# Gold coated metal nanostructures grown by glancing angle deposition and pulsed electroplating

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## ARTICLE INFO

## ABSTRACT

Nickel based nanostructures are grown by glancing angle deposition (GLAD) on flat and pre-patterned substrates. These fabricated porous thin films were subsequently coated by pulsed electroplating with gold. The morphology and conformity of the gold coating were investigated by scanning electron microscopy and X-ray diffraction. Controlled growth of closed gold layers on the nanostructures could be achieved, while the open-pore structure of the nanosculptured thin films was preserved. Such gold coated nanostructures are a candidate for optical sensing and catalysis applications. The demonstrated method can be applied for numerous material combinations, allowing to provide GLAD thin films with new surface properties.

## 1. Introduction

Nanostructured surfaces can provide completely new properties compared to bulk materials. The shape and size of the nanostructures influence the properties of a surface. A powerful way to grow nanostructures is the so-called Glancing Angle Deposition (GLAD) [1]. This is a physical vapor deposition (PVD) technique, where the substrate is tilted to a highly oblique angle $\theta$ with respect to the incoming particles and an azimuthal substrate rotation is applied. This deposition geometry allows fabricating various nanostructure morphologies, for example vertical and helical nanostructures can be obtained by slow and fast azimuthal substrate rotation, respectively. From the physical point of view, the film growth is determined by a self-shadowing effect and surface diffusion. To further functionalize the nanostructures, various techniques such as electroless chemical deposition [2], atomic layer deposition (ALD) [3] or electroplating [4], have been developed to coat complex shaped nanostructures with different materials. Electroplating is in-between the both other methods, as the need for an external driving force (electrical current) provides a possibility to control the electro-chemical reaction. The main advantage of this technique is that the deposition reaction can be interrupted by stopping the external current. This allows an exact control of the amount of deposited materials (that is proportional to the total transferred charge) and opens the possibility to pause the deposition for a defined period of time. Periodic interruption of the deposition process is known as pulsed electrodeposition [5], which is especially suited for coating of high aspect-ratio holes or porous thin films [6].

The distinguished property of the GLAD method is the high flexibility and precise control of the design of nanostructures. However, this method is only restrictedly usable for materials (an example is gold) which show a high surface diffusion already at low temperatures, resulting in the growth of smeared or dissolved nanostructures [7]. Otherwise gold nanostructures would be interesting for surface enhanced Raman sensing (SERS) [8] and catalysis applications [9]. Because the SERS effect and catalytic reactions only require a few nm thick layers, a thin gold shell on another core metal nanostructure would be sufficient. In the present study, Ni and NiFe GLAD nanostructures were chosen as substrates for two reasons. Firstly, Ni rich alloys have a conductive surface, since strong surface oxidation, as known for various other metals, does not occur at room temperature. Secondly, gold and nickel are immiscible at room temperature, which is important for creating a pure closed gold shell around the nickel core.

## 2. Material and methods

Nickel and nickel-iron (81/19 wt-%) nanostructures were grown by a GLAD process, utilizing an electron-beam evaporator in an

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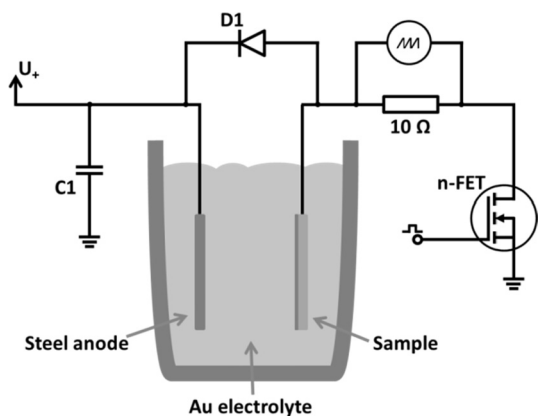
**Fig. 1.** Schematic illustration of the pulsed electrodeposition setup. The capacitor C1 is realized as parallel connection of a 4.7 mF electrolyte and a 100 nF ceramic capacitor. Diode D1 is of Schottky type. The pulse shape and current are controlled by an oscilloscope over a 10 Ω resistor.

ultra-high vacuum system with a base pressure of approximately $10^{-8}$ mbar. Carbon crucibles were used for the evaporation and natively oxidized planar and pre-patterned Si (100) pieces were used as substrates. The depositions were carried out at room temperature. Pre-patterning was realized by shadow nanosphere lithography (NSL), using a nanosphere monolayer prepared as described in [10]. Nanospheres with a diameter of 1.59 μm were utilized. To obtain a closed metal layer that guarantees the electrical conductivity of the substrate, 100 nm Ni or NiFe were deposited at normal incidence onto all samples prior to glancing angle deposition. Atop of this layer, nanostructures were grown with an angle of incidence $\theta = 86°$ and a substrate rotation frequency of 5 revolutions per minute (rpm). Using a quartz crystal microbalance allowed monitoring the deposition rate, which was held constant at about 1 nm/s during deposition.

