## **Electronic Supplementary Information**

## Towards the understanding of formation of micro/nano holes of Ge/GeO<sub>2</sub> through phase mapping

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**Figure S1.** Optical images of PL emission at different excitations light from  $Ge/GeO_2$  wafer and microcrystallites. PL spectra of (a) wafer, (b) microcrystallites with 325 and 532 nm of excitation.



Figure S2. Schematic of the experimental setup used for the synthesis of Ge/GeO<sub>2</sub> holes.



**Figure S3.** SEM images of Ge a) wafer and b) microcrystallites. Inset of (b) shows the magnified image of single microcrystal. (c) Ge wafer heated at 600  $^{\circ}$ C for 12 h (inset shows the magnified image of single hole).



Figure S4. Schematic of single hole showing the position where EDX, Raman and PL have been taken. The distance between two consecutive positions is ~ 0.5  $\mu$ m.



Figure S5. EDS of Ge/GeO<sub>2</sub> wafer taken at, a) inside the hole b) outside the hole.



4.84 **(a) (b)** 4.85 Weight (%) Weight (%) 4.80 4.80 4.76 4.75 100 200 200 400 600 0 300 0 Temperature (°C) Time (min)

Figure S6. XRD of  $Ge/GeO_2$  wafer and microcrystallites. The Ge phase peaks are shown in solid circle.

Figure S7. Oxidation kinetics curves of Ge wafer oxidized in air ambient at 600 °C for 4 h. (a

& b) Variation of weight % with temperature and time, respectively.



Figure S8. TEM/HRTEM images of portion of GeO<sub>2</sub> microcrystal.



**Figure S9.** (a & b) Absorbance and luminescence spectra of  $\text{GeO}_2$  microcrystallites, respectively. The excitation wavelength is 355 nm for luminescence spectra. It may be noted that the microcrystallites as shown in Fig. 6(a) has been ball-milled to obtain fine powders and absorbance and PL studies have been carried out in water solvent. Inset of (a) shows the Tauc plot for indirect band GeO<sub>2</sub> (3.48 eV).



Figure S10. PL excitation spectra of Ge/GeO<sub>2</sub> wafer. The detection wavelength is 442 nm.

Table S1. Excitation dependent emission from GeO<sub>2</sub>.

References	Morphology	Excitation	Emission
No.			
8	Ge/GeO <sub>2</sub> core/shell nanoparticles	325 nm	400 nm
9	GeO <sub>2</sub> nanocrystals	325 nm	410 nm
		441 nm	620 nm
10	Ge/GeO <sub>2</sub>	325 nm	410 nm
	nanoparticles		560 nm
11	GeO <sub>2</sub> nanowires	221 nm	485 nm
	GeO <sub>2</sub> bulk powder	221 nm	340 nm
		234 nm	345 nm
		325 nm	420 nm
12	GeO <sub>2</sub> nanowire	221 nm	347 nm
			364 nm
		305 nm	403 nm
			490 nm
13	GeO <sub>2</sub> nanowire network	265 nm	404 nm
14	Oxidized Germanium	488 nm	560 nm
15	hollow GeO <sub>2</sub> walnuts	325 nm	452 nm,
			538 nm
	solid walnut		569 nm

Table S2. EDX analyses.

Elem.	Wt %	At %
O K	3.42	13.84
GeK	96.58	86.16
Total	100.00	100.00

Elem.	Wt %	At %
O K	40.05	75.19
GeK	59.95	24.81
Total	100.00	100.00