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Chemical Microsensors with Ordered Nanostructures

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1. Introduction

Current issues solved in Microsensors are focused on finding of new approaches to increase sensitivity with decreasing dimensions at the same time, together with low-cost ability in manufacturing. The chapter deals with non-lithographic techniques of nanostructuring surfaces on sensing layers of microsensors which are promising to improve their parameters, mainly to amplify sensitivity. Especially (bio)chemical sensors for environmental, pharmaceutical and medical applications employ nanostructures in their construction.

2. Template based techniques for ordered nanostructures fabrication

One of the ways to achieve better and better detection characteristics of sensors is the use nanoparticles to modify the surface of the sensitive detection sensor part. A big challenge in fabricating various nanostructures fixed on solid supports is the uniformity and reproducibility in size and spatial distribution. This can be accomplished in several ways. Among proven methods, the lithography is very popular. It allows creating very precise structures and reliefs, but the price for the acquisition of apparatus and the service are very high.

On the other hand, the template based methods are exceptional techniques how to create freestanding, non-oriented and oriented nanostructures like nanotubes, nanorods, nanowires as well as nanodots over large areas on substrates in a fast, cheap and easy reproducible way. The possibility of using these well aligned nanosized structures as sensor arrays makes them very attractive candidates for potential applications in chemical analysis and medicine, especially for biosensing purposes. The template based methods can be applied in the current technology of thick film sensors, but it increasingly penetrates into areas of thin film applications. The other well known applications include electronic (e.g. as embedded capacitors) and optoelectronic devices, for example dye-sensitized solar cells, light emitting diodes and so on.

There is variety of the material which can be used for nanostructures fabrication by the template based methods; from semiconducting oxide (selenide, telluride) to pure metals such as Ni, Au and Pd.

Regarding to above mentioned applications, the microsensor for mentioned applications is build up on (bio)chemical transducer as can be seen on Fig. 1. The transducer contains a sensing layer where nanostructures are very promising formation of the sensing layer to obtain advanced sensing properties.

Fig. 1. Microsensor fabricated by hybrid technology (a), microsensor on a single chip (b)

2.1 Template fabrication and properties

Among various materials (activated carbon or carbon nanotubes, polymer gel, radiation track-etched polycarbonate or mica, zeolites, porous silicon prepared by electrochemical etching of silicon wafer and nanochannel array on glass) used as templates, alumina is the most frequently used one (G. Z. Cao & D. W. Liu, 2008). The pores in an anodic aluminum oxide mask are self ordered as a close-packed array of columnar hexagonal cells, each containing a central pore normal to the substrate. Similarly like alumina, the other metals (e.g. titanium) with specific characteristics can be changed by the electrochemical method to porous oxides, so called ceramics, with periodic nanoporous hexagonal structure (Alivov, 2009; Chu, 2005). Aluminum and titanium have a special ability, which was discovered in 1970 by a group of Wood, Sullivan and others. The controlled anodic oxidation means creating of nanoporous structure (Shingubara, 2003). During the 90s, the production process was being improved. The research team of Japanese scientists Masuda and Fukuda, who developed the production of porous ceramics using the "two-steps" method, which greatly contributed to improving the quality of the resulting structures, was of great importance in nanoporous ceramic research (Masuda & Fukuda, 1995).

During anodization process, the diffusion of metal ions or oxygen through the oxide layer growing in an electric field generated in this layer by applying an external voltage is the steering process. The rate of oxide layers growth during anodization depends exponentially on the electric voltage. The diameter and density of nanopores in template can be tuned in a wide range (from 3 to 500 nm) by controlling the anodization conditions, namely anodization voltage, time, and electrolyte. Kokonou et al. found, that anodization conditions strictly depend on aluminium layer thickness (Kokonou, 2007). In other words, the conditions for thin Al layers differ significantly from those used to grow thicker films. Particularly, much lower electric fields are necessary in the case of aluminium thin films, since the strong electric field causes fast dissolution of the grown alumina. Generally, the lower voltage is applied, the smaller pore size, the higher pore density and the better homogeneity. Concerning the temperature, the lower value is maintained during the

anodization process, the slower growth of pores and consequently their better uniformity can be reached. The uniformity of the template can be also influenced by number of anodization steps. The well-ordered nanoporous alumina masks can be obtained by two-step or even by three-step anodization of aluminum layer (Mozalev, 2009; Zhou, 2006).

