ChemComm

Preparation and functionalization of hydride terminated porous germanium†

Hee Cheul Choi and Jillian M. Buriak*

Department of Chemistry, 1393 Brown Laboratories, Purdue University, West Lafayette, IN 47907-1393, USA.
E-mail: buriak@purdue.edu

Received (in Irvine, CA, USA) 17th May 2000, Accepted 20th July 2000

Porous germanium (PG) is prepared by a novel bipolar electrochemical etching (BEE) technique; scanning electron microscopy (SEM) clearly reveals formation of a porous layer up to a few microns thick that is Ge–H$_x$ terminated as indicated by FTIR spectroscopy; the hydride terminated PG material is quite resistant to oxidation, even under thermal conditions, but can be induced to undergo hydrogermylation reactions with alkenes and alkynes.

Porous semiconducting materials are a topic of intense interest because of their unique electronic,[1] optoelectronic,[2] and morphological[3] properties, and biocompatibility[4] characteristics. Up to now, the vast majority of research efforts have concentrated on porous silicon, although other materials such as porous GaAs, InP, SiC, Si_xGe_{1-x}, GaP, and GaN,[5] have also been investigated to a lesser extent. The unusual light emitting properties of porous silicon through photo-, electrochemi- and chemi-luminescence routes are a result of the highly complex nanoscale architecture. Embedded nanocrystallites and nanowires of silicon within the porous silicon matrix exhibit quantum confinement effects, and thus the material acts very differently from the bulk parent. There is a surprising dearth of knowledge about porous silicon's congener, porous germanium (PG), and thus any potentially important properties intrinsic to this material remain unknown. There are two published procedures[6,7] for preparation of PG involving an anodic etch with aqueous HF electrolytes, but in our hands yield an oxidized surface instead of hydride terminated germanium surface. Little morphological investigation and no chemical reactivity studies have been carried out on the reported PG surfaces prepared in this manner.[8,9] Here, we describe the formation of highly ordered PG with a nanoscale architecture, as determined from plan and cross-sectional views of the porous layer by scanning electron microscopy (SEM), utilizing a novel and reproducible etching technique, termed *bipolar* electrochemical etching (BEE), with an HCl-based etchant. Through transmission FTIR studies of the PG, we have determined that the surface is Ge–H$_x$ terminated, and can undergo surface hydrogermylation reactions with alkynes and alkenes, yielding alkenyl and alkyl terminated interfaces respectively. Light emission upon UV irradiation is also observed at 77 K in air.

The porous germanium (PG) was prepared from polished single crystalline Ge(100) wafers, either n- or p-doped, using an ethanoic HCl solution (1 : 1.8 of 48% HCl : EtOH v/v) in air. A wide variety of conditions were examined, but only a bipolar electrochemical etching (BEE) procedure produced the desired results.‡ BEE was carried out in a homemade Teflon etching cell, identical to that used to prepare porous silicon.[10] Initially, the germanium surface is anodized at 350 mA cm^{-2} for 5 min, followed by cathodization for 1 min with a negative bias, at the same current density, as outlined in Fig. 1. Longer cathodization leads to surface damage due to electropolishing. Upon anodization, the surface turns visibly gray, and is believed to be composed of surface hydroxide or surface chloride, as suggested by the lack of Ge–H$_x$ vibrations in the transmission FTIR spectrum and literature precedent.[11] Scanning electron microscopy indicates formation of a *ca*. 700 nm thick amorphous layer after 2 min anodization, which fully dissolves after 5 min, leaving no observable film on the surface of the bulk germanium within the resolution of the instrument (10 nm). Germanium oxide is soluble in aqueous solution, and thus appears to be formed transiently before dissolution under these conditions. The subsequent cathodization step is critical for formation of the porous layer and hydride termination. Presumably, the weak Ge–Ge bonds are protonated under the cathodic potential[11] which eventually leads to GeH_4 production, and dissolution of the bulk germanium, resulting in hydride termination and pore formation[12] (Fig. 1). Formation of thin porous layers on silicon has been reported under cathodic conditions.[13] Without the prior anodic step, only hydrogen evolution from the cathodic germanium electrode occurs. The PG layer shows false colors due to Fabry–Perot fringes, resulting from constructive and destructive interference of the reflected white light from the top and bottom of the thin porous layer, as is observed with thin porous silicon layers.[14,15]

