

MODIFICATION OF THE SURFACE ROUGHNESS OF PLATINUM THIN FILM ELECTRODES BY ALLOY FORMATION WITH ALUMINUM

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Platinum is a widely used electrode material in electrochemistry. For many applications like conductometric and amperometric sensors a high effective surface area over the geometric surface area is desired. This is usually realized by electrodeposition of platinum-black on individual devices. For electrochemical sensors made by thin film technology, such a step is preferably performed on-wafer. Even if galvanic deposition is possible on whole wafer, platinum black is too fragile to sustain the necessary cleaning step after the dicing. In this contribution we have studied alloy formation between aluminum and platinum as a method to increase the surface area.

Alloy formation in thin film processing is often subject of concern as it can have disastrous effects on the functioning of the devices. During the processing of electrochemical sensors we were also confronted with the problems of alloy formation between aluminum and platinum. However, we found that when platinum had been in contact with aluminum at relatively mild conditions there was a beneficial effect on the sensors' characteristics. Analysis showed that this was caused by an increase of the surface roughness. In contrast to platinum-black the material is as robust as normal thin film platinum.

Thin film layers of platinum and aluminum were subsequently deposited on an oxidized silicon substrate. Platinum thickness was varied while the aluminum thickness kept constant (large excess of aluminum). Anneal temperatures up to 400°C were investigated. After the anneal the remainder of the aluminum was etched away, exposing the Pt/Al alloy. Because of the light-brownish color, and in analogy to platinum-black, the term platinum-brown is introduced.

The samples were investigated using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM). Electrodes produced according to this method were characterized with cyclic voltammetry.

Alloy formation starts at a relatively low temperature of 150°C and should not be performed at temperatures higher than 250°C. At higher temperatures the material becomes resistive and SEM-images reveal the presence of cracks. Roughness factors were determined from the hydrogen desorption region of the cyclic voltammogram. Values as high as high as 50 were observed (ideally smooth polycrystalline platinum having a roughness factor of 1). The cyclic voltammogram of platinum brown is almost exactly the same as of thin film platinum, only now the current is much higher, see Fig. 1 and 2. The chemical resistance was not tested extensively, but seems comparable to normal thin film platinum, while samples annealed at temperatures above 250°C were readily attacked in KOH solutions. EDS analyses on the TEM-samples showed that Al diffuses into the Pt-layer.

In Figure 3 a SEM picture is presented of the surface of platinum brown annealed for 23 h at 200°C. For comparison, in Figure 4 the surface of resistive platinum-brown, annealed for 1h25 at 300°C, is presented; cracks can be seen on the surface.

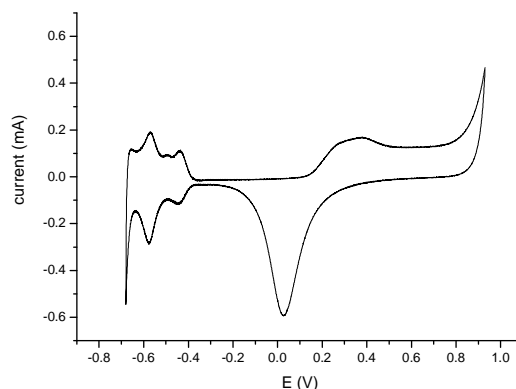


Figure 1. Cyclic voltammogram of thin film platinum electrode (1 M H₂SO₄; vs. Hg/HgSO₄; 100 mV/s).

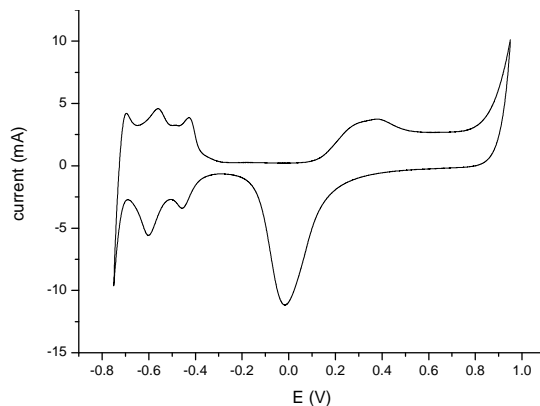


Figure 2. Cyclic voltammogram of platinum-brown electrode (1 M H₂SO₄; vs. Hg/HgSO₄; 100 mV/s).

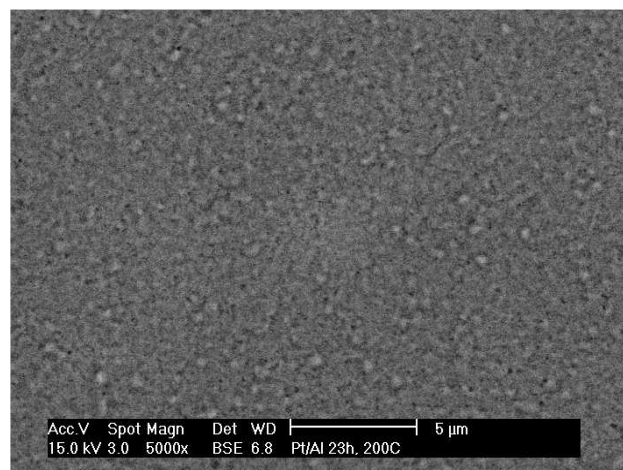


Figure 3. SEM picture of the surface of a platinum brown electrode (23h, 200 °C).

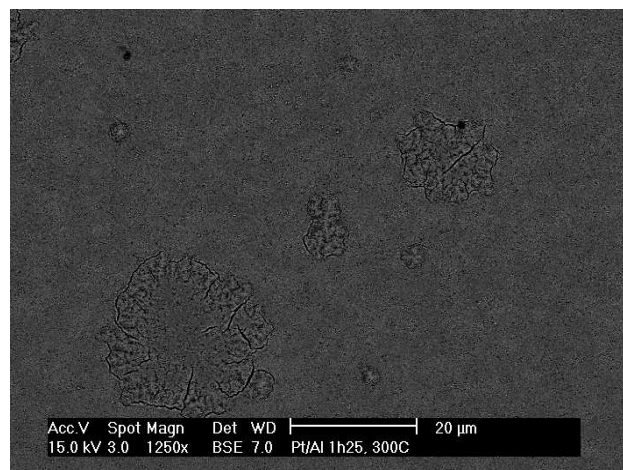


Figure 4. SEM picture of the surface of resistive platinum brown (1h25, 300 °C), revealing cracks.