Giant corrugations in Bi$_2$Se$_3$ layers grown on high-index InP substrates

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Epitaxial growth of Bi$_2$Se$_3$ layers usually takes place in the (0001) orientation due to the stability of this surface terminated by the van der Waals bonds. Here, we show that the layers grown on InP(11n) substrates (n = 3, 4, and 5) are not (0001) oriented. The approximate lattice match at the heterointerface leads to an alignment between the [0001] direction of Bi$_2$Se$_3$ and the [111] direction of InP. The consequent tilt of the Bi$_2$Se$_3$(0001) plane with respect to the surface of the high-index substrates gives rise to a formation of giant corrugations consisting of the (0001) and (1100) facets. We demonstrate critical influences of the in-plane polarization and miscut of the substrates which emerge owing to the strong overlayer-substrate interaction in the semicoherent heteroepitaxy: Twin domains are eliminated and the layers are strained to the extent that the lattice symmetry is altered. We examine the Dirac band structure under strain using density functional calculations. The Dirac point shifts away from the $\Gamma$ point and the spin degeneracy is lifted when the strain is in the Bi$_2$Se$_3[1100]$ direction as the spatial inversion symmetry is removed.

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I. INTRODUCTION

There has been a dramatic surge in the number of publications on the epitaxial preparation of Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ layers in recent years. The rush was triggered by the discovery that these materials are three-dimensional topological insulators (TIs). The surface of TIs hosts gapless conductive states having a linear dispersion. The spin and momentum associated with the Dirac cone are orthogonal to each other due to strong spin-orbit coupling. The spin-momentum locking yields unconventional electronic properties for the surface states, which may be utilized for applications. High-quality single-crystal layers are obviously desirable in exploiting the exotic properties of TIs. It is noteworthy that, while these chalcogenides have been known as thermoelectric materials for decades, producing self-organized nanostructures has been a major issue for the latter purpose to improve the thermoelectric figure of merit by quantum confinements and/or the reduction of thermal conductivity.

If one regards the rhombohedral Bi$_2$Se$_3$ crystal (space group $R_{3m}$, no. 166) as a trigonal system (space group $P_{3m1}$, no. 156), five monoatomic sheets are bonded strongly in a sequence of Se-Bi-Se-Bi-Se in the c-axis direction. The material is constructed as an assembly of the quintuple layers (QLs), where adjacent QLs are coupled weakly by the van der Waals forces. The stacking sequence of the monoatomic sheets in terms of the atom location is described by three components as $\ldots$ ABCABC $\ldots$. The unit cell in the c-axis direction is hence completed by 15 monoatomic sheets.

The termination by the van der Waals bonds at the surface of the QLs is responsible for the fact that Bi$_2$Se$_3$ layers typically grow in the manner of van der Waals epitaxy. In this growth mode, the epilayers achieve their own lattice parameters from the beginning of the growth due to the weak epilayer-substrate interaction. This is advantageous as Bi$_2$Se$_3$ layers can be grown, in principle, on any substrates regardless of the lattice mismatch. The growth direction of epitaxial Bi$_2$Se$_3$ layers is thus generally [0001] to benefit from the surface stability.

A problematic consequence of the van der Waals epitaxy is that the in-plane crystalline orientations become random, unless a directional stress is imposed from the substrates to induce alignments. The randomness results in generating grains. From the viewpoint of avoiding scattering of the TI surface states from the grain boundaries, coherent heteroepitaxy on lattice-matched substrates is, therefore, attractive although Bi$_2$Se$_3$ is a suitable material for the van der Waals epitaxy. In principle, the TI surface states are protected from the backscattering caused by nonmagnetic impurities. Nevertheless, the states can be vulnerable, for instance, against the quantum scattering caused by fluctuations in the quantized energy levels associated with size variations. In addition, the TI surface states can be scattered to the bulk states when the bulk states also contribute to the transport, which is the case in reality for Bi$_2$Se$_3$ as crystalline defects act as donors. Moreover, the helical surface states may even be induced at the grain boundaries if the orientations of the Bi$_2$Se$_3$ lattice in the adjacent domains are highly dissimilar. Monocrystalline layers are hence ideal in examining the fundamental physical properties of TIs.

