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Sputtering deposition, XPS and X-ray diffraction characterization of hard nitrogen–platinum thin films

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Nitrogen–platinum thin films have been prepared by reactive sputtering. The surface and the bulk of these films for which nitrogen incorporation promotes adherence and hardness, have been investigated by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), nuclear analysis and electrical measurements. The XPS data (core lines and conduction band) support the existence of a PtN_x compound (x of the order of 0.1) characterized by a very limited metal to non-metal charge transfer. Concerning the XRD results, peak shifts, broadening and asymmetries have been observed and are related to the hardness improvement.

1. Introduction

It is well known that the presence of a large number of dislocations and other types of imperfections (grain boundaries, impurities, etc.) improves the hardness of metals [1, 2]. Moreover in an A–B supersaturated solid solution, the dissolved B atoms may precipitate and form a compound AB in the matrix. These precipitates can interact with dislocations and hence increase the hardness of materials [3, 4].

However, the quality of a film depends not only on intrinsic properties of the film but also on the film adherence to the substrate. Nitrogen has recently been used to improve adherence of sputtered metal–ceramic couples [5] and of sputtered titanium carbide on steel [6].

In the course of a larger investigation into the incorporation of non-metals into platinum, we have found an improvement of both the adherence and the hardness of platinum films sputtered in nitrogen on glass and on polished stainless steel substrates. The objective of this paper is to present the results of both surface and bulk characterization (mainly by X-ray photoelectron spectroscopy (XPS), X-ray diffraction and electrical measurements) of those films for which nitrogen incorporation promotes adherence and hardness.

2. Experimental conditions

Nitrogen–platinum thin films have been sputtered in a d.c. discharge. The apparatus has been described elsewhere [7]. Argon–nitrogen mixtures and ammonia have been used as reactants to coat either glass or polished stainless steel substrates. Discharge voltages varying from 3500 to 900 V (with a current density varying, respectively, from 2 to 0.1 mA cm^{-2}) were used at an average pressure of 6.6 Pa. For the purpose of this study an average thickness of metal of 100 nm was deposited onto the substrates which were maintained at 50° C in order to avoid thermal decomposition.

Detection of the incident ions on the substrate was achieved by glow discharge mass spectrometry (GDMS) [8]. In GDMS, the neutral species are ionized in the plasma and then detected in a quadrupole filter without using the ionization chamber of the spectrometer. In the nitrogen discharge at 6.6 Pa, the PtN^+ contribution is

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nearly 10% of the Pt^+. The different ionic currents recorded are $N_2^+ = 5 \times 10^{-7}$ A, $N^+ = 1 \times 10^{-8}$ A, $Pt^+ = 9 \times 10^{-9}$ A, $PtN^+ = 1 \times 10^{-9}$ A and $PtN_2^+ = 1 \times 10^{-10}$ A, for an applied target voltage of 1400 V.

3. Experimental results

Most of the sputtered films, which always had the same metallic aspect as pure platinum, exhibited very good adherence to the various substrates. Hardness coefficients around 7 mohs (platinum bulk hardness equals 4.3) were measured for films sputtered at low power.

3.1. Evaluation of nitrogen concentrations in platinum

Nuclear reactions $^{14}N\,(d,\alpha)\,^{12}C$ induced in nitrogen by 1.7 MeV deuterons were used to determine the nitrogen content in the platinum films. The description of this method, which is now routinely used, will not be reported here [9]. The nitrogen concentrations of various selected platinum films are calculated with an AlN crystal as reference. These values are plotted against the electrical power of the discharge in Fig. 1. In this figure, the error bars give the accuracy of the data. If one excepts the statistical errors, the main indeterminations come from the experimental evaluation of the Rutherford cross-section [9] and from the calculated stopping power of deuterons [10, 11] in platinum.

3.2. Thin film electrical measurements

Four-point probe measurements were made to determine the sheet resistance. The film resistivity increased as the sputtering power decreased from $1.5 \times 10^{-5}\,\Omega$ cm to $8 \times 10^{-5}\,\Omega$ cm (for nitrogen discharge) and to $2 \times 10^{-4}\,\Omega$ cm (for ammonia discharge). In the same way, the temperature coefficient of resistance (TCR) decreased from $2 \times 10^{-3}\,°C^{-1}$ to $4 \times 10^{-4}\,°C^{-1}$ (Fig. 2). For reference, the pure platinum thin films were characterized by a resistivity of $1 \times 10^{-5}\,\Omega$ cm and a TCR of $3 \times 10^{-3}\,°C^{-1}$.

