

Pulsed Electrochemical Deposition of Pt and Bi₂Te₃ in Porous InP: a Comparative Study

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Abstract — Porous InP templates with parallel pores possessing diameters of 80 nm have been fabricated by anodic etching of commercially available *n*-InP substrates with (100) orientation in neutral electrolyte (NaCl). Comparative studies of pulsed electrochemical deposition of Pt and Bi₂Te₃ and evolution of nanodots growth have been investigated. The dependence of Pt and Bi₂Te₃ deposition uniformity upon the cathodic potential, duration of voltage pulse and delay time between pulses was studied systematically. As a result technological conditions for uniform deposition of Pt on inner surface of pores in porous InP were identified.

Keywords — pulsed electrochemical deposition, nanodots, nanotubes, porous InP.

I. INTRODUCTION

Deposition of metal nanoparticles on semiconductor substrates and matrices is of great importance for subsequent controlled growth of semiconductor nanostructures, enhancement of solar energy absorption in thin-film photovoltaic structures, fabrication of plasmonic nanoarchitectures for surface enhanced spectroscopy etc. [1,2]. Among many explored methods such as vapour, solution, electrochemistry-based approaches, the electrochemical deposition of metal dots proves to be one of the most cost-effective and efficient, especially when the dots are to be created on semiconductor substrates or matrices exhibiting electrical conductivity.

Precisely controlling the shape of nanomaterials and forming well-aligned arrays from these nanomaterials will stimulate further investigation of their physical properties and will widen the potential applications of metal nanodots in many areas, for instance in the area of plasmonic photonic crystals

II. EXPERIMENT

A. Preparation of porous layers

Crystalline 500- μm thick *n*-InP(100) substrates with the free electron concentration of $1.3 \times 10^{18} \text{ cm}^{-3}$ were supplied by CrysTec GmbH, Germany. To make use of industrial approaches of planar semiconductor technologies, it is important to develop methods for the preparation of templates with pores oriented parallel to the top surface of the substrate.

To fabricate porous layers with pores parallel to the top surface, the InP substrates were subjected to anodic etching

in 3.5M NaCl aqueous solution at 25°C through photolithographically prepared windows, as described elsewhere [3].

As shown in Fig. 1, we used a design where some areas of the front surface of the substrate are covered by a photoresist, while other areas are exposed to the electrolyte in the electrochemical etching process. In this case, it is expected that the pores will grow from the surface exposed to the electrolyte initially in a direction perpendicular to the top surface. However, with further propagation of pores, they will be deflected in directions parallel to the top surface, and will grow under the regions covered by the photoresist.

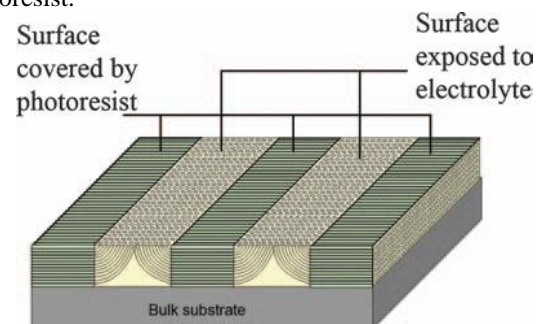


Fig. 1. Illustration of the approach for the preparation of porous templates with pores parallel to the top surface of the sample.

B. Pulsed electrochemical deposition

An electrolyte containing 10 mM Bi³⁺ and 15 mM HTeO²⁺ ions in 1 M HNO₃ prepared by dissolution of bismuth(III)-nitrate pentahydrate Bi(-NO₃)₃ · 5H₂O (Sigma Aldrich) and pure Te powder (99.999% Fluka) was used for pulsed electrodeposition of Bi₂Te₃.

Electroplating of Pt was realized in a commercially available gold bath containing 5 g/l Pt (DODUCO). The electrochemical deposition of Pt was performed at T = 25°C in a common two-electrode plating cell where the porous sample served as working electrode, while a platinum wire was used as counter electrode.

A pulsed voltage with rectangular pulses was provided by a home-made generator. During the pulse time with duration 100 μs a cathodic voltage of -16 V was applied between the two electrodes to electrochemically reduce the metal species on the surface of the sample being in contact

with the electrolyte. After each pulse, a delay time as long as one second was kept. Besides, magnetic stirring provided appropriate conditions for the recovery of the ion concentration in the electrolyte.

