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Scalable Production of Light-Sensitive Devices from Liquid-Phase Exfoliated Transition Metal Monochalcogenide Flakes

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Abstract

Layered semiconductors of IIIA–VIA group, have attracted considerable attention in (opto)electronic applications thanks to their atomically thin structures and their (opto)electronic properties. Currently, two-dimensional (2D) indium selenide (InSe) and gallium selenide (GaSe) are emerging as promising candidates for the realization of light-driven thin-field effect transistors (FETs) and photodetectors due to their high intrinsic mobility ($10^2 - 10^3$ $cm^2V^{-1}s^{-1}$) and their direct bandgap in an energy range ($1.3 - 3.2$ eV) suitable for UV, visible and NIR light detection. A requirement for large-scale electronic applications is the development of low-cost, reliable industrial production processes. In this context, it has been recognized that liquid-phase exfoliation (LPE) of InSe and GaSe is a cost-effective and environmentally friendly way to formulate inks for FETs, presenting a significant advantage over conventional methods. In this study, printed InSe and GaSe phototransistors are presented showing high responsivity ($13 - 274$ AW^{-1}) and fast response velocity ($15 - 32$ ms). Furthermore, GaSe phototransistors show an on-off current ratio of $\sim 10^3$ in the dark, which can be readily achieved without the need for complex design of drain/source contacts or gating techniques. The gate-dependent photoresponse shows that the phototransistors can be modulated by the gate voltage. These results demonstrate that liquid-phase exfoliated InSe and GaSe are valid candidates for low-cost high-performance (opto)electronic devices.

1 Introduction

Two-dimensional layered materials (2DLMs), formed by layers of bonded atoms held together in the out of plane direction by weak van der Waals forces, have been employed in many research fields, including fundamental physics [1, 2] photonics [3, 4], (opto)electronics [5, 6] and energy storage and conversion [7–10]. In particular, ultra-thin layered semiconductors of IIIA–VIA group such as InSe and GaSe have recently been recognized as a topic of interest for the scientific community [11]. Unlike transition metal dichalcogenides (TMDs) that exhibit a direct bandgap only in the few-layered (< 5 nm) form, InSe and GaSe show an indirect gap in the monolayer and a gradual transition to a direct bandgap when the thickness increases [5, 6, 11]. This can be advantageous for light detection because few-layer films ensure high absorption of light while being more stable than monolayers towards degradation. Moreover, their bandgap energy can be tuned in a wide range from ~ 1.3 eV to ~ 3.2 eV (at room temperature) depending on the material under consideration and the thickness [5, 6]. This leads to a wide spectral response from UV and visible light to near-infrared (NIR) due to quantum-size confinement effects of the natural quantum-well determined in few-layer InSe and GaSe flakes [5, 6]. Several groups reported high-performance field-effect transistors based on single-layer and few-layer InSe and GaSe, but despite the great potential demonstrated by these excellent figures of merit, the above-mentioned results were obtained using laboratory-scale production methods [5, 6]. Another way to produce layered materials is provided by liquid-phase exfoliation (LPE), which is capable to produce large quantity of liquid dispersions of thin 2D crystals with high crystalline integrity [7, 12]. The as-produced liquid dispersions of 2D crystals are suitable for large-scale and on-demand deposition with established methods (*e.g.*, spray-coating, dip-coating, spin-coating, screen-printing, inkjet-printing) [5, 6], making LPE a viable technique for all the applications demanding high volume and cost-effective solutions. In this work, it has been investigated the potential of spray-coating deposition, a widespread industrial coating process, for the fabrication of high-performance solution-processed InSe photodetectors and GaSe phototransitors. It has been shown that light-sensitive devices based on spray-coated films of liquid-phase exfoliated flakes of InSe and GaSe in isopropyl alcohol (IPA) exhibit very high responsivity ($13 - 274$ AW^{-1}) to light in a broad spectrum (350 nm

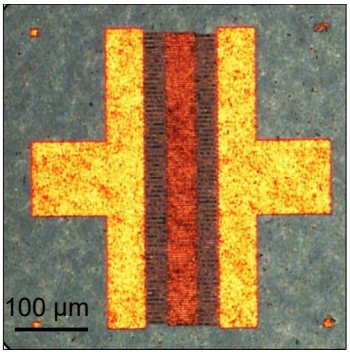

Figure 1. Optical microscope image of the complete photodetector.

