

Classification

Physics Abstracts

79.20F — 68.55 — 81.15C

Study of epitaxial films of Ag, Pd and AgPd deposited by dc sputtering

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(Received June 18, 1990; accepted September 05, 1990)

Résumé. — Nous décrivons les conditions de préparation de films minces épitaxiaux d'argent, de palladium et d'alliages argent-palladium déposés sur des faces (100) de MgO par pulvérisation cathodique. L'orientation parallèle $(100)_d/(100)_s$ (d pour dépôt et s pour substrat) est observée pour les deux derniers systèmes. Les films sont caractérisés par THEED, RHEED, SAD, TEM et AES. La composition massive des alliages est déterminée par ICP. La pureté superficielle des films condensés est étudiée et discutée.

Abstract. — The experimental conditions to condense epitaxial films of silver, palladium and silver-palladium alloys onto (100) air-cleaved MgO faces by glow discharge sputtering are related. The orientation $(100)_d/(100)_s$ (where d indicates deposit and s substrate) is observed for the two last systems. The films are characterized by THEED, RHEED, SAD, TEM and AES. The bulk composition of the alloys is determined by ICP. The surface purity of the condensed films is examined and discussed.

1. Introduction.

Silver-palladium coatings have many industrial applications such as electrical contacts, dental alloys, catalysis,... As the properties of thin films depend strongly on their structure, composition and purity, we propose to condense silver-palladium alloy films onto single-crystal substrates by glow discharge sputtering.

In a previous paper [1] we have shown that epitaxial films of Ag, Pd and AgPd alloys deposited onto NaCl were chloride contaminated. In order to overcome this, we tried to prepare single crystal films of Ag, Pd and AgPd on MgO single crystals. The deposition of such films by thermal evaporation was the subject of several investigations [2, 4]. Asskali [5] obtained good epitaxial (100) palladium films onto MgO by glow discharge sputtering. We showed [1] that by simultaneous sputtering of both elements, it was possible to obtain monophase alloys at various concentrations. In the present work, we examined the purity of epitaxial alloy films deposited onto MgO (100).

2. Experimental technique.

The substrates were air cleaved (100) faces of MgO single crystals (purity 99.9%). After chemical polishing in a HCl (4M)–CH₃OH solution and annealing two hours at 973 K in vacuum [6] they showed reflexion high energy electron diffraction (RHEED) patterns characteristic of (100) single crystal faces (Fig. 1). Auger electron spectroscopy was used for purity testing of the films. Auger measurements were performed on a V.G. LEED-Auger spectrometer with a retarding field analyser using a 2.5 keV electron gun incident at 77° with respect to the sample normal. This grazing incidence is known to increase the surface sensitivity of Auger electron spectroscopy.

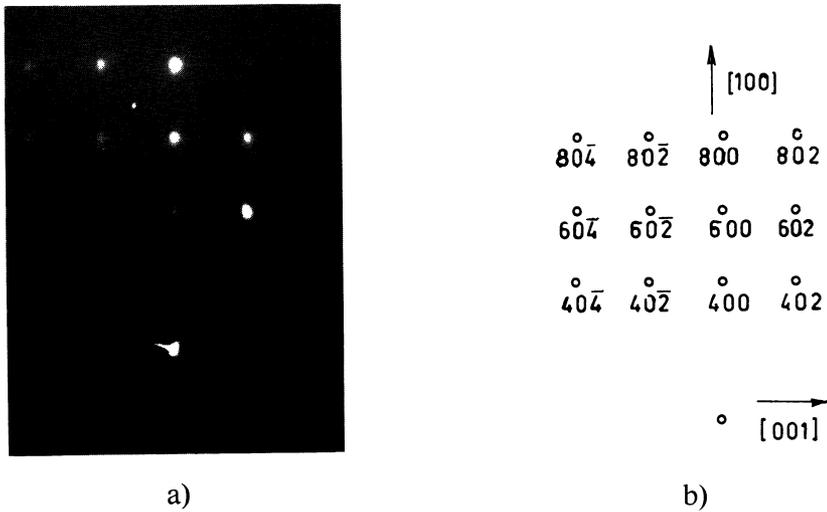


Fig. 1. — a) RHEED pattern of a MgO (100) face after chemical polishing and annealing.
b) Pattern interpretation: orientation (100) azimuth $\langle 010 \rangle$.

After chemical (HCl (6M) CH₃OH) stripping from the MgO substrate, the films were studied by transmission electron microscopy (TEM), selected area diffraction (SAD) and transmission high energy electron diffraction (THEED). The films compositions were determined using inductively coupled plasma atomic emission spectroscopy (ICP).

