Electrochimica Acta 232 (2017) 422–430

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Fast growth synthesis of mesoporous germanium films by high frequency bipolar electrochemical etching☆

Youcef A. Bioud[a], Abderraouf Boucherif[a], Ali Belarouci[a,b], Etienne Paradis[a], Simon Fafard[a], Vincent Aimez[a], Dominique Drouin[a], Richard Arès[a,*]

[a] Laboratoire Nanotechnologies Nanosystmes (LN2) - CNRS UMI-3463, Institut Interdisciplinaire d'Innovation Technologique (3IT), Universit de Sherbrooke, 3000 Boulevard Universit, Sherbrooke, J1K OA5, Qubec, Canada
[b] Lyon Institute of Nanotechnologies INL, CNRS UMR 5270, Ecole Centrale de Lyon, Universit de Lyon, 36 Avenue Guy de Collongue, 69134 Ecully cedex, France

ARTICLE INFO

Article history:
Received 29 November 2016
Received in revised form 16 February 2017
Accepted 20 February 2017
Available online 24 February 2017

Keywords:
Porous germanium
Bipolar electrochemical etching
Nucleation
Passivation
Refractive index
Sensing

ABSTRACT

Mesoporous germanium (MP-Ge) has been predicted to play an important role in a wide range of potential applications. These porous Ge networks are characterized by physical and chemical properties that contrast with their bulk counterpart. For more than two decades, the methods that were used to synthesize these materials were extremely slow and yield non-uniform layers, which limit their applications. Here we demonstrate the synthesis of thick MP-Ge films with high growth rate (up to 300 nm/min) by using high-current density and high-frequency bipolar electrochemical etching. An optimized nucleation procedure is also reported. It enables a much better lateral homogeneity of the MP-Ge films. Following these results a refined electrochemical Ge etching model is proposed. The model is confirmed by Fourier Transform Infrared Spectroscopy and Cyclic Voltammetry measurements. Reflectivity measurements were also used to demonstrate that the effective refractive index of MP-Ge can be adjusted as a function of layer porosity. It has been reduced down to 1.76 due to the presence of the mesopores. Finally, a basic interferometric porous Ge sensor is demonstrated, a detection sensitivity of 711 nm/RIU was measured upon exposure to glycerol-water solutions.

1. Introduction

Recently, germanium (Ge) nanostructures have attracted a lot of attention because of their unique physicochemical properties, which differ significantly from those of bulk crystals. Due to their unique and versatile properties, nanocrystals, nanowires and porous forms of Ge have the potential to be used in a broad range of applications such as electrochemical energy storage [1], [2], sensing [3], [4], photovoltaics [5], microelectronics [6], and photonics [7]. Porous Ge is a very promising material and has been already leveraged for various uses, such as a template for epitaxial growth of III-V materials with high crystalline quality [8], a viable anode material of Lithium Ion Batteries [9] and has been predicted as an ideal candidate for thermoelectric applications [10]. Additionally, it was recently reported by Gerasimos *et al.* that mesoporous Ge (MP-Ge) with hexagonal pore ordering and very high surface area, exhibits strongly size-dependent optical properties as well as photoluminescence [11], [12]. Besides, near-infrared emission from MP-Ge formed by electrochemical etching is evidence that luminescence originates from quantum confinement effect [13]. Moreover, germanium has one of the largest refractive indices (n~4.0) amongst classical semiconductors, making it a promising material for optical applications. The synthesis approaches to fabricate Ge nanoparticles [14], [15] and nanowires [16,17], are well-established, but the routes to the large-scale manufacturing of porous materials are much less developed. Very few techniques are available to fabricate MP-Ge films by a variety of chemical and physical techniques, among them, spark processing [18], inductively coupled plasma chemical vapor deposition (ICPCVD)[19], Wet-chemical synthesis in a template mold [14], Se^+ and Te^+ ions implantation [20] or Ge^+ self-implantation [21], reduction alloying/dealloying approach [22] and electrochemical etching [23–26]. But mesoporous nanostructures fabricated from electrochemical etching have some

---

Abbreviations: MP-Ge, Mesoporous Germanium; FBEE, Fast Bipolar Electrochemical Etching; CBEE, Conventional Bipolar Electrochemical Etching; DC, Direct current; CV, Cyclic Voltammetry; LLL, Landau-Lifshitz-Looyenga; SCE, Saturated Calomel Electrode; QC, Quantum Confinement; SCR, Space Charge Region.

☆ Fully documented templates are available in the elsarticle package on CTAN.

* Corresponding author.

E-mail address: Richard.Ares@USherbrooke.ca (R. Arès).

