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Improved structural and electrical properties in native $\text{Sb}_2\text{Te}_3/\text{Ge}_x\text{Sb}_2\text{Te}_{3+x}$ van der Waals superlattices due to intermixing mitigation

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Superlattices made of $\text{Sb}_2\text{Te}_3/\text{GeTe}$ phase change materials have demonstrated outstanding performance with respect to GeSbTe alloys in memory applications. Recently, epitaxial $\text{Sb}_2\text{Te}_3/\text{GeTe}$ superlattices were found to feature $\text{Ge}_x\text{Sb}_2\text{Te}_{3+x}$ blocks as a result of intermixing between constituting layers. Here we present the epitaxy and characterization of $\text{Sb}_2\text{Te}_3/\text{Ge}_x\text{Sb}_2\text{Te}_{3+x}$ van der Waals superlattices, where $\text{Ge}_x\text{Sb}_2\text{Te}_{3+x}$ was intentionally fabricated. X-ray diffraction, Raman spectroscopy, scanning transmission electron microscopy, and lateral electrical transport data are reported. The intrinsic 2D nature of both sublayers is found to mitigate the intermixing in the structures, significantly improving the interface sharpness and ultimately the superlattice structural and electrical properties. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4976828]

Phase change materials (PCMs) are nowadays used as the active material for non-volatile solid-state memories, based on reversible phase transitions from amorphous to crystalline and vice versa induced by short current pulses. The most promising materials are the alloys along the GeTe–$\text{Sb}_2\text{Te}_3$ pseudo-binary line. An impressive achievement has been accomplished when it was realized that PCM memory cells based on superlattices (SLs), structures made of alternating GeTe and $\text{Sb}_2\text{Te}_3$ layers, showed dramatically improved performance in terms of reduced switching energies with ultra-low energy consumption, enhanced write-erase cycle lifetimes, and faster switching speeds. However, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) investigations carried out on molecular beam epitaxy (MBE) grown $\text{Sb}_2\text{Te}_3/\text{GeTe}$ SLs have shown that the constituting materials intermix at the interfaces, forming alternating layers of $\text{Sb}_2\text{Te}_3$ and natural $\text{Ge}_x\text{Sb}_2\text{Te}_{3+x}$ (GST) blocks with 7- to 15-atomic layers randomly distributed along the growth direction. Such phenomenon, explained in terms of the different bonding dimensionality of GeTe and $\text{Sb}_2\text{Te}_3$, is thermodynamically driven and therefore it cannot be easily controlled during the growth. Furthermore, the formation of GST with a different number of atomic planes results in an intrinsic loss of the vertical ordering.

In the present work, we aim at verifying whether intentionally grown $\text{Sb}_2\text{Te}_3/\text{GST}$ SLs would offer better control of the deposited layers, allowing for higher SL structural quality. Both $\text{Sb}_2\text{Te}_3$ and natural GST are in fact van der Waals (vdW) materials, enabling in principle their implementation in epitaxial vdW superlattice structures. This would facilitate the material optimization as severe requirements to reduce intermixing would no longer be necessary. Furthermore, highly ordered SL structures would potentially enable to discriminate between the role of interface quality and SL ordering during the phase transition, unveiling the switching mechanism. Moreover, if the dispersion
in the GST composition along the growth direction could also be suppressed, it would be possible to engineer new SL structures by changing both the stacking and the composition of the constituting layers.