As a matter of fact, the growth of smooth semicoherently aligned Bi$_2$Se$_3$ layers has been demonstrated on InP substrates. The small lattice mismatch between the Bi$_2$Se$_3$(0001) and InP(111) planes enables semicoherent growth at the heterointerface. The crystal orientations of the overlayers are thereby directly dictated by the substrates, in contrast to the weak overlayer-substrate interaction in the van der Waals epitaxy. Apart from establishing in-plane crystal orientations, the semicoherent heteroepitaxy was found to give rise to giant steps in the overlayers when the substrate surface was inclined to be away from the (111) plane. The step
bunching occurred as the [0001] direction of Bi$_2$Se$_3$ remained parallel to the [111] direction of InP even on the vicinal InP(111) substrates. Emergence of broad (0001)-oriented terraces in the course of the growth produced the giant steps.

In this paper, we explore the step-bunching phenomenon systematically by growing Bi$_2$Se$_3$ layers on high-index InP substrates. As the substrate surface is inclined from (111) towards (001), Bi$_2$Se$_3$ layers exhibit unconventional growth orientations. We show that these nominal surface orientations occur as the Bi$_2$Se$_3$[0001] direction follows the tilt of the InP[111] direction. The resultant step bunching is demonstrated to develop regular corrugations. In addition, we present two findings that manifest overwhelming influences of the substrates. (1) Twin domains are found to disappear due to the selection of the stacking sequence by the in-plane polarization of the substrate surface. That is, the Bi$_2$Se$_3$ layers on the high-index InP substrates are truly of a single crystalline domain. (2) The strain imposed by the substrates can be as large as to alter the crystal symmetry of the overlayers. We further investigate the effects of the strain on the Dirac surface states by performing density functional simulations.

II. EXPERIMENT

Bi$_2$Se$_3$ layers were grown on InP substrates by hot wall epitaxy.\textsuperscript{7,8,20} The source and substrates were placed in an evacuated quartz tube with an inner diameter of 21 mm. We used pieces of Bi$_2$Se$_3$ (about 0.5 g) as the source material. The source was heated to about 500 °C by employing a horizontal three-zone furnace. The substrate temperature was set to a number of values by placing the substrates at different horizontal positions in the tube along the temperature gradient.\textsuperscript{7} Each growth was carried out for 5 h. The substrates were cooled immediately to room temperature at the end of the growth.

We examined the surface morphology of the layers using scanning electron microscopy. The structural properties were investigated using x-ray diffraction (XRD). Cu K$_{\alpha1}$ radiation was used as the x-ray source.

With respect to the surface preparation for the substrates, the growth outcome, specifically the appearance of the corrugations, was qualitatively unaffected by the presence of the native oxides. We have employed the InP substrates provided by a supplier without surface treatments in the present work, for simplicity. We point out, however, that the corrugations appeared over a wider substrate temperature range if the native oxides had been removed by chemically etching the substrates immediately before the sample mounting. The presence of the native oxides is hence indicated to delay the formation of the initial Bi$_2$Se$_3$ layers. The thickness of the layers was not the same even under nominally identical growth conditions due to this influence of the native oxides and to the fact that the thermal contact between the substrates and the quartz tube differed slightly in each growth run.

III. CORRUGATIONS

We show the surface morphology of the Bi$_2$Se$_3$ layers in Fig. 1. The InP substrates were (113)A-, (114)B-, and (115)A-oriented in Figs. 1(a)–1(c), respectively. One finds stripes as a common surface feature, which are developed in the direction orthogonal to the [110] direction of the substrates.

The XRD curves obtained from the layers are shown in Figs. 2 and 3. The ω-2θ-scan curves plotted in Fig. 2 reveal a number of strong peaks that neither originate from the InP substrates nor correspond to the usual (000l)/ reflections of a (0001)-oriented Bi$_2$Se$_3$ layer. (Here, $i$ are integers.) That is, the orientation of the Bi$_2$Se$_3$ layers on the high-index substrates is other than (0001). For instance, the layer on InP(115) appears to be (11011)-oriented. However, this non-C-plane surface orientation is purely incidental. As we evidence by the φ-scan curves in Fig. 3(a), the [0001] direction of Bi$_2$Se$_3$ is rigorously aligned to be along the [111] direction of InP. This alignment is the essential feature that is common among the layers grown on the high-index substrates.

The lattice periodicity in the (111) surface of InP, $a_{\text{InP}}/\sqrt{2}$ with $a_{\text{InP}}$ being the lattice constant of InP, is almost identical to the lattice parameter of Bi$_2$Se$_3$.\textsuperscript{6,8} In the illustration in Fig. 4(a), the filled circles show the atoms in the Bi$_2$Se$_3$ lattice. Their different size represents the three stacking components A, B, and C. The lattice periodicity in the InP(111) surface is indicated by the rectangular grid. The lattice mismatch is merely 0.3%, and so the surface of the Bi$_2$Se$_3$ layers grown on the InP(111) substrates is markedly smooth, as shown in Fig. 1(d). The [0001], [1120], and [1100] directions of coherently grown Bi$_2$Se$_3$ layers are fixed to be parallel to the [111], [110], and [112] directions of InP, respectively.

