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Rate equation model for the time dependence of the reflectance of a Ge$_2$Te$_2$Sb$_5$ film during optical switching processes

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We apply a rate equation model in order to simulate the measured change of the reflectance of an epitaxially grown Ge$_2$Te$_2$Sb$_5$ (GST) film during optically induced switching between the amorphous and crystalline phases of the material. The amorphization and the re-crystallization process are considered to exhibit different switching rates, which depend on the actual value of the energy fluence of the applied laser pulse. The measured time dependence of the reflectance of the GST film as a measure of its degree of crystallinity is qualitatively reproduced by the rate equation model demonstrating that both processes can occur simultaneously during the switching process, but with different rates. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4803543]

I. INTRODUCTION

Devices based on phase-change random access memory (PCRAM) are very promising candidates to meet the ever growing demand for higher memory densities and faster read/write cycles. In contrast to conventional memory cells, a bit in PCRAM devices is stored as a difference in the structural phase (amorphous or crystalline) of the phase-change material (PCM) and not as an electrical charge. In particular, the PCM composition Ge$_5$Sb$_3$Te$_3$ (GST) of the (GeTe)(Sb$_2$Te$_3$) system is currently investigated very actively. Key parameters are the speed of the phase transformation, the stability of the crystal structure, and the scalability of the total memory cell. Recent investigations demonstrate a scalability down to 2 nm thin GST films. The switching time of a complete PCRAM cell can be faster than 5 ns using superlattice-like structures of the PCM. Very recent results show that for GST superlattices based upon a Ge flip-flop mechanism the phase change from the amorphous to the crystalline phase can be on the sub-ps time scale, if fs pump pulse pairs are used. However, the sub-ps time scale can be currently reached only by optical means using sophisticated fs-lasers. Our investigation focuses on the phase transformation induced by single or multiple pulses with durations in the ps time range, since this timescale is the practical limit of todays electronics.

II. EXPERIMENTAL DETAILS

The investigated GST film with a thickness of about 90 nm has been grown by molecular beam epitaxy (MBE) on a lattice-matched GaSb(001) substrate in order to guarantee a high structural quality. Due to the MBE growth and the selected growth parameters, the epitaxial film is completely crystalline directly after growth. Using x-ray diffraction and reflection high-energy electron diffraction, the investigated film is shown to exhibit a cubic crystal structure. In contrast, GST films for commercial applications and most other scientific investigations are produced by sputter deposition and are usually amorphous directly after growth. Therefore, the sputtered films need first to be heated to the crystallization temperature in order to become crystalline. For the optical switching experiments, we used a high-power Nd:YAG laser (Continuum Leopard SV-20) operating at a wavelength of 532 nm and providing pulses of 60 ps duration with a maximum repetition rