

# Preparation of functional Ga<sub>2</sub>S<sub>3</sub> and Ga<sub>2</sub>Se<sub>3</sub> shells around Ga<sub>2</sub>O<sub>3</sub> nanowires via sulfurization or selenization

Edgars Butanovs<sup>1,\*</sup>, Luize Dipane<sup>1</sup>, Aleksejs Zolotarjovs<sup>1</sup>, Sergei Vlassov<sup>2</sup>, Boris Polyakov<sup>1</sup>

<sup>1</sup>Institute of Solid State Physics, University of Latvia, Kengaraga street 8, Riga, Latvia, LV-1063

<sup>2</sup>Institute of Physics, University of Tartu, W. Ostwaldi Str. 1, 50412, Tartu, Estonia

\*e-mail: edgars.butanovs@cfi.lu.lv

## Abstract

Combining defect semiconductors Ga<sub>2</sub>S<sub>3</sub> and Ga<sub>2</sub>Se<sub>3</sub> in Ga<sub>2</sub>O<sub>3</sub>-based heterostructured nanowires (NWs) have potential in photonics and optoelectronics applications due to the materials appealing optical properties. In this work, we have developed and studied Ga<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>S<sub>3</sub> and, for the first time, Ga<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>Se<sub>3</sub> *core-shell* NWs. Ga<sub>2</sub>S<sub>3</sub> and Ga<sub>2</sub>Se<sub>3</sub> shell was obtained during high-temperature sulfurization and selenization process of pure Ga<sub>2</sub>O<sub>3</sub> NWs, respectively, in a chemical vapour transport reactor. As-grown nanostructures were characterized with scanning and transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy and photoluminescence measurements. Single-nanowire photodetector devices were fabricated in order to demonstrate their electric and photoconductive properties. Such novel *core-shell* NW heterostructures could potentially be used in next-generation nanoscale electronic and optoelectronic devices.

**Keywords:** *nanowire; gallium oxide; Ga<sub>2</sub>S<sub>3</sub>; Ga<sub>2</sub>Se<sub>3</sub>; core-shell; heterostructure*

## 1. Introduction

One-dimensional (1D) nanostructures – nanowires (NWs) – have been actively investigated for different applications in nanoelectronics and optoelectronics [1], for example, photodetectors, transistors, LEDs [2–4], sensors [5,6], energy storage and

conversion [7,8] due to their unique physical characteristics, which arise from the high surface-to-volume ratio and the size confinement effects. Modification of NW surface is a promising approach how to tune their properties [9]. Compared to the conventional thin films growth, NWs surface can exhibit a considerably lessened constraint for the lattice mismatch during heterostructure preparation [10–12], therefore, making NWs as a potential template for growth of high-quality films and introducing new possibilities to engineer novel nanostructures in *core-shell* configuration [9,13].

Gallium oxide ( $\text{Ga}_2\text{O}_3$ ) has recently attracted a lot of scientific attention as a prospective ultra-wide bandgap semiconductor in a form of thin films and NWs [14,15].  $\text{Ga}_2\text{O}_3$  has five different polymorphs among which the most stable one is monoclinic  $\beta$ - $\text{Ga}_2\text{O}_3$  with a bandgap value of around 4.9 eV [16]. While  $\text{Ga}_2\text{O}_3$ -based thin films, NWs and heterostructures have been researched extensively in the last few years mainly for applications in power electronics [17,18] and UV photodetectors [19–21], as well as there are reports on NW sensing [22] and memory [23] devices have been demonstrated,  $\text{Ga}_2\text{O}_3$ -based hybrid NW materials still lack the variety of studies, especially in the *core-shell* configuration. There have been only few reports over the years on  $\text{Ga}_2\text{O}_3$ - $\text{TiO}_2$  [24],  $\text{Ga}_2\text{O}_3$ - $\text{ZnO}$  [25],  $\text{Ga}_2\text{O}_3$ - $\text{WO}_3$  [26] and  $\text{Ga}_2\text{O}_3$ - $\text{Ga}_2\text{S}_3$  [27] *core-shell* NWs demonstrating the materials potential in various applications.

Gallium chalcogenide compounds can be divided in two groups based on their stoichiometry:  $\text{GaX}$  compounds, such as  $\text{GaS}$  and  $\text{GaSe}$ , are layered van der Waals materials, which have been very actively studied in the 2D form for the last decade [28–30]; and  $\text{Ga}_2\text{X}_3$  compounds like  $\text{Ga}_2\text{S}_3$  and  $\text{Ga}_2\text{Se}_3$ .  $\text{Ga}_2\text{S}_3$  and  $\text{Ga}_2\text{Se}_3$  are commonly called ‘defect semiconductors’, since their  $\beta$  (monoclinic) and  $\gamma$  (orthorhombic) phases can be built with the cubic  $\alpha$ - $\text{Ga}_2\text{X}_3$  fundamental unit, which is basically a defect zincblende structure with the  $\text{Ga/X}$  stoichiometry ratio of only 2:3. Ordered or

randomly oriented structural Ga vacancies in the lattice result in the  $\beta$ - or  $\alpha$ -phase, respectively [31–34].  $\text{Ga}_2\text{S}_3$  is a p-type semiconductor with a direct bandgap of 3.0-3.4 eV [31,35] and has shown promise in photonics and optoelectronics [36–38], mainly due to its intriguing optical properties, as well as in sensing [39] and possibly sodium ion batteries [40]. In comparison,  $\text{Ga}_2\text{Se}_3$  is a slightly less studied semiconductor with the direct bandgap measured from 1.8 eV to 2.4 eV [32], which has potential applications in optoelectronic devices [31,32] and lithium ion batteries [41].

$\text{Ga}_2\text{O}_3$ , especially in the form of NWs, is a convenient template for  $\text{Ga}_2\text{S}_3$  and  $\text{Ga}_2\text{Se}_3$  growth, since synthesis of 1D  $\text{Ga}_2\text{S}_3$  and  $\text{Ga}_2\text{Se}_3$  nanostructures is complicated – only  $\text{Ga}_2\text{Se}_3$  NWs growth from GaAs has been recently demonstrated [34]. It has been previously shown that  $\text{Ga}_2\text{O}_3$  exposure to  $\text{H}_2\text{S}$  gas at elevated temperature leads to formation of either GaS or  $\text{Ga}_2\text{S}_3$  phase [27,42] and vice versa –  $\text{Ga}_2\text{O}_3$  was obtained via gallium sulfide annealing in an oxygen containing atmosphere [43,44]. On the other hand, to the best of our knowledge, no  $\text{Ga}_2\text{O}_3$ - $\text{Ga}_2\text{Se}_3$  1D heterostructures have been previously demonstrated.  $\text{Ga}_2\text{S}_3$  and  $\text{Ga}_2\text{Se}_3$  are semiconductors with a narrower bandgap than  $\text{Ga}_2\text{O}_3$ , thus giving the freedom to tune the optical properties in the visible range, especially if control over their defects could be achieved during the synthesis. Furthermore, electrical and optical properties of such heterostructures could be tuned even further through doping of the  $\text{Ga}_2\text{O}_3$  core, either with Si or Sn to increase the electrical conductivity [16] or with rare earth elements for light emission applications [45].

