Nowadays, the era of miniaturization brings many demands on modification of common materials properties. In recent years, this challenge is well accepted in the field of nanotechnology. This work is focused on low cost technology of metal surfaces modification with high ordered metal nanowires or nanorods. Nanoparticles are composed of various metals such as Au, Ni, Cu, Pd or Pt. In the principle, the fabrication of nanostructured surfaces is based on electrodeposition of metal ions to the prepared nanoporous template of alumina oxide. The template was obtained by anodic oxidation of thin sputtered or evaporated aluminum film. The anodization process was performed under specific conditions such as voltage, temperature and suitable electrolyte. The changing of anodizing conditions can influence the geometrical parameters of templates and subsequently the diameter and position of nanowires, as well. The length is determined by the deposition time. The nanostructured surfaces have a wide spectrum of applications in the field of electronics, sensors, surface engineering and optics. The main goals of nanostructured surface are to increase the sensing area and the usage of nanoparticles influence on interference and light focusing in magnetic and biological applications.

Key words: anodized alumina, nanopores, micro sensor, intermetallic layer

1. INTRODUCTION

The using of template base methods is a very low cost technology in comparison with lithographic method and pore anodized alumina is one of templates base methods. Highly ordered nanopores in a thin-film alumina template have been prepared for electrochemical micro sensors fabrication with nanopatterned surface of electrodes. The template has been grown on the micro system composes by two gold comb-like electrodes. The template is used for nanopillars or nanotubes formation on the electrodes surface. The preparation highly ordered hexagonal pore [1,2,3] structure as template is done using anodization of Al film adhered on the micro system, which is the first phase of device fabrication. The second is the nanorods or nanotubes growing on the system. The anodized alumina (AA) as a template was used for its good dielectric properties and for ability of self ordering of aluminum under anodization [2,4]. The aluminum was directly evaporated on gold microelectrodes. The film thickness was obtained about 2 µm. The transformation thin aluminum film to nanopore alumina was reached by electrochemically controlled oxidation of aluminum. In this paper the two-step anodization [1] of thin Al film deposited on Si wafer was experimentally carried out with the aim to grow thin alumina on aluminum layer where alumina has double growing ratio causing high mechanical strain. Decreasing of the mechanical stress had to be done. The pore diameter and inter-pore distance vary in the range 15 – 30 nm and 20 – 50 nm respectively. Since 1995, when the self-ordered porous alumina was discovered, [2] the effort to utilize of that extremely interesting material started. Up to now, self-ordered porous alumina with many different parameters was obtained, e.g. porous templates with inter-pore distance from 50 nm to 500 nm. [3,4,5] After this invention, many groups begun to find a use in many spheres of science like electronic, magnetic, optoelectronic devices. Also, the porous alumina has been found the use in orthopedic surgery like a component in bone implants with low coefficient of friction. [6,7] But the most interesting sphere is the applications of anodized alumina (AA) with various materials in sensors technology. Especially, the AA is used for increase areas of sensors active layers. The AA has been
applied as template for deposition nanowires or nanotubes on substrate or as mask for etching tiny ordered motives. [8] Various forms of AA has been studied for different application. [5,9] AA, which is fabricated from aluminum foils with thickness 250 μm, is one of them. This process of porous alumina fabrication is managed very well and it is described on Fig. 1. The disadvantage of this template lies on its difficulty manipulation. Better way is to deposit aluminum thin film directly on the substrate and after that to anodize porous alumina. [8,10,15]. However, it requires deposition equipment and clean rooms. This technique has made possible fabrication of AA and subsequently nanowires on various metallic layers without necessity to solve problems allied to manipulation and dissolving of remainder aluminum. Therefore, this technique is more suitable for industry.

Nowadays we can see a tendency to fabricate still smaller sensors elements but it is required the same or higher sensitivity. [8] One of many solutions could be enlargement of detection area by force of nanopillars or nanotubes deposited on surface. The utilization of different AA templates makes possible to produce nanoparticles with various sizes. Unfortunately, there are still many outstanding challenges in production multi metallic systems with perfectly ordered nanoparticles surface.

2. EXPERIMNETS

Here, the fabrication process of the porous alumina is described. First, we used to N-type of silicon substrate for sputtering of thin aluminum film. The thickness of film was 2 μm and the purity 99,999%. The first problem of the AA creation was appeared at once with deposition of aluminum film. The film was not homogenous and it was molded by much bigger crystals than 100 nm. Crystal's boundaries were very apparent and deep. Fig. 2. They avoided the creation of ordered structure. [11] Indeed, the porous AA structure was created, but it was not absolutely applicable as a template for arrayed deposition.

Fig. 1. The porous alumina starts to grow on thin electrode and the pores are spontaneous formed to hexagonal structure (a). The aluminium layer is gradually consumed and the pores grow (b) to the point when the oxide barriers on aluminium/aluminium oxide interface on bottom of alumina templates touched on based metal electrodes. Next step are following: electrodeposition of metal through the pores (c), aluminium templates dissolution and exposing of nanowires (nanocolumns) (d).

