Patterning of high-quality two-dimensional chalcogenide crystals with unique planar structures and various fascinating electronic properties offers great potential for batch fabrication and integration of electronic and optoelectronic devices. However, it remains a challenge that requires accurate control of the crystallization, thickness, position, orientation and layout. Here we develop a method that combines microintaglio printing with van der Waals epitaxy to efficiently pattern various single-crystal two-dimensional chalcogenides onto transparent insulating mica substrates. Using this approach, we have patterned large-area arrays of two-dimensional single-crystal Bi$_2$Se$_3$ topological insulator with a record high Hall mobility of $\sim 1,750$ cm$^2$ V$^{-1}$ s$^{-1}$ at room temperature. Furthermore, our patterned two-dimensional In$_2$Se$_3$ crystal arrays have been integrated and packaged to flexible photodetectors, yielding an ultrahigh external photoresponsivity of $\sim 1,650$ A W$^{-1}$ at 633 nm. The facile patterning, integration and packaging of high-quality two-dimensional chalcogenide crystals hold promise for innovations of next-generation photodetector arrays, wearable electronics and integrated optoelectronic circuits.
Two-dimensional (2D) chalcogenide crystals are single- and few-layer chalcogenides with a unique planar structure, such as 2D transition-metal chalcogenides NbSe$_2$ and MoS$_2$, III–VI In$_2$Se$_3$ and GaSe, IV–VI SnSe and V–VI Bi$_2$X$_3$ (X = Se or Te). This big family offers a potentially high mobility and rich electronic band structures ranging from semimetals to semiconductors and even topological insulators, having emerged as attractive candidates for the applications in electronics and optoelectronics$^{1-10}$. In this family, layered Bi$_2$X$_3$ were recently discovered as topological insulators, a new state of quantum matter with an insulating bulk state and gapless Dirac-type edge/surface states$^{11-13}$. Compared with bulk materials, 2D crystals of Bi$_2$X$_3$ topological insulators with large surface-to-volume ratios and enhanced exotic surface states provide excellent 2D geometry for the fabrication and integration of functional devices$^{3,14,15}$. In$_2$Se$_3$, another intriguing chalcogenide was recently synthesized in atomically thin flakes. Transistors based on 2D In$_2$Se$_3$ crystals showed an efficient photoresponsivity, made them promising candidate in high-performance optoelectronics$^{16}$.

Herein, by combining microintaglio printing with van der Waals epitaxy, we have developed a method to efficiently pattern various 2D chalcogenide crystals onto mica substrates. Large-area arrays of 2D single-crystal chalcogenides with remarkable properties can be readily prepared. We believe that this patterning method paves the way for the application of 2D chalcogenide crystals in electronics and optoelectronics.

Results

Patterning of 2D chalcogenide crystals. Figure 1a illustrates the patterning process of 2D chalcogenide crystals on layered pseudohexagonal fluorophlogopite mica [KMg$_3$(AlSi$_3$O$_{10}$)F$_2$] substrates. As an ideal van der Waals epitaxy substrate$^{21}$, freshly cleaved mica surface was first intaglio printed by solvent ink using a polydimethylsiloxane (PDMS) stamp, which has a surface relief structure containing the desired patterns. After microintaglio printing and vacuum drying of solvent ink, the mica surface modified with intaglio patterns was released from the PDMS stamp and used for selective-area van der Waals epitaxy of various 2D chalcogenide crystals in a set-up similar to our previous nanoribbon and nanoplate synthesis (see Methods, Supplementary Fig. 1, Supplementary Fig. 2 and Supplementary Note 1 for a detailed description)$^8,14$. The pattern of as-grown various 2D crystals is faithfully reproduced from the relief pattern of the PDMS stamp.

The crystal structure of layered Bi$_2$X$_3$ is schematically depicted in Fig. 1b. Each covalently bonded X–Bi–X quintuple layer
Mechanism of patterning 2D chalcogenide crystals. Understanding the crystal growth mechanism of 2D arrays is related to how to precisely control the patterning process and is therefore critical to achieve high device uniformity and high device yield for the practical applications in the large-area nanoelectronics and optoelectronics. To this end, we systematically investigated the intaglio printing process, nucleation and growth of 2D crystals. The solvent ink is usually made from the PDMS oligomer, which is dissolved in the most common organic solvent such as acetone, ethanol and cyclohexane. During the intaglio printing, the solvent ink is transferred onto the mica surface from microwells or cells of the patterned PDMS stamp (Fig. 2a). We in situ observed the transfer process of the solvent ink between the PDMS stamp and the mica surface using a contact angle goniometer (Fig. 2b). Interestingly, the ink surface inside the wells of PDMS forms a concave meniscus due to the capillary action and wettabiity during the solvent evaporation (Supplementary Table 1), which gives rise to the additional aggregation of residue along the edge of imprint patterns. After drying of the solvent ink, imprints are formed on the non-contacted regions between the PDMS stamp and mica surface. AFM measurements show that the imprints of PDMS oligomer have an average thickness of ~0.5 nm and an root mean squared roughness of ~0.4 nm at room temperature (Fig. 2c). After 1 h heating at 700°C, the imprints can still be seen by AFM (Fig. 2d). In a controlled experiment, an aqueous solution ink of NaCl was used to form a heat-stabilized inorganic crystal imprint on mica, which further confirms the intaglio printing process (Supplementary Fig. 8 and Supplementary Note 4).

