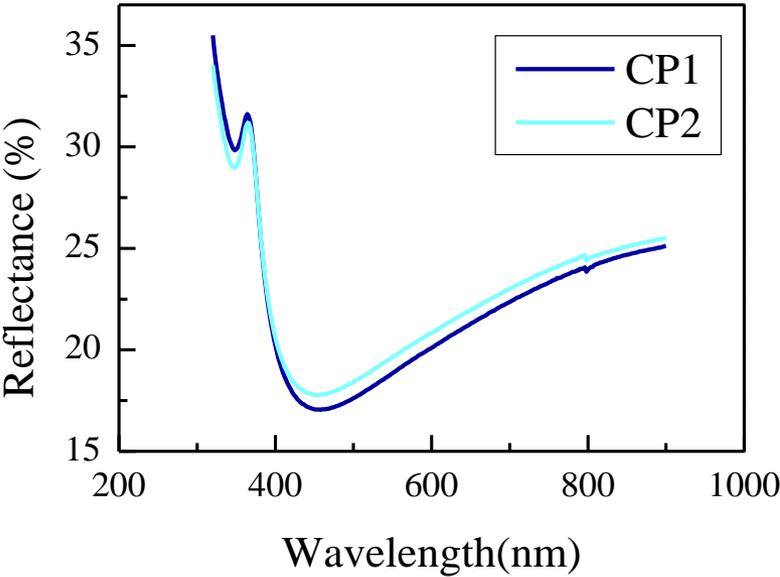


Thin polymer films' optical characterization

Reflectance spectra are measured



Refractive index n , extinction coefficient k and thickness d are determined from reflectance spectra by using two-stage nonlinear curve fitting method.

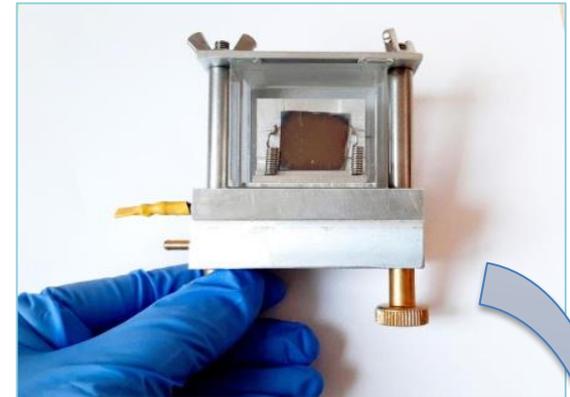


<i>sample</i>	<i>d</i>	<i>n</i>	<i>k</i>
CP1	73	1.35	0.017
CP2	71	1.34	0.018

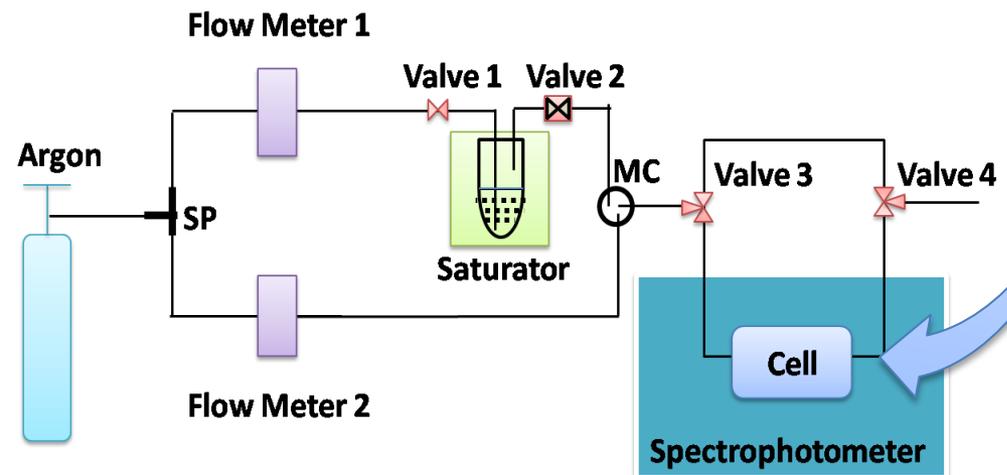
The thickness of CP1 and CP2 films is almost equal ($72 \text{ nm} \pm 1$) which allows us to compare their characteristics. The optical constants are identical.

