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Resistivity of Bilayers Ni/Pd Films and $Ni_{1-x}Pd_x$ Alloys Films

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Abstract: In this study, we present the resistivity measurements on pure metal films Ni, Pd, on binary alloys films $Ni_{1-x}Pd_x$ and on bilayers Ni/Pd films. We will analyze the effect of disorder related to the random distribution of elements in solid solution on the alloy $Ni_{1-x}Pd_x$ film resistivity. We used two types of substrates: glass-Corning and a polycrystalline α-alumina. The resistivity $Ni_{1-x}Pd_x$ alloy films at ambient temperature presents two maxima, one maximum near atomic composition $Ni_{72}Pd_{28}$ and the other near $Ni_{30}Pd_{70}$. The resistivities of $Ni_{1-x}Pd_x$ films deposited on the α-alumina substrates are 30% larger than the resistivities of the $Ni_{1-x}Pd_x$ films deposited on the glass-Corning substrates. When one changes the degree of order in the mixture (Ni, Pd) while passing from a solid solution Ni_xPd_{1-x} to bilayers Ni/Pd films, the apparent resistivity decreases by a factor -larger than 2.

Keywords: $Ni_{1-x}Pd_x$ thin films, resistivity, bilayers Ni/Pd films, atomic order disorder.

1 Introduction

In the context of an increased production and wide use of hydrogen, the safety is an essential condition.

The purpose of the present work is to develop transition metal alloys thin films of Pd_x-Ni_{1-x} as hydrogen sensors.

The Pd_xNi_{1-x} alloys have interesting properties: they are not easily oxidizable, and can operate in a wide range of temperatures and hydrogen pressures.

The hydrogen solubility can be controlled by varying the alloy composition.

The sensors can be used in the form of thin films or as bilayers deposited on an insulating substrate (alumina, glass).

The thin films reactivity is monitored by the change in their electrical properties under atomic hydrogen insertion. In the bilayers version, the functionality of the sensors will depend on the physicochemical modifications of the layer of palladium buried.

2 Méthod of preparation of Thin Films

2.1 Mode of obtaining Pure Metals and Bilayers Films

The thin films were prepared by sputtering (RF) vacuum in the presence of a low pressure partial of argon [1]. The pure metal films are deposited on plates of glass-Corning-1737, 1 mm thickness in the shape of a disc of diameter equal to 30.5 mm and on polycrystalline α-alumina substrates with an average grain size G.
= 5 ± 4 μm,**Fig**-1.

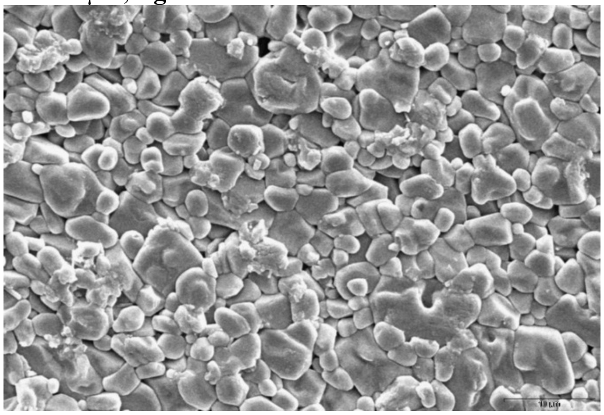

Fig.1: Surface of α-alumina substrate.

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The mean velocities of deposit of palladium and nickel films are V_{Ni} = 1.94 Å.s-1, and V_{Pd} = 7.11 Å.s-1.

2.2 Principle of Obtaining Ni_xPd_{1-x} Alloy Films with Chemical Compositions Gradient

The technique consists in co-depositing alloy films of two different material targets, Fig- 2a-2b.

The theoretical principle of co-pulverization method is addressed in the works of R.J. Gnaedinger [2], G.C. Schwartz [3] and J.J. and J.J. Hanak [4, 6]. This technique was used to elaborate Ni_xPd_{1-x} alloys films.