We find that imprints of solvent intaglio-printed onto mica provide the control over the nucleation of vapour-grown 2D chalcogenide crystals on the contacted regions of mica. Interestingly, the additional aggregation of residue at the edge of the imprints facilitates the nucleation of 2D seeds (Fig. 2e). As the growth continues, 2D seeds grown up from different nuclei can coalesce to form large-size seed aggregates, rings, and eventually continuous nanocrystals on mica (Fig. 2f,g). Thicker nanocrystals were obtained with the layer-by-layer growth mode by varying the growth time and deposition temperature (Fig. 2h). Figure 2i,j shows typical AFM images of merged areas at which adjacent islands coalesced together. To further examine the microstructure of merged areas by transmission electron microscopy (TEM), as-grown discrete 2D crystals were faithfully transferred from the mica substrate to a lacey carbon support film on a TEM grid using an efficient poly(methyl methacrylate)-mediated transfer technique (Supplementary Fig. 9, Supplementary Fig. 10 and Supplementary Note 5). Importantly, extensive TEM studies indicated that these discrete 2D crystal islands with six-fold symmetry are unidirectionally aligned and then merge to uniform single-crystal nanoplate rings with predefined orientation and smooth surface (Fig. 2k,l, Supplementary Fig. 10 and Supplementary Note 6). Note no discontinuous lines or wrinkles were observed in the merged areas. Eventually, 2D-ordered arrays of continuous nanocrystals without any noticeable grain boundary defects were formed on prepatterned mica. Besides the identical orientation of multiple islands, both the ultraflat mica surface (root mean squared roughness ~0.07 nm, Supplementary Fig. 11) and weak interlayer interaction facilitate seamless, defect-free coalescence of the adjacent layered islands during the van Waals epitaxy.

Evaluation of patterned 2D chalcogenide arrays. We have systematically evaluated the crystal structure and electronic structure of as-grown 2D chalcogenide crystals. In the case of Bi2Se3, a well-ordered array of truncated triangular Bi2Se3 nanoplates was patterned on the mica surface, in which the edges of nanocrystals on mica were oriented predominantly at multiples of ~60° (Fig. 3a,b), consistent with the 2D hexagonal lattice of the Bi2Se3 QL. TEM and selected area electron diffraction further indicate the excellent alignment and the epitaxial nature of 2D-ordered nanoplate arrays patterned on mica. HRTEM (high-resolution TEM) and corresponding fast Fourier transformation pattern of individual Bi2Se3 nanoplates reveal that nanoplates are single-crystalline rhombohedral phase with atomically smooth edges parallel to the (11–20) direction (Fig. 3c,d). Energy-dispersive X-ray spectroscopy analyses revealed uniform chemical composition along the entire plane with a Bi/X atomic ratio of 2:3 (Supplementary Fig. 12). In addition to highly crystalline structure, the electronic band structure of the individual 2D Bi2Se3 crystal was directly measured by microspot angle-resolved photoemission spectroscopy (micro-ARPES) with high spatial resolution (Fig. 3e,f, Supplementary Fig. 13 and Supplementary Note 7), which unambiguously reveals clear linear dispersion of the topological surface state, characteristic of the topological insulator11.

The high crystalline quality and robust topological surface states of 2D Bi2Se3 crystals allow us to explore their high mobility transport. We first measured the temperature-dependent carrier concentration and carrier mobility of a Hall bar device of a ~30-QL-thick Bi2Se3 nanoplate directly fabricated by electron beam lithography (EBL) on mica substrates (Fig. 3g, Supplementary Fig. 14 and Supplementary Note 8). It was
observed that the carrier concentration decreases and the carrier mobility increases with decreasing temperature from 300 K down to 80 K, showing a semiconductor-like behaviour. Remarkably, a room temperature carrier mobility $m_n = 1,750 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is obtained, which is the highest value reported for Bi$_2$Se$_3$ nanostructures such as nanowires, nanoribbons, nanoplates and thin films. Statistical measurements of carrier mobility indicate that our Bi$_2$Se$_3$ crystals have high mobility and reasonable uniformity. We speculate that the ultrahigh mobility is attributed to the suppression of scattering at grain boundaries and inter-terrace steps with improved quality of 2D crystals.