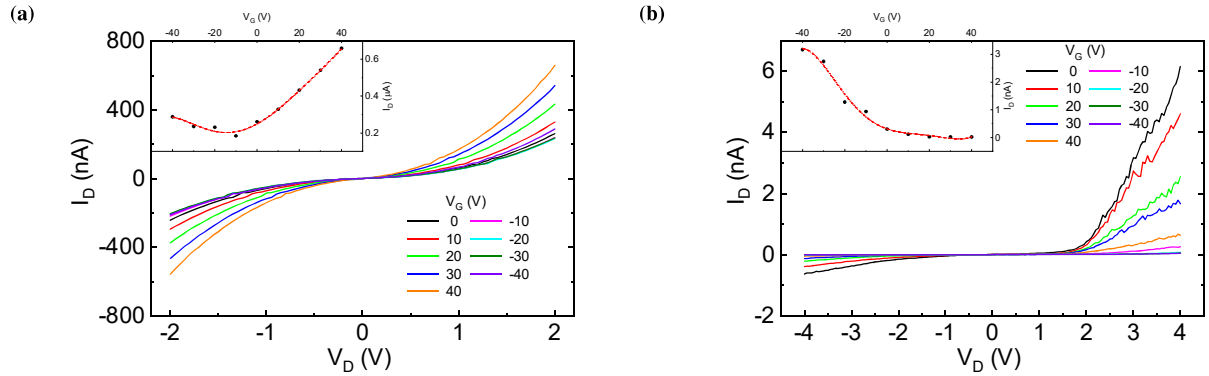

Figure 2. Source-drain current (I_D) *vs.* source-drain voltage (V_D), recorded in the dark at bottom-gate voltage (V_G) values between -40 and 40 V, for both a) InSe and b) GaSe. In inset, I_D *vs.* V_G curves.

- 900 *nm*), surpassing previous records of responsivity in photodetectors based on percolating networks of solution-processed 2D flakes by more than one order of magnitude [5]. In addition, The GaSe phototransistor exhibits a p-channel gate-voltage dependent behavior with a high on/off ratio of $\sim 10^3$.

2 Materials and Methods

2.1 Material Production

The synthesis of $\beta-$InSe and $\varepsilon-$GaSe bulk crystals was performed with the Bridgman-Stockbarger method. Solvents commonly used for the production of 2D-material-based dispersions (*e.g.*, N$-$methyl$-$2$-$pyrrolidone – NMP, dimethylformamide – DMF) present serious health hazards. Moreover, they contaminate the substrates degrading the properties of the printed materials, due to their low vapour pressure and high boiling point of the solvents ($T_b \sim 200^oC$). For these reasons, alternative low boiling temperature ($< 100^oC$) and environmentally friendly liquid mediums are investigated for LPE. It has been performed LPE of InSe and GaSe in IPA followed by sonication and ultracentrifugation in order to achieve a good compromise between ink stability, lateral size, and thickness of the flakes. Isopropyl alcohol, thanks to its low toxicity with respect to other organic solvents (*e.g.*, NMP, DMF, etc. health code ≥ 2 NFPA704) and its low boiling point [5] is a suitable solvent for LPE of InSe and GaSe crystals.

2.2 Photodetector Fabrication

The InSe and GaSe dispersions were sprayed on different samples. Several electrode arrays were deposited on the same substrate in order to exploit the large area deposition capability of the spray coating process. Electrodes with small length ($L = 1\ \mu m$) and large total width of the conduction channel ($W = 5760\ \mu m$), provide an active area $W \cdot L$ for photodetection. The interdigitated gold electrode array was fabricated using e-beam lithography and lift-off on highly doped silicon (100) with 100 *nm* thermal oxide on the surface. Each electrode consists of 65 interdigitated fingers with an overlap of 40 μm (Fig. 1). A volume of 30 *ml* of the as-obtained InSe and GaSe dispersions in IPA were deposited by spray-coating onto the patterned substrate, which was heated to 60^oC to favour quick solvent evaporation during the deposition. The coated samples was placed under vacuum overnight at room temperature to stabilize the deposited film and remove residual solvents. A 200^oC annealing for 30 *min* in argon atmosphere was then performed to improve the interface between flakes and the contact with electrodes.

