Graphene-porous semiconductor nanocomposites scalable synthesis for energy applications

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Abstract. The aim of this work is to develop a cost effective and scalable fabrication process for graphene-enhanced porous semiconductor nanocomposite (GPNC). This class of materials combines the remarkable properties of graphene with the unique properties of porous semiconductors, such as porous silicon (PSi) and porous germanium (PGe). The experimental results show that these nanocomposites are chemically resistant to most of the commonly used microfabrication solutions and have enhanced electrical and thermal properties. Besides, we demonstrate the potential of graphene-porous germanium nanocomposite (GPGNC) for energy storage application.

1. Introduction
Integration of graphene-based composites presents a rising interest due to graphene’s unique properties [1]. Graphene sheets are usually fabricated on patterned and non-patterned surface by many techniques. In applications such as energy storage or sensing, the benefits of graphene are proportional to its surface area. There is a clear advantage in synthesizing graphene inside a solid with a high specific area, with the condition that a certain degree of crystallinity is maintained. Only few reports on graphene integrated into bulk matrix of porous semiconductors are found in literature, even though the porous materials seems as ideal hosts [2]. It was shown by Uhlir in 1956 [3] that electrochemically etched silicon (i.e. porous silicon (PSi)) has a large specific surface area, e.g. 900 m$^2$/cm$^3$ for 55% porosity. This property paved the way for new applications in optoelectronic, bio-sensors and energy harvesting. Salonen et al. were the first to associate porous silicon with carbon by using a non-catalytic synthesis technique [4]. This method was improved to create graphene-enhanced porous silicon nanocomposite (GPSNC) through an infiltration step. It was shown later on, that coating the porous Si with graphene, improves the chemical and thermal stability, as well as the electrical conductivity of porous structures. Recently, porous germanium (PGe) was developed by bipolar electrochemical etching [5]. Due to the higher electrical and thermal conductivities compared to PSi an improved efficiency is expected for similar applications. In this work, we report the first application of GPGNC as on-chip anode for lithium-ion batteries.
2. Fabrication

Our approach consists of two low cost and scalable process steps which are schematically illustrated in Figure 1. Firstly, the substrates are porosified by electrochemical etching to obtain a mesoporous layer. Further on, the porous layer is carbonized leading to a graphene coated porous semiconductor as shown below.

![Schematic view of the process to synthesize GPNC.](image)

2.1. Electrochemical etching

Commercially available, boron doped p-type Si (0.001 - 0.002 Ω·cm) and gallium doped p-type Ge wafers (0.01 Ω·cm) were porosified in a single bath electrochemical etching cell. The doping concentration of both materials was around $1 \cdot 10^{18}$ cm$^{-3}$. The wafers were (100) oriented with an miscut of 6° for Ge. In the case of Ge wafer, backside SiN film was removed by immersing the sample in HF(49%) solution at 25°C for 5 min. Next, the sample was dried under a N$_2$ flow and placed between the Cu working electrode and Pt counter-electrode. In the case of Si substrate, the porous layer was obtained by applying a pulsed current in a HF(49%):Ethanol (1:1, v-v) electrolyte. On the other hand, for Ge, the etching was carried out in a HF(49%):Ethanol (5:1, v-v) solution under non-symmetric pulsed bipolar current. Also, a pre-etching step was applied in order to increase the number of nucleation sites on the surface [5]. This leads to a homogeneous porosification. The morphology of both PSi and PGe is shown by cross-sectional SEM images in Figure 2-a and b.

2.2. Chemical Vapor Infiltration

Graphene coating was performed in a 2inch quartz tube furnace. To avoid the presence of oxygen, the pressure inside the furnace is maintained higher than atmospheric pressure. Initially, the samples were dried at 50 °C under continuous Ar flow. After a H$_2$ flow was introduced and added to Ar for 20 min. Further on, the temperature was increased up to 120 °C where the impregnation step was carried out under a C$_2$H$_2$ flux. The carbonization process was performed at a temperature of 500 °C for PGe and at 700 °C for PSi, respectively. Finally, the samples were cooled down to room temperature under Ar+H$_2$ flow. More details on carbonization process can be found in references [6, 7]. The presence of graphene-like material within the matrix was confirmed by Raman spectroscopy by observing carbon sp$^2$ and sp$^3$ orbital modes (see Figure 2-c below). It is an allotrope of carbon that exhibits a significant amount of sp$^3$-hybridized bond as evidenced by the D-band (~1350 cm$^{-1}$). From the Raman spectra, we can observe that the I$_D$/I$_G$ ratio is lower in the case of GPGNC sample (I$_D$/I$_G$ $\sim$ 0.7) compared to GPSNCG (I$_D$/I$_G$ $\sim$ 1.1). This may suggest a better graphene quality on PGe, that can be explained by the low miscibility of carbon into Ge which facilitates during carbonization the creation of sp$^2$ bond and limits the defect density [8].
3. Characterization

