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A two-step growth method is proposed for the fabrication of highly-oriented Sb$_2$Te$_3$ and related superlattice films using sputtering. We report that the quality and grain size of Sb$_2$Te$_3$ as well as GeTe/Sb$_2$Te$_3$ superlattice films strongly depend on the thickness of the room-temperature deposited and subsequently by annealing at 523 K Sb$_2$Te$_3$ seed layer. This result may open up new possibilities for the fabrication of two-dimensional electronic devices using layered chalcogenides. © 2016 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/).

Demand for highly-oriented two-dimensional (2D) chalcogenide films, such as transition metal dichalcogenides (TMDC) and topological insulators (TI), has sharply increased due to their possible application for future electronic devices. Among these materials, Sb$_2$Te$_3$ is a key compound. This material is known not only as a representative topological insulator material, but also as a phase change material used in both optical disc and non-volatile memory applications as well as a thermoelectric material. Phase change random access memory (PCRAM) is one of the most promising next generation non-volatile memories. The current authors proposed and developed a GeTe/Sb$_2$Te$_3$ superlattice structure for use with PCRAM, and revealed that this superlattice memory exhibits faster switching speeds and lower energy consumption than conventional PCRAM. Furthermore, several superlattice structures including GeTe/Sb$_2$Te$_3$ have been theoretically predicted to exhibit unusual properties forming topological insulators or Dirac semimetals, leading to the experimental confirmation of unusual magnetic properties despite the lack of magnetic elements.

The most widely used techniques to fabricate 2D chalcogenides are exfoliation from a bulk single crystal, chemical vapor deposition (CVD), and molecular beam epitaxy (MBE). However, the area of films that can be fabricated by exfoliation is limited and sample sizes are not uniform. Although CVD and MBE techniques are well suited for industry, to the best of the authors’ knowledge, there have been no reports on the deposition of the GeSbTe phase change material by these processes in industry for non-volatile memory applications, but sputtering has been widely used to grow chalcogenide phase change materials. However, it has been believed up to now that 2D chalcogenide thin films with strong orientation and large grain size cannot be deposited by sputtering. Recently, the present authors proposed a novel deposition mechanism for the growth of highly oriented Sb$_2$Te$_3$ and related superlattice films by sputtering with the nomenclature “self-organized van der Waals epitaxy (SO-vdW epitaxy)”. This method enables the fabrication of highly-oriented 2D chalcogenide thin films on a wide variety of substrates using an amorphous Si layer deposited underneath the film. However, lateral grain size is limited and further improvement is required. Recently, a two-step growth method was proposed for the growth of epitaxial topological insulators using MBE. In this paper, we employ a similar method for the fabrication of highly-oriented Sb$_2$Te$_3$ and related superlattice films by sputtering. Significant improvements in film quality are reported using the two-step growth method.
A single-crystal Si(100) was used as a substrate. In the first step, reverse sputtering was used to remove the native oxide of the Si substrate surface in the growth chamber. The base pressure of the chamber was below $3.0 \times 10^{-5}$ Pa and the working pressure during reverse sputtering was $5.5 \times 10^{-1}$ Pa using Ar plasma source. The sputtering power was 200 W and the sputtering duration was 20 min. The use of reverse sputtering significantly improved the degree of out-of-plane orientation of the film as reported previously. Immediately after the completion of the reverse sputtering process, an amorphous Sb$_2$Te$_3$ seed layer was deposited at room temperature without breaking the vacuum. An Sb$_2$Te$_3$ alloy target was used with a sputtering power of 20 W and a working pressure of $4.2 \times 10^{-1}$ Pa. The thickness of the seed layer was varied from 0 to 10 nm. After the growth of the Sb$_2$Te$_3$ seed layer, the sample was heated to 523 K at a ramp rate of 10 K/min in the same chamber and held at 523 K for 60 min. The remainder of the deposition was carried out at the same temperature and the total film thickness was fixed at 50 nm. After growth, the sample was allowed to cool to room temperature in vacuum for a period of over 3 hours. In addition to the Sb$_2$Te$_3$ samples, GeTe/Sb$_2$Te$_3$ superlattice samples were also fabricated for non-volatile memory applications. For the superlattice samples, a 3-nm-thick Sb$_2$Te$_3$ seed layer was initially deposited at room temperature as well as at 523 K for comparison. The growth of superlattice samples was carried out at 523 K using GeTe and Sb$_2$Te$_3$ alloy targets. An alternating layer structure was achieved by opening and closing shutters in front of each sputtering target. The thickness of each layer was 1 and 4 nm for GeTe and Sb$_2$Te$_3$, respectively, and the growth of these layers was repeated for 8 cycles (40 nm in total thickness). The sample thickness was measured by means of a stylus profiler, BRUKER, Dektak XT, with a vertical resolution of 0.1 nm. For thickness measurements, part of the substrate surface was covered with a thin marker before the deposition. After deposition, the marker was removed by ethanol to create a step. The step was sharp enough to measure the thickness accurately. The crystal structure of the films was analyzed by x-ray diffraction (XRD) using a Cu-Kα source ($\lambda = 1.5418$ Å) in a Bragg-Brentano geometry. Glancing angle in-plane measurements were also performed at a fixed incidence angle of 0.4°. The surface roughness and morphology was measured by atomic force microscopy (AFM). The microstructure was observed using transmission electron microscopy (TEM).

The out-of-plane XRD results for films with different seed layer thicknesses are shown in Fig 1(a). Regardless of the seed layer thickness, all films exhibited a strong 001 orientation normal to the substrate, namely, only $<00l>$ reflections were observed with the exception of the Si substrate peak. The peak intensities of the 006, 009 and 0015 reflections are plotted as a function of the seed layer thickness in Fig. 1(b). It was found that the intensity of all the peaks initially increased with increasing seed layer thickness and then decreased. These results suggest that an optimum thickness exists of around 3–4 nm.

