Interaction of the Electromagnetic Radiation with the Surface of Palladium Hydride Cathodes

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Introduction

- The dissolution of hydrogen within a metal lattice and the formation of a metal hydride greatly perturb the electrons and phonons of the host material. Several are the relevant observed effects

  - The generally observed expansion of the lattice, often including a change in the crystal structure, involves a modification of the symmetry of the states and a reduction of the band width.

  - The attractive potential of the protons affects those metal wave-functions which have a finite density at the H site and leads to the so called metal hydrogen bonding band below the metal d-band.

  - The additional electron brought by the H atoms into the unit cell produces a shift of the Fermi level.

- **Consequently, the electronic Density of State of Palladium changes as deuterium solubilized inside metal lattice increase.**

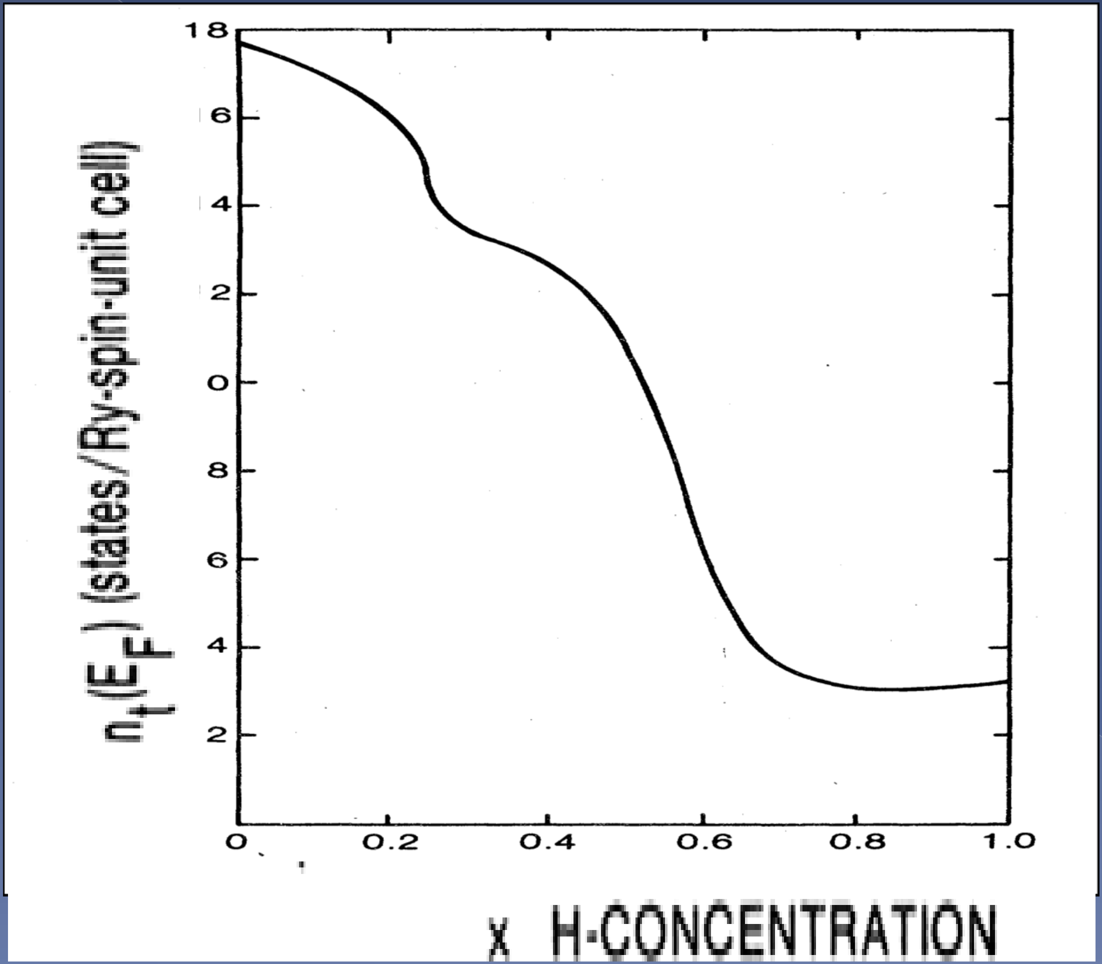
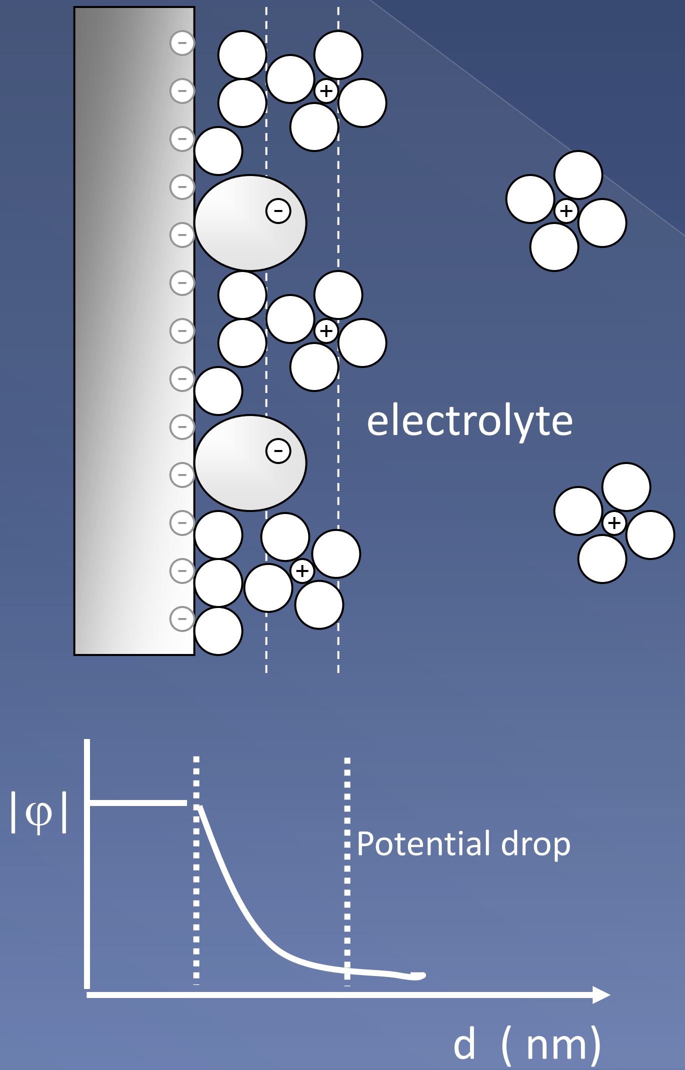


Fig. 1 - Total Density of States at the Fermi level plotted versus hydrogen concentration in PdHx

