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Study of formation, stabilization and properties of porous silicon and porous silica

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ABSTRACT

The large specific surface area of porous silicon (PS) gives it a high degree of chemical surface reactivity. Formation of silicon oxide (silica, SiO_2), via different oxidation methods (thermal or electrochemical) within the porous matrix turns out to be an additional factor of PS stability and an improvement of its chemical, structural, morphological, crystalline and optical properties. In this work, PS reactivity is justified by the presence of siloxane (SiOSi) and silanol (SiOH) free and bound sites. Oxidation and densification effects on mesoporous silicon layers properties were investigated. The influence of operating parameters (current density, electrolyte concentration, treatment time, temperature, and oxidizing gas) on PS morphology and oxide quality were assessed. Sample characterization was performed using FTIR, SEM, EDS, XRD and UV–Visible spectrophotometry. Our results showed that oxidation provides stabilization and chemical modification of PS specific surface by creation of SiOH and SiOSi active sites. The optical and crystalline properties are dependent on oxidation temperature. Wet thermal oxidation, preceded by a short dry oxidation under O_2, followed by densification under N_2, with an oxidation rate of greater than 62%, improves PS properties for a functionalization via silanization.

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1. Introduction

Porous silicon (PS) is a crystalline material obtained through pores structuration in a monocrystalline substrate. Its high specific surface area and its high reactivity makes it an excellent candidate for various recent applications, such as in biomedical and pre-clinical Imaging [1,2] photoluminescence [3,4], microsystems microstructuring [5], photovoltaic devices [6], optical devices [7] and chemical technology (gas sensors or bio-sensors) [8,9].

PS is a very unstable material that needs a passivation for stability purposes in order to resist pre-treatment protocols, functionalization, silanization, activation and/or grafting. Indeed, the anodized PS surface, freshly prepared, offers termini of hydrogen bonds (Si–H) which, according to Grossman et al. [10] and Jarvis et al. [11], provides a hydrophobic character. These surfaces show no resistance to ambient air and alkaline media treatment. The air surface contact causes a random and uncontrolled oxidation which strongly affect layers stability by surface oxide formation (SiOSi) of imperfect structure.

In order to stabilize PS surface layers and improve their properties (structural, morphological, crystalline and optical) an enhanced oxidation is necessary. Two main methods of oxidation are used: the electrochemical method and (wet or dry) the thermal method. They both lead to the formation of porous silica (OPS), rich in siloxane (SiOSi) and silanol (SiOH) active sites necessary to silanization and enabling increased reactivity of the porous surface. Indeed, Imai [12] is the first to have carried out an oxidation process to achieve insulating dielectric layers, basis of FIPOS process (Full Isolation by Porous silicon oxidized).

It was reported that PS oxidation particularly improves morphological and structural properties. Parasteh et al. [13] and González-Díaz et al. [6] showed, while studying evolution of the characteristics of infrared bands amplitude as a function of temperature and oxidation time, that SiO_2 formation, in pores outer layers and on silicon nanostructures, is accompanied simultaneously by a decrease in pore size, porosity, specific surface area and roughness while pore shape is maintained. Fang et al. [14] showed that, despite considerable decrease in mico-pores size and porosity with increasing temperature oxidation, stability of porous layers is improved, particularly at high annealing temperatures

However, very few studies on the effect of oxidation at high temperatures (1000 °C) on PS crystal structure changes are available. Cisneros et al. [15] showed that anodized PS, while keeping its

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