Измерение сопротивления тонкой пленки на поверхности электрода

M. A. Vorotyntsev[1,2,3], D. V. Konev[3], M. Skompska[4]

[1] ICMUB-UMR 6302 CNRS, Universite de Bourgogne, Dijon, France

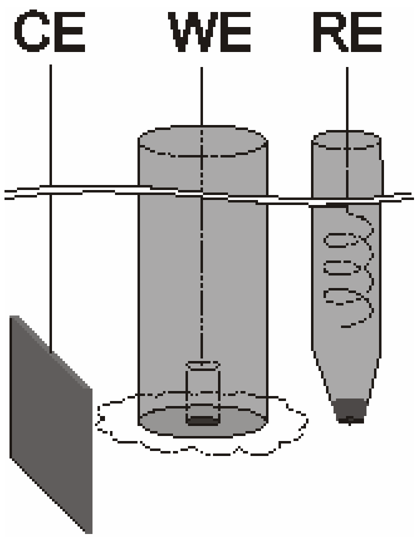
[2] M. V. Lomonosov Moscow State University, Russia

[3] Institute for Problems of Chemical Physics, Chernogolovka, Russia

[4] University of Warsaw, Poland

mivo2010@yandex.com, mv@elch.chem.msu.ru, mv@u-bourgogne.fr

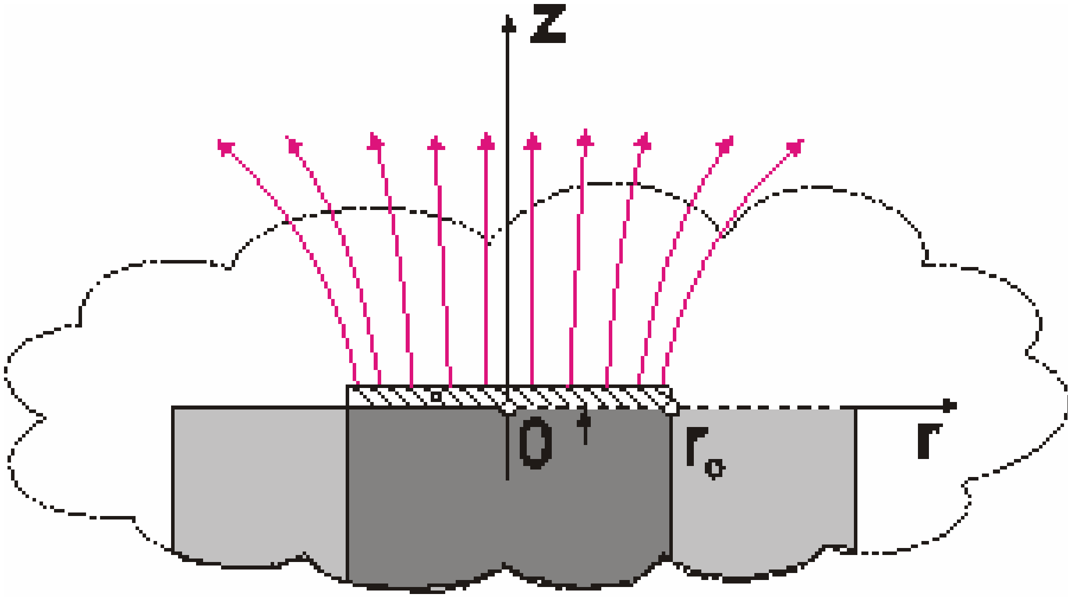
In situ measurements of specific conductivity of films on electrode surface



Specific conductivity: function of potential

Impedance problems:

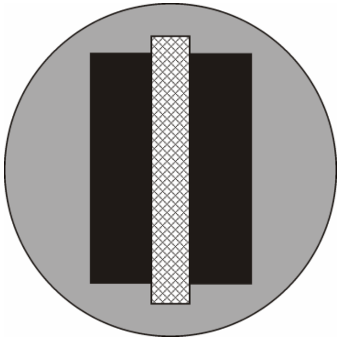
1. Special equipment
2. Interpretation (electrode/film resistance!)
3. Non-uniform electric field distribution