Model of the Electrochemical Interface

- The electrochemical interface is well represented by a double layer structure in contact with a space of charges

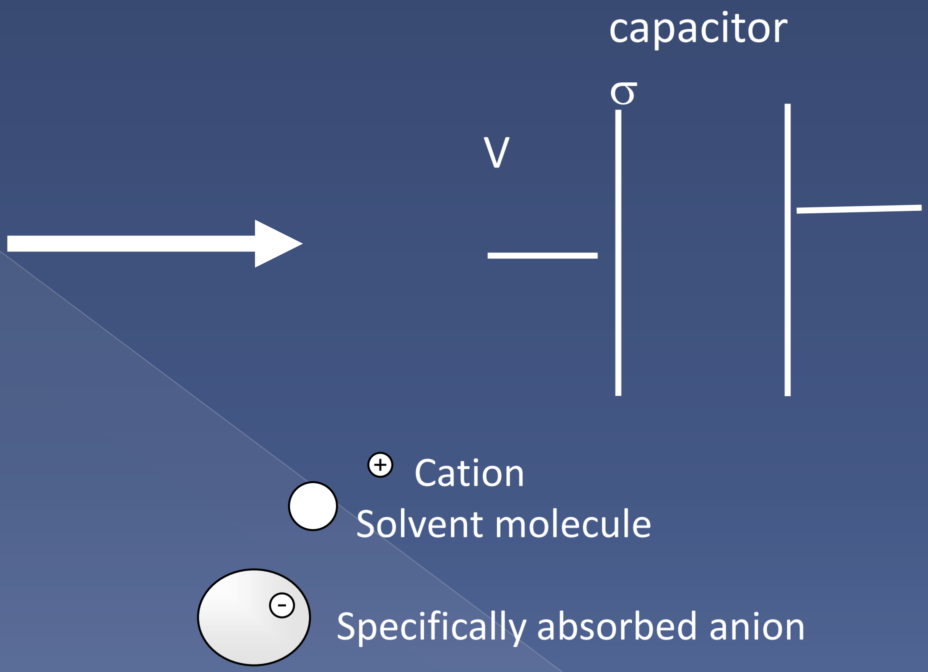


electrolyte

|φ|

Potential drop

d (nm)



capacitor

σ

V

⊕ Cation

Solvent molecule

Specifically absorbed anion

$$\frac{d\varphi}{dx} = -\left(\frac{8KTn_0}{\varepsilon\varepsilon_0}\right)^{1/2} \sinh\left(\frac{ze\varphi}{KT}\right)$$

$$\varphi = \frac{2KT}{ze}\ln\left(\frac{1+\beta e^{-\tilde{k}x}}{1-\beta e^{-\tilde{k}x}}\right)$$

$$\varphi_2 = \varphi_0 + \left(\frac{d\varphi}{dx}\right)_{x=x_2} x_2$$

$$\sigma^m = \left(8KT\varepsilon\varepsilon_0 n_0\right)^{1/2} \sinh\left(\frac{ze\varphi_2}{2KT}\right)$$

$$\tilde{k} = \left(\frac{2n_0 z^2 e^2}{\varepsilon\varepsilon_0 kT}\right)^{1/2}$$

$$\beta = \tanh(ze\varphi_0 4KT)$$

$$E_{dl} = \left.\frac{d\varphi}{dx}\right|_{x_2}$$

$$\sigma^m = 10^{14} C/m^2$$

$$\varphi_0 = 250 mV$$

$$E_{dl} = 10^8 V/m$$

PdH Dielectric Function Estimation

- The purpose is to obtain a reasonable, consistent dielectric function value suitable to be used in our model

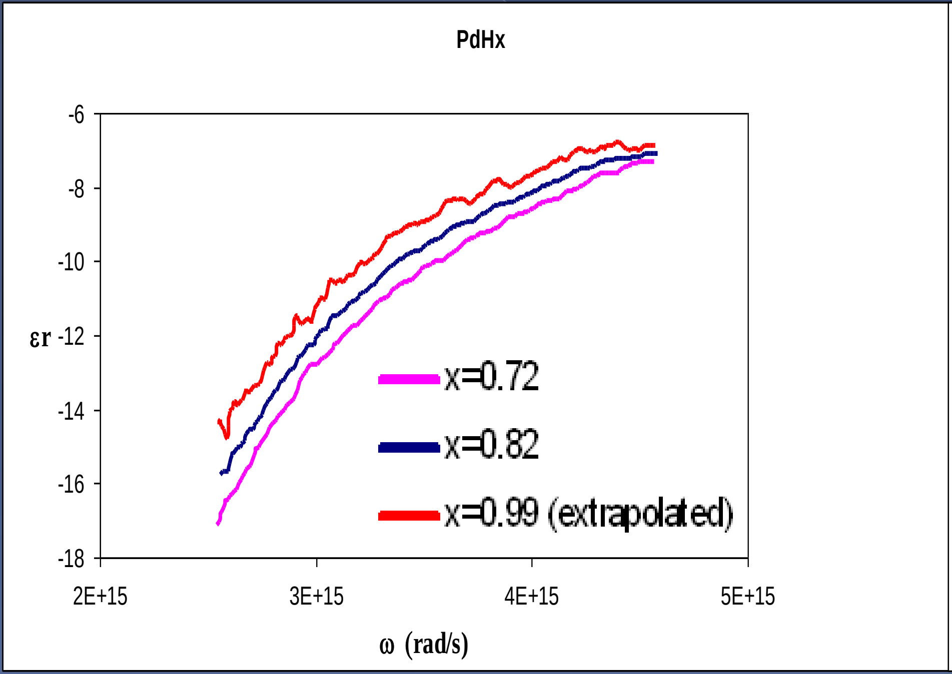


Fig.2- Dielectric function real component , palladium hydride

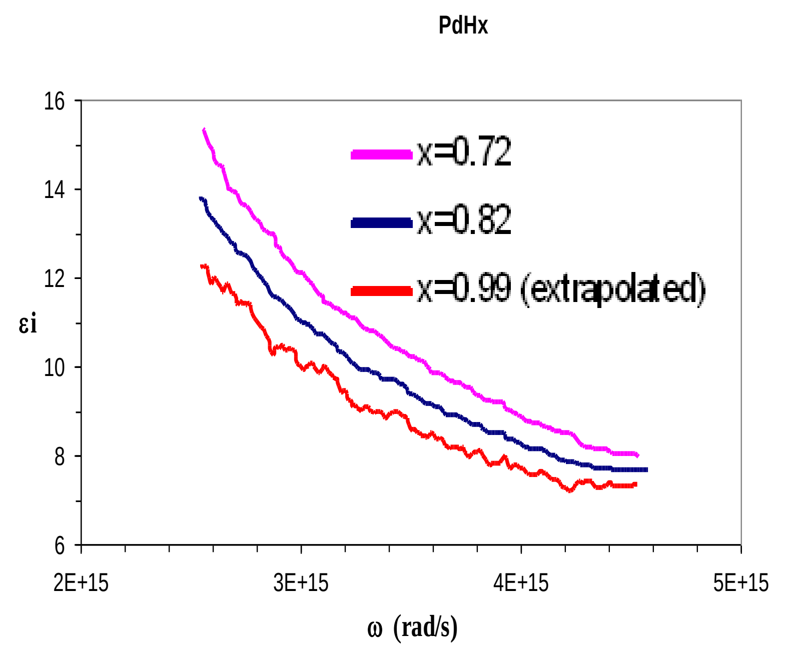


Fig. 3- Dielectric function imaginary component , palladium hydride

- Double layer is characterized by a high density of charges: it is necessary to describe a metal foil having on its surface a very high charge density, which results in an intense electrostatic field

