MATERIALS SCIENCE

Tunable and laser-reconfigurable 2D heterocrystals obtained by epitaxial stacking of crystallographically incommensurate Bi$_2$Se$_3$ and MoS$_2$ atomic layers

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Vertical stacking is widely viewed as a promising approach for designing advanced functionalities using two-dimensional (2D) materials. Combining crystallographically commensurate materials in these 2D stacks has been shown to result in rich new electronic structure, magnetotransport, and optical properties. In this context, vertical stacks of crystallographically incommensurate 2D materials with well-defined crystallographic order are a counterintuitive concept and, hence, fundamentally intriguing. We show that crystallographically dissimilar and incommensurate atomically thin MoS$_2$ and Bi$_2$Se$_3$ layers can form rotationally aligned stacks with long-range crystallographic order. Our first-principles theoretical modeling predicts heterocrystal electronic band structures, which are quite distinct from those of the parent crystals, characterized with an indirect bandgap. Experiments reveal striking optical changes when Bi$_2$Se$_3$ is stacked layer by layer on monolayer MoS$_2$, including 100% photoluminescence (PL) suppression, tunable transmittance edge (1.1–0.75 eV), suppressed Raman, and wide-band evolution of spectral transmittance. Disrupting the interface using a focused laser results in a marked the reversal of PL, Raman, and transmittance, demonstrating for the first time that in situ manipulation of interfaces can enable “reconfigurable” 2D materials. We demonstrate submicrometer resolution, “laser-drawing” and “bit-writing,” and novel laser-induced broadband light emission in these heterocrystal sheets.

INTRODUCTION

Atomiﬁcally thin layered materials, such as graphene, transition metal dichalcogenides, and a range of other layered compounds (1), remain as one of the most exciting systems for exploring a wide range of novel electronic (2), excitonic (3), valley (4), and correlated (5) physics under two-dimensional (2D) confinement and have immense potential in nanoelectronics (6), optoelectronics (7), photodetection (8, 9), memory (10), and energy technologies (11). Appropriate stacking of two such crystallographically similar or commensurate 2D layers has been shown to result in exotic charge and spin states due to lattice matching, long-range interlayer coupling, strain, or formation of Moiré bands (12–24). Stacked 2D materials have also been used to demonstrate a variety of functional applications (19, 22, 25–27).

Recent progress in direct synthesis of various stacked layers of similar and dissimilar crystals with atomically clean interfaces using chemical vapor deposition (CVD) growth (27–34) has opened up the possibility for exploring functional synergy in beyond-commensurate 2D crystal pairs. However, most studies have shown that other than trivial charge transfer, crystallographically dissimilar 2D materials such as molybdenum disulfide (MoS$_2$)/graphene heterolayers largely retain their independent properties (31, 32, 34). One might conjecture that novel properties would result only if the layers interact sufficiently to form a new heterocrystal with a modiﬁed unit cell and electronic structure, conditions that, to our knowledge, have not been demonstrated before.

Here, we present a new type of vertical stacking between 2D crystals of MoS$_2$ trilayers (TLs) and bismuth selenide (Bi$_2$Se$_3$) quintuple layers (QLs), where 3 × 3 unit cells of Bi$_2$Se$_3$ stack congruently on 4 × 4 unit cells of MoS$_2$, maintaining perfect rotational alignment. 2D MoS$_2$ remains as one of the most intensely studied 2D materials beyond graphene, characterized by a bulk indirect bandgap ($E_g$ ~ 1.29 eV) that increases with decreasing thickness, becoming a direct gap with strong photoluminescence (PL) at ~1.85 eV in its monolayer (1TL) form. Bi$_2$Se$_3$, another layered material, is a well-known 3D topological insulator with strong spin-orbit coupling-induced exotic physics including spin momentum–locked, topologically protected surface Dirac states superposed on low–energy gap ($E_g$ ~ 300 meV) bulk semiconducting states (35). Beyond its fascinating topological properties, Bi$_2$Se$_3$ exhibits interesting optical properties in the few-nanometer limit, including a tunable bandgap exceeding 2.5 eV (36) and emergent multiplet PL (37). 2D Bi$_2$Se$_3$ and 2D MoS$_2$ display substantial differences in structures, compositions, lattice parameters, and their electronic and optical properties. Despite these differences, their 2D heterocrystals develop new layer thickness–dependent electronic band structures, including a direct-to-indirect bandgap transition, emergent spectral transmittance, and suppressed PL and Raman spectra. When the interface is disrupted using a laser, MoS$_2$ behaves like an individual layer and demonstrates an efﬁcient recovery of its PL. Moreover, this process can be reversed by annealing the heterocrystals.