2.1 GLOW DISCHARGE SPUTTERING. — Films were deposited in a d.c. glow discharge in pure argon (99.995%) between two planar electrodes. The residual pressure before argon admission was never greater than 6×10^{-5} Pa. The cathode was either a disc of pure silver (99.99%), a high pressure compacted disc of palladium powder (99.9%) or a disc of pure silver partially covered with palladium. A drawing of the experimental system was presented in part I [1]. The MgO substrate was 40 mm away from the cathode and was in close contact with a copper block heated by an inserted Xenophot 100 W, 12 V lamp. The substrate temperature was measured by a Ni/NiCr thermocouple located in the heated copper block. We do not obtain the real surface temperature by this method but it gives a good reproducibility. The pumping system consisted of a turbomolecular pump in order to minimize carbon contamination.

2.2 INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY (ICP). — The alloy films were dissolved in HNO_3 65 % p.a. (Merck) then diluted to obtain 5 ml of a 5 % acid solution. Two standard solutions containing 10 ppm of Ag and Pd were prepared by dissolution of AgNO_3 and $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in a 5 % HNO_3 solution. The measurements were performed on an ICP spectrometer IL-100 from Instrumentation Laboratory.

3. Experimental results.

The epitaxial conditions for various systems are summarized in table I and electron diffraction patterns are shown in figures 2-5. Although the lattice misfit is small between Ag and MgO (see Tab. II), no good epitaxy was observed for this system. This result agrees partly with the literature : Green *et al.* [7] could not obtain epitaxial silver films onto air-cleaved MgO faces by thermal evaporation and Kahn *et al.* [8] condensed polycrystalline silver films on MgO by sputtering. However, a beginning of orientation is observed (Fig. 2). As it is possible to prepare epitaxial silver films onto vacuum-cleaved MgO [7], the surface state of the substrate probably plays a critical role in the epitaxy of silver.

Table I. — Epitaxial conditions by glow discharge sputtering.

Cathode composition	$T(\text{K})$	$V(\text{kV})$	$p(\text{Pa})$	$I(\text{mA})$	$t(\text{nm})$	annealing	remarks
Ag	748	3.0	6.7	6	62	—	a
$\text{Ag}_{70}\text{Pd}_{30}$	888	4.0	4.0	6	80	—	
$\text{Ag}_{50}\text{Pd}_{50}$	913	3.0	10.6	6	75	2h at 863 K	c
$\text{Ag}_{30}\text{Pd}_{70}$	973	3.0	10.1	5 – 6	64	1h at 893 K	d
$\text{Ag}_{13}\text{Pd}_{87}$	1023	3.0	10.0	5 – 6	76	1h at 893 K	
Pd	1053	2 – 2.6	8.0	6	72	—	b

T = temperature I = current density
 V = voltage t = thickness
 p = pressure

Remarks :

- a) no epitaxy of silver is observed. However a beginning of orientation is shown in figure 2
- b) perfect parallel epitaxy of palladium was obtained. The Kikuchi lines in figure 3 show the perfection of the crystal lattice
- c) a diffraction pattern is presented figure 4
- d) a diffraction pattern is presented figure 5

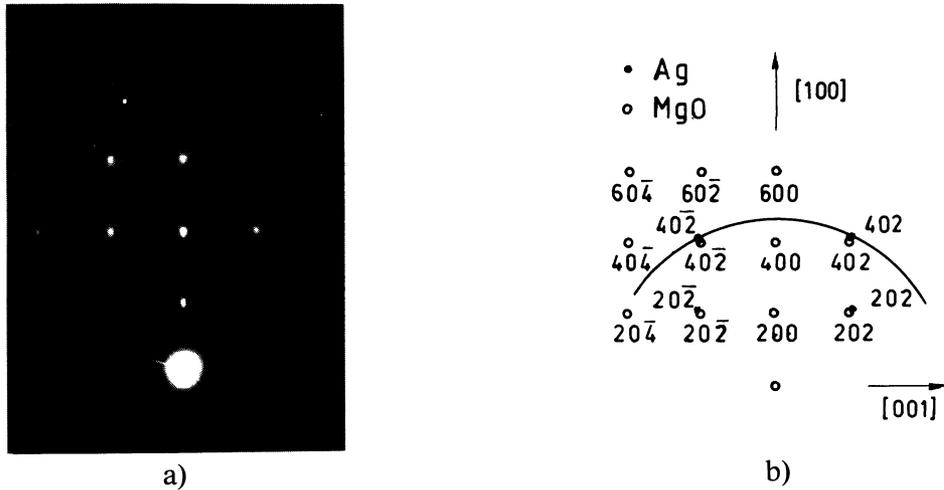


Fig. 2. — a) RHEED pattern of a Ag film deposited on MgO under the conditions listed in table I. b) Pattern interpretation.

