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Laser induced structural transformation in chalcogenide based superlattices

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Superlattices made of alternating layers of nominal GeTe and Sb₂Te₃ have been studied by micro-Raman spectroscopy. A structural irreversible transformation into ordered GeSbTe alloy is induced by high power laser light exposure. The intensity ratio of anti-Stokes and Stokes scattering under laser illumination gives a maximum average temperature in the sample of 177 °C. The latter is lower than the growth temperature and of 400 °C necessary by annealing to transform the structure in a GeSbTe alloy. The absence of this configuration after *in situ* annealing even up to 300 °C evidences an electronic excitation induced-transition which brings the system into a different and stable crystalline state. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4953158>]

Phase change materials (PCMs) play an important role in information technology due to their property of fast and reversibly changing from the crystalline to the amorphous state both exhibiting dissimilar optical contrast and huge difference in resistivity.¹⁻⁴ The most interesting compounds having PCM properties that can be exploited for new non-volatile phase change random access memory (PCRAM) applications are the alloys along the GeTe-Sb₂Te₃ pseudobinary line.^{5,6} Recently, superlattice (SL) structures built with alternating GeTe and Sb₂Te₃ layers have been proven to be optimal candidates as new non-volatile solid-state memory since they combine scalability and fast switching speed with low power dissipation.⁷ Important advances⁸⁻¹⁰ show that the ground state in nominal GeTe-Sb₂Te₃ SLs grown by molecular beam epitaxy (MBE) on Sb passivated Si (111) consists of van der Waals heterostructure of Sb₂Te₃ and rhombohedral natural GeSbTe of different compositions. Momand *et al.*⁸ also showed that annealing of such SLs at 400 °C induces a complete transition to bulk rhombohedral Ge₁Sb₂Te₄. Moreover, in spite of the fact that laser light alters the temperature of the sample,¹¹ a combination of electrical and optical studies on similar SLs highlighted the influence of the electric field on the switching properties.¹² In this letter, we perform Raman spectroscopy on chalcogenide-based SL consisting of nominally alternating layers of Sb₂Te₃ and GeTe, where intermixing at the interface occurs leading to the formation of inclusions of GeSbTe.⁸⁻¹⁰ By analyzing the intensity ratio of anti-Stokes and Stokes scattering, we estimate the heat transfer to the sample during illumination. We find that at high laser power, the spectrum changes irreversibly with the formation of an ordered GeSbTe at a local sample temperature lower than that used for the growth of such alloys. In addition, we show that this configuration cannot be obtained by annealing, and thus, we conclude that the structural change is induced by the interaction with the exciting light.

In this work, the SL structure is grown by solid source MBE equipped with a reflection high-energy electron diffraction (RHEED) setup.^{8,10} The 112 nm-thick sample

consists of nominal 10 repetitions of GeTe (4.4 nm) and Sb₂Te₃ (6.8 nm) grown on Si (111)-(√3 × √3)R30°-Sb, at a substrate temperature of 227.5 °C and the RHEED intensity during deposition confirms that the film grows crystalline from the very beginning until the end of the growth. For more details on the surface preparation and growth see, for instance, Refs. 10, 13, and 14. Micro-Raman spectroscopy is employed to measure the anti-Stokes and Stokes scattering. The sample is excited by a continuous wave He-Ne laser 632.8 nm, and the Raman signal is analyzed by a spectrometer equipped with a LN₂-cooled charge-coupled device (CCD) detector. The laser light is focused by a microscope objective and the same objective is used for the collection of the backscattered light. The spectral resolution achieved is 0.7 cm⁻¹, and the stray light is suppressed by a notch filter. The vibrational modes are assigned by means of polarization resolved spectroscopy. The background from the sample is measured by considering the Raman signal from the Si (111) substrate. The *in situ* annealing is realized by using the THMS600 microscope stage. The sample was cooled down to -195 °C and heated up to 300 °C with a rate of 20 °C min⁻¹.

