Enhanced photoluminescence of ordered macroporous germanium electrochemically prepared from ionic liquids

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Abstract: Recently we reported our results on the successful synthesis of 3-D highly ordered macroporous (3DOM) structure of germanium via the template-assisted electrochemical deposition from air- and water stable ionic liquids. Herein we report our new results on the photoluminescence (PL) properties of the obtained ordered macroporous Ge and the Ge/polystyrene composite opal structure. The latter showed a strong green emission compared to a Ge film and a Ge inverse opal. The enhancement of PL intensity was ascribed to the disorder multiple scattering in polystyrene colloidal crystal structure which increased both the excitation light absorption efficiency and the light extraction efficiency. The X-ray photoelectron spectroscopy (XPS) results suggested that the ordered macroporous Ge was capped with an oxide layer including a considerable amount of GeO$_2$. The observed green emission (539 nm) was related to GeO$_2$, likely resulting from the Ge-O bond related intrinsic defects.

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1. Introduction

Since Yablonvich and John proposed the idea of photonic bands in periodic dielectric structures in 1987, these materials have attracted much attention for future optical devices [1,2]. The optical properties of photonic crystals (PCs) are entirely determined by a photonic band gap (PBG). It has been theoretically demonstrated that a full PBG can exist if the dielectric constant (ε) of the backbone is 7.8 or higher [3]. Therefore, much effort has been devoted to the synthesis of various semiconductor photonic crystals, especially Si and Ge inverse opal PCs. The routes mainly include chemical vapor deposition (CVD) [4], electrodeposition [5], and sol-gel techniques [6].

Germanium has the highest dielectric constant (ε = 16) among materials that are transparent in the near infrared (IR) regime (λ>1850nm) [7]. It also has quite a high refractive index (n = 4.12 at λ = 2 μm), making it a very promising candidate for photonic applications in the IR spectral range. As the width of the photonic band gap in a photonic crystal increases with the dielectric contrast, germanium PCs in the periodic structure can deliver wider PBGs than those made of silicon, which makes it to be the best material for producing a wider PBG. Moreover, in comparison with the electronic properties of silicon, germanium has smaller effective masses for electrons and holes, and the energy difference between the indirect energy gap (0.67 eV) and the direct one (0.8 eV) is smaller (E = 0.13 eV). Germanium also has a larger effective excitonic Bohr radius (24.3 nm) which implies that the quantum confinement effect could be easier achieved and is more prominent. The observation of visible luminescence in the nanostructured porous silicon and germanium have attracted much attention recently. It has been found that Ge quantum dots embedded in Si matrices exhibit photoluminescence (PL)
originating from the spatially indirect no-phonon recombination between holes confined within the Ge dots and electrons from the conduction band of Si [8].

From the optical and electronic properties mentioned above, it can be concluded that germanium has quite a high potential as an excellent material for PCs. The main drawback associated with synthesizing high quality Ge PCs has been the need of ultra high vacuum techniques like CVD. However, recently we reported, for the first time, that 3-dimensional highly ordered macroporous (3DOM) germanium can be prepared by a simple and relatively cheap electrochemical pathway [9]. The process is quite simple: Germanium is electrodeposited inside polystyrene (PS) colloidal crystal templates (on ITO glass) with sphere sizes of e.g. 370 and 560 nm from the air- and water stable ionic liquids, 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([HMIm]FAP) and 1-ethyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)amide ([EMIm]Tf$_2$N) containing (each) GeCl$_4$ as a Ge source, respectively. The template was then removed by simply dissolving in a suited solvent like tetrahydrofuran (THF). The obtained 3D structure, which is a replica of the template (opal) and called inverse opal photonic crystal, consisted of air spheres arranged on a face-centered cubic (fcc) lattice. Interestingly, the whole sample which had a surface area of 0.3 cm$^2$ (only limited by the size of the electrochemical cell) showed strong Bragg reflections upon changing the angle of incident of visible light which can be seen even by the naked eye (see references 9 and 10 for details). This demonstrated the potential of our method to obtain high quality Ge PCs.

