Abschließender Sachstandsbericht
Leibniz-Wettbewerb

"Epitaxial Phase Change Superlattices Designed for the Investigation of Non-Thermal Switching"

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Federführendes Leibniz-Institut: Paul-Drude-Institut für Festkörperelektronik

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Inhalt

1. Zielerreichung und Umsetzung der Meilensteine

The main goal of the present proposal was to design and fabricate epitaxial phase change material superlattices (PCMSLs), consisting of alternating layers of GeTe and Sb_2Te_3, to investigate the role of non-thermal and electronic excitations during the state transformation.

2. Aktivitäten und Hindernisse

The overall activity was constituted by two major taskes

Fabrication of epitaxial GeTe/Sb_2Te_3 superlattices
Pump probe experiments on GeTe/Sb2Te3 superlattices

3. Ergebnisse und Erfolge

Fabrication of epitaxial GeTe/Sb_2Te_3 superlattices

The growth by molecular beam epitaxy of GeTe and Sb_2Te_3/GeTe superlattices on three differently reconstructed Si(111) surfaces is demonstrated. Namely, these are the Si(111)−(7×7), Si(111)−(√3×√3)R30°−Sb, and Si(111)−(1×1)−H reconstructions. Through X-ray diffraction, the epitaxial relationship of GeTe is shown to depend on the passivation of the surface; in-plane twisted and twinned domains could be suppressed on a passivated surface. This behavior which resembles what would be expected from lamellar materials, is attributed to the relative weakness of resonant dangling bonds, that are further weakened by Peierls distortion. In the superlattice structure, the epitaxial relationship of the whole stack is shown to be decided by the very first layer already. Thus, no twisted domains are observed if they are suppressed in the initial layer. At the interfaces, intermixing between GeTe and Sb_2Te_3 into an ordered ternary GeSbTe (GST) alloy is observed and demonstrated by scanning-transmission electron microscopy and X-ray diffraction (XRD). The resulting structure is a stack of 2D materials. Taking advantage of the high-angle annular dark field detector's ability to discriminate atomic species by their contrast in atomic mass, the tendency toward ordering of each species into separate layers within the GST blocks is resolved. However, due to kinetic limitations and to the effect of diffusion, mixed Ge/Sb layers are observed, especially in the top-side of each GST sublayer. Revealed by XRD and Raman, then demonstrated by scanning transmission electron microscopy (STEM), intermixing is observed between the GeTe and the topmost Sb_2Te_3 quintuple layer of each sublayer, forming different GST compounds at the interface. Using the ability of the STEM to discriminate between heavy and lighter atomic species, an asymmetry in the Ge concentration inside the GST blocks is discovered. Mainly from this observation, a growth model is drafted, attributing the intermixing specifically to the deposition of GeTe on top of Sb_2Te_3. From these results, a model describing the intermixing during growth is presented. Finally, through Rflection High Energy Electron Diffraction monitoring, a surprising variation of the in-plane lattice spacing is observed during the growth of the superlattices. It could be ascribed neither to classical epitaxy nor to van der Waals epitaxy. This is explained by a certain degree of coupling, even across van der Waals bonds. Supported by grazing-incidence XRD, the possibility for strain engineering in van der Waals bonded superlattices is demonstrated.

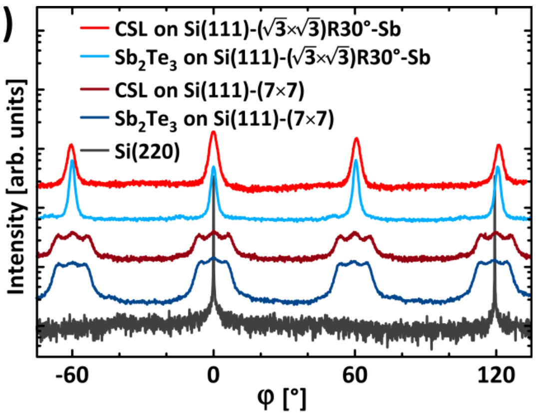

Figure 1: *XRD φ−scans showing the {0 1 $\bar{1}$ 5} reflections from Sb_2Te_3 films grown on Si(111)-(7x7) and Si(111)-(√3×√3)R30°-Sb, compared with reflections from the equivalent planes in CSLs grown on the same surfaces, with Sb_2Te_3 as their first layer. Substrate Si{220} reflections (the equivalent planes in silicon) are shown as a reference.*