- **The dielectric function variation related to surface charge density is**

$$\Delta\varepsilon_{PdH_x} = \left(\varepsilon_{x_{free}} - 1\right)\frac{\Delta N_{e\sigma_{PdH_x}}}{Ne_{PdH_x}}$$

$$\Delta N_{e\sigma_{PdH_{0.99}}} = \frac{\sigma^m}{q\cdot d}$$

$$Ne_{PdH_x} \approx \frac{2DOS\cdot KT}{Ry}\frac{1}{V_{cell}}$$

$$d = \frac{c}{\sqrt{8\pi\mu_{0\,Pd}\,\rho^{-1}_{PdH_{0.99}}}}$$

$$\varepsilon_{PdH_x\,TOT} = \varepsilon_{PdH_x} + \Delta\varepsilon_{PdH_x}$$

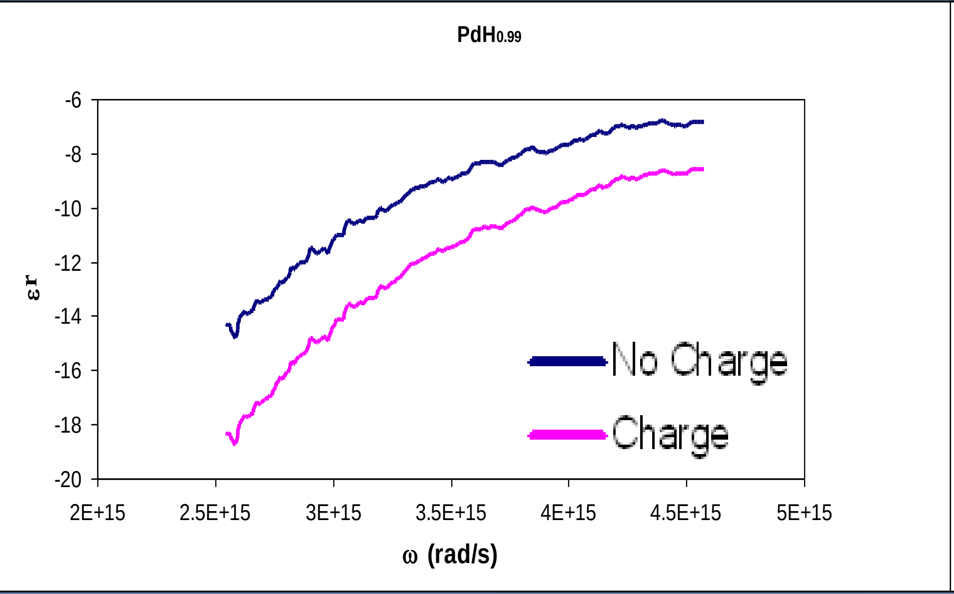


Fig. 4- PdH0.99 dielectric function real component versus angular frequency.
The shift to negative values due to surface charge is shown

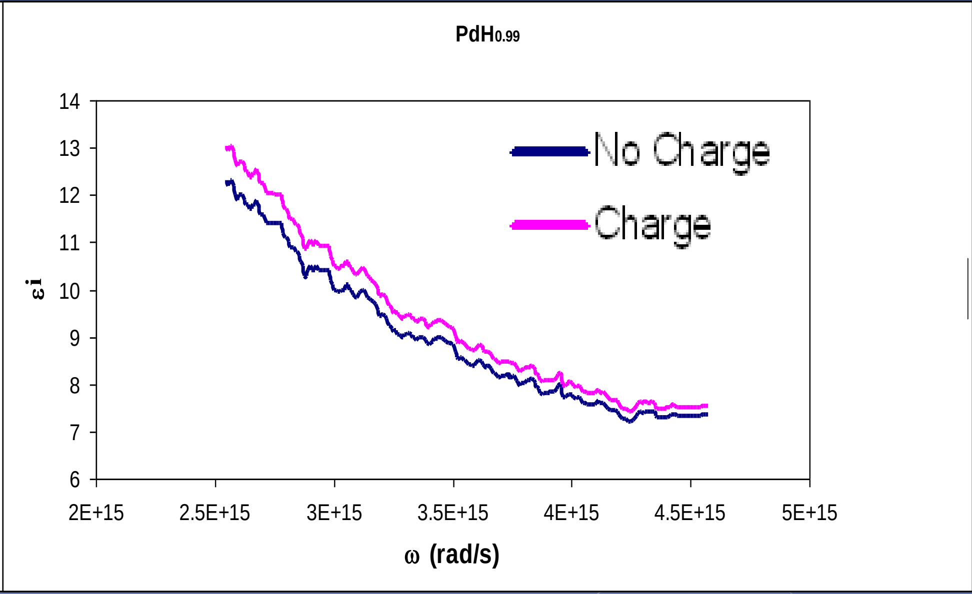
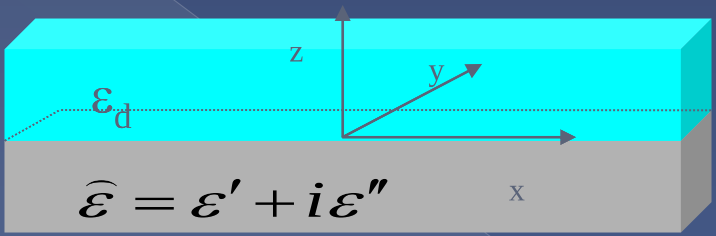


Fig. 5- PdH0.99 dielectric function imaginary component versus angular frequency.
The shift to higher values due to surface charge is shown

Surface Plasmons

- Surface plasmons (polaritons) are quanta of plasma oscillations created by the collective oscillation of electrons on a solid surface.

