Int. J. Thin. Film. Sci. Tec. **11**, No. 3, 321-326 (2022)

International Journal of Thin Films Science and Technology

http://dx.doi.org/10.18576/ijtfst/110309

Interface Resistivity in Ni/Cu Bilayers, and Ni/Pd bilayers Comparison of the Mode of Electrical Transport in Ni/Cu bilayers and Ni/Pd bilayers in Relation with the Chemical Reactions at the Interfaces of bilayers

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Received: 22 Jun. 2022, Revised: 2 Jul. 2022, Accepted: 12 Aug. 2022

Abstract: In this study we determined and compared interphases-interfaces-resistivity between nickel/copper bilayers and nickel/palladium bilayers in relation to the chemical reactions which can take place at the interfaces of bilayers and deduced the electric transport mode in bilayers.

Keywords: bi-layered Ni/Cu and Ni/Pd , interphases-interfaces-resistivity, electric transport mode in a bilayer.

1 Introduction

The electrical resistance measurement by the method of collinear four probes was used to determine the interphases-interfaces-resistivity. The metal samples studied of f.c.c structure, copper, nickel, palladium, bilayer nickel on copper (Ni/Cu) and bilayer nickel on palladium (Ni/Pd) are deposited on insulating substrates. We prepared single thin films of copper, nickel, palladium, bi-layered Ni/Cu and Ni/Pd of various thicknesses. In the case of films with two superimposed layers we applied the model developed by Schumann and Gardner [1,2] and modified by C. W. Wang [3], to extract the resistivity related to the interface interphases in bi-layered Ni/Cu. and Ni/Pd thin films. A combination of various techniques including chemical analysis by Energy Dispersive X-Ray-Spectrometry, and the observations by Scanning Electron Microscopy (S.E.M.) of the surface bilayers were associated to the electrical measurements in order to elucidate the modification of electrical properties of bi-layered thin films observed with time.

2 Preparations of Thin Films

The thin films are prepared by cathode sputtering (RF) under vacuum (~1.5 Pa) in the presence of a low partial pressure of argon-U. At the beginning of each pulverization, an ionic etching, in situ, target is necessary before each deposit. The films, in the form of discs of 30.5 mm diameter, are then deposited on plates of 1 mm thickness, out of glass-Corning-1737. The setting under air of the samples at the end of the preparation is carried out under inert atmosphere (nitrogen-gas). The mean velocities of deposit of copper, nickel and palladium films are respectively of $V_{Cu} = 1.94$ Å.s^{-1}, $V_{Ni} = 3.54$ Å.s^{-1}, and $V_{Pd} = 7.11$ Å.s^{-1}. During the preparation of bi-layered films the second layer is deposited after that the first layers was exposed to air.

3 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 at the ambient temperature the automatic measurements of voltage and current by the technique of the four collinear probes, as shown in Fig-1. The automatic measurements are controlled by computer, using an interface GPIB and a Labview program.

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

$$\rho = R.W.C(S, d_0) \qquad (1)$$

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With : $$C = \frac{\pi}{\ln 2 + \ln\left(\frac{\left(\frac{d_0}{S}\right)^2 + 3}{\left(\frac{d_0}{S}\right)^2 - 3}\right)}$$

where S is the distance between two successive probes (S = 2.54 mm), and d_0 the sample diameter.

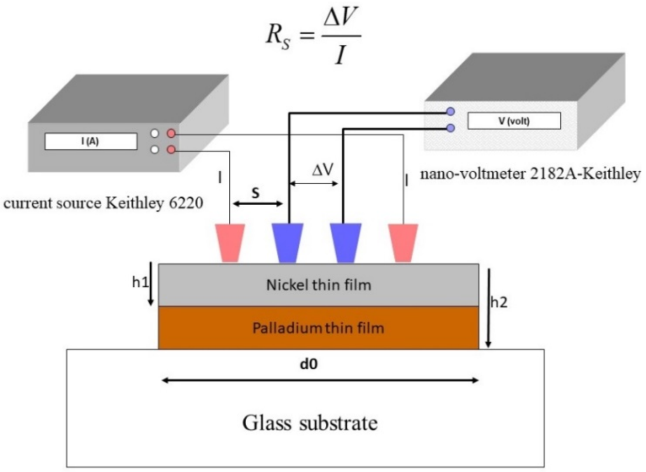

Fig.1: General diagram of the measurement of the electrical resistance of a bi-layered thin films by collinear four probes.

