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Analysis Of Ni-Hydride Thin Film After Surface Plasmons Generation By Laser Technique

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A nickel-hydride thin film was studied by the Attenuated Total Reflection (ATR) method. The differences between a "black" film and a pure nickel film "blank" behaviour are showed. The black Ni-hydride film has been obtained by a short electrolysis with 1 M Li_2SO_4 electrolyte in light water. A shift in the minimum of the observed reflected light occurs, together with a change in the minimum shape, i.e. its half-height width increases. This two phenomenon are due to the change in the electronic band structure of the metal induced by the electron added in the lattice by hydrogen. The changing of the electronic structure, revealed by the laser coupling conditions, leads to consider that an hydride phase was created. Both the blank (not hydrogenated) and black (hydrogenated) specimens were taken under He-Ne laser beam at the reflectance minimum angle for about three hours. A SIMS analysis was also implemented to reveal differences in the isotopic composition of Cu, as marker element, between the blank and black films, in order to study the coupled effect of electrolysis and plasmon-polariton excitation on LENR processes in condensed matter.

1 Introduction

Surface Plasmons - Polaritons excitation by laser stimulation has been produced on pure Ni (blank) and Ni-Hydride (black) thin films by applying the Attenuated Total Reflection (ATR) method.

After loading hydrogen in Ni by electrolysis, SIMS surface analysis on the blank and on the irradiated black samples allowed to reveal differences in the isotopic composition of the marker element: Cu.

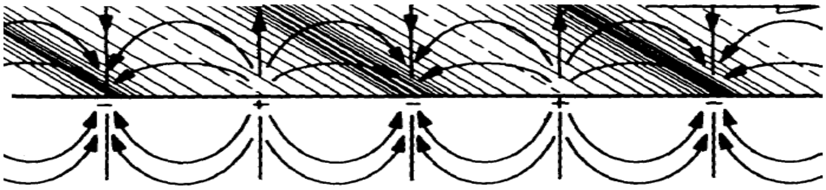


Figure 1. Charge separation, at the interface between two media, created, for instace, by an e.m. field

Cu is an impurity in Ni and is also deposited as impurity during the electrochemical loading of hydrogen in the metal. Cu was selected as marker since it has only two isotopes : ^{63}Cu and ^{65}Cu They don't overlap with isotopes of other elements.

Analysis revealed that isotopes having masses in the range 125-140 are absent before and after the H loading, so that one may exclude that SIMS analysis of ^{63}Cu and ^{65}Cu are affected by masses 126 and 130 twice ionized.

Surface plasmons (polaritons) are quantum of plasma oscillations created by the collective oscillation of electrons on a solid surface (Fig. 1).

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):

1) Electrons beam
2) Laser irradiation
3) Lattice vibrations = Phonons
4) Charged particles impinging on a surface

The change in zero-point energy of the surface plasmon oscillator system precisely corresponds to the classical image potential energy; so that external point charge induces a polarization charge density in a metal that is identical to the distribution induced by a set of surface plasmons.

Existence of plasmons has been revealed at the Gas/Metal and Electrolyte/Metal Interfaces[1].

A strong electric field enhancement arises during surface plasmons excitation. This phenomenon could be explained both with classical[2] or quantum mechanical[3] considerations.

2 Theoretical aspects

Bulk plasmon frequency is:

$$\omega_p{}^2 = \frac{Ne^2}{m_{eff}\varepsilon_0} \qquad (1)$$

Electric field created by charge separation:

$$E = \frac{Ne}{\varepsilon_0}u \qquad (2)$$

where N is the electron density at the Fermi level, e the electron electric charge, m_{eff} the electron effective mass, ε_0=8.854x10^{-12} Fm^{-1} the vacuum dielectric constant, u the separation distance.

