Porous silicon: morphology and formation mechanisms

Claude Lévy-Clément
CNRS-LCMTR 2/8 rue Henri Dunant, 94320 Thiais, France
levy-clement@glvt-cnrs.fr

Porous materials are generally obtained by localized electrochemical corrosion under anodic polarization (anodization). Some metals such as aluminum or stainless steel can be made porous. Comparatively a far larger number of semiconductors can be made porous, leading to important changes in the physical properties. The best and first known example is that of porous silicon, which exhibits strong photoluminescence in the visible range instead of the weak luminescence of bulk silicon. Since its discovery more than forty years ago and recognition of its porous nature ten years latter, it has attracted considerable research interest due to its morphological, electrical and optical properties which are different from those of bulk silicon.

Porous Si exhibits distinctive appearances. The size of the structures varies by three orders of magnitude, ranging from nanoporous silicon (including microporous and mesoporous Si) with pores and crystallites in the nanometer scale, up to macroporous silicon with pore and pillar dimensions in the micrometer scale. Qualitatively, the diverse morphological features of porous Si can be schematically summarized with respect to four different aspects: pore orientation, filling of macropores, branching and depth variation of porous Si. Generally, porous Si-formed p-Si and n-Si have distinct differences in term of pore size, orientation and degree of branching. Also porous Si formed in the dark and under back illumination are very different in these aspects. The formation process of porous Si is a very complex function of numerous factors, among which the doping concentration appears to show the clearest functional effect on morphology.

Many theories on the formation mechanisms of porous Si have emerged, but most of them have dealt with certain aspects of the very complex morphology and formation of porous Si (1). Two main categories of models have been proposed. The first one is basically electrostatic in nature, based on the consideration that physical effects associated with the SCR play a major role in the pore formation mechanism. The second category is based on computer simulations. The disadvantages of the most popular models proposed to explain porous Si formation are that they do not take into account the chemical aspects which may influence the kinetics at the Si/electrolyte interface.

Recently, an integrated view of formation mechanisms that can be coherent with various morphological features and with understanding of the fundamental anodic reaction process at the Si/electrolyte interface has been published by Zhang based on a very large body of information (2). During this lecture, the rich morphology of porous Si will be described in the light of this paper. The basic concept is that the formation of pores is the consequence of spatially and temporally distributed reactions at the semiconductor/electrolyte interface. The fundamental reason for the uneven distribution of reactions is that the rate of electrochemical reactions on a semiconductor is sensitive to the radius of curvature of the surface. This sensitivity can either be associated with the thickness of the space-charge layer or the resistance of the substrate. Because of the intricate relations among the kinetic factors and geometric elements, the detailed features of porous Si morphology and the mechanisms for their formation are complex and greatly vary with each situation. In summary, the diverse types of porous Si can be categorized in three groups: (i) Space-charge layer controlled: this include all porous Si formed except for the macro-porous Si formed on p-type Si and micro-porous Si formed under illumination (the diameter of the pores in these porous Si types is comparable to the width of the space-charge layer; (ii) Substrate resistance controlled: this include the macroporous Si formed on low doped p-Si; (iii) Photocarrier controlled: this includes all microporous Si formed under illumination. This approach allows for the first time to explain the formation of two-layer porous Si with a microporous Si on top of a macroporous Si.

Other semiconductors can be made porous, but their properties have been studied rather scantily. However, some important findings have recently been reported, in particular with porous III-V compounds. A comparative study with porous Si rich morphology and formation mechanisms will be presented.

References

1. "Macro Porous Micro Structures Including Silicon", *C. Lévy-Clément*, Chapter 3.2, in Semiconductor Electrodes and Photoelectrochemistry, S. Licht, Editor, ISBN 3-527-30250-6 (Vol. 6 in "Encyclopedia on Electrochemistry," A. Bard, Series Editor), WILEY-VCH, Weinheim, Germany, (2002).
2. X. G. Zhang, J. Electrochem.Soc. 151 (1) C69-C80 (2004).