We experimentally investigate these emergent and reversible electronic/optical properties and examine the underlying mechanism of our ﬁndings via ab initio density functional theory (DFT)–based computations. These unique optical properties are also used to demonstrate novel laser-reconfigurable 2D sheets with submicrometer-resolution patterns and laser-induced tunable broadband light emission.

RESULTS

1TL MoS$_2$ single crystals were ﬁrst synthesized on various substrates, followed by depositing Bi$_2$Se$_3$ QLs, both using CVD (36,38). 1TL...
MoS\textsubscript{2} has a very strong PL signature, and we have used it as the starting crystal to grow 1QL and few-QL Bi\textsubscript{2}Se\textsubscript{3} on top of MoS\textsubscript{2}. Because the heterocrystal unit cell contains dissimilar numbers of MoS\textsubscript{2} and Bi\textsubscript{2}Se\textsubscript{3} unit cells, we will refer to the corresponding layers as TL and QL (instead of Mo\textsubscript{16}S\textsubscript{32}, Bi\textsubscript{18}Se\textsubscript{27}, etc.), respectively. By varying the synthesis conditions, it was possible to obtain samples whose overall thicknesses were those corresponding to 1TL@nQL, where nQL denotes the thickness equivalent of n quintuple layers of Bi\textsubscript{2}Se\textsubscript{3}.

Figure 1 (A and B) shows typical optical images of 1TL@1QL and 1TL@2QL heterocrystals grown on quartz and SiO\textsubscript{2}/Si substrates, where the QLs have uniform one- or two-layer coverage, respectively. (Our notation of 1TL@1QL is meant to denote that Bi\textsubscript{2}Se\textsubscript{3} was grown on top of MoS\textsubscript{2}.)

Figure 1C shows a low-magnification transmission electron microscopy (TEM) image of a QL growth-arrested sample, revealing grains formed from multiple QL nucleation sites on the 1TL surface. Despite the multinucleation growth, selected-area electron diffraction (SAED) (Fig. 1D) of the composite structure reveals a single distinct set of points representing a superposition of Mo\textsubscript{2}X\textsubscript{2} type (39) and Bi\textsubscript{2}Se\textsubscript{3} type (40) diffraction patterns (red and green hexagons, respectively), with perfect crystallographic alignment. Analysis of the diffraction spots leads to MoS\textsubscript{2} lattice spacing of 3.1622 ± 0.0276 Å, similar to a previous report on pristine MoS\textsubscript{2} (~3.2 Å) (41), and Bi\textsubscript{2}Se\textsubscript{3} lattice spacing of 4.1401 ± 0.0223 Å, very close to previous reports on pristine Bi\textsubscript{2}Se\textsubscript{3} (~4.136 Å) (42, 43). The ratio of these two lattice parameters \(d_{\text{MoS}_2} : d_{\text{Bi}_2\text{Se}_3} \approx 3 : 4\) is within the accuracy of our TEM and suggests a novel lattice matching between 4 × 4 unit cells of MoS\textsubscript{2} and 3 × 3 unit cells of Bi\textsubscript{2}Se\textsubscript{3}.

Figure 1E shows the atomic force microscopy (AFM) topographic image of a crystal with a QL step edge separating the 1TL@1QL and 1TL@2QL regions, with the QLs being about 0.9 to 1.1 nm in height (see section S1). The geometry-optimized DFT structure of a proposed 1TL@1QL heterocrystal with various atomic dimensions is shown in Fig. 1F (side view) and Fig. 1G (top view). The in-plane lattice parameters were fixed to experimental values while allowing the atoms to relax along the c axis. This resulted in a QL step height of 1.06 nm, which is in excellent agreement with our experimental results. The unit cell of the 1TL@1QL heterocrystals contains 16 MoS\textsubscript{2} parent unit cells and 9 Bi\textsubscript{2}Se\textsubscript{3} unit cells; both AA- and AB-type stacking were present within the same unit cell, as shown in Fig. 1F. The parent unit cells are shown in Fig. 1H for comparison. We conclude that MoS\textsubscript{2} and Bi\textsubscript{2}Se\textsubscript{3} can form rotationally aligned epitaxial stacks through space filling (along each crystallographic axis) by a ratio of number of unit cells that is the inverse of the ratio of their lattice parameters. To our knowledge, this is the first instance of such a unique 2D crystal structure built from completely incommensurate parent unit cells.