Surface plasmons frequency for plane interface between two semi-infinite mediums, being the first a metal and the second a solution, is:

$$\omega_{sp} = \frac{\omega_p}{\sqrt{1+\varepsilon_1}} \tag{3}$$

where ε_1 is the relative dielectric constant (in the follow simply dielectric constant) of the medium 1. The dielectric function of a metal is complex :

$$\varepsilon_2 = \hat{\varepsilon} = \varepsilon' + i\varepsilon'' \tag{4}$$

The average electronic scattering time is the attenuation constant τ (for metals $\tau \sim 10^{-14}$ s)

If the conditions[4]

$${\omega_p}^2 >> \frac{1}{\tau^2} \tag{5}$$

$$\omega^2 >> \frac{1}{\tau^2} \tag{6}$$

are satisfied, it follows

$$\varepsilon' = n^2 - k^2 = 1 - \frac{{\omega_p}^2}{\omega^2} \tag{7}$$

$$\varepsilon'' = 2nk = \frac{1}{\tau}\frac{{\omega_p}^2}{\omega^3} \tag{8}$$

where n is the refraction index, k the attenuation index.

The dependence of the wave vector

$$K = K' + iK'' \tag{9}$$

of the plasma oscillation from the frequency at the surface of two semi-infinite mediums (Fig. 2) is the dispersion relation, which under certain conditions could be written as[5]

$${K_x}' = \frac{\omega}{c}\sqrt{\frac{\varepsilon_1\varepsilon'}{\varepsilon_1+\varepsilon'}} \tag{10}$$

$${K_x}'' = \frac{\omega}{c}\sqrt{\left(\frac{\varepsilon_1\varepsilon'}{\varepsilon_1+\varepsilon'}\right)^3} \cdot \frac{\varepsilon''}{2\varepsilon'^2} \tag{11}$$

The s. p. propagation length is:

$$L_p = \frac{1}{K_x''} \tag{12}$$

If conditions

$$\varepsilon' < 0 \tag{13}$$

$$\varepsilon'' < |\varepsilon'| \tag{14}$$

$$\varepsilon_1 < |\varepsilon'| \tag{15}$$

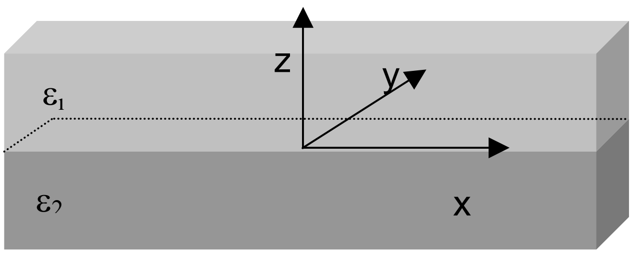


Figure 2. Interface between two semi-infinite mediums and reference axis

are satisfied, it follows:

$$K_x' = \frac{\omega}{c}\sqrt{\frac{\varepsilon_1(\omega^2 - \omega_p^2)}{\omega^2(\varepsilon_1 + 1) - \omega_p^2}} \tag{16}$$

Similarly one has, for the z component of the wave vector

$$K_{z1} = \frac{\omega}{c}\frac{\varepsilon_1}{\sqrt{\hat{\varepsilon} + \varepsilon_1}} \tag{17}$$

$$K_{z2} = \frac{\omega}{c}\sqrt{\frac{\hat{\varepsilon}^2}{\hat{\varepsilon} + \varepsilon_1}} \tag{18}$$

Then the penetration length of the plasma wave into the two media is:

$$z_{pj} = \frac{1}{|K_{zj}''|} \qquad j = 1, 2 \tag{19}$$

It is quite easy to plot the simplified expression (16) of s.p. dispersion law (Fig. 3).

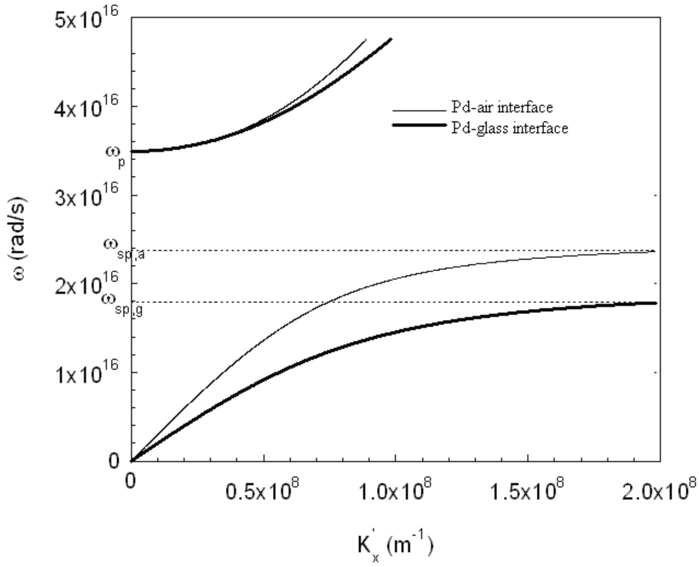


Figure 3. Surface Plasmon Dispersion Law for an air-Pd surface and a glass–Pd surface