The nominal surface orientations of the Bi$_2$Se$_3$ layers on the high-index substrates are no longer (0001). As we plot in Fig. 5, the (11014), (11011), and (11010) planes of Bi$_2$Se$_3$ happen to be nearly parallel to the substrate surface on the (113), (114), and (115) surfaces of InP, respectively. The
Bi$_2$Se$_3$ layers grown on high-index InP substrates. The orientation indicates the positions at which the (0003) reflections of Bi$_2$Se$_3$, with $i$ being integers, are expected to produce peaks. The layer on InP(115)A contains a small amount of (0001)-oriented component as (0001) plane with respect to the substrate surface, the (115) surface of InP. In Fig. 4(b), we show schematic views of the Bi$_2$Se$_3$(0001) and InP(115) surfaces. The periodicity in the [552] direction of the InP(115) surface is three times longer than that in the [112] direction of the InP(111) surface. That is, the Bi$_2$Se$_3$(0001) surface is lattice-matched to the InP(115) surface as well as to the InP(111) surface. As a matter of fact, the Bi$_2$Se$_3$ layer prepared on InP(115) is, in fact, lattice-matched to the InP(111) surface as well as to the InP(111) surface. The alignment between the Bi$_2$Se$_3$(0001) and InP[111] directions is maintained even for the high-index substrates. Semicoherent heteroepitaxy is thus evidenced to be favored over van der Waals epitaxy. The dominance of the formation of bunched steps due to Bi$_2$Se$_3$(0001) || InP[111] is, however, not trivial as the (0001) plane of Bi$_2$Se$_3$ is, in fact, lattice-matched to the (115) surface of InP. In Fig. 4(b), we show schematic views of the Bi$_2$Se$_3$(0001) and InP(115) surfaces. The periodicity in the [552] direction of the InP(115) surface is three times longer than that in the [112] direction of the InP(111) surface. That is, the Bi$_2$Se$_3$(0001) surface is lattice-matched to the InP(115) surface as well as to the InP(111) surface. As a matter of fact, the Bi$_2$Se$_3$ layer prepared on InP(115) contains a small amount of (0001)-oriented component. The vertical bars in Fig. 2 indicate the positions at which the (0003) reflections arising from a (0001)-oriented Bi$_2$Se$_3$ layer are expected to appear. Some of the numerous peaks are seen to be attributed to the (0001)-oriented component. We speculate that this minority component is incorporated in the 

FIG. 2. (Color online) $\omega$-2$\theta$-scan x-ray-diffraction curves of Bi$_2$Se$_3$ layers grown on high-index InP substrates. The orientation of the substrates is (113)A, (114)A, and (115)A for the curves from top to bottom, respectively. Some of the peaks associated with InP and Bi$_2$Se$_3$ are identified using the three- and four-index notations, respectively. The Bi$_2$Se$_3$ layers grown on the high-index substrates are not (0001) oriented, in contrast to the typical Bi$_2$Se$_3$ layers prepared with the growth mechanism of the van der Waals epitaxy. The bars indicate the positions at which the (0003) reflections of Bi$_2$Se$_3$, with $i$ being integers, are expected to produce peaks. The layer on InP(115)A contains a small amount of (0001)-oriented component as (0001)-oriented Bi$_2$Se$_3$ is approximately lattice-matched to InP(115). The curves are offset for clarity.

The small amplitude of this peak is regarded as evidence of a large uniaxial strain in the layer imposed by the substrate. The curves are offset for clarity. Further continuation of the growth results in extending the terraces. Due to the small surface diffusion during growth at low substrate temperatures, the corrugations are composed of small segments in Fig. 6(c). For all the images, the terraces are clearly seen to originate from the van der Waals–terminated (0001) plane.