- Surface plasmons may be generated by mechanisms able to produce charge separation between Fermi level electrons and a background of positive charges (i.e. lattice atoms)



- Surface Plasmons Wave Vector x component dispersion relation is expressed by

$$K_x = \frac{\omega}{c}\sqrt{\frac{\varepsilon_d \hat{\varepsilon}}{\varepsilon_d + \hat{\varepsilon}}}$$

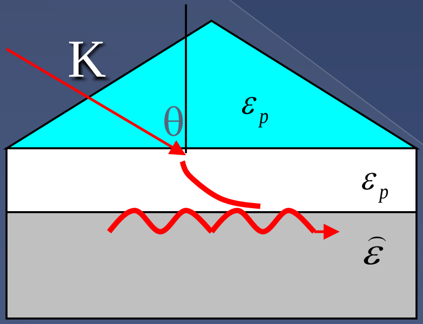
  - Under certain conditions one could use the simplified expression:

$$K_x' = \frac{\omega}{c}\sqrt{\frac{\varepsilon_d(\omega^2 - \omega_p{}^2)}{\omega^2(\varepsilon_d + 1) - \omega_p{}^2}}$$

$$\omega_p{}^2 = \frac{Ne^2}{m_{eff}\,\varepsilon_0}$$

Surface Plasmons Excitation Conditions

- Prism Coupling



$$\begin{cases} K_x = \dfrac{\omega}{c}\sqrt{\dfrac{\varepsilon_d \varepsilon'}{\varepsilon_d + \varepsilon'}} \\ K_x = \dfrac{\omega}{c}\sqrt{\varepsilon_p}\,\sin\theta \end{cases}$$

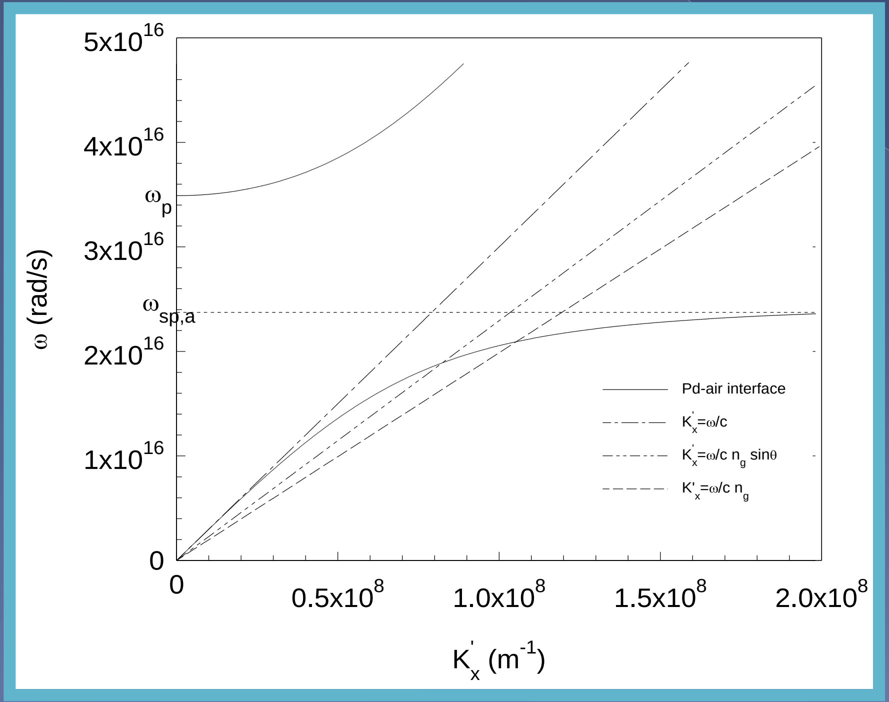


Fig.6 - Matching condition given by interception between s.p. and laser beam dispersion law, achievable using a prism coupler

- Roughness Coupling

$$K_x = \frac{\omega}{c}\sin\theta \pm \Delta K_x = K_{sp}$$

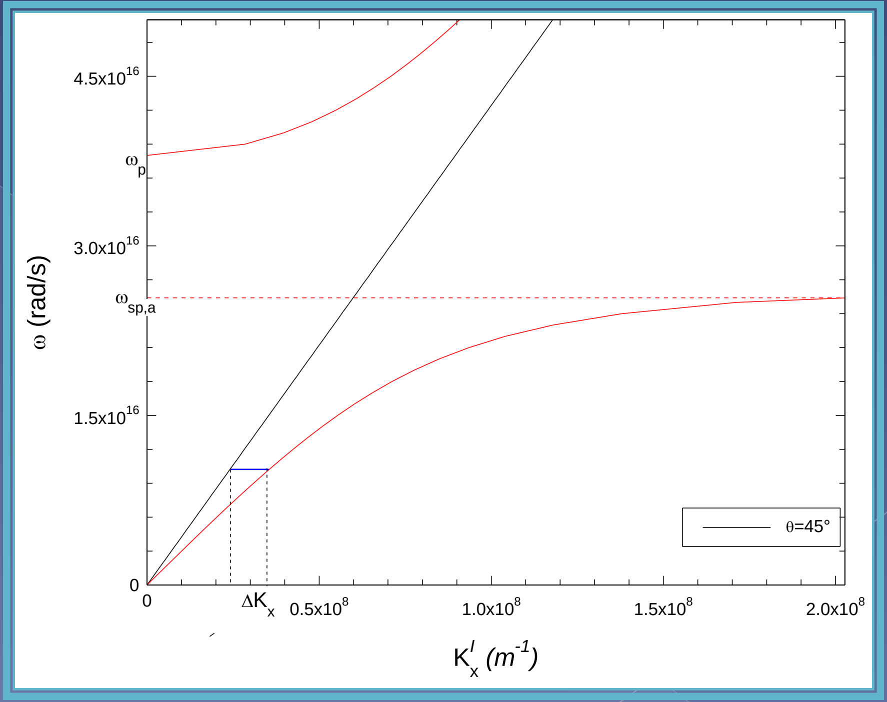


Fig.7 - Matching condition given by laser beam wave vector increment due to a corrugation lattice

Electro-Magnetic field Enhancement due to Surface Plasmons Excitation

- ➢ Surface Plasmons resonance could give rise to a huge local field enhancement, due to a focusing effect: a broad e.m. wave is confined in a surface.