Platinum films with an electrical resistivity greater than $5 \times 10^{-5}\,\Omega$ cm were unstable when heated to temperatures greater than 130° C. Fig. 3 shows the change of resistivity as a function of temperature, for an applied heating rate of about $5°\,C\,min^{-1}$. This change may be related to a film decomposition as will be shown by the X-ray diffraction data.

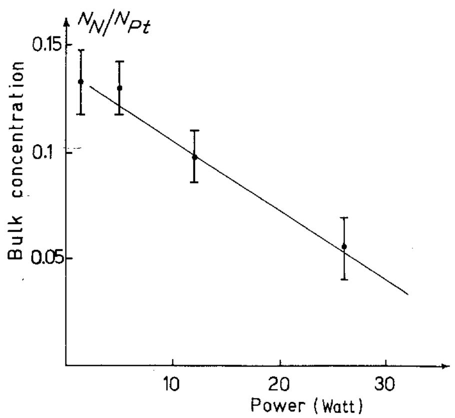

Figure 1 Atomic concentration of nitrogen determined by nuclear reaction in platinum sputtered films as a function of the electrical power of the discharge (Discharge gas: N_2).

3.3. X-ray diffraction

X-ray diffraction patterns of these films exhibited the (1 1 1) line corresponding to the highest atomic density plane parallel to the substrate. However, the (1 1 1) peak appeared at lower angles. The observed shifts depended on the sputtering power and corresponded to a dilatation of the platinum lattice (± 1.6%) normal to the (1 1 1) plane (Fig. 4). Moreover, annealing the films at 300° C for 24 h in air, removed these peak shifts, as indicated by the arrows in Fig. 4. By extrapolation of values measured by Cadeville and Lerner [12] for the Pd–H, Pd–B, Pd–C and Pt–B systems as a function of the Goldsmith radii, we obtained a value of $\sim 5 \times 10^{-3}$ Å $(\text{at}\,\%)^{-1}$ for the parameter increment per interstitial per cent. Using this value, the increase of the lattice parameter observed may be attributed to the incorporation of about 12% nitrogen for the films sputtered at low power. This is in good agreement with the nitrogen concentrations found by nuclear analysis.

Broadening of the (1 1 1) platinum line was observed when the sputtering power decreased. The (1 1 1) line half-width varied from ~ 0.006 radian for the films sputtered in argon to ~ 0.02 radian for the films sputtered in nitrogen at low voltage. In addition, an asymmetry of the peak has also been detected; in short, the smaller the sputtering power, the larger is the displacement of the centre of gravity of the peak from the peak maximum towards the larger angles.

Peak shifts, broadening and asymmetries are normally associated with ultra-small particle sizes,

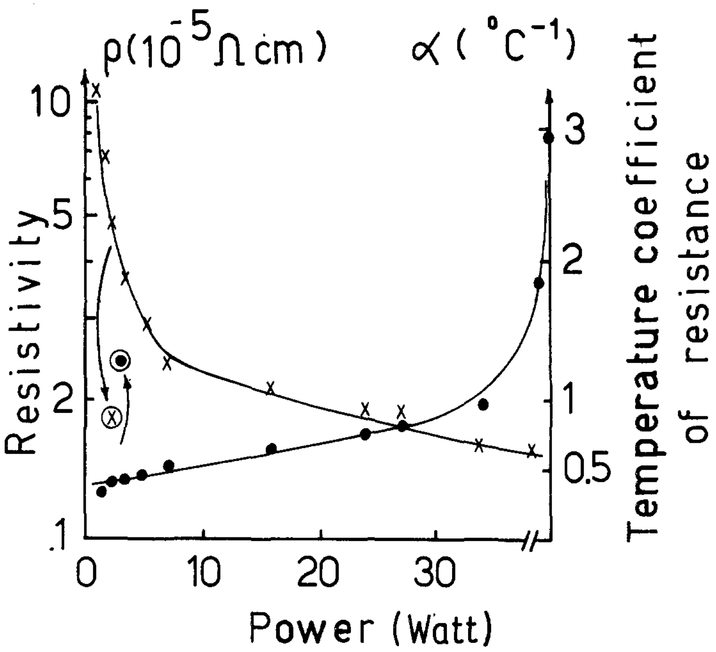

Figure 2 Electrical resistivity and temperature coefficient of resistance as a function of the sputtering power. (Discharge gas: NH_3; X ● before annealing, ⊗ ⊙ after annealing at 300° C during 24 hours in the air).

