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# MESOPOROUS GERMANIUM BY HIGH FREQUENCY BIPOLAR ELECTROCHEMICAL ETCHING FOR OPTICAL SENSOR APPLICATIONS

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## SUMMARY

Mesoporous germanium layers (MP-Ge) were prepared with high growth rate (up to 300 nm/min) by using a new high-current-density, high-frequency bipolar electrochemical etching (BEE) process. The potential of porous semiconductor layers for optical sensing has been assessed by examining the resonance wavelength shift in the reflectance spectra before and after infiltration of ethanol.

## 1. INTRODUCTION

Germanium has one of the largest refractive indices ( $n \sim 4.0$ ) amongst semiconductors, making it a promising material for optical applications. Additionally, porous germanium nanostructures have rapidly attracted attention over the last few years. Their unique properties have been leveraged for various uses, such as templates for epitaxial growth of III-V materials with high crystalline quality [1], Near-infrared emission from mesoporous Ge formed by electrochemical etching and the evidence that luminescence originates from quantum confinement effect have been also demonstrated [2]. Mesoporous Ge nanostructures have been prepared by a variety of chemical and physical techniques [3, 4]. But mesoporous nanostructures fabricated from electrochemical etching have some distinctive advantages: (i) high density of nanocrystals, (ii) pure material (iii) low fabrication cost. Despite all these advantages, the use of the electrochemical etching process to produce self-assembled Ge nanostructures remains limited. This is mainly due to the poor lateral homogeneity of the process and the relatively low growth rate.

## 2. EXPERIMENTAL RESULTS AND DISCUSSIONS

### *Preparation of mesoporous Germanium substrates (MPGe)*

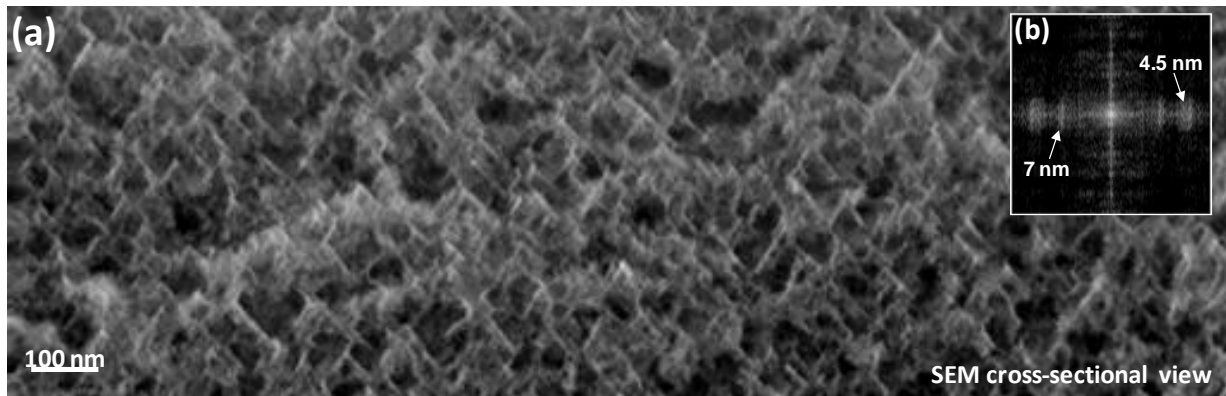
In this work, two types of experiment are reported, namely fast BEE and the classical BEE which is used as a reference. Both experiments are conducted for a total duration of 40 min in 49% HF solution. For the fast BEE, the current densities and duration of the anodic and cathodic pulses are respectively 20 mA/cm<sup>2</sup> for 0.05 s and -60mA/cm<sup>2</sup> for 0.05 s. For the classical BEE, the corresponding values are respectively 2 mA/cm<sup>2</sup> for 1 s and -2mA/cm<sup>2</sup> for 1 s.

### *Fast and Conventional electrochemical etching*

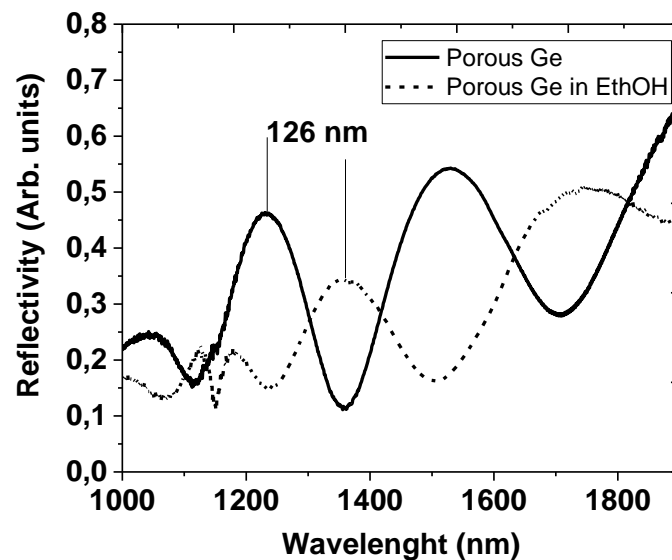
We have systematically studied the influence of the etching parameters on both the fast BEE and classical BEE processes. These parameters include: current density, electrolyte concentration, pore initiation on p-type Ge electrodes for the formation of mesoporous Ge layers. In particular, we have identified the parameters that lead to the formation of homogeneous, thick mesoporous layers with various morphologies and etching rates up to 6.2 μm/hour. We propose to use a controlled nucleation step, which consists in applying an initial very high direct current for 10 seconds before alternating the current. This procedure forces the nucleation of uniformly distributed mesopores. Then, by applying fast BEE, we obtain homogeneous MPGe with a porosity of 53% (see **Fig (1)**); we observe uniformly distributed mesopores with size of several nanometers. We also notice a diamond-like shaped pore formation following the <111> directions. On the opposite, by classical BEE, we obtain a total dissolution of porous Ge in the HF electrolyte with thick, high-porosity layers with a “spongy” morphology.

### *Reflectivity measurement*

Selective and accurate sensing of different chemical or biochemical analytes is currently a major need in many areas of industrial activity. We have chosen ethanol to demonstrate the value of PGe as a platform for analyte sensing. Porous germanium is emerging as a unique and promising material for sensing applications because of its sponge-like structure, high surface to volume ratio, low-cost, and compatibility with standard microfabrication technology. As can be seen from **Fig (2)**, during the ethanol adsorption, the Fabry-Perot oscillation fringes are red-shifted. This phenomenon is attributed to the capillary adsorption of ethanol within the pores. The ethanol-filled pores increase the structure overall effective refractive index and consequently increases its optical thickness. This effect promotes the wavelength shift in the reflectance spectrum.



**Figure 1:** (a) Cross-section SEM image of porous Ge layers formed at  $20\text{mA}/\text{cm}^2$  by Fast BEE technique. (b) Average crystallite size obtained by FFT.



**Figure 2:** Reflectance-FTIR spectra evolution of a  $1.8\ \mu\text{m}$  thick porous Ge layer with a 70% porosity fabricated by the fast BEE technique immersed in ethanol. A 126 nm red-shift is inferred with respect to the reference.

## 5. CONCLUSIONS

In conclusion, an optimized nucleation procedure by conventional BEE and fast BEE has been reported. It allows a much better lateral homogeneity of the mesoporous Ge layers. Furthermore, porous Ge offers the possibility to modulate its refractive index with its porosity and the effective medium; this quality is much appreciated for photonic applications. It could be an important building block for creating various photonic devices such as anti-reflection coatings, waveguides, biosensors and photonic crystals.

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