3 Results and Discussion

The current *vs.* voltage (I–V) curves of the InSe photodetector and GaSe phototransistors are first described in dark conditions and were measured at room temperature and under vacuum in order to avoid the influence of moisture and atmospheric gases. The doped silicon substrate was electrically contacted to apply a gate bias V_G. For both InSe and GaSe, as shown in Fig. 2a and Fig. 2b, the drain-source current (I_D) varies with V_D under different V_G (from -40 to 40 V), indicating that I_D can be effectively controlled by electrostatic doping. In particular, for InSe, the inset in Fig. 2a shows the $I_D - V_G$ transfer curves in dark at the drain bias voltage of 15 V. The device shows an ambipolar behaviour with a minimum I_D current at $V_G \sim -10\ V$ and a distinct asymmetry in electron and hole conductance (inset Fig. 2a) showing apparent mobility of $3 \cdot 10^{-5}\ cm^2V^{-1}s^{-1}$ for electrons and $1 \cdot 10^{-5}\ cm^2V^{-1}s^{-1}$ for holes. The transistor is n-doped at $V_G = 0\ V$ and never appears in the off-state, which could be explained by the presence of the defect states in the gap of InSe. On the other hand, in the case of GaSe, the transistor is p-doped at $V_G = 0\ V$ and is in the off-state ($I_D \sim 25\ pA$) for $V_G > 20\ V$, exhibiting a unipolar behavior (inset of Fig. 2b). An on/off current ratio (I_{on}/I_{off}) of $\sim 10^3$ was determined from I_D *vs.* V_G measurements by taking the ratio of maximum to minimum I_D with gate voltage between -40 and $+40\ V$. Moreover, it has been found a a field-effect differential mobility of the film of $\sim 10^{-3}\ cm^2V^{-1}s^{-1}$ for a V_G in the range between -40 and 0 V (inset of Fig. 2b). In order to study the behaviour of the devices as photodetectors, the photoresponse