Table II.

system	lattice misfit for	
	$(100)_d < 011 >_d // (100)_s < 011 >_s$	$(100)_d < 011 >_d // (100)_s < 001 >_s$
Ag/NaCl	-27.5 %	-48.8 %
Pd/NaCl	-31.0 %	-51.2 %
Ag/MgO	-3.0 %	-31.4 %
Pd/MgO	-7.7 %	-34.7 %
Ag/Pd	-5.0 %	-25.7 %

We obtained a perfect parallel orientation of Pd (Fig. 3) and AgPd alloys (Figs. 4, 5) on MgO (100). The epitaxial temperature is higher on MgO than on NaCl (see Tab. III). Tables I and III suggest also that the epitaxial temperature of the alloys increases with the Pd concentration.

We studied the spectral lines of silver at 328.068 nm and palladium at 340.458 nm by ICP-atomic emission spectrometry. The spectrometer was calibrated with the first standard solution and a blank solution containing 5% HNO₃. The reliability of the method was checked with the two standard solutions. The deviation was never larger than 2%. Table IV shows the relation between the target composition and the film composition. The silver concentration is always higher in the film than on the target. This is probably due to the relative sputtering yield of silver and palladium. Seah [9] gives a ratio Y_{Ag}/Y_{Pd} of 1.4 and Mathieu and Landolt [10] a ratio of 1.89.

AES was used to estimate the purity of our films. We showed [1] that films deposited onto heated rocksalt (100) faces were heavily chloride contaminated even in the bulk. Figure 6 shows an AES spectrum of a silver-palladium alloy film deposited onto MgO (100) at 973 K.

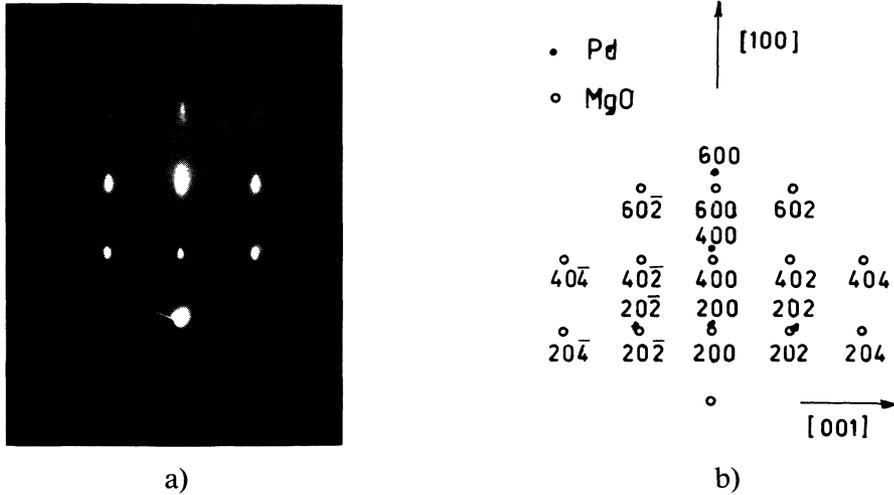


Fig. 3. — a) RHEED pattern of a Pd film deposited on MgO under the conditions listed in table I.
 b) Pattern interpretation: orientation : $(100) \langle 011 \rangle // (100) \langle 011 \rangle$

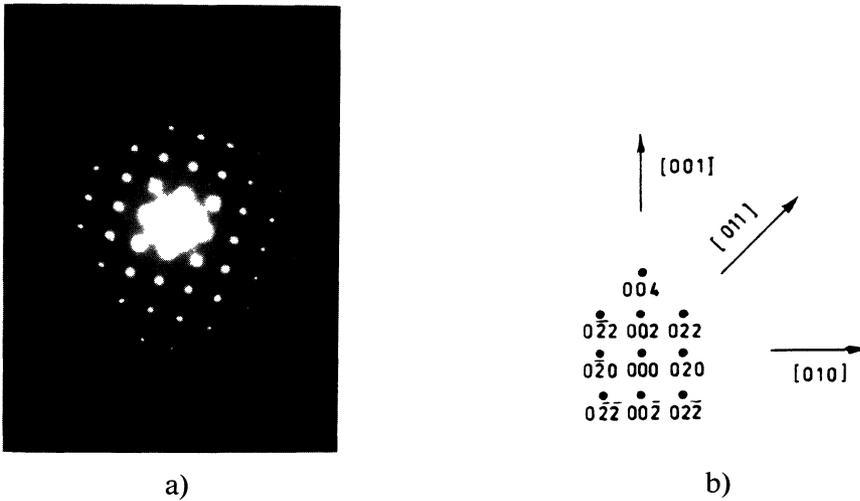


Fig. 4. — a) SAD pattern of a AgPd film deposited on MgO under the conditions listed in table I.
 b) Pattern interpretation.