Table 2.1. Characteristic parameters for surface plasmons excitations on some metals, by using a 632 nm incident radiation

Element	$\hat{\varepsilon}$	L_p(μm)	z_{p1}(μm)	z_{p2}(μm)
Ag	-16+0.5i	88	0.4	0.02
Au	-10+0.8i	21	0.3	0.03
Pd	-15+15i	5.7	0.5	0.02
Ni	-9+14i	3.8	0.4	0.03

Surface plasmons (polaritons) excitation by electromagnetic stimulation turns out when the real part of the *x* component of the wave vector of the incident wave results to be equal to the one of the surface plasmon.

The laser beam dispersion relation is:

$$K_x = \frac{\omega}{c}\sqrt{\varepsilon_1}\,sin\,\theta \qquad (20)$$

Electric field has to belong to the incidence plane, i.e. the wave has to be polarized in the p mode: if the electric field is perpendicular to incidence plane, and thus parallel to the interface (s-type polarization), it would assume the same value in the two mediums, without giving rise to the charge displacement needed to excite surface plasmons[6].

The comparison between the expressions (16) and (20) gives the following plot (Fig. 4).

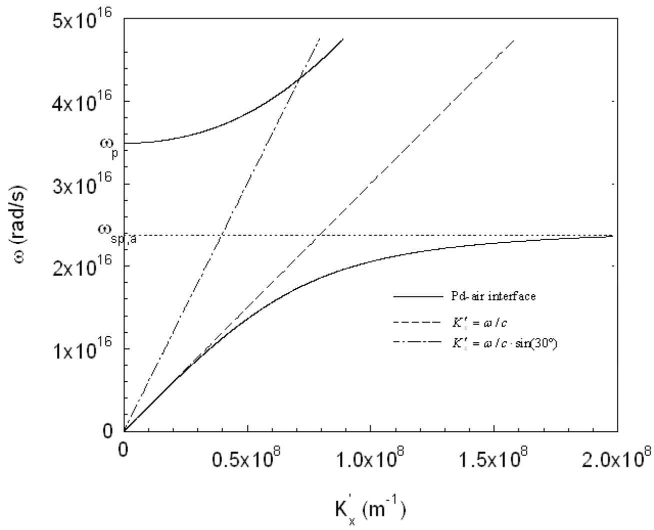


Figure 4. Comparison between s.p. and laser beam dispersion law at two different incidence angles

No matching condition results to be possible between light lines and surface plasmon dispersion curve at an air-Pd interface: the matching condition can not be satisfied on smooth

surface, because the interaction between photons and plasmons can not simultaneously satisfy the energy and momentum conservation.

Using a prism coupler the light lines modify and coupling conditions are achievable. The two most used configurations, Otto and Kretschmann (or Raether-Kretschmann) are showed below (Fig. 5):