- ➢ This phenomenon could be understood considering the wave vector component perpendicular to the interface between the two media:

$$K_{z2} = \frac{\omega}{c}\sqrt{\frac{\hat{\varepsilon}^2}{\hat{\varepsilon} + \varepsilon_1}}$$

$$K_{z1} = \frac{\omega}{c}\frac{\varepsilon_1}{\sqrt{\hat{\varepsilon} + \varepsilon_1}}$$

- ➢The field enhancement could be in a phenomenological way expressed as

$$\frac{\left|\vec{E}_j\right|^2}{\left|\vec{E}_0\right|^2} \approx \frac{\left|K_{zj}''\right|}{K_x''}$$

- Enhancement of about 10^2 factor could be obtained in this classical calculation. On appropriate structures and by quantum mechanical computation the enhancement factor could be equal to several magnitude orders

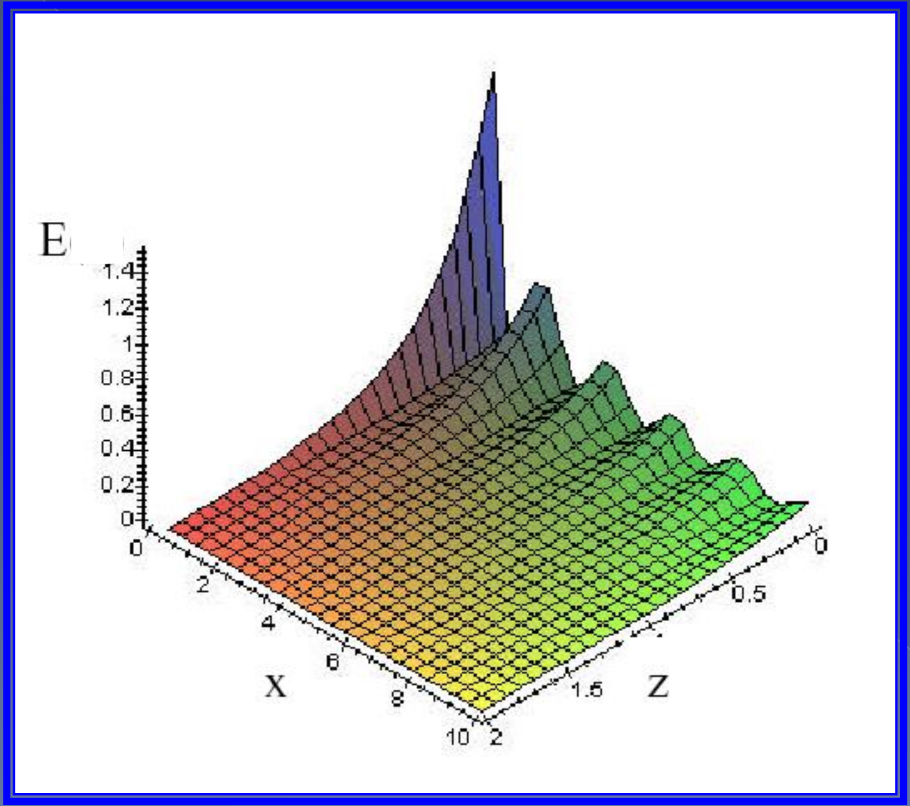
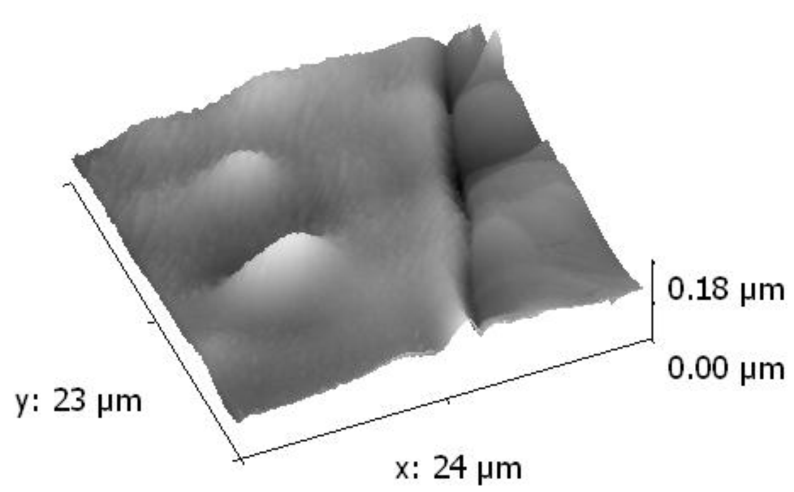
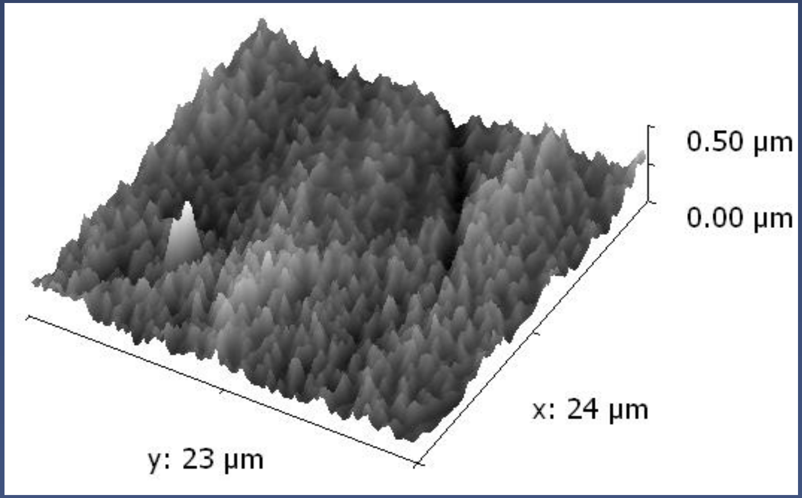


