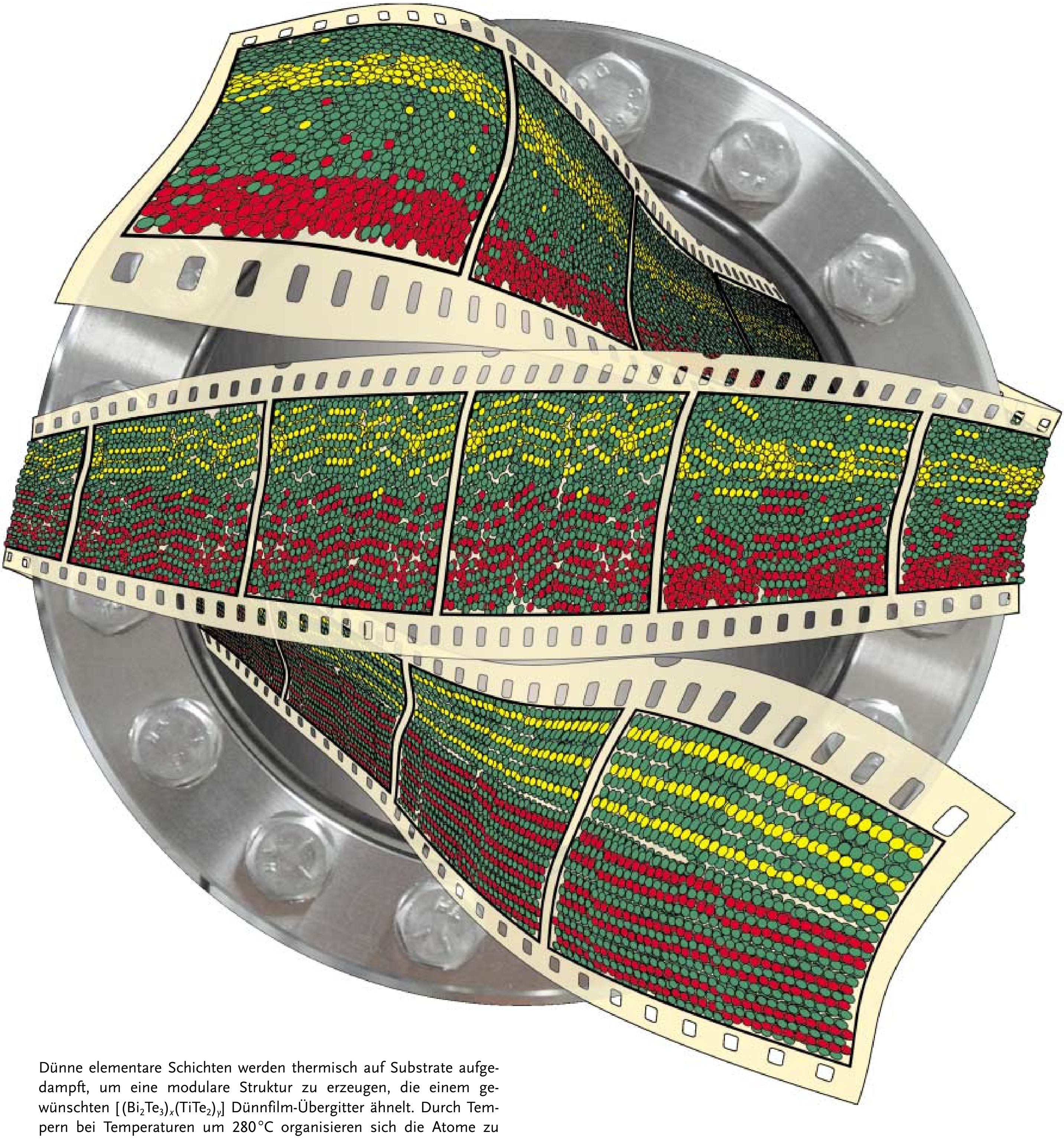
Zuschriften



Dünne elementare Schichten werden thermisch auf Substrate aufgedampft, um eine modulare Struktur zu erzeugen, die einem gewünschten $[(Bi_2Te_3)_x(TiTe_2)_y]$ Dünnfilm-Übergitter ähnelt. Durch Tempern bei Temperaturen um 280°C organisieren sich die Atome zu einem wohldefinierten Übergitter. Mehr dazu entnehmen Sie auf den folgenden Seiten der Zuschrift von D. C. Johnson et al.