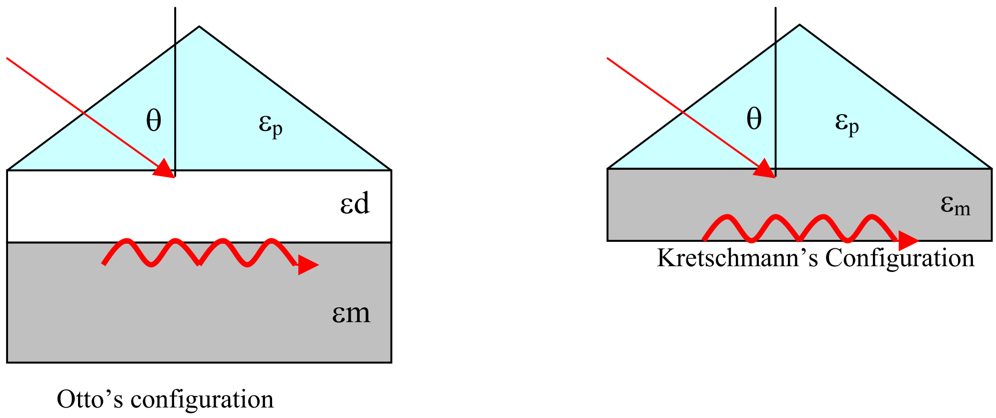


Figure 5. Two most used configuration in prism coupling

ε_p is the prism (or lens) dielectric constant, ε_d the dielectric medium one and ε_m is the metal dielectric function

The interception between the two curves (10) (or (16) in the simpler situation) and (20) is given by the solution of the system of equations:

$$\begin{cases} K_x = \dfrac{\omega}{c}\sqrt{\dfrac{\varepsilon_1\varepsilon'}{\varepsilon_1+\varepsilon'}} \quad \Leftrightarrow K_x = \dfrac{\omega}{c}\sqrt{\dfrac{\varepsilon_1(\omega^2-\omega_p{}^2)}{\omega^2(\varepsilon_1+1)-\omega_p{}^2}} \\ \\ K_x = \dfrac{\omega}{c}\sqrt{\varepsilon_p}\, sin\theta \end{cases} \tag{21}$$

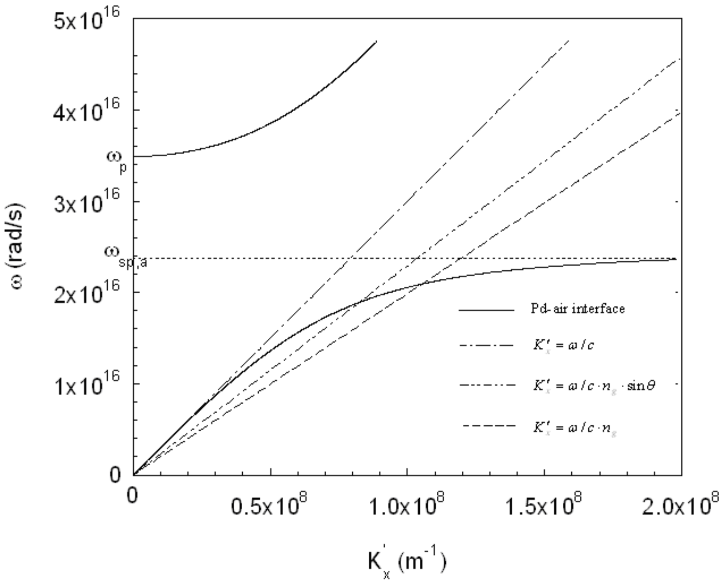


Figure 6. Matching condition given by interception between s.p. and laser beam dispersion law, achievable using a prism coupler

The corresponding plot (Fig. 6) shows now interception, observable between the light line relative to the total reflection condition (· -) and the one relative to incidence parallel to surface (-): the generic line (· · -) has one common point (except the origin) with s.p. dispersion law curve.

It is possible to obtain s.p. excitation also using a corrugation lattice or by corrugating the metal surface itself: such a corrugation increases the x component of the laser beam wave vector, making thus possible the coincidence with s.p. wave vector[5]:

$$K_x = \frac{\omega}{c} sin\,\theta \pm \Delta K_x = K_{sp} \tag{22}$$

where ΔK_x is defined as

$$\Delta K_x = \pm ng \tag{23}$$

$$g = \frac{2\pi}{a} \tag{24}$$

The plot below (Fig. 7) shows the possibility to satisfy the matching condition between the wave vectors of the two curves of interest.

