

R. V. GHITA*, M. NEDELCU, M. F. LAZARESCU

National Institute for Materials Physics, P.O.Box MG 7, Magurele, Bucharest, Romania

Chemical Deposited Pd on GaAs

The chemical deposition of palladium on *n* and *p*-GaAs from an aqueous solution of PdCl₂, in strong acid medium can be an alternative technique for contacts on GaAs. This paper presents the variations of palladium films thickness (measured by an interferometric method) as a function of solution concentration, reaction time and substrate conductivity. There are presented data concerning the adhesion of palladium films (measured by a mechanical method) related to the film thickness. From a comparative study concerning the adhesion of evaporated films such as: Au/*n*-GaAs, Ag/*n*-GaAs, Au-Ge/*n*-GaAs and Pd/*n*-GaAs, it results the conclusion that the adhesion of palladium films are of the same order of magnitude as the metallic films evaporated without an annealing procedure.

Keywords: palladium, GaAs, chemical deposition, adhesion measurement

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1. Introduction

Palladium chemical deposition on GaAs is an alternative technique for contact deposition, besides vacuum deposition or rf-sputtering. Ohmic behaviour of both *n* and *p*-type GaAs provide indications of an intriguing electrical aspect related to Schottky barriers. (OELHAFEN et al. 1983). Palladium on GaAs is stated to be a class of a reactive interface (OELHAFEN et al. 1983), obtained initially by Pd sublimation upon cleaned GaAs substrate, a interface in which the unoccupied intrinsic surface semiconductor states are apparently unaffected by metallization.

This paper studies the general aspects of the kinetics of palladium chemical deposition reaction on *n* and *p*-type GaAs, coupled with the adhesion properties of deposited films. The adhesion of Pd film without annealing is compared with usual ohmic contacts on GaAs such as Au, Ag or Au-Ge obtained by vacuum deposition.

2. Experimental Results and Discussion

2.1 Palladium film deposition

Palladium film was deposited on (100) GaAs substrate of *n* and *p*-type doped $\sim 10^{18} \text{cm}^{-3}$ (*n*-type:Te, *p*-type:Si), from an aqueous solution of PdCl₂ at different concentrations and reaction times. The GaAs substrates had a medium thickness of 360 μm , a diameter of $\Phi=2.54 \text{ cm}$ and a deposition area of 1 cm^2 . Before deposition the wafers were cleaned in

*corresponding author: ghitar@alpha1.infim.ro

organic solvents but were not chemically etched. The adherence of palladium film is strongly dependent on the cleaning procedure which should therefore be made as stringent as possible. The starting solution was : PdCl₂: H₂O (1.2 g/l) in HCl (37 %) :(40 ml) and for the other concentrations a dilution method was used. In literature (FLORES 1983) the formation of a Pd-GaAs compound is activated by maintaining the bath at 50 °C. The metallic deposition on GaAs wafer is uniform and this means that the semiconductor surface has a high density of nucleation sites. An appreciable etching of GaAs in the activator solution was present on the surface and from transmission electron microscopy (TEM) literature data (D'ASARO et al. 1980) was observed that there, exist Pd grains that are randomly oriented . The mechanism of chemical reactions leading to the nucleation and growth of metallic palladium, starts with the activator solution that contains in excess HCl which serves to dissolve PdCl₂ by complexing it to form PdCl₄²⁻. The deposition of metallic palladium from this species occurs according to the reaction (D'ASARO et al. 1980):



The required electrons must be supplied by the substrate, and in the case of GaAs the following reactions may proceed from right to left (D'ASARO et al. 1980):



The values of E⁰ indicate that both Ga and As may be oxidised by PdCl₄²⁻. Palladium will deposit at the cathodic sites, while substrate oxidation (dissolution) will take place at the anodic sites. The deposition of palladium will involve nucleation and growth as in a conventional electrodeposition processes. The uniform distribution of very small Pd grains observed on GaAs indicates that nucleation is highly promoted on this substrate.

The chemical deposited palladium films have not been exposed to an annealing procedure and the thickness of palladium films has been established using an interferometric method, with a Linnik type microscope at λ= 540 nm. The measurement was performed in a rectangular geometry defined by a photoresist mask for dividing the unprotected areas. The results have been compared as order of magnitude with the ones obtained using a α-step profiler. The thickness of Pd films as a function of reaction time in the interval (20-100) sec. at the concentration c=1.2 g/l and temperature T=313 K has a linear dependence related to the exposed mechanism. For long reaction times the chemical deposition act is accompanied by the removing of the film due to the lack of adherence.