Optoelectronic measurements of patterned 2D crystals. The excellent transport properties of 2D chalcogenide crystals facilitate high-performance optoelectronic applications because of their sizable bandgaps, large surface-to-volume ratio and the absence of dangling bonds. Large-area, high crystalline quality nanoplates of 2D crystals grown on transparent dielectric mica substrates can provide a platform for transfer-free fabrication and measurements of flexible optoelectronic devices, such as transparent electrodes and photodetectors. Grid networks containing 2D Bi$_2$Se$_3$ crystals with metallic surface states synthesized by this patterning technique are presented in Supplementary Fig. 16 and Supplementary Note 9, which can be used as novel broadband transparent flexible electrodes. On the other hand, the patterned In$_2$Se$_3$ crystal is n-type semiconductor with suitable direct bandgap ($\sim 1.3 \text{ eV}$) and extraordinary photoresponse (Supplementary Fig. 17 and Supplementary Note 10). For practical high-performance photodetector applications, flexible In$_2$Se$_3$ photodetector arrays with several individual channels were directly fabricated by photolithography on the transparent mica substrate (Fig. 4a,b). Photocurrent ($I_{\text{ph}}$) signals from individual channels as well as their additions were collected by illuminating the single and multiple channel devices (Fig. 4c, Supplementary Fig. 18), indicating realizable, stable, cooperative operations of high spatial resolution photodetector arrays.

Figure 2 | Mechanism of patterning 2D chalcogenide crystals. (a) Schematic of microintaglio printing process to form imprints on mica surface. (b) Charge-coupled device camera photos showing the transfer of solvent ink from a microwell of PDMS stamp onto mica. (c,d) AFM images of the imprints on mica surface captured directly after microintaglio printing (c) and after heating at 700 °C for 1 h (d). Scale bars in c and d, 5 µm. (e-h) Transmission-mode OM images of Bi$_2$Se$_3$ crystals on mica at different nucleation and growth stages: the nucleation of Bi$_2$Se$_3$ crystal islands starting from the edge of the imprints (e), epitaxial growth of Bi$_2$Se$_3$ crystal ring from the edge to the middle (f), formation of complete patterns after merging of different islands (g), the formation of thicker, single crystals at longer growth time (h). Scale bars in e–h, 10 µm. (i) AFM image of a patterned Bi$_2$Se$_3$ crystal in the middle stage of the growth process. Scale bar, 3 µm. Inset of i, reflection-mode OM image of the same crystal. Scale bar of i inset, 5 µm. (j) Enlarged AFM image of the merging region of two domains indicated in the box of i. Scale bar, 500 nm. Below panel of j, height distribution diagram of the indicated area. (k) TEM image of a patterned Bi$_2$Se$_3$ crystal in the middle stage of the growth process. Scale bar, 2 µm. Inset of k, diffraction pattern of the common merged area indicated by a red square showing single-crystal nature. (l) HRTEM image from the merging region indicated in k. Scale bar, 2 nm.
from a 2D array. Scale bar of inset, 5 μm. Temperature for an individual Bi2Se3 crystal with the thickness of 5 0.1 nm, a hallmark of the topological insulator. The conduction band (CB), valence band (VB), surface state (SS) and Dirac point (DP) are indicated, together with Fermi energy (EF), the energy level of Dirac point (E_D) and wave vector k. Hall mobility (μ_h) and carrier density (n) as a function of temperature for an individual Bi2Se3 crystal with the thickness of ~30 nm. Inset: OM image of a Hall-bar device fabricated on an individual Bi2Se3 crystal from a 2D array. Scale bar of inset, 5 μm. (h) Statistic distribution of room temperature mobility of five devices based on the 2D Bi2Se3 crystal array, indicating high mobility and reasonable uniformity of 2D crystals.