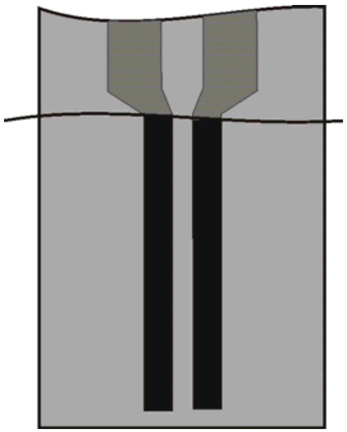
Principal in situ method: microband electrodes

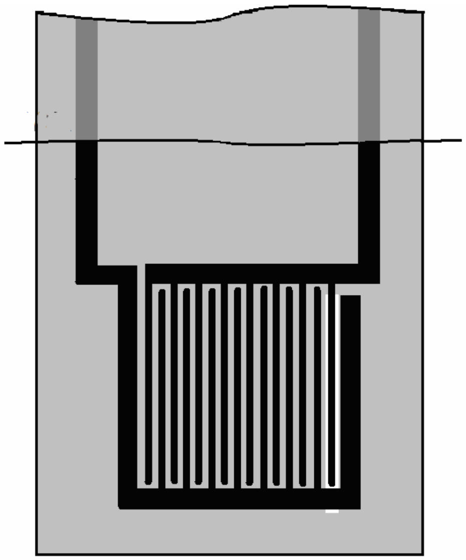
Various constructions (no commercial supply!):

2 metal plates separated
by a thin insulating layer
One can clean by polishing



Lithographic metal layers:





Film above electrodes and gaps.

Current between them via film

Film resistance $\Delta U / I = R_f$ Film conductivity: $R_f = G / \kappa$

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Problem of two electrodes configuration:

contribution of electrode/film resistance

4 microband electrodes: separation of R_f and $R_{m/f}$

U.Lange, V.M.Mirsky, Analyt. Chim. Acta, 2011, 687,105

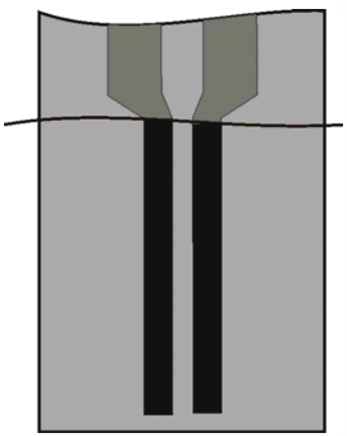
Another problem: Is the film uniform? Which thickness?

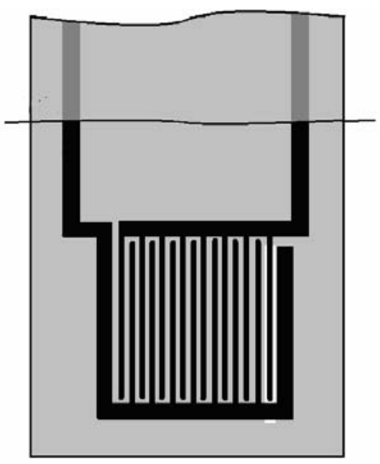
One opinion: only R_f Another opinion: $G = L_g / A_f$

Gap width: 5-100 µm

Film thickness?

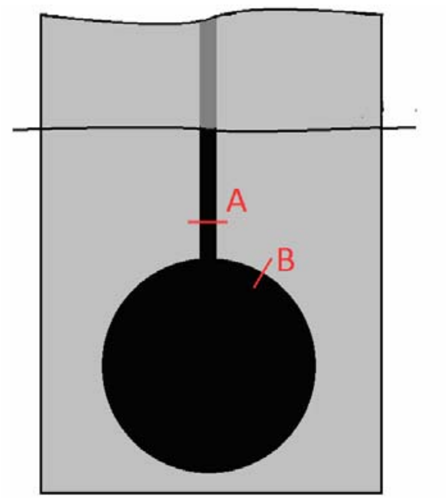
Microband height?