There is no doubt that the quality of aluminium layer used for template fabrication plays a key role in reaching the uniform growth and regular distribution of nanopores. In other words, the level of film surface roughness has a direct effect on the regularity of pore arrangement (A. P. Li, 1998; Masuda, 1998; A. W. Wang & White, 1995). For sensor applications, a porous mask can be made in two ways. One of them is the production of several tens of micrometers thick membranes of high purity aluminum foil (thickness of 250 μm), and the other one is direct anodization of thin aluminum layer deposited on the substrate. Both of these options bring several problems. When using foil, the first step is electrochemical polishing of the surface followed by annealing step for aluminium recrystallization and to increase homogeneity. The homogeneity of thin aluminum deposited layer depends strongly on the deposition technique. Usually, the aluminium layer is deposited by several PVD techniques like pyrolytic evaporation, magnetron sputtering or ion sputtering on various solid supports, most currently on insulating substrate, like SiO_2 coated silicon wafer, glass, sapphire or on some semiconducting materials (e.g. GaAs, InP). During anodizing it is also necessary to consider the influence of adhesion between the aluminum layer and the underlying substrate (Hrdy & Hubalek, 2005).

As mentioned above, the choice of electrolyte is also a very important factor influencing the anodization process. The most frequently used electrolytes for alumina template fabrication are sulphuric, oxalic or phosphoric acid aqueous solutions at low concentration. The smallest pore size is generally reached using the sulphuric acid which is commonly used under lower constant voltage (in the range of 18 V up to 30 V) compared to oxalic acid (constant voltage from 30 to 60 V). The highest pore size is reached in the case of phosphoric acid. The other electrolytes composition was studied as well. Anitha and colleagues tested the influence of three different fluorine containing electrolytes (aqueous hydrofluoric acid (HF), HF containing dimethyl sulphoxide and HF containing ethylene glycol) on fabrication of TiO_2 nanotubes (Anitha, 2010). The experiments were carried out over a broad voltage range (2-200 V) and HF concentrations (0.1–48 wt%) which resulted in variation of anodization time from 5 s to 70 h. The authors observed that the composition of the electrolyte and its fluorine inhibiting nature has significant impact on nanotube formation as well as on controlling the aspect ratio. In other work, Song et al. examined the influence of defined water additions to an organic anodization electrolyte on wall thickness oscillations in electrochemically grown TiO_2 nanotube arrays (Song & Schmuki, 2010).

Finally, the choice of etching conditions during subsequent chemical etching step after anodization process can induce the type (shape) of prepared nanostructures. For example, the hole array structure can be obtained by the selective removal of silicon oxide from the Si substrate using wet etching in HF solution while the column array structure can be obtained by the selective etching of Si substrate in KOH solution using silicon oxide as a mask (Oide, 2006).

Sometimes, it is necessary to use other post-processing methods such as thinning to obtain very thin nanoporous template. Graham et al. employed the anodized nanoporous alumina to form aluminium electrodes on integrated circuit (IC) which can be applied as biocompatible material enabling a low-cost solution for drug discovery pharmacology, neural interface systems, cell-based biosensors and electrophysiology (Graham, 2010). The

porous alumina was electrochemically thinned to reduce the alumina electrode impedance. For applications where a porous electrode surface is either preferred or acceptable, the authors demonstrated that porosity can be manipulated at room temperature by modifying the anodizing electrolyte to include up to 40% polyethylene glycol and reducing the phosphoric acid concentration from 4% (w/v) to 1%. For applications requiring a planar microelectrode surface, a noble metal was electrodeposited into the pores of the alumina film. Limited success was achieved with a pH 7 platinum and a pH 5 gold cyanide bath but good results were demonstrated with a pH 0.5 gold chloride bath which produced planar biocompatible electrodes. A further reduction in impedance was produced by deposition of platinum-black, which may be a necessary additional step for demanding applications such as neuronal recording.

Montero-Moreno studied a barrier layer thinning (BLT) process to decrease the high electrical resistance generated by the barrier layer that isolates the metallic base from the electrodeposition bath (Montero-Moreno, 2009). The authors showed that during thinning, a controllable branched-shaped porous structure of AAO is generated. Finally, the use of stepped techniques to obtain alumina templates with narrower pores than expected in an oxalic acid bath was also analyzed.