Fig.8 - Electromagnetic Field due to SP excitation, arbitrary units

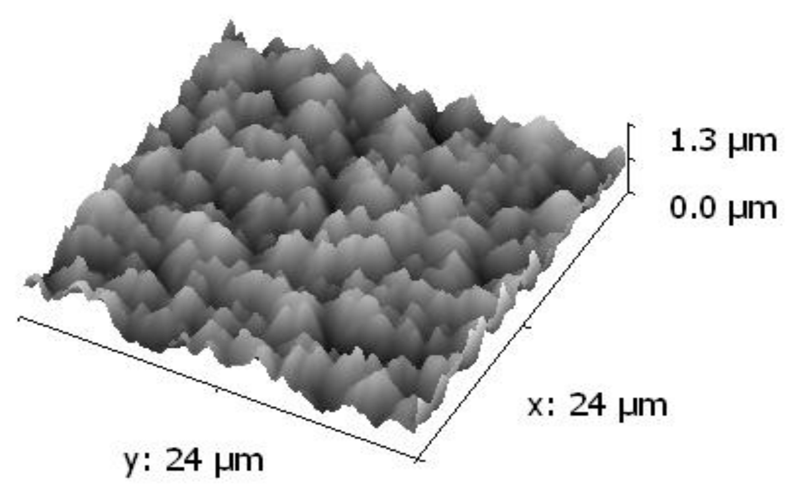
Palladium Cathodes Roughness



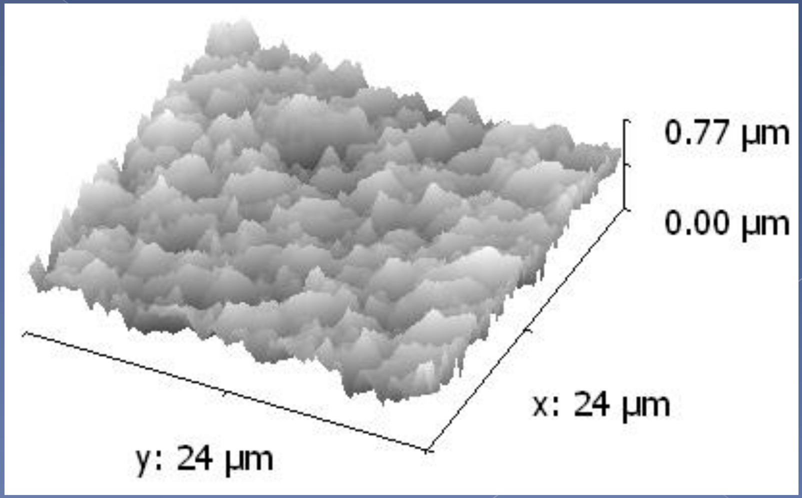
L72a(207-225)RA_4.jpg



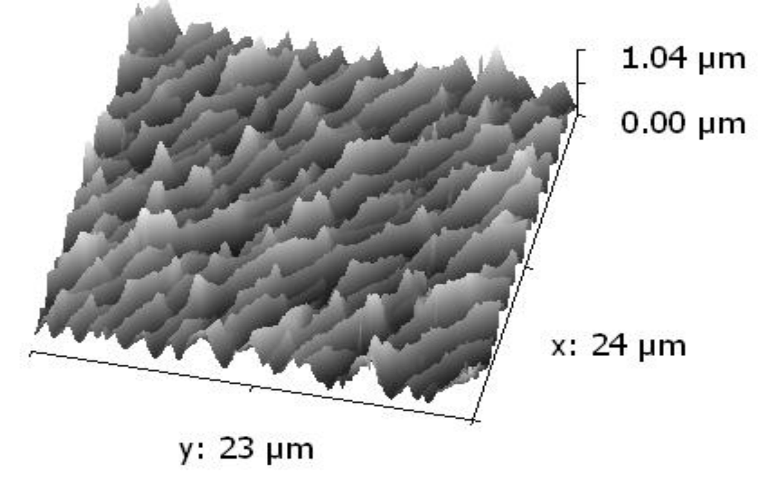
L68(0-20)RAE_5.jpg



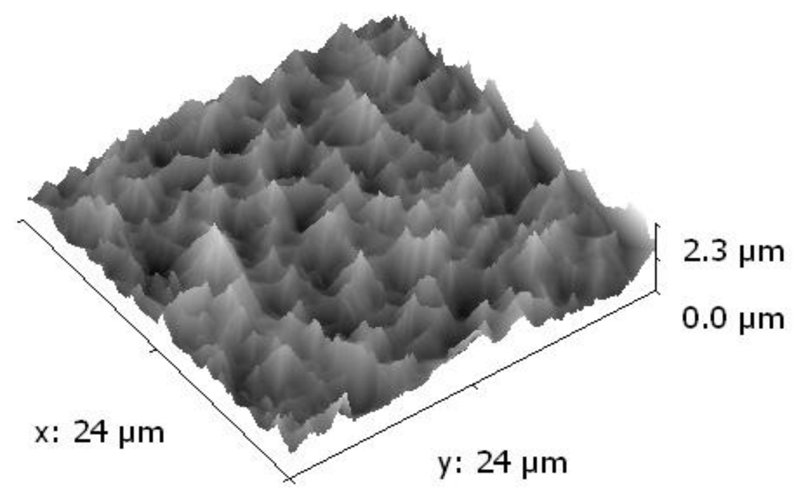
L68(20-40)RAE_3.jpg



L51(43-81)RAE_5.jpg



L55(215-254)RAE_7.jpg



L56(6-26)RAE_5.jpg

Sample	**Roughness (µm)**	**Surface Profile Average Wave Length (µm)**
L72a(207-225)RA	0.024	2
L68(0-20)	0.109	2.3
L68(20-40)	0.175	3
L51(43-81)RAE	0.112	1.8
L55(215-254)RAE	0.132	1.6
L56(6-26)RAE	0.205	1.5

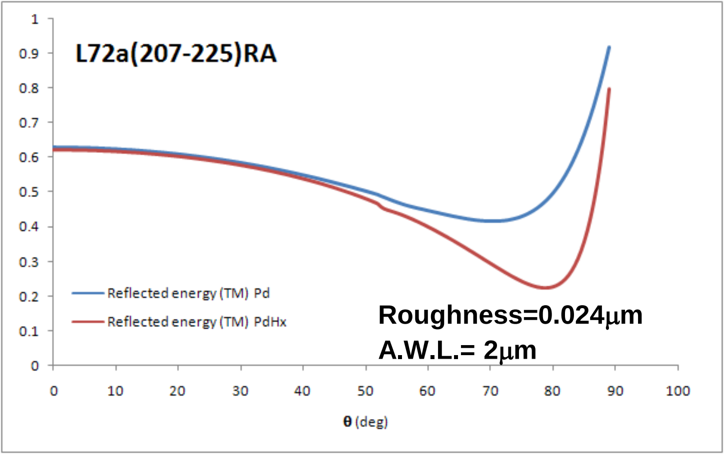
Rough Surface Reflectance Simulation

- A surface Plasmon can not be excited by direct impinging of an electromagnetic radiation on a smooth surface

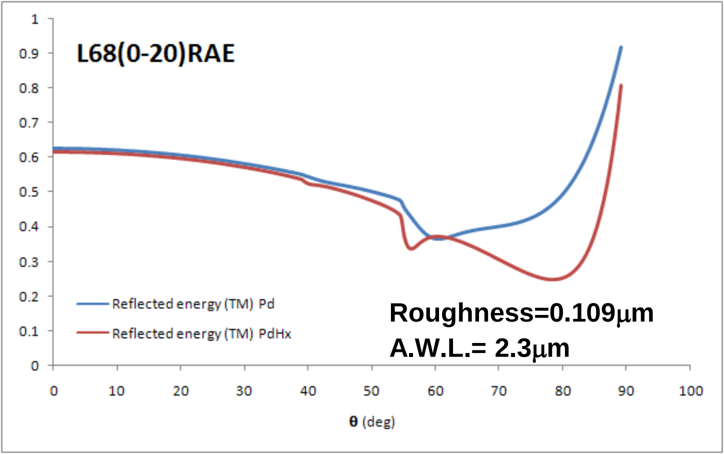
- A rough surface increases incoming electromagnetic wave momentum