or strains produced by dislocations, stacking faults or twin faults. These strains will also be related to the hardness improvement of the films. Working on chromium films, Komaiya *et al.* [13] have observed that the hardness is approximately proportional to the square root of the line broadening.

It was observed that, on annealing out the faults at 300° C, the hardness of the films decreased. A detailed study of the X-ray diffraction line profile is in progress.

3.4. XPS results

Although it has not been possible to obtain a depth-profile analysis of the films by using argon ion etching, the XPS results of various platinum films sputtered in N_2 and in NH_3 are presented in this section. The spectra were recorded in part with a VG ESCA 1 electron spectrometer (non-monochromatized AlKα radiation) and in part with a HP 5950 A electron spectrometer (monochomatized AlKα radiation). The main data are given in Table I.

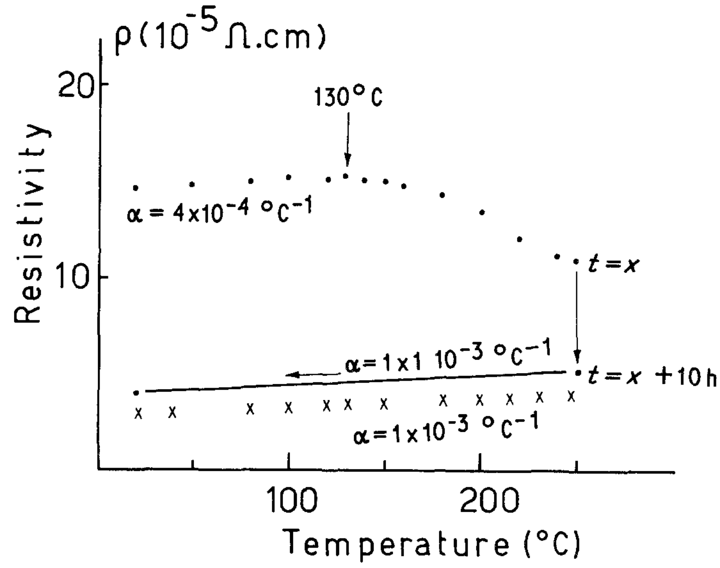

Figure 3 Electrical resistivity plotted against temperature of annealing.

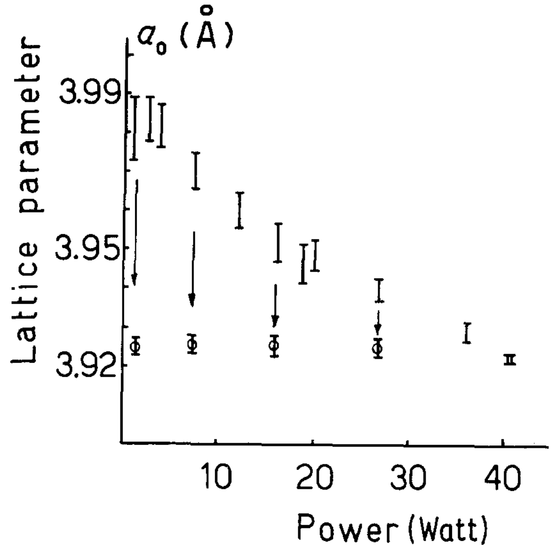

Figure 4 Platinum lattice parameter as a function of the sputtering power. (Discharge gas: NH_3; I sputtered films, Φ films annealing at 300° C during 24 hours, II bulk platinum as reference).