Scanning electron microscopy (SEM) clearly reveals PG in both cross-sectional and plan views (Fig. 2) for both n- and p-type wafers. The porous layer of a PG sample prepared from n$^+$ Ge is *ca*. 15 μm thick (Figs. 2(*a*) and (*b*)), and features down to the resolution of the instrument, *ca*. 10 nm, can be discerned.

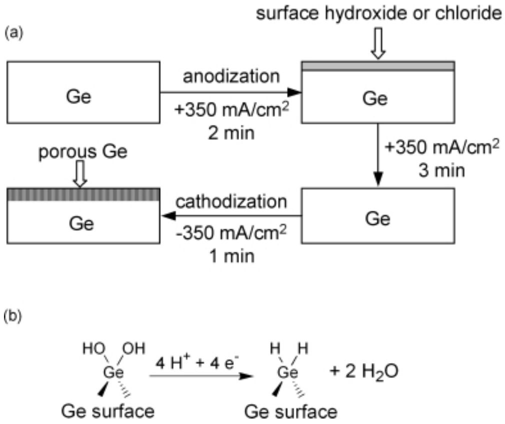

Fig. 1 (*a*) Schematic representation of the bipolar electrochemical etching (BEE) of Ge(100) wafers. (*b*) Surface electrochemical conversion of oxidized Ge(100) surfaces to hydride-terminated Ge(100) under cathodic bias in an acidic medium.[12]

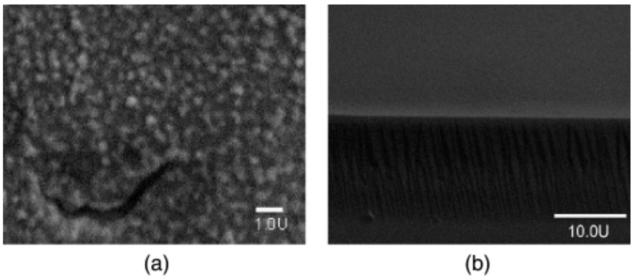

Fig. 2 Plan (*a*) and cross-sectional (*b*) views of n$^+$ type derived PG.

---

† Electronic supplementary information (ESI) available: FTIR thermal stability measurements and SEM images. See http://www.rsc.org/suppdata/cc/b0/b004011h/

DOI: 10.1039/b004011h

The pores are tilted by 9° from the surface normal due to the 9° miscut of the starting wafers. The thickness of the porous layer can vary somewhat across an etched surface (1–15 μm), most likely due to heterogeneities in the electrical field during the etch as a result of the simplicity of our set-up. PG prepared from p-type Ge shows similar features, and is *ca.* 1.5 μm thick (Figs. 2(*c*) and (*d*)). Higher magnification of the surface layer in plan view of either n- or p-type samples reveals a highly porous top layer in the center of the 0.3 cm^2 etched area (Fig. 2(*a*) and (SI5†)), which progressively becomes populated by crystallites with an average size of 500 nm towards the edge.†

FTIR analysis of PG reveals a broad ν(Ge–H$_x$) vibration with features at 2044 cm^{-1} and 2015 cm^{-1}, as shown in Fig. 3(*a*), which appear at slightly lower energies than gas phase Me$_{4-x}$GeH$_x$.[16] Oxygen back-bonded Ge–H$_x$ vibrations, expected at higher energies[11] are not observed. Because of the surface roughness and broad Ge–H$_x$ stretching region, it is expected that the surface is terminated with mono-, di- and trihydrides, like porous silicon.[17] In order to definitively prove the formation of the Ge–H bonds, a deuterated surface (Ge–D$_x$) was made by same etching technique using deuterated ethanol and DCl solution. The resulting Ge–D$_x$ stretching mode appears at 1455 cm^{-1}, as expected, with a very weak Ge–H$_x$ band observed at 2020 cm^{-1} (Fig. 3(*b*)). The thermal stability of the hydride termination is surprising and is described in the ESI†.