3. Vertically ordered nanostructures

Vertically ordered nanostructures fabricated using template-based method can be used for sensor surface modification to enhance its sensitivity or they can create nanosensor array. High surface area and unit impedance behavior is expected from this formation. These nanostructures can be also functionalized with various biomolecules with specific sensitivity for biorecognition transducer construction. The usage of template-based techniques for nanostructures fabrication (especially nanorod, nanowire and nanotube arrays) can be performed either in the solution or with the help of other deposition methods. One of the greatest advantages of template-based synthesis for the growth of nanotubes and nanotube arrays is the independent control of the length, diameter, and the wall thickness of the nanotubes. While the length and diameter of resulted nanotubes are dependent on the templates used for the synthesis, the wall thickness of nanotubes can be readily controlled by the growth duration. Another great advantage of template-based synthesis is the possibility of multilayered hollow nanotube or solid nanocable structures formation [1].

The deposition from solution is known as electrochemical deposition or simply as electrodeposition, which involves oriented diffusion of charged reactive species through a solution when an external electric field is applied, and reduction of the charged species at deposited surface which also serves as an electrode. In industry, electrochemical deposition is widely used in making metallic coatings in a process known as electroplating. In general, this method is only applicable to electrical conductive materials such as metals, alloys, semiconductors, and electrically conductive polymers and oxides. After the initial deposition, the electrode is separated from the depositing solution by the deposit and the electrical current must go through the deposit to allow the deposition process to continue. When deposition is confined inside the pores of template membranes, nanocomposites are produced. If the template membrane is removed, nanorod or nanowire arrays are prepared. However, when the deposition occurs along the wall surface of the pore channels, nanotubes would result (G. Z. Cao & D. W. Liu, 2008). The example of deposition from solution can be the work of Wang, who prepared vanadium pentoxide nanotube arrays (Y.

Wang, 2005). Another example is formation of mesoporous oxides with well defined and ordered porous structure, which can be readily synthesized using surfactant or copolymer micelles as templates through sol-gel processing. Next recent example is Au nanoparticle templated synthesis of poly(N-isopropoylacrylamide) nanogels (G. Z. Cao & D. W. Liu, 2008).

The second mentioned case, i.e. the nanostructures formation using other deposition methods, is for example atomic layer deposition (ALD) as a perfect technique for the synthesis or fabrication of alumina nanotube arrays with well controlled wall thickness and morphology (C. C. Wang, 2007). ALD has also been employed for the fabrication of TiO₂ coated alumina membranes and TiO₂-coated Ni nanowires, and TiO₂ nanotube arrays were readily obtained by dissolving the templates (Kemell, 2007; Y. Wang, 2005).

3.1 Nanodots and nanocolumns

Nowadays, there are lots of papers dealing with ordered nanotubes array fabricated using template methods, but only very few works concerning the application of anodization technique for nanodots preparation. Sometimes, the scientists combine the usage of nanoporous mask and other ways of nanodots deposition, like ion beam evaporation, electron gun evaporation, nanoscale selective epitaxial growth (Y. D. Wang, 2006a), selective anodization using AFM tip, electrodeposition etc.

In order to achieve nanocrystals directly grown by anodization with sizes in the range of 1 to 10 nm which is essential for their quantum effect, the diameter of pores in the template must also be in this range. Beside the pore diameter, the template film thickness is also a crucial parameter which determines the quality of prepared nanostructures. In the case of nanodots, the scientists found that thinner template is more convenient in order to reach the high density of QDs array; particularly the thickness must be in the maximum 3 to 5 times higher than template pore size. Mao et al investigated well reproducible direct preparation of ultrathin template with thickness about 50 nm by utilizing a stop signal, a vivid color appearing at the air-electrolyte interface (Mao, 2009).

From the chemical point of view, several materials can be used for nanodots fabrication. Wang et al. prepared ordered GaN nanodot arrays with an average dot diameter and height of 60 and 100 nm by nonlithographic nanopatterning technique combined with nanoscale selective epitaxial growth for application in high efficiency nitride light emitting diodes (Y. D. Wang, 2006a). The same group of scientists also studied InGaN nanorings, nanodots, and nanoarrows fabrication using GaN layer on a sapphire substrate coated with a thin layer of SiO₂ (around 100 nm) by PECVD and finally coated with evaporated aluminium layer (about 1 µm) (Y. D. Wang, 2006b). The aluminium layer was then anodized to nanoporous template in a two-step anodization process and used to pattern nanopores in SiO₂ transfer layer. The patterned SiO₂ layer was applied as a template for nitride growth by MOCVD. The diameter of the deposited nitride nanostructures varied from 35 to 250 nm and their type was determined by controlling the nitride growth time.