Figure 2A shows the calculated first-principles band structures of the 1TL@1QL heterocrystals, superimposed on those of the parent monolayer crystals for comparison (see section S3 for details of band structures for greater clarity). 1TL MoS\textsubscript{2} has a direct bandgap located at the K and K’ points of the first Brillouin zone that results in a signature PL peak at \(E \sim 1.85\) eV (44), whereas 1QL Bi\textsubscript{2}Se\textsubscript{3} is characterized by an indirect transition gap of ~0.5 eV, with the direct gap being much larger (~0.75 eV), located at the \(\Gamma\) point at the center of the first Brillouin zone. Compared to that of 1TL MoS\textsubscript{2}, the electronic band structure of the 1TL@1QL heterocrystal displays an indirect DFT bandgap, as seen in Fig. 2A. Figure 2B demonstrates how this gap rapidly decreases further as a function of increasing QL thickness. The significant differences between the band structure of the parent crystals and the daughter heterocrystals are attributed to strong TL-QL interaction despite their incommensurate lattices. Our Raman spectroscopic investigations reveal (see section S2) that in 1QL and 2QL heterocrystals, the interlayer interactions are strong enough to substantially suppress the dominant Raman peaks of both MoS\textsubscript{2} and Bi\textsubscript{2}Se\textsubscript{3} in stark contrast with heterolayers of 2D materials with weak, van der Waals interactions, where signature Raman peaks of individual layers are largely undiminished (27, 45–47). Figure 2B shows the band structure...
of the 1TL@2QL and 1TL@3QL heterocrystals, according to which the bandgap continues to decrease with increasing QL thickness, which is consistent with the decreasing gap obtained from optical measurements (section S4).

Figure 2C shows the PL spectrum of 1TL@nQL (n = 1 to 4) samples, compared to that of pristine 1TL MoS$_2$. We find a marked (near-100%) suppression of the PL spectrum of the 1TL@1QL sample, which suggests a direct-to-indirect bandgap transition (44), in agreement with our DFT results. Addition of further QLs completely quenches the PL, as shown in the inset to Fig. 2C. To ascertain whether interlayer charge transfer (46, 48) could be responsible for the PL suppression, we also performed PL measurements on structures where CVD-grown 1TL MoS$_2$ samples were mechanically transferred (with random position and orientation) onto freshly cleaved Bi$_2$Se$_3$ layers (see section S5). Figure 2D compares the PL spectra from such a “transferred” heterolayer sample, where only a partial PL modification is observed, suggesting that directly grown heterocrystal formation is necessary for the observed complete PL suppression. We will show later on that disrupting the interface alignment of TLs and QLs in the heterocrystals immediately recovers the PL, providing further evidence that the observed PL suppression is not merely an outcome of thermodynamic charge transfer—a mechanism that is sometimes responsible for PL quenching in other heterosystems (46, 48). The charges in heterocrystals appear to redistribute into periodic layers of electrons and holes at the interface in the heterocrystals, as discussed in section S3.

Figure 2E shows the energy-resolved optical transmittance ($T$) of pristine MoS$_2$ and heterocrystals with increasing thickness below 6 nm (corresponding to n = 1 to 5 QL). The highest transmittance curve corresponds to that of 1TL MoS$_2$, with dips at 1.9 and 2.04 eV, corresponding to the formation of A and B excitons from the two spin-orbit split edges of the valence band at the K points. This is followed by a gradual decrease in transmittance with increasing energy ending in a broad transmittance valley centered around the lowest transmittance ($T_m$) at 2.88 eV, possibly associated with degenerate exciton states near the Γ point. The broadband absorbance between $\approx$1.9 and 2.9 eV has been proposed to arise from strong electron-phonon effects that smear out several higher-order excitonic peaks within this region (49). With increasing QL thickness, there is a steady decrease in transmittance over the entire region of the measured spectra. Note that although the PL of these samples is completely quenched, the dip-like A and B excitonic features in the transmittance spectra are retained, suggesting that these excitons can survive in the heterocrystals although the material as a whole becomes an indirect-gap system, in a manner similar to few-layered MoS$_2$ (50). Because of the large size of the heterocrystal supercell, we were unable to carry out a calculation of the absorption spectrum that accounts for electron-hole interactions (49), and hence, we could not theoretically ascertain whether excitonic peaks survive in the heterocrystals. However, our analysis of the projected band structures (see section S3) reveals that despite the overall systematic changes in the band structures with increased QL thickness and dominance of the bandgap near the Γ point by the Bi$_2$Se$_3$ bands, the nature
of the valence band peaks at the K and K’ points, which are responsible for the A and B excitons, is mostly MoS2-type, analogous to how the valence band peaks are retained at the K and K’ points in few-layered MoS2 (44). These considerations provide a plausible reason for why we continue to observe the A and B excitons despite the formation of an indirect gap in our heterocrystals.