A comparison could be made between surface plasma frequency, ω_{sp}, and phonon frequency,

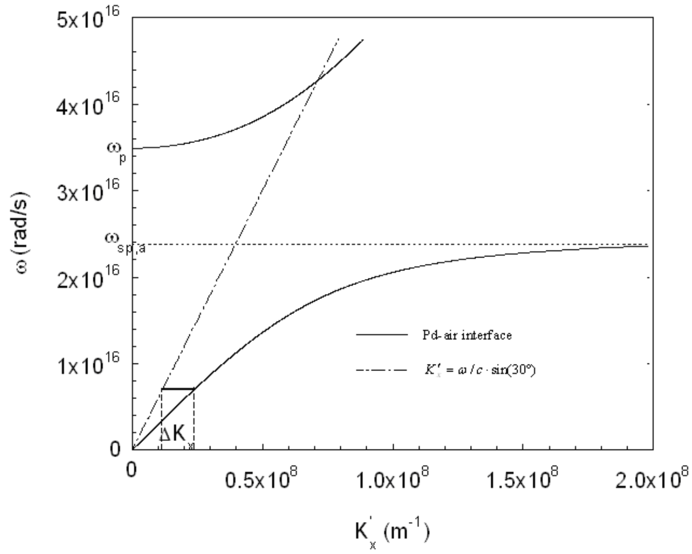


Figure 7. Increment ΔK_x of laser beam wave vector due to roughness, giving rise to s.p. resonance

both longitudinal (ω_{LO}) and transverse (ω_{TO}). Surface plasmons frequency is located between the two phonon frequency, and it assumes almost the same value of the longitudinal one[7].

3 Reflectance Measurement to Reveal Surface Plasmons

The interception between laser beam and s.p. dispersion curves (Fig. 6) could not be used to obtain a quantitative value for the frequency and for the angle of incidence giving resonance condition, as s.p. dispersion law is derived for two semi-infinite mediums, while using the prism coupler a layered structure is obtained (Fig. 5). A corrective factor is needed. However, is it possible to use an easier, indirect method, based on the Attenuated Total Reflection (ATR) principle.

Under certain conditions, light wave propagating along a layered structure, containing a metal layer, produces a reflectance minimum instead of total reflection[8].

A measurement of the reflectance R allows to reveal the resonant conditions. R is defined as

$$R = \left| \frac{E_r}{E_i} \right|^2 = \frac{I_r}{I_i} \tag{25}$$

where r stands for reflected and i for incident

The reflectivity rjk

$$r_{jk} = \frac{\dfrac{K_{zj}}{\varepsilon_j} - \dfrac{K_{zk}}{\varepsilon_k}}{\dfrac{K_{zi}}{\varepsilon_j} + \dfrac{K_{zk}}{\varepsilon_k}} \tag{26}$$

where j,k = 0,1,2 point prism, dielectric and metal respectively, leads the following relationship for reflectance

$$R = |r_{012}|^2 = \left|\frac{E_r}{E_i}\right|^2 = \left|\frac{r_{01} + r_{12}e^{2iK_{z1}d}}{1 + r_{01}r_{12}e^{2ik_{z1}d}}\right|^2 \tag{27}$$

A minimum of the reflectance for an incidence angle larger than the total reflection one, indicates a resonant condition for plasmons creation. The reason is the coupling between the light wave and the electronic surface plasma on the metal.

4. Experiment Design towards Simulation

A calculation of the reflectivity allows a calculation of the beam incidence angle to have a reflectance minimum for the experimental set-up[9]:

$$r = \frac{m_{12} - (z_s \cdot m_{22} - z_u \cdot m_{11}) - z_u \cdot z_s \cdot m_{21}}{m_{12} - (z_s \cdot m_{22} + z_u \cdot m_{11}) + z_u \cdot z_s \cdot m_{21}} \tag{28}$$

where

$$\begin{bmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{bmatrix} = M_l M_{l-1} \ldots M_2 M_1 \tag{29}$$

being

$$M_j = \begin{bmatrix} cos(K\tau_j z_j) & iZ_j\, sin(K\tau_j z_j) \\ iY_j\, sin(K\tau_j z_j) & cos(K\tau_j z_j) \end{bmatrix} \tag{30}$$

$$K = \frac{2\pi}{\lambda} \tag{31}$$

$$K_x = \sqrt{\varepsilon_p}\, sin\,\theta \tag{32}$$

$$Z_j = \frac{1}{Y_j} = \frac{\tau_j}{\varepsilon_j} \tag{33}$$

$$\tau_j = \pm\sqrt{\varepsilon_j - K_x{}^2} \tag{34}$$

$$j = u, 1, 2, \ldots, l-1, l, s \tag{35}$$

where j points the configuration layers.