Discussion

One of the most striking properties of 2D chalcogenide crystals is their high photosensitivity, where the responsivity is the photocurrent I_p divided by the incident power: R_p = I_p/P_in. To gain further insight into the characteristics of the 2D photodetector, we extracted the representative I_p = V_{SD} output curves (Fig. 4d) and calculated the photoresponsivity (Fig. 4e) of 2D In2Se3 crystals illuminated at 633 nm under different incident light intensities. As the light intensity increases, more excited photocarriers are produced by interband transition and transported to the electrodes under the fixed bias, leading to more current. The photoresponsivity presents a non-linear dependence on the increasing incident light intensity and a final saturation behaviour, which may be attributed to the defects and/or charged impurities on the surface of the channel materials. This phenomenon has also been observed in 2D MoS2 photodetectors. Under low incident power (P_in = 622 nW cm$^{-2}$, 40 μm$^2$), the In2Se3 device shows a remarkable responsivity of 1,650 AW$^{-1}$ at 5 V bias, 10$^3$ times higher than graphene-based photodetector ($R_p = 0.1 \sim 10$ mAW$^{-1}$) and approximately two times higher than the best 2D MoS2 photodetector ($R_p = 880$ AW$^{-1}$)$^3$. From the three-dimensional photoresponsivity map of In2Se3 photodetector (Supplementary Fig. 19), the photoresponsivity can be modulated by the bias voltage $V_{SD}$, suggesting higher responsivity can be readily achieved by applying a larger bias voltage. Spatial photocurrent mapping of 2D In2Se3 crystals array shows a reasonable uniformity of the patterned crystal array (Supplementary Fig. 18), and the statistic measurements of 18 semiconductor In2Se3 photodetectors indicate 2D In2Se3 crystal arrays have high photoresponsivity with a reasonable uniformity (Fig. 4f).

The photoresponsivity can range from several hundred to several thousand A/W, depending on the sample thickness, bias, incident light power and so on. The highest photoresponsivity of 2D In2Se3 crystal is measured as 4,470 A/W at a bias of 5 V (Supplementary Fig. 20).

The packaging is another important aspect for practical applications of optoelectronic devices. We exploited a lamina-based packaging method of patterned 2D chalcogenide crystals on mica$^{28}$. Figure 4g shows a schematic diagram, representative photograph and OM image of packaged 2D optoelectronic devices. The device typically consists of three parts—a transparent polyethylene terephthalate (PET) previously coated with thin metal electrodes, a transparent flexible mica flake that supports 2D crystal array and a transparent PET substrate coated with a polyimide adhesive layer. When the three portions are put together to form a sandwiched configuration by OM-assisted physical lamination, van der Waals interactions between 2D crystals and metal electrodes facilitate the formation of intimate contact with clean interfaces, which may avoid the degeneration of devices introduced by standard lithography process and metal evaporation. This packaged photodetector exhibits a remarkable photoresponse (Fig. 4h) after switching incident light on or off many times. In addition, we investigated the mechanical durability of packaged 2D crystal photodetectors after repeated bending. Figure 4i shows the current as a function of bending cycles with the laser on or off at a bias voltage of 5 V. The packaged 2D In2Se3 photodetector kept its structural integrity, with little variation in both photocurrent and dark current. 

Figure 3 | Evaluation of the crystal structure and electronic structure of 2D chalcogenide crystal arrays. (a) Typical transmission-mode OM image of a 7 × 10 Bi2Se3 nanoplate array with the same orientation on a transparent mica substrate. Scale bar, 20 μm. (b) Histogram of the orientation distribution of Bi2Se3 nanoplates in a. (c) TEM image of a patterned Bi2Se3 crystal array transferred to a lacey carbon support film on a TEM copper grid. Scale bar, 5 μm. (d) HRTEM image obtained from the same Bi2Se3 crystal array, with corresponding fast Fourier transformation pattern shown in the inset. Scale bar, 1 nm. (e) Full valance spectra contrast map of a 2D Bi2Se3 crystal array measured by micro-ARPES with beam spot size of ~1μm and a 1-μm step scan. Scale bar, 20 μm. (f) Electronic band structure of individual Bi2Se3 crystals, showing a direct bulk gap and surface states consisting of a single Dirac cone, a hallmark of the topological insulator. The conduction band (CB), valence band (VB), surface state (SS) and Dirac point (DP) are indicated, together with the Fermi energy (EF), the energy level of Dirac point (E_D) and wave vector k. The...
current after repeated dynamic bending tests, respectively, indicating its excellent flexibility and durability.

In summary, we have developed an efficient method to pattern high crystalline quality 2D chalcogenide crystals on mica substrates by the combination of microintaglio printing with van der Waals epitaxy. Accurate control of the crystallization, thickness, position, orientation and layout of patterned 2D chalcogenide crystals has been achieved. Large arrays of 2D single-crystal Bi$_2$Se$_3$ topological insulator with a record high Hall mobility show promise as broadband transparency flexible transparent electrodes. Furthermore, patterned 2D In$_2$Se$_3$ crystal arrays with an extraordinary photoresponsivity were integrated and packaged to flexible photodetectors. This facile patterning of high-quality 2D chalcogenide crystals would pave the route for next-generation photodetector arrays, wearable electronic and optoelectronic systems.