Our transmittance data also reveal a significant red-shift of transmittance spectral weight below the exciton energy values with increasing QLs. Although increased reflectance is evident (changing sample contrast in the insets to Fig. 2E) with growing QLs, we could not independently estimate the percentage of light reflected (R) or absorbed (A) by the crystals under our microscopy-based measurements. However, because $T(\%) = 100 - [R(\%) + A(\%)$, and both A and R depend on the density of states (DOS), the decreasing transmittance values and the comparatively larger drop in spectral transmittance at lower energy values (with increasing number of QLs) suggest that energy ranges below the excitonic dips are now also occupied by electronic bands with a steady increase in the heterocrystal DOS near the Fermi level. From these curves, approximate transmittance edges of the heterocrystals could be estimated using a modified Tauc plot approach (see section S4). A clear, monotonically decreasing thickness dependence of transmittance edge values is observed in the heterocrystals, ranging from ≈1.1 to 0.75 eV, saturating at the higher thickness values. These values are consistent with all PL spectra of heterocrystals that show no detectable indirect peak above 1.2 eV (detection limit of our PL spectrometer). We note that these values are significantly distinct from the energy gaps in either of the participating parent crystals.

The DFT DOS of 1TL MoS2 and representative heterocrystals are plotted in Fig. 2F, which shows that as QL thickness increases, the DOS spectral weight near the bottom of the conduction band also shifts to lower energies, which is in excellent agreement with our experimental observation of red-shift of transmittance spectral weight with increased QL thickness. Detailed analysis of A and B excitons in our heterocrystals (presented in Discussion) also reveals gradual decrease in peak amplitude and peak shift toward lower energies (red-shift) with increasing QL thickness (50). We thus conclude that heterocrystal formation is responsible for giving rise to several fundamentally new and functionally attractive observed electronic and optical properties.

We next discuss another attractive feature of our heterocrystals. We have discovered that application of a high-intensity laser spot on the heterocrystals results in nearly complete reversal of their optical properties. Figure 3A schematically depicts the laser treatment process on a heterocrystal sample supported on a substrate. Typically, samples were exposed to a 488-nm laser focused onto a spot size down to <1 μm with an intensity of 76 μW/μm². Figure 3B shows a scanning electron microscopy (SEM) image of a sample that has been exposed to spots of various sizes, the affected areas of which are highlighted. The inset to Fig. 3B is an AFM topographic image of one of the “treated” spots, denoted by the submicrometer outlined area. The laser-treated area typically undergoes a small increase in height and surface roughness (discussed later), suggesting that the laser treatment is not “etching/sublimating out” the materials but possibly induces structural changes, whereas the lighter SEM contrast suggests modified electronic properties. The most remarkable outcome of the laser treatment is the recovery of the MoS2 PL peak. Figure 3C summarizes this rather surprising result, where a sample was laser-treated for various time intervals. A strong PL peak (measured using a low-intensity laser) is recovered at nearly the same photon energy as that of the parent 1TL MoS2 crystal, indicating that the laser treatment results in the reversion of the electronic structure to that of a pristine 1TL MoS2. In addition to the PL recovery, prolonged laser treatment of the heterocrystals results in a complete change of their color (as seen in the optical image inset to Fig. 3C), further indicating the marked change in their electronic properties. PL spectra were also measured in samples of different QL thicknesses after identical, 10-min laser treatment (Fig. 3D). The degree of PL recovery was found to be inversely related to the QL thickness, confirming that most of the changes observed occurred in the Bi₂Se₃ region. As discussed later, the recovered PL slightly red-shifted compared to the pristine PL, possibly because the Bi₂Se₃ layers were still attached to the MoS2 layer.