Jung et al. examined the growth of CdTe QDs array (with dot size of 80 nm) on the GaAs substrate by molecular beam epitaxy method using the porous alumina masks (with thickness about 300 nm) for applications in optoelectronic devices in visible range (M. Jung, 2006). Similarly, Alonso-Gonzalez et al. investigated the fabrication of InAs QDs using epitaxial growth on GaAs nanoholes pre-patterned surface (Alonso-Gonzalez, 2006). Their particular approach consists of using the anodic aluminium oxide (AAO) prepared from epitaxially grown aluminium layer on GaAs substrates as a mask for creation of ordered

nanoholes in GaAs, which act as preferential nucleation sites for InAs QDs. Liang et al. used highly ordered AAO porous membrane as template for fabrication of hexagonal close-packed nanopore arrays on Si, GaAs, and GaN substrates via reactive ion etching (Liang, 2002). These nanopore structures were then utilized for QDs arrays formation from various metals and semiconductors (ZnO, TiO₂) through evaporation and subsequent etching. Kouklin et al. electrodeposited the hexagonal close-packed array of CdS QDs in a nanoporous AAO template and studied them by capacitance-voltage spectroscopy (Kouklin, 2000). The authors found that these structures are ideally suited for quantum-dot flash memories.

Lim et al. fabricated epoxy nanodots array sensors with sputtered Au electrodes for electrochemical determination of whole blood coagulation time. The authors used the titanium layer instead of aluminium for the replication of nanopatterns into epoxy (Lim, 2009). Even though the ordering of dimples in the titanium is not as good as that in the aluminium, the usage of titanium in this case was found more convenient due to the better hardness of titania and lower surface energy which facilitates the separation of a replica film from the substrate. The fabrication process started by anodization of a titanium foil, which leads to formation of highly ordered nanotubular TiO₂ film. After its removal by epoxy, the hexagonal nanoarrays on the titanium surface are formed similarly to those of the aluminum substrate after the removal of the first anodic oxide. The second epoxy film formation on the titanium substrate mold with hexagonally arrayed dimples. The height of created nanodots was around 28 nm and their diameter was 120 nm.

Nanoporous AAO membrane can also serve as a host material for a variety of magnetic materials which can be embedded for example by electrodeposition, sputtering or infiltration routes. The work of Jung et al. deals with the electrochemical growth of Ni nanodots array using the long-range ordered cylindrical alumina nanopores as a template created on titanium precoated silicon wafer (J. S. Jung, 2008). Such Ni nanodots array is suitable for high density data storage materials.

Another approach of AAO template usage was tested by Yan et al., who prepared the composite of highly ordered nanoporous AAO films loaded with ZnO nanoparticles (10.8 nm) by simple soaking the AAO films in an aqueous solution of zinc acetate followed by annealing at 500 °C (J. L. Yan, 2008). The composite exhibited intense and broad emission spectra in the wavelength range of 350–600 nm.

In other paper, the authors demonstrated an application of ultrathin porous AAO layers (about 50 nm) on Si as templates for Ba_xSr_{1-x}TiO₃ nanodot array fabrication (B. Yan, 2007). Furthermore, these aluminum oxide nanotemplates can be employed as lithographic masks to transfer the nanopattern into the silicon substrate.

Yang et al. prepared ordered arrays of Ta₂O₅ nanodots with diameter of 80 nm at the bottom and of 50 nm in height using AAO as a template (C. J. Yang, 2007). The structures were synthesized in a two-step anodization process from TaN (50 nm) and Al (1.5 μm) films deposited successively on p-type Si wafers. Similar approach was applied in the work of Vorozhtsova et al. and Mozalev et al., who used Ta layer as a starting material for Ta₂O₅ nanocrystals or nanocolumns fabrication through AAO template (Mozalev, 2009; Vorozhtsova, 2010). Ta₂O₅ is a material of great interest for fabricating capacitor, semiconducting and photonic devices as well as resistive humidity sensor. This is due to its unique properties such as high dielectric constant, low leakage current density, high index of refraction and low optical propagation losses. Its high dielectric constant and low leakage current density make it popular for a use in the next generation semiconductor electronics.