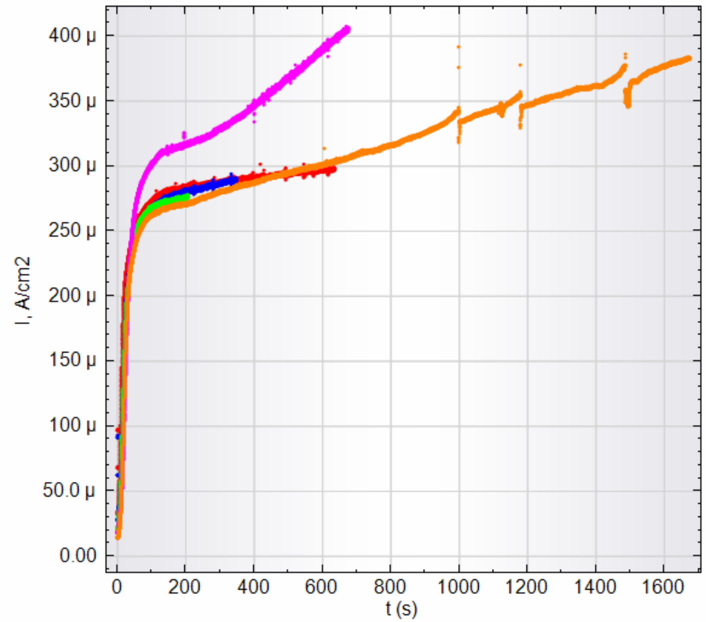




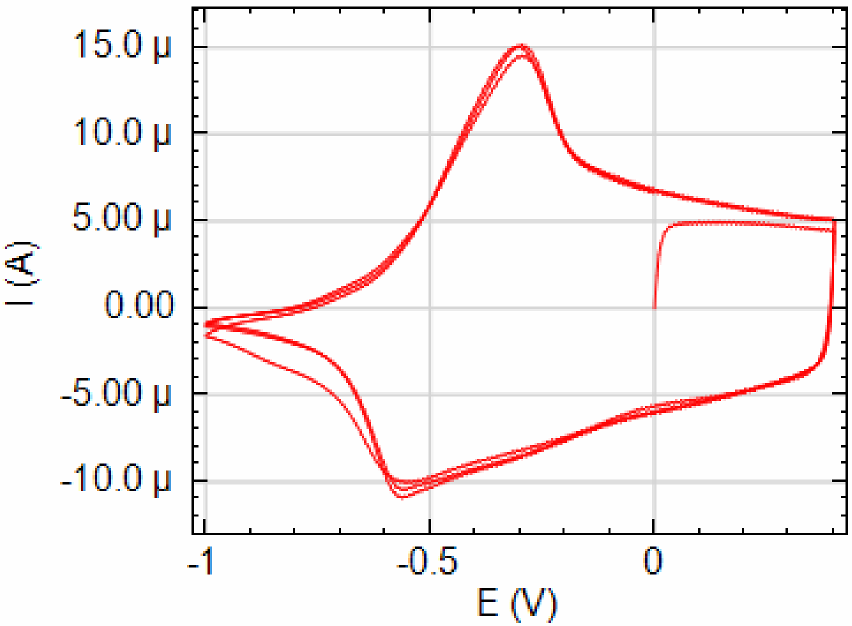
Our study: film growth on microband electrodes

Disk + single microband





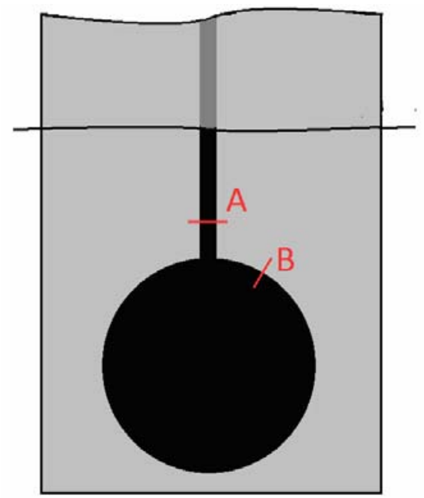
Series of pot-static depositions various PPy film thicknesses