Pump probe experiments on $GeTe/Sb_2Te_3$ superlattices

Pump/probe schemes based on optical-pump and Terahertz (THz) spectroscopy-probes have been employed to access ultrafast dynamics necessary for the understanding of switching mechanisms. The sensitivity of THz-probe to conductivity in both GST and $GeTe/Sb_2Te_3$ superlattices showed that the non-thermal nature of switching in superlattices is related to interface effects, and can be triggered by employing up to one order less laser fluences if compared to GST. Such result agrees with literature, in which a crystal to crystal switching of superlattice based memory cells is expected to be more efficient than GST melting, therefore enabling ultra-low energy consumption. $GeTe/Sb_2Te_3$ based superlattices resemble in their structure that of ordered GST due to the presence of periodic vdW gaps in between building blocks alternating Te, Sb and Ge layers. For this reason it is surprising that the switching mechanism of GST and superlattices is so different. Multilayer model simulations have been performed in order to evaluate the absorbed/transmitted power of the 800 nm laser-pump in the samples and determine the optimal thickness for the time resolved experiments. In the simulation n and k are taken from literature, and the heterostructure is simulated according to its really obtained structure considering the intermixing. A minimum thickness of 60 nm thickness resulted to be ideal compromise in order to have high quality sample and good pump/probe signal detection, with around 60% absorbed power in the film and negligible <1.7% of transmitted power. In fig.2 a) THz transmittance change of $GeTe/Sb_2Te_3$ (1nm/3nm x 15times) as function of delay time is shown for different pump fluence (see labels). The curves are plotted with an offset for clarity. It is interesting to note that a peculiar transmittance evolution is present. A first remarkable consideration concerns the fluence range employed, which is much lower if compared with amorphous and crystalline GST: Up to 1 order of magnitude lower fluences with 0.02 mJ/cm^2 for superlattices, while 0.1 mJ/cm^2 for amorphous-GST and 0.4 mJ/cm^2 for cristalline-GST. Immediately after excitation (at deleay 0 ps), the three curves corresponding to fluences from 0.02 to 0.1 mJ/cm^2 show an increase of transmission above the 100% starting value (indicated for each curve by horizontal dotted lines) from 0.3 to 0.5% of the initial value, indicative of a small effect. Such transmittance increase subsequently decreases till the original 100% value within few ps (8 ps for the highest fluence of 0.1 mJ/cm^2). A pump-induced increase of the THz transmission, or a decrease of the THz absorption corresponds to a decrease of the THz conductivity. When incident fluence is further increased (0.13 mJ/cm^2), a drop in the signal is visible after initial excitation (0.4% decrease) followed by a recovery, which actually leads to an increase of transmittance above 100% and a further drop, as for the lower fluence cases. A long recovery for t >8 ps is also visible. Similar transmittance evolution is found for 0.19 mJ/cm^2 too. Here, however, the higher number of excited carriers (larger drop of signal 0.9%) does not lead to an increase above the starting value. The transmittance maximum observed for 0.02 mJ/cm^2 at 1.1 ps shifts toward 4.1 ps for 0.19 mJ/cm^2. Two major time constants have been considered to describe the carrier dynamics: τ_2 is the time constant which stems for the increase of transmittance [see label in fig.2 a)], τ_3 describes the recovery from the previous transmittance increase [see label in fig.2