So that

$$R = R[r(\theta)] \tag{36}$$

since R is defined as

$$R = |r|^2 \tag{37}$$

5 Experimental Set-Up

The minimum of the reflectance is revealed by a photo detector The pictures (Fig. 8) show the entire set-up used for the experiment: it is possible to observe the laser source, the focusing lens, the rotating support, the coupling lens and the photo detector

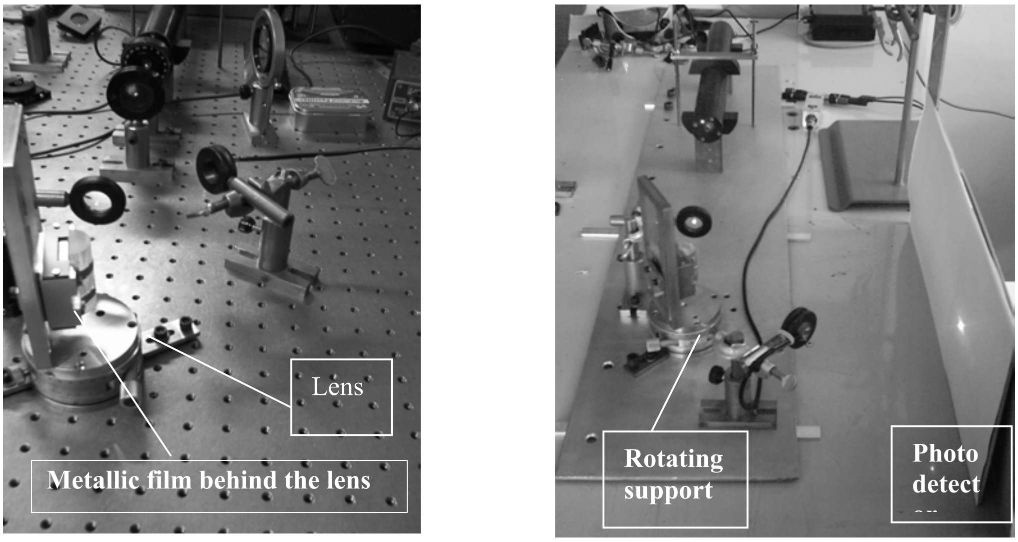


Figure 8. The minimum of the reflectance is revealed by a photo detector

6 Experimental Results

- Nickel-Hydride thin films (blank and black) on a polyethylene support have been studied by the Attenuated Total Reflection (ATR) method.

- Blank and black films (NiE) have been produced during the same sputtering process.

- The black Ni-hydride film has been obtained by a short electrolysis with 1 M Li_2SO_4 electrolyte in light water (40 minutes, current ranging between 10 to 30 mA).

- The specimen was taken under He-Ne laser beam at the reflectance minimum angle (Fig. 9, Fig. 10) for about three hours.

- The same laser treatments has been done on the blank (not electrolysed film).

-After electrolysis a shift in the minimum of the observed reflected light occurred, together with a change in the minimum shape, i.e. its half-height width increases (Fig. 11).

- This two phenomenon are due to the change in the electronic band structure of the metal induced by the electron added in the lattice by hydrogen.

- The changing of the electronic structure, revealed by the laser coupling conditions, leads to consider that an hydride phase was created.