The submicrometer-resolution laser treatment could be advantageously used to demonstrate proof-of-concept 2D sheets with laser-patterned or laser-written optical/electronic properties. Figure 3E shows two such examples: (i) In the top panel, a moving laser spot was used to define rectangular windows and arrays of parallel lines on the 2D heterocrystals with modified properties. These laser-written patterns are highly attractive for optoelectronic circuits or plasmonic crystals. (ii) In the bottom panel, a moving laser spot was periodically chopped to mimic “bit-writing,” where the alternating submicrometer “laser-treated, light-emitting” and “pristine, dark” regions could code 1’s and 0’s, respectively. This represents an interesting new way of optical information storage in atomically thin materials. Figure 3F shows the spectral transmittance curves of two heterocrystals before and after laser treatment along with that of pristine 1TL MoS2. After treatment, the transmittance curves of the heterocrystals look markedly similar to those of 1TL MoS2 over the entire spectrum of energies tested, suggesting that the laser treatment results in near-complete reversal of band structure to that of pristine 1TL MoS2. Similar recovery is also seen in Raman spectroscopy (see section S2) after laser treatment for A1g (~385 cm⁻¹), E1₂g (~405 cm⁻¹), and 2LA(M) (phonon at the M Brillouin zone edge) modes (450 to 460 cm⁻¹). Moreover, by annealing the laser-treated samples at 175°C in argon environment, partial PL quenching and recovery can be repeated a few times, proving that the “reconfiguration” is reversible (as discussed later). To our knowledge, this is the first instance of such a laser-induced optical/electronic property reconfiguration/reversal demonstrated in atomically thin crystals. We next investigate the mechanism underlying this laser-induced reversal.

Figure 4 (A and B) shows AFM images of two laser-treated areas of a 1TL@3QL heterocrystal. Analysis of the surface heights reveals that the laser-treated areas have a slightly greater mean height and surface roughness, indicating that the material under the laser spot has become more uneven or granular. Figure 4 (C and D) shows optical and TEM images of another heterocrystal sample, part of which was laser-treated, as shown. Higher-magnification TEM images from representative regions of this crystal reveal that whereas the pristine heterocrystal retains its planar, homogenous topology (Fig. 4E), spatially distinct nanoscale domains appear in the laser-treated sample (Fig. 4F), consistent with the granular morphology observed in our AFM measurements. SAED patterns from each of these regions confirm that whereas rotational orientation of the Bi₂Se₃ and MoS2 patterns remain aligned in the pristine heterocrystal (Fig. 4G), the Bi₂Se₃ layer breaks into smaller domains and undergoes small rotations relative to the original MoS2 orientation, resulting in multiple, closely rotated patterns in the laser-treated regions (Fig. 4H). It appears that the laser treatment provides sufficient energy to the Bi₂Se₃ layer to break down into smaller nanoscale domains and to sufficiently detach them from the MoS2 TL to rotate away from their original direction. As we have shown in previous reports (36, 37), markedly different from its bulk
Fig. 3. Laser-induced recovery of “1TL MoS2”–like optical properties and designer 2D crystals. (A) Schematic depicting the laser treatment procedure: exposure of a heterocrystal to a focused laser spot ($I = 76 \mu W/\mu m^2$). (B) SEM image showing laser-treated areas (lighter contrast) on a heterocrystal, with the inset showing an AFM image of one of the treated spots. (C and D) The laser treatment results in the recovery of 1TL MoS2–like PL, shown as a function of exposure time in (C) and samples of different QL thickness in (D). (E) 2D materials by design. Top: Schematic and optical image of a laser-written heterocrystal showing a rectangular “window” and an array of lines drawn with submicron spatial resolution. Bottom: An SEM image of a heterocrystal exposed to an optically chopped moving laser, intended to represent an alternating sequence of 1’s and 0’s in a proof-of-concept optical storage device. (F) Variation of energy-resolved transmittance before and after laser treatment in the heterocrystals. The insets show optical images of a 1TL MoS2 and two post–laser-written heterocrystals with different thicknesses, from which the spectra were collected, before and after the laser treatment. A near-complete recovery to pristine MoS2–like behavior is obtained in the posttreated samples.