Fig. 2. SEM image of the porous alumina surface anodized in sulfuric acid at 25V at 10°C. Anodization time was 13 minutes.
In the second experiment, the alumina film was deposited by vapor deposition (VD) method. The surface was glossier than sputtered film. In Fig. 3, the crystal's boundaries are evident but they did not affect the anodized process as much as in the first case. On the other hand, the problem with adhesion was appeared. The evaporated aluminum films were cracked or involved by anodization in many cases.

In both experiments, samples with alumina film were cleaned and degreased in acetone at first. After that, they were put on a cell, where the sample was the anode and a stainless steel was the cathode. Sulfuric acid at 10% was used as electrolyte. The temperature of electrolyte was ranging from 0 °C to 24 °C. The voltage was set on value 25 V. The electrolyte was rigorously stirred. [3, 12, 13] Samples were anodized between 13 minutes and 15 minutes. During this time, current value decreased to value of 100 μA. After that, samples were etched in 5% phosphoric acid at 39°C in ordered to open the pores and dissolve the porous barriers. The etching time was between 2 and 3 minutes. After 3 minute of etching, the ceramic structure was started breaking down. The pore diameter and inter-pore distance vary in the range of 15 – 30 nm and 20 – 50 nm respectively, see Fig. 4.

Anodization of thin aluminum film in oxalic acid was done [2,5,14] However, the result was unsatisfactory. The layer did not appear of porous structure. The result is shown in Fig. 5. The anodization of aluminum foil is easier to manage than the aluminum film.

Next the next application of the opened alumina, the template was used for the electrodeposition of nanowires. The metal used for experiments on the nanostructure growth was gold (component of electrolyte: 6 g.L⁻¹ of K[Au(CN)]₂ and 2.32 g.L⁻¹ of H₃BO₃). The current density of deposition over the total area of nanopores was usually 0.25 mA.cm⁻² for Au nanostructures. The deposition time was 10 seconds. The temperature of plating bath was approx. 50 °C. In the next phase, the filled template was dissolved in 5% H₃PO₄. The surface morphology and homogeneity of the fabricated samples were investigated with MIRA II Tescan field scanning electronic microscope operated at 1–30 keV in high vacuum mode. The original porous structure can be seen in Fig. 6.
RESULT AND DISCUSSION

Fig. 2 and 3 show that the alumina structures are not enough self-organized. The pores have been created chaotically and they have different sizes. Nanocrystals of aluminum are the main cause of this issue. The size of nanocrystals grows is time dependent. Nanocrystals of aluminum are evident in Fig. 2, where many defects can be found between nanocrystals. Using VD technique this problem was solved, see Fig. 3. The aluminum layer, which was deposited by sputtering, was turbid. On the other hand the layer, deposited by VD, had brilliant polished surface. Because the VD run in many steps and the alumina film has a thickness of 200 nm, nanocrystals do not grow up as much as nanocrystals in sputtered film. Therefore the alumina thin film deposited by VD is more quality.

Next issue is to improve the adhesion between silicon substrate, inter metallic layer and alumina film. One of the solutions is decreasing the stress, which is raised by the deposition process. The other solution is heating the substrate which results in better adhesion but it decreases the speed of deposition. Next solution is using different intermetallic layers like titanium or titanium dioxide which have better adhesion and they can also create porous structure by special conditions. The using of anodic porous titanium oxide is going to bring benefit due to its conduction advantages. Titanium dioxide can be used as conductive matrix for deposition of nanopillars. [6]

Another task is finding conditions for creating ordered porous structure. In comparison, it is much difficult to apply anodization by Two-step method because it often terminates in dissolving or breaking up of aluminum films by anodization at second step. This problem is much dependent on adhesion of alumina layer. Anodization in one step was success managed and conditions were determined but then an initiation of second step is done, it is necessary to dissolve a first anodized layer of AA. This part of fabrications is in progress during higher temperature in range 40 – 60°C and the anodization process is done at the same or lower a room temperature. This thermal difference causes very high mechanical stress between AA and bottom layer. The problem solving is in very slow increasing/decreasing of the temperature. The next very important condition is the electrolyte stirring. If the stirring is insufficient or it is stopped during anodization, free aluminum ions, which are usually stirred up in solution, begin to imbed on alumina surface. They cause the interruption of anodization process. [3] The stirring is very important for drawing-off rising hydrogen’s molecules from AA surface. They usually stay on alumina surface, where they are reduced from water.
molecules, if a position is suitable or intensity of stirring is small. They cause non-uniform anodization of some alumina areas.

CONCLUSION

The conditions of the anodization process using aluminum thin films deposited by evaporation and sputtering were found. The optimal conditions of anodization processes have been determined for the first step. The self-organized process of thin films is dependent on high purity, homogeneity of aluminum film and adhesion between aluminum and silicon layers. Finally the VD method shows to be more suitable for deposition of aluminum thin film on silicon substrate than the sputtering method. Through the obtained template, the array of nanowires was deposited on electro-conducting metal layer and the nanowires have got the same geometrical parameters such as porous anodic alumina. We believe that the reported method brings several benefits. The first one is a very simple preparation of nanowires-based vertically aligned structures directly on conductive electrode.

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