Figure 1 shows both anti-Stokes and Stokes scattering of the SL, [(GeTe)(4.4 nm)/(Sb₂Te₃)(6.8 nm)]₁₀, after excitation with different intensities of the laser illumination and the spectral region of Rayleigh scattering has been removed for the sake of clarity. The density filters range between 1% and 100% corresponding to power densities of 10³-10⁵ W/cm², respectively, and the exposure time is 70 s for all the spectra of this work. At low power (see Fig. 1(a)), the SL resembles the typical vibrational modes and intensity ratio of Sb₂Te₃¹⁵ with A_{1g} (1) at 69 cm⁻¹, E_g (2) at 114 cm⁻¹, A_{1g} (2) at 171 cm⁻¹ and a weak E_g (1) at 45 cm⁻¹. The intensity of the two A_{1g} modes, especially the A_{1g}(1), decreases once the Sb₂Te₃ is stacked into a SL whereas the E modes remain unchanged. In fact, the A_{1g} modes are associated with the out of plane stretching of the crystal.¹⁶ The shoulder at higher frequencies of A_{1g}(1) is located at the position of the E mode of GeTe at 78.5 cm⁻¹ (see light blue curve in Fig. 1(b)). The fact that we observe faint GeTe features indicates that the intermixing is occurring only at the interfaces and does not concern the full sublayer, as shown for thinner sublayers⁸ where the GeSbTe modes were observed already at

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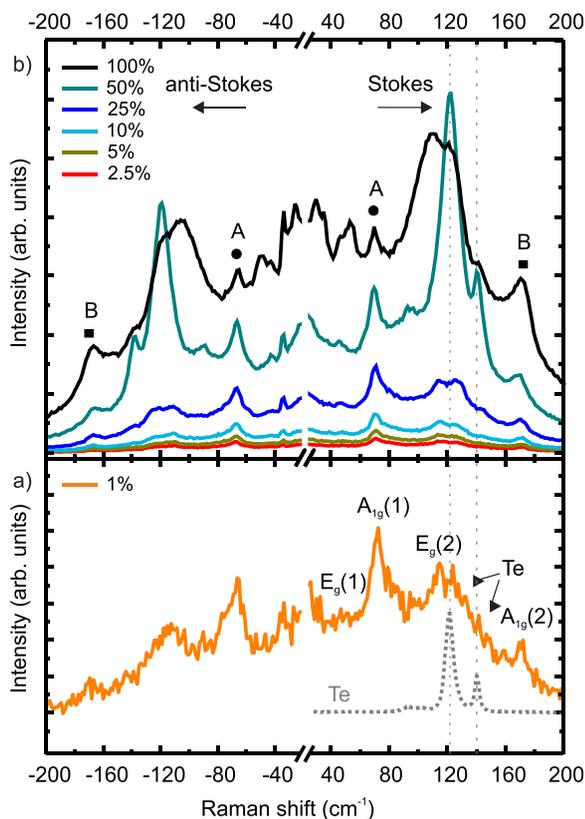


FIG. 1. Raman spectra of the chalcogenide superlattice (SL) $10x[(\text{GeTe})_{4.4}/(\text{Sb}_2\text{Te}_3)_{6.8}]$ recorded at room temperature (RT) with laser illumination of (a) 1% (orange) and (b) 2.5% (red), 5% (dark yellow), 10% (light blue), 25% (blue), 50% (dark cyan), and 100% (black). The dotted light gray curve in (a) represents the Te sample for comparison. The peaks denoted by circle (A) and square (B) symbols are the $A_{1g}(1)$ and $A_{1g}(2)$ modes, respectively. The central portion of the spectra due to Rayleigh scattering is removed for the sake of clarity.

low Raman laser power. Moreover, two additional peaks appear at 126 cm^{-1} (A_1) and 143 cm^{-1} (E), which are the result of some Te formation. Both modes are blueshifted with respect to Te bulk¹⁷ of about 5 and 2 cm^{-1} , respectively, due to the Sb_2Te_3 environment which changes the Te bond length. After exposure of the same sample to higher laser power, the spectrum changes: The Te peaks become more pronounced at 25% illumination until the characteristic double peak turns into a single pronounced mode at 120 cm^{-1} (see dark cyan curve at 50% laser power), in accordance with similar observation in different Te based compounds,¹⁸ and two additional Te modes at 93 cm^{-1} and 140 cm^{-1} are visible. The redshift of these emissions underlines the Te segregation (see the overlap of the peak positions with the Te reference). Most importantly, at maximum laser power (100%), the spectrum changes dramatically and a peak at 109 cm^{-1} along with two low frequency modes at 35 cm^{-1} (E) and 51 cm^{-1} (A_1) appear, which are evidences of GeSbTe formation (see later in the text). In order to find out the thermal contribution of the laser, the average temperature in the sample was estimated by measuring the intensity ratio of anti-Stokes (I_{AS}) to Stokes (I_S) scattering. In the following, we consider the narrower modes $A_{1g}(1)$ and $A_{1g}(2)$, labeled as A and B in Fig. 1(b), respectively. The rate of I_{AS}/I_S follows the Boltzmann distribution law and the temperature in the sample is given by¹⁹

$$\frac{1}{T} = \frac{1}{1.4387\Delta\nu_i(T)} \left\{ \ln\left(\frac{I_S}{I_{AS}}\right) + 4\ln\left[\frac{(\nu_0 + \Delta\nu_i(T))}{(\nu_0 - \Delta\nu_i(T))}\right] \right\},$$

where ν_0 is the wave number of the exciting laser (15802.8 cm^{-1}) and $\Delta\nu_i(T)$ is the temperature dependent wave number of $i = A, B$ Raman mode (cm^{-1}). For each peak at different laser power, the intensity I and the spectral position $\Delta\nu_i(T)$, which has weak temperature dependence, were considered. The intensity ratio was corrected by subtracting the Raman scattering of the Si (111) substrate in order to discard the contribution of the Rayleigh scattering to the measured spectra, given that the phonon energies of the film are very close to ν_0 . The obtained values of the temperature for the A and B modes and their average value (T_{av}) with the respective deviations are reported in Table I. First of all, T_{av} shows that the heating effect of the laser is negligible until 5% laser power. However, T_A and T_B differ at lower power, due to the weaker signal especially for the B mode, thus making these values unreliable till 10% laser power. A little increase in T_{av} is observed at 10%, but it starts rising substantially from 25%. Interestingly, the maximum temperature obtained at 100% laser exposure is 177°C , which is lower than the growth temperature (227.5°C) and much below the melting temperatures of the single compounds ($\text{Sb}_2\text{Te}_3 \sim 580^\circ\text{C}$,²⁰ $\text{GeTe} \sim 500^\circ\text{C}$,²⁰ and $\text{Ge}_2\text{Sb}_2\text{Te}_5 \sim 627^\circ\text{C}$ (Ref. 21)), so should not induce any sensible change in the material. The laser light might induce preferential segregation of Te¹⁸ with formation of Te compounds on the surface, as already discussed.

In order to understand whether the configuration obtained under 100% laser light illumination can be achieved also by simple thermal means, an *in situ* annealing experiment during Raman spectroscopy of the same sample was performed. The SL was cooled down to -195°C , and the stabilized Raman signal was detected during the ramp up to 300°C . It should be noted that the laser power was chosen low enough (10%) to prevent any material transformation. The peak shift of the Stokes scattering is reported in Fig. 2(a) as a function of stage temperature for the A and B modes (black and red circles, respectively). As a result of the thermal expansion of the sample, by increasing the temperature, the emission redshifts with a rate of $-0.01481\text{ cm}^{-1}\text{ }^\circ\text{C}^{-1}$ for the A mode and $-0.01285\text{ cm}^{-1}\text{ }^\circ\text{C}^{-1}$ for the B mode. In addition, the blue and rose triangles represent the respective shift of their power dependent Raman as a function of the estimated T_{av} (see Table I). By comparing the temperature trend of the two

TABLE I. Temperature estimation from anti-Stokes and Stokes scattering of the $A_{1g}(1)$ and $A_{1g}(2)$ modes (T_A and T_B , respectively) and T_{av} at different laser illumination.

Laser power (%)	$T_A \pm \Delta T_A$ ($^\circ\text{C}$)	$T_B \pm \Delta T_B$ ($^\circ\text{C}$)	$T_{av} \pm \Delta T_{av}$ ($^\circ\text{C}$)
1	20.3 ± 0.4	7.1 ± 0.1	13.7 ± 0.3
2.5	32.5 ± 0.6	9.7 ± 0.1	21.2 ± 0.3
5	24.1 ± 0.5	12 ± 0.1	18.0 ± 0.3
10	30.3 ± 0.4	37.2 ± 2	33.7 ± 1.2
25	61.1 ± 1.4	69.6 ± 7.2	65.3 ± 4.3
50	106.9 ± 3	102.5 ± 5.2	104.7 ± 4.1
100	176 ± 7.4	178.4 ± 8.8	177.2 ± 8.1