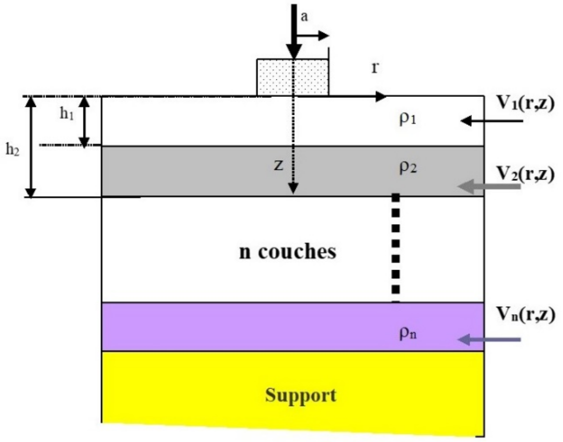

Fig.2: Working hypotheses in the model of Schumann-Gardner.

4 Resistance of bilayers deposited on insulating substrate (Model of Shumann and Gardner (S-G))

This model was developed in the case of a diffusion layer of single-phase material divided into n layers, and presenting a gradient of resistivity on all the thickness of the layer. In the case of a layer divided into n layers, the electric potential at a point M (r, z) of the $n^{\text{ième}}$ layer is determined by Schumann-Gardner in cylindrical co-ordinates. "r" is the distance from the probe and "z" the depth measured from surface of the first layer. The extremity of each probe is of finite size, it has a circular surface contact of radius a, with the first layer, (Fig.-2). The potential at a point of $n^{\text{ième}}$ layer is given by the expression:

$$V_n(r,z) := \int_0^\infty \theta_n(\lambda) J_0(\lambda r) e^{(-\lambda z)} d\lambda + \int_0^\infty \psi_n(\lambda) J_0(\lambda r) e^{(\lambda z)} d\lambda \quad (2)$$

J_0 is the Bessel function of first species of order "zero", a the radius of contact of the probe, $\psi_n(\lambda)$ and $\theta_n(\lambda)$ are two functions which depend on the boundary conditions and the initial conditions (the number of layers, the thicknesses of the layers, the resistivity of the different layers, and the shape of the current density distribution at the end of each current probe).

In the case of a system with two layers having a contact resistance at the interface between the first and the second layer, the condition of continuity of the current density in the model of S-G is replaced by the condition [3]: $V_1(r, z = h_1) - V_2(r, z = h_1) = -J.\rho_I$.

The expressions of the potentials at the two points of measurement~~s~~ of surface external and located respectively at the distances "r = s, and r = 2s" of the probes of current are given by:

$$V_1(r = s, z = 0) = \frac{I_0 \rho_1}{2\pi a} \int_0^\infty \frac{(1 + 2\theta_1(\lambda)\sin(\lambda a)(J(0, \lambda s)}{\lambda} d\lambda, \quad (3a)$$

$$V_1(r = 2s, z = 0) = \frac{I_0 \rho_1}{2\pi a} \int_0^\infty \frac{(1 + 2\theta_1(\lambda)\sin(\lambda a)(J(0, 2\lambda s)}{\lambda} d\lambda, \quad (3b)$$

The function $\Theta_1 = 1 + 2\theta_1$ is written: $\Theta_1 = \frac{N_1 + N_2}{D_1 + D_2}$