3.1. Chemical stability

Despite of its unique physical properties, PSi suffers from poor thermal and chemical stability [2]. In order to study chemical resistance of GPSNC, several solutions: fluoro-hydric acid (HF, 49%), potassium hydroxide (KOH, 30% at 80 °C), and most commonly used in microfabrication mixtures: Piranha (H₂SO₄:H₂O₂), RCA (H₂O₂:NH₄OH:H₂O₂) and HNA (HF:H₂NO₃:C₂H₄O₂) were tested. Also, the tests were applied for four different solvents: OptiClear, methanol, isopropanol and acetone to evaluate the passivation potential of graphene coating layer. Etching tests were performed during 5 min. The overall chemical resistance of PSi, PGe and GPSNC are represented in Table 1, based on the change in I_D/I_G ratio of graphene coating obtained from the Raman spectra.

| Sample     | Solvent        | HF | KOH | RCA | Piranha | HNA |
|------------|----------------|----|-----|-----|---------|-----|
| PSi        | ✓              | ✓  | ×   | ×   | ×       | ×   |
| PGe        | ✓              | ✓  | ×   | ×   | ×       | ×   |
| GPSNC      | ✓              | ✓  | ✓   | ✓   | ✓       | ✓   |
| GPGNC*     | ✓              | ✓  | ✓   | ✓   | ✓       | ✓   |

*Expected results without experimental confirmation.

Table 1. Chemical resistance of non-graphenized and graphenized porous Si and Ge semiconductors. Three symbols are used to describe the materials dissolution: "✓" resistant and "X" etching or morphological variation.

None of the solutions presented in this study were able to etch the GPSNC samples. Only a morphological change was observed for the one dipped in HNA. This behaviour is due to the presence of H₂NO₃ which reacts with carbon resulting in sample surface oxidation and nitration [9].

3.2. Physical properties

Three physical properties were mainly studied in literature concerning porous semiconductors and graphene-based porous silicon as shown in Table 2. Kolhatkar et al demonstrated two of them for GPSNC, i.e. thermal stability (R_T) and thermal conductivity for GPSNC [7]. More precisely, they showed GPSNC stability at 900 °C for 10 sec and the influence of coating quality on this stability. In the same work, thermal conductivities of PSi and GPSNC were measured using micro-Raman spectroscopy. The authors highlighted that graphene-coating induces any change in thermal conductivity at room temperature and at 120 °C. The decrease
in this conductivity value is mainly explained by a blocking of the phonon scattering due to the non-continuous porous structure.

| Sample | $R_T$ (°C) | $\lambda$ (W/(m.K)) | $\sigma$ (S/m) |
|--------|------------|---------------------|---------------|
| PSi    | 500        | 13 [7]              | $2 \cdot 10^{-6}$ |
| PGe    | 300        | 0.6 [10]            | $9 \cdot 10^{-4}$ [11] |
| GPSNC  | 900 [7]    | 17 [7]              | $1.2 \cdot 10^{-4}$ |

Table 2. Physical properties of non-graphenized and graphenized porous Si and Ge semiconductors

The electrical properties for PSi and GPSNC were studied by four probes I-V measurement, two at the top and two on the back of the sample. Only the transverse conductivity was measured. Before the measurements, aluminium metallization was performed by evaporation on both faces of the sample. Before etching, the electrical conductivities of silicon and germanium monocrystals are 2 S/m and 1 S/m respectively. After porosification, PSi and PGe conductivity decrease sharply as shown in table 2. This decrease can be explained by a carrier depletion due to low size of crystallites. Concerning GPSNC, the graphene coating provides an $60 \times$ higher conductivity. No measurement was performed on GPGNC sample, but a similar trend is expected.