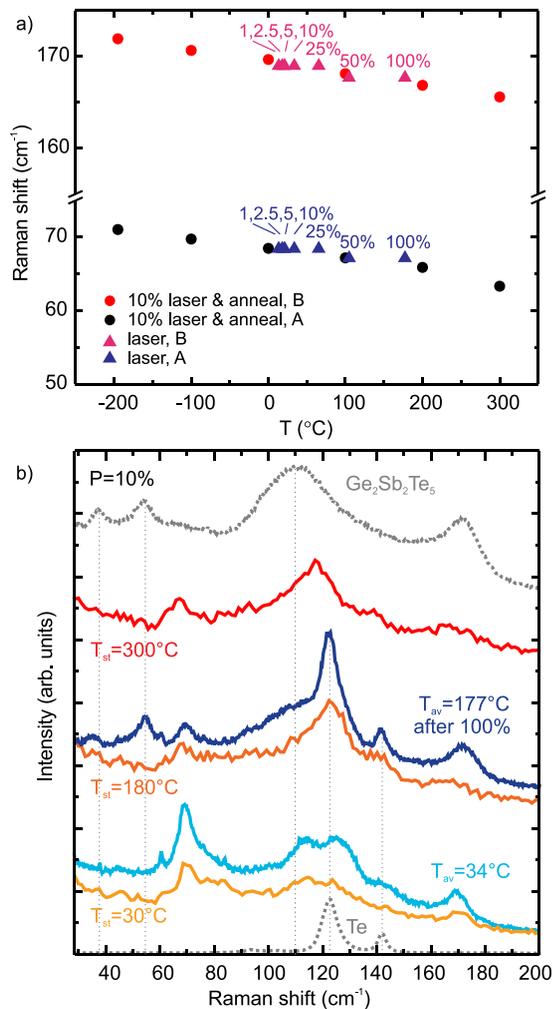


FIG. 2. (a) Comparison of the Raman peak shift for the SL after 1%–100% laser illumination (triangles) and under stage annealing at 10% laser illumination (circles) both for the A mode (blue and black) and the B mode (rose and red) as a function of the temperature. (b) Stokes scattering of the SL at 10% laser illumination after *in situ* annealing at stage temperature (T_{st}) of 30 °C, 180 °C, 300 °C (yellow, orange, and red curves, respectively), at RT before (average temperature, T_{av} = 34 °C) and after (T_{av} = 177 °C) 100% laser illumination (light blue and blue curves, respectively). The dotted light and dark gray curves represent, respectively, the Te and Ge₂Sb₂Te₅ samples for comparison.

different experiments, the overlap of the data points demonstrates that the temperature estimation is accurate. To disclose the effect of the laser light at high power, it is useful to compare spectra obtained at 10% before and after 100% laser power illumination (corresponding to T_{av} = 34 and 177 °C) with that of *in situ* annealing for stage temperature (T_{st}) of 30 and 180 °C. The Stokes scattering spectra are reported in Fig. 2(b) where the same acquisition time after stabilization is always used. Despite the fact that the penetration depth of the laser in these materials is 22.4 nm (Refs. 22 and 23) (two periods of the SL) and that the stage heat distributes in the sample from the Si substrate, temperatures above T_{av} = 177 °C are approached in the annealed case, as obtained after careful anti-Stokes and Stokes analysis similar to the power series of Fig. 1. A comparison of the yellow and light blue curves shows only a small redshift of the characteristic double peak, which can be attributed to the slightly different temperature (T_{st} = 30 °C versus T_{av} = 34 °C). After increasing T_{st} to

180 °C, the double peak merges in a single one at 122 cm⁻¹ due to segregation of Te (see orange curve and Te reference). This is the same behavior observed at 50% laser power in Fig. 1(b). The correspondence of the Te peak evolution at T_{st} = 180 °C and T_{av} = 177 °C confirms the consistency of the temperature estimation. Surprisingly, the spectrum does not change significantly even up to T_{st} = 300 °C, only a larger redshift of the central mode by 5 cm⁻¹ is observed (see the red curve in Fig. 2(b)). On the contrary, for T_{av} = 177 °C, we detected a different configuration with modes appearing at 109 cm⁻¹ and at 35 and 54 cm⁻¹, as shown by the blue curve. Similar low frequency modes have been calculated in Ref. 24 by considering the ordered stacking of the Ge–Sb planes as reported in Ref. 25. However, if we compare such modes with the MBE grown ordered Ge₂Sb₂Te₅^{26,27} (see dotted gray curve), we note that only some of the peaks are in fair agreement. The choice of Ge₂Sb₂Te₅ as reference sample derives from the estimation of the Ge concentration in our SL. In fact, by considering the number of Ge atomic layers in 4.4 nm of GeTe and Sb atomic layers in 6.8 nm of Sb₂Te₃, we get a Ge concentration of 0.48 (Ge/(Ge + Sb)), which is very close to the value for Ge₂Sb₂Te₅ (0.5) whereas for Ge₁Sb₂Te₄ is 0.33. Thus, we conclude that a transformation of the SL into a structure resembling ordered Ge₂Sb₂Te₅ is possible at temperature of 177 °C only by means of laser light application, but further investigation is necessary for assessing the structure after high laser power exposure in all details. Nevertheless, the A and B modes from Sb₂Te₃ are still pronounced with a strong enhancement of the E_g (1), but a rearrangement of the atomic structure takes place with the intercalation of GeTe layers leading to GeSbTe formation, as confirmed by other works.^{8–10} As a result, the dominant peak is the E mode at 109 cm⁻¹. The pronounced GeSbTe peaks observed are explained by the vacancy ordering, which breaks the symmetry and enables the vibrations.^{27–30}