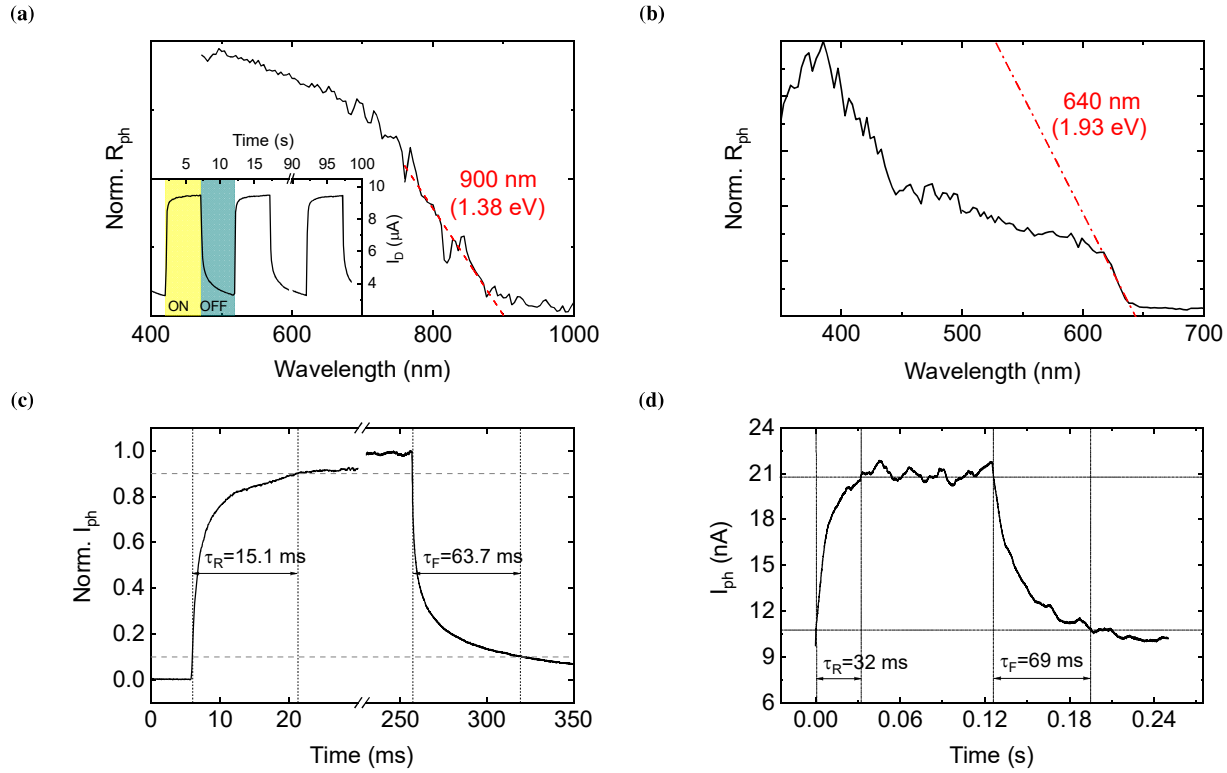

Figure 3. Spectral responsivity of a) InSe and b) GaSe photodetectors. The dashed line is a linear fit of the tail of the spectrum. The inset of a) plots the response to 0.1 *Hz* pulsed light (530 *nm*). Photocurrent rise and decay during pulsed light excitation for c) InSe and d) GaSe.

(R_{ph}) was measured under the exposure to different light stimuli for both InSe and GaSe (Fig. 3). In the case of InSe, the maximum R_{ph} is $\sim 274\ AW^{-1}$ at 455 *nm*, corresponding to an irradiance of $\sim 0.53\ mWcm^{-2}$. It has been obtained a R_{ph} much higher than photodetectors based on solution-processed 2D crystals, and InSe in particular [5]. The spectral response of the device is shown in Fig. 3a in the visible and NIR range at bias voltages $V_D = 2\ V$ and gate voltage $V_G = 0\ V$. The R_{ph} is higher at short wavelength and decreases around 800 *nm*, resulting in a bandgap value (E_{gap}) of 1.38 eV. In the case of GaSe, the photodetector is responsive in the UV-visible range, as shown in Fig. 3b, and it was measured at bias voltages $V_D = 3\ V$ and gate voltage $V_G = 0\ V$. It has been found that R_{ph} has a peak at 385 *nm*, with a value of $\sim 13\ AW^{-1}$ and decreases toward longer wavelengths with a pronounced drop at ~ 600 *nm*. The bandgap can also be estimated from the spectral responsivity. The resulting value of ~ 640 *nm* corresponds to $E_{gap} \sim 1.93\ eV$. Finally, it has been reported the time response of the InSe and GaSe devices, obtained by measuring the current during slow modulation of light source. For both devices, excellent long-term stability is observed with fast switching and reproducible transition from "ON" to "OFF" conditions. In particular, for InSe, the measured rise (fall) times, defined as the time to go from 10% (90%) to 90% (10%) of the maximum current, are $\tau_R = 15.1\ ms$ ($\tau_F = 63.7\ ms$), which are among the fastest reported for photodetectors made with films of LPE flakes of InSe (Fig. 3c). On the other hand, for GaSe, the measured rise (fall) times are $\tau_R \sim 32\ ms$ ($\tau_F \sim 69\ ms$) (Fig. 3d).

4 Conclusions

In this paper, it has been reported that spray-coated liquid phase exfoliated networks of InSe and GaSe flakes are suitable for the production of light-sensitive devices with good photoresponsivity to a wide range of excitations from UV to visible and NIR light, and can be used as semiconductor channel material in phototransistors, obtaining a high-throughput and low-cost method to implement photodetectors with high sensitivity and fast response time. The use of spray coating and environmentally friendly solvents in the fabrication process is essential to control the morphology and connectivity of the flakes network in order to substantially improve the mobility, the on-off ratio and the switching speed, making these materials interesting alternatives for photodetectors in the UV, visible and NIR spectral range, also for applications on flexible substrates.

References

[1] S. Sunku, D. Halbertal, R. Engelke, H. Yoo, N. Finney, N. Curreli, G. Ni, C. Tan, A. McLeod, C. Lo, C. Dean, J. Hone, P. Kim, and D. Basov, "Dual-gated graphene devices for near-field nano-imaging," *Nano Letters*, vol. 21, no. 4, pp. 1688–1693, 2021.

