Basal-plane growth of cadmium arsenide by molecular beam epitaxy

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The three-dimensional Dirac semimetal cadmium arsenide (Cd3As2) is distinguished among the expanding ranks of gapless topological materials by the fact that its two Dirac nodes—doubly degenerate band crossings along the kz direction—that are protected by a symmetry of the crystal lattice—lie at the Fermi level and are isolated from other (parabolic) bands [1]. Its high electron mobility, large Fermi velocity, and chemical stability [2–8], make it attractive for future high-performance electronics. In epitaxial thin films, electrostatic gating, quantum confinement, and strain engineering afford separate, extra degrees of control over the electronic states, making such films an attractive platform for the study and realization of topological phases. The combination of Cd3As2’s unusual band structure with the tunability of thin film samples has led to the demonstration of the Dirac nature of the two-dimensional (2D) states [9] that give rise to the quantum Hall effect in very thin films [10–12].

To date, epitaxial thin film growth of Cd3As2, whether by molecular beam epitaxy (MBE) [13,14] or pulsed laser deposition [12,15], has been achieved on the tetragonal (112) plane, which is also the easy cleavage plane of single crystals [16]. The (001) plane differs from the (112) plane and indeed all others in that the two bulk nodes project onto one point, rather than two, in the surface Brillouin zone [1]. As the film thickness is reduced to the point when finite size effects become apparent (less than about 40 nm), the subbands alternate between an inverted and trivial ordering, and the material transitions between a quantum spin Hall insulator phase and a trivial band insulator phase [1]. The properties of films grown on the (001) plane are also likely to provide perspectives on the nature of the quantum Hall effect and surface transport in (112) films. Furthermore, (001) oriented films may be required to observe Weyl fermions under applied magnetic fields [6].

Here we report on a MBE approach for the growth of reproducible, smooth (001) Cd3As2 films, with carrier mobilities comparable to the better-established (112) Cd3As2 films [10]. In particular, we demonstrate that the introduction of a thin InAs wetting layer significantly improves the structural characteristics. Signatures of quantum transport confirm the quality of these samples and suggest avenues for further research.

Samples were grown using conventional MBE techniques. A schematic of the heterostructure is shown in Fig. 1(a). After a solvent rinse, a cleaved piece of an undoped (001) GaSb wafer was loaded into a buffer chamber for outgassing. The chip was adhered to a tungsten plate with liquid gallium to improve temperature homogeneity and consistency in thermometry. The native oxide was thermally desorbed in the growth chamber under Sb flux, and a 150-nm-thick layer of GaSb was grown to smooth out any resulting pits before growth of a Ga1−xAlxSb1−yAsy buffer layer for electrical isolation from the GaSb. While in principle an AlSb buffer layer electrically isolates the Cd3As2, the +0.649% lattice mismatch with GaSb can result in defects. The incorporation of small amount of Ga is thought to suppress the oxidation besides slightly reducing the lattice mismatch [17]; addition of As further reduces the lattice mismatch, allowing for the growth of thick buffer layers with low densities of extended defects. For example, high quality InAs quantum wells have been grown using GaAlSb buffer layers [18]. In quaternary alloys of Al, Ga, Sb, and As, the incorporation of the incident Al and Ga atoms is unity across a wide range of viable substrate temperatures, and as a result the desired group III composition can be achieved by setting the absolute flux of the sources. The relative Sb versus As incorporation, however, depends strongly on the substrate temperature. Here, the desired composition was achieved by maintaining a constant substrate temperature, measured by a
FIG. 1. (a) Schematic of the heterostructure (not to scale). (b) Out-of-plane $2\theta-\omega$ XRD scans from a 450-nm-thick (001) Cd$_3$As$_2$ film grown on an AlGaSb buffer layer with a 1.2-nm-thick InAs wetting layer. The vertical lines show literature values for the GaSb substrate (solid) and Cd$_3$As$_2$ layer (dashed). The reflections around 00$l$ GaSb ($l = 2, 4, 6$ from left to right) are shown in more detail in the insets. The 00$24$ Cd$_3$As$_2$ reflections have $l = 8, 16, 24$, but the 00$24$ Cd$_3$As$_2$ reflection is too faint to be seen. Unindexed peaks are from the AlGaSb buffer layer. (c) Reciprocal space map in the vicinity of the 224 GaSb reflection performed on the same film as shown in (b). The axes show the out-of-plane and in-plane components of the scattering vector, $q_{[001]}$ and $q_{[110]}$, respectively. The diagonal line (gray, solid) shows the cubic condition, i.e., $a = c$, or $q_{[110]} = (\sqrt{2}) q_{[001]}$. The short vertical line (gray, dashed) shows the condition for the buffer layer being fully strained to the substrate. The Cd$_3$As$_2$ peak is not expected to fall along the cubic condition line because its lattice is tetragonal. (d) Out-of-plane $2\theta-\omega$ x-ray diffraction scan in the vicinity of 004 GaSb for $\sim$45-nm films grown on different wetting layers, InAs, AlSb, and GaSb [see legend in (e)]. The buffer layer (second most intense peak) is a quaternary alloy Ga$_{0.2}$Al$_{0.8}$Sb$_{0.9}$As$_{0.1}$. The scans are offset for clarity. Two literature values for the 0016 Cd$_3$As$_2$ scattering angle are indicated with vertical lines, one in agreement with the reflections in (b) [22] (dot-dash, teal), and the other corresponding to a slightly smaller lattice constant (dot, black) [16]. The fact that the 0016 Cd$_3$As$_2$ peak in the top trace (InAs wetting layer) does not fall along the dot-dash line is likely due to residual epitaxial strain. (e) XRR of the three films shown in (d). The film grown on InAs is the smoothest and also apparently thinnest, judged by the tail-off of the oscillations and their period, respectively, even though all growth parameters were held constant.