(3c), with

$$N_1 = -e^{(z\lambda - 2h_2\lambda)}(\rho_1 + \rho_2 - \lambda\rho_I) + e^{(-2d\lambda - z\lambda)}(\rho_1 - \rho_2 + \lambda\rho_I), \quad (3d)$$

$$D_1 = e^{-2h_2\lambda}(\rho_1 + \rho_2 - \lambda\rho_I) + e^{(-2d\lambda)}(\rho_1 - \rho_2 + \lambda\rho_I), \quad (3e)$$

$$N_2 = e^{(z\lambda - 2h_1\lambda)}(\rho_1 - \rho_2 - \lambda\rho_I) - e^{(-z\lambda)}(\rho_1 + \rho_2 + \lambda\rho_I), \quad (3f)$$

$$D_2 = e^{-2h_1\lambda}(\rho_1 - \rho_2 - \lambda\rho_I) - (\rho_1 + \rho_2 + \lambda\rho_I), \quad (3g)$$

I_0 is the intensity of the current delivered by each of the two probes, ρ_1 is the resistivity of the first layer (nickel) located at the depth z = 0, ρ_2 the resistivity of the second layer (copper or palladium), ρ_I represents the resistivity of the interface between the two layers Ni/Cu or Ni/Pd [5, 6], h_1 and h_2, are respectively the depths of the interfaces limiting the two layers, and $d = h_2 - h_1$ the thickness of the second layer as shown in Fig.1.

The potential difference measured between the two internal probes, $\Delta V = V_1(0,2s) - V_1(0,s)$, as well as the apparent electric resistance between these two probes are respectively equal to:

$$\Delta V = \frac{I_0\rho_1}{2\pi a}\int_0^\infty \frac{\sin(\lambda a)(1+2\theta_1(\lambda))(J(0,\lambda s)-J(0,2\lambda s))}{\lambda}\,d\lambda, \quad R_S = \frac{\Delta V}{I_0} \tag{4}$$

To calculate this integral numerically we used the method of approximation of Simpson.

To fit the interface resistivity ρ_I, the thicknesses of the Ni, Cu and Pd layers as well as the resistivity of the monolayers are fixed to within 5%. The adjustment calculation between the calculated resistance $R_{S\text{-calculated}}$ and the experimental resistance $R_{S\text{-experimental}}$ is considered satisfactory if:

$$\left|\frac{R_{S-calculated} - R_{S-\exp erimental}}{R_{S-\exp erimental}}\right| * 100 < 0.5\% \tag{5}$$

4.1 Resistivity of Interfaces Interphases in Nickel/copper bilayers Films:

Bilayers resistivity deduced from spread resistances R_S measured to the external surface of Ni/Cu bilayers, Fig.-3 and those calculated according to the model of Schumann and Gardner (eq-4) are given in the Table-1. The average resistivity of interface interphases determined by this method for the three bilayers studied is: $\rho_I = (0.34 \pm 0.2)$ mΩ.cm^2. This average value is obtained by fixing the geometrical parameters equal to: a = 15 µm and S = 2.54 mm, and by adjusting in the equations (3a-3d) the parameters d, h_1, ρ_1 and ρ_2, characterizing the bilayers with less than 5% close to the experimental values obtained on copper and nickel films: $d = w_{Cu}$, $h_1 = w_{Ni}$, $\rho_1 = \rho_{Ni}$ and $\rho_2 = \rho_{Cu}$. By this method the calculated spread resistance R_S agrees with the experimental value within less than 0.5%.

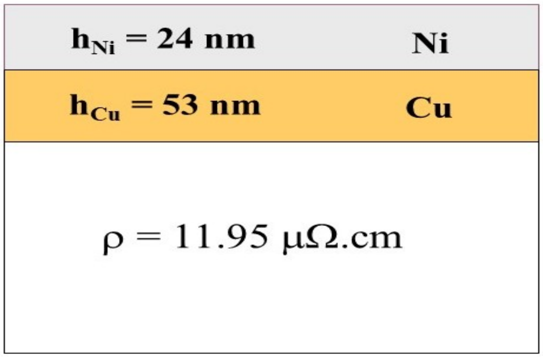

Fig.3a: Interface resistivity in bilayer-1ρI = 0.11*10-3 Ω.cm^2.