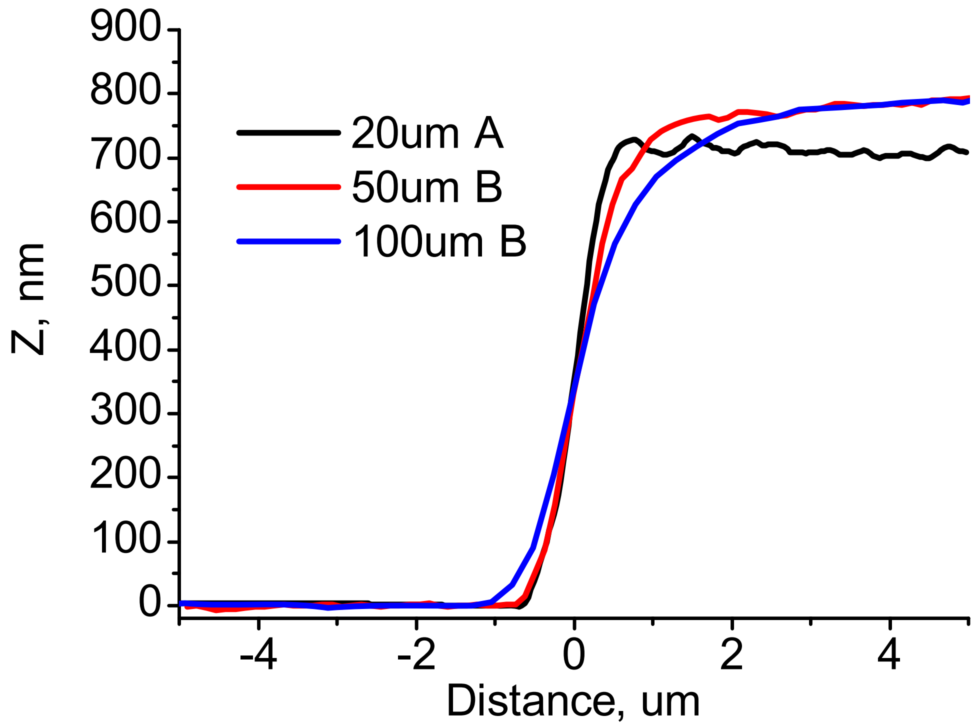


Disk + single microband

Large scale AFM device

Contact mode

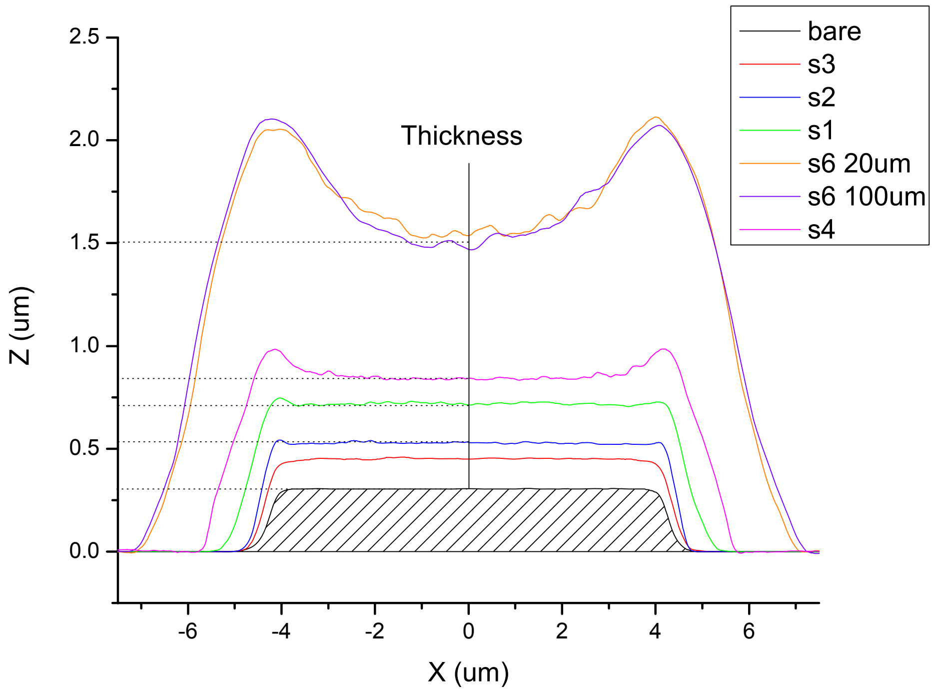