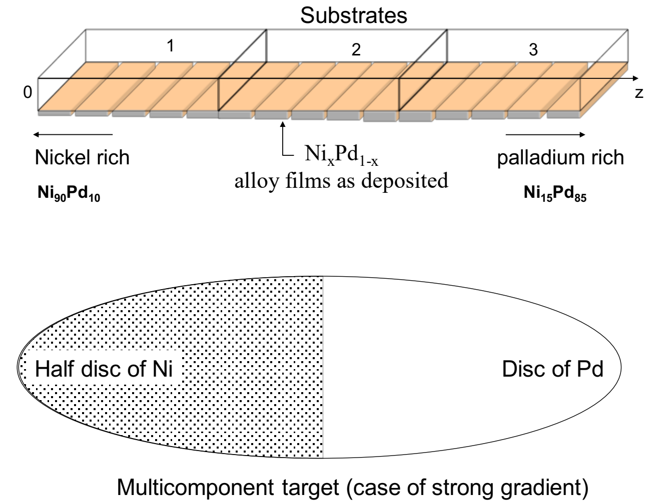


Fig.2a : Geometry of the target (Ni, Pd) in the case of development of Ni_xPd_{1-x} films ~~to~~ with strong gradient of composition, LOS6 (1/2Pd, 1/2Ni).

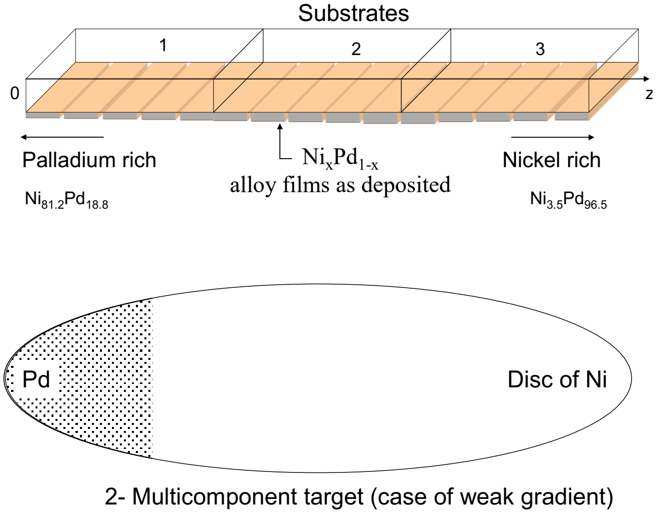


Fig.2b: Geometry of the targets (Ni, Pd) in case of development of Ni_xPd_{1-x} films with weak gradient of composition, LOS8 (1/3Pd, 2/3Ni).

Two geometries of targets were selected to prepare solid solutions Ni_xPd_{1-x}, Fig.2a-2b. In the first configuration, LOS6- (½ Pd + ½ Ni), the target consists of a palladium disc partially hidden by a half disc of nickel with the same diameter Fig.2a, and in the second configuration, LOS8- (1/3 Pd, 2/3 Ni), the palladium disc is hidden by a sector of nickel of the same diameter and representing a surface fraction of 66.7% compared to that of palladium (Fig.2b).

To prepare a large range of composition in each co-sputtering run, three square substrates of 35 mm side and 1 mm thickness, juxtaposed are used as shown in Fig.-2a-2b. Before each deposit a periodic network of parallel strip of 0.7 mm width and distance of 6.5 mm, is drawn with a felt pen, on the surface of each substrate. These strips allow after dissolution with acetone (lift off technique) to delimit separated rectangular (6.5x35) mm films samples. The steps obtained are used for local thicknesses measurements. In the case of alumina substrate, two rectangular sheets of 50 mm length, 35 mm width, and 1 mm thickness are used for each deposit.

3 Thicknesses Measurements

Thicknesses measurements, at the level of each step separating two bands, are obtained using an interference microscope. The average thicknesses, h, of the films vary between 70 nm ≤ h ≤ 252 nm **(Fig-3 and Fig-7).**