The PBG structure and spectra properties of Ge PCs have been widely studied in literature, but a detailed study on the PL properties of Ge PCs has not been given yet. In the present paper, we report for the first time on the PL properties of ordered macroporous Ge and germanium-filled PS colloidal crystal nanocomposites. The 3DOM structure of germanium was prepared via the template-assisted electrochemical deposition in air- and water stable ionic liquids from GeCl$_4$. The effect of the PBG on the PL emissions of the bare and composite structure of Ge PCs is studied. The origins of emission and the enhancement of the PL intensity in the Ge PCs are discussed.

2. Experimental

Germanium was deposited from 0.1 M GeCl$_4$ in [HMIm]FAP. The ionic liquid was purchased in the highest available (ultrapure) quality from Merck KGaA (Germany) and was used after drying under vacuum at 100 °C to a water content of below 1 ppm. GeCl$_4$ (99.9999%) was purchased from Alfa Aesar. The working electrode was indium tin oxide (ITO) coated glass with a polystyrene colloidal structure on top of it. A Pt ring was used as a counter electrode and an Ag wire was used as a quasi-reference electrode. Monodisperse PS spheres with an average diameter of 370 ± 2 nm were obtained by using an emulsifier-free emulsion polymerization technique. ITO slides (50 mm × 10 mm) were used as substrates for PS template growth. The PS colloidal crystals were self-assembly grown by using controlled vertical sedimentation method. The electrochemical cell was made of polytetrafluoroethylene (Teflon) and clamped over a Teflon-covered Viton O-ring onto the substrate yielding a geometric surface area of 0.3 cm$^2$. The electrochemical measurements were performed in an argon filled glove box with water and oxygen contents below 2 ppm (OMNI-LAB from Vacuum Atmospheres) by using a VersaStat™ II (Princeton Applied Research) potentiostat/galvanostat controlled by powerCV software. For more experimental details see reference [10]. The deposits were characterized by using a field-emission scanning electron microscope (FE-SEM, S-470, Hitachi), energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM, JEM-2100HR) and X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI5700 ESCA system with MgK$\alpha$ source). For the XPS analysis, the beam energy was 3kV, the current was 1uA, and the analyzed area was 4 um × 4 um. The C 1s line (284.5 eV) was used as a reference to correct charge shift.
The PL measurements were carried out at room temperature by Renishaw inVia Raman microscope (He–Cd Laser, 325 nm).

3. Results and discussion

The ionic liquid 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)-trifluorophosphate ([HMIm]FAP) has been used for the electrodeposition of Ge inside the PS template as it has an excellent hydrolytic and has a high electrochemical stability [11]. Figure 1 shows the cyclic voltammogram (CV) of pure [HMIm]FAP on ITO glass. The ionic liquid has quite a broad electrochemical window of about 6.0 V. The organic cation starts to decompose at a potential of about −2.8 V vs. the Ag quasi reference electrode.

![Fig. 1. CV of pure [HMIm]FAP on the ITO surface showing the electrochemical window of the ionic liquid. The scan rate is 10 mV s⁻¹, at 25 °C.](image1)

![Fig. 2. CV of 0.1 M GeCl₄ in [HMIm]FAP acquired at a scan rate of 10 mV s⁻¹ on ITO covered with a polystyrene colloidal crystal template at 25 °C.](image2)

Figure 2 shows the cyclic voltammogram of 0.1 M GeCl₄ in [HMIm]FAP on the polystyrene-modified ITO substrate. GeCl₄ in this ionic liquid on ITO shows quite a similar electrochemical behavior to that reported for the ionic liquid [Py1,4]TF₂N on Au(111) [12]. The
The first reduction peak at $-1.2$ V corresponds to the reduction of Ge(IV) to Ge(II). The second peak at $-1.67$ V is correlated with the bulk deposition of elemental germanium, as can be proved by XPS (Fig. 4) where a brownish deposit formed on the ITO substrate. The rising current at about $-2.5$ V is attributed to the irreversible reduction of the organic cation $[\text{HMIm}]^+$. The oxidation peaks in the reverse scan are only partly due to the electrochemical oxidation of Ge, as there is also a chemical oxidation of the deposit by GeCl$_4$ [13].

