Positron Annihilation as a Method to Characterize Porous Materials

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Abstract:

- Beam-based Positron Annihilation Spectroscopy (PAS)
- nondestructively pore-size determination and distribution of 0.3nm-30nm pores
- Depth profiling:
  - interconnection length of pores
  - depth-dependent inhomogeneities
  - damage in pore-structure
  - hidden porosity (dense layers, diffusion barriers)
Main spectroscopies:

- time domain
- energy of annihilation gamma rays
- momentum of gamma rays:
  - doppler Energy shifts
  - Angular distribution
Most interesting parameters:

- pore size
- pore size distribution (PSD)
- Pore interconnection length $L_{\text{int}}$
  - Scale length over which pores are connected to each other
Ps in nanoporous films:

- Closed pores
- Open pores
- Capping layer
Ps in nanoporous films:

- Positrons (50 eV-15 keV):
  - scatters of atoms and electrons
  - slows down to atomic scale energy (several eV) in pico-seconds

- Typically 10%-50%:

- Capture bound molecular electron (Ore-model)

- Recombines with „spur“ e\(^-\) from e\(^+\) ionizing collisions (Spur-model)

- Forming Ps
Note:
Relationship between these formation mechanisms and contribution of material to them are largely unknown
Ps

- **p-Ps**
  - singlet (para-) Ps
  - S=0
  - LT=125 ps
  - 2\(\gamma\)-annihilation conserving momentum and energy
  - narrow peak at 511 keV

- **σ-Ps**
  - triplet (ortho-)
  - S=1
  - LT=142 ns
  - 3\(\gamma\)-annihilation
  - \(\gamma\)-ray energy distribution increases linear
  - cutoff at 511 keV
  - Annihilation strongly perturbed by interaction with surrounding e⁻
    - reduces σ-Ps lifetime while localized in pores
inside potential well of void Ps is trapped with small loss of energy

- singlet interaction of $e^+$ in $\sigma$-Ps with surrounding molecular $e^-$ of opposite spin SHORTENS Ps-lt. Mixing in fast $2\gamma$ decay during wall collisions
  - “pick-off” annihilation decreases lifetime from 142ns to $\sim$1ns
  - annihilation with Ps-bound $e^-$
most useful property to find out: **PORESIZE**

- Micropores ($R \leq 2\text{nm}$) → good correlation to QM-Tao-Eldrup model (RTE: extension to mesopores ($R > 2\text{nm}$))
  - if pores closed → Ps trapped (“bounces like gas-atom”)
    - smaller pores → faster pickoff
      → more $2\gamma$-annihilation
  - if PSD → distribution of Ps-lifetime
Connected pores:

- Length scale of connection $L_{\text{int}}$
- Ps light and mobile
  - Can diffuse over great distances (greater than film thickness)
  - $\sim 10^6$ pore-wall collisions before annihilation
- Ps escaping into vacuum: $LT=142$ ns
  - Indicates connection
- but only part of Ps escapes
  - Profiling into various depths
• profiling into various depths
  • average pore size by mean free path of Ps
    (material must be capped by thin film)

\[
\text{mean free path} = 4 \frac{V}{S}
\]

V-pore volume; S-pore surface area
PAS-techniques:

- Doppler-broadening spectroscopy (DBS)
- Angular correlation of annihilation radiation (ACAR)
- Ps-time of flight (PS-TOF)
- $3\gamma$ annihilation spectroscopy ($3\gamma/2\gamma$ branching ratio)
- Positronium annihilation lifetime spectroscopy (PALS)
- Implantation directly from $\beta^+$ source in sample (bulk-PAS)
**Bulk-PAS**: unsuitable for thin films
- high energies
- broad energy range

**Positron beam:**
- focused, mono energetic $e^+$, defined energy
- vacuum system
- depth profiling (varying energies)
DBS and ACAR:

- Sensitive to momentum
  - determined by momentum of $e^-$ in Ps and free $e^+$ annihilation
  - probe electronical and physical environment
DBS:

- high energy resolution γ-detectors (germanium)
- needs sufficient calibration
- no pore size
Coincidence DBS:

- 2 γ-detectors (germanium) simultaneously
- better energy resolution
- useful probing pore surface chemistry
ACAR:

- measures not energy broadening of 511 keV γ-rays but relative angle between them
- component of pair momentum in transverse to γ-ray direction
- at rest: p-Ps, Ps quenching
  - deviation angle θ from 180° of the back to back gamma rays
  - θ typically ~10mrad
  - θ larger for high momentum annihilations
ACAR Setup:

- 2 positron sensitive detectors (ACAR cameras)
- 5 meters apart → angular resolution ~mrads
- Θ calculated from 2 coincident 511 keV gamma rays
- Difference to DBS: only p-Ps annihilation contributes
- Needs intense positron beam for beam based depth-profiling
Ps-TOF:

- porous media with highly interconnected pores
- beam forms Ps near surface of film
- narrow collimated gamma shield placed in front of one detector near front of the film
- Ps escaping film annihilates in collimator
  ➔ TOF recorded

- Time histogram can be converted to energy distribution
Ps TOF:

- beam energy varies:
- degree of Ps than can thermalize and its escape-energy varies
- useful to understand thermalisation and diffusion in pores
  - check interconnection
- no pore size, not suitable for closed pores
PALS and $3\gamma/2\gamma$:

- most used and useful methods
- determine pore size, interconnectivity, depth-dependent film inhomogeneities
- use of positron beam
- **Lifetime measurement:**
  - **Start Signal:** While being implanted into the film, positrons knock off secondary electrons which starts the timing clock. (The time for positrons to form Ps is on the order of picosecond, i.e., 10-12 sec, which can be neglected compared to Ps lifetime on the order of nanosecond.)
  - **Stop signal:** Ps annihilates into gamma-rays, which stops the timing clock.
Figure 2  The magnetically guided PAS beam/spectrometer at Washington State University. From Reference 4.
A typical PALS spectrum with three film Ps lifetimes fitted using POSFIT. The points for each channel have been connected with a line for visual clarity. Each channel corresponds to 1.25 ns.
$3\gamma/2\gamma$:

- Energy spectrum
- Calculation of $3\gamma/\gamma^2$ ratio
- Increasing in larger pores
Tao-Eldrup:
- useless for pore sizes approaching thermal De Broglie wavelength of $P_s$
  $\sim 6$ nm
- extension for larger pores: RTE

- Pore-size calibration calculated at different temperatures using a cubical pore shape model. The 0K (ground state) curve given by the Tao-Eldrup model and the dashed curve given by the classical model are presented for comparison.
RTE: at given temperature and assumed pore shape curve measuring lifetime versus pore dimension can be calculated

- conversion to classical mean free path mean distance between Ps pore wall collisions pore size
- not specific to pore geometry

\[ \lambda = \frac{1}{\tau} = \lambda_{\text{pickoff}} + \lambda_{\text{vac}} \]

\[ \lambda_{\text{vac}} = \frac{1}{142 \, \text{nS}} \]
round-robin:

SANS: small angle neutron scattering
EP: ellipso-metric porosimetry
BET: gas absorption
PSD:

- Fitting of decay spectrum to a continuum of lifetimes using CONTIN or MELT

- Converted into fractional pore volume as a function of a f. e. spherical pore diameter
Figure 6  Plausible PSDs in a low-k film for a variety of positron beam energies (in keV) determined from continuum lifetime fitting. This film has a complicated depth dependence to porosity. The curve labeled “matrix” has no engineered pores.
Determination of Film Porosity:

- complicated dependence of Ps-annihilation intensity on pore size and porosity
- no unique correspondence from fitted Ps-intensity or $3\gamma/2\gamma$ to porosity
- independent measures of porosity required
Determination of Film Porosity:

![Graph showing the relationship between Ps Intensity in Film and Film Porosity](image)

- **Linear Nucleation and Growth**
- **Small Molecule**
- **Particle Template**
Determination of Film Porosity:

Graph showing the relationship between film porosity and cylindrical pore diameter for different conditions:
- Particle Template
- Small Molecule
- Linear Nucleation and Growth

Matrix Micropores
Depth-profiling of films:

- powerful feature of beam-based PAS
- Mean positron implantation depth: \( \bar{Z} = \frac{40}{\rho} E^{1.6} \)
  
  \( E \) - beam energy; \( \rho \) – film density in g/cm\(^3\)

- corresponds well to Ps-forming profile but not to annihilation profile (connected pores)
- Depth-dependent variations of Ps-intensity reflect changes in porosity
- Lifetime indicates pore size variations (closed pores)
Figure 8  Positron implantation profiles for several beam energies calculated for $\sim 45^\circ$ incidence on a film of density 1 g cm$^{-3}$. 
Depth-profiling of films:

- Reveals $L_{\text{int}}$:
- Ps-light and mobile - can diffuse 1000nm-thick film (fully interconnected pores)
- Annihilation in vacuum (142 ns, high $3\gamma/2\gamma$ ratio)
- Measuring escaping-Ps fraction of film as function of implantation length
- Calculation of mesopore $L_{\text{int}}$:
  - mean implantation depth from which 50% Ps escape the film
Depth-profiling of films:
Figure 9  Plot of the Ps escape fraction ($F_{esc}$) as a function of mean positron implantation depth ($top$) used to calculate the mesopore interconnection length ($L_{int}$) ($bottom$) for films of increasing porosity. This film is a cyclodextrin-based porogen in a MSSQ matrix.
Depth-profiling of films:

- Information from 3γ/2γ ratio:

*Figure 10* Typical depth-profile of the 3γ fraction for several porogen weight fractions. The lower panel is a fit of the data to a diffusion model to determine L_int. Reprinted with permission from Reference 28. Copyright 2005, American Institute of Physics.
Depth-profiling of films:

- DBS parameters s, w are also sensitive:

\[
\Delta S/S_0 \quad \Delta MW/MW_0
\]

\[\text{Porosity (\%)}\]

\[\text{low momentum} \quad \text{high momentum}\]

\[\text{Porogen Load (wt. \%)}\]

**Figure 11** Plot of the change in low-momentum (S) and high-momentum (W) parameters as a function of film porosity. Reprinted with permission from Reference 5. Copyright 2003, American Chemical Society.
Porosity variations in film depth:

- What if film not homogeneous?
- Beam-based PAS can study hidden porosity (diffusion barriers, capping layers…)
- diffusion barriers sealing can be tested
Porosity variations in film depth:

- multilayer model:

- PALS depth-profiling must be combined with etching off upper layers (interconnections)
Pore shape and growth:

- Understanding important for controlled pore design (determined pore size and interconnectivity)
- PALS can simultaneously characterize size and interconnection length
- Study nanoporousity from isolated pores to interconnected network

3 porogens:
- CA: calix arene porogens
- CD: cyclodextrin porogens
  - tCD-methoxyl functional group
  - sCD-trimethoxyl functional group
Figure 13  Plots of pore diameter (*left*) and pore interconnection length (*right*) as a function of porosity for MSSQ films made with three different porogens. The growth modes for the porogens are dramatically different.
Pore shape and growth:

- **sCD**: produces cylindrical growth
- **tCD**: three-dimensional growth
- **CA**: explosive growth beyond critical concentration (7%-15% porosity)
Thanks for listening!

- http://positron.physik.uni-halle.de
- http://positrons.physics.lsa.umich.edu