Li et al. fabricated the hexagonally ordered arrays of ferromagnetic nanodot with narrow size distribution by electron beam evaporation of Fe, Ni of $\text{Fe}_{20}\text{Ni}_{80}$ into AAO template and subsequent mask lift-off (C. P. Li, 2006). Moreover, exchange-biased bilayer nanodots were fabricated using argon-ion milling instead of the mask lift-off. The authors found that when magnetic dots are fabricated using mask lift-off, the phosphoric acid etching before magnetic materials deposition should be long enough to remove the alumina barrier layer remaining at the bottom of pores. Otherwise, the dots would also be removed during subsequent mask lift-off. On the other hand, with the argon-ion milling, the barrier layer cause any problems. Thus, shorter etching times resulting in smaller pore diameters can be used.

Next frequently used material in QDs array fabrication using AAO template is titanium dioxide. The group of researchers with Chen P. L. intensively studied the uniform nanodot arrays of titanium oxide prepared by electrochemical anodization of Al/Ti film stack on silicon (Chen, 2005), Al/TiN bilayered film on a sapphire (Chen, 2004) or TiN/Al films on silicon substrates (Chen, 2003). In the first case, the authors applied such self-organized nanodot arrays as the electron emission source in field emission triode device. In the second mentioned work, they found that the phase development of the isolated TiO_2 nanodots is very much different from TiO_2 thin films and powders. After high temperature annealing, the nanodots are polycrystalline and consist of a mixed phase of anatase and rutile instead of single rutile phase. While in the third work, the as-prepared nanodots were basically composed of amorphous TiO_x with a hexagonal arrangement and an average diameter of about 60 nm.

Similarly to these papers, Chu et al. reported the TiO_2 nanodots and nanorods (diameter of 20–100 nm, height of 30–260 nm and distance of 50–380 nm) fabricated by combined anodization from superimposed Al/Ti layers sputtered on glass substrates (Chu, 2005a, 2005b). These nanostructures can be applied e. g. as DNA sensors. The authors also tested new anodizing electrolyte, a diluted nitric acid solution, for fabricating uniform, self-organized, ordered nanoporous titania films with parallel cylindrical pores (pore diameter approximate to 30 nm and thickness around 1100 nm). After heating at 600 °C for 2 h, the nanoporous titania films exhibited high photocatalytic activity under UV illumination.

Cha et al. presented a method for fabricating SiO_2 nanodot arrays with average diameter of 68 nm through pattern transfer of self-organized tantalum oxide hard masks onto a Si wafer (Cha, 2004). Tantalum oxide nanopillar arrays are formed at the bottom of anodic aluminum oxide by electrochemical anodization of the Al/Ta films on a Si wafer. Then the tantalum oxide nanopillars were used as hard masks for formation of SiO_2 nanostructures. Ion milling was used for the pattern transfer. The density and diameter of the SiO_2 nanodot arrays could be controlled by varying the anodizing conditions.

3.2 Nanowires and nanotubes created by electrodeposition of metal ions

A variety of metal nanowires, including Ni, Co, Cu and Au with nominal pore diameters between 10 and 200 nm have been synthesized by electrodeposition. For example, Possin prepared various metallic nanowires using radiation track-etched mica (Possin, 1970). Likewise, Williams and Giordano produced silver nanowires with diameters below 10 nm (Williams & Giordano, 1984). Whitney et al. fabricated the arrays of nickel and cobalt nanowires, also using polycarbonate templates (Whitney, 1993). The growth of Au nanorod arrays has also been well studied (G. Z. Cao & D. W. Liu, 2008; J. G. Wang, 2004; H. W. Wang, 2006).

Vertically aligned nanowire arrays realized on interdigitated electrodes are very promising for applications where high active surfaces are needed, i.e. sensors and biosensors. Fabrication of nanoparticles takes place in electrolyte by inserting conductive substrate with a porous non-conducting mask. The conductive substrate represents a cathode. After applying a constant current between two electrodes, metal ions are attracted to the cathode. On the cathode, ions diffuse through the open pores to form nanowires, respectively nanotubes. After complete deposition, the porous mask is dissolved usually in NaOH (Matefi-Tempfli, 2009). The step by step anodization process is schematically illustrated on Fig. 2.