4. Application as on-chip anode for Lithium-ion batteries (LIB)

There is an important interest to use GPSNC and GPGNC as anode for LIB. First of all, due to the high specific capacity of both Si (4200 mAh/g) and Ge (1900 mAh/g) and secondly, to the porous structure which offers free space for volumic expansion during lithiation and high specific area. The graphene coating plays an important role for protection against electrochemical degradation and limits the solid electrolyte interphase (SEI) layer formation [12]. The first on-chip GPSNC anode was shown by Oakes et al [13]. Later, Westover et al. [14] proved the use of GPSNC as supercapacitor anode as well as high power density anode. No studies on GPGNC on-chip anode have been reported up to now from our knowledge. In this work, a 1 cm$^2$ GPGNC anode was fabricated and packaged in a CR2032 cell with a 250 $\mu$l of DC/DMC electrolyte solution placed on the anode. Then, a Celgard paper was set as separator between...

Figure 3. a) Voltage profiles of GPGNC between 0.8 and 3 V vs Li/Li+ and b) Lithiation and delithiation curves with coulombic efficiency for 1000 cycles.
the anode and the pure Li cathode to avoid any short circuit. Pre-lithiation step was performed during 135h to activate graphene coating and form the SEI layer. In figure 3-a the battery voltage profile as a function of surfacic capacity is shown. Cycling was performed between 3 V and 0.8 V vs Li/Li+. This range was chosen to avoid the deep-intercalation of Li and the substrate lithiation. A decrease of irreversible surfacic capacity is observed from the first cycle up to the 500th. Figure 3-b shows the charge/discharge capacity at current rate of 10C. Thus, a high power density half-cell can be obtained with a surfacic capacity of 3 mAh/cm\(^2\) for 1000 cycles, which represents an energy density of 0.13 mWh/cm\(^2\). This result shows that GPGNC is promising material as high power density anode.

5. Conclusion

The advantages of the graphene coating on porous semiconductors properties were discussed. It was shown that this coating enhances the physical properties of porous semiconductor. Also, due to the chemical and thermal stability, the GPNC material can be used in microfabrication process of microdevices for on-chip energy conversion and storage applications.

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References

[1] Geim A K and Novoselov K S 2010 The rise of graphene Nanoscience and Technology: A Collection of Reviews from Nature Journals (World Scientific) pp 11–19
[2] Canham L 2014 Handbook of porous silicon (Springer)
[3] Uhlir A 1956 Bell Labs Technical Journal 35 333–347
[4] Salonen J, Laine E and Niinistö L 2002 Journal of Applied Physics 91 456–461
[5] Bioud Y A, Boucherif A, Belarouci A, Paradis E, Fafard S, Aimez V, Drouin D and Arès R 2017 Electrochimica Acta 252 422–430
[6] Boucherif A R, Boucherif A, Kolhatkar G, Ruediger A and Arès R 2017 Small 13 1603269
[7] Kolhatkar G, Boucherif A, Boucherif A R, Dupuy A, Fréchette L G, Arès R and Ruediger A 2018 Nanotechnology 29 145701
[8] Haller E, Hansen W, Luke P, McMurray R and Jarrett B 1982 IEEE Transactions on Nuclear Science 29 745–750
[9] Anglin E J, Cheng L, Freeman W R and Sailor M J 2008 Advanced drug delivery reviews 60 1266–1277
[10] Isaiev M, Tutushkono S, Jean V, Termentzidís K, Nychyporuk T, Andrusenko D, Marty O, międzEnc minister D, Lacroix D and Lysenko V 2014 Applied Physics Letters 105 031912
[11] Beattie M N, Bioud Y A, Hobson D G, Boucherif A, Valdivia C E, Drouin D, Arès R and Hinzer K 2018 Nanotechnology 29 215701
[12] Chatterjee S, Carter R, Oakes L, Erwin W R, Bardhan R and Pint C L 2014 The Journal of Physical Chemistry C 118 10893–10902
[13] Oakes L, Westover A, Mares J W, Chatterjee S, Erwin W R, Bardhan R, Weiss S M and Pint C L 2013 Scientific reports 3 3020
[14] Westover A S, Freudiger D, Gani Z S, Share K, Oakes L, Carter R E and Pint C L 2015 Nanoscale 7 98–103