Nitrogen concentrations as measured by XPS are found to depend on discharge conditions (Fig. 5) and correlate fairly well with the electrical resistivity of the films (Table I). Concerning the N (1s) binding energy, a value of 400.3 eV, corresponding to zero charge on nitrogen, has been proposed from an extensive compilation of nitrogen-compound series [15]. On the basis of this reference point, a mean chemical shift of − 1.6 eV was recorded in the case of the samples deposited in N_2, whereas the shift was reduced to − 0.6 eV for the sample sputtered in NH_3 discharge.

In the case of samples deposited in N_2 the binding energy (398.5 to 399 eV) should be compared with the values reported in the literature for some 1st-series transition metal nitrides, e.g. VN and FeN_x (397.2 eV) [16, 17], CrN and TiN (396.8 eV) [16, 6]. On the other hand, the shift of the Pt ($4f_{7/2}$) line should not exceed + 0.2 eV, while the shifts reported for V (2p) and Cr (2p) amount to + 1.5 and + 2.1 eV. These data support the existence of an interstitial-type PtN_x compound (with x of the order of 0.1), characterized by a very limited metal to non-metal charge transfer.

Concerning the sample deposited in NH_3, the N(1s) maximum is shifted to a higher binding energy (399.7 eV), which is in fact very close to that of ammonia condensed on metallic surfaces (399.8 eV) [15, 17]. It is clear that a substantial amount of adsorbed nitrogen species contributes to the N(1s) profile, presumably mostly in the higher binding energy region ($\geqslant$ 399 eV). This surface effect leads to an overestimation of the n_N/n_{Pt} ratio with regard to the actual concentration in the bulk.

Comparing with the Pt–C system [18], it is worth pointing out the decrease in asymmetry of the Pt ($4f_{7/2}$) line when the intensity of the N(1s) peak at lower binding energy increases (Table I). Following the explanation proposed in the case of the Pd–H system [19, 20], this effect may be tentatively related to the change of the nearly free

TABLE I XPS results

Sample	Electrical resistivity (10^{-5} Ω cm)	Pt ($4f_{7/2}$)* (eV)	Asymmetry† of Pt ($4f_{7/2}$)	FWHM‖ of Pt ($4f_{7/2}$) (eV)	ρ (eV)	N (1s)* (eV)	$\frac{n_N}{n_{Pt}}$‡
Evaporated Pt	1.5	71.19	2	1.29	0.86	–	–
Pt + N_2 (I)	2	72.13	1.6	1.15	0.89	398.5	0.08
Pt + N_2 (II)	6	71.36	1.4	1.45	1.21	398.5	0.23
Pt + N_2(III)	9	71.3	§	§	–	399	0.45
Pt + N_2(II) heated in O_2 at 165° C	3.5	71.18	1.85	1.45	1.02	399 400.4	0.18
Pt + NH_3	18	71.2	¶	¶	–	399.7	0.45

*Binding energies referred to the Fermi level of Pt.

†Ratio λ/ρ of the left (λ) to the right (ρ) half-width at half maximum of the peak recorded with monochromatized radiation.

‡Rough estimate of atomic concentrations obtained from Scofield's cross-section values [14].

§Recorded with unmonochromatized radiation; comparable to the values recorded for the preceding sample (Pt + N_2 II) examined in the same condition.

¶Recorded with unmonochromatized radiation; this sample shows a slightly lower asymmetry than evaporated platinum but the same FWHM (1.93 eV) as the sample Pt + N_2 II (these samples being examined in the same condition).

‖FWHM = Full wave half maximum.

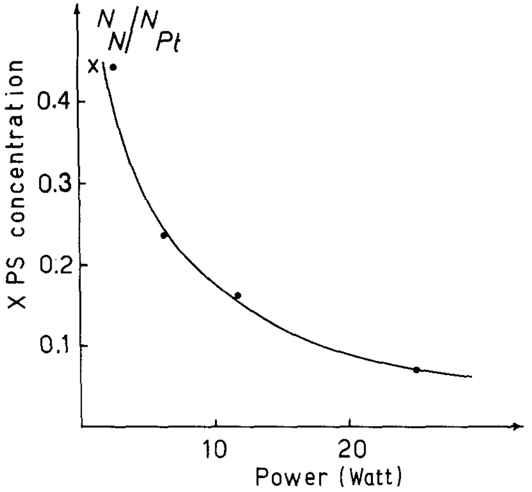

Figure 5 Surface atomic concentration of nitrogen determined by XPS as a function of the sputtering power. (Discharge gas: ● N_2, X NH_3).

electron from d to s character when increasing the nitrogen concentration in the metallic lattice. Addition of s-electron density (or d–s interchange) results in a decreased efficiency for the creation of electron-hole pairs at the Fermi surface. It must be added that the right half-width of the Pt ($4f_{7/2}$) peak shows a fairly regular variation with the electrical resistivity of the films (Table I).