Fig. 4. Evidence of laser treatment–induced breakdown of rotational alignment. (A and B) AFM topography images comparing the surface morphology of pristine versus laser-treated areas in few-nanometer-thick heterocrystals. Both root mean square surface roughness and the mean height of the laser-treated [denoted with an asterisk (*)] areas are slightly greater than those of pristine areas. (C) Optical and (D) low-magnification TEM image of a few-nanometer-thick heterocrystal grown on a Si$_3$N$_4$ TEM membrane, with part of the crystal being laser-treated as shown. Corresponding higher-magnification TEM images are shown in (E) pristine and (F) laser-treated demarcated areas. The laser-treated area is seen to have lost its homogeneity and becomes polycrystalline with nanoscale grains. SAED patterns from the (G) pristine and (H) laser-treated areas reveal that the Bi$_2$Se$_3$ crystal nanodomains in the laser-treated samples lose their rotational alignment, with the MoS$_2$ crystal resulting in their rotationally spread-out diffraction patterns (outlined by green dashed circles). Note that the MoS$_2$ pattern remains intact. (I) Typical SAED of laser-treated, suspended (see section S5) heterocrystals, revealing rotational reorientation and spread of both Bi$_2$Se$_3$ and MoS$_2$ crystals, suggesting that both form polycrystalline nanodomains. (J) PL in a similar sample before and after [denoted with an asterisk (*)] laser treatment. Laser treatment in suspended samples is seen to result in a characteristic broadband PL, which is different from the sharply defined PL of supported samples (see fig. S11 for a larger version).
form, quantum-confined few-layered Bi2Se3 can have bandgaps $E_g > 2.5$ eV, absorbing little or no light over the range of photon energies investigated here, and thus, heterocrystals after laser treatment become more transparent and similar to 1TL MoS2 (Fig. 3F). Although these nanodomains of Bi2Se3 retain their crystal structure (as evident from the strong diffraction patterns), breakdown of rotational alignment results in the heterocrystals losing their electronic identity. The underlying MoS2 TL hence regains its PL and other optical properties, as summarized in Fig. 3.

The crystallographic and optical modifications are even more marked when the laser treatment is performed on “suspended” heterocrystals (see section S6). The Bi2Se3 and MoS2 layers appear to break down into smaller domains with a range of rotational orientations, resulting in ring-like patterns characteristic of polycrystalline samples, as seen in the SAED pattern in Fig. 4I. Additional diffraction rings appear in between the patterns formed by the Bi2Se3 and MoS2 layers, corresponding to lattice spacings ranging from 3.54 to 3.57 Å (see section S6), which is consistent with the spacing between (201) planes of orthorhombic Bi2Se3 (51), indicating the possible formation of this phase within the laser-treated region. These regions are optically characterized by a broadband PL spectrum ranging from ~1.7 to 2.2 eV, as seen in Fig. 4I. This response is very unlike the PL emission from the 1TL MoS2 or from laser-treated substrate-supported samples (shown in the same graph for comparison), but its presence is consistent with our recent report on broadband, multipeak PL in nanoscale Bi2Se3 (37) and with size-dependent PL in nanoscale MoS2 (52, 53). It appears that laser treatment is a versatile and powerful tool for “designing” a variety of light-emission properties from the same heterocrystal enabled by nanocrystal formation of the parent crystals without any deleterious effects.

**DISCUSSION**

Variation of optical properties of our heterocrystals as a function of layer thickness and laser treatment reveals a number of interesting features. In pristine MoS2, the A and B excitons are known to be localized at the valence band peaks at the K and K’ points of the first Brillouin zone (49). Figure 5A shows a close-up of the associated excitonic “dips” obtained after a polynomial background subtraction from the transmittance curves of Fig. 2E. Going from pure 1TL MoS2 to the indirect bandgap heterocrystals, the excitonic dips are seen to systematically become somewhat smaller and red-shifted. This behavior is remarkably similar to the manner in which excitonic peaks evolve with increasing layer thickness in pure 2D MoS2 samples (50), although the related valence band peaks shift gradually away from the Fermi level (54). By projecting the states with MoS2 and Bi2Se3 characters, our first-principles computations show that the valence band peaks and their nearly pure MoS2 character are retained at the K and K’ points with an increasing number of QLs in the heterocrystals, some mixing with Bi2Se3 bands notwithstanding (see section S3). These results indicate that the effective electronic interactions between MoS2 and Bi2Se3 layers in our heterocrystals are similar in strength to those between pure MoS2 layers, despite the mismatch between the lattice parameters. Notably, red-shift in the excitonic peaks in both MoS2 and our heterocrystals reflects the effects of a decreasing bandgap energy with an increasing number of layers and the associated changes in the screening environment at K and K’.