Fig. 2. Nanostructures fabrication process by template-based method: (a) Thin aluminum film with a intermetallic layer. Start of anodization process; (b) Progress of process; (c) Nanoporous template with oxide barrier; (d) Alumina layer with hexagonally arrayed pores created by anodization; (e) Nanostructures which are formed through the template; (f) Nanostructures after the template dissolving

The size of resulting structure is influenced by the geometry of porous mask. The diameter of nanoparticles and their mutual distance are given by the size of individual cells in relation to the pore size, so-called mask porosity. Creating a specific type of nanostructures depends on the mask and electrodeposition conditions. Length of the formed nanostructures is directly proportional to the current density and electrodeposition time. The amount of deposited material is based on Faraday's law. The growth of metallic nanostructures is also affected by temperature and solution concentration, electric potential and pH of the solution. The example of alumina template created in various electrolytes and characterized by SEM can be seen on Fig. 3.

The type of the structure is given by the specific conditions under which the nanostructures are being created. The probability of making nanotubes through a mask grows with the size of pores in the mask. Nanowires almost always occur at very small diameters of nanopores (20 nm). The most frequently used metals for the nanostructure fabrication are nickel, gold, palladium and silver. Some examples of the fabricated nanostructures observed under SEM analysis by Hubalek et al. are presented on following figures: nanotubes on Fig. 4 (left), Fig. 5 (left) and nanowires on Fig. 4 (right), Fig. 6 (left, right).

Fig. 3. Alumina layer with hexagonally arrayed pores (top view): Anodization process in $(\text{COOH})_2$ solution (left) and anodization process in H_2SO_4 solution (right)

Fig. 4. Nickel nanostructures: Ni nanotubes (left) and Ni nanowires (right)

Fig. 5. Gold nanostructures: Au nanotubes (left) and Au nanowires (right)

Fig. 6. Examples of metal nanostructures: Pd long nanowires (left) and Ag nanowires (right)

Very important parameter is the pH of the used electrolyte. At low pH values nanowires are created, while nanotubes grow at high values. It is possible that the formation of nanotubes is somehow connected with the release of gaseous hydrogen at the cathode (the metal layer on the bottom of the pores). This hydrogen release is just affected by the pH of the electrolyte. Among other parameters that were examined, if they have an impact on the type of nanostructures, was the current density. Nevertheless, it was found there was no correlation between the different values of current density and types of nanostructures. Moreover, it is assumed that usage of ultrasound during electrodeposition also affects the type of nanostructure. Even the influence of electrolyte concentration is not precluded (Klosova, 2006a, 2006b).

3.3 Nanotubes created by anodization of metal layers

Most of papers concerning the usage of template based methods for ordered nanotubes fabrication deal with titanium dioxide since this material has a very large surface area and thus it is very attractive for battery, gas sensor, photocatalytic applications, as biomaterial and so on. Li et al. reported a morphologic characterization of the anodic titanium oxide (ATO) films with highly-ordered titania nanotube arrays grown perpendicularly to a titanium foil (L. L. Li, 2010). The ATO film was annealed in an air furnace, forming anatase TiO_2 . After TiCl_4 post-treatment to enhance the ruthenium-based dye loading on the ATO surface, the optimized ATO arrays were used as a photoanode in a dye-sensitized solar cell. Zhao et al. investigated a novel solid state pH sensor fabricated by anodization of titanium substrate electrode (Zhao, 2010). They found the amorphous TiO_2 nanotubes had better pH response than TiO_2 nanotubes in anatase phase. After being irradiated by ultraviolet light (UV), the potential response of the electrode modified by amorphous TiO_2 nanotube was close to Nernst equation (59 mV/pH). Wang and colleagues employed vertically aligned TiO_2 nanotubes array film produced using electrochemical anodization of Ti foil followed by a nitrogen-doping process in order to form relative humidity sensors (Q. Wang, 2010). These sensors showed resistive and capacitive humidity-sensing properties in the range of 11.3–93.6 %.

Cao et al. discussed a layer-by-layer growth model of anodic TiO_2 nanotube arrays (C. B. Cao, 2010). Many phenomena appeared during the anodization and can be reasonably explained by this model, such as the first sharp slope of current in initial period, current fluctuation, occurring of ridges in adjacent tubes, and the rings broken off from the tube

mouths. Furthermore, key factors which determine the morphology of TNT are discussed which is helpful for the design of nanoarchitectures in related material systems.

Sennik et al. synthesized highly ordered, vertically oriented TiO₂ nanotubes arrays grown by anodic oxidation of titanium foil and investigated their hydrogen sensing properties in the temperature interval of 20–150 °C (Sennik, 2010). The fabricated TiO₂ nanotubes were approximately 1 μm in length and 90 nm in diameter. For the sensor measurements, two platinum pads were used as electrodes on the TiO₂ nanotube arrays. The authors found the sensitivity increased at higher temperature. The sensing mechanism of the TiO₂ nanotube sensor could be explained with chemisorption of H₂ on the highly active nanotube surface.