Similar to the step bunching reported in Ref. 8, the stable (0001) plane of Bi$_2$Se$_3$ will show up as terraces for the high-index substrates. To compensate the inclination of the (0001) plane with respect to the substrate surface, the (1100) plane is expected to emerge as the side facet of the steps. The highly regular stripes are hence produced in the fashion of self-organization. The details in the appearance of the stripes depend on the growth conditions. We show in Fig. 6 the variations of the corrugations. The growth at the initial stage takes place by forming elongated islands; Fig. 6(a). Regular corrugations are produced when the islands coalesce, as shown in Fig. 6(b). The layer thickness differed here due to the temperature gradient within the sample piece at the growth. (See Ref. 7 for details.) Further continuation of the growth
FIG. 4. (Color online) Lattice matching between Bi$_2$Se$_3$(0001) surface and (a) (111) and (b) (115) surfaces of InP. The filled circles show the atoms in the Bi$_2$Se$_3$(0001) surface. The different size corresponds to the A, B, and C components in the ABC stacking. The periodicity in the (111) and (115) planes of InP is shown by the rectangular grids. The (0001) surface of Bi$_2$Se$_3$ is approximately lattice-matched to both the (111) and (115) surfaces of InP. The open circles at the lower-right corners show the atom configuration in the InP surfaces. The atom configurations of Bi$_2$Se$_3$ and InP are similar on InP(111) but differ considerably on InP(115).

FIG. 5. (Color online) Angle between surface planes. The filled circles show the angle between the (0001) and (1 10$n$) planes of Bi$_2$Se$_3$. The lattice parameters of Bi$_2$Se$_3$ used in the calculations are $a = 0.4138$ nm and $c = 2.864$ nm. The angle between the (111) and (11$n$) planes of InP is shown by the open circles. The horizontal lines indicate the angles corresponding to the (113), (114), and (115) surfaces of InP. The inset illustrates the configuration of the planes. The dotted arrow corresponds to the InP[111] and Bi$_2$Se$_3$[0001] directions. For coherently grown Bi$_2$Se$_3$ layers on the InP(113) and InP(115) substrates, the substrate surface is nearly parallel to, respectively, the (11014) and (11010) planes of Bi$_2$Se$_3$, provided that the layers are unstrained.

Bi$_2$Se$_3$ layer as clusters. In contrast to the case on InP(115), the lattice mismatch is large on InP(113) and InP(114). The (0001)-oriented minority component is, as a consequence, absent for these cases in Fig. 2.

Despite the small lattice mismatch on InP(115), Bi$_2$Se$_3$ layers prefer to align their [0001] axis in the [111] direction of the substrates. The energy arising from the broken bonds at the heterointerface when the layers are oriented in the [0001] direction is suggested to be larger than the energy cost for exposing the Bi$_2$Se$_3$(1100) plane as the side facet of the corrugations. We show the ball-and-stick models of the (111) and (115) surfaces of InP at the lower-right corners in Figs. 4(a) and 4(b), respectively. The atoms in the Bi$_2$Se$_3$(0001) and InP(111) surfaces overlap well with each other. The alignment between the [0001] axis of Bi$_2$Se$_3$ and the [111] axis of InP(111) is thus seen to be advantageous also from the viewpoint of lowering the bonding energy. The surface energy eventually becomes too large when the inclination of the InP[111] axis is further increased. As reported in Ref. 8, the step bunching vanishes on the InP(001) substrates as the surface fraction of the Bi$_2$Se$_3$(1100) plane becomes too excessive, where the Bi$_2$Se$_3$ layers are (0001) oriented.

Under some growth conditions, such as at low substrate temperatures, Bi$_2$Se$_3$ layers predominantly grow in the (0001) orientation on InP(115). The morphology of these layers is rough, as we show in Fig. 1(e). While the $\omega$-2$\theta$ scan confirms the islands to be (0001) oriented, no peak was detected in the $\phi$ scan (not shown). We hence speculate that
these islands grew by the van der Waals epitaxy rather than the semicoherent heteroepitaxy. Indeed, we do not recognize in-plane alignments of the hexagon geometry of the islands with respect to the substrate in Fig. 1(e). In other words, even if a (0001)-oriented layer is realized on InP(115), the growth is not due to semicoherent heteroepitaxy resulting from the lattice coincidence depicted in Fig. 4(b). The energy increase caused by the broken bonds at the heterointerface is suggested to be enormous.

As the role of broken bonds appears to be crucial, we have investigated the bonding at the heterointerface by the first-principle calculations in the framework of density functional theory (DFT). For the Bi$_2$Se$_3$(0001) heterostructure, we take into account two QLs that are exposed to vacuum at one side and attached to the substrate at the other side. Here, we examine two situations. In case 1, the Se atoms of the Bi$_2$Se$_3$ layer are initially placed on top of the In atoms of the InP substrate at the heterointerface. In case 2, the Se atoms are placed on the interstitial positions of the In atoms. The Bi and Se atoms were allowed to move to minimize the total energy of the system, whereas the substrate atoms were set to be rigid.

