Scalable Thin-Film GaSe Epitaxy and Chemical Conversion into Ga_2O_3

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Van der Waals (vdW) semiconductors offer new avenues for advanced technologies beyond the constraints of Moore's law [1]. However, their widespread application necessitates precise and scalable manufacturing processes. Here, high-quality GaSe vdW semiconductor crystals are grown by molecular beam epitaxy (MBE) [2] with electronic properties controlled during growth or post-growth thermal oxidation. High-temperature annealing of GaSe in an oxygen-rich environment triggers its full conversion into the crystalline oxide Ga_2O_3, providing multiple-functionalities on a unified platform, from electrical insulation to deep ultraviolet (UV) optoelectronics [3].

High-quality wafer-scale GaSe crystals with a range of layer thicknesses are produced by MBE on 2-inch c-plane (0001) sapphire (Al_2O_3) wafers (Fig. 1a). The grown GaSe layers feature a dominant D_{3d} polymorph, referred to as γ'-GaSe (Fig. 1a) [2]. Thermal annealing in a tube furnace under a controlled atmosphere of oxygen (0.5 sL/min) and argon (2.0 sL/min) and a range of annealing temperatures T_a (from 400 to 900 °C), produces a sequential conversion of GaSe into the intermediate Ga_2Se_3 phase, followed by transformation into amorphous Ga_2O_3, and ultimately the formation of crystalline Ga_2O_3 (Fig. 1b). This process departs from a Fickian oxygen-diffusion model and indicates that the diffusion and reaction kinetics in thin layers is assisted by strain.

The absorption spectra of as-grown GaSe and Ga_2O_3 reveal a lower absorption coefficient in the oxide across a wide spectral range and a clear shift of the absorption edge from 2.3 eV in GaSe to 4.5 eV in Ga_2O_3 (Fig. 1c). Due to their wide bandgap, both amorphous and crystalline Ga_2O_3 are transparent across a broad spectrum that extends from UV to visible wavelengths with selective absorption the UV-C band (200-280 nm) that provides a platform for sensors in this important technological spectral range. The UV-C band is free of solar background at ground level, enabling deployment of wide field-of-view receivers for better signal detection and low background noise for non-line-of-sight and line-of-sight communication. The devices have low (< 0.1 nA) dark current, high (> 10^3) on/off ratio and fast (< 1 ms) UV-C photoresponse under low (V = 2 V) applied bias (Fig. 1d).

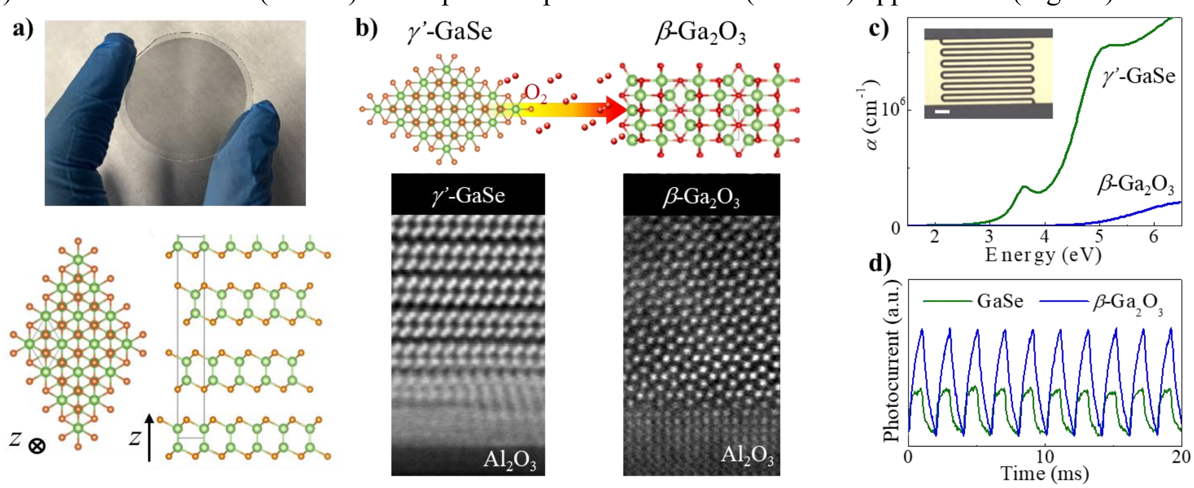

Fig.1. a) Photograph of GaSe on sapphire and schematic of crystal structure. b) Schematic of the conversion of GaSe into Ga_2O_3 by thermal annealing and high-resolution STEM images of GaSe and Ga_2O_3. c) Absorption spectra for GaSe and Ga_2O_3. Inset: optical image of device with interdigitated Au-contacts (scale bar: 1 mm). d) Temporal modulation of the photocurrent in GaSe and Ga_2O_3 under UV-C excitation (λ = 260 nm, P = 3.3 μW).

References: [1] K. S. Novoselov et al., Science, **353**, 6298 (2016); [2] M. Shiffa et al., Small, **20**, 7, 2305865 (2024); [3] N. D. Cottam et al., unpublished.