http://dx.doi.org/10.1016/j.electacta.2017.02.115

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. In the recent years, bipolar electrochemical etching (BEE) has been introduced for the fabrication of porous Ge layers [27], [28]. For this technique, the anodic polarization is used for etching, while a cathodic polarization is used for the passivation of the already formed mesoporous layer to avoid its dissolution [23]. Buriak *et al.* produced porous n-doped Ge layers with thicknesses in a range of 1 μm to 15μm using highly concentrated HCl-based electrolytes diluted in ethanol [27], [29]. But, no structural details regarding the germanium layer were reported. A few years later, Foll *et al.* studied the nucleation and growth of n- and p-type porous Ge with various types of electrolytes, crystal orientations and doping concentrations [28]. However, the formation of MP-Ge layers with different morphologies by BEE have been reported for the first time by our groue [24]. An optimized anodic/cathodic sequence was used and showed very diverse nanoscale morphologies which allowed the observation of size dependent photoluminescence [30], [13]. Once more, the importance of anodic/cathodic ratio to engineer different morphologies has been reported [31]. But despite the effectiveness of BEE to form stable MP-Ge layers, etch rates obtained by this method on p-doped Ge are rather low, ranging between 15nm/min [30] and 50 nm/min [24]. So far, the etch rates obtained from the electrochemical etching of p-doped Ge are quite different from that of the n-doped type. For n-Ge, the material pore density, pore dimension and layer structure depend on the doping density and the crystallographic orientation of the wafer. However, for p-Ge, the holes are the majority carriers and are certainly omnipresent, which will lead to a uniform dissolution even without backside illumination [32]. As a consequence, etch rates during porous p-Ge formation is very slow, which is a major drawback, making the synthesis of MP-Ge time consuming and thereby preventing its large-scale deployment in many industrial processes. In this paper, we introduce a new technique called fast bipolar electrochemical etching (FBEE) to fabricate thick MP-Ge films with high growth rate (above 300nm/min). Additionally, we demonstrate an optimized procedure for nucleation that allows an enhanced uniformity in the pores formation and a much better lateral homogeneity of the MP-Ge films. Then, we propose a refined electrochemical model based on FTIR (Fourier Transform Infrared Spectroscopy) and CV (Cyclic Voltammetry) results. Finally, we report optical properties of MP-Ge layer by IR reflectivity measurements, as well as a first proof of concept of an optical interferometer device.

2. Experimental Section

Galvanostatic etching of germanium has been performed in a two-electrode electrochemical cell with a Pt wire counter electrode. The p^+ type Ge wafers are (100) oriented with a 6° miscut and have a nominal resistivity of 0.025 Ω.cm. The electrical contact was ensured by pressing the backside of the sample on a gold-coated copper electrode. The electrolyte is a 5:1 mixture of hydrofluoric acid (49%) and anhydrous ethanol. Two types of experiments are reported in this study, namely fast bipolar electrochemical etching (FBEE) and the conventional bipolar electrochemical etching (CBEE), which is used as a reference as shown in Fig. 1. Both experiments are conducted for a total duration of 40 min. For the FBEE, the current densities of anodic and cathodic pulses and their duration are respectively 20 mA/cm^2 for 0.04s and 60mA/cm^2 for 0.04s. For the CBEE, the current densities of anodic and cathodic pulses and their duration are respectively 20 mA/cm^2 for 1s and 20 mA/cm^2 for 1s. The morphology and thicknesses of the porous layers are extracted from the Scanning Electron Microscopy (SEM) pictures and the bulk porosity is determined by gravimetric measurements and IR reflectivity. All spectra were recorded with a VERTEX 80/80v FTIR spectrometer using a Globar source, a KBr beam splitter and a MCT D15 detector. The spectral resolution in transmission mode was 2.0 cm^{-1} with a total scanning time of 5 min. For FTIR microscopic reflectance analysis, a standard 15x objective is used with gold surface as reference. Cyclic Voltammetry (CV) was performed using an O-ring electrochemical cell. This cell consisted of a Teflon bath with a classical three-electrode arrangement: p-Ge substrate as a working electrode (WE), counter electrode (CE) being Pt wires and a saturated calomel reference electrode (SCE) HF resistant. The best results were obtained with an electrolyte consisting of 49% HF at 2°C.

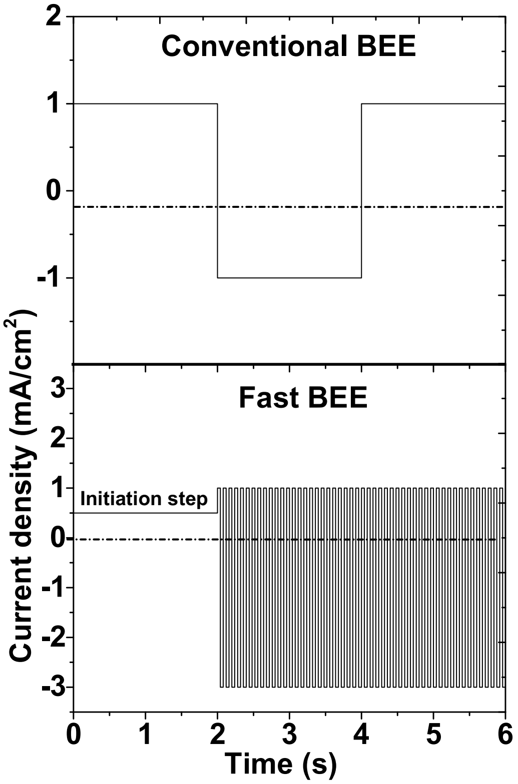

Fig. 1. Electrical etching regime of Conventional BEE and Fast BEE (note that in FBEE, the switching time is much faster than CBEE).

3. Results and Discussion

3.1. MP-Ge morphologies by CBEE and FBEE

The lateral homogeneity of porous Ge layers is of paramount importance for future applications of this material. Homogeneous porous Ge layers can be in many cases challenging to obtain as can be seen in Fig. 2a. Possible reasons for this inhomogeneity are a random initiation due to current lines, which pass preferentially through defects on the surface where the local electric field is amplified as shown in Fig. 2c. To circumvent this type of nucleation, we propose to use a controlled nucleation step, which consists to apply a higher direct current for 10 seconds before alternating current; this procedure forces the nucleation of uniformly distributed mesopores as shown in Fig. 2d. The result of this procedure is shown in Fig. 2b; we can clearly see a high difference of porous Ge spot quality after the initiation step.