To this end, here we present the MBE growth and characterization of Sb$_2$Te$_3$/GST SLs (GST-SL) on Si(111)-(√3 × √3)R30°-Sb passivated surfaces. The repeating unit of the GST-SL investigated in this work consists of 2 quintuple layers (QLs) of Sb$_2$Te$_3$ and a Ge$_2$Sb$_2$Te$_5$ (GST225) block, giving a bilayer thickness of ~3.7 nm, as shown schematically in Figure 1(a). The GST225 features mixed occupation of Sb and Ge layers, as found in MBE grown Sb$_2$Te$_3$/GeTe SLs. The number of repetitions was set to 10 and 2 QLs of Sb$_2$Te$_3$ were deposited at the end of the growth to serve as the capping layer, resulting in a 10 × [Sb$_2$Te$_3$(2 nm)/GST225(1.7 nm)]/Sb$_2$Te$_3$(2 nm) structure. Two SL samples are presented here: the first one (GST-SL A) was realized to precisely match the nominal structure, while the second (GST-SL B) features an excess of ~0.2 QL of Sb$_2$Te$_3$ meant to promote intermixing in the structure, similar to what has been found in Sb$_2$Te$_3$/GeTe SLs. In order to better compare the two SL structures, the excess of Sb$_2$Te$_3$ was compensated by reducing the thickness of GST to maintain the same SL periodicity. During the growth, substrate (227.5 °C) and cell temperatures were kept constant. Flux ratios of ~0.5 and ~1.8 were used for Ge/Sb and Te/Sb, respectively.

The SLs, together with Sb$_2$Te$_3$ and GST reference samples, have been characterized by high resolution X-ray diffraction (XRD), Raman spectroscopy, and HAADF-STEM. The diffractometer used for the XRD characterization of the samples is a PANalytical X'Pert PRO MRD system with a Ge (220) hybrid monochromator, employing a CuKα1 (λ = 1.540598 Å) X-ray radiation. The Raman spectra were acquired in backscattering z(y,xy)-z geometry, the sample was excited with the 632.8 nm line of a He–Ne laser, and the scattered light was analyzed using a spectrometer equipped with an LN$_2$-cooled charge-coupled device (CCD) detector. HAADF-STEM measurements were...
carried out using a JEOL ARM200F. Lateral electrical transport properties of both the GeTe- and GST-SL samples were studied by temperature dependent Hall measurements in the range between 4 and 300 K. In order to avoid a contribution of the substrate, the two SLs have been grown also on high-resistivity Si(111) (>5000 Ωcm). A four-contact van der Paw configuration was realized by wire bonding the samples to the chip carriers using In droplets and Au wires. The measurements were performed applying currents and magnetic fields of 0.5 mA and 0.5 T, respectively.

The XRD radial scans of the GST-SL A and B are shown in Figure 1(b) together with those of Sb$_2$Te$_3$ and GST reference samples (red, magenta, green, and green-yellow curves, respectively). The radial scan of a 15 × (Sb$_2$Te$_3$(3 nm)/GeTe(1 nm)] SL (GeTe-SL) sample grown in analogous conditions and the simulated curve of the ideal GST-SL structure are also shown for comparison (blue and black curves, respectively). All the peaks visible in the radial scans of the GST-SLs, except the much sharper ones at ∼2, 4 and 6 Å$^{-1}$ corresponding to the (111), (222), and (333) Bragg reflection of the Si substrate, are satellite peaks attributed to the SL. The position of the 0th order SL satellite peaks, the most intense in the satellite series for each diffraction order, is in between the ones of the corresponding Sb$_2$Te$_3$ and GST building blocks, as expected (see dotted line at the second order diffraction peaks). The periodicity of the SL, calculated from the satellites separation, is D$_{SL}$ = 3.9 ± 0.4 nm, in good agreement with the nominal one. The XRD radial scan of the SL shows an intensity modulation of the satellite peaks which follows the one of the 00.3/ peaks of Sb$_2$Te$_3$. Notably, none of the satellites is found exactly at the Q$_2$ position of Sb$_2$Te$_3$ peaks, as generally expected in the case of SLs. The average composition of the GST reference sample, measured from the separation between the main GST peak and the corresponding 1st order vacancy layer peak, is GST225. The broadening of the vacancy layer peak and the smearing out of higher order peaks is related to the coexistence in the film of different GST blocks and both cubic and rhombohedral stackings. The improvement of the structural quality of the GST-SLs with respect to the GeTe-SL is immediately evident when comparing the diffraction curves: less and much broader satellites are present for the structure nominally featuring GeTe layers. Furthermore, there is a correspondence between the position of some features in the curve and that of Sb$_2$Te$_3$ and GST peaks, which indicates that structural disorder is present in the SL and is responsible for the smearing out of the satellite series. In the XRD curve of GST-SL B, the SL features are weaker and broader compared to GST-SL A, as expected for intentionally intermixed SL structures, but nevertheless most of the satellite peaks are still present. Despite the additional disorder induced in the structure, GST-SL B is still characterized by a higher degree of vertical ordering as compared to the nominal GeTe-SL, which is a further indication that Sb$_2$Te$_3$/GST SL structures are intrinsically less prone to the intermixing of their constituting layers. This result also suggests that interface sharpness in vdW SLs can be controlled by accurately calibrating the growth of the constituting materials, ensuring each 2D layer in the SL to be terminated. The simulated XRD curve, which has been calculated for the ideal GST-SL structure based on the dynamical theory of diffraction, shows that all expected satellite peaks can be resolved in the experimental curve of GST-SL A. However, the intensity profile of the satellites in the simulation does not perfectly match the experimental one across the whole Q$_2$ range: this is mainly related to the slight difference between the periodicity of the grown and simulated SLs. SL models featuring less ideal structures would need to be implemented in order to accurately fit the experimental curves.