Concerning conduction band profiles, the most significant changes also seem to be connected with the presence of the N (1s) peak at lower binding energy (398.5 eV). Besides a slight reduction of the density of occupied states near the Fermi energy, E_F, a complex structure at about 3 eV fills the region between the two maxima characteristic of the pure platinum conduction band (Fig. 6). Moreover, a small peak at 5 to 5.5 eV comes out of the tail at higher binding energy. These modifications are in fact reminiscent of the profile found in the Pt–O system [7, 21], which suggests a peak structure arising from the Pt (5d)–N (2p, 2s) orbital interaction. The perturbation of metallic density of states concerns some 5% of the d-electrons in the whole band. In a localized picture this would involve the existence of some 5% of chemically modified Pt atoms in the metal.

The XPS spectral characteristics of the metal lines, including the conduction band profile, tend to be recovered after heating at 165° C under an O_2 atmosphere (Table I). However, as far as the N (1s) line is concerned, the decrease in intensity is rather limited. Moreover, a new N (1s) peak appears at higher binding energy (Table I). It is possible that this results from a balance between elimination of adsorbed nitrogen species and surface enrichment by diffusion from the bulk [17].

4. Conclusions

Thin films of platinum containing up to 13 at% nitrogen have been prepared by d.c. reactive sputtering using nitrogen–argon and ammonia as discharge gases. Nitrogen incorporation into platinum is mainly determined by the sputtering power.

The films are characterized by good adherence to the different substrates and by great hardness.

Although the chemical shifts of the Pt ($4f_{7/2}$) line are small (< 0.2 eV), the relative intensity and the binding energy (~ 398.5 eV) of the N (1s) line, the decrease of the Pt (4f) asymmetry and the profile of the conduction band, support the existence of a PtN_x phase (with x of the order of

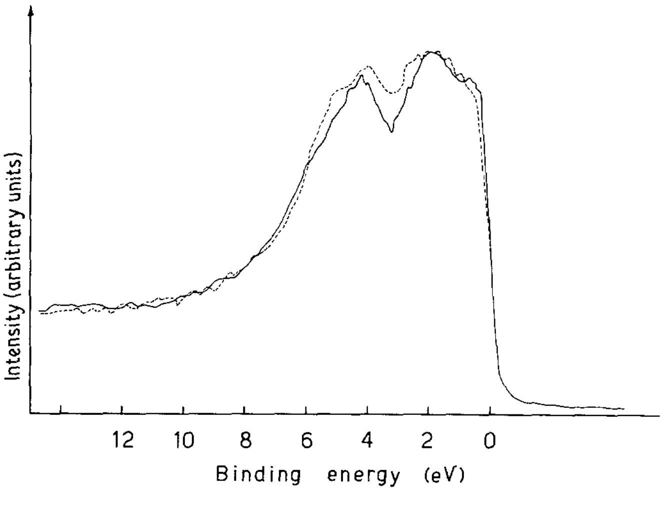

Figure 6 Pt 5d band profile of evaporated platinum (full line) and of platinum sputtered in nitrogen (sample N_2II) (dashed line) recorded with monochromatized AlKα radiation.

0.1) characterized by a very limited metal to non-metal charge transfer.

X-ray diffraction measurements show that the films exhibit preferred orientations with the most dense (1 1 1) planes parallel to the substrate. Nitrogen incorporation gives rise to peak shifts, broadening and asymmetries of the Pt (1 1 1) line which should be related to a diminution of the particle size, to the presence of dislocations and microdistortions.

XPS, X-ray diffraction and electrical measurements indicate that the nitrogen–platinum films are relatively unstable during thermal treatment.

Finally considering the X-ray diffraction results, we think that the hardness improvement can be related to the presence of a large number of dislocations and grain boundaries produced by the incorporation of several per cent of nitrogen in the platinum lattice.

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