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Superlattices

Design and Synthesis of $[(Bi_2Te_3)_x(TiTe_2)_y]$ Superlattices**

*Fred R. Harris, Stacey Standridge, Carolyn Feik, and David C. Johnson**

The synthesis of new compounds has often been a necessary precursor to the discovery of new physical phenomena.[1] Unfortunately, predicting the structure and composition of undiscovered compounds with extended structures is quite difficult.[2] This is a result of many different possible coordination numbers and local environments for atoms in compounds. Most solid-state compounds are discovered serendipitously; however, solid-state chemists have recently begun searching for means to predict the structures of new compounds. For example, a prediction method proposed by Schön and Jansen utilizes energy calculations as a function of changes in the internal coordinates of atoms to find local energy minima.[3]

Another approach to predicting new compounds, used in the work presented here, is to combine the structural features of two or more known materials into a targeted new phase. We chose to target new materials consisting of interleaved layers of compounds containing van der Waals gaps (VWGs). We hypothesized that interleaving layers of already quasi 2D materials will result in products that are at local energy minima on the multidimensional energy surface. VWGs exist in many compounds, including layered transition-metal dichalcogenides (TMDC),[4] structural analogues of Bi_2Te_3,[5] and MPX_3 compounds (where M is a metal atom and X is a chalcogen),[6–8] to mention a few. Structural properties of the known VWG compounds support the hypothesis that the targeted structures are at local energy minima. For example, the existence of different stacking registries resulting in different polytypes suggests that there is only small free energy differences between them.[9–13] Additionally, interwoven TMDC films grown with molecular-beam epitaxy have been made with large lattice mismatches, thus implying that little strain energy is present between layers.[14] This reinforces the idea that there is little contribution to the stabilization energy of compounds from the weak, nondirectional VWG bonding between layers.

When considering which compounds to interleave to explore the effect of superstructure on physical properties, compounds that contain VWGs are also a logical choice. The bonding requirements of these compounds are satisfied within each layer, thus leaving interfaces between the layers with no dangling bonds. In addition, the weak bonding across the gaps reduces the effects of strain and eliminates the formation of dislocations that often result from lattice mismatch. The minimization of these defects between the layers in the targeted materials should result in the superstructure dominating the physical properties.

While dichalcogenide superlattices have been prepared (containing XMX layers)[15] and superlattices exhibiting the bismuth telluride structure have been prepared (containing XMXMX layers),[16] we believe this report of the synthesis of $[(Bi_2Te_3)_x(TiTe_2)_y]$ superlattices is the first preparation of a mixed superlattice (containing XMX–XMXMX layers), thus illustrating the general nature of the local energy arguments made above. This is an intriguing component pair in that Bi_2Te_3 is a narrow-bandgap semiconductor[17] while $TiTe_2$ is a semimetal.[18,19] An additional challenge in the $[(Bi_2Te_3)_x(TiTe_2)_y]$ superlattices is the immiscibility of the components. In the XMX–XMX and XMXMX–XMXMX superlattices made previously, the binary compounds formed solid solutions.[16,20–22]

The immiscibility of the components of the targeted superlattice presents a synthetic challenge that requires a low temperature synthesis approach.[23] We used a modulated elemental reactants (MER) synthesis technique to synthesize superlattice precursors. These films were prepared by thermally evaporating elements sequentially in an high vacuum chamber ($<5\times10^{-7}$ torr) onto an ambient temperature substrate.[21] Bilayers of bismuth and tellurium, followed by bilayers of titanium and tellurium, were sequentially deposited to give the desired compositions of Bi_2Te_3 and $TiTe_2$ in the superlattice structure. The ratio of layer thicknesses was calibrated to yield the correct stoichiometry for each binary system. Samples were made by systematically changing the layer thickness of bismuth while holding the layer thickness of tellurium constant. Composition was determined by electron microprobe analysis (EPMA), and the ratio of layer thicknesses resulting in Bi_2Te_3 stoichiometry was selected for synthesis of the subsequent superlattice precursors. Similarly, titanium–tellurium binaries were synthesized and analyzed by EPMA to determine the thicknesses resulting in a $TiTe_2$ stoichiometry. Once the thickness ratios in the binaries were determined, samples with an approximate 1000 Å thickness were made by combining both binary systems into alternating layers. Absolute amounts of each binary multilayer were adjusted by analyzing X-ray reflectivity (XRR) for series of systematically changed superlattice precursors. These optimized precursors were then annealed to 280 °C for 20 minutes in a preheated box furnace under an inert N_2 atmosphere to kinetically trap the desired product.