The palladium film thickness dependence of PdCl₂ solution concentration are presented in Fig.1 and Fig.2 in the following deposition conditions : reaction temperature: T₁ = 313 K and T₂ = 323 K; reaction time: t= 60 sec, substrate type: *n*-GaAs and *p*-GaAs (with corresponding errors for thickness measurement).The general trend is proportional behaviour, that presents a noticeable difference for the electric character of the substrate. From this point of view, in Fig.1 and Fig.2 a more rapidly deposition rate reaction on *n*-GaAs relative to *p*-GaAs is to be remarked.

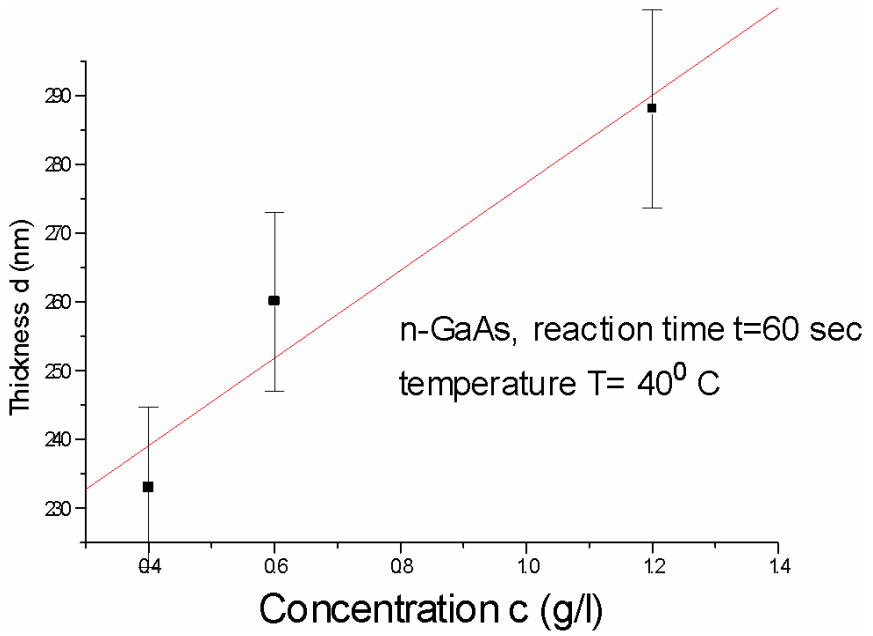


Fig. 1: The thickness of chemical deposited palladium films as a function of solution concentration for *n*-GaAs

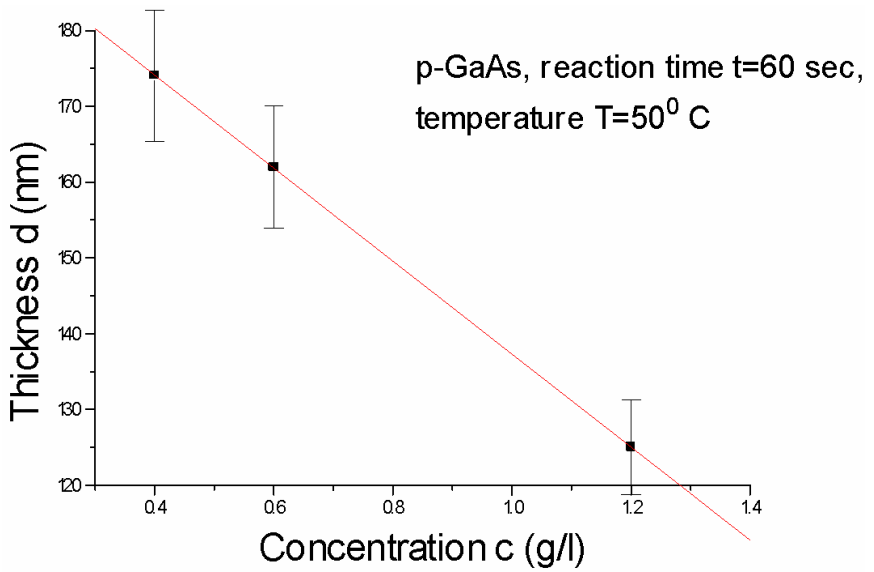


Fig. 2: The thickness of chemical deposited palladium films as a function of solution concentration for *p*-GaAs

A possible explanation for this fact could be that the *n*-GaAs substrate has an excess of free electrons, to neutralise Pd^{2+} ions from the chloride solution, so the deposition has the

condition to increase with concentration. On the *p*-GaAs substrate there exists a lack of free electrons and according to reaction (1) the neutralisation of Pd²⁺ ions is more efficient at low concentration of chloride solution, so the general trend is a decreasing one.