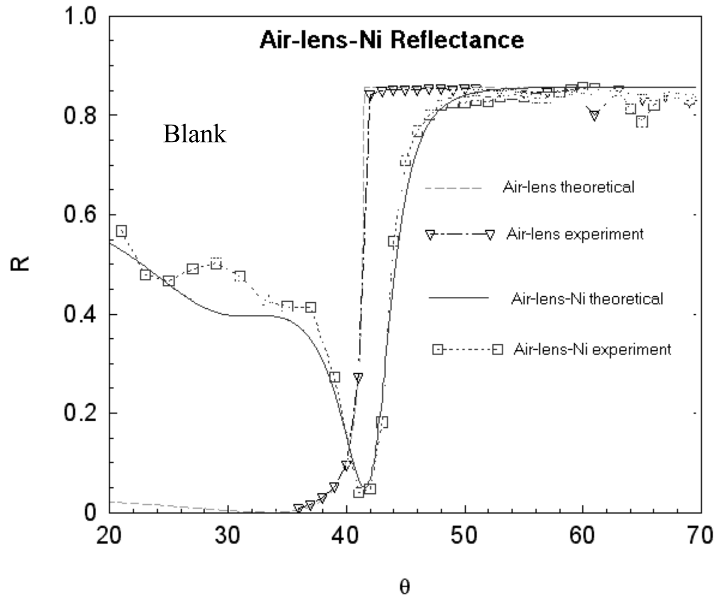
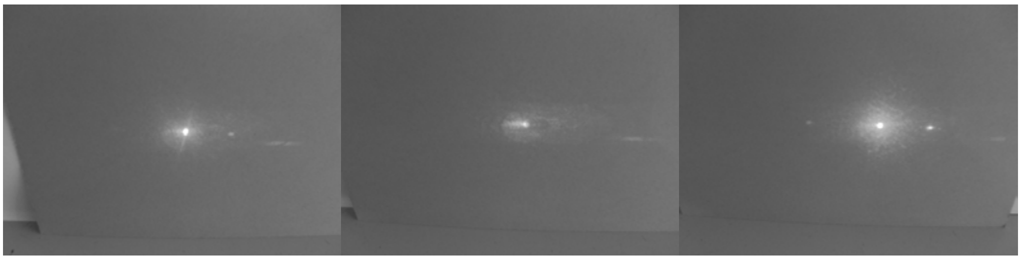


Figure 9. Blank Film Air/lens/Ni Reflectance



(a) (b) (c)

Figure 10. Reflected laser beam spot for increasing incidence angles: (a) before reflectance minimum, (b) in reflectance minimum, (c) after reflectance minimum

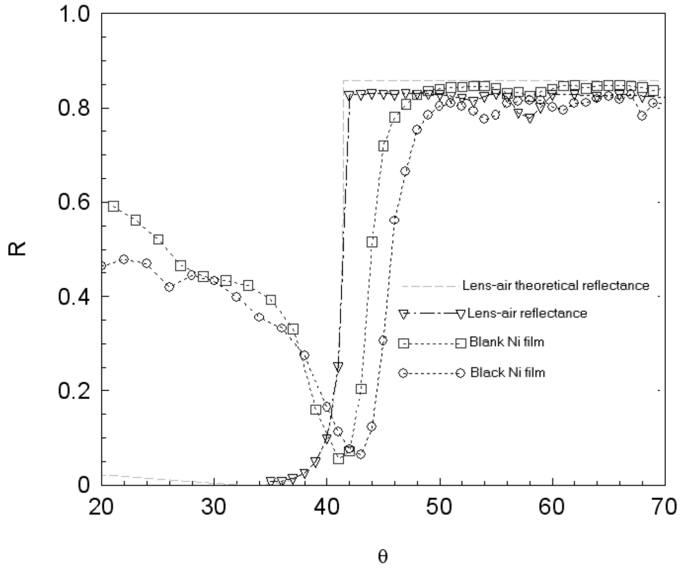


Figure 11. Reflectance of a cylindrical lens - air- Ni layered structure. The plot for the blank film and the black one are showed. The shift in the minimum angular position is due to the hydrogen in the metal lattice

7 SIMS Analysis

SIMS analysis has been carried out on both black and blank films. The analysis revealed a strong difference between the samples (Fig. 12, Fig. 13).

Measurements have been done in several points of the sample giving always the same results both in the blank and in the black, so that the idea that there are regions of the film enriched in one of the two isotopes can be discharged.