We summarize the results of the simulations in Table I. As listed in the top two rows in Table I, the Bi$_2$Se$_3$ lattice in case 2 is highly deformed. That is, the interstitial configuration is not the energy minimum. The Se atoms at the heterointerface are suggested to have relocated to be on top of the In atoms of the InP substrate at the heterointerface. In case 2, the Se atoms are placed on the interstitial positions of the In atoms. The Bi and Se atoms were allowed to move to minimize the total energy of the system, whereas the substrate atoms were set to be rigid.

Table I. Total energy $E_{\text{total}}$, bulk modulus, stress, lattice parameters ($a$, $b$, and $c$), and angles ($\alpha$, $\beta$, and $\gamma$) of Bi$_2$Se$_3$ layers on (111) and (001) surfaces of InP substrates calculated using density functional theory. The Se atoms of Bi$_2$Se$_3$ are placed initially on the In atoms of InP for case 1 and at the interstitial positions for case 2. The simulations involved 12 atoms for the cases of the InP(111) substrate, i.e., two QLs and one In and one P atoms. For the cases of the InP(001) substrate, the number of atoms was 14, i.e., two QLs and two In and two P atoms.

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<tr>
<th>Model</th>
<th>$E_{\text{total}}$ (eV/atom)</th>
<th>Bulk modulus (GPa)</th>
<th>Stress (GPa)</th>
<th>$a$ (nm)</th>
<th>$b$ (nm)</th>
<th>$c$ (nm)</th>
<th>$\alpha$ (deg)</th>
<th>$\beta$ (deg)</th>
<th>$\gamma$ (deg)</th>
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</thead>
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<tr>
<td>InP(111), case 1</td>
<td>−325.858</td>
<td>76.828</td>
<td>−0.001</td>
<td>0.4145</td>
<td>$=a$</td>
<td>2.979</td>
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<td>$=a$</td>
<td>120.00</td>
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<tr>
<td>InP(111), case 2</td>
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<td>3.408</td>
<td>0.008</td>
<td>0.4137</td>
<td>$=a$</td>
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<td>$=a$</td>
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<tr>
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<td>−0.012</td>
<td>0.4113</td>
<td>0.4095</td>
<td>3.973</td>
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<td>89.80</td>
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<tr>
<td>InP(001), case 2</td>
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<td>3.408</td>
<td>−0.073</td>
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<td>0.4094</td>
<td>3.983</td>
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<td>89.65</td>
<td>119.74</td>
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IV. ABSENCE OF TWIN DOMAINS

To confirm the realization of the expected in-plane epitaxial orientation relationships, we have performed a series of additional XRD measurements for the Bi$_2$Se$_3$ layers grown on the high-index substrates. While the lattices of the overlayer and the substrate were indeed adjusted at the heterointerface as in our previous report, the $\phi$-scan measurements for the high-index substrates exhibited unusual characteristics in comparison to those when the substrate was InP(111).

We show the results for the Bi$_2$Se$_3$(11025) reflection in Fig. 7.24 The logarithm of the intensity is plotted here using a gray scale. With our measurement setup, the azimuthal rotation for a $\phi$ scan is possible only around the surface normal of the substrates. We have, therefore, performed a pole-figure-like scan over the azimuthal angle $\chi$ instead of rotating the sample around the [111] axis of the substrate. The closed loop indicated in Fig. 7 corresponds to the $\phi$ scan of the Bi$_2$Se$_3$(11025) reflection if the angle $\phi$ were rotated with respect to the InP[111] axis. Such a $\phi$ scan generally produces sixfold symmetric peaks, as shown by the bottom curve in Fig. 3(b) obtained from a layer grown on InP(111)B. However, only threefold symmetric peaks indicated by the arrows were detected for the layers grown on InP(115).
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![Figure 7](image)

**FIG. 7.** (Color online) X-ray-diffraction pattern for Bi$_2$Se$_3$ layer grown on InP(115)B when azimuthal angle $\phi$ and tilt angle $\chi$ are varied. The azimuthal rotation was carried out around the surface normal of the substrate. The logarithm of the diffraction intensity is plotted using a gray scale. The closed loop corresponds to the $\phi$ scan of the (11025) reflection of Bi$_2$Se$_3$ if the sample were rotated around the InP[111] axis. The loop concerns the majority Bi$_2$Se$_3$ component for which the [0001] direction is aligned to be parallel to the [111] direction of InP. The InP(333) reflection is also indicated. The arrows indicate threefold symmetric peaks. The anticipated positions for exact sixfold symmetry are marked by the dotted circles. The threefold symmetry of the peaks demonstrates the absence of the twin domains in the layer.