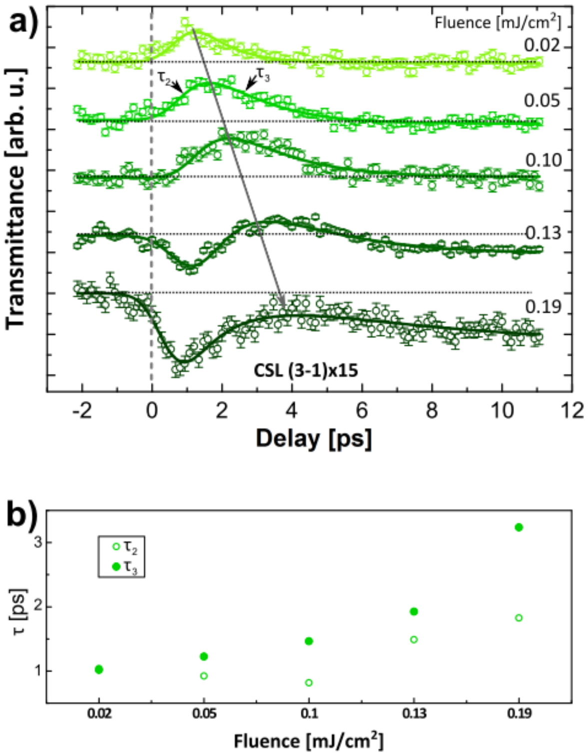

***Figure 2**: a) THz transmittance change in superlattice for different applied laser fluencies. Fits of the experimental data are superimposed; b) time constants as function of applied fluence are shown.*

b)]. The change of τ_2 and τ_3 depending on the applied fluence is shown in fig.2 b). Both display a non linear increase for increasing fluence values. The interpretation of the transmittance evolution is not trivial, especially due to the fact that for higher fluence values different dynamics seem to come into play. If we start from the first three curves, which present only one characteristic feature, a first complication arises from the fact that an increase of transmittance above the 100% line might be ascribed to an amorphization of the CSL upon laser pumping. However, the reversibility of the process (signal recovery to 100% line), strongly suggests that it is more reasonable to assume an ultrafast "disordering" that leads to a decrease in conduction, without invoking a permanent phase transition. Based on the structural knowledge we have on the as grown CSL, it is reasonable to assume that such disordering is happening at the interfaces between Sb_2Te_3 and GST blocks, which presents many discontinuities of the vdW gaps. At higher fluence values, a sub-ps transmittance drop, and a very long recovery time above 8~ps occurs [see last two curves in fig.2 a)]. Such behavior has been observed also in crystalline GST. All these observations suggest that the superlattices transmittance evolution might be arising from a competing bulk/interface effect. Let us recall that bulk GeTe, Sb_2Te_3 and GST shows dynamics only starting from 0.4 mJ/cm^2, with transmittance drop and immediate recovery through single τ for bulk material (measured as references). If a transmittance drop and recovery is the sign for a bulk-like behavior, we have to notice that for superlattices this effect can be achieved at lower fluences and follows that of crystalline GST with two recovery time constants. In a superlattice annealing study, it has been shown that for 400°C, the superlattice transforms into ordered GST. This highlights an intrinsic thermodynamic tendency toward intermixing, as found also during growth, above a certain energy barrier. This result and the evolution of the curves in fig.2 suggest that for increasing fluences, if enough heat is accumulated into the lattice, the superlattice would start to transform into GST, and the corresponding THz signal would be comparable with the one of GST. Such intermixing and consequent loss of the superlattice structure is therefore expected to happen earlier than a permanent amorphization of the heterostructure. Within the employed fluences, reproducibility of the measurements shown in fig.2 a) indicates that intermixing can be excluded. A superlattice GeTe/Sb_2Te_3 (4nm/6nm x 7 times) has also been measured for comparison. In this sample we increase the bulk at the expenses of the interface. In addition, the relative presence of the two constituents changes from 3 to 1.5. The result of the time-resolved measurement is shown in fig.3 for two fluences in which also a rise and drop are obtained. Curves are plotted with an offset and smoothed with an adjacent-average method for clarity. 100% transmittance lines are shown as guide for the eye. For fluence of 0.08 mJ/cm^2, a total transmittance increase of ~0.1% is obtained (see label in fig.3). By increasing the fluence 0.13 mJ/cm^2, the signal drops ~0.3% (see label in fig.3), and subsequently rises above the 100% original transmission. A recovery to the original value follows. The overall lower effect made the measurements of such superlattices more challenging, requiring longer integration times. In particular, the smaller effect of the interface disordering might support the fact that a superlattice with higher proportion of interfaces in the film is desirable for switching application. This is in agreement with literature results. Switching in superlattices happens between two crystalline states, i.e. one conducting [low resistive state (LRS)] and the other highly resistive (HRS), as opposed to conventional GST where switching occurs between amorphous and crystalline phases. Electrical characterization show that superlattice memory cells as grown display a resistance value of $10^4\Omega$, instead,