Figure 1a shows X-ray diffraction (XRD) patterns collected with $Cu_{K\alpha}$ (1.54 Å) radiation which correspond to five isomeric superlattices with the formula $[(Bi_2Te_3)_x(TiTe_2)_x]$ synthesized by using the MER approach. Rietveld refinement of these superlattices shows that the structure within the layers and the VWG distance between Bi_2Te_3 sections is close to that of the distance found in bulk Bi_2Te_3 (2.6 ±0.1 Å experimental; 2.60 Å reported in the literature,[24] and the same is true for the structure of and VWG distance between

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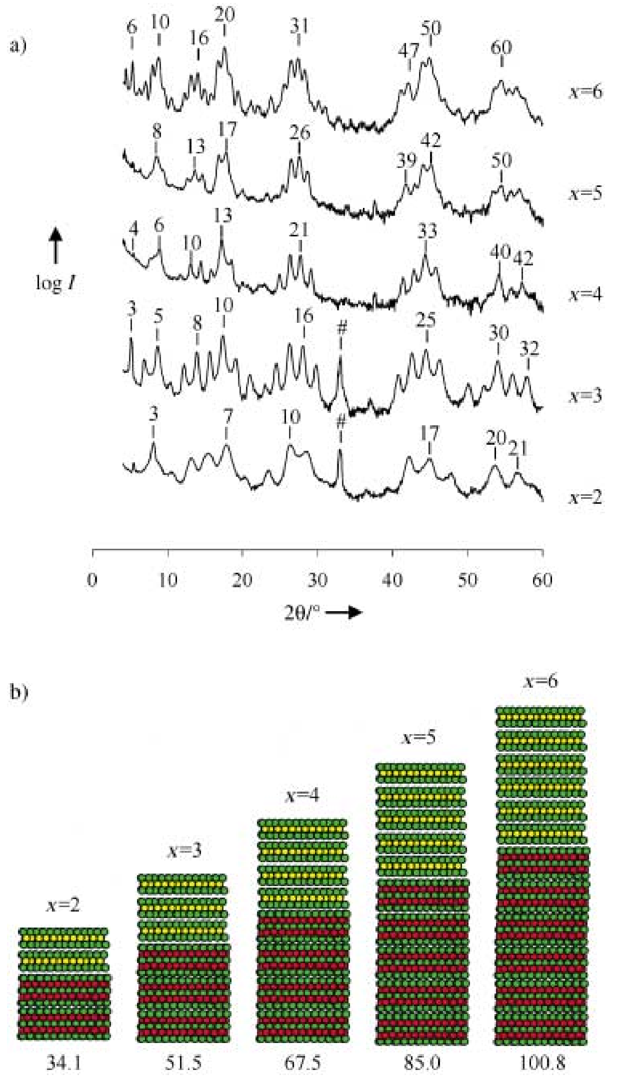

Figure 1. a) X-ray diffraction of five isomeric superlattices with the formula $[(Bi_2Te_3)_x(TiTe_2)_x]$, I = intensity. The # sign indicates peaks from the substrate. The numbers above the peaks are the l component of the Miller indices of the superlattice. While all of the l can be indexed, only some are listed owing to space restrictions. b) Idealized structures of each isomeric superlattice. The numbers listed underneath each structure indicates its c lattice parameter.

$TiTe_2$ layers (3.2 ±0.1 Å experimental; 3.08 Å reported in the literature)[25] The VWG distance between the Bi_2Te_3 and $TiTe_2$ layers is closer to that found in the pure $TiTe_2$ phase (3.2 ± 0.1 Å experimental).[26] This suggests that these isomeric structures along the c axis look similar to the idealized structures shown in Figure 1b. Grazing incidence X-ray diffraction provides no evidence of alignment of the layers in the a direction. Transmission electron microscopy shows that the films consist of small grains of the targeted superlattices (Figure 2).