[2] A. C. Ferrari, F. Bonaccorso, V. Fal'Ko, K. S. Novoselov, S. Roche, P. Bøggild, S. Borini, F. H. Koppens, V. Palermo, N. Pugno *et al.*, "Science and technology roadmap for graphene, re-

lated two-dimensional crystals, and hybrid systems," *Nanoscale*, vol. 7, no. 11, pp. 4598–4810, 2015.

[3] C. Trovatello, A. Marini, X. Xu, C. Lee, F. Liu, N. Curreli, C. Manzoni, S. Dal Conte, K. Yao, A. Ciattoni, J. Hone, X. Zhu, P. Schuck, and G. Cerullo, "Optical parametric amplification by monolayer transition metal dichalcogenides," *Nature Photonics*, vol. 15, no. 1, pp. 6–10, 2021.

[4] F. Bonaccorso, Z. Sun, T. Hasan, and A. Ferrari, "Graphene photonics and optoelectronics," *Nature photonics*, vol. 4, no. 9, pp. 611–622, 2010.

[5] N. Curreli, M. Serri, D. Spirito, E. Lago, E. Petroni, B. Martín-García, A. Politano, B. Gürbulak, S. Duman, R. Krahne, V. Pellegrini, and F. Bonaccorso, "Liquid phase exfoliated indium selenide based highly sensitive photodetectors," *Advanced Functional Materials*, vol. 30, no. 13, p. 1908427, 2020.

[6] N. Curreli, M. Serri, M. Zappia, D. Spirito, G. Bianca, J. Buha, L. Najafi, Z. Sofer, R. Krahne, V. Pellegrini, and F. Bonaccorso, "Liquid-phase exfoliated gallium selenide for light-driven thin-film transistors," *Advanced Electronic Materials*, vol. 7, no. 3, p. 2001080, 2021.

[7] S. Bellani, E. Petroni, A. Del Rio Castillo, N. Curreli, B. Martín-García, R. Oropesa-Nuñez, M. Prato, and F. Bonaccorso, "Scalable production of graphene inks via wet-jet milling exfoliation for screen-printed micro-supercapacitors," *Advanced Functional Materials*, vol. 29, no. 14, p. 1807659, 2019.

[8] A. Capasso, S. Bellani, A. Palma, L. Najafi, A. Del Rio Castillo, N. Curreli, L. Cina, V. Miseikis, C. Coletti, G. Calogero, V. Pellegrini, A. Di Carlo, and F. Bonaccorso, "Cvd-graphene/graphene flakes dual-films as advanced dssc counter electrodes," *2D Materials*, vol. 6, no. 3, p. 035007, 2019.

[9] M. Zappia, G. Bianca, S. Bellani, N. Curreli, Z. Sofer, M. Serri, L. Najafi, M. Piccinni, R. Oropesa-Nuñez, P. Marvan, V. Pellegrini, I. Kriegel, M. Prato, A. Cupolillo, and F. Bonaccorso, "Two-dimensional gallium sulfide nanoflakes for uv-selective photoelectrochemical-type photodetectors," *Journal of Physical Chemistry C*, 2021.

[10] M. Ghini, N. Curreli, A. Camellini, M. Wang, A. Asaithambi, and I. Kriegel, "Photodoping of metal oxide nanocrystals for multi-charge accumulation and light-driven energy storage," *Nanoscale*, vol. 13, no. 19, pp. 8773–8783, 2021.

[11] N. Curreli, A. Fanti, G. Mazzarella, and I. Kriegel, "Linear and nonlinear optical propagation in 2d materials," *arXiv preprint arXiv:2103.13884*, 2021.

[12] A. Del Rio Castillo, V. Pellegrini, A. Ansaldo, F. Ricciardella, H. Sun, L. Marasco, J. Buha, Z. Dang, L. Gagliani, E. Lago, N. Curreli, S. Gentiluomo, F. Palazon, M. Prato, R. Oropesa-Nuñez, P. Toth, E. Mantero, M. Crugliano, A. Gamucci, A. Tomadin, M. Polini, and F. Bonaccorso, "High-yield production of 2d crystals by wet-jet milling," *Materials Horizons*, vol. 5, no. 5, pp. 890–904, 2018.