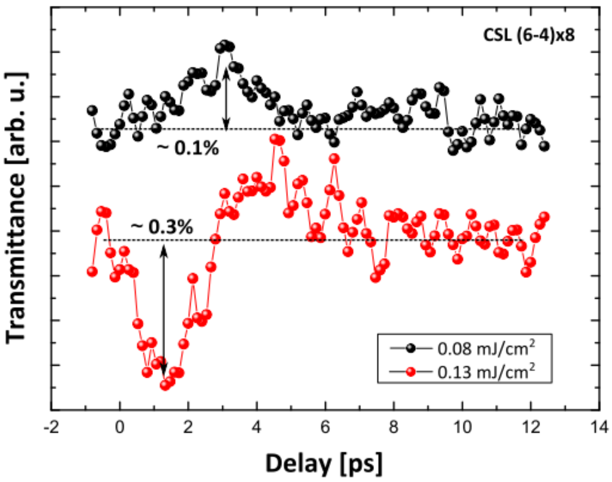

Figure 3: THz transmittance change in superlattice GeTe/Sb_2Te_3 (4nm/6nm x 7 times) for 0.13 and 0.08 mJ/cm^2 applied laser fluences is shown. 100 % transmittance line are shown as guide for the eye.

HRS of $10^7\Omega$ is obtained after electrical switching with a programming current at least 1/3 lower than that necessary to switch GST. Therefore, interface response might represent the key to understand the HRS in PCMSLs. The comparison of electrical data with optical pump/probe reveals that in both cases lower power (low programming current, low fluences) is used to induce the switching or its precursor. In both cases the sample undergoes a strong disordering process. The latter, as from pump/probe data, is possibly arising at the interface, thus it explains why superlattices with relatively too high bulk contribution do not switch as nicely as those with larger interface contribution.

4. Chancengleichheit

Within the project we actively committed to provide to all employees working in the project equal opportunity as well as the equality of women and. The project responsibles are a female and a male. Between the group members a Ph.D student female was strongly encouraged and she delivered very important results. All employed male PostDocs could make their scientific career compatible with family commitments requesting the parental child care opportunities provided by our institute. The project leader Dr. R. Calarco has been elected in 2018 equal opportunity officer at PDI.

5. Qualitätssicherung

Our academic work was and is based on the fundamental principle of honesty with oneself and others. We always work in compliance with the principles of good scientific practice. All such principles have been communicated by the elder group members to the younger and openly discussed as central concerns by all team members. The most relevant results obtained in this project have been published in 18 peer reviewed scientific journals, many of them in open access. Between those 3 have been invited review papers. In addition to normal participation more than 30 invited seminars at conferences or at academic institutions have been delivered.

6. Zusätzliche eigene Ressourcen

The project leader Dr. R. Calarco (50%) and Dr. T Flissikowsky (10%) participated to the project with large part of their working time.

7. Strukturen und Kooperation

To be able to succesfully perform the project several beam times at the BESSYII synchrotron have been requested. Such requests have been developed with a very tight cooperation with the beam line scientist K. Holldack responsible of the THz beamline at BESSYII.

1. THz investigation of Phase Change Materials superlattices 2015 THz- beamline
2. Femtosecond dynamics of optical switching in rewritable optical media II 2016 Femtoslicing (UE56-1-ZPM)
3. Time-resolved THz magneto-optical Kerr effect in Sb2Te3/GeTe superlattices 2016 THz- beamline

8. Ausblick

As an outlook for the future, it would be interesting to grow superlattices with controlled atomic inclusions in the van der Waals gaps at the interfaces, which are expected to influence the switching performances of the superlattice itself. Such atomic inclusions could be accessed by structural characterization methods. The different superlattices would then be characterized electrically and by THz-probe. Such a strategy is expected to unveil the exact interface effect discovered in this project, and would offer a path for an optimization work in order to maximize the performance of superlattices based memory cells.