pyrometer, and iterating on the beam equivalent pressure ratio of the group V sources. After the buffer layer, four monolayers (1.2 nm) of a thin wetting layer, either InAs, GaSb, or AlSb, were grown. The lattice constant of InAs differs from that of GaSb by $-0.614\%$. We call the four monolayers a wetting layer because, given that the layer grows pseudomorphically on the underlying buffer layer, the differences in subsequent Cd$_3$As$_2$ growth on each must reflect differences in surface and/or interfacial energies. Finally, the growth parameters for (001) Cd$_3$As$_2$ were in most respects identical to those reported previously [13]. High flux from a molecular Cd$_3$As$_2$ source ($2.6 \times 10^{-6}$ torr on a flux monitoring ion gauge) was supplied to a low-temperature substrate (thermocouple temperature around 200 $^\circ$C).

After structural characterization by atomic force microscopy (AFM) and x-ray diffraction (XRD) and reflectivity (XRR), Hall bar structures were fabricated using standard photolithographic techniques. Mesas were isolated by argon ion milling, and ohmic contacts were deposited as Au/Pt/Ti stacks. Unless stated otherwise, samples were exposed to a nitrogen plasma treatment prior to electrical measurement to reduce the density of low-mobility $p$-type carriers on the top surface [19]. Electrical measurements were performed in a Quantum Design Physical Properties Measurement System using standard lock-in techniques. Unless stated otherwise, the longitudinal magnetoresistance data shown was symmetrized and the Hall magnetoresistance antisymmetrized under a change in magnetic field ($B$) direction.

Cross-section transmission electron microscopy (TEM) samples were prepared using a focused ion beam system with a final milling energy of 2 keV Ga ions. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging was performed on an FEI Titan S/TEM ($C_s = 1.2$ mm) operated at 300 kV with a convergence semiangle of 9.6 mrad. The experimental HAADF-STEM images were denoised by the Wiener filter [20]. The simulated image of Cd$_3$As$_2$ (space group I4$_1$/acd [16]) was calculated using the Kirkland multislice algorithm [21].

Figure 1(b) shows a high-resolution, out-of-plane $2\theta-\omega$ XRD scan of a sample with a 450-nm-thick Cd$_3$As$_2$ film on an InAs wetting layer and AlGaSb buffer layer. In the vicinity of the 002 GaSb substrate reflection (magnified in the left
inset), the 008 Cd₃As₂ and 002 AlGaSb reflections are seen. The 1.2-nm-thick InAs wetting layer does not have enough volume to scatter x-rays above the detection limit. Another sequence of peaks is visible near the 004 GaSb reflection (center inset), starting with 0016 Cd₃As₂. The kinematical scattering intensity of the 0024 Cd₃As₂ reflection, expected near 006 GaSb (right inset), is less than that of the 008 Cd₃As₂ peak by a factor of more than 10³ and is not observed. The lack of other film peaks confirms the (001) orientation of the Cd₃As₂ film.

To verify the in-plane epitaxial alignment, the reciprocal space map in Fig. 1(c) shows a region in the vicinity of the 224 GaSb reflection. The diagonal line indicates the 224 peak position for a relaxed cubic layer. The vertical dashed line shows the position for a coherently strained film (i.e., in-plane lattice parameter identical to that of the substrate). The buffer layer peak falls between the two lines, which indicates partial strain relaxation, and its lattice parameter is about 0.5% larger than that of the substrate. From the position of the 4416 Cd₃As₂ peak, its lattice parameters are determined to be \( a = 12.65 \text{ Å} \) and \( c = 25.44 \text{ Å} \), which agree well with the published values for bulk Cd₃As₂ [16,22]. The \( c/a \) ratio is 2.01, consistent with (001)-oriented Cd₃As₂ films.