Another issue that merits careful consideration is identifying which of the two mechanisms—disruption of rotational alignment or a possible “delamination” of the Bi2Se3 layers—plays a more dominant role in the recovery of optical properties after laser treatment. As mentioned earlier (Fig. 4, A and B), we noticed a slight increase in sample height after laser treatment. This could partially reflect the fact that the average height of a rough surface appears larger than that of a flat surface, because a continuous sheet of material redistributes into small grains (even smaller than the AFM tip size) of increased heights. On the other hand, the increased height of laser-treated Bi2Se3 could also potentially indicate a certain degree of delamination of the Bi2Se3 from the MoS2 layer. We have analyzed our data to understand which of these two effects is more dominant. Although laser treatments recover the transmittance curve shapes, we find that positions of the excitonic “dips” continue to be red-shifted by about 30 to 45 meV after laser-treated recovery (Fig. 5B). Similarly, the post-laser-treated PL peaks remain red-shifted by 20 to 25 meV compared to those of pristine MoS2 (see Fig. 5C). As discussed earlier, these peak shifts are associated with the immediate dielectric environment of the excitons. That is, the red-shifted excitonic features after laser treatment (transmittance and PL) appear to indicate that the Bi2Se3 layers were still physically adhered to MoS2 and provide a modified dielectric environment, despite their rotational rearrangement. These observations, in addition to the absence of any diffraction patterns (other than pure rotational spots), suggest that after laser treatment, the formation of randomly oriented nanograins that remain attached to the MoS2 surface is the more dominant reason for PL, transmittance, and laser recovery.

In addition, we find that PL quenching and recovery, when measured from the same spot of a heterocrystal, can be partially repeated through annealing of the laser-treated samples, as shown in Fig. 5D. SAED patterns measured from laser-treated areas before and after the annealing process (see section S7) reveal the remarkable fact that upon annealing, the Bi2Se3 sublattice almost completely recovers its original rotational alignment with respect to the MoS2 crystal. This provides clear evidence that annealing of the samples results in rotational realignment and re-formation of the heterocrystals and recovery of their pristine (pre-laser-treated) properties including the re-quenching of the PL. To our knowledge, this is the first demonstration of reconfigurable interface engineering with a functionally attractive outcome in atomically thin materials. Although further fine-tuning of laser treatment and recovery is required to obtain better reproducibility, we conclude that the laser-induced heterocrystal modification is reversible, which makes it attractive for possible rewritable optical storage devices.

Finally, a key question concerns the identification of the driving forces responsible for the formation of heterocrystals presented in this study. Our analysis indicates that a favorable lattice parameter ratio alone is not sufficient for achieving either rotational alignment or heterocrystal formation. Interlayer interactions, which could overcome stresses due to residual in-plane strains needed for heterocrystal formation, likely play an important role in stabilizing the rotational alignment and crystallographic long-range order. For example, although the ratio of lattice parameters of MoS2 and hexagonal boron nitride (hBN) is close to 5:4, past reports reveal no evidence of perfect rotational alignment between heterolayers of this pair of materials, and moreover, the PL spectrum of MoS2 grown on hBN is close to that of freestanding MoS2 (55–58). An important role will also be played in this connection by how the electronic and optical properties are modified through the presence of the interface in a heterocrystal. It is possible that because h-BN is sp$^3$-bonded, its out-of-the-plane interactions with MoS2 might be weak and thus hinder the ability of this
pair of 2D materials to form heterocrystals. Other layered materials that inherently have beyond–van der Waals out-of-plane characteristics may be more suitable for heterocrystal formation. It is clear that further theoretical and experimental efforts are needed to understand the main factors underlying heterocrystal formation.

To summarize, we have presented controlled synthesis of a uniquely new class of vertically stacked 2D heterocrystals with a novel “switchable” PL and widely tunable optical transmittance values and transmittance edges. The range of edge energies is highly attractive for beyond-silicon electronics and optoelectronics, especially for telecommunication wavelengths that require active electronics at the 1550-nm (0.8 eV) standard. Tunable absorbance, reflectance, and photoluminescence properties make these crystals potentially important for various photovoltaic and photodetection applications in the visible range. We have also presented a novel laser-induced reversal of the electronic and optical properties, especially the striking manner in which the PL can be reversed and its sharp versus broadband nature can be tuned. To our knowledge, this is the first instance of a 2D material where the optical properties can be tuned very markedly with submicrometer spatial resolution. We have used this laser-writing approach to demonstrate 2D heterocrystals with patterns, arrays, and optical information (bit) storage abilities. It is possible to conceive various photonic, plasmonic, and optoelectronic applications that may benefit from these highly precise optical arrays and circuit-drawing in an atomically thin material. Because the formation of heterocrystals from significantly incommensurate parent crystals is a fundamentally new approach for designing 2D materials, this idea could potentially be explored in a variety of other incommensurate 2D materials, thereby opening up a range of novel electronic, optical, magnetic, thermal, and mechanical properties that are inconceivable through the common van der Waals stacking. We believe that our work represents a significant and important step in furthering fundamental knowledge and potential applications development using 2D materials.

