ELECTROCHEMICAL PROCESSES AND CHARACTERISATION OF DOPED TiO_2 THIN FILMS; RELATIONSHIP BETWEEN PREPARATION CONDITIONS AND NANOSTRUCTURE

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Abstract: *In this paper, we report an experimental study on electrochemical anodization using different acidic electrolytes of high purity Ti thin film deposited on silicon substrate by sputtering. The aim of this paper is to provide further insight into the nanostructures of undoped and doped titanium oxide layers prepared by anodization of pure titanium thin films deposited on silicon substrate by sputtering with different mixtures as electrolytic media and different doping procedures, using information provided by SEM, FTIR and Raman spectroscopy. Nanoporous titania was investigated in order to achieve an n-TiO_2/Si heterojonction by anodization and doped processes being compatible with silicon technology. The dependence of pore morphology and pore formation rate on process parameters was evaluated. In order to investigate the crystallization, after anodization, samples were annealed in a quartz tube furnace at different temperatures using nitrogen gas for annealing. The influence of electrolyte composition and annealing temperature on the nanostructure and morphology of the oxide layer and the changes induced by the heat treatment, were also investigated by SEM, FTIR and Raman spectroscopy. TiO_2 film was doped with phosphorus and palladium to improve electrical conduction.*

Keywords: ***Ti thin films, nanoporous doped oxide, anodization, and nanostructured thin films***

EXPERIMENTAL DETAILES

Nanoporous titanium oxide films were formed by titanium thin films deposited by sputtering on the silicon substrate, using different mixtures (with and without fluorinated compound) as electrolyte. Anodization was conducted at a low potential using a three electrodes system.Ti film (~ 90 nm) was deposited on silicon wafer substrate, p – type, 1 - 2 Ω×cm rezistivity, by DC magnetic sputtering.

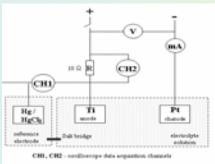

Figure 1 – Setup anodization cell

Figure 2 - Experimental assembly

The anodization was stopped when the current dropped to zero, proving the complete anodization of the Ti thin film.

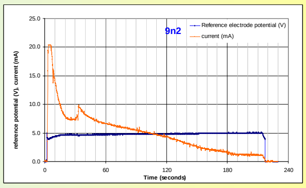

Figure 3 – Dependence of the current density on the anodization time

Morphologies of nanostructures, thickness dependence of TiO_2 layers and pores geometry on the parameters of the anodizing process was established from the SEM measurements.

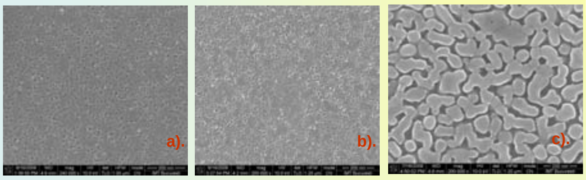

Figure 4 - SEM image of TiO_2 layer

a). Untreated; b). Treated at 723 K; c). Treated at 1133 K

The formation process of the porous structure and the change in surface morphology induced by heat treatments is evident. Annealing at 723 K in N_2 for 30 minutes proves improving of the anodic thin film (from amorphous to anatase phase) crystallization and increases its transparency. After annealing at 1133 K in N_2, for 30 minutes the anatase is converted in rutile phase.

CHARACTERISATION

The crystalline transformation into anatase phase of nanoporous TiO_2 after heat treatment at 723 K and 773 K was confirmed by Raman spectroscopy measurement.

From the Raman spectra one can conclude that the titania follows a structural transformation at each stage of the annealing process. At sample treated at 723 K, anatase phase becomes the major one proved by the bands at 144 cm^{-1} and 639 cm^{-1} of Eg Raman active mode in anatase crystal. As annealing temperature is increased over 773 K a rutile peak at 439 cm^{-1} grows.