- Modelling: Laser Angular Reflectance from gratings

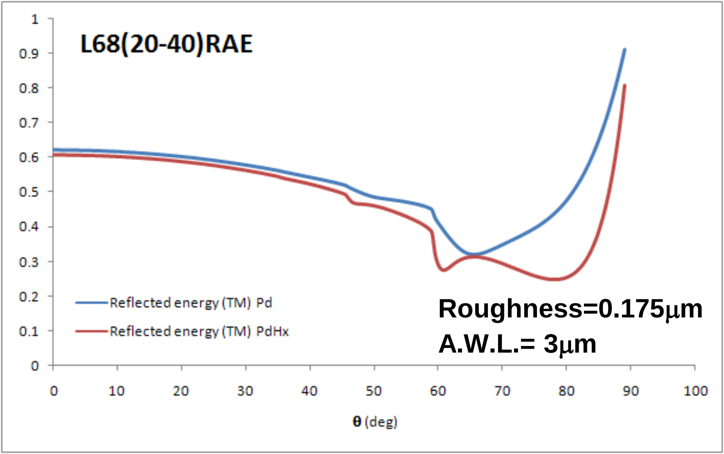
- Deepenings → **S10_O3**


L72a(207-225)RA

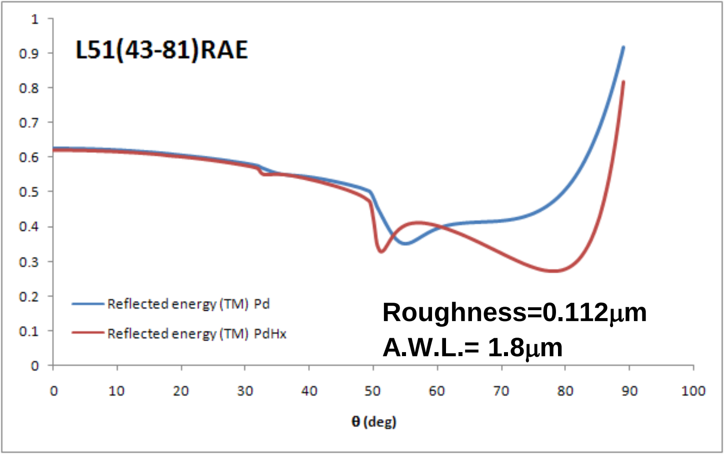
Roughness=0.024μm
A.W.L.= 2μm


L68(0-20)RAE

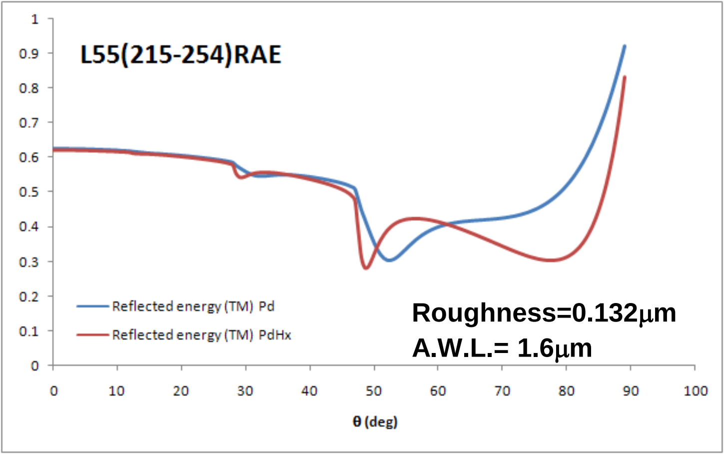
Roughness=0.109μm
A.W.L.= 2.3μm



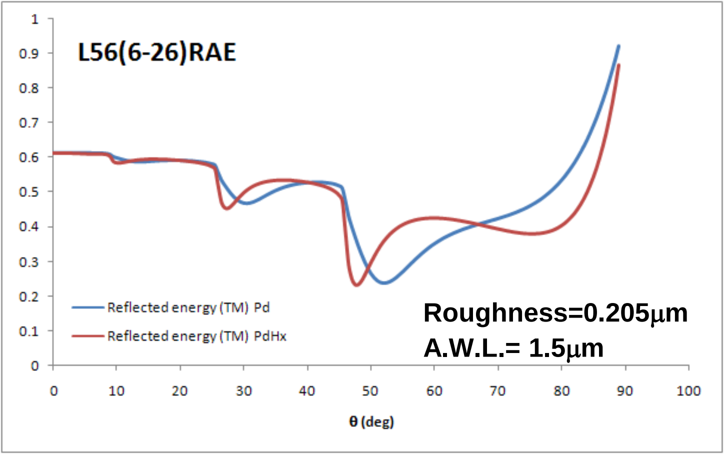
Roughness=0.175μm
A.W.L.= 3μm



Roughness=0.112μm
A.W.L.= 1.8μm



Roughness=0.132μm
A.W.L.= 1.6μm



Roughness=0.205μm
A.W.L.= 1.5μm

Finite Element Method Model

- **Previous Model:**
  - No information on Electromagnetic Field localization
  - Source terms can not be included in the Analytical Model

- **FEM implemented to solve differential Maxwell equations.**

- **Adequate boundary conditions are needed: Perfectly Matched Boundary Conditions (PML)**

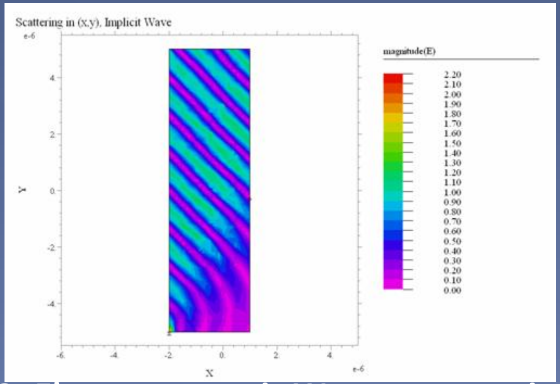


Fig. 9- Electromagnetic Wave propagation in free space

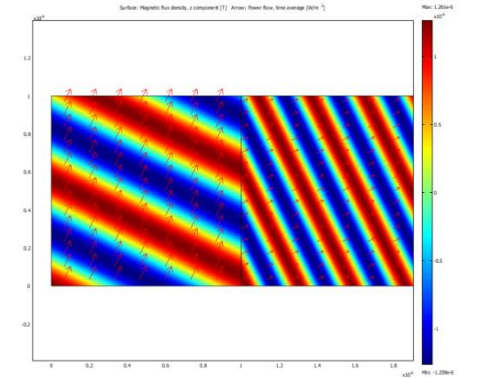


Fig. 10- Plane wave propagating in a two semi-infinite media domain

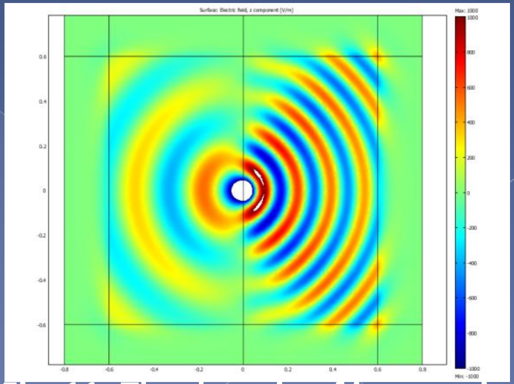


Fig. 11- The domain of interest is surrounded by outer PML elements.

