

# A Method to Produce Porous Platinum Film

SIMPLE ROUTE GIVING HIGH PURITY FILM OF VARYING THICKNESS

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*A simple low cost hydrothermal method is described for producing thin films of porous platinum. The films are formed from  $[Pt(NH_3)_4]Cl_2$  and comprise platinum agglomerates ~ 200–300 nm in size with internal grains of ~ 20–60 nm.*

Thin metal films, especially those of the platinum group metals, are of interest to the semiconductor industry and to material engineering. They can be used, for instance, in optics, in optoelectronics, in the processes of micro- and ultrafiltration, as electrodes and as anticorrosion layers, and as the catalytic materials in chemical sensors (1–5).

Several methods of producing platinum films are known. The oldest involves spreading a thin layer of a solution containing a platinum salt onto a glass surface and then burning off at “dark heat” (~ 400°C) (6). Metal can also be deposited onto various supports from solutions of platinum salts, complexes or compounds by chemical or electro-

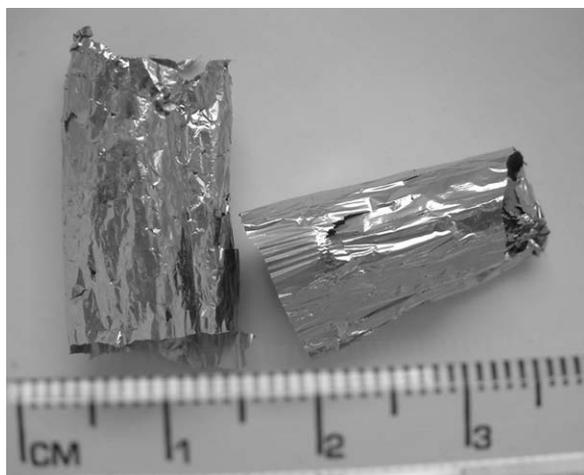
chemical reduction. In addition, platinum can be sputtered cathodically or evaporated *in vacuo* onto supports.

There is now more interest in depositing films onto supports by adsorption processes or by gas phase reactions of platinum compounds, that is chemical vapour deposition (CVD). Modified methods, such as plasma-enhanced or plasma-assisted, thermal laser-assisted, photolytic CVD, are also available (7).

To obtain free thin platinum films using the above methods the support must be removed. The support has to be dissolved in acids, such as HF (in the case of glass, Si, or SiO<sub>2</sub>), HNO<sub>3</sub> (if the platinum is deposited onto metals such as silver or gold) or in water (if platinum was evaporated onto the surface of NaCl crystals). The thin platinum films obtained usually contain impurities from the carrier.

However, if the films are obtained from precursors that contain carbon, then carbon is always a contaminant, and this narrows their applications. Carbon can be removed by burn-off, but this requires temperatures higher than 400°C. The films, which consist of fine thermally-unstable crystallites recrystallise during burn-off. During recrystallisation the size of the crystallites increases. Also, in the case of porous films, the size of the pores increases.

We have now produced porous platinum films by heating aqueous solutions of  $[Pt(NH_3)_4]Cl_2$  at concentrations of 3–60 g dm<sup>-3</sup> for several hours in cylindrical



*Fig. 1 Thin platinum films as removed from a cylindrical glass tube. The film can be easily flattened and cut*

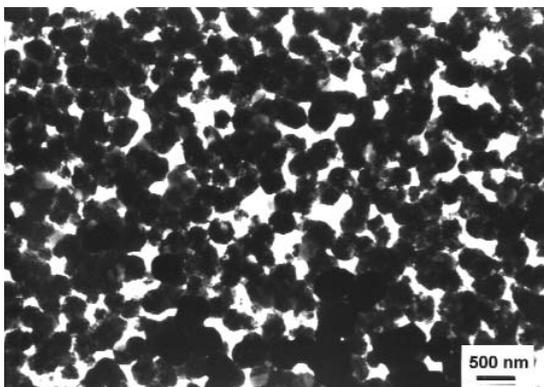


Fig. 2 TEM image of platinum film obtained from aqueous  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$  solution at concentration of  $3 \text{ g dm}^{-3}$ . The film formed inside a vessel of surface area  $26 \text{ cm}^2$ . The film is  $140 \text{ nm}$  thick with agglomerates  $\sim 200$  to  $300 \text{ nm}$

tubes of glass or quartz of  $10 \text{ mm}$  diameter in a pressure reactor at  $8\text{--}10$  atmospheres and a temperature of  $170\text{--}180^\circ\text{C}$  (8). Films were formed at the interface between the vessel and the  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$  solution phase. The films consisted of mutually-joined platinum agglomerates of size  $\sim 200\text{--}300 \text{ nm}$ , with spaces of similar dimensions between them. The films let through light (of wavelengths  $200\text{--}2200 \text{ nm}$ ). The films, of surface area up to several tens of  $\text{cm}^2$ , could be easily removed from the liquid and freely placed on a different support, such as ceramic, glass or plastic. The amount of platinum in the films weighed from  $3$  to  $120 \text{ g m}^{-2}$  (related to the wide range of platinum salt concentrations from  $3$  to  $60 \text{ g dm}^{-3}$ ). Film area was measured from the surface area of the vessel moistened by the aqueous platinum solution. The high purity of the films was confirmed by energy dispersive spectroscopy. The platinum films are shown in Figure 1; they were not brittle nor easily torn and were easy to flatten.