In fact, the trigonally symmetric Bi$_2$Se$_3$ crystal should produce threefold symmetric peaks. For Bi$_2$Se$_3$, rotating the lattice by 180° around the $c$ axis is equivalent to mirror-reflecting the lattice along the $c$ axis. The sixfold symmetry in the $\phi$ scan, therefore, originated from the coexistence of twins described by the stacking sequences of “...ABC...” and “...CBA...”. On InP(111) substrates, the two stacking sequences take place with the same probability, and so the existence of twin domains cannot be avoided. Naturally, the coexistence of the two twin domains has undesirable consequences similar to grain boundaries. Apart from the ordinary disorder effects associated with twin domain boundaries, one cannot even rule out the possibility of the surface states being induced at the boundaries as the translational symmetry of the crystal is broken. In support of this speculation, Seixas et al. have demonstrated by DFT calculations that the surface states are affected by stacking faults.

The threefold symmetry of the $\phi$-scan peaks in our pole figure indicates that the layers contain exclusively only one of the twins. The absence of twin domains was observed also for the (0001)-oriented minority component in the layer grown on InP(115)B, as manifested by the top curve in Fig. 2(b). The twin elimination is attributed to the in-plane surface polarization of the high-index substrates. As one finds for the ball-and-stick model of the InP(115) surface in Fig. 4(b), the surface is polarized in the [nn2] directions of the (11n) substrates. The bonding energy is no longer the same for the twins, and so the low-energy stacking sequence is enforced. A similar selection of epitaxial orientations by the in-plane polarization was observed for MnAs layers grown on the (113) surface of GaAs. The growth on the high-index InP substrates thus produces truly monocrystalline Bi$_2$Se$_3$ layers.

We note that Li et al. reported the absence of twin domains in a Bi$_2$Se$_3$ layer grown on the vicinal Si(111) surface. The twin elimination was driven by the asymmetric elastic strains that triangularly shaped Bi$_2$Se$_3$ islands experienced from the steps on the vicinal surface. The surface of the high-index InP substrates may have contained steps produced by (110)-oriented terraces. We hence cannot rule out the possibility that the absence of the twin domains in our samples was caused by such steps on the substrate surface rather than by the in-plane polarization.

**V. UNIAXIAL STRESS**

As one finds for the top curve in Fig. 3(b), the three peaks in the $\phi$ scan were not identical in amplitude. In contrast to the two strong peaks at $|\phi| \sim 120^\circ$, the third peak marked by the bar at $\phi \sim 0$ is significantly weak. In order to confirm misalignments of the sample not being the cause for the small intensity of the third peak, we have examined the amplitude of the (11025) reflection of Bi$_2$Se$_3$ while $\chi$ was varied in addition to $\phi$ similar to the measurement plotted in Fig. 7. As one finds in Fig. 8(a), the peak is negligibly small at $\phi \sim 0$ even when $\chi$ was varied over a range sufficient to compensate possible misalignments.

As indicated by the wobbling of the peak position of the symmetric InP(115) reflection plotted over $\phi$, Fig. 8(b), the orientation of the InP(115) substrate is inclined by about 0.3° along the [110] direction of the substrate due to miscut. Given the coincidence in the symmetries between Figs. 8(a) and 8(b), we attribute the nonidentical peak amplitudes in the $\phi$ scan to the uniaxial distortion of the Bi$_2$Se$_3$ lattice imposed from the vicinal substrate. Such a stress from the twofold symmetric substrate will change the crystal structure of Bi$_2$Se$_3$ to monoclinic. For the space group $C_m$ (no. 8), one out of the three reflections in the $\phi$ scan becomes weak.

Let us roughly estimate the lattice constants in the presence of epitaxial strains. For simplicity, we assume complete...
relaxation of the lattice-mismatch stress at the growth temperature. The stress at room temperature arises solely from the thermal expansion mismatch in this circumstance. As the atomic structures at the heterointerface are unknown, we consider two situations Bi2Se3(0001)/InP(111) and Bi2Se3(1100)/InP(112) instead of exactly treating the Bi2Se3 layers on the high-index substrates.

The strain-altered lattice constant for the C-plane Bi2Se3 layer on InP(111) is obtained as

$$\varepsilon /\varepsilon_r = -2C_{13}/C_{33},$$

(1)

where

$$\varepsilon_r = (a - a_r)/a_r, \varepsilon /\varepsilon_r = (c - c_r)/c_r.$$  

(2)

The suffix r indicates the lattice constants in a relaxed layer. The a-axis lattice constant a obeys the thermal expansion of InP and the c-axis lattice constant c is determined by the consequential elastic distortion. For the elastic constants, we have employed Voigt’s contracted notation Cij.