Methods

**PDMS stamp fabrication.** Relief structures consisting of desired patterns were fabricated in PDMS (Sylgard 184, Dow Corning) stamps using standard photolithography and replica molding$^{29}$. One layer of photoresist (diluted SU-8 2050, Microchem) with a thickness of $\approx 10$ μm was first patterned on a SiO$_2$/Si wafer using a Cr/quartz photomask to produce a master with a positive relief pattern. The master was cured for 20 min at 200 °C and then cooled down to room temperature. A PDMS stamp was cast onto the master by a mixture of the PDMS precursor and...
cross-linker (10:1 by mass), cured for 1 h at ~90 °C and peeled away. For pre-
traction of PDMS oligomers, the PDMS stamp was allowed to swell in hexanes for 24 h. After draining it off, the stamp was tritiumated three times in 2:1 ethanollwater mixture for 5 min. The overall pre-extraction process was repeated for
three times to remove low molecular weight oligomers.54

Microintaglio printing. Solvent ink (0.5–1 ml) such as acetone, ethanol or
cyclohexane containing saturated PDMS oligomers was first pipetted onto the
surface of PDMS stamps with microwell arrays. The array of microwells on the
PDMS stamp filled with solvent ink was gently placed well-side down on the
surface of freshly cleaved mica sheet, which were put in a vacuum chamber con-

2D chalcogenide crystal growth. We performed the growth of 2D chalcogenide
crystals inside a 12-inch horizontal tube furnace (Lindberg/Blue M) equipped with a
1-inch diameter quartz tube. Chalcogenide powder (Alfa Aesar, Purity 99.9999
cavities were partially covered with aligned arrays of carbon nanotubes dry-transferred
from the vertical array of carbon nanotube forests. The surface of the 2D crystal
were cleaned by several cycles of Ar-sputtering and annealing under vacuum
before the micro-ARPES measurements.

Photodetector array fabrication. Standard photolithography was used to define the
selected region and fabricate photodetector arrays of as-grown 2D chalcogenide
crystals on mica substrates. The metal electrodes (10 nm In and 60 nm Au) were
reused to prevent the charge accumulation on the insulating mica
substrate during EBL. The metal electrodes (5 nm Cr and 60 nm Au) were deposited by
thermal evaporation, which were found to form nearly ohmic contact without
annealing process. Silver paste was used to bond the devices for Hall measurements.

Characterization. Characterization was done using OM (Olympus DX51 micro-
scope), AFM (Veeco Nanoscope IIIa), scanning electron microscopy (Hitachi
S-4800, acceleration voltage 5–30 kV) and TEM (FEI Tecnai F30, acceleration
voltage 300 kV). Lacey carbon film supported on copper grids was used for TEM
characterization. Micro-ARPES measurements were conducted at the spectro-
scopy beamline at Elettra Synchrotron Radiation Lab in Italy, with energy resolution
of 70 meV and a single resolution energy of 0.2 eV. The ARPES spectra were
acquired after thermal evaporation of the sample. The ARPES measurements were
performed at 70 meV resolution and 0.5° angular resolution. The sample was put in a
vacuum chamber connected by an ultrahigh vacuum line. The vacuum chamber was
flushed with the carrier gas repeatedly to remove the oxygen residue. The van der
Waals effective force constant is 801–1001 N m. The laser power was calibrated
with a power meter (Newport, model 840–C) and the laser power was kept constant
during the entire measurement. The energy and momentum resolutions were
50–500 meV and 0.1×0.1 eV, respectively. The measurement was carried out under
vacuum pressure of 10–10–6 Torr.

Transport and photocurrent measurements. A semiconductor analyzer
(Keithley, SC-4200) combined with a Micromanipulator 6,200 probe station was used
to characterize the electrical performance of the PDMS photodetectors. The electrical
measurements were performed in a vacuum chamber at room temperature.

Acknowledgements

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**Author contributions**
H.P. conceived and designed the experiments. W.Z., T.X. and Y.Z. performed the synthesis, structural characterization, device fabrication, transport measurements and analyses. Y.L.C. performed the micro-ARPES measurements. W.J., S.Z., J.Y., J.W., Y.J., Y.G., Y.W., G.C., S.H., H.Q.X. and Z.L. assisted in experimental work and contributed to the scientific discussions. W.Z., T.X., Y.Z. and H.P. wrote the paper. All the authors discussed the results and commented on the manuscript.

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