Figure 2 shows an electron microscopy image. The thickness of the film depends on the ratio of the  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$

concentration to the surface of the vessel wetted by the solution.

No 'gaps' were observed on the TEM images at higher concentrations of the  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$  solution, but empty spaces were visible when lower  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$  concentrations were applied.

The platinum agglomerates comprise grains of size  $20\text{--}60 \text{ nm}$ . These dimensions were determined from the TEM image shown in Figure 3. The average size of the crystallites,  $D$ , forming the film was  $35 \text{ nm}$ , calculated from X-ray line broadening of the (111) line, using the Scherrer formula:

$$D = k\lambda / (\beta \cos \theta)$$

where  $k$  is a constant ( $k = 0.9$ ),  $\lambda$  is the X-ray wavelength ( $0.15418 \text{ nm}$ ),  $\beta$  is equal to the full width at half-maximum (FWHM) intensity of the diffraction line and  $\theta$  is the angle of diffraction. The average crystallite sizes obtained from XRD data were in good agreement with corresponding TEM measurements. The size of the crystallites increase  $\sim 10\text{--}20 \%$  during reordering and recrystallisation after heat treatment up to  $1000^\circ\text{C}$ .

It is interesting that platinum films obtained from solutions of much higher concentrations of  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ , which are much thicker (for example,  $5500 \text{ nm}$  at concentrations of  $60 \text{ g dm}^{-3}$ ) and

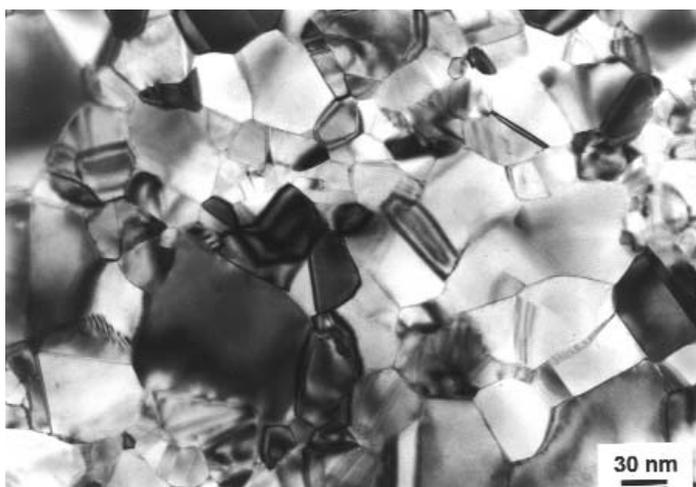


Fig. 3 TEM image of the platinum film in Figure 2, but at higher magnification. The platinum agglomerates are composed of fine grains of size  $20\text{--}60 \text{ nm}$

impervious to the TEM electron beam, also consist of fine crystallites of average size  $\sim 37$  nm, as found by X-ray diffraction.

## Conclusion

The grain sizes in platinum films produced by this route from  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$  solutions appear to be independent of film thickness. We believe that this method of obtaining porous platinum films could be widely used. It is very simple, proceeds in mild conditions and gives reproducible results. Such platinum film may find application in filtering or possibly as catalytic material.

## References

- 1 R. Lenigk, H. Zhu, T.-C. Lo and R. Renneberg, *Fresenius J. Anal. Chem.*, 1999, 364, (1–2), 66
- 2 M. Matsumiya, W. Shin, N. Izu and N. Murayama, *Sens. Actuators B: Chem.*, 2003, 93, (1–3), 309
- 3 S. C. Pak, W. Penrose and P. J. Hesketh, *Biosens. Bioelectron.*, 2001, 16, (6), 371
- 4 A. Arora, A. J. de Mello and A. Manz, *Anal. Commun.*, 1997, 34, (12), 393
- 5 K. D. Harris, J. R. McBride, K. E. Nietering and M. J. Brett, *Sens. Mater.*, 2001, 13, (4), 225
- 6 J. W. Döbereiner, *Schw. J.*, 1828, 54, 414
- 7 Y. Iwasawa, ‘Supported Catalysts from Chemical Vapor Deposition and Related Techniques’, in “Handbook of Heterogeneous Catalysis”, eds. G. Ertl, H. Knözinger and J. Weitkamp, VCH Wiley, Weinheim, 1997, Vol. 2, p. 853
- 8 J. Wrzyszczyk, H. Grabowska and M. Zawadzki, *Polish Patent Appl.* 371,715; 2004

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