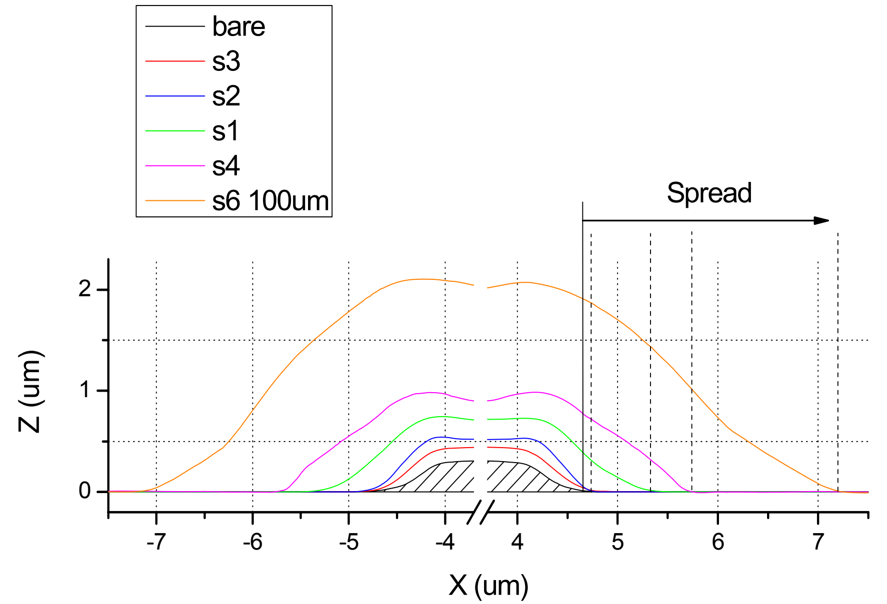


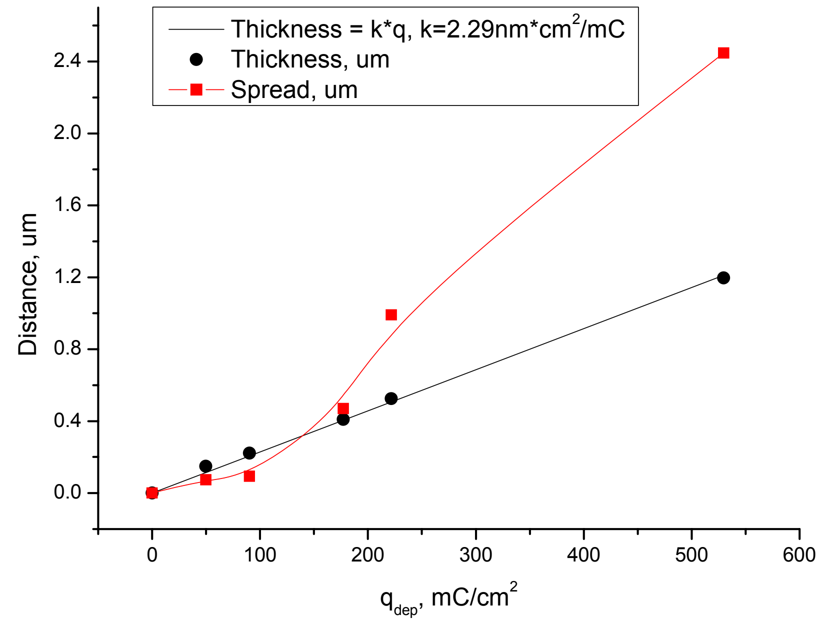
Similar profiles near edges of microband and macrodisk

