# FORMATION OF POROUS SILICON/COPPER OXIDES/TITANIUM DIOXIDE HETEROSTRUCTURES

*Belarusian State University of Informatics and Radioelectronics, Minsk, Republic of Belarus*

*Denisov N. M.*

*Liahushevich S. I. – PhD, Associate Professor*

Composite porous silicon/copper oxides/titanium dioxide structures have been formed via electrochemical etching/deposition and sol-gel method. SEM has been employed in order to investigate structural properties. The key parameters of the obtained structures for photocatalytic applications are discussed.

Ecological safety of many modern industrial processes leaves much to be desired. Not only do the toxic emissions harm the environment, they are also resistant to conventional purification methods. One of its results is insufficient access to pure water sources, which is becoming a serious threat, as millions of children die from water-related diseases annually. However, photocatalysis, being an advanced oxidation method, is believed to have the potential to yield major steps in meeting clean energy demands and tackling environmental pollution.

$TiO_2$photocatalysis is widely used in a variety of applications and products in the environmental and energy fields. It is generally based on the process, in which a specific wavelength light absorption by a semiconductor leads to generation of electron-hole pairs, which then interact with the adsorbed molecules, turning them into active radicals. These radicals, namely •OH and •$O_2^-$, and other intermediate species are capable of reducing complex chemicals to $H_2O$ and $CO_2$.

One of the main drawbacks of $TiO_2$ is its wide band gap, which limits its activity to only ultraviolet spectrum region. Therefore, The CuO-$TiO_2$ materials, which are highly active photocatalysts, are of special interest, since they naturally absorb both visible and ultraviolet irradiation. Moreover, CuO, being a p-type semiconductor, is expected to form a p-n junction if combined with n-type $TiO_2$. Thus, the aim of this study is formation of porous silicon/copper oxides/titanium dioxide heterostructures.

The porous silicon substrate was formed via electrochemical etching of p-type silicon wafers in hydrofluoric acid solution. Subsequently, electrochemical deposition technique was employed to fill the pores with copper. Then the sol containing $TiO_2$ nanoparticles was obtained by mixing 9.6 g of 1-butanol, 0.16 g of acetylacetone, 0.78 g of titanium isopropoxide and 0.1 g of distilled water. Finally, the samples were covered with the sol by spin coating technique, and then dried and heated at 500 ºC in air.

The anodic etching of silicon wafer has resulted in formation of porous layer with the depth of approximately 15 µm and pore diameter of 0.5 – 1 µm. The pores have a cylindrical shape and are uniformly distributed along the surface of silicon.

The cathodic deposition of copper into porous layer has led to formation of faceted copper particles inside the pores. Diameter of the particles varies from 0.1 to 1 µm.

The performed sol-gel spin coating has resulted in formation of thin $TiO_2$ coating covering both porous silicon and copper oxides. The presence of $TiO_2$ in the obtained structures is not evident from the SEM images since both the contrast between different materials and magnification are low while the formed $TiO_2$ film is relatively thin.

Nevertheless, the oxidation of copper particles can be confirmed by the change of their shape. Faceted copper particles with sharp edges have become slightly roundish after the heating. Cupric oxide (CuO) mainly forms from copper at 500 ºC in air, although a small amount of cuprous oxide ($Cu_2O$) may also be presented.

The nature of the substrate, which in our case is porous silicon, plays an important role in photocatalytic processes. Its porosity benefits both the adhesion of the particles and the adsorption capacity, increasing the active surface area and diminishing the pollutant diffusion rate limitation during photocatalysis. The electronic properties of the substrate, such as band gap and conductivity type, also influence the behavior of photogenerated charge carriers.

The second important factor is the size of copper oxides particles. Ideally, copper oxides would form nanosized structures, which possess large surface area and evenly cover porous silicon to form heterojunction, while in our case the formed particles are relatively large and sometimes even block the entrance of the pores, decreasing the effective surface of the final structures. Unfortunately, the cathodic deposition technique has its limitations, especially in case of porous substrates.

Finally, considering the intended photocatalytic applications of these structures the optimal thickness of $TiO_2$ film is yet to be determined. On the one hand, it enhances charge separation and covers underlying copper oxides protecting them from aggressive chemicals. On the other hand, it reflects the considerable amount of visible light before it reaches the surface of copper oxides, decreasing electron-hole pairs' photogeneration efficiency.

In conclusion, composite porous silicon/copper oxides/titanium dioxide structures have been formed. Copper oxides microparticles deposited into the porous silicon and covered by thin $TiO_2$ layer have been observed on SEM images. Our future efforts are going to be focused on investigation of these structures' photocatalytic properties and their further improvement.

References

1. Leary, R. Carbonaceous nanomaterials for the enhancement of $TiO_2$photocatalysis / R. Leary, A. Westwood // Carbon. – 2011. – Vol. 49. – P. 741–772.

2.Nakata, K. $TiO_2$photocatalysis: Design and applications / K. Nakata, A. Fujishima // Journal of Photochemistry and Photobiology. – 2012. – Vol. 13. – P. 169–189.