Fig. 3. (a) FESEM images of the surface of PS colloidal crystal template. The scale bar is 1µm; (b) A cross-section of Ge PCs before dissolution of the PS spheres. Arrows indicate the Ge nanocrystals grown in opal voids. The scale bar is 5 µm; (c) Ge PCs after removing the PS matrix obtained after applying a constant potential of $-1.6$ V vs. Ag for 1 h at room temperature. The scale bar is 1µm; (d) A high-resolution FESEM image of the Ge PC shown in (c).

Figure 3(a) shows a FESEM image of the surface of the PS colloidal crystal template. The PS spheres have an average diameter of 370 ± 2 nm. Figure 3(b) shows a cross-section of Ge/PS before dissolution of the PS template. According to the SEM images in Fig. 3(a) and 3(b), we can conclude that the PS crystal template is arranged in a face-centered cubic lattice. Figure 3(c) shows a Ge PC (after removal of the PS matrix) obtained after applying a constant potential of $-1.6$ V vs. Ag for 1 h at room temperature. The holes formed at the former contact points between the polystyrene spheres of the template and their arrangement on a triangular lattice shows that the hollow voids represent an fcc- array. Figure 3(c) and 3(d) show that Ge has grown from the electrode surface through the template towards the solution. As ionic liquids have a low surface tension which allowing a perfect wetting of electrode and template, Ge grows easily through the template. Figure 3(d) shows a high-resolution SEM image of a Ge PC, where the triangular positions have been highlighted. For a PS colloidal crystal template with a sphere diameter ($D$) of 370 nm, the spacing $d$ for the Ge PCs is given by: $d = \sqrt{3}D = 0.577D$.  

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The in-plane particle diameter \( a \) defined as the perpendicular bisector of the largest inscribed equilateral triangle that fills the threefold hole, is given by:
\[
a = \sqrt[3]{3} (1 - \gamma_p) D = 0.233 D
\] [14]. With a theoretical value of 86 nm a Digital Micrograph software gives a size distribution of 84–96 nm, which supports the high order of the material.

Representative XPS spectra of the surface of the Ge PCs are shown in Fig. 4(a) and Fig. 4(b). The measured photoelectron energy is sensitive to the chemical environment, thus different oxidation states can be extracted from spectra by fitting several Gauss curves to the measured spectra. In our case the subpeaks within the 3d_{5/2} peak are due to Ge atoms with a different oxidation state (Ge, GeO, GeO_2) and the subpeaks provide information on their relative contributions. The 3d_{5/2} deconvoluted XPS spectra of the deposit (Fig. 4(a)) shows that germanium was considerably oxidized during ex situ treatment.

![Fig. 4. The Ge 3d decomposed XPS spectra of the Ge PCs surface. (a) no Ar\(^+\) ion sputtering (b) after 2 min Ar\(^+\) ion sputtering](image)

The deposit is a mixture of GeO_2 (32.3 eV) and GeO (30.9 eV), were dominant with a small amount of Ge-Ge bonds (29.4 eV) and 69.5\% GeO_2, 20.5\% GeO and 10\% Ge can be calculated. After 2 min of Ar\(^+\) ion sputtering (Fig. 4b) amount of GeO_2 decreases to 35\%, the amount of Ge increases to 51\% and the amount of Ge remains nearly constant with 14\%. As XPS only probes the topmost 5–10 nm of a sample we can conclude that there is GeO on top of Ge and GeO_2 on top of GeO as a natural oxide layer. We should mention that there is hardly no surface oxidation of electrodeposited Ge if it is stored in an argon filled glove box.