The surface of the sample has been cleaned by ion bombardment (Ar^+ , energy = 4 keV, pressure = 1.33×10^{-4} Pa) and annealed (> 773 K). Therefore, no significant contamination of the restored sample is observed by Auger electron spectroscopy. It must be stressed that the carbon 272 eV peak is overlapped by the Pd 279 eV peak, so it is difficult to assert that no carbon is present. We obtain a ratio Pd (279 eV)/Pd(330 eV) = 0.16. This value is given by Vankar and Vook [11] for a palladium surface free of carbon. Even when the sample was heated for 5 hours at 843 K, the ratio didn't increase. The C 272 eV peak may also overlap with the Ag 261-266 eV. In order to

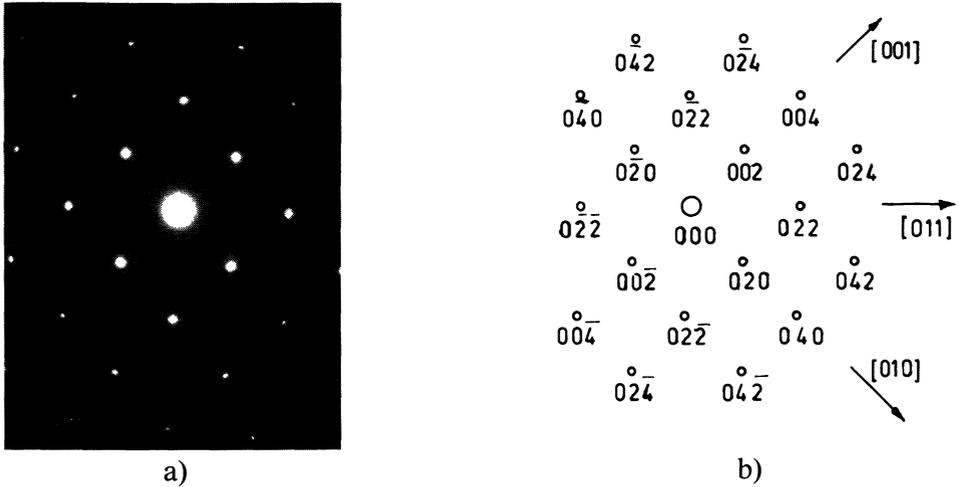


Fig. 5. — a) THEED pattern of a AgPd film deposited on MgO under the conditions listed in table I.
b) Pattern interpretation.

Table III. — A comparison between epitaxial temperatures (K) on NaCl (100) and MgO (100).

Target composition	Ag	Pd	Ag ₇₀ Pd ₃₀	Ag ₅₀ Pd ₅₀
NaCl [1]	383	898	783	863
MgO	(748)	1053	888	913

Table IV. — Comparison between the target composition and the film composition.

target composition		film composition	
% Pd	Ag	% Pd	% Ag
87	13	72	28
70	30	52	48
50	50	40	60
30	70	14	86

establish the absence of carbon, most investigators rely on the ratio $R = (C_{272} + Ag_{261-266}) / Ag_{303 \text{ eV}}$ [12]. R values for clean silver are in the range of 0.42-0.55 depending on the modulation voltage. We found a ratio of 0.5. No oxygen was detected after ion cleaning and sample