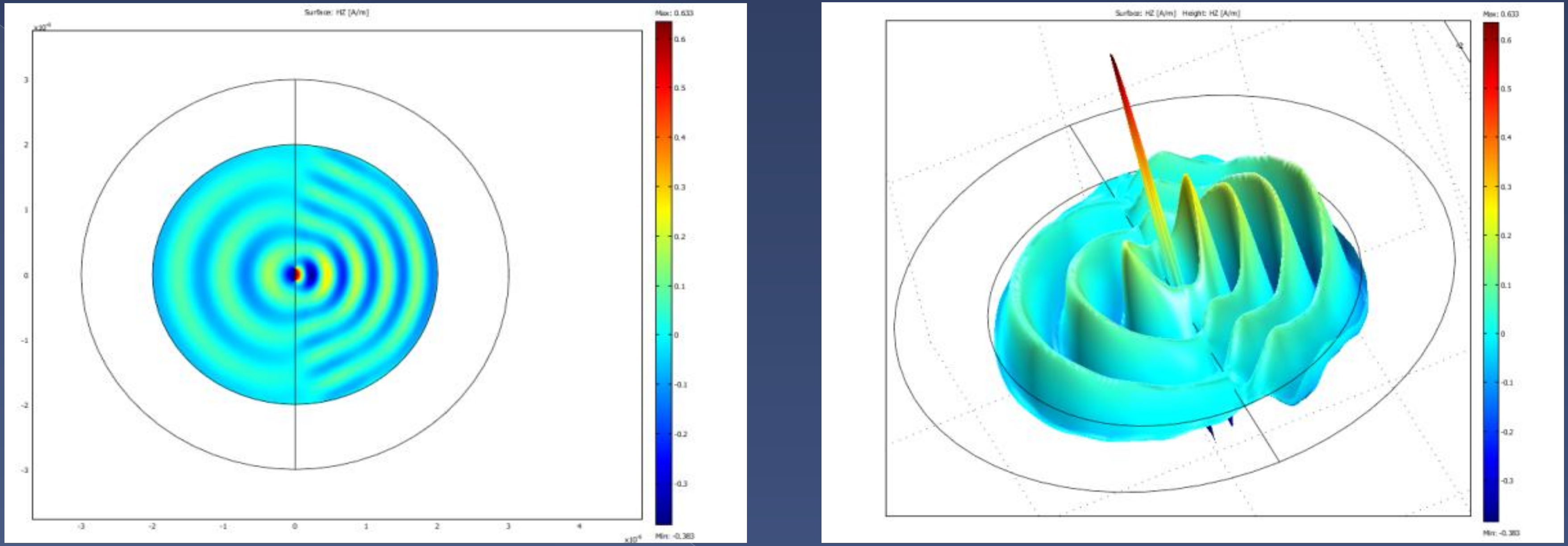


Fig. 12- Magnetic field originated by a surface current flux

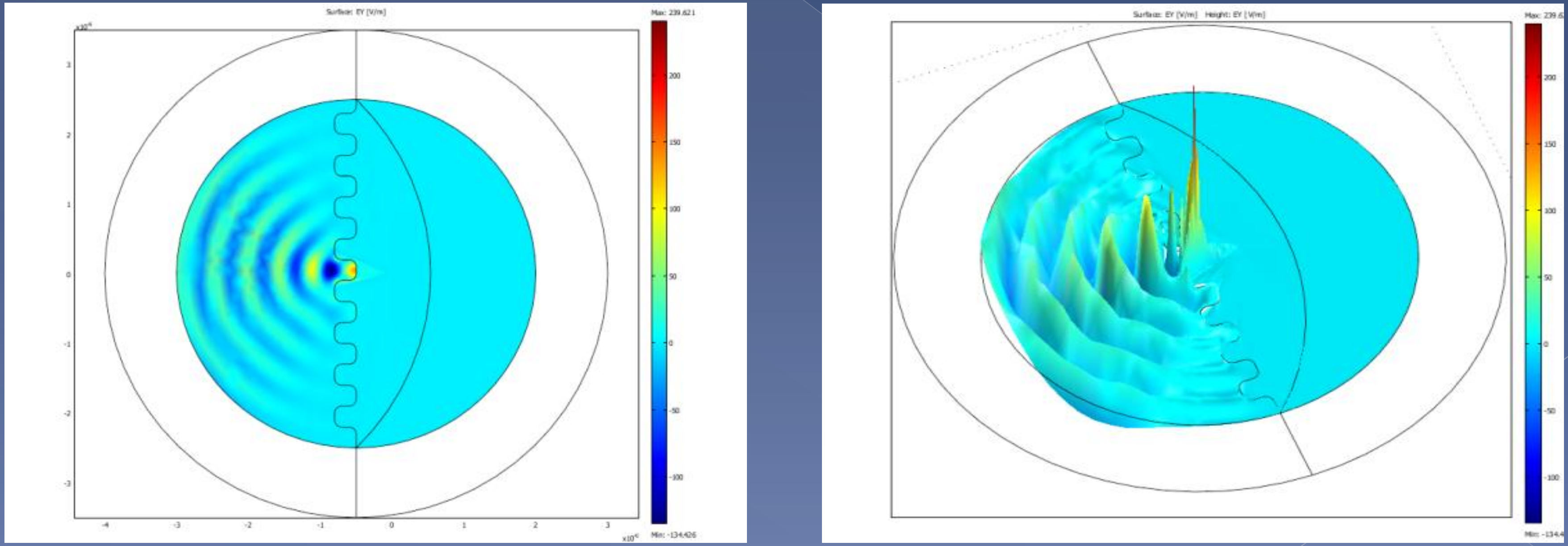


Fig. 13- Electric field distribution originated by an alternate surface current density flowing on a corrugated interface between air and PdHx

Conclusions

- **Description of Pd samples surface under cathodic polarization has been performed by including the effects of high charge density at the inter-phase**

- **On suitable surfaces electron plasma oscillation may occur. Their frequency is depending on the material electronic properties and surface profile properties**

- **The models developed show that under adequate conditions strong electromagnetic field localization and magnification arises.**

- **Advanced modelling of process occurring at the interface and into the bulk is the first step towards material engineering**