Slightly different film thicknesses in central areas

Single microband: film cross-section







Growth rates in normal and tangent directions are comparable

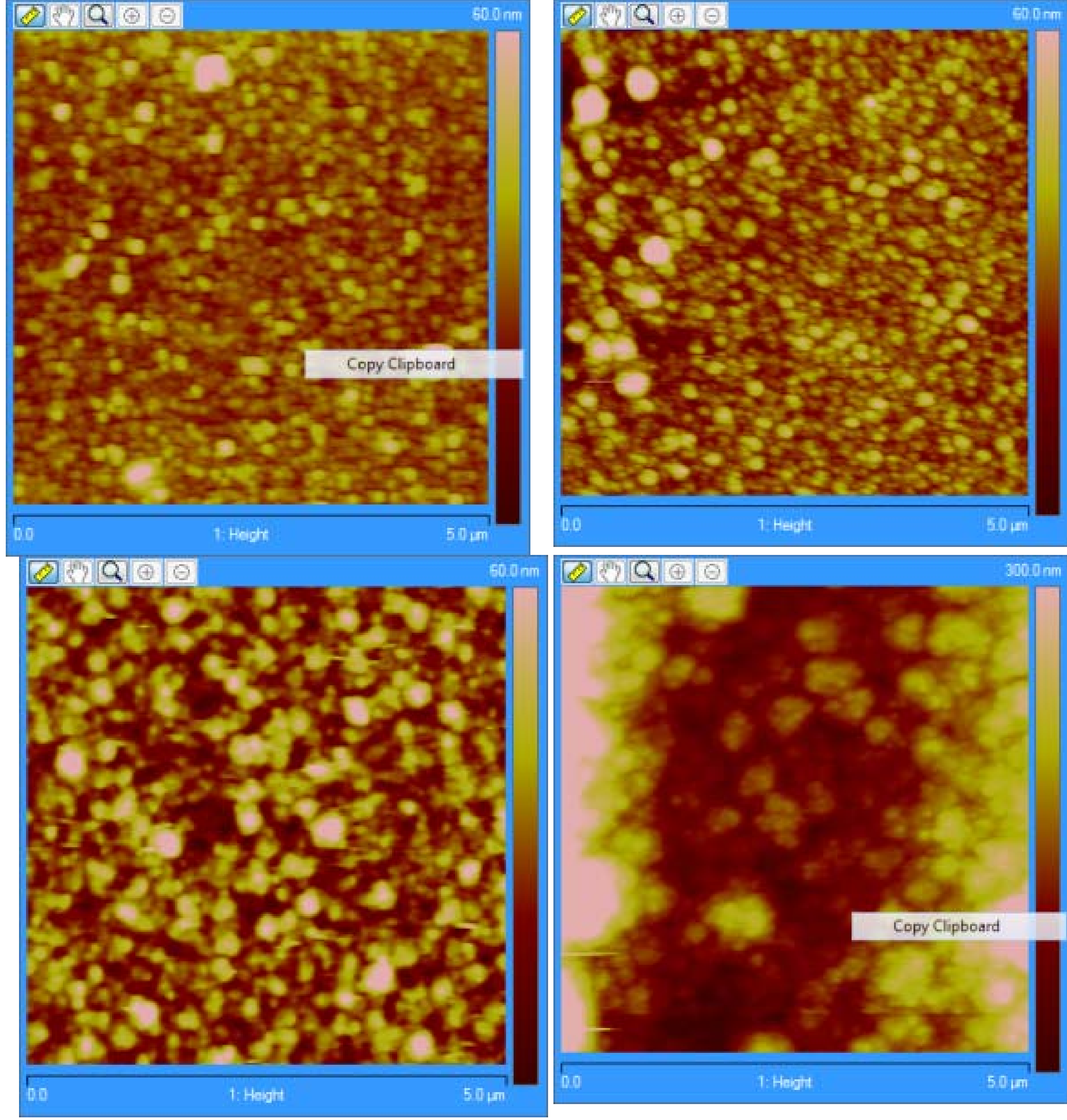
Disk: AFM images

Increase of film thickness:

Greater elements

Higher roughness

Impossible to estimate G, i.e. film conductivity κ



Film conductivity: novel method

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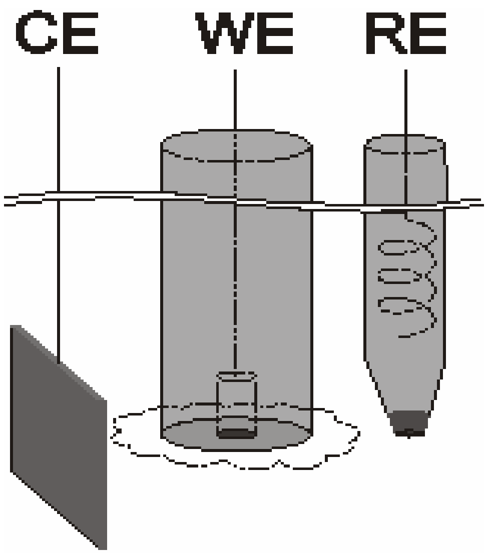
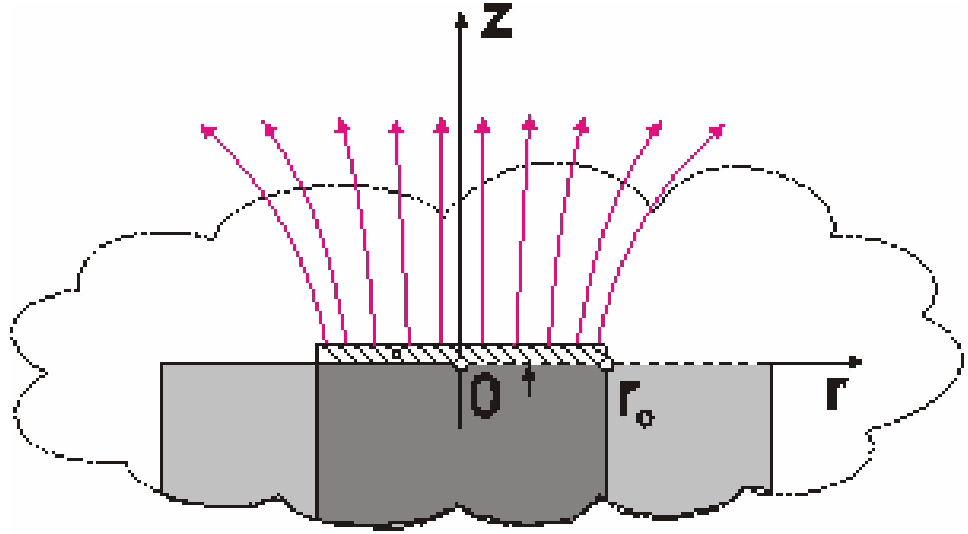
Standard 3-electrode cell with static disc electrode





Solution: 3D distribution. Thin film: 1D distribution

Film conductivity: novel method

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Potential step:

non-stationary potential/current distributions

Primary (short-time) potential/current distributions:

1)no concentration changes, 2) no changes at interfaces

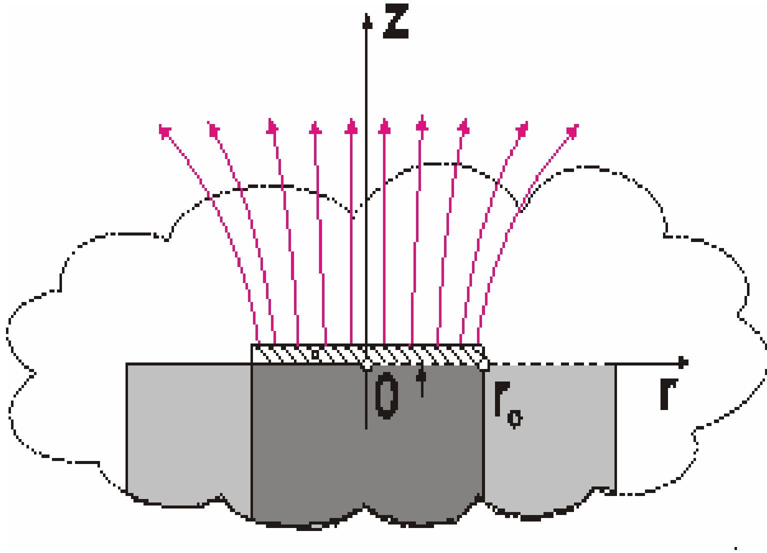
Only induced fluxes of mobile charges in solution & film

$\Delta\Phi = 0$ at $z > 0$ (solution)

$\mathbf{i} = -\kappa_s \nabla\Phi$ at $z > 0$ (solution)

$i_z \cong \kappa_f (V - \Phi_o) / L_f$ (thin film)

V: amplitude of potential step



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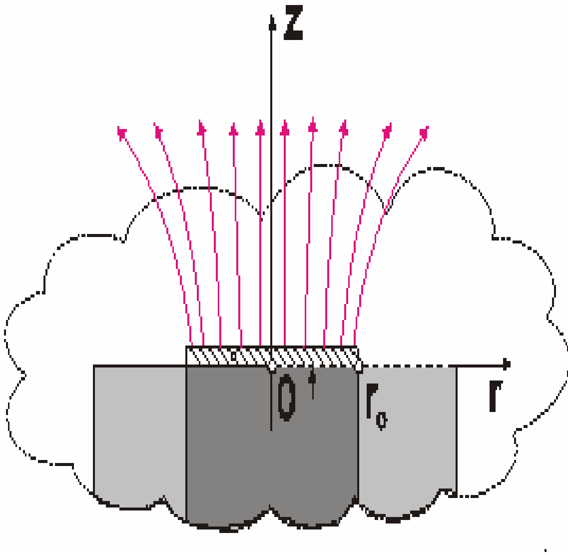

Total short-time resistance: $R_{tot} = V/I_o$

Nonadditive contributions of solution (R_s) and film (R_f) resistances

Analytical formulas:

$R_{tot}(R_s, R_f)$ & $R_f(R_s, R_{tot})$

If R_{tot} is measured for a set of electrode potentials, $R_{tot}(E)$, one can determine $R_f(E)$

Specific conductivity of the film, $\kappa_f(E)$:

$R_f = G_f / \kappa_f$, $\quad G_f = L_f / A_f$, $\quad A_f = \pi r_o^2$

Conclusions

- For the first time: study of polymer film growth on non-uniform surfaces (single- and double-bands)
- Contrary to a widely-used hypothesis: no preferential film propagation along the surface
- To measure the interband current, i.e. film resistance the film thickness should be about a half of the interband gap, i.e. micrometer range, while the local and global film morphologies become non-uniform

Novel "potential-step method for disk electrode" to measure absolute values of in situ specific conductivity $\kappa_f(E)$ of film on electrode surface, i.e. in contact with solution under electrode potential control.

Advantages:

- Standard electrochemical cell,
- Measuring device = potentiostat (short-time signals),
- Normal-size (about mm) disk electrode, no need of micro/nanoelectrodes or larger-size (cm) electrodes,
- Standard film deposition procedure,
- Thin films (from a few tens of nm),
- Electronic or ionic or mixed (electron-ion) conductivity,
- Non-destructive type of measurement

Limitations of potential step method:

1) $R_f << R_s$, 2) too low conductivity (displacement current)

Combination of microband and potential step methods:

matching dependences resistance vs potential.

Another method to determine film conductivity, $\kappa(E)$