The FTIR spectra of samples were recorded at 45°, in the 4000-370 cm^{-1} spectral range.

The FTIR spectra showed only the peak attributed to TiO_2 with no signals from the organic compounds and indicating the successful removal of organic groups following thermal annealing.

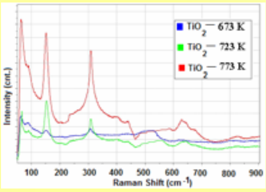

Figure 5 – Raman spectra of TiO_2 layers treated at 673 K, 723 K and 773 K

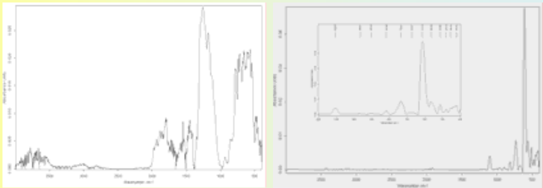

Figure 6 – ATR-FTIR spectra of TiO_2 before (a) and after annealing (b)

➢***TiO_2 film was doped with phosphorus and palladium to improve electrical conduction.*** Doping was realized using different processes like chemical deposition during anodizing process and low temperature treatment in a doping furnace at 723 K using nitrogen atmosphere for phosphorous and electrolyze of palladium chloride solution or a chemical reduction process of palladium chloride with hydrofluoric acid for palladium doping.

➢***The p-n junctions were measured from an electrical point of view.***

➢***The influence of used parameters was studied using SEM.***

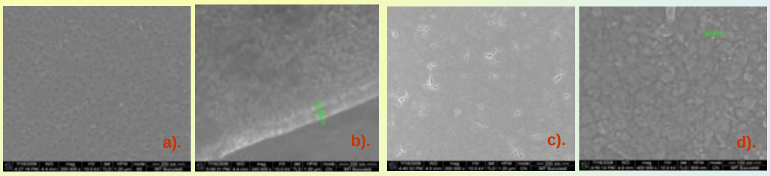

Figure 7 – SEM images for TiO_2 phosphorus doped

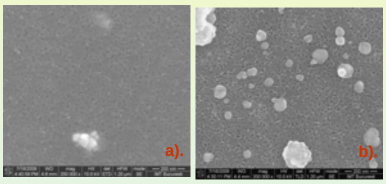

Figure 8 – SEM images for TiO_2 palladium doped

A relative uniform distribution of the doping substance can be seen on the surface of the oxide for samples presented in figure 7 a-d and 8 a. Chemical deposition of palladium in a solution of $PdCl_2$ 0,005% in DIP 1:10 leading us to a full defects layer related to the excess of Pd present there (figure 8 b).

CONCLUSION

- *The dependence of layers morphology on anodizing parameters was evaluated in order to optimize the process. The influence of anodization conditions (e.g. electrolyte composition, current density, pH and time) on the structure and morphology of the oxide layer and the changes induced by the heat treatment, were investigated using different methods.*
- *The best results have been obtained using a mixture of ammonium fluoride (0.42 %wt) - monoethylene glycol (84.32 %wt) – hydrogen peroxide (15.25 %wt) as electrolyte, at 5V applied voltage, anodization time 228 seconds and 303 K bath temperature.*
- *Annealing at 723 K in N_2, for 30 minutes proves improving the crystallisation of the anodic thin film (from amorphous to anatase phase) and increases its transparency. After annealing at 1133 K in N_2, for 30 minutes the anatase is converted in rutile phase.*
- *FTIR results indicate the presence of Ti-O, Si–O–Ti, Si–O, C-H, C-O, C-C and O-H/Ti-OH bonds for TiO_2 anodization film, whereas after heat treatment the peaks attributed to the organic groups and O-H groups disappeared. The band at 614 cm^{-1} demonstrates the synthesis of the TiO_2- anatase form.*
- *Doping with phosphorus and palladium improve TiO_2 films electrical conduction.*

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