To further verify the influence of the laser light on the structural change, we performed a polarization resolved measurement by exciting the sample along the cleaved edge, as shown in Fig. 3. In fact, due to the anisotropy between the in plane and the out of plane directions of the SL, a different switching behavior was reported in Ref. 12, when the electric field is polarized in the SL plane (x, y) or out of plane. Here, when high laser illumination (100%) is irradiated and the sample is measured at low power, a permanent structural change of the SL is observed for both polarization directions with the formation of the GeSbTe feature around 109 cm⁻¹, as already observed in Fig. 2(b) for the sample excited perpendicular to the SL plane. It should be noted that a different position on the sample was chosen in the two cases due to the irreversibility of the structural transformation. Strikingly, in the case of the electric field aligned in the SL plane peaks attributed to ordered Ge₂Sb₂Te₅ appear at 35 cm⁻¹ and 54 cm⁻¹ (see blue curve), where the weak intensity of the lower frequency peak is due to the background of the scattered light. On the contrary, in the case of the out of plane polarized light, almost no change is observed in the same spectral range (see dark red curve). This is a clear indication of the laser light effect on the structural change and whether such difference could be attributed to the SL anisotropy or to the crystal symmetry is the subject of a dedicated study.

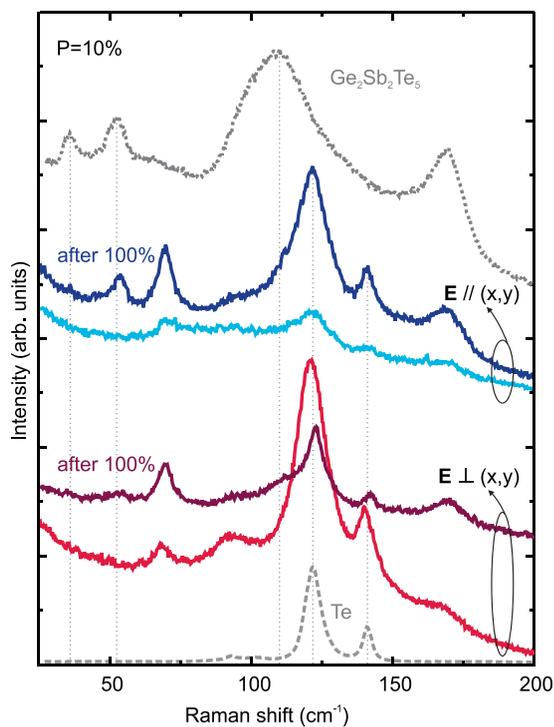


FIG. 3. Stokes scattering of the SL at 10% laser illumination before and after high laser power (100%) excited from the cleaved edge with polarization in the SL plane ((x,y), light blue and blue, respectively) or orthogonal (red and dark red, respectively). The dotted light and dark gray curves represent, respectively, the Te and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ samples for comparison.

The in plane electric field of the continuous wave laser is able thus to excite the electronic system of the SL structure leading to a permanent change into ordered crystalline GeSbTe . Interestingly, this effect was not observed in thin chalcogenide SLs previously.

In conclusion, we have shown clear experimental evidence that after high power laser exposure a SL formed by alternating layers of nominal Sb_2Te_3 and GeTe transforms into a structure that closely resembles ordered crystalline $\text{Ge}_2\text{Sb}_2\text{Te}_5$. The temperature of the sample was estimated by Raman anti-Stokes and Stokes scattering, and a maximum value of 177°C was obtained. Such GeSbTe structure is not observed after annealing of the same sample up to 300°C ; thus, we conclude that it results from the interaction of the laser light with the SL material. We therefore envision that the application of ultra short laser pulses by an optimized fluence on such as grown SL might pave the way to control the structural phase of chalcogenide SLs at temperature lower than the melting point. The present findings provide intriguing future perspectives for the next generation of PCRAM.

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