Evaluation of thin polymer films' sensing properties

Copolymer aqueous dispersion

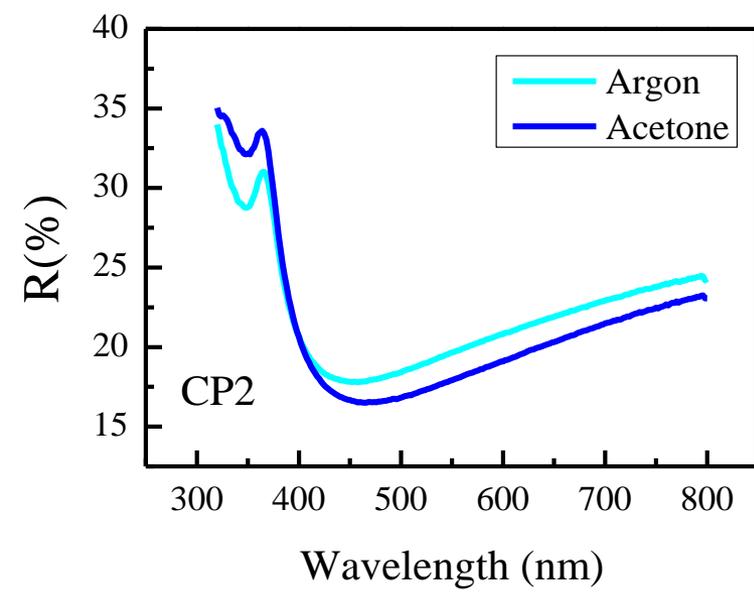
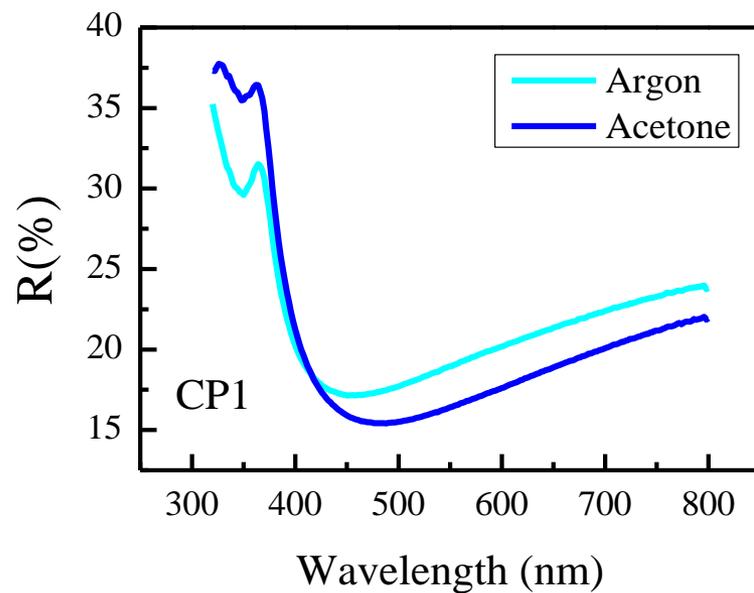


- To evaluate sensing properties of the films they were placed in quartz cell and the atmosphere inside is changing from air to acetone by using homemade bubbler system.
- Reflectance spectra in air and acetone are measured and maximum difference ΔR is calculated.