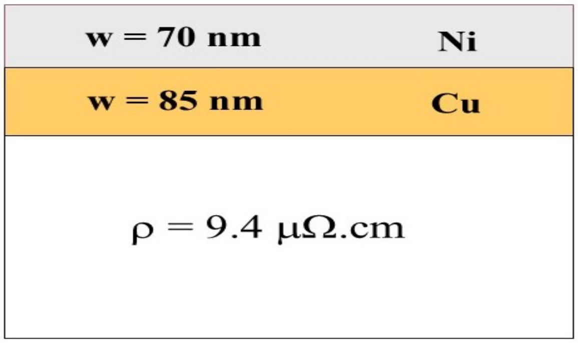

Fig.3b: Interface resistivity in bilayer-2 ρI = 0.55*10^{-3} Ω.cm^2.

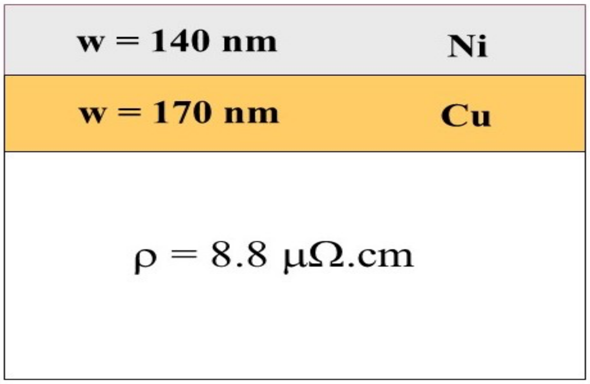

Fig.3c: Interface resistivity in bilayer-3 ρI = 0.18*10^{-3} Ω.cm^2.

Fig.3: Thicknesses and resistivity of Ni, Cu films and interface resistivity in Ni/Cu bilayers.

4.2 Resistivity of Interfaces Interphases in Nickel/Palladium bilayers:

Spread resistances «R_S» measured to the external surface of Ni/Pd bilayer, are given in Fig.-4 and-Table 2. The average of interfaces interphases resistivity determined by this method for the tow bilayers studied is: $\rho_I = (2.3 \pm 0.4)$ mΩ.cm^2. We find that the interface resistivity determined in Ni/Pd bilayers is approximately 10 times larger than the interface resistivity determined in Ni/Cu bilayers.

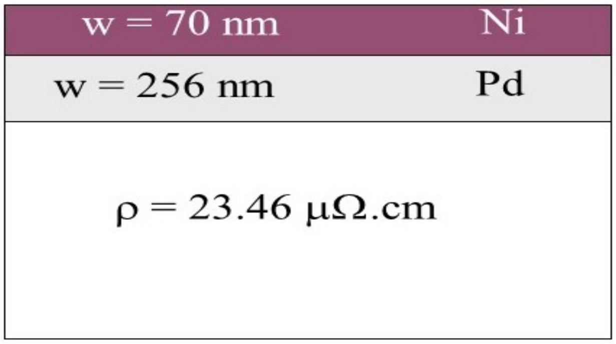

Fig.4a : Interface resistivity in bilayer-4 ρI = 2*10^{-3} Ω.cm^2.

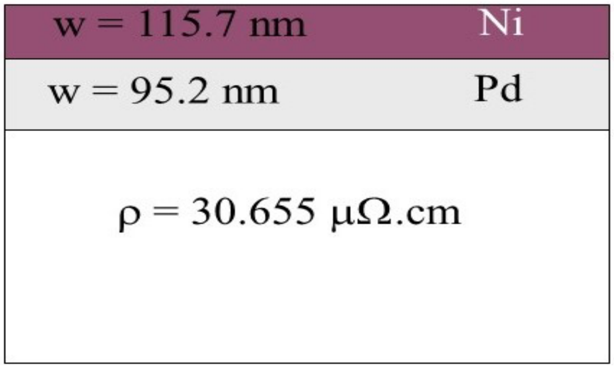

Fig.4b : Interface resistivity in bilayer-5 ρI = 1.98×10^{-3} $\Omega.cm^2$.

Fig.4: Thicknesses and resistivity of Ni, Pd films and interface resistivity Ni/Pd bilayers.