The regular structure of the MER precursors provides a useful X-ray probe for studying the mechanism of product formation and optimizing annealing conditions. We chose to study the $[(Bi_2Te_3)_3(TiTe_2)_3]$ superlattice with a series of diffraction experiments designed to identify key structural changes and their associated annealing temperatures. Figure 3 contains a summary of a XRD study as a function of annealing temperature showing the increase in structural order perpendicular to the substrate. The 10.0 Å Bi_2Te_3 layer spacing produces diffraction maxima at 2θ values of 8.8, 17.7, 26.7, and 45.3°, while the 6.5 Å $TiTe_2$ layer spacing results in diffraction maxima at 2θ values of 13.6, 27.4, 41.6, and 56.6°. In the initially deposited sample, weak diffraction maxima are

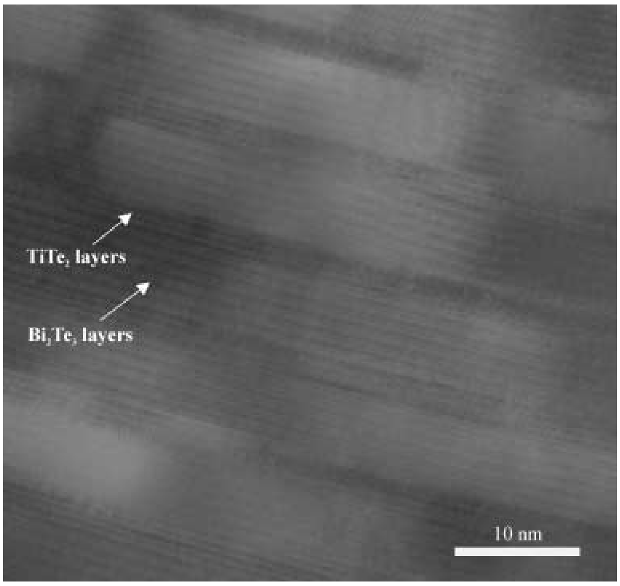

Figure 2. TEM of $[(Bi_2Te_3)_6(TiTe_2)_3]$ superlattice. The different VWG spacings make the Bi_2Te_3 and $TiTe_2$ areas clearly visible.

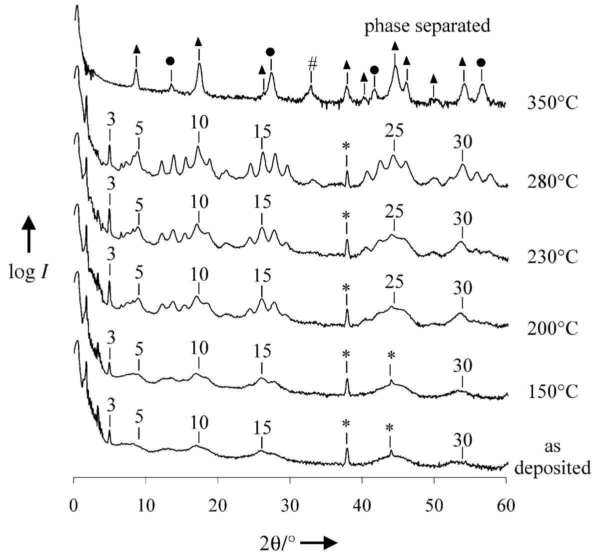

Figure 3. X-ray diffraction study of a forming $[(Bi_2Te_3)_3(TiTe_2)_3]$ superlattice. (*) indicates diffraction from the sample holder. Numbers above the peaks indicate the L component of the Miller Indices. Because of space restrictions, only a some of the peaks are labeled. In the phase separated material (▲) and (●) indicate peaks from Bi_2Te_3 and $TiTe_2$ respectiviely. (#) indicates substrate peaks.

observed at around 8 and 13°, thus indicating the presence of small crystallites of Bi_2Te_3 and $TiTe_2$ respectively. With annealing, these peaks grow in intensity and split. Higher-order Bragg peaks also grow and have the greatest intensity at the angles mentioned above. This reflects increased order and growth of crystallites perpendicular to the substrate containing layers similar to those found in the respective binary compounds. Only 00*l* diffraction lines are observed indicating the crystallographically aligned nature of the resulting superlattice. The superlattice disproportionates into a mixture of the binary compounds on annealing to 300 °C, thus reflecting the metastable nature of the superlattice structure.