Similarly like previous authors, Joo et al. examined the formation of TiO₂ nanotube films on pure Ti, Ti-Pt, and Ti-Pd thin films by anodization in a mixture of glycerol and water (1:1 volume ratio) containing 0.5 wt % NH₄F (Joo, 2010). These nanotubes arrays were applied as a resistance-type hydrogen gas sensor. The Pt or Pd particles dispersed in the wall of nanotubes effectively improved the performance of the hydrogen gas sensor perhaps due to the acceleration of hydrogen chemisorption on the wall of the nanotube.

Mun et al. applied TiO₂ nanotube array in label-free sensing of rabbit immunoglobulin G (IgG) using optical interferometry (Mun, 2010). The authors examined the aqueous stability of the TiO₂ nanotube array and compared it with porous silica (SiO₂), which is a more extensively studied thin film optical biosensor. They found that TiO₂ nanotube array is stable in the pH range 2 to 12, whereas the porous SiO₂ sensor displays significant degradation at pH > 8.

Yang et al. studied properties and sensing applications of highly ordered TiO₂ nanotube arrays made by anodic oxidation in fluoride containing electrolytes (L. X. Yang, 2010). The effect of anodization parameters (electrolyte, pH, and voltage) on the titania nanotube size and shape were discussed. The excellent biocompatibility of TiO₂, the high orientation, the large surface area with tunable pore sizes, as well as the high electron transfer rate along with the nanotubes make TiO₂ nanotube array an ideal substrate for the sensor's fabrication and application. The sensors based on the TiO₂ nanotube arrays for sensing hydrogen, oxygen, humidity, glucose and hydrogen peroxide all exhibited low detection limit, high stability, very good reproducibility and high sensitivity.

Tan et al. prepared transparent, well-aligned TiO₂ nanotube arrays on glass substrates via atomic layer deposition of TiO₂ onto free-standing porous anodic alumina template (Tan, 2010). The authors investigated their photocatalytic activity on degradation of aqueous methylene blue solution and solid stearic acid film. They found that Pd functionalized TiO₂ nanotubes revealed the highest photodegradation efficiency thus these nanonstructures might have potential applications in self-cleaning coating, transparent electronics, and solar cells.

Similarly, Liu et al. tested the photocatalytic activity of self-organized, well-crystallized and high aspect-ratio TiO₂ nanotube arrays prepared by anodic oxidation in dimethyl sulfoxide containing 5 wt% HF at 40 V (vs. Pt) (Liu, 2009). The authors compared the TiO₂ nanotubes length influence on photocatalytic degradation of methylic orange. They observed that the photocatalytic efficiency of ultralong nanotubes (19.4 μm) arrays was 1.55 times as high as the short nanotube with length about 500 nm.

Hassan et al. fabricated TiO₂ nanotubes (TiNTs) using electrochemical anodization of titanium in 2-propanol/water containing 0.14 M NH₄F as the supporting electrolyte (Hassan, 2009). The authors studied the effects of the water content, time of anodization and potential on the growth behavior of TiNTs. The TiNTs obtained under optimum conditions had heights of up to 1800 nm and inner diameters of about 90 nm. The ellipsometric characterization confirmed the presence of a thin barrier layer at the nanotubes/metal

interface, which was enriched with the rutile phase, whereas the nanotubes were enriched with the anatase phase. Cho et al. prepared titanium oxide nanotubes via anodization of titanium in various electrolytes: 1 M KH_2PO_4 water solution, glycerine, and ethylene glycol with 0.15 M, 0.17 M or 0.075 M NH_4F (Cho, 2008). The maximum lengths of nanotubes were 3.0 μm in the case of KH_2PO_4 water solution under potential of 25 V, 14 μm in the case of glycerine under potential of 50 V and 164 μm in the ethylene glycol solution under potential of 60 V, respectively. Concerning the TiO_2 nanotubes diameters the smallest one was reached in glycerine (60 nm), then 100 nm using KH_2PO_4 water solution and 150 nm in ethylene glycol. The nanotubes annealed at 500 °C for 30 min appeared in the anatase phase.