In order to determine whether the hydride terminated PG surface could be functionalized, hydrogermylation of alkynes was examined. Refluxing a PG sample in a 20% 1-dodecene solution in mesitylene (v/v) for 2 h resulted in incorporation of surface-bound dodecyl moieties[18] (Fig. 3(*c*)). Application of other known reaction conditions for formation of Si–C bonds on porous and flat silicon to PG were unsuccessful, including Lewis acid[19] mediated hydrogermylation, and Ge–Ge bond attack with Grignard reagents.[20] The crystalline PG structure may be more sensitive to Lewis acids and nucleophilic attack under these conditions. In any case, the surface of PG may be tailored through thermally induced hydrogermylation reactions.

Homogeneous red photoluminescence is observed by eye across the entire PG surface at 77 K in a darkened room upon illumination with 365 nm irradiation, but is considerably weaker than that observed from porous silicon; the weak light emission, unfortunately, fell below the optical detection limit of our CCD set-up, and thus a $\lambda_{\max}$ could not be collected. Samples etched only anodically, as opposed to the bipolar etching procedure, on the other hand, emit yellow-white photoluminescence under 254 nm UV illumination at 77 K. Since there are no observable Ge–H$_x$ bonds formed after anodization by FTIR, nor a porous layer by SEM, the source of the photoluminescence is believed to arise from germanium oxide layers, as opposed to germanium nanoparticles. This supposition is supported by the fact that all emission is eliminated after washing the sample with 25% aqueous HF, while the Ge–H$_x$ terminated samples are unaffected. We propose that the weak red light emission observed from Ge–H$_x$ terminated PG arises from Ge nanoparticles, whilst that from the anodically etched samples results from oxide.

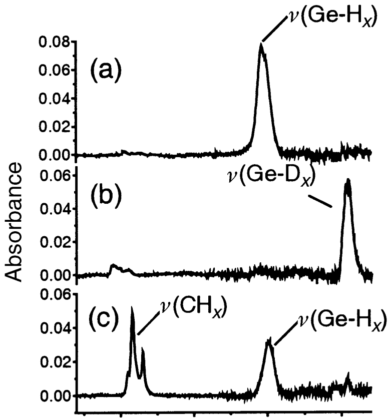

Fig. 3 FTIR spectrum of PG: (*a*) etched by BEE using ethanoic HCl, (*b*) using deuterated ethanol and DCl, and (*c*) thermally hydrogermylated using 1-dodecene.

To summarize, we report a new and highly reproducible etching procedure to produce hydride-terminated porous germanium. Through a bipolar HCl etch, porous layers up to 15 microns thick can be prepared and subsequently functionalized with alkyl monolayers through a thermally induced hydrogermylation reaction. Detailed mechanistic studies are presently underway in our laboratories to further elucidate the complex etching process. Optimization of the etching procedures through a better understanding of the PG formation process should permit us to improve the light emission from this material.

Notes and references

‡ *Experimental*: electrochemical etching of Ge was conducted using highly P doped (100) n-type (0.004–0.020 Ω cm) or Ga doped p-type (7–23 Ω cm) Ge wafers in a homemade Teflon etching cell equipped with an aluminium tongue in contact with the Ge wafer, and a Pt loop wire as a counter electrode, and ethanoic HCl (1 : 1.8 of 48% HCl : EtOH v/v) as the etchant/electrolyte. A Princeton Instruments 273 potentiostat was utilized as the current source. 350 mA cm^{-2} current density was applied for 5 min during anodization of n-type Ge followed by cathodization with the same current density. Light illumination was applied during cathodization for the p-type PG to harness the photocurrent, allowing for this high current density to pass. Thermal hydrogermylation of the PG was performed in a Schlenk flask with 20% 1-dodecyne in mesitylene solvent under nitrogen atmosphere, and was refluxed at 250 °C for 2 h. After completion of the reaction, the sample was washed with CH$_2$Cl$_2$, THF, ethanol and pentane, then dried under N$_2$ stream. All FTIR spectra were taken with a Nicolet Nexus FTIR spectrometer 670 equipped with a MCT detector cooled with liquid nitrogen. SEM images were taken using a JEOL JSM-35CF scanning electron microscope at an accelerating voltage of 10 kV.