5 Comparison of the mode of electric transport in a Ni/Cu bilayers and a Ni/Pd bilayers

We have shown in a previous study [5] that bilayers Ni/Cu films in a constant electric field can be modeled by an electrical circuit equivalent of two parallel drivers. Electric transport in the bilayer Ni/Cu films is equivalent to that of two electrical resistances (R_{Ni}, R_{Cu}) laid out in parallel. Indeed, we have experimentally verified the following relation:

$$\frac{1}{\rho_{bilayer/Parallel}} = \frac{h_{Ni}}{h_{Ni}+h_{Cu}}\frac{1}{\rho_{Ni}} + \frac{h_{Cu}}{h_{Ni}+h_{Cu}}\frac{1}{\rho_{Cu}} \tag{6}$$

where h_{Ni} and h_{Cu} are the thicknesses of the nickel and copper layers, ρ_{Ni} and ρ_{Cu} the resistivities of the nickel and copper layers. We have shown that the resistivities of the bilayers, calculated from the surface resistances measured on the three bilayers, are equal to a few percent, to those calculated from relation (6) (Table-1). Whereas if we would model the electrical transport in the bilayers considered by two layers in series the difference between the measured resistivity and that calculated by the relation (7) is about 28-115%:

$$\rho_{bilayer/series} = \frac{h_{Ni}}{h_{Ni}+h_{Cu}}\rho_{Ni} + \frac{h_{Cu}}{h_{Ni}+h_{Cu}}\rho_{Cu} \tag{7}$$

Table 1: Experimental and calculated results for Ni/Cu bilayers.

Ni/Cu bilayers	Films thiknesses (nm)	Experimental resistivity (μΩ.cm)	Resistivity Calculated layers in parallel circuits (μΩ.cm)	Resistivity Calculated layers in series circuits (μΩ.cm)	Interface resistivity ($m\Omega.cm^2$)
Film-11 Ni	24	61.9	**11.99** (3.44%)	**25.03** (115.8%)	0.11
Film-12 Cu	53	8.8			
Bilayer-1	24/53	**11.95**			
Film-21 Ni	70	23.4	**8.4** (7.5%)	**13.58** (49.55%)	0.55
Film-22 Cu	85	5.5			
Bilayer-2	70/85	**9.4**			
Film-31 Ni	140	18.8	**8.2** (9.2%)	**11.56** (27.9%)	0.18
Film-32 Cu	170	5.6			
Bilayer-3	140/170	**8.8**			

This behavior is no longer valid in the case of a Ni/Pd bilayer. Indeed, the equivalent circuit which describes the mode of electric transport is that of a hybrid circuit made up of a circuit where the resistances of the nickel films R_{Ni} and that of the palladium film R_{Pd} are in parallel associated with a circuit where the resistances of the films are in series. Indeed, the resistivity of the Ni/Pd bilayers modeled by an electrical circuit of two layers in parallel gives the same result as if we considered the two layers in series; in other words, the resistivity of the bilayers calculated by equations (6) and (7) and measured give the same result to within a few percent, (Table-2). This behavior is explained by the existence of a chemical reaction at the interface between the atoms of the nickel layer and the atoms of the palladium layer, as shown by the images of the external surface of the Ni/Pd bilayers obtained in SEM, (Fig-4).

Table 2: Experimental and calculated results for Ni/Pd bilayers.

Ni/Pd bilayers	Films thiknesses (nm)	Experimental resistivity (μΩ.cm)	Resistivity Calculated layers in parallel circuits (μΩ.cm)	Resistivity Calculated layers in series circuits (μΩ.cm)	Interface resistivity (mΩ.cm^2)
Film-41 Ni	70	23.3	**21.86** (2%)	**21.88** (1.9%)	2
Film-42 Pd	256	21.5			
Bilayer-4	70/256	**23.46**			
Film-51 Ni	115	20.96	**23.28** (0.21%)	**23.65** (2.8%)	1.98
Film-52 Pd	95.2	26.9			
Bilayer-5	115/95.2	**30.655**			

6 Evolution of the SEM Morphology of the External Surface of Ni/Cu and Ni/Pd Bilayers:

Unlike the appearance of the external surface observed by SEM of the Ni/Cu bilayers which remains unchanged over Time, the appearance of the external surface of the Ni/Pd bilayers changes over time, Fig-5: one observes after about four weeks a distribution of dark areas distributed homogeneously over the entire external surface then at the level of these areas there is germination and growth of micro-crystals of $Ni_xPd_{(1-x)}$ after about 12 months.