Yoriya et al. described the fabrication of fully separated self-organized titania nanotube arrays by Ti anodization in diethylene glycol containing either HF or NH_4F (Yoriya, 2008). They studied the effect of the fluoride bearing species used in the anodization electrolyte on the tube morphology, degree of tube-to-tube separation, and crystallization.

On contrary to above mentioned papers, Hu et al. described the preparation of highly ordered, vertically oriented TiO_2 nanotube arrays using HF-free aqueous solution (Hu, 2009). The authors investigated the TiO_2 crystalline phase influence on photocurrent generated by an anode consisting of a titanium foil coated by TiO_2 nanotubes and a platinum cathode in an electrochemical cell. It was determined that the anatase crystalline structure converts light into current more efficiently and it is therefore a better photocatalytic material for hydrogen production via photoelectrochemical splitting of water. Other semiconducting material used for nanotubes fabrication through anodization process was studied by Hahn et al. (Hahn, 2010). Self-organized nanotubular layers of ZrO_2 were electrochemically grown by tailored anodization in an $(\text{NH}_4)_2\text{SO}_4$ electrolyte containing small amounts of fluoride ions. This semiconducting material is usually used as sensing layer of chemical gas sensors and humidity sensors. Photoluminescence and cathodoluminescence measurements revealed very bright white luminescence of as-grown ZrO_2 nanotubes, hence these nanotubes are suitable for optoelectronic applications.

3.4 Films

Berger et al. demonstrated in their work that highly ordered porous anodic zirconia (PAZ) arrays with cell diameters ranging from 70 to 120 nm can be grown in fluoride containing glycerol electrolytes (Berger, 2008). They showed that this morphology (in contrast to the typically observed nanotubular layers) can simply be obtained by controlling the water content in the electrolyte during the anodization process. It is proposed that the morphology transition from pores to tubes is based on the rate of preferential etching at the hexagonal cell triple points in the oxide.

Zhang prepared the highly ordered TiO_2 thin films by anodic oxidation followed by calcination at various temperatures (300, 400, 500 and 600 °C) (Zhang, 2008). The author investigated the humidity sensing behaviours of prepared samples. The samples calcined at 600 °C showed high sensitivity with nearly two orders change in the resistance and short response and recovery time (< 190 s) during the relative humidity variation from 11 to 95%.

Another method is the deposition of WO_3 thin films on highly ordered nanoporous alumina template. Nanoporous anodic oxide layers were formed by anodizing aluminum films in malonic acid electrolyte. Tungsten trioxide sensing films were deposited on the top of nanoporous alumina layers by rf magnetron sputtering of a metallic target (Fig. 7). The tungsten oxide gas sensing structures supported by nanoporous alumina templates showed high responsiveness to toxic gases, especially to NO_2 (Gorokh, 2006; Khatko, 2009, 2006; Vallejos, 2008).

Fig. 7. SEM images of cross-fracture (left) and the surface (right) of alumina films with sputtered WO₃

4. Conclusion

Described non-litographic techniques are based on template-assisted method. The template preparation of thin film with highly ordered pores is a suitable way for nanostructured material synthesis since they are cheap, fast and easy reproducible. Due to the special properties arising from their behavior, these highly ordered nanostructures can find various applications in environmental analysis as well as medicine and pharmacy.

In the case of environmental analysis application, the nanostructures are used to modify either the sensing elements from the semiconducting materials of vapor and gas sensors or the electrodes of electrochemical sensors.

Concerning the pharmacy and medicine, quantum dots (QDs) in planar form (so-called lab-on-chip) deposited on various solid surfaces seems to be a new approach of template-based method application. The sensor array created from separately deposited QDs, also called “fluorescence array detector”, can be used for in-vitro large-field imaging. This allows the easy detection of many different biomolecules at the same time, since each QD can emit the light at different wavelength. Electrochemical biosensors with functionalized electrodes for rapid detection and mass screening are very promising in near future in cases of pandemic and epidemic. Cultivation of cells on gold nanodots has also high impact in biochemistry research for medicine.

5. Acknowledgment

This work has been supported by Grant Agency of the Academy of Sciences of the Czech Republic under the contract GAAV KAN208130801 (NANOSEMED) and by Grant Agency of the Czech Republic under the contract GACR 102/08/1546 (NANIMEL).

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Microsensors

Edited by Prof. Igor Minin

ISBN 978-953-307-170-1

Hard cover, 294 pages

Publisher InTech

Published online 09, June, 2011

Published in print edition June, 2011

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