In Figure 1(c) the Raman scattering measurements for GST-SL A, GST-SL B, and GeTe-SL samples are shown (red, magenta, and blue curves, respectively), together with the ones measured for Sb$_2$Te$_3$ and GST reference samples (green and green-yellow curves, respectively). Each spectrum is normalized to its maximum and an offset for the intensity is added for a better comparison. For Sb$_2$Te$_3$, four sharp modes are excited at 48 (E$_g$(1)), 71 (A$_{1g}$(1)), 114 (E$_g$(2)), and 169 (A$_{1g}$(2)) cm$^{-1}$. On the other hand, Ge$_2$Sb$_2$Te$_5$ alloy is characterized by broader features, with modes at 108 (overlap of E$_g$ and A$_1$) and 172 (A$_{1g}$) cm$^{-1}$. The spectrum of the SL clearly features a superposition of the modes present in the constituent materials. The A$_{1g}$ modes in the SLs are slightly shifted with respect to their corresponding ones in Sb$_2$Te$_3$, as found also for GeTe-SLs. The broadening of the Raman modes could be attributed to the presence of structural disorder due to imperfect stacking of the SL building blocks with respect to the stoichiometric Sb$_2$Te$_3$. When comparing the Raman spectra of SL samples, the differences are rather small with GST-SLs having
sharper modes, particularly true for GST-SL A (see mode $A_{1g}^{(1)}$ at 69.5 cm$^{-1}$). The sharpening of Raman modes in GST-SLs is an indication that Sb$_2$Te$_3$/GST vdW SL structures lead to improved structural quality due to the mitigation of intermixing, in accordance with the HAADF-STEM characterization presented in the following paragraph. As described in the work of Wang et al.,$^{10}$ none of the two Raman modes of GeTe is present in the spectrum of GeTe-SL, while instead the shoulder at $\sim$101 cm$^{-1}$ has been assigned to the presence of GST Raman modes. This points out the intermixing of GeTe in the SL and is in accordance with the HAADF-STEM characterization, where only GST blocks were found along the stacking.$^8$ Such a shoulder is also evident in GST-SLs. Moreover, in the case of GST-SL B a broad feature at $\sim$130 cm$^{-1}$ is visible, which is at present under further investigation.