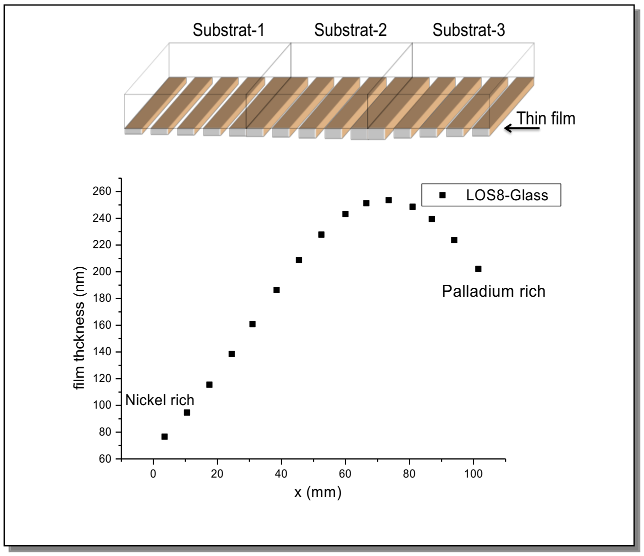


Fig.3: thicknesses distribution of the various NixPd1-x films.

4 Chemical Analysis of Ni_xPd_{1-x} Alloy Thin Films

The chemical profiles of nickel and palladium compositions along the direction of the gradient are obtained on MEB-Leica equipped with an X-ray detector from Röntech Company. The kinetic energy of the primary electrons used for the chemical analysis is of 25 keV. The concentrations of nickel and palladium, obtained from the intensities of $K_{\alpha\text{-Ni}}$ and $L_{\alpha\text{-Pd}}$ emission lines, are carried out along the axis of each rectangular band with an average step of 2 mm. From the apparent experimental concentrations of nickel and palladium atoms, $(C_{Ni})_{exp}$, $(C_{Pd})_{exp}$, we calculated the real concentrations $(C_{Ni})_F$ and $(C_{Pd})_F$ of the chemical elements in Ni_xPd_{1-x} thin films. The standard samples used for this quantitative analysis are Ni/Pd bilayers films. The mean atomic composition of nickel and palladium in the Ni/Pd bilayers films is calculated according to equations (1a-1b):

$$(C_{Ni})_{et} = \frac{h_{Ni} a_{Pd}^3}{h_{Ni} a_{Pd}^3 + h_{Pd} a_{Ni}^3} \qquad (1a)$$

$$(C_{Pd})_{et} = \frac{h_{Pd} a_{Ni}^3}{h_{Pd} a_{Ni}^3 + h_{Ni} a_{Pd}^3} \qquad (1b)$$

where a_{Ni} and a_{Pd} are the cubic CFC cells parameters of nickel and palladium layers and h_{Ni}, h_{Pd} are the thicknesses of these two layers. The total thickness of Ni/Pd bilayers films was intended to be equal to that of the Ni_xPd_{1-x} alloy films. This method enabled us to check the conservation of the ratio of the concentrations in the Ni/Pd bilayers films:

$$\frac{(C_{Ni})_F}{(C_{Pd})_F} = \frac{(C_{Ni})_{\exp}}{(C_{Pd})_{\exp}} \qquad (2)$$

Combining equation-2, and equation (3) that express the mass law conservation:

$$(C_{Ni}) + (C_{Pd}) = 1 \qquad (3)$$

we deduced the local concentration of nickel $(C_{Ni})_F$ and palladium $(C_{Pd})_F$ in Ni_xPd_{1-x} alloys films. The results of chemical analyzes relating to the two limits of composition are given in Fig.4. In configuration LOS6 (½ Pd + ½ Ni). , the atomic concentration of palladium (% At.) varies in the interval 19 ≤ % X ≤ 95 whereas in configuration LOS8(1/3 Pd, 2/3Ni), this concentration varies in the interval 10 ≤ % X ≤ 79.

5 Principles of Electrical Measurements and Model of Calculations of the Resistivity

A power current source Keithley 6220 and one nano-voltmeter 2182A-Keithley are used to take the automatic measurements of voltage and current by the technique of the four colinear probes (Fig-5). The automatic-command of the measuring instruments is controlled by computer thanks to an interface GPIB and a Labview program.

The calculation of the resistivity is deduced from the resistances measured by the model developed by Smits [1, 7]. In case of thin film thickness W, the resistivity ρ of a sample of rectangular shape a*d is connected to electric the resistance R, by the relation (4):

$$\rho = R.W.C(S, a, d) \quad (4),$$

S denotes the distance between two successive probes (S = 2.54 mm) and C(S, a, d) is the geometrical factor correction of the sample.