After electroplating the samples were rinsed in distilled water. The morphology has been investigated by using Scanning Electron Microscopes (SEM) Zeiss Sigma and TESCAN Vega TS 5130 MM equipped with an Oxford Instruments INCA Energy EDX system operated at 20 kV.

III. RESULTS AND DISCUSSION

As one can see from Fig. 2 (a,d), the formation of small dots at short duration of pulsed electrochemical deposition occurs. With increasing of time of electroplating, the number of dots and their diameters increase until they interconnect with each other (see Fig. 2b,e). Overlapping of neighboring dots leads to the formation of tubular structures with the smooth surface, as illustrated in Fig. 2c.

In premiere, recently, the mechanism of Au dots nucleation and growth was proposed and demonstrated [4].

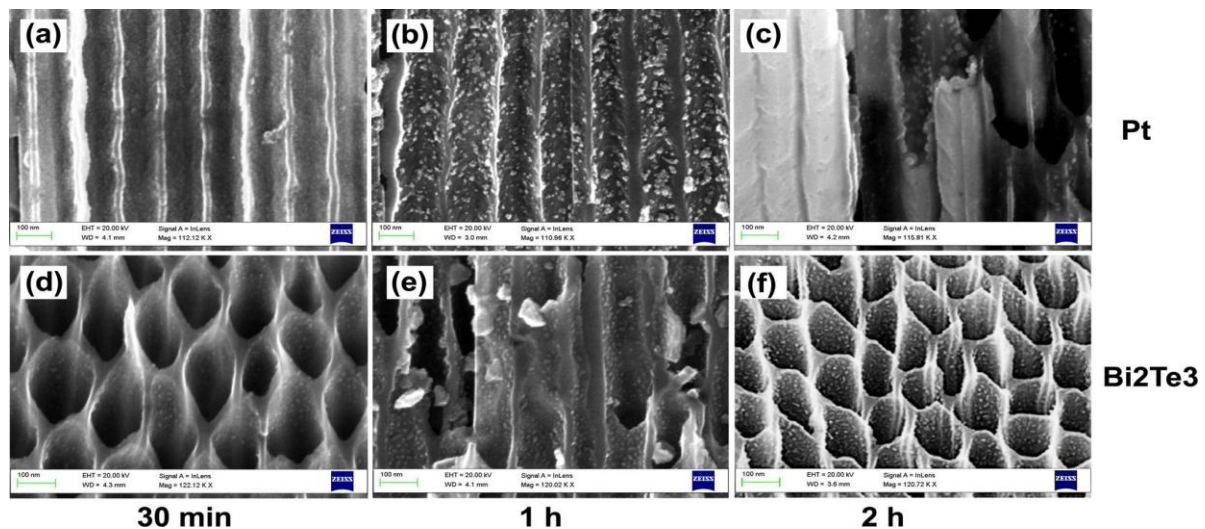


Fig. 2 SEM images of pulsed electrochemical deposition of Pt (a,b,c) and Bi_2Te_3 (d,e,f) at different durations of deposition.

We found that after nucleation each dot increases in sizes up to a critical transverse dimension of about 20 nanometers, the process of hopping electrodeposition of Au being continuously supported by the formation of new nanodots. The process continues until the entire surface exposed to the electrolyte is covered by a monolayer of self-assembled gold nanodots. It is interesting to note that after the self-assembled monolayer is formed, further electroplating of gold is spatially non-uniform and leads to the deposition of particles with relatively large diameters.

It is obvious, that in case of Pt deposition, formation and growth rate of dots is higher in contrast to Bi_2Te_3 (Fig. 2c,f), which requests longer durations of deposition. But the problem is that porous InP skeleton starts to dissolve at the process durations more than 3 h in the electrolyte containing Bi_2Te_3 .

IV. CONCLUSIONS

In conclusion, electroplating starts with the deposition of metal dots, their density increasing with time. Overlapping of the neighboring dots leads to the formation of tubular structures in case of Pt deposition as shown in Fig. 1c. The deposition of Bi_2Te_3 nanodots is more similar with those of Au deposition mechanism, but with much slower deposition velocity.

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