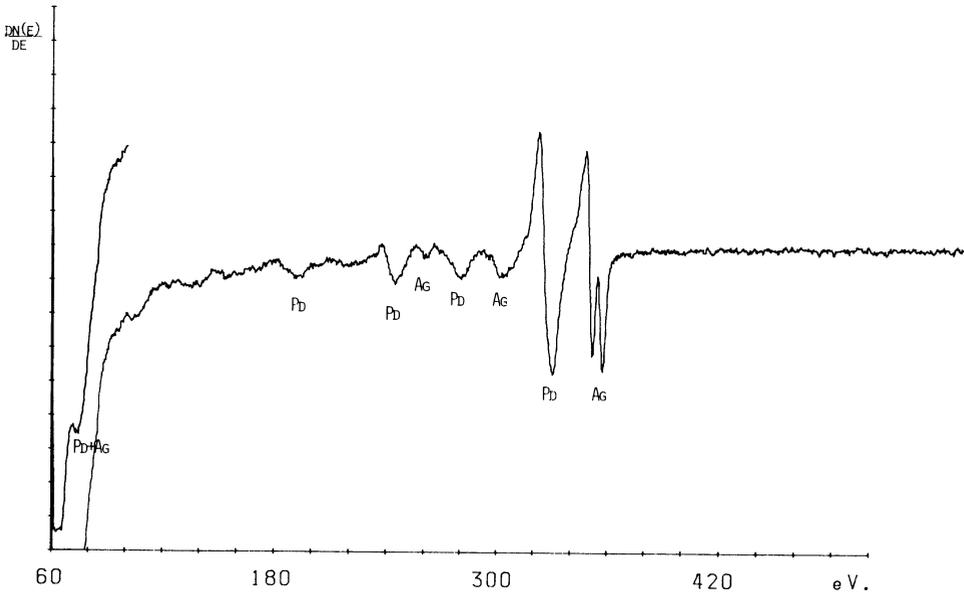


Fig. 6. — AES spectrum of an AgPd alloy deposited onto MgO after ion cleaning; modulation voltage = 2.75 V, $E_p = 2.5$ keV.

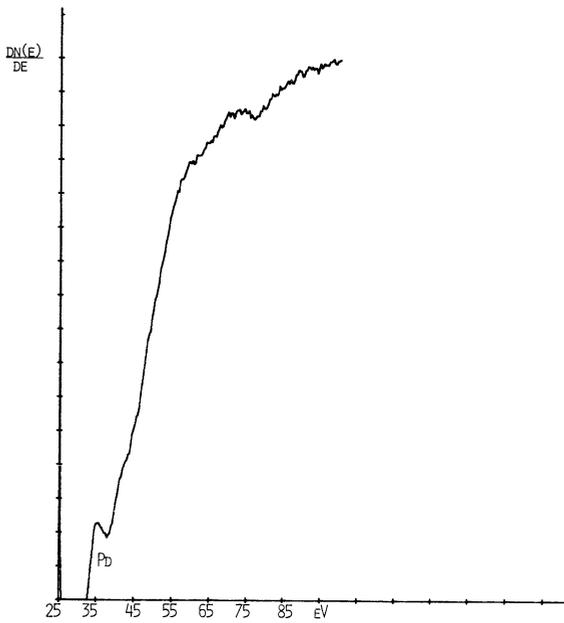


Fig. 7. — AES spectrum of an AgPd alloy deposited onto MgO after ion cleaning; modulation voltage = 1.75 V, $E_p = 2.5$ keV.

heating. This justifies the choice of magnesium oxide as a high stability substrate. No sulfur is present on the sample after bombardment but a small sulfur segregation is observed when heating. The sulfur contamination remains however weak (< than 6% on the surface).

The surface cleanliness of a sample can also be qualitatively studied by observing the low energy region of the Auger spectrum. As it is known that low energy Auger peaks are typical of the very first atomic layers, the presence of the Pd peak at 39 eV in figure 7 proves the cleanliness of the surface. Indeed, according to the Pons *et al.* model [13] and using the Seah and Dench formula for the attenuation length [14], more than 80 % of the signal of the Pd $N_{2,3}N_{4,5}N_{4,5}$ transition comes from the two first atomic layers. The energy shift relative to the literature (44 eV) is probably due to charging effects of the substrate. A palladium foil half-covered with silver was used to determine a relative Auger yield (S). With a primary beam energy of 2.5 keV and a modulation voltage of 2.7 V, $S_{Ag} (351-356 \text{ eV})/S_{Pd} (330 \text{ eV}) = 1.14$. This value corresponds to the value given by Mathieu [15]. After several ion-sputtering and heating cycles, the silver and palladium atomic concentrations remain constant for all the films studied. This demonstrates the good bulk homogeneity of our films.

4. Conclusions.

Preparation of epitaxial films of palladium and silver-palladium alloys on MgO (100) faces proved to be easy by glow discharge sputtering. The epitaxial temperature is higher for films deposited on MgO than for films deposited onto NaCl and increases with the palladium concentration. Excellent parallel orientations were obtained. The purity of films deposited on MgO is very good, no significant surface contamination is observed by AES. The bulk composition of the alloy films can easily be determined by ICP.

Acknowledgements.

The authors are most grateful to the Fonds National de la Recherche Scientifique for financial support. Thanks are also due to OTAN for grant 48.81. We wish to thank M. Hoenig from the laboratory of the Belgian Ministry of Agriculture for ICP measurements. F. Reniers is grateful to the Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture for a specialisation grant.

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Cet article a été imprimé avec le Macro Package "Editions de Physique Avril 1990".