MATERIALS AND METHODS

Growth of MoS₂-Bi₂Se₃ heterocrystals
MoS₂ substrates were grown using CVD. The growth setup consisted of quartz tubes [1 inch (2.54 cm) in diameter] in a horizontal tube furnace (Lindberg/Blue M). A quartz boat, containing a thin layer of MoO₂ powder (3 mg) with SiO₂/Si or polished quartz (MTI Corporation) substrates suspended over the powder with the growth side facing down, was placed in the hot center of the furnace. Sulfur powder (150 mg) was placed near the insulating edge of the furnace upstream. The setup was pumped down and purged with argon gas before it was filled with an Ar atmosphere. Downstream was then opened to atmosphere in addition to a constant 200 standard cubic centimeter per minute (SCCM) Ar flow. The furnace was heated at a rate of 50°C/min to 780°C and then held there for 15 to 25 min. After the elapsed time, the furnace was opened and allowed to cool rapidly.
Bi$_2$Se$_3$ growth was performed in an identical CVD setup. Bi$_2$Se$_3$ powder (50 mg) was placed in the hot center of the furnace. The MoS$_2$ substrate was placed downstream 14 to 16 cm to a temperature range of 315° to 290°C. The system was pumped down to a base pressure of ~10 mtorr before a 20-SCCM Ar flow was introduced, raising the growth pressure to ~350 mtorr. The furnace was heated at a rate of 50°C/min to 480°C and then held there for 10 to 20 min depending on the desired thickness. Once growth was completed, the furnace was opened and allowed to cool rapidly.

Instrumentation

Raman and PL spectra were measured using a Renishaw Raman microscope equipped with a 488-nm laser and a grating of 1800 lines/mm. A ×100 objective focused the laser at a ×50 objective and chopped at 200 Hz. The power was attenuated below 10 μW to avoid additional effects. All Raman, PL, AFM, and UV-Vis experiments were performed under ambient condition.

DFT computational details

The ab initio calculations were performed using the pseudopotential projected augmented wave method (59) implemented in the Vienna ab initio simulation package (60, 61) with an energy cutoff of 420 eV for the plane-wave basis set. Exchange-correlation effects were treated using the generalized gradient approximation (GGA) (62), and van der Waals corrections were included using the DFT-D2 method of Grimme (63), where a 7 × 7 × 1 Γ-centered k-point mesh was used to sample the Brillouin zone. The stacking spacing and bandgap were further studied using the new SCAN (strongly constrained and appropriately normed) meta-GGA scheme (64), and we found the same trends as with GGA–PBE (Perdew-Burke-Ernzerhof). A large enough vacuum of 15 Å in the z direction was used to ensure negligible interaction between the periodic images of the films. All the structures were relaxed using a conjugate gradient algorithm with an atomic force tolerance of 0.05 eV/Å and a total energy tolerance of 10$^{-5}$ eV. The spin-orbit coupling effects were included in a self-consistent manner.

Annealing experiments on heterocrystals

The PL of the samples was first measured on as-grown heterocrystals. The samples were then laser-treated for 90 s, and the low-power PL was measured again. After identifying the region where the laser treatment was performed with respect to markers on the substrate, the samples were then annealed in pure argon (flowing at a rate of 2 SCCM) at 175°C overnight. After annealing, low-power PL was measured at the same locations as before. The cycle was then repeated.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/7/e1601741/DC1 section S1. Optical and AFM images of MoS$_2$–Bi$_2$Se$_3$ heterocrystals.

section S2. Raman spectra of MoS$_2$–Bi$_2$Se$_3$ heterocrystals.

section S3. DFT calculations of band structure and charge density differences of heterocrystals.

section S4. Calculation of transmittance edge from DFT DOS and experimental transmittance data.

section S5. Investigations of mechanically transferred Bi$_2$Se$_3$/MoS$_2$ heterostructures.
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Tunable and laser-reconfigurable 2D heterocrystals obtained by epitaxial stacking of crystallographically incommensurate Bi$_2$Se$_3$ and MoS$_2$ atomic layers

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