Evaluation of thin polymer films' sensing properties

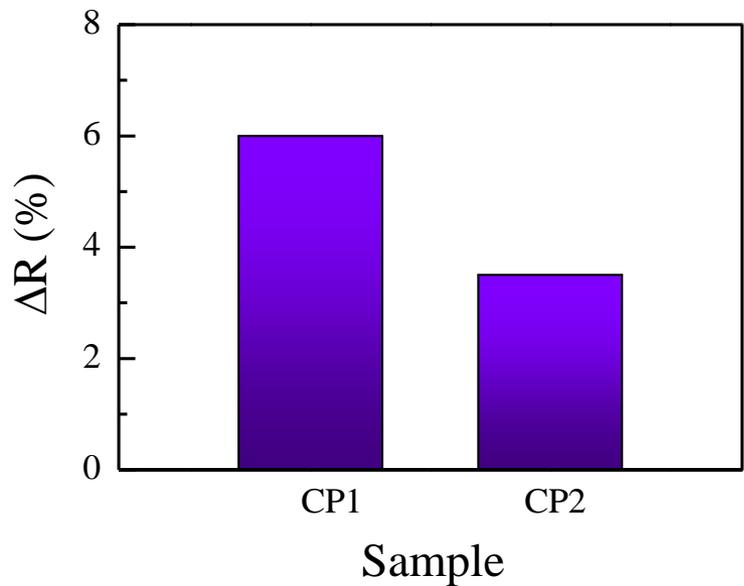


➤ Maximum reflectance change ΔR is calculated:

$$\Delta R = | R_{ar} - R_{ac} |$$



Evaluation of thin polymer films' sensing properties



Maximum reflectance change ΔR of CP1 thin film is almost twice as CP2's sample!

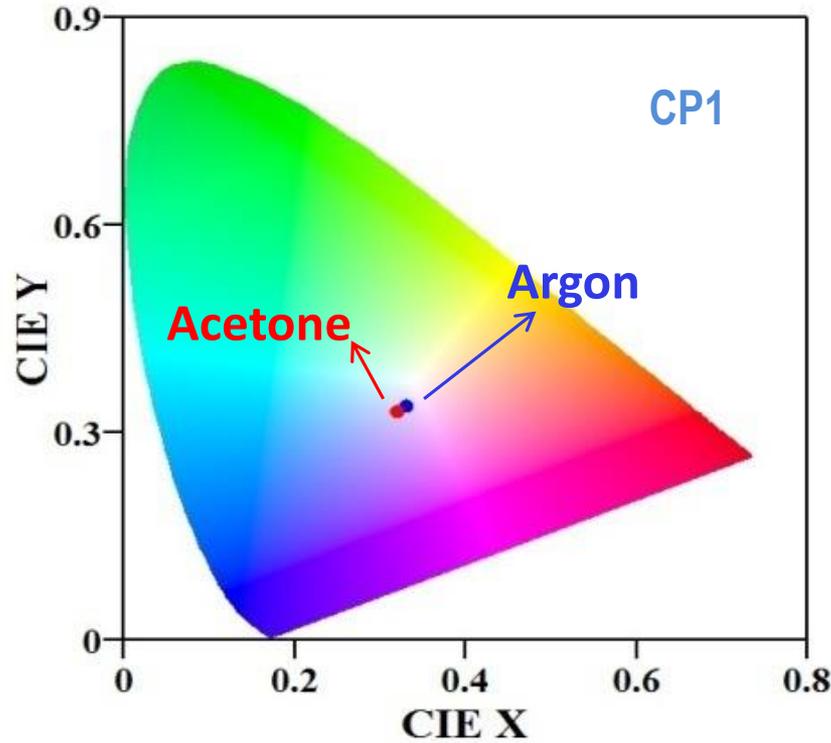
CP1: $\Delta R_{\max} = 6.00$
CP2: $\Delta R_{\max} = 3.50$

Maximum reflectance change ΔR of CP1 and CP2 thin film samples



Evaluation of thin polymer films' sensing properties

- To check the applicability of these samples for uses in color sensing, CIE color coordinates are calculated and plotted on the color scheme.
- The two points that represent the colors of CP1 at argon and acetone are separated in the color space, thus enabling color sensing of acetone.





Summary

- Acetone-sensitive copolymers are successfully designed by grafting poly(methyl acrylate) side chains onto poly(vinyl alcohol) precursor.
- Thin films of poly(vinyl alcohol)-*graft*-poly(methyl acrylate) of different composition are successfully deposited via spin-coating method.
- Refractive index n of 1.35, extinction coefficient k of 0.018 and thickness of 72 nm are determined for studied copolymers' films from measured reflectance spectra. It is found that the influence of copolymer grafting density on the optical characteristics is negligible.
- The successful sensing of acetone vapors by using thin films of poly(vinyl alcohol)-*graft*-poly(methyl acrylate) copolymers was demonstrated. Maximum reflectance change ΔR of CP1 thin film (6.0 %) is almost twice higher as compared to CP2's sample (3.5 %).
- A possibility of color sensing in reflectance mode is demonstrated.

Thank you for your
attention!!!



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