



Self-Assembled Monolayer of Au Nanodots Deposited on Porous Semiconductor Structures

Ion Tiginyanu,^{a,b,*} Eduard Monaico,^b and Kornelius Nielsch^c

^aInstitute of Electronic Engineering and Nanotechnologies, Academy of Sciences of Moldova, Chisinau 2001, Moldova

^bNational Center for Materials Study and Testing, Technical University of Moldova, Chisinau 2004, Moldova

^cInstitute of Applied Physics, University of Hamburg, Hamburg 20355, Germany

We demonstrate the possibility to cover the surface of GaP and InP porous structures by a self-assembled monolayer of electrochemically deposited nanoscale Au nanodots. After nucleation, each dot was found to increase in sizes up to a critical transverse dimension, the process of pulsed electrodeposition of gold being continuously supported by the formation of new nanodots. The density of deposited Au dots is shown to be dependent upon the number and width of the applied voltage pulses. The deposition of “size-saturated” dots continues until the entire surface exposed to the electrolyte is covered by a monolayer of self-assembled Au nanodots.

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Deposition of metal nanoparticles on semiconductor substrates and matrices is of great importance for controlled growth of semiconductor nanostructures, enhancement of solar energy absorption in thin-film photovoltaic structures, fabrication of plasmonic nanoarchitectures for surface enhanced spectroscopy etc.¹⁻³ Among many explored methods such as vapor, 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. Using pulsed electroplating, Sato et al. demonstrated uniform deposition of Pt dots with the diameters ranging from 20 to 30 nm on *n*-GaAs and *n*-InP substrates with the free electron concentrations of 2×10^{16} and $5 \times 10^{16} \text{ cm}^{-3}$ respectively.^{4,5} The authors found the Fermi-level pinning at the metal-semiconductor interface to be greatly reduced, resulting in a strong dependency of the Schottky barrier height on the metal workfunction.

The goal of this paper is to demonstrate, in premiere, electrochemical deposition of size-saturated noble metal dots on GaP and InP porous semiconductor structures. We show the possibility to reach full coverage of the surface of porous structures by a self-assembled monolayer of nanoscale Au dots. The gold dots were chosen in our research due to their unique plasmonic characteristics promising for a myriad of applications.

Experimental

Crystalline 500- μm thick *n*-GaP(111) and *n*-InP(100) substrates with the free electron concentration of 2×10^{17} and $1.3 \times 10^{18} \text{ cm}^{-3}$ respectively were supplied by CrysTec GmbH, Germany. To fabricate porous layers, the GaP and InP substrates were subjected to anodic etching in 500 ml of 1 M HBr and 5% HCl aqueous solution, respectively, at 25°C through photolithographically prepared windows, as described elsewhere.⁶

Electroplating of Au was realized in a commercially available gold bath containing 5 g/l Au (DODUCO). The electrochemical deposition of Au was performed at $T = 25^\circ\text{C}$ 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 from 2 to 100 μs a cathodic voltage of -16 and -25 V for InP and GaP, respectively, 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.

Results and Discussion

Fig. 1 illustrates SEM images taken from fragments of low-porosity GaP fabricated under potentiostatic anodic etching conditions (applied voltage 10 V) with subsequent electrochemical deposition of Au dots. The applied cathodic voltage was -25 V, while the duration of voltage pulses was 50 μs . The image presented in Fig. 1a corresponds to 5 s of pulsed electrodeposition, while the image shown in Fig. 1b corresponds to 100 s of electroplating. After application of five voltage pulses, a random but uniform distribution of dots is observed along the surface of the porous structure, the individual dots being spatially separated from each other. Remarkably, after application of approx. 100 voltage pulses a uniform full coverage of the surface by a monolayer of Au dots is reached, see Fig. 1b. Thorough analysis of the images presented in Fig. 1a and 1b shows that, in spite of a certain distribution in the dot sizes, the transverse dimensions of the dots do not exceed 20 nm.

Fig. 2 illustrates SEM images taken from fragments of porous GaP with pores generated at applied anodic voltage of 20 (a) and 15 V (b). Note that the pores are parallel to each other and oriented perpendicular to the initial top surface of the substrate. Like in the previous case, Au electroplating was carried out at applied cathodic voltage of -25 V with the duration of voltage pulses of 50 μs . The images presented in Fig. 2a and 2b correspond to 5 and 100 voltage pulses respectively. Random but uniform distribution of individual dots was evidenced in depth of the porous layers after 5 s of electrodeposition, see Fig. 2a. At the same time, after 100 s of electrodeposition we registered a complete coverage of the surface by a monolayer of Au dots with diameters not exceeding 20 nm (Fig. 2b).

To illustrate the dynamics of nucleation and formation of Au dots with continuous increase in their density, we researched electroplating of gold on the top surface of porous *n*-InP, applying ten cathodic voltage pulses of different widths: 2; 10 and 100 μs . The results are illustrated by images presented in Fig. 3a, 3b, and 3c, respectively, while Fig. 3d represents an enlarged section selected from Fig. 3c. Note that in this specific case the growth of pores during anodic etching took place in directions parallel to the top surface, for details see Ref. 7. Actually the buried pores grew under a 60-nm thick surface layer of virgin InP covered by photoresist, the latter being removed chemically after anodic etching. As one can see from Fig. 3a–3d, the distribution of Au dots on the top surface is rather uniform, and the nucleation and formation of dots occur along the entire surface with the same probability, in spite of the changing morphology in depth, i.e. alternation of buried pores and InP walls. Electroplating for 10 s with 100- μs pulses proves to be enough to cover practically the whole surface by a monolayer of Au dots, see Fig. 3c and 3d.

*Electrochemical Society Active Member.

^zE-mail: tiginyanu@asm.md