1 M. V. Wolkin, J. Jorne, P. M. Fauchet, G. Allan and C. Delerue, *Phys. Rev. Lett.*, 1999, **82**, 197.

2 L. T. Canham, T. I. Cox, A. Loni and A. J. Simons, *Appl. Surf. Sci.*, 1996, **102**, 436.

3 A. G. Cullis, L. T. Canham and P. D. J. Calcott, *J. Appl. Phys.*, 1997, **82**, 909.

4 J. Wei, J. M. Buriak and G. Siuzdak, *Nature*, 1999, **399**, 243.

5 (*a*) P. Schmuki, D. J. Lockwood, H. J. Labbe and J. W. Fraser, *Appl. Phys. Lett.*, 1996, **69**, 1620; (*b*) T. Takizawa, S. Arai and M. Nakahara, *Jpn. J. Appl. Phys. 2*, 1994, **33**, L643; (*c*) A. G. Cullis, L. T. Canham and P. D. J. Calcott, *J. Appl. Phys.*, 1997, **82**, 909; (*d*) J. N. Chazalviel, R. B. Wehrspohn and F. Ozanam, *Mater. Sci. Eng. B*, 2000, **69**, 1.

6 S. Miyazaki, K. Sakamoto, K. Shiba and M. Hirose, *Thin Solid Films*, 1995, **255**, 99.

7 S. Bayliss, Q. Zhang and P. Harris, *Appl. Surf. Sci.*, 1996, **102**, 390.

8 S. Bayliss, L. Buckberry, P. Harris and C. Rousseau, *Thin Solid Films*, 1997, **297**, 308.

9 S. S. Chang and R. E. Hummel, *J. Lumin.*, 2000, **86**, 33.

10 E. J. Lee, T. W. Bitner, J. S. Ha, M. J. Shane and M. J. Sailor, *J. Am. Chem. Soc.*, 1996, **118**, 5375.

11 F. Maroun, F. Ozanam and J.-N. Chazalviel, *J. Phys. Chem. B*, 1999, **103**, 5280.

12 E. A. Efimov and I. G. Erusalimchik, *Electrochemistry of Germanium and Silicon*, Sigma Press, Washington D.C., 1963.

13 S. P. Zimin, M. N. Preobrazhenskii and D. S. Zimin, *Tech. Phys. Lett.*, 2000, **26**, 12.

14 A. Janshoff, K. P. S. Dancil, C. Steinem, D. P. Greiner, V. S. Y. Lin, C. Gurtner, K. Motesharei and M. J. Sailor, *J. Am. Chem. Soc.*, 1998, **120**, 12108.

15 K. P. S. Dancil, D. P. Greiner and M. J. Sailor, *J. Am. Chem. Soc.*, 1999, **121**, 7925.

16 D. F. Van De Vondel and G. P. Van der Kelen, *Bull. Soc. Chim. Belg.*, 1965, **74**, 453.

17 P. Gupta, A. C. Dillon, A. S. Bracker and S. M. George, *Surf. Sci.*, 1991, **245**, 360.

18 A. B. Sieval, V. Vleeming, H. Zuilhof and E. J. R. Südholter, *Langmuir*, 1999, **15**, 8288.

19 F. Glocking, *The Chemistry of Germanium*, Academic Press, New York, 1969, p. 85.

20 J. L. He, Z. H. Lu, S. A. Mitchell and D. D. M. Wayner, *J. Am. Chem. Soc.*, 1998, **120**, 2660.

21 K. Choi and J. M. Buriak, *Langmuir*, 2000, in press.