Infrared Analysis of Thin Multilayered Polymer Film Using Cantilever Enhanced Photoacoustic Detector

Kaori Watanabe and Fumiko Hiwatashi Systems Engineering

Systems Engineering Inc. *www.systems-eng.co.jp info@systems-eng.co.jp*

Introduction

Polymer thin film is used in...

- Structural material
- Electronic device
- Adhesive
- Paint and printing
- Biomaterial

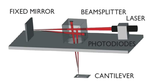
nm to μm ordered polymer structure
Multilayered films for hybrid and novel functions
Depth profiling analysis is necessary

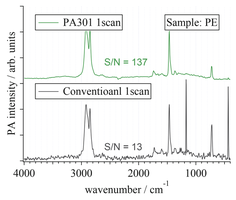
Surface analysis

- XPS, SSIMS, SPM, XRD etc.
- Vibrational spectroscopy -> definitive molecular information
  » PAS: Non-destructive (little sample preparation), depth-profiling

Novel PAS detector (GASERA; booth 555)

- Cantilever and laser interferrometer based detector
- **Ten times more sensitive than traditional acoustic microphone**





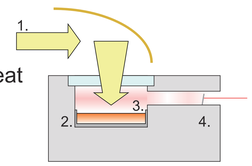
This study

- Infrared PAS analysis of multilayered films
- Determination of accurate sampling depth of PAS with cantilever detector

Photoacoustic Spectroscopy (PAS)

Photoacoustic spectroscopy

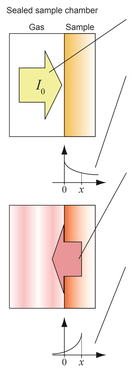
1. Sample absorbs incident light
2. Absorbed energy partially transformed into heat (non-radiating relaxation)
3. Heat diffuses back to sample surface
4. Thermal expansion of surrounding gas detected



PAS advantage

- Highly sensitive
- Non-destructive
- Depth-profiling
- Versatile
  » Irregular shaped, small, or opaque sample etc.
  » THz, IR, NIR, UV-Vis etc.

PAS Sampling Depth



Incident light beam irradiated onto sample

Light intensity at position x

$I = I_0 \exp(-\beta x)$ (β: Absorption coefficient)

Heat generated at position x

$\Delta T \propto \beta I = \beta I_0 \exp(-x/\beta)$

Heat diffused from position x to the sample surface

$\Delta T_s = \Delta T \exp(-x/\mu) \propto \beta I_0 \exp(-x/\beta - x/\mu) \approx \beta I_0 \exp(-x/\mu)$

μ: Thermal diffusion length $\mu = \sqrt{2\alpha/\omega}$

μ: "PAS Sampling Depth"
Generated heat decays to $1/e$

α: Thermal diffusivity $\alpha = k/\rho C$ [cm^2 s^{-1}]
k: Thermal conductivity [W cm^{-1} K^{-1}]
ρ: Density [kg cm^{-3}]
C: Specific heat [J kg^{-1} K^{-1}]
ω: Angular modulation frequency $\omega = 2\pi V v$
V: Mirror velocity [cm s^{-1}]
v: Infrared wavenumber [cm^{-1}]

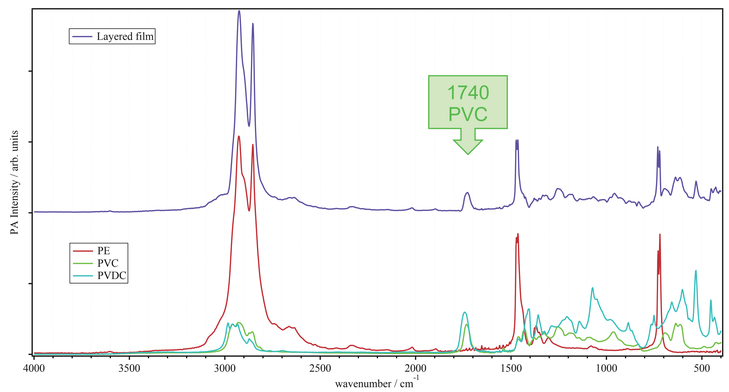
Results and Discussion

1. PAS spectrum of multilayered film

Layered sheets of food wrap
PE, PVC, PVDC; 10 um each

PE 10 μm
PVC 10 μm
PVDC 10 μm

Mirror velocity V = 5 kHz = 0.32 cm s^{-1}



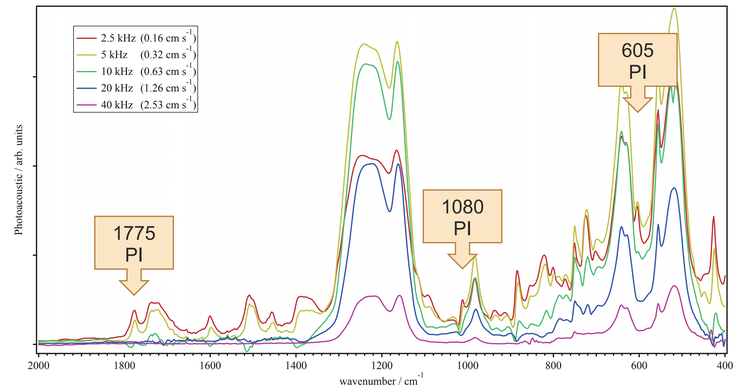
1740 cm^{-1} peak of PVC observed

Sampling depth > 10 μm ↔ PAS sampling depth μ = 7.6 μm

Photoacoustic signal observed beyond μ

2. PAS spectrum of multilayered film, various mirror velocity

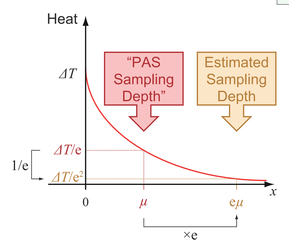
Multilayered polyimide film
Kapton® 300F929



Estimation of accurate samping depth Aμ (A: factor)

- 1775 cm^{-1} peak: Observed at 10 kHz, not observed at 20 kHz
  » 3.8A < 12.5 μm < 5.3A
- 1080 cm^{-1} peak: Observed at 10 kHz, not observed at 20 kHz
  » 3.4A < 12.5 μm < 4.8A
- 605 cm^{-1} peak: Observed at 20 kHz, not observed at 40 kHz
  » 4.6A < 12.5 μm < 6.4A

Estimated factor
2.6 < A < 2.7
i.e., A ≈ e



Heat generated at depth eμ can be detected
Generated heat decays to $1/e^2$ at surface

Conclusion

Photoacoustic signal can be detected beyond PAS sampling depth μ. Accurate sampling depth is estimated to be ~eμ, where the generated signal decays to $1/e^2$ upon reaching the sample surface.