The case of Bi2Se3(1100)/InP(112) is unlikely to be realized in the real system as the two lattices do not match with each other. Nevertheless, we assume that the two systems are strongly bonded at the heterointerface to evaluate the upper bound of the thermal distortion of the trigonal symmetry of bulk Bi2Se3. The lattice constant in this circumstance is given by

$$\varepsilon_{yy} = -(C_{12}\varepsilon_{xx} + C_{13}\varepsilon_{zz} + C_{14}\varepsilon_{xy})/C_{11},$$

(3)

where \(\varepsilon_{xx}, \varepsilon_{yy}, \) and \(\varepsilon_{zz}\) are defined in manners similar to Eq. (2).

We assume the shear strain \(\gamma_{zz}\) to be zero.

For numerical evaluations, we use the thermal expansion coefficients of Bi2Se3 at room temperature up to the growth temperature. We note that the coefficients \((a_r = 1.9 \times 10^{-5} \text{ K}^{-1} \text{ and } a_c = 1.1 \times 10^{-5} \text{ K}^{-1} \text{ in the } c- \text{ and } a-\text{axis directions, respectively})\) are significantly larger than that of InP \((a_{\text{InP}} = 4.6 \times 10^{-6} \text{ K}^{-1})\). As we are not aware of any reports of the elastic moduli of Bi2Se3, we use the values measured for Bi2Te3.\(^{29}\) The values are expected to be similar due to the identical crystal structure and the similarity in the thermal expansion.\(^{28}\) The thermal expansion mismatch for the C-plane Bi2Se3 layer gives \(\varepsilon_x = 1.6 \times 10^{-3} \). The strain in the c-axis direction is thus estimated to be \(\varepsilon_{yy} = -1.8 \times 10^{-3} \). For the (1100)-oriented Bi2Se3 layer, \(\varepsilon_{xx} = \varepsilon_{yy}\) and the thermal expansion mismatch in the c-axis direction is \(\varepsilon_{zz} = 3.6 \times 10^{-3} \). The consequential strain in the out-of-plane direction is \(\varepsilon_{xy} = -1.8 \times 10^{-3} \). The strain in the corrugated Bi2Se3 layers on the high-index substrates is thus roughly estimated to be on the order of \(10^{-3} \).

By performing a ω-2θ scan in the [111] direction of the substrate (not shown here), we have obtained the c lattice parameter for the inclined majority component of Bi2Se3 on InP(115) to be 2.8567 nm. For the (0001)-oriented minority component, the c lattice parameter is estimated to be 2.9034 nm from the bottom curve in Fig. 2. It ought to be emphasized that the boundary conditions assumed in the above theoretical models, which are appropriate for a flat film, would not be realized even for the (0001)-oriented component as this minority component is likely to be incorporated in the majority layer as clusters. The lattice parameter value is 0.25% smaller and 1.4% larger than the bulk value for the majority and minority components, respectively. The strain in the (0001)-oriented minority component is roughly one order of magnitude stronger than that in the majority component. This is consistent with the negligibly small suppression of the third peak in Fig. 7.

If the two major peaks from the layer in the bottom curve in Fig. 2 are indeed associated with the (1101) plane, the a lattice parameter has to be about 10% smaller than the bulk value. As such a huge strain is unrealistic; asymmetrical distortion of the lattice resulting from the large inclination of the Bi2Se3[0001] axis on the high index substrate is rather suggested to be responsible for the fact that the reflections from the (1101) plane anticipated in Fig. 5 were not observed experimentally. The dotted circles in Fig. 7 indicate the positions anticipated for the (11025) reflection in the unstrained situation. The upper peak is within the loop corresponding to the φ scan, whereas the lower two peaks are outside the loop. That the three peaks are considerably shifted from the expected positions in the approximately twofold symmetric manner in accordance with the substrate miscut may be regarded as another evidence for the layer being strongly strained by the substrate.

If the space group alteration is indeed responsible for the peak suppression in Fig. 3(b), the strain effect implies that the band structure associated with the Dirac cone of the TI layers can be manipulated by engineering the stress imposed from the substrates.\(^{30}\) We emphasize that such a modification is not possible for the layers grown by the van der Waals epitaxy as the growth is, on the contrary, based on negligible epilayer-substrate interaction. We have, therefore, investigated by DFT calculations how the band structure of Bi2Se3 is modified in the presence of strain. Strain effects on the Dirac cone were previously investigated for graphene.\(^{31-34}\) It has been found that no intrinsic gap opening at DP is induced by strains. The location of the DP in the momentum space, nevertheless, may shift with the strain, and so extrinsic gap opening may occur when the multiple DPs in graphene cross with each other. (This gap opening thus corresponds to the hybridization of the surface states in thin TI layers.\(^{35}\) Moreover, simultaneous presence of the strain and a magnetic field was shown to give rise to the Hofstadter spectrum of the Landau levels.\(^{36}\)