The data shown in Figs. 1(d) and 1(e) are from samples grown under nominally identical conditions but on GaₓAl₁₋ₓSb₁₋₀.₃As₀.₃ buffer layers with different wetting layers, InAs, AlSb, and GaSb, respectively. Figure 1(d) shows out-of-plane \( 2\theta-\omega \) XRD scans in the vicinity of the 004 GaSb reflection. The GaₓAl₁₋ₓSb₁₋₀.₃As₀.₃ buffer layer composition can be calculated using \( x = 0.8 \) (from flux calibration) and regarding the alloy as a mixture of Ga₀.₂Al₀.₈Sb and Ga₀.₂Al₀.₈As. Assuming a fully relaxed buffer layer, we find \( y = 0.09 \); in the case of a fully strained buffer layer, \( y = 0.11 \). The lattice mismatch relative to the Cd₃As₂ layer is \( -4\% \). Despite the large mismatch, thin Cd₃As₂ films grown on heterostructures with InAs wetting layers show an elongation of the out-of-plane lattice parameter [cf. lines in Fig. 1(d)] that is, at least in part, due to residual epitaxial coherency strain (estimated to be about \( -0.7\% \) in-plane). Furthermore, the differences in the scattered intensity of the 0016 Cd₃As₂ peak reflect differences in the defect densities on the three wetting layers. The film on InAs is also smoother, because oscillations in XRR survive to higher scattering angles [see Fig. 1(e)] and this is also evident in the AFM images shown in Fig. 2. Nevertheless, the morphology of the (001) films differs from the smooth, step-like surfaces of (112) Cd₃As₂ MBE films.
Figure 3(a) shows a cross-section HAADF-STEM image viewed along [001]. Shown are the Cd$_3$As$_2$/InAs interface and the top few unit cells of the buffer layer. Comparison with simulations [Fig. 3(b)], and especially the orientation of rows of subtly elongated butterfly-shaped features, which are caused by a displacements of cadmium atoms, further confirms the [001] growth direction, consistent with the lattice constants found in XRD.

Electrical transport measurements on three Hall bar devices of ~45-nm-thick Cd$_3$As$_2$ films on different wetting layers, measured at 2 K, are shown in Fig. 4(a). The similarity [23]. Furthermore, as judged by the period of the fringes in XRR, Cd$_3$As$_2$ films grown on AlSb and GaSb are thicker than on InAs.

Figure 3(b) shows a magnified image of the Cd$_3$As$_2$ film, simulated image, and schematic. Due to the displacement of Cd atoms, the projected Cd atomic columns are seen as a characteristic elongated, butterfly-like shape (purple shaded ellipses), which form rows parallel to [010].
in the longitudinal magnetoresistance ($R_{xx}$) for films on AlSb and GaSb may be attributed to the granularity of the Cd$_3$As$_2$ films on both wetting layers (Fig. 2), which causes the current traveling through a small number of paths that are only weakly coupled to each other. By contrast, the device on the film with the InAs wetting layer [solid lines in Fig. 4(a)] shows a factor of 50 lower zero-field resistance. This is especially evident in Fig. 4(b), which shows only the results from the film on InAs. The incipient quantum Hall effect seen in Figs. 4(a) and 4(b) is a further sign of the high quality of the Cd$_3$As$_2$ film grown on InAs.

The differences in the longitudinal resistance between the three devices cannot be attributed solely to the difference in carrier concentration. Specifically, the 2D carrier concentrations, as determined by the Hall effect [Fig. 4(a)] are $1.0 \times 10^{12}$ cm$^{-2}$ (on InAs), $7.8 \times 10^{11}$ cm$^{-2}$ (on AlSb), and $6.5 \times 10^{11}$ cm$^{-2}$ (on GaSb), i.e., they vary by less than a factor of two. The differences in carrier concentrations correlate with the relative positions of the conduction bands in the three wetting layers [24], which suggests that band bending at the bottom interface may play a role. It is important to note, however, that transport is not through the wetting layer itself. The low-energy nitrogen plasma changes the band bending at the top surface appreciably. As seen in Fig. 4(c), the condition of the top surface, (2) the behavior of the resistance relative to the carrier density across the three wetting layers, and (3) a similar response to the nitrogen plasma surface treatment, are together predominantly characteristic of the Cd$_3$As$_2$ films.

In summary, we have demonstrated a method for growing high-quality, (001)-oriented epitaxial thin films of Cd$_3$As$_2$ on (001) III-V substrates. A thin InAs wetting layer improves the nucleation on (001) growth surfaces, resulting in smoother, coalesced films. An avenue of future studies is buffer layers with a lattice parameter matched to that of Cd$_3$As$_2$ to encourage layer-by-layer or step-flow growth, or at least further improve the surface morphology. Nevertheless, the carrier mobility demonstrates that these (001)-oriented Cd$_3$As$_2$ films can be viable counterparts to the more established (112)-plane films. The observed onset of a quantum Hall regime sets a clear path for future study of the nature of the 2D states in this system and their relationship to the topological states as controlled in semiconductor-topological semimetal heterostructures.

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