Rocking curve scans were collected as a function of annealing to monitor the evolution of interfacial roughness in the multilayer (from the 001 reflection) and the changes in alignment of the crystallites that are forming from the 008 and 0010 reflections (related to the layer spacing of $TiTe_2$ and Bi_2Te_3 respectively). The 001 rocking curve shows little change in the diffuse scattering up to 240 °C. Above this temperature, the diffuse scattering becomes more intense, which suggests that the interfacial roughness of the multilayer is increasing.[27] The full width at half max (FWHM) of both the 008 and 00 10 high angle rocking curves narrow steadily from 8 and 10° respectively at 160 °C to 3.2° at 280 °C reflecting a steady increase in the alignment of the crystallites as a function of annealing temperature. The crystallite size, determined from the FWHM of the XRD patterns collected at the same annealing temperatures, increases as well.

A possible mechanism for the formation of these superlattices consistent with this diffraction data is presented in Figure 4. The broad high angle maxima in the XRD scan of the as-deposited sample (Figure 3) suggest small crystallites of both Bi_2Te_3 and $TiTe_2$ are present as represented in Figure 4 a. After annealing at 150 °C, the increased definition of the high angle 00*l* diffraction maxima (Figure 3) reflects the developing long range order in the *c* direction and rocking curve data shows a Gaussian distribution of orientation with a width of ~9° (Figure 4 b). By 240 °C, TEM studies show that most of the material in the sample has crystallized while diffraction measurements show that the particle size and degree of orientation have significantly increased (Figure 4 c). Continued Ostwald ripening increases alignment and decreases defects between 240 °C and 280 °C (Figure 4 d). Annealing above 300 °C induces disproportionation into Bi_2Te_3 and $TiTe_2$ (Figure 4 e). The diffraction data resulting from the modulated nature of the precursors track the evolution of the sample with temperature and time permitting the annealing conditions to be efficiently optimized.

The formation of these XMX–XMXMX superlattices suggests that there are a multitude of kinetic products that can potentially be made by interleaving VWG compounds. Properties are more likely to be dominated by the superlattice structure because of the lack of interfacial defects, such as dangling bonds, between the components. Fortunately VWG compounds have a host of intriguing properties including superconductivity, interesting magnetic properties, and charge density waves.[4,28–30] The understanding of how properties change with superlattice structure could ultimately lead to the tuning of the macroscopic properties of a material through the control of superlattice stoichiometry and unit cell size.[31,32]

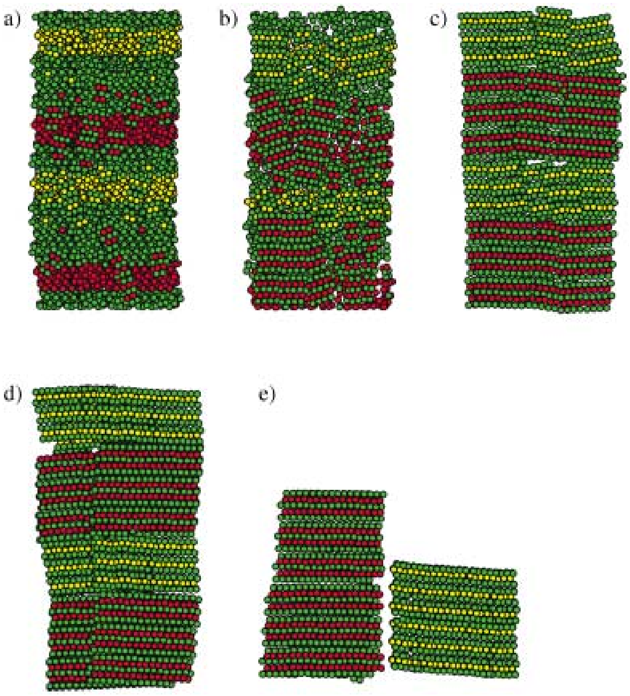

Figure 4. Proposed mechanism of superlattice formation from MER. a) Shows the deposited precursor. Crystallites have begun to form. b) ~100 °C. Crystallites are growing larger and beginning to exhibit long range order. c) ~230 °C. Most of the material has crystalized. d) 240–300 °C Grains continue to grow by Ostwald ripening. e) >300 °C The superlattice dissociates into its constitutes.

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