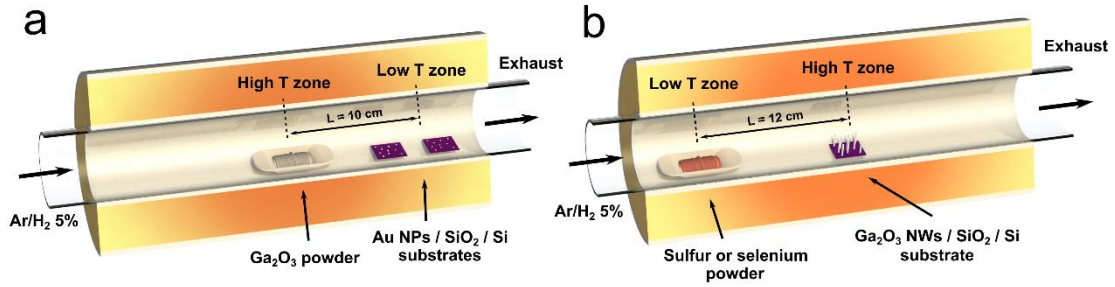
In this work, we demonstrated growth of  $\text{Ga}_2\text{O}_3$ - $\text{Ga}_2\text{S}_3$  and  $\text{Ga}_2\text{O}_3$ - $\text{Ga}_2\text{Se}_3$  *core-shell* NWs through sulfurization and selenization, respectively, of pure  $\text{Ga}_2\text{O}_3$  NWs at elevated temperatures. Phase composition and structural evolution was studied for samples prepared at different temperatures. Furthermore, single-nanowire

photodetector devices were fabricated in order to demonstrate their electric and photoconductive properties, which show promise for the nanostructure application in next-generation nanoscale electronic and optoelectronic devices.

## 2. Experimental details

Pure  $\text{Ga}_2\text{O}_3$  NWs were grown in a horizontal quartz tube (18 mm inner diameter) reactor via atmospheric pressure chemical vapour transport (see *Fig. 1(a)*). A ceramic boat was filled with 0.15g  $\text{Ga}_2\text{O}_3$  powder (99.99%, *Alfa Aesar*) and loaded in the centre of the quartz tube, oxidized silicon wafers  $\text{SiO}_2/\text{Si}(100)$  (*Semiconductor Wafer, Inc.*) coated with Au nanoparticles (NPs, *Alfa Aesar*, water suspension, 100 nm diameter) were placed downstream in a lower temperature (T) region 10 cm away from the centre of the furnace. Au NPs were used as a catalyst for the vapour-liquid-solid (VLS) growth. The reactor was heated up to  $1010^\circ\text{C}$  (high T zone) under a flow of carrier gas mixture  $\text{Ar}/\text{H}_2$  5%, the temperature and flow was then maintained for 30 minutes for the NWs to grow, followed by natural cooling to the room temperature. Typically, up to 100  $\mu\text{m}$  long  $\text{Ga}_2\text{O}_3$  NWs were synthesised on the  $\text{SiO}_2/\text{Si}$  substrates, the temperature at the low T zone being around  $850\text{-}900^\circ\text{C}$ . Characterization data for the as-grown pure  $\text{Ga}_2\text{O}_3$  NWs is shown in *Fig. S1*.

In order to grow either  $\text{Ga}_2\text{S}_3$  or  $\text{Ga}_2\text{Se}_3$  shell around  $\text{Ga}_2\text{O}_3$  NWs, the horizontal quartz tube (18 mm inner diameter) reactor, containing  $\text{Ga}_2\text{O}_3$  NWs in the centre (high T zone) and sulfur (99%, *Enola*) or selenium (99+%, *Alfa Aesar*) powder, respectively, upstream in the low T zone 12 cm from the centre, was heated up to the required temperature (temperatures mentioned further are in high T zone) under  $\text{Ar}/\text{H}_2$  5% carrier gas flow, kept for 15 minutes and then cooled naturally (see *Fig. 1(b)*). An excessive amount of sulfur and selenium powders were placed in the reactor in order to



**Figure 1.** (a) A schematic diagram of the reactor setup used for pure  $\text{Ga}_2\text{O}_3$  NWs growth. (b) A schematic diagram of the reactor setup used for the sulfurization and selenization of the  $\text{Ga}_2\text{O}_3$  NWs. Sulfur and selenium powders were used as precursors for sulfurization and selenization process, respectively. The high T zone temperature corresponds to the ones used throughout the article.

maintain chalcogen-vapour-rich atmosphere. The temperature for sulfurization or selenization of  $\text{Ga}_2\text{O}_3$  to start to occur significantly enough was found to be  $400^\circ\text{C}$  and  $500^\circ\text{C}$ , respectively. The synthesis procedures were performed at various temperatures in order to study its impact on the shell formation (growth rate, morphology, phase composition).

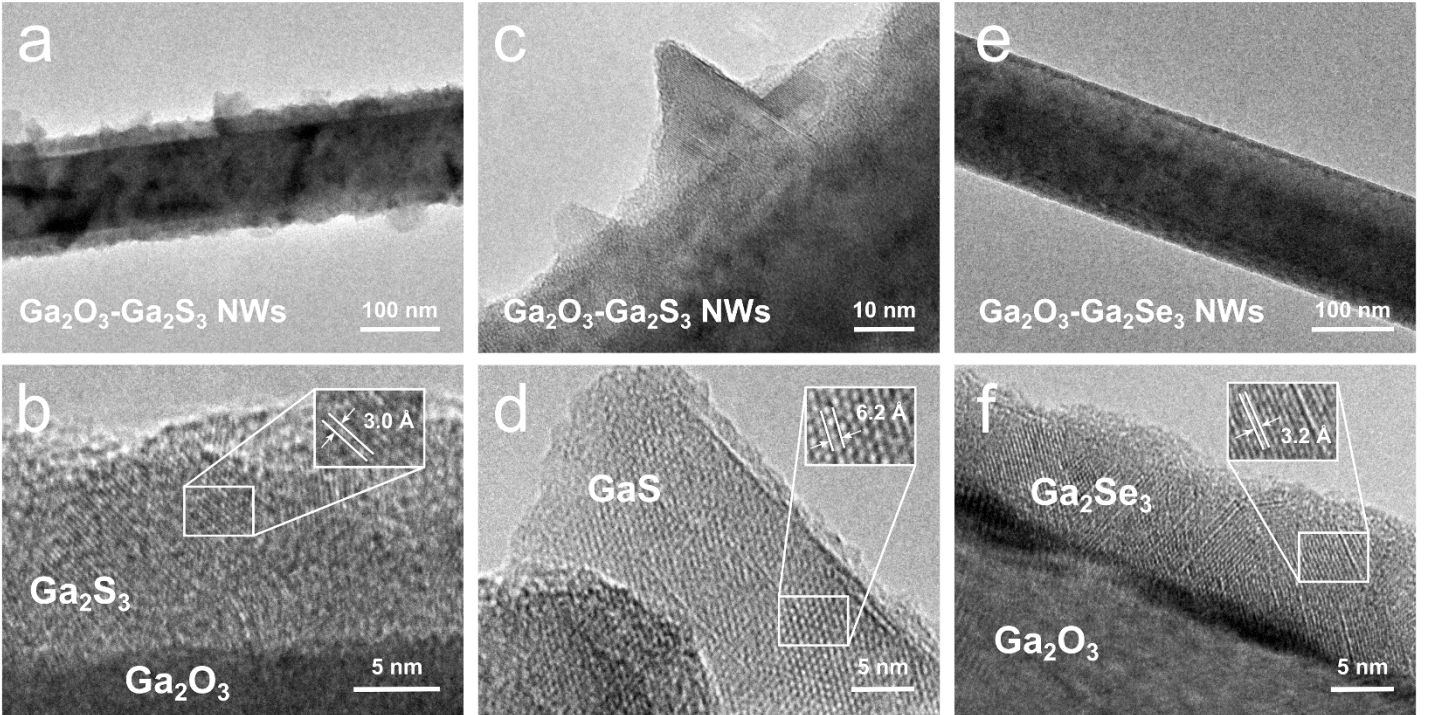
As-grown NW morphology was studied using a scanning electron microscope (SEM, Lyra, Tescan) together with energy dispersive X-ray (EDX) elemental analysis, while their inner crystalline structure was characterized using a transmission electron microscope (TEM, Tecnai GF20, FEI) operated at a 200 kV accelerating voltage. NW phase composition was examined by X-ray diffraction (XRD) using Rigaku MiniFlex 600 powder diffractometer with Bragg-Brentano  $\theta$ - $2\theta$  geometry and a 600W Cu anode X-ray tube (Cu  $K\alpha$  line,  $\lambda = 1.5406 \text{ \AA}$ ). Micro-Raman spectroscopy measurements were performed using a TriVista 777 confocal Raman system (Princeton Instruments, 750 mm focal length, 1800 lines/mm grating) equipped with an upright Olympus microscope with UIS2 MPlanN 100x/0.90 objective, a continuous-wave single-frequency diode-pumped laser Cobolt Samba 150 ( $\lambda=532 \text{ nm}$ ) and Andor iDus DV420A-OE CCD camera. X-ray photoelectron spectroscopy (XPS) spectra were