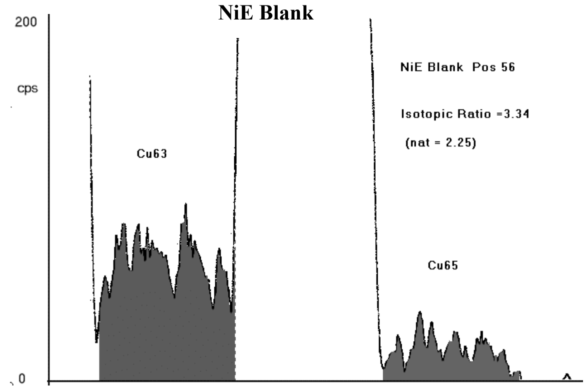


Figure 12. Blank of NiE, ^{63}Cu results to be more abundant of ^{65}Cu, the difference with the natural isotopic ratio is due to the small signal on mass 65. The sample was undergone to laser excitation of plasmons-polaritons for 3 hr

NiE blank

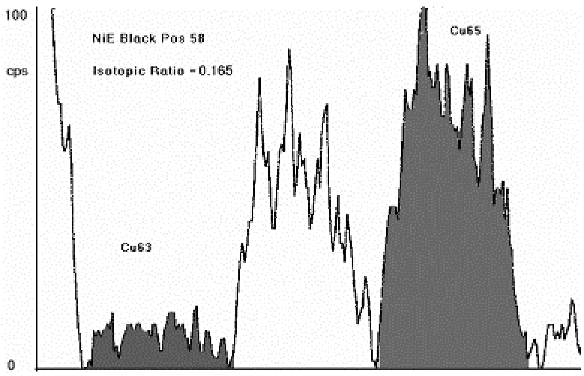


Figure 13. Black of NiE, after 40 min electrolysis + 3 hr of plasmons-polaritons excitation by laser. Isotopic ratio is changed of 1360%

SIMS analysis in deep (200 Å, just half of the Ni film thickness, Fig. 14) revealed that the isotopic shift is maintained in the bulk, so that also the hypothesis that the effect is due to the support can be discharged.

Measurements have been repeated over more than 10 points of both blank and black samples giving always the same isotopic shift, so that an isotopic enrichment effect should be excluded. Ni hydride formation giving an increasing of mass 65 can be also excluded since the abundance of ^{62}Ni is larger than the ^{64}Ni one, so that such an effect should give an increasing of mass 63 peak larger than the increasing of the mass 65 one.

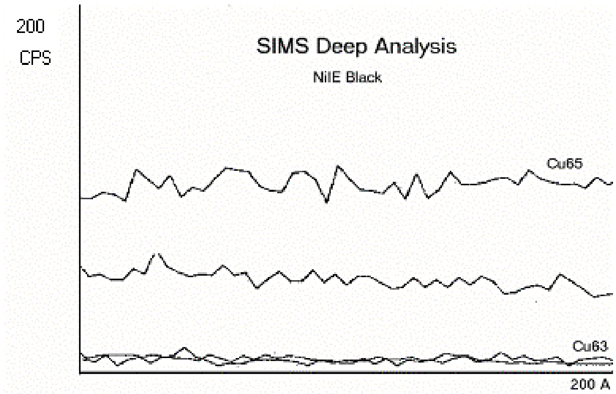


Figure 14. SIMS analysis in deep (200 Å) in the black sample

8 Conclusions

The measurements revealed a very clear effect on the $^{63}Cu/^{65}Cu$ isotopic ratio shift, very difficult to explain in terms of isotopic enrichment.

In the blank the isotopic ratio between ^{63}Cu and ^{65}Cu shows the larger abundance of the first one as expected.

The situation is completely changed in the black where the most abundant cupper isotope results to be ^{65}Cu with a shift that is 1360%.

Such a result reproduces the data obtained with some hours of electrolysis, when a weak emission of X rays was detected, but the effect seems to be enhanced.

Results seem to be a clear signature of a LENR process occurring in condensed matter under the electro-dynamic trigger of plasmons - polaritons.

The local e.m. field created by plasmons (polaritons) should also be responsible of the energy transfer mechanism from composite nucleus to the lattice [10-11] because of the field effect on nuclear decay process.

Cross analysis by SIMS and NAA are foreseen for enhancing the study.

Such a result should be considered as preliminary and requires to be repeated in order to confirm the effect and to understand the role of the electrolysis and the role of the laser in producing a so wide isotopic shift on copper.

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