In Figure 2(a) a HAADF-STEM cross section image of the GST-SL A sample is shown. The SL structure with its constituting Sb$_2$Te$_3$ and GST blocks is clearly regular along the growth direction, which confirms indeed the higher structural quality of native vdW SL structures found by XRD analysis. With respect to GeTe-SLs,$^8$ the Sb$_2$Te$_3$ blocks in GST-SLs feature much sharper interfaces and less stacking faults, which is most probably a result of the mitigation of the intermixing between constituting layers, as already evidenced in the Raman scattering analysis. It is worth to stress that, when intermixing takes place during growth, the nucleation of the GST along the in-plane direction cannot be controlled. This in turn results in the formation of GST blocks with different compositions and worsens the vertical ordering of the SL. With respect to the GST reference film, in which 5-, 7-, 9-, 11-, and 13-layer vdW systems are present and follow a Gaussian distribution around the 9-layer one, as expected for the average GST225 composition,$^{15}$ the present SL contains mainly 5-, 7- and 9-layer vdW systems, and 7-layer GST blocks seem to form from 9-layer blocks in the presence of 2-atomic-plane stacking faults. Further analysis will be carried out to clarify this aspect. Figure 2(b) shows a high resolution HAADF-STEM cross section image of the GST-SL A sample, in which the nominal structure of the SL is precisely reproduced, demonstrating the high degree of structural perfection of such SLs.

In Figure 3 the GeTe- and GST-SLs resistivity as well as the carrier mobility as a function of temperature are shown (blue and red data points, respectively). The resistivity (black lines and circles), though close, is slightly higher for the GST-SL sample. Both samples are characterized by a clear metallic behavior, as Sb$_2$Te$_3$ and GST featuring at least a partial degree of vacancy ordering.$^{14,22}$ Besides the expected decrease of the mobility as the temperature increases, the GST-SL sample has a factor $\sim$2 higher mobility compared to the GeTe-SL (gray lines and triangles). At the same time, the 3D carrier concentration, which does not change significantly as a function of temperature, is higher in the case of the GeTe-SL ($n_{\text{GeTe-SL}} = 5.91 \times 10^{20}$ cm$^{-3}$ and $n_{\text{GST-SL}} = 2.78 \times 10^{20}$ cm$^{-3}$ at room temperature). To interpret these results, it is worth to mention that in the presence of stacking faults the density of vacancies, and consequently of intrinsic carriers, is higher compared to the case of a perfect crystal with ordered vacancies. Moreover, such defects might act as scattering centers for carriers, reducing their mobility. It is then possible to directly correlate the electrical data with the
We reported the MBE growth and characterization of Sb$_2$Te$_3$/GST van der Waals SLs, where the GST was intentionally fabricated. The investigated structure is characterized by a superior structural quality with respect to epitaxial Sb$_2$Te$_3$/GeTe SLs. In particular, the 2D nature of the constituting layers is found to mitigate the intermixing peculiar of the Sb$_2$Te$_3$/GeTe system, allowing the SL vertical ordering and interface sharpness to be precisely controlled. Notably, the Sb$_2$Te$_3$ QLs in the Sb$_2$Te$_3$/GST SLs are found to be to a great extent less defective compared to those in Sb$_2$Te$_3$/GeTe SLs, approaching the quality of Sb$_2$Te$_3$ epitaxial films. The dispersion of composition found in epitaxial GST is also remarkably reduced in the SL, where almost only 7- and 9-layer blocks are present. The interface sharpness can be controlled by accurately calibrating the growth of the SL constituting materials, ensuring each 2D layer in the SL to be terminated. Interestingly, the improved structural quality is found to give rise to a factor $\sim 2$ increase in the lateral carrier mobility. The present results constitute a significant step forward in the control of the structural quality of Sb$_2$Te$_3$/GeTe based SL structures, potentially allowing to discriminate between the role of interface quality and SL ordering during the phase transition. Moreover, it paves the way for the engineering of new SL structures by changing both the stacking and composition of the constituting layers.

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