![FIG. 1. (a) XRD out-of-plane results for Sb$_2$Te$_3$ films with different room-temperature seed layer thickness. (b) XRD peak intensities as a function of seed layer thickness.](image-url)
In-plane diffraction results are shown in Fig. 2(a). Fig. 2(a) shows the results of an in-plane scan of an Sb$_2$Te$_3$ film, where a 3-nm-thick seed layer was deposited at room temperature followed by the deposition of a 47-nm-thick film at 523 K (total thickness 50 nm). It can be clearly seen that only the 110 peak was present underscoring the strong orientation of the $<00l>$ planes parallel to the substrate. The inset shows a magnified view of the 110 peaks for different samples. The intensity and full-width half maximum of the 110 peaks are plotted as a function of the thickness of the seed layer in Fig. 2(b). It was found that presence of a seed layer, even as thin as 1 nm, resulted in an increase in the peak intensity relative to a film grown without a seed layer, an effect which saturated for thicker seed layer samples. On the other hand, the full-width half maximum decreased with increasing thickness of the seed layer and increases again for thicker samples. Since the full-width half maximum of the XRD peak is typically inversely proportional to the grain size, this result suggests that a seed layer of around 3~4 nm thickness results in the largest grain size.

To elucidate the reason for an optimum thickness, AFM measurement of three films with different seed layer thicknesses were carried out. Fig. 3 shows the surface morphology of the 1, 3, and 5-nm-thick Sb$_2$Te$_3$ films deposited at room temperature followed by annealing at 523 K for 1 hour for crystallization. The thicknesses of the film were determined in the amorphous state and the actual thickness may be slightly lower than the initial value due to the density increase upon crystallization. The surface of the 1-nm-thick Sb$_2$Te$_3$ film clearly exhibits island features as
illustrated in Fig. 3(a). In contrast, the surface of the 3-nm-thick sample shows a uniformly smooth film (Fig. 3(b)). When the seed layer thickness exceeds 5 nm, island features become visible again as indicated by the arrows in the inset of Fig. 3(c), which may prevent the crystal grains from maintaining a strong orientation. The $R_{\text{MS}}$ roughness was 0.39, 0.20, and 0.27 nm for 1, 3, and 5 nm films, respectively, a trend consistent with the discussion above. Therefore, it can be concluded that a 3-nm-thick $\text{Sb}_2\text{Te}_3$ seed layer is optimum to ensure the growth of a highly-oriented film due to seed layer homogeneity and the lack of large grains. We also confirmed the reproducibility of the 3 nm seed layer being optimum by additional samples prepared under the same conditions.

Here, the advantages of room-temperature seed layer deposition rather than high temperature are discussed focusing on the following two points. The first is the surface termination effect of a Te layer. Since $\text{Sb}_2\text{Te}_3$ is a layered compound composed of quintuple layers, which are terminated by Te atoms (Te-Sb-Te-Sb-Te), once a Te-terminated surface is formed, layer-by-layer growth can easily be occur. It is suggested that the as-deposited $\text{Sb}_2\text{Te}_3$ film is in an amorphous state at room temperature; during heating it crystallizes and forms a Te-terminated surface that plays an important role as the seed layer for subsequent growth. The second point regards lateral crystal growth. $\text{Sb}_2\text{Te}_3$ is known to exhibit growth-dominated crystallization, indicating that the nucleation rate is low and once crystal nuclei are formed, the crystallization proceeds by the growth of the nuclei. When an $\text{Sb}_2\text{Te}_3$ film is deposited at high temperature, the nucleation rate may be relatively high because deposited atoms possess large amounts of kinetic energy sufficient to enhance surface mobility, and consequently, a large number of nucleation sites can be formed. When an amorphous $\text{Sb}_2\text{Te}_3$ film is deposited at room temperature and crystallized gradually upon heating, the nucleation rate is very low resulting in the coarsening of crystal grain. It is expected that subsequent film will grow following the crystalline grains of the initial seed layer.

Finally, two cross-sectional microstructures were compared using TEM. The SL structure was Si/$\text{Sb}_2\text{Te}_3$ (3 nm)/[GeTe(1 nm)/$\text{Sb}_2\text{Te}_3$ (4 nm)]$_8$, which were deposited on seed layers formed at room temperature and at high temperature (523 K). It is clearly seen from Fig. 4(a)–4(d) that the lateral grain size significantly increased for the former SL films. The grain size of the latter film is ca. 50–100 nm, while in the former film the grains are ca. 200–300 nm. The coarsening of the crystal grain is consistent with XRD in-plane measurement. Additionally, the strong preferred orientation of the film was also confirmed by selected area electron diffraction, as shown in Fig. 4(e), indicating a near-perfect match to the XRD out-of-plane results.

In summary, in this work, the effect of deposition temperature on the crystallinity of a seed layer for chalcogenide superlattice films was investigated. The XRD peak intensities of both out-of-plane and in-plane measurements as well as the full width at half maximum of in-plane measurement were found to depend on the thickness of the room-temperature $\text{Sb}_2\text{Te}_3$ seed layer. A
seed layer with a thickness of about 3–4 nm showed the best results in terms of the degree of orientation and the lateral grain size of the films. The fabricated GeTe/Sb₂Te₃ chalcogenide superlattice film demonstrated a grain size of more than 200 nm, a size large enough for non-volatile memory applications, in which typically less than a 50 nm contact area is required. Furthermore, this result may open up new possibilities for other novel applications, especially, the fabrication of electronic devices that use the lateral direction of chalcogenide superlattice films.

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