We compare the band structures of a Bi2Se3 slab under various strains in Fig. 9. To highlight the influences of the strain, we assumed a large of strain of 5%. As references, we show the band structures of the bulk and an unstrained slab in Figs. 9(a) and 9(b), respectively. We note that the surface states are mostly constructed of the mixture of the p orbitals of Se and the s orbitals of Bi. The thickness of the slab was assumed to be of three QLs. An energy gap is present at the DP in Fig. 9(b) as the hybridization of the surface states is not negligible for such a thin slab.

In Figs. 9(c) and 9(d), the Bi2Se3 lattice was expanded and squeezed in the [1120] direction, respectively. The lattice parameter was assumed to be unchanged in the [1100] direction, whereas the c lattice parameter was varied correspondingly to keep the volume identical for all the cases. In comparison to the unstrained case, both the hybridization gap and the bulk band gap are larger (smaller) for the compressive (tensile) strain. While the coupling between the surface states as well as the quantum confinement for the bulk states should be stronger...
the Bi$_2$Se$_3$ lattice is strained by 5% for (c)–(f). For (c) and (d), tensile and compressive strain is applied in the [11\bar{2}0] direction, respectively. For these strained cases, the in-plane lattice parameter in the direction orthogonal to the strain direction was kept to be the bulk value, whereas the c lattice parameter was varied correspondingly to maintain the cell volume to be unchanged. The Fermi energy is shown by the horizontal lines. The arrows indicate the Dirac point. The Dirac cone as well as the bulk band structure are modified by the strains. The Dirac point moved away from the \Gamma point in (c) and (f).

when the c lattice parameter is smaller under tensile strain, the observed behaviors in Figs. 9(c) and 9(d) are opposite to the expectations. The changes are thus suggested to be due to direct strain effects.

The effects of strain are more dramatic when the strain is applied in the [1\bar{1}00] direction; Figs. 9(e) and 9(f). The narrowest energy gap associated with the hybridization is not at the \Gamma point, indicating that the DP moved away from the \Gamma point. The DP shift originates from the fact that the space group of the Bi$_2$Se$_3$ lattice is no longer P$_{3m1}$ under the strain. The DP remains at the \Gamma point when the strain is in the [1\bar{1}20] direction, as we have shown above, as such strain does not alter the space group. One finds, in addition, that the band degeneracy of the surface states is lifted. Here, Kramer’s degeneracy becomes nonapplicable as the centrosymmetry is eliminated. The giant spin splitting is thus another consequence of the strain in the [1\bar{1}00] direction.

VI. CONCLUSIONS

In conclusion, we have investigated the epitaxial orientation relationships when Bi$_2$Se$_3$ layers are grown on (113)-, (114)-, and (115)-oriented InP substrates. The layers develop stripes in the in-plane direction orthogonal to the [1\bar{1}0] direction of the substrates. We have demonstrated that the alignment between the Bi$_2$Se$_3$[0001] and InP[11\bar{1}] directions is responsible for the generation of the highly regular corrugations. The self-organized structure is thus a manifestation that the growth on the InP substrates takes place based on the semicoherent heteroepitaxy instead of the van der Waals epitaxy. The layers are strongly strained by the substrates owing to the tight bonding at the heterointerface. The strong bonding has been found also to forbid the coexistence of the twin domains through the in-plane polarization of the substrate surface. These observations demonstrate that the structural properties of the semicoherently grown Bi$_2$Se$_3$ layers are strongly affected by the substrates. Using DFT calculations, we have evidenced that the Dirac band structure can be modified by means of strain engineering. The modification depends dramatically on the direction of the strain, which can be controlled in the experimental system by choosing the direction of the substrate miscut.
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21The surface energy of the Bi₂Se₃(0001) plane was estimated to be 6–13 meV/Å² in T. Björkman, A. Gulans, A. V. Krasheninnikov, and R. M. Nieminen, Phys. Rev. Lett. 108, 235502 (2012).
24We have chosen the (11025) reflection as it has a relatively low tilt angle of 17.7° in φ scans for the Bi₂Se₃ component having the c axis perpendicular to the surface. This reflection was used throughout the present work for the convenience in comparing the results in the various measurements.
25The peak at the center of the loop belongs to the tail (crystal truncation rod) of the InP(333) reflection. The 2θ angle of the pole figures was 89.8°. The InP(333) reflection was detected since the slit was relatively wide (wider than one degree).