In order to get more information on the optical properties of the material we measured the PL spectra of the samples with different structures at room temperature. Figure 5 shows the PL spectra of the Ge PC (red curve) together with a compact electrodeposited Ge film as a reference, the excitation power was 30 mW. The PL spectra reveal three main peaks at 539 nm (2.3 eV) with 2 shoulders at 552 and 585 nm, at 399 nm (3.1 eV) and at 654 nm (1.9 eV). The latter one is only obtained for the Ge PC. The shoulders at 552 nm and 585 nm are attributed to the emission center of In_2O_3 from the ITO glass as confirmed by the measured PL spectra of ITO glass (not shown). Surprisingly, although the volume fraction of Ge in the inverse opal is only one fourth of that in the compact film, the visible emission of the Ge PC reveals higher intensities than that of the film sample. As there is no distinct difference in the experimental conditions the enhancement of PL intensity must be due to the ordered porous structure of the Ge PC. As the walls of the inverse opal are in contact with air, the Ge porous structure can be regarded as a semiconductor–insulator nanostructure in which the semiconductor (Ge) is surrounded by an insulator (air) with a smaller dielectric constant. Such a structure would induce an increase in oscillator strength and exciton binding energies due to the dielectric confinement effect [15]. This effect could determine the exciton properties of semiconductors.
due to the long-range nature of the electron-hole Coulomb interaction. Therefore, a more intensive exciton emission is expected from Ge inverse opals due to the dielectric-confinement effect. This effect is one of the possible explanations for the PL enhancement of the Ge inverse opal. The two PL peaks at $\lambda = 539$ nm and 399 nm, corresponding to the orange-green PL ($\sim$2.3 eV) and the blue PL ($\sim$3.1 eV) respectively, are related to emission centers in GeO$_2$. XPS measurements (Fig. 4) demonstrated that Ge in the macroporous structure was covered with an oxide layer that included a considerable amount of GeO$_2$. GeO$_2$ nanocrystals are usually a blue PL material with two weak peaks around 3.1 eV (400 nm) and 2.2 eV (563 nm) [16]. Structural properties of amorphous GeO$_2$ nanoparticles have been reported by using molecular dynamics simulations [17]. Calculations showed that the surface of amorphous GeO$_2$ nanoparticles contained large numbers of structural point defects such as vacancies or those with low coordination number. The strong green PL of amorphous GeO$_2$ nanoparticles was attributed to the defects at their inner surfaces. It was also pointed out that the intrinsic point defects were the origin of the optical band-gap narrowing in ordered porous Ge nanostructure. The exciton states of the $\alpha$-semiconductor are similar to those of the crystalline semiconductor [18]. Furthermore, the PL properties of amorphous GeO$_2$ are similar to that of crystalline GeO$_2$. Gao et al [19] suggested that the emission of Ge nanocrystals in the visible region was not related to quantum confinement, and indicated that the blue-PL band centered at 3.1 eV (410 nm) was attributed to GeO$_2$ defects. Zacharias et al [20] also reported that the blue PL did not originate from the radiative recombination of excitons confined in the nanocrystals and suggested that the blue-PL band was related to Ge/O related defects.

![Fig. 5. The room temperature PL spectra of the Ge films (electrochemically prepared) and Ge PCs at an excitation power of 30 mW](image)

We employed transmission electron microscope (TEM) to investigate further the structure of our electrochemically made Ge PC and to check if Ge/GeO$_x$ nanocrystallites are present. Figure 6(a) shows a fraction of the Ge PC and Fig. 6(b) indeed reveals Ge nanocrystallites with a diameters of a few. Unfortunately, the lattice fringe and the interface of the crystallites cannot be clearly resolved in the dark area of the HR-TEM. The formation of these inhomogenous dark areas might be due to the crystallites that are not oriented in a way that allows lattice fringes to be observed. For smaller sizes (<3 nm), even in the HR-TEM observation, we cannot get a
distinct nanocrystallite image that can be well assigned. Photonic crystal composite materials have interesting physical properties associated with the interaction of electromagnetic radiation with their framework [21], especially with semiconductor nanocrystals filled with artificial opal structures [22].

Fig. 6. (a) The TEM image of Ge PCs. The scale bar is: 400 nm; (b) The HRTEM image of the border of Ge PCs. The scale bar is: 4 nm.

Fig. 7. (a) PL spectra of Ge PCs and Ge infilled PS composite; (b) Normalized PL spectra of Ge PCs and Ge-PS composite at an excitation power of 9 mW. The PL spectra are normalized at the peak intensity of the green emission band.

Therefore, it is of interest to study the PL of Ge/PS opal composites. Figure 7(a) shows the PL spectra of a Ge PC and that of Ge-infilled PS (Ge/PS opal composite) with an excitation power of 9 mW. Obviously, the broad green light emission band is markedly enhanced in the Ge/PS opal composites, with reference to the Ge PC alone. The PL intensity of the Ge/PS opal composites becomes several orders of magnitude higher than that of the Ge PC film. In order to reveal the effect of the PBG environment on the Ge emission, the PL spectra were normalized (Fig. 7(b)) to the peak intensity of green emission for both the Ge/PS and Ge PCs. It is noteworthy that the peak position and shape of the green light emission band of the Ge/PS opal composites corresponds to that of GeO$_2$ nanocrystals (see Fig. 5), implying that the green emission in the Ge/PS composites originates as expected from the same emission centers. In turn this suggests that the enhancement of the PL of the GeO$_2$ covered Ge nanocrystallites results from the PS opal structure. There are several possible mechanisms for the enhancement of PL intensity in Ge/PS opal composites: (1) an interfacial coupling between Ge nanocrystallites and the PS opal; (2) an increased absorption efficiency of excitation light; (3)
an increased light extraction efficiency. Yang et al. reported on an enhanced yellow-green PL form ZnO/SiO$_2$ opal composites and found that the PL intensity of the composite increased with increasing the diameter of the SiO$_2$ microsphere [23]. The enhancement of the PL intensity was attributed to the increase in the excitation light absorption efficiency and the light extraction efficiency caused by the disorder scattering in opals. Furthermore, the multiple scattering of incident excitation light can increase the absorption probability of photons due to a longer optical path length in the PS matrix before it leaves the sample. At low carrier densities, the electron and hole distributions are described by classical statistics. The frequency dependence of the emission spectrum can be described by the following Eq. (1):

$$I(hv) \propto (hv - E_g)^{1/2} \exp\left(-\frac{hv - E_g}{k_BT}\right).$$  \hspace{1cm} (1)

The $(hv - E_g)^{1/2}$ prefactor represents the joint electron-hole density of states for the inter-band transition and the final factor is due to the Boltzmann statistics [24]. As the absorbed probability of photons increases, the intensity of the excitation light also increases. The scattering in opal colloidal crystals is mainly caused by the disorder present in the lattice. The origin of the disorder in opal colloidal crystals can arise from the size distribution of the sphere, lattice periodicity fluctuations, missing spheres and interstitials which can hardly be avoided especially when employing the vertical sedimentation method to grow opal matrix templates. As seen in Fig. 7(b) the emission peaks centered at wavelengths of 399 nm and 653 nm are observed in the Ge PCs but they disappear in the Ge/PS composites. The disappearance of the first peak (at 399 nm) might be attributed to the absorption of the UV emission by the polystyrene colloidal spheres. As the polystyrene spheres filled the voids between Ge array and the ITO layer in the Ge/PS opal composite, the 653 nm peak disappeared, too. Therefore, this suggests that the 653 nm emission is due to the interface defects between the Ge ordered array and the ITO layer.

The emission enhancement can also be caused by the improvement of the light extraction efficiency of the Ge/PS opal colloidal crystal film. Yamasaki has demonstrated that an organic light-emitting device with an ordered monolayer of silica microspheres can improve the high scattering efficiency, resulting in an enhancement in the light extraction efficiency [25]. In the Ge/PS composite structure the improved extraction can lead to a PL intensity enhancement. The transmission spectra indicate that the position of the PBG centre for the 22 layer PS colloidal crystal template is at about 517 nm. Since the wavelength of incident rays (325nm) is far away from the PBG, the PL enhancement is not directly related to the PBG structure.

4. Conclusions and outlook

In summary, we reported the PL measurements for Ge PCs and Ge/PS composite opals prepared at room temperature by electrochemical deposition of Ge, inside a PS template, from the air- and water-stable ionic liquid [HMIm]FAP containing GeCl$_4$ as precursors. An enhancement of the green emission from the Ge/PS opal composite opal was observed. This enhancement of the PL intensity was ascribed to the disorder multiple scattering in polystyrene opals colloidal crystal that increased the excitation light absorption efficiency and the light extraction efficiency. XPS results have demonstrated that the macroporous Ge was covered with a thin oxide layer (including both GeO$_2$ and GeO), therefore, the green PL near 2.3 eV (539nm) and the blue PL near 3.1 eV (400nm) was related to GeO$_2$ exciton centers. The experimental results indicate that photoluminescent semiconductor nano-array can be made by using the highest quality ultra-pure ionic liquids.
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