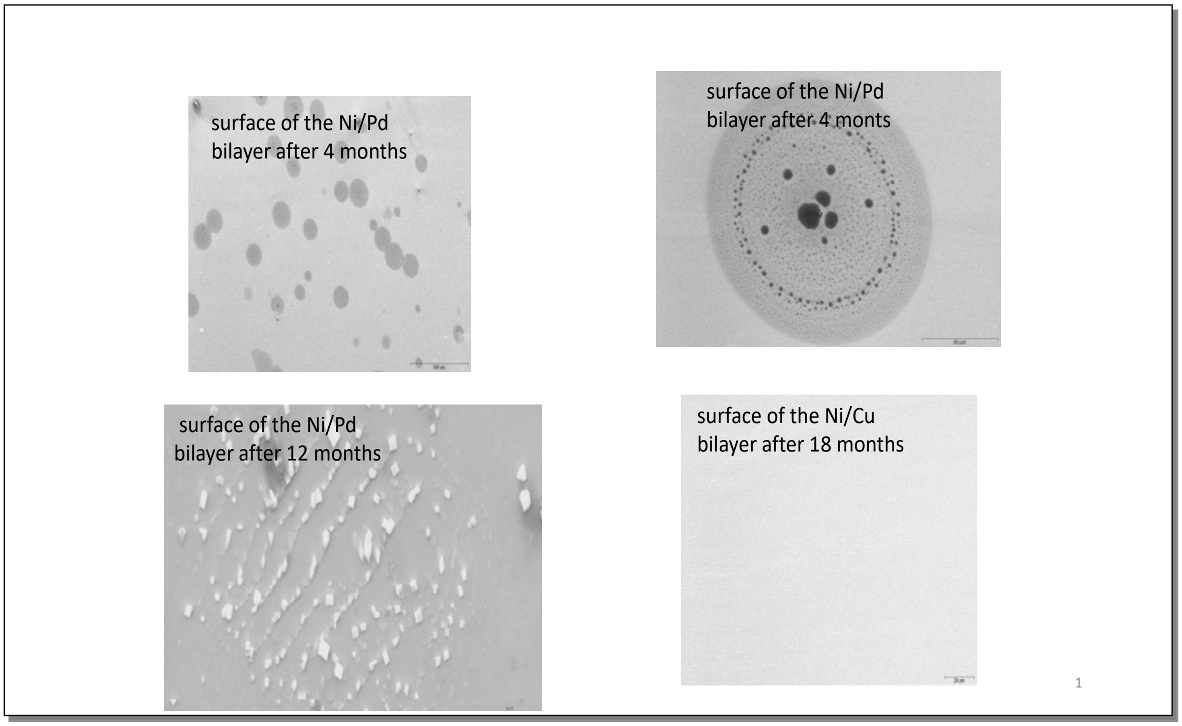

Fig.5: Evolution of the SEM morphology of the external surface of Ni/Pd and Ni/Cu bilayers over time.

7 Conclusions

During this study we determined the interfaces resistivity in Ni/Cu and Ni/P bilayers by applying the Schumann and Gardner model, modified by C. W. Wang. We have found that the interface resistivity in Ni/Pd bilayers is about ten times larger than that determined in Ni/Cu bilayers. When there are no chemical reactions at the interface, between the two superimposed films, which is the case of Ni/Cu bilayers, the electrical transport in the bilayers is equivalent to that of two parallel circuits represented by the two layers of nickel and copper. When chemical reactions occur at the interface, which is the case of Ni/Pd bilayers, the electrical transport in the bilayers can be represented by a hybrid circuit made up of a parallel circuit, associated to a series circuit.

Acknowledgment: The author profoundly grateful to the staff who contributed to the various stages of this work.

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