Afterwards, the GLAD coated samples were cleaved into pieces of approximately 0.5 cm$^2$ size. For the electrodeposition, a commercial available gold electrolyte containing chloroauric acid and potassium ferrocyanide was used. The concentration of pure gold was 3 g/l. The galvanic cell consisted of a 10 ml glass beaker, a steel anode and a conductive clamp for the samples. An electric circuit created the current pulses, as illustrated in Fig. 1. A microcontroller controlled the pulse number and timing. Rise and fall times of less than 200 ns were achieved with this assembly. The surface area of nanostructured thin films is not experimentally accessible and therefore remains unquantified. However, the macroscopic area of the substrate on which the nanostructures are grown is known. Hence, the given current densities refer to the substrates area. Notice that the substrate area is smaller than the area of the nanostructured thin films, resulting in an overestimation of the real current densities. After the Au deposition, the samples were removed from the galvanic bath and rinsed with water. For analysis, the samples were cleaved and the fresh edges were examined with a scanning electron microscope (SEM). A primary electron energy of 8 kV was chosen and the secondary electrons were used for imaging. Due to the large difference in atomic masses of Ni and Au, a strong contrast between Ni and Au can be observed even in secondary electron mode.

## 3. Results and discussion

In all experimental approaches applying non-pulsed DC currents, the films rapidly peeled off from the substrate, and gold condensation was observed only on top of the nanostructures. In these cases, the continuous reaction leads to a diffusion driven coating, where exposed parts of the sample show a faster coating
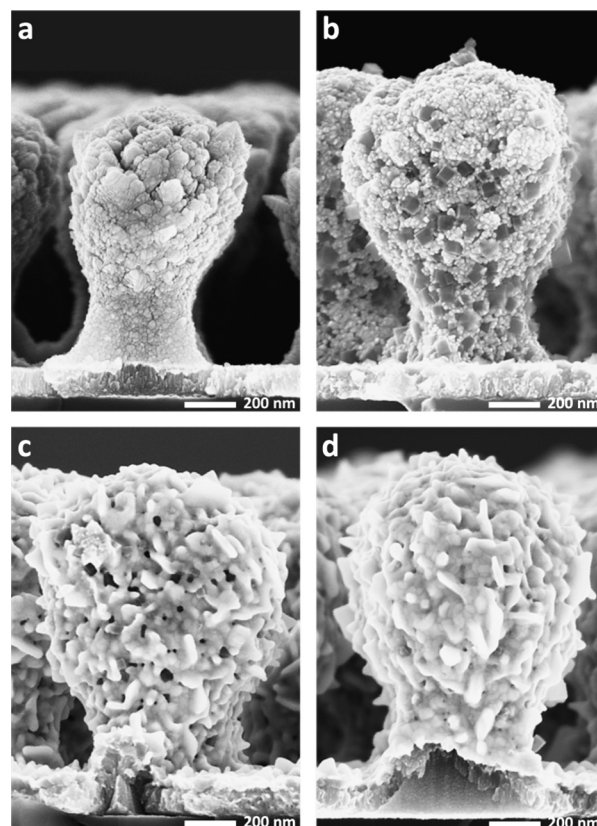


**Fig. 2.** Cross-sectional SEM images of periodically arranged NiFe nanostructures that are coated by electrodeposition. All samples were deposited with $t_{on}/t_{off} = 1$ μs/9 μs and a pulse current density of about $(92 \pm 5)$ mA/cm$^2$. (a) uncoated NiFe structures. (b), (c) and (d) Au coated structures after $0.5 \cdot 10^7$, $1.0 \cdot 10^7$ and $1.5 \cdot 10^7$ pulses, respectively. In (b), the formation of gold crystallites is shown, while in (d) a nearly closed gold layer is achieved.

process than deeper located parts, leading to a non-equal final film thickness. Thus, the reaction must be stopped before the concentration of material ions in the solution between the nanostructures drops too low. During the reaction break, new material diffuses into the depleted regions, so that in the next reaction interval a uniform deposition can be realized. As a rough estimation, a cylindrical hole with a depth of 1000 nm and a diameter of 100 nm is completely depleted in around 100 μs, if typical values for the current density of 100 mA/cm$^2$ and an initial concentration of 3 g/l of Au(III) ions are assumed. This would correspond to a gold thickness of about 0.004 nm per current pulse on the walls of the hole. To assure a homogeneous coating, the on-time $t_{on}$ of a pulsed deposition has to be much smaller than this, while the off-time $t_{off}$ has to be sufficiently long to allow new ions to diffuse into the hole.

For all following deposition experiments an on-time $t_{on}$ of 1 μs and an off-time $t_{off}$ of 9 μs was chosen. Fig. 2 (a) shows a NiFe nanostructure grown on a NSL substrate. Interseed growth is not obtained and the structures are well separated. Figs. 2 (b), (c) and (d) demonstrate the development of the gold coating on NiFe nanostructures with increasing pulse number. The current density during the pulses was 89, 88 and 97 mA/cm$^2$, respectively. At the beginning of the coating process, small isolated gold crystals can be obtained on the nanostructure surface and the substrate layer that interconnect with increasing deposition time. Finally, a rough closed layer was observed after a charge transfer of approximately 1.45 C/cm$^2$, and a total deposition time of 150 s. In Fig. 3 (a), NiFe nanostructures grown on planar substrates are presented. These well separated structures have diameters between 30 nm and 150 nm. Some of the nanocolumns broaden with in-