As a general remark is to be said that the dependence of palladium films thickness of solution concentration is much weaker than in the case of gold on GaAs (DONZELLI et al. 1978).

2.2 Palladium thin film adhesion

The adhesion of coating to substrate is one of the critical factors. With inadequate adhesion, the coating may detach prematurely and consequently cause the failure of the coated part. Therefore, it is important to evaluate the adhesion between coating and substrate in a quantitative way. (ZHONGWEI et al. 1998). The critical load measurement in scratch test have been used in assessing adhesion in film/substrate systems (PARK et al 1997).

The study of palladium thin film adhesion on GaAs have been performed using a mechanical method (BENJAMIN et al. 1960) that consists in the action of a vertical force at the interface film/substrate. The critical loads are strongly affected by various parameters such as scratching speed, indenture tip radius, film thickness (PARK et al. 1997) The vertical force applied at the interface should have a maximum value in the local removing of the film for the horizontal motion of the point in which the load is applied. The vertical force is applied on a rounded point of sapphire characterised by a curvature radius *r*. This force produces a plastic deformation in GaAs substrate in a circle contact of radius *a*. The deformation depends on: substrate hardness (*H*), vertical applied load (*W*), circle contact ($a = (W/pH)^{1/2}$). In horizontal motion for rounded point appeared a shearing force *F* which is tangent at deformed surface and depends on the normal pressure *P* (equal to hardness *H*) by relation as is presented in Fig.3 (BENJAMIN et al. 1960) :

$$F = \frac{aP}{(r^2 - a^2)^{1/2}} = \frac{aH}{(r^2 - a^2)^{1/2}} = \frac{(W/pH)^{1/2}H}{(r^2 - (W/pH)^{1/2})^{1/2}} \tag{5}$$

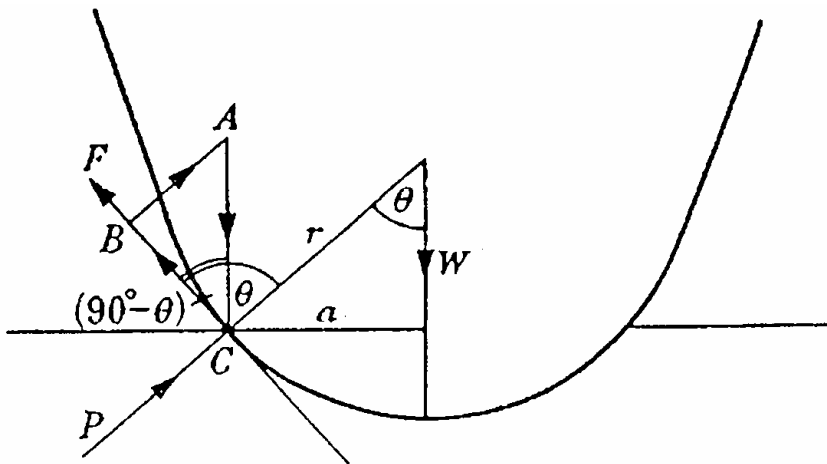


Fig. 3: Forces at lip of indentation produced by rounded point

This expression permits the computation of the shearing force as a function of vertical load. The dependence for vertical load $W(g)$ versus palladium thickness $d(nm)$ curve is presented in Fig.4., and as can be observed there exists a linear decreasing for adhesion as a function of the thickness of deposited Pd film on n -GaAs. This aspect is explained by an internal layer strain and represents a normal behaviour for a thin film without annealing, in the sense that as the film is thinner, its adherence is improved. For palladium thin films the physical explanation of the larger adhesion (expressed in the vertical applied load) is related to a metallic character of the bonds developed between different successively deposited Pd layers.