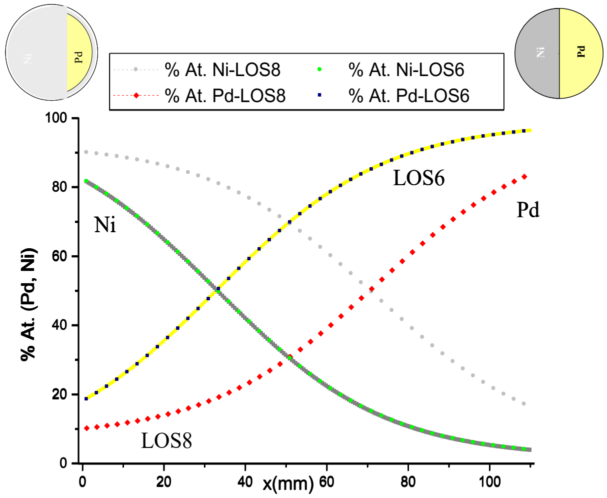


Fig.4: Chemical analyzes of the Ni_xPd_{1-x} films corresponding to the two geometries of the targets.

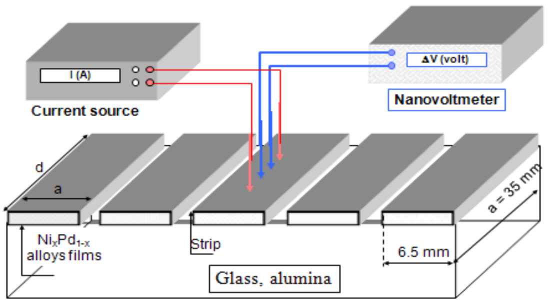


Fig.5: General diagram of the measurement of the electric resistance of a thin film by collinear four probes.

The resistivity of films $Ni_{1-x}Pd_x$ alloy at the ambient temperature presents two maxima, one maximum near atomic composition $Ni_{72}Pd_{28}$ and the second near $Ni_{30}Pd_{70}$ (Fig. 6). This is attributed to the difference in the level of stress between nickel rich films and palladium rich films. Thickness of films rich in nickel is smaller than that of films rich in palladium, Fig-3.

The position of the maxima obtained on our $Ni_{1-x}Pd_x$ films is different from the results published by Mott [8] and other authors [9-12] on bulk $Ni_{1-x}Pd_x$ alloys for which the maximum of resistivity is obtained for the atomic composition $Ni_{30}Pd_{70}$.

In addition the resistivities of $Ni_{1-x}Pd_x$ films deposited on the α-alumina substrates are 30% larger than the resistivities of the $Ni_{1-x}Pd_x$ films deposited on the glass-Corning substrates. This difference is attributed to the defects in thin film because the alumina substrate presents a porosity of about 2%. and a surface roughness comparable with the grains size.

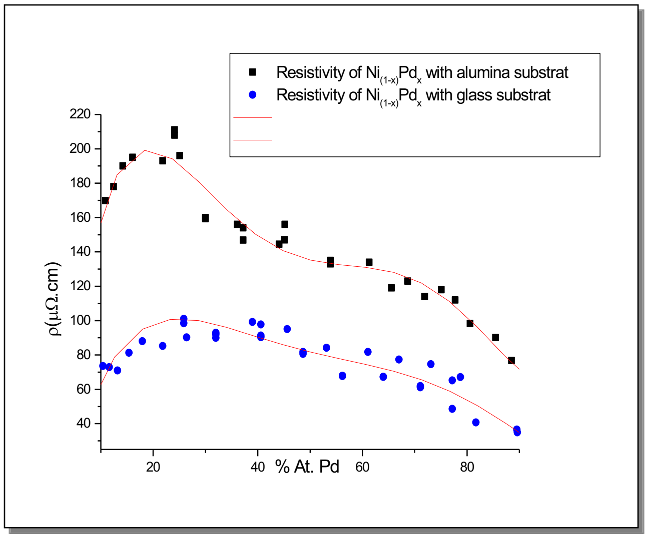
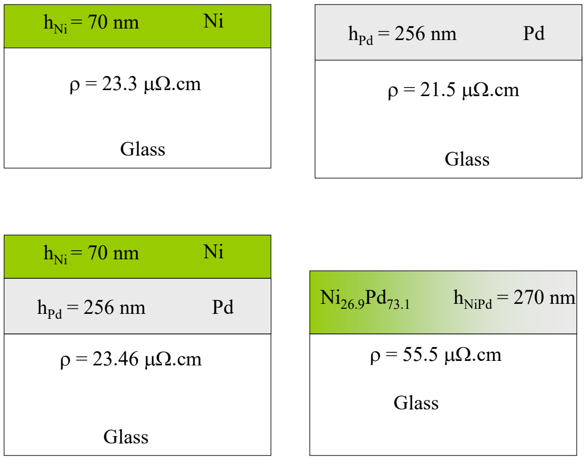