obtained using an ESCALAB Xi (ThermoFisher) spectrometer. Photoluminescence (PL) spectra and its dependence on the temperature was recorded using Andor Shamrock B303-I spectrometer coupled with Andor DU401A-BV CCD camera. Sample temperature was controlled in a vacuum chamber with Sumitomo HC-4 closed-cycle helium cryostat operating within temperature range ~9–325 K. For temperature control, LakeShore 331 Temperature controller was used. Excitation of PL was performed with a 266 nm excitation wavelength - fourth harmonic of CryLas FQSS266-Q Q-switched Nd:YAG laser, with pulse energy 0.3  $\mu$ J at 15kHz. All PL spectra were not corrected to compensate for the sensitivity changes of experimental setup as only the qualitative comparison is performed.

Two-terminal individual NW photoconductor devices were fabricated via conventional photolithography process. First, NWs were mechanically transferred to an oxidized silicon wafer chip (300 nm thick SiO<sub>2</sub>), followed by spin-coating it with AZ1518 photoresist. The optical mask with the microelectrode pattern (5  $\mu$ m gap between the electrodes) was aligned on top of a single NW and exposed using SUSS MicroTec MA/BA6 Gen4 mask aligner. A 10/90/20 nm thick Cr/Ag/Al electrodes, respectively, were deposited via thermal evaporation method followed by a lift-off procedure. At least five devices for each material were fabricated in order to make consistent conclusions. Current–voltage ( $I$ – $V$ ) characteristics and photoresponse of the fabricated single-NW photodetector devices were measured with a two-contact microprobe station connected to a low-noise current preamplifier (SR570, Stanford Research Systems) and oscilloscope (TDS2004B, Tektronix). A 405 nm wavelength semiconductor diode laser (CNI Laser) with 0.5 W/cm<sup>2</sup> power was the illumination source for the photoresponse measurements. All the measurements were performed at room temperature and in air.

### 3. Results and discussion

As-grown *core-shell* NW morphology and the inner structure was characterized using TEM (see *Fig. 2*). In the case of sulfurized  $\text{Ga}_2\text{O}_3$  NWs, it was possible to obtain a continuous, few nanometres thick  $\text{Ga}_2\text{S}_3$  shell around NWs at  $600^\circ\text{C}$  (*Fig. 2(a)*). A uniform shell is a prerequisite for good electrical properties of the nanostructure. On the other hand, protruding GaS crystals start to form at such temperature as has been shown at a higher resolution in *Fig. 2(c)*. Similarly, a continuous  $\text{Ga}_2\text{Se}_3$  shell was obtained after selenization of  $\text{Ga}_2\text{O}_3$  NWs at  $600^\circ\text{C}$  (see *Fig. 2 (e)*). Here, the shell is smoother in comparison to the sulfurized NWs, since only one new phase forms. The NWs maintain their length after sulfurization/selenization and the formed shell is