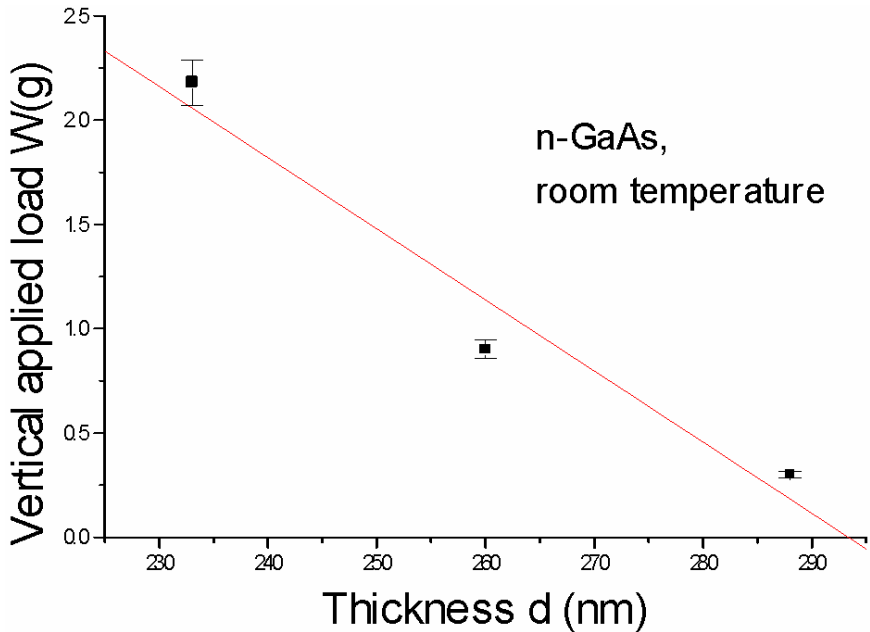


Fig. 4: The dependence for vertical rupture load versus palladium film thickness curve

In order to compare the adhesion of chemical deposited Pd films on GaAs, there are presented results concerning the shearing force for metallization GaAs substrate for vacuum deposited metal films and alloys such as: Au/GaAs, Ag/GaAs, Au-Ge/GaAs. In Table 1 the film type, substrate type, film thickness, computed shearing force and deposition conditions including annealing procedure (usually at 763 K in low vacuum: (0.00136-0.0136) mbar) are listed. As can be observed, the computed shearing force F for chemical deposited Pd/ n -GaAs had the same order of magnitude as evaporated Au/ n -GaAs and Ag/ n -GaAs films without annealing. There exist an important increasing for the computed shearing force F in the case of vacuum deposited Au/ n -GaAs and Au-Ge/ n -GaAs films followed by an annealing procedure, due to the reactivity of metals at annealing temperature. The Fig.4 is related to the chemical deposited palladium on different n -GaAs samples and the corresponded sample used for quantitative measurements of adhesion respectively the shearing force in Pd film had a thickness of 260 nm in the limit of experimental errors of the order 20 nm. In the case of Pd/ p -GaAs the shearing force is the same as for chemical deposited Pd/ n -GaAs in spite of

different reaction conditions as concentration, temperature and reaction time. In this peculiar case the only common point is the shearing force computed from vertical applied force, according to equation (5) where the hardness of the substrate corresponds to GaAs and is $H_B = 750 \pm 40 \text{ Kg/mm}^2$. These experimental observations are important in the perspective of electroless plating (as for gold (D'ASARO et al. 1980)) on III-V compound crystals.

Table 1: Comparative study for the adhesion of thin films deposited on GaAs substrate

Film	Substrate GaAs	Thickness d(nm)	Shearing force F (x 10 ⁷ N/m ²)	Remarks
Pd	n	256±20	0.511±0.01	Chemical
Pd	p	188±20	0.51±0.01	Chemical
Ag	n	300±20	0.25±0.01	Evaporated
Au	n	150±20	0.75±0.01	Evaporated
Au	n	150±20	1.96±0.01	Evaporated/annealed
Au-Ge	n	500±20	2.64±0.01	Evaporated/annealed

3. Conclusions

Palladium chemical deposition can be an alternative technique to obtain contacts on GaAs. The reaction mechanism is a galvanic displacement of Pd²⁺ ions on an unoxidised substrate of GaAs due to the presence of a strong acid solution. The dependence of chemical parameters suggests that the reaction on *n*-GaAs is preferred due to the presence of free electrons on the surface.

The palladium thin film adhesion measurement performed with a mechanical method, established that as the chemical deposited films are thinner, they have a large bonding to the substrate. This fact expresses a general tendency for deposited thin films. The comparative adhesion study between palladium chemical deposited films without annealing and the common contacts on GaAs substrate as Au/*n*-GaAs or Ag/*n*-GaAs vacuum deposited films revealed a similar behaviour.

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