Fig.6: Variation of the resistivity of films of Ni$_x$Pd$_{1-x}$ alloys, as a function of % atomic of palladium on alumina and glass substrates.

6 Comparison between the Resistivity of Bilayers Ni/Pd Film and that of a Film of Ni$_{1-x}$Pd$_x$ alloy with the Same Average Atomic Composition

This section is devoted to the comparative study, Fig-7, of the electric properties of bilayered Ni/Pd films on ~~the~~ one hand and those of binary Ni$_{1-x}$Pd$_x$ alloys films, ($0.269 \leq X \leq 0.524$) presenting the same average atomic composition as the bilayers on the other hand.

This study shows that the resistivity of film of the solid solution Ni$_x$Pd$_{1-x}$ is at least twice the resistivity of bilayers Ni/Pd. When one changes the degree of order in the mixture (Ni, Pd) while passing from a solid solution Ni$_x$Pd$_{1-x}$, where the spatial distribution of the chemical elements palladium and nickel in the same crystal lattice is random with that of a system with two completely ordered networks corresponding to bilayers Ni/Pd, the apparent resistivity decreases by a factor larger than 2.



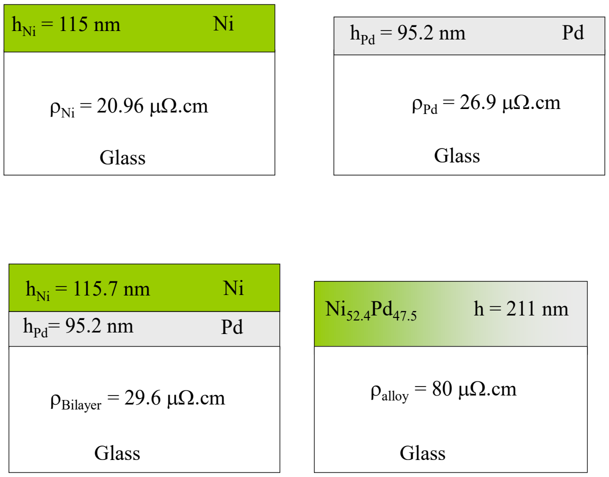


Fig.7: Resistivities (ρ_i) and thicknesses (h_i) of films of Ni, Pd, of bilayers Ni/Pd and the Ni$_x$Pd$_{1-x}$ alloys films.

7 Conclusions

The resistivity of Ni$_{1-x}$Pd$_x$ alloy films at ambient temperature presents two maxima**:** one maximum near atomic composition Ni$_{72}$Pd$_{28}$ and the other near Ni$_{30}$Pd$_{70}$

The resistivities of Ni$_{1-x}$Pd$_x$ films deposited on the α-alumina substrates are 30% larger than the resistivities of the Ni$_{1-x}$Pd$_x$ films deposited on the glass-Corning substrates.

We have shown that the film resistivity of a Ni$_x$Pd$_{1-x}$ solid solution is at least twice the resistivity of a Ni/Pd bilayer with the same average atomic composition. When in the solid solution Ni$_x$Pd$_{1-x}$ we pass from a system in which the spatial distribution of the chemical elements palladium and nickel in the crystal lattice is random, to that of the completely ordered system corresponding to the two networks of the Ni/Pd bilayer, the apparent resistivity decreases by a factor of at least two.

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