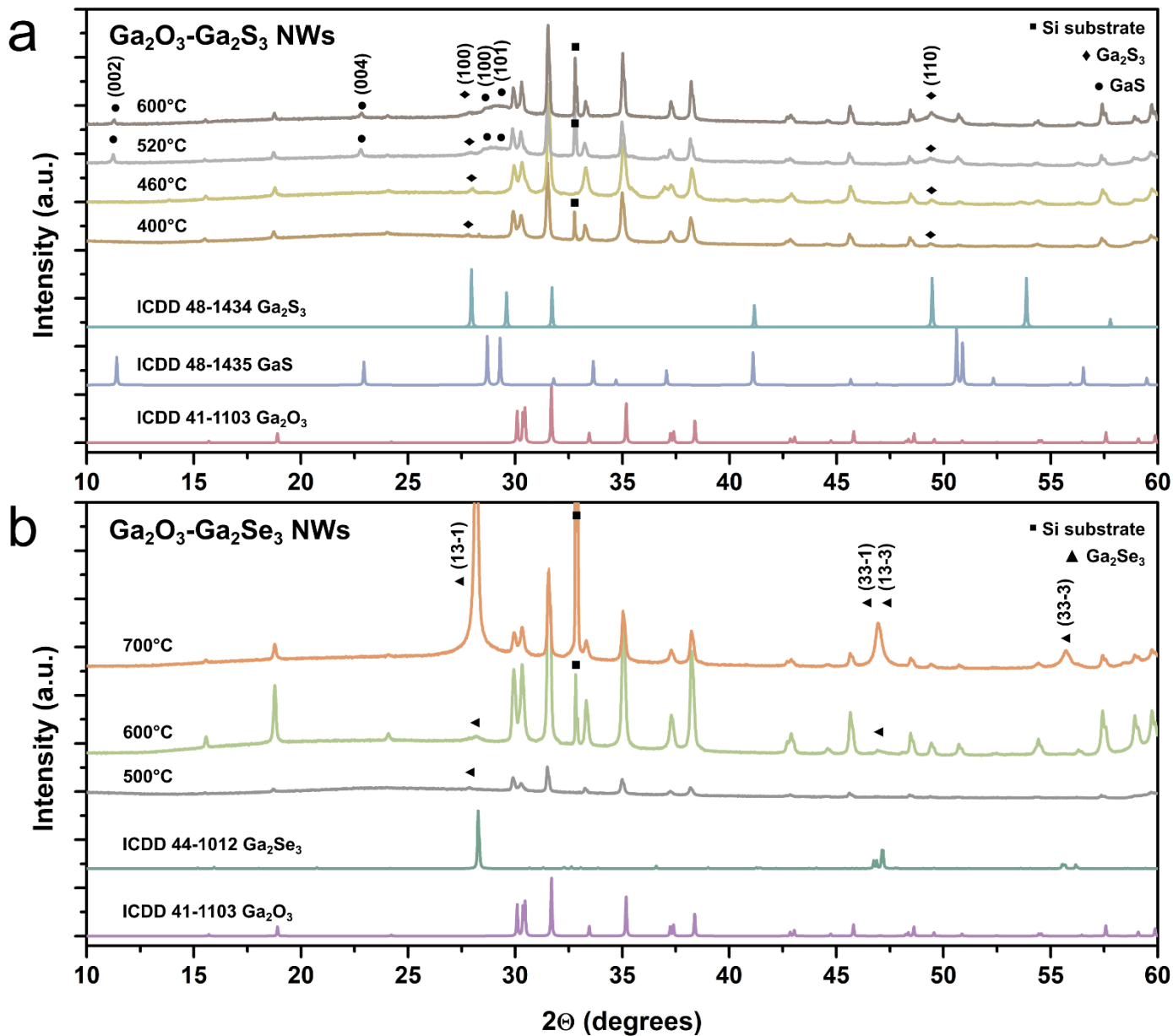


**Figure 2.** Transmission electron microscope images at different magnifications of (a-d)  $\text{Ga}_2\text{O}_3$ - $\text{Ga}_2\text{S}_3$  *core-shell* NWs prepared at  $600^\circ\text{C}$  and (e,f)  $\text{Ga}_2\text{O}_3$ - $\text{Ga}_2\text{Se}_3$  *core-shell* NWs prepared at  $500^\circ\text{C}$ . Note that  $\text{Ga}_2\text{O}_3$  NWs sulfurized at higher temperatures also contain crystals of GaS phase. The insets show the measured atomic interlayer distances in the formed phases.

uniformly distributed along the NWs, as was confirmed by SEM and EDX measurements (see *Fig. S2*), however, the surface roughness of the *core-shell* NWs increases at higher temperatures (see *Fig. S3*) because of the more active reaction between  $\text{Ga}_2\text{O}_3$  and the chalcogenide vapour. In order to control the shell thickness, process time can be used with some limitations. At higher TEM resolution (*Fig. 2(b,d,f)*) the inner crystalline structure of the formed phases is revealed and interplanar distance values measured. Interplanar distance in the  $\text{Ga}_2\text{S}_3$  shell was determined to be  $3.0 \text{ \AA}$ , which is in a good agreement with the lattice parameter  $c=6.031 \text{ \AA}$  in ICDD-PDF #48-1434. The protruding GaS crystals exhibit interplanar distance of  $6.2 \text{ \AA}$ , which corresponds to lattice spacing between (101) planes in GaS [46]. As for the  $\text{Ga}_2\text{Se}_3$  shell, interplanar distance was measured to be  $3.2\text{-}3.3 \text{ \AA}$ , closely matching the lattice parameter  $c=6.6491 \text{ \AA}$  in ICDD-PDF #44-1012. The TEM measurements show the high crystalline quality of the prepared *core-shell* NWs. The processed NWs preserve their length, inner composition and crystalline structure in comparison to pure  $\text{Ga}_2\text{O}_3$  NWs, since the reaction with chalcogenide vapour occurs close to the surface, mainly leading to morphological changes.

To confirm the presence of the phases in the as-grown *core-shell* NW samples, XRD measurements were performed on the NW arrays on the Si(100)/ $\text{SiO}_2$  substrates, prepared at various temperatures (see *Fig. 3*). Worth noting that all the unmarked peaks belong to the monoclinic  $\text{Ga}_2\text{O}_3$  core (ICDD-PDF #41-1103) and are interpreted in *Fig. S1(a)*. In the case of the sulfurized  $\text{Ga}_2\text{O}_3$  NWs (*Fig. 2(a)*), formation of monoclinic  $\text{Ga}_2\text{S}_3$  phase (ICDD-PDF #48-1434) takes place in the whole tested temperature range from  $400^\circ\text{C}$  to  $600^\circ\text{C}$ . On the other hand, hexagonal GaS phase (ICDD-PDF #48-1435) start to appear at  $520^\circ\text{C}$  and above. As for the selenized  $\text{Ga}_2\text{O}_3$  NWs (*Fig. 3(b)*), monoclinic  $\text{Ga}_2\text{Se}_3$  phase (ICDD-PDF #44-1012) is present in the samples prepared at



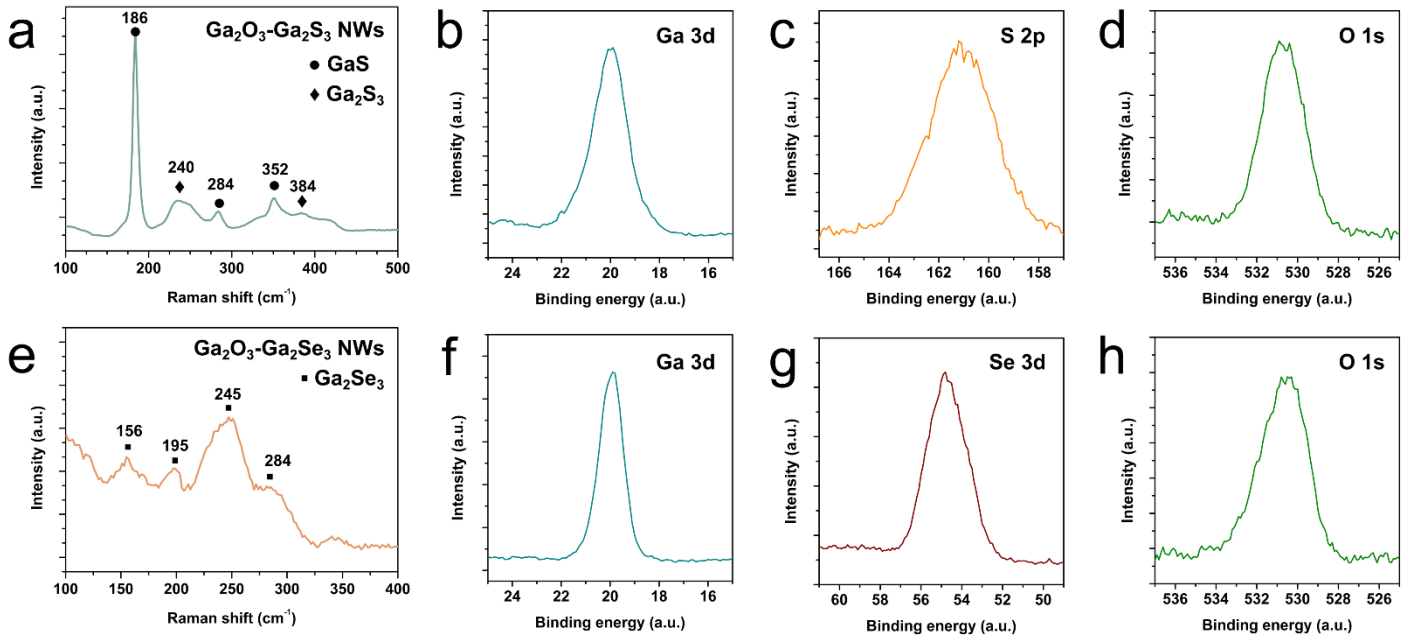


**Figure 3.** X-ray diffraction patterns of (a)  $\text{Ga}_2\text{O}_3\text{-Ga}_2\text{S}_3$  and (b)  $\text{Ga}_2\text{O}_3\text{-Ga}_2\text{Se}_3$  *core-shell* NW arrays on Si(100)/ $\text{SiO}_2$  substrates, prepared at various temperatures. The respective ICDD patterns for each phase are provided for reference.

temperatures starting from 500°C and above. The intensity of the  $\text{Ga}_2\text{Se}_2$  peaks in relation to the  $\text{Ga}_2\text{O}_3$  ones increases significantly with rising temperature, indicating that selenium vapour reacts more aggressively with  $\text{Ga}_2\text{O}_3$  NWs. This is accompanied by significant increase of surface roughness, as can be seen in *Fig.S3*. Bragg peak at  $2\theta \approx 33^\circ$  can be attributed to the Si(100) substrate (forbidden Si(200) reflection). XRD results match well with the visual observations made by TEM – the samples with the

visible protruding crystals correspond to the ones containing GaS phase. The formation of the hexagonal phase during the sulfurization and not during selenization could occur because sulfur and  $\text{H}_2\text{S}$  vapour are not as reactive as the selenium counterparts, which might lead to anion deficiency and preferable formation of GaS phase alongside  $\text{Ga}_2\text{S}_3$  in our tested synthesis parameter range. On the other hand, the chemically more active selenium and  $\text{H}_2\text{Se}$  vapour leads to the cation deficient  $\text{Ga}_2\text{Se}_3$  phase [47]. GaSe can be produced from  $\text{Ga}_2\text{Se}_3$  at higher temperatures ( $960^\circ\text{C}$ ) and lower pressure (330 Pa) as it was shown by Wu *et al.* [48]. In our case the synthesis was carried out at atmospheric pressure in a temperature range  $500\text{--}700^\circ\text{C}$  resulting in pure  $\text{Ga}_2\text{Se}_3$  shell formation. Furthermore, since GaS hexagonal layered crystal structure does not match the  $\text{Ga}_2\text{S}_3$  monoclinic structure, GaS crystals grow outwards due to the large lattice mismatch.

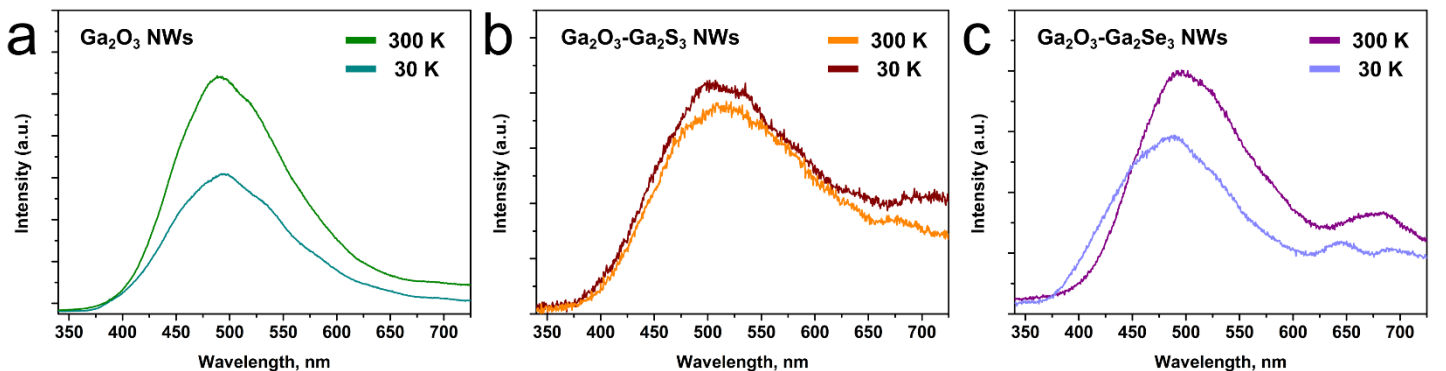
Room-temperature micro-Raman spectroscopy was used to confirm the presence of the respective compounds in the as-prepared *core-shell* NWs. Raman



**Figure 4.** Micro-Raman spectra of (a)  $\text{Ga}_2\text{O}_3\text{-Ga}_2\text{S}_3$  and (e)  $\text{Ga}_2\text{O}_3\text{-Ga}_2\text{Se}_3$  *core-shell* NWs, both prepared at  $600^\circ\text{C}$ . XPS spectra of the same (b-d)  $\text{Ga}_2\text{O}_3\text{-Ga}_2\text{S}_3$  and (f-h)  $\text{Ga}_2\text{O}_3\text{-Ga}_2\text{Se}_3$  NWs, showing the peak scans of the detected elements.

spectra of Ga<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>S<sub>3</sub> NWs (*Fig. 4(a)*) contains several peaks: the ones at 186, 284 and 352 cm<sup>-1</sup> can be attributed to GaS A<sub>1g</sub>, E<sub>2g</sub><sup>1</sup> and A<sub>2g</sub><sup>1</sup> modes, respectively [49], while the 240 and a weaker 384 cm<sup>-1</sup> peak belong to Ga<sub>2</sub>S<sub>3</sub> A<sub>1g</sub> and F<sub>2g</sub> modes, respectively [37]. As for Ga<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>Se<sub>3</sub> *core-shell* NWs (see *Fig. 4(e)*), Raman peak features measured at 156, 195, 245 and 284 cm<sup>-1</sup> can be indexed to A<sub>1</sub>, A<sub>1</sub>, A' and F<sub>2</sub> vibration modes in Ga<sub>2</sub>Se<sub>3</sub>, respectively [32]. Furthermore, an XPS analysis was performed in order to verify the chemical composition of the *core-shell* NW arrays on the Si(100)/SiO<sub>2</sub> substrates. Survey spectra are depicted in *Fig. S4(a,b)* and did not contain any peaks of possible contaminant elements. High-resolution spectra of Ga3d, O1s, S2p and Se3d were acquired (see *Fig. 4(b-d)* and *(f-h)* for sulfurized and selenized Ga<sub>2</sub>O<sub>3</sub> NWs, respectively) and calibrated relative to adventitious C 1s peak at 285 eV binding energy. None of the peaks exhibited any observable shift in binding energy due to the change of the chemical states after sulfurization or selenization, as well as no distinction between Ga<sub>2</sub>S<sub>3</sub> and GaS chemical states was possible to be made. The characteristic Ga3d peak is located at 20.2 eV binding energy, while the O1s peak at around 530.4 eV. After sulfurization of Ga<sub>2</sub>O<sub>3</sub> NWs, S2p peak, characteristic for metal sulfides, emerged at 161.3 eV. Worth noting that S2p peak in gallium sulfide compounds also contains contribution of Ga2s peak, as shown in the fitted scan in *Fig. S4(c)*. Lastly, Ga<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>Se<sub>3</sub> *core-shell* NW samples exhibited Se3d peak at 54.8 eV, thus confirming the formation of a selenide compound in the nanostructures.

PL spectra, measured at room and 30K temperature, for  $\text{Ga}_2\text{O}_3\text{-Ga}_2\text{S}_3$  and  $\text{Ga}_2\text{O}_3\text{-Ga}_2\text{Se}_3$  *core-shell* NWs and pure  $\text{Ga}_2\text{O}_3$  NWs are depicted in *Fig. 5*. The PL intensity is depicted in arbitrary units and does not contain information about relative intensities between the measured spectra. PL of all samples consists of many overlapping peaks and thus analysis is challenging; however, some features can be identified. Pure  $\text{Ga}_2\text{O}_3$  (see *Fig.5(a)*) commonly exhibits a wide blue-green PL defect band ranging from around 380 to 650 nm, which is well studied and consists of various overlapping contributions of recombination between donor and acceptor bands, formed by oxygen vacancy /  $\text{Ga}^{2+}$  and gallium vacancy / gallium-oxygen vacancy pairs, respectively [50,51]. This blue-green  $\text{Ga}_2\text{O}_3$  defect band is present in all the measured spectra for the sulfurized and selenized samples. The PL spectrum of the  $\text{Ga}_2\text{O}_3\text{-Ga}_2\text{S}_3$  NWs (see *Fig.5(b)*) contains another defect band centred at around 680 nm, which is attributed to transition between two deep acceptor and donor levels in  $\text{Ga}_2\text{S}_3$ , located at 0.4 eV above the valence band and 1.1 eV below the conduction band, respectively [27,35]. Some contribution to the PL spectrum might also come from GaS [52]. As for the  $\text{Ga}_2\text{O}_3\text{-Ga}_2\text{Se}_3$  *core-shell* NW PL spectrum (see *Fig.5(c)*), two peaks can be resolved at 645 and 695 nm while measuring at 30K, matching free exciton and bound

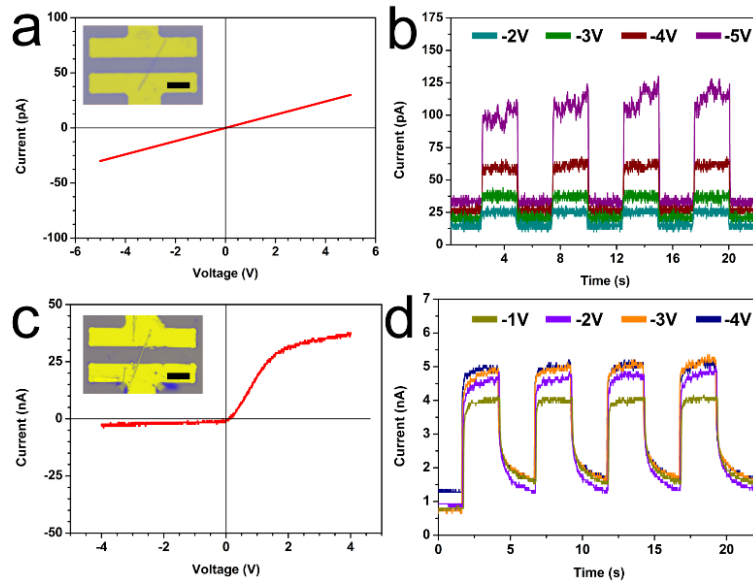


**Figure 5.** Photoluminescence spectra of (a) pure  $\text{Ga}_2\text{O}_3$ , (b) sulfurized and (c) selenized (both at  $600^\circ\text{C}$ ) NW array. Spectra were measured at 30K and room temperature with 266 nm excitation wavelength.

exciton emissions in Ga<sub>2</sub>Se<sub>3</sub>, respectively [32]. At room measurement temperature only one peak can be distinguished at 680 nm, which consists of contributions from the band-edge free exciton combined with the bound exciton and defect emissions, as previously shown by Ho [32].

Two-terminal single-nanowire photodetectors were fabricated from the as-prepared *core-shell* NWs, as well as from the pure Ga<sub>2</sub>O<sub>3</sub> NWs. Ga<sub>2</sub>O<sub>3</sub> NWs exhibited very low conductivity (see *Fig.S5*) and no response to visible light. *Fig. 6(a)* and *(c)* shows the measured dark state current-voltage (I-V) characteristics for Ga<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>S<sub>3</sub> (prepared at 600°C) and Ga<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>Se<sub>3</sub> (prepared at 500°C) *core-shell* NWs, respectively. The insets show optical microscope images of typical single-nanowire two-terminal photodetector devices for each material. I-V curve for Ga<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>S<sub>3</sub> NWs shows linear behaviour, indicating that ohmic contacts formed between Cr layers in electrodes and Ga<sub>2</sub>S<sub>3</sub> as has been demonstrated previously [39]. In contrast, the I-V curve for Ga<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>Se<sub>3</sub> NWs exhibits asymmetric Schottky behaviour in pA range [33]. The strong current saturation at higher positive bias voltages could be explained by contribution of space-charge limited current (SCLC), which is often observed in nanoscale devices when charge carriers are forced into small volume and start screening each other [53]. Since the pure Ga<sub>2</sub>O<sub>3</sub> NWs demonstrated very poor conductivity, most probably the current in the prepared *core-shell* NWs mainly flows through the few nanometres thick shell. The devices were periodically illuminated with 405 nm wavelength light in order to study their photoresponse properties as shown in *Fig. 6(b)* and *(d)* for Ga<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>S<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>Se<sub>3</sub> *core-shell* NWs, respectively. The devices were also tested for 532 nm and 660 nm laser light; however, no response was observed. On-off measurements demonstrate a steady, rapid and repeatable increase and decrease of the current when the illumination of Ga<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>S<sub>3</sub> NWs is turned on or off,

respectively; therefore, showing good stability and reversibility of the devices. Rise and decay time of the devices, defined as the required time for the photocurrent to increase or decrease to 90% or 10%, was determined to be around 30 ms. Important to note that the role of the GaS phase, present in the  $\text{Ga}_2\text{O}_3\text{-Ga}_2\text{S}_3$  *core-shell* NWs, on device performance is still unclear and should be elucidated – presumably the mixture of two semiconductors introduces structural defects, which degrade the electrical properties of the shell. Similar results were obtained for  $\text{Ga}_2\text{O}_3\text{-Ga}_2\text{Se}_3$  *core-shell* NW devices, however, the dark current (around 1 nA) and the generated photocurrent (3-4 nA) was more than a magnitude higher (tens of pA in  $\text{Ga}_2\text{S}_3$ ), meaning higher responsivity, and the rise and decay time was measured to be around 40 and 900 ms, respectively. The longer decay time is typically associated with charge carrier trapping centres [54]. The current enhancement ratios ( $I_{\text{on}}/I_{\text{off}}$ ) for the both prepared materials nanostructures were



**Figure 6.**  $\text{Ga}_2\text{O}_3\text{-Ga}_2\text{S}_3$  single nanowire, prepared at  $600^\circ\text{C}$ , (a) dark state I-V characteristics, (b) on-off photoresponse at different bias voltages.  $\text{Ga}_2\text{O}_3\text{-Ga}_2\text{Se}_3$  single nanowire, prepared at  $500^\circ\text{C}$ , (c) dark state I-V characteristics, (d) on-off photoresponse at different bias voltages. 405 nm wavelength light with  $0.5 \text{ W/cm}^2$  intensity was used for illumination in the photoresponse measurements. The insets show optical microscope images of typical single-nanowire two-terminal photodetector devices for each material. Scale bars correspond to  $10 \mu\text{m}$ .

measured to be at around 4-5. Ultimately, Ga<sub>2</sub>O<sub>3</sub> NWs show promise as a convenient template for Ga<sub>2</sub>S<sub>3</sub> and Ga<sub>2</sub>Se<sub>3</sub> semiconductor growth, which could enable the materials applicability in next-generation nanoscale optoelectronic devices, such as photodetectors.

## 5. Conclusions

In this work, we demonstrated growth of Ga<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>S<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>Se<sub>3</sub> *core-shell* NWs, in which the shell was obtained during high-temperature sulfurization and selenization process of pure Ga<sub>2</sub>O<sub>3</sub> NWs, respectively, in a chemical vapour transport reactor. Synthesis of pure Ga<sub>2</sub>S<sub>3</sub> and Ga<sub>2</sub>Se<sub>3</sub> 1D nanostructures is complicated, however, Ga<sub>2</sub>O<sub>3</sub> is a convenient template for Ga<sub>2</sub>S<sub>3</sub> and Ga<sub>2</sub>Se<sub>3</sub> growth due to the simple synthesis process and the similar crystal structures. In the case of sulfurization, Ga<sub>2</sub>S<sub>3</sub> shell formation was observed above 400°C, however, GaS phase also forms as protruding crystallites at temperatures higher than 520°C. As for Ga<sub>2</sub>Se<sub>3</sub>, formation of other phases was not observed at 500-700°C. Generally, at lower reaction temperatures continuous, few nanometres thick shells grow, while higher process temperature leads to increase of nanostructure surface roughness. Furthermore, single-nanowire photodetector devices were fabricated in order to demonstrate their electric and photoconductive properties, which show promise for the nanostructure application in next-generation nanoscale electronic and optoelectronic devices.

## Acknowledgements

This research is funded by the Latvian Council of Science project “Epitaxial Ga<sub>2</sub>O<sub>3</sub> thin films as ultrawide bandgap topological transparent electrodes for ultraviolet optoelectronics” No. lzp-2020/1-0345. S.V. was supported by the European

Union's Horizon 2020 program, under Grant Agreement No. 856705 (ERA Chair “MATTER”). Institute of Solid State Physics, University of Latvia as the Center of Excellence has received funding from the European Union’s Horizon 2020 Framework Programme H2020-WIDESPREAD-01-2016-2017-TeamingPhase2 under grant agreement No. 739508, project CAMART<sup>2</sup>. The authors are grateful to Jevgenijs Gabrusenoks for micro-Raman measurements and Valts Minders for assistance with materials synthesis.

### Supplementary information

Supplementary information is available and contains characterization data on pure Ga<sub>2</sub>O<sub>3</sub> NWs, SEM images of the *core-shell* NWs prepared at different temperatures, XPS survey spectra and detailed analysis of S2p peak, and dark-state I-V curve of single Ga<sub>2</sub>O<sub>3</sub> nanowire two-terminal device.

### References

- [1] Dasgupta, N. P. *et al.* 25th Anniversary Article: Semiconductor Nanowires - Synthesis, Characterization, and Applications. *Adv. Mater.* **26**, 2137–2184 (2014)
- [2] Jia, C., Lin, Z., Huang, Y. & Duan, X. Nanowire Electronics: From Nanoscale to Macroscale. *Chem. Rev.* **119**, 9074–9135 (2019)
- [3] Soci, C. *et al.* Nanowire Photodetectors. *J. Nanosci. Nanotechnol.* **10**, 1430–1449 (2010)
- [4] Yan, R., Gargas, D. & Yang, P. Nanowire photonics. *Nat. Photonics* **3**, 569–576 (2009)
- [5] Fennell, J. F. *et al.* Nanowire Chemical/Biological Sensors: Status and a Roadmap for the Future. *Angew. Chemie Int. Ed.* **55**, 1266–1281 (2016)



- [6] Chen, X., Wong, C. K. Y., Yuan, C. A. & Zhang, G. Nanowire-based gas sensors. *Sensors Actuators B Chem.* **177**, 178–195 (2013)
- [7] Mai, L., Tian, X., Xu, X., Chang, L. & Xu, L. Nanowire Electrodes for Electrochemical Energy Storage Devices. *Chem. Rev.* **114**, 11828–11862 (2014)
- [8] Chen, Z. *et al.* Core–shell MoO<sub>3</sub>–MoS<sub>2</sub> Nanowires for Hydrogen Evolution: A Functional Design for Electrocatalytic Materials. *Nano Lett.* **11**, 4168–4175 (2011)
- [9] Sun, Y., Sun, B., He, J. & Wang, C. Compositional and structural engineering of inorganic nanowires toward advanced properties and applications. *InfoMat* **1**, 496–524 (2019)
- [10] Li, Y., Qian, F., Xiang, J. & Lieber, C. M. Nanowire electronic and optoelectronic devices. *Mater. Today* **9**, 18–27 (2006)
- [11] Dong, Y., Tian, B., Kempa, T. J. & Lieber, C. M. Coaxial Group III–Nitride Nanowire Photovoltaics. *Nano Lett.* **9**, 2183–2187 (2009)
- [12] Polyakov, B. *et al.* Unexpected Epitaxial Growth of a Few WS<sub>2</sub> Layers on {11 $\bar{1}$ 00} Facets of ZnO Nanowires. *J. Phys. Chem. C* **120**, 21451–21459 (2016)
- [13] Butanovs, E. *et al.* Synthesis and characterization of GaN/ReS<sub>2</sub>, ZnS/ReS<sub>2</sub> and ZnO/ReS<sub>2</sub> core/shell nanowire heterostructures. *Appl. Surf. Sci.* **536**, 147841 (2021)
- [14] Yuan, Y. *et al.* Toward emerging gallium oxide semiconductors: A roadmap. *Fundam. Res.* **1**, 697–716 (2021)
- [15] Pearton, S. J. *et al.* A review of Ga<sub>2</sub>O<sub>3</sub> materials, processing, and devices. *Appl. Phys. Rev.* **5**, 011301 (2018)
- [16] Teherani, F. H. *et al.* A review of the growth, doping, and applications of  $\beta$ -

- Ga<sub>2</sub>O<sub>3</sub> thin films. *Proc. SPIE 10533, Oxide-based Mater. Devices IX, 105330R* (2018)
- [17] Pearton, S. J., Ren, F., Tadjer, M. & Kim, J. Perspective: Ga<sub>2</sub>O<sub>3</sub> for ultra-high power rectifiers and MOSFETS. *J. Appl. Phys.* **124**, 220901 (2018)
- [18] Perez-Tomas, A., Chikoidze, E. & Rogers, D. J. A walk on the frontier of energy electronics with power ultra-wide bandgap oxides and ultra-thin neuromorphic 2D materials. in *Oxide-based Materials and Devices XII* (eds. Teherani, F. H., Look, D. C. & Rogers, D. J.) 63 (SPIE, 2021)  
doi:10.1117/12.2590747
- [19] Kaur, D. & Kumar, M. A Strategic Review on Gallium Oxide Based Deep-Ultraviolet Photodetectors: Recent Progress and Future Prospects. *Adv. Opt. Mater.* **9**, 2002160 (2021)
- [20] Xie, C. *et al.* Catalyst-Free Vapor–Solid Deposition Growth of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Nanowires for DUV Photodetector and Image Sensor Application. *Adv. Opt. Mater.* **7**, 1901257 (2019)
- [21] Wang, S. *et al.* In situ synthesis of monoclinic  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanowires on flexible substrate and solar-blind photodetector. *J. Alloys Compd.* **787**, 133–139 (2019)
- [22] Afzal, A.  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanowires and thin films for metal oxide semiconductor gas sensors: Sensing mechanisms and performance enhancement strategies. *J. Mater.* **5**, 542–557 (2019)
- [23] Sivakumar, C. *et al.* High-Quality Single-Crystalline  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Nanowires: Synthesis to Nonvolatile Memory Applications. *Nanomaterials* **11**, 2013 (2021)
- [24] Chang, K.-W. & Wu, J.-J. Formation of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> Nanobarcodes from Core-Shell Nanowires. *Adv. Mater.* **17**, 241–245 (2005)

- [25] Jin, C., Park, S., Kim, H. & Lee, C. Ultrasensitive multiple networked Ga<sub>2</sub>O<sub>3</sub>-core/ZnO-shell nanorod gas sensors. *Sensors Actuators B Chem.* **161**, 223–228 (2012)
- [26] Park, S., Kim, S., Sun, G. J. & Lee, C. Synthesis, structure and ethanol sensing properties of Ga<sub>2</sub>O<sub>3</sub>-core/WO<sub>3</sub>-shell nanostructures. *Thin Solid Films* **591**, 341–345 (2015)
- [27] Othonos, K. M., Zervos, M., Christofides, C. & Othonos, A. Ultrafast Spectroscopy and Red Emission from  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>/ $\beta$ -Ga<sub>2</sub>S<sub>3</sub> Nanowires. *Nanoscale Res. Lett.* **10**, 304 (2015)
- [28] Late, D. J. *et al.* GaS and GaSe Ultrathin Layer Transistors. *Adv. Mater.* **24**, 3549–3554 (2012)
- [29] Hu, P. *et al.* Highly Responsive Ultrathin GaS Nanosheet Photodetectors on Rigid and Flexible Substrates. *Nano Lett.* **13**, 1649–1654 (2013)
- [30] Jung, C. S. *et al.* Red-to-Ultraviolet Emission Tuning of Two-Dimensional Gallium Sulfide/Selenide. *ACS Nano* **9**, 9585–9593 (2015)
- [31] Ho, C.-H., Lai, X.-R., Chuang, C.-A., Kuo, W.-L. & Tiong, K.-K. The Study of Optical Properties of III<sub>2</sub>–VI<sub>3</sub> Defect Semiconductor Group Compounds Ga<sub>2</sub>S<sub>3</sub>, Ga<sub>2</sub>Se<sub>3</sub>, In<sub>2</sub>S<sub>3</sub>, and In<sub>2</sub>Se<sub>3</sub>. *Adv. Photonics Res.* **2**, 2000110 (2021)
- [32] Ho, C.-H. Ga<sub>2</sub>Se<sub>3</sub> Defect Semiconductors: The Study of Direct Band Edge and Optical Properties. *ACS Omega* **5**, 18527–18534 (2020)
- [33] Xue, W. *et al.* Discovery of Robust Ferroelectricity in 2D Defective Semiconductor  $\alpha$ -Ga<sub>2</sub>Se<sub>3</sub>. *Small* **18**, 2105599 (2022)
- [34] Berto, F. *et al.* Ga<sub>2</sub>Se<sub>3</sub> Nanowires via Au-Assisted Heterovalent Exchange Reaction on GaAs. *J. Phys. Chem. C* **124**, 17783–17794 (2020)
- [35] Yoon, C.-S. *et al.* Blue photoluminescence of  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> and  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub>:Fe<sup>2+</sup>

- single crystals. *Appl. Phys. Lett.* **83**, 1947–1949 (2003)
- [36] Liu, H. F. *et al.* Synthesis and Phase Evolutions in Layered Structure of Ga<sub>2</sub>S<sub>3</sub> Semiconductor Thin Films on Epiready GaAs (111) Substrates. *ACS Appl. Mater. Interfaces* **6**, 3501–3507 (2014)
- [37] Zheng, Y., Tang, X., Wang, W., Jin, L. & Li, G. Large-Size Ultrathin  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> Nanosheets Toward High-Performance Photodetection. *Adv. Funct. Mater.* **31**, 2008307 (2021)
- [38] Ho, C.-H. & Chen, H.-H. Optically decomposed near-band-edge structure and excitonic transitions in Ga<sub>2</sub>S<sub>3</sub>. *Sci. Rep.* **4**, 6143 (2015)
- [39] Alsaif, M. M. Y. A. *et al.* Atomically Thin Ga<sub>2</sub>S<sub>3</sub> from Skin of Liquid Metals for Electrical, Optical, and Sensing Applications. *ACS Appl. Nano Mater.* **2**, 4665–4672 (2019)
- [40] Wang, P. *et al.* Exploring the sodium ion storage mechanism of gallium sulfide (Ga<sub>2</sub>S<sub>3</sub>): a combined experimental and theoretical approach. *Nanoscale* **11**, 3208–3215 (2019)
- [41] Ding, J.-J., Zhou, Y.-N., Cui, Y.-H. & Fu, Z.-W. Ga<sub>2</sub>Se<sub>3</sub> Thin Film as a Negative Electrode Material for Lithium-Ion Batteries. *ECS Electrochem. Lett.* **1**, A7–A9 (2012)
- [42] Zervos, M., Othonos, A., Gianneta, V., Travlos, A. & Nassiopoulou, A. G. Sn doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> and  $\beta$ -Ga<sub>2</sub>S<sub>3</sub> nanowires with red emission for solar energy spectral shifting. *J. Appl. Phys.* **118**, (2015)
- [43] Leontie, L. *et al.* Synthesis and optical properties of Ga<sub>2</sub>O<sub>3</sub> nanowires grown on GaS substrate. *Thin Solid Films* **689**, (2019)
- [44] Sprincean, V. *et al.* Crystallinity and optical properties of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>/Ga<sub>2</sub>S<sub>3</sub> layered structure obtained by thermal annealing of Ga<sub>2</sub>S<sub>3</sub> semiconductor.

- Mater. Sci. Semicond. Process.* **121**, 105314 (2021)
- [45] Khartsev, S. *et al.* Reverse-Bias Electroluminescence in Er-Doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky Barrier Diodes Manufactured by Pulsed Laser Deposition. *Phys. Status Solidi Appl. Mater. Sci.* **219**, 1–5 (2022)
- [46] Carey, B. J. *et al.* Wafer-scale two-dimensional semiconductors from printed oxide skin of liquid metals. *Nat. Commun.* **8**, 14482 (2017)
- [47] Liu, J. *et al.* Self-assembled epitaxy of Ga<sub>2</sub>Se<sub>3</sub> on the oxidized GaSe surface and atomic imaging of the Ga<sub>2</sub>Se<sub>3</sub>/GaSe heterostructure. *Appl. Surf. Sci.* **586**, 152774 (2022)
- [48] Wu, C.-Y. *et al.* Controlled synthesis of GaSe microbelts for high-gain photodetectors induced by the electron trapping effect. *J. Mater. Chem. C* **8**, 5375–5379 (2020)
- [49] Yang, S. *et al.* High performance few-layer GaS photodetector and its unique photo-response in different gas environments. *Nanoscale* **6**, 2582–2587 (2014)
- [50] Mi, W. *et al.* Ultraviolet–green photoluminescence of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> films deposited on MgAl<sub>6</sub>O<sub>10</sub> (100) substrate. *Opt. Mater. (Amst)*. **35**, 2624–2628 (2013)
- [51] Yu, D. ., Bubendorff, J.-L., Zhou, J. ., Leprince-Wang, Y. & Troyon, M. Localized cathodoluminescence investigation on single Ga<sub>2</sub>O<sub>3</sub> nanoribbon/nanowire. *Solid State Commun.* **124**, 417–421 (2002)
- [52] Chiricenco, V., Caraman, M., Rusu, I. . & Leontie, L. On the luminescence of GaS(Cu) single crystals. *J. Lumin.* **101**, 71–77 (2003)
- [53] Zhang, P. *et al.* Space–charge limited current in nanodiodes: Ballistic, collisional, and dynamical effects. *J. Appl. Phys.* **129**, 100902 (2021)
- [54] Jiang, J. *et al.* Defect Engineering for Modulating the Trap States in 2D Photoconductors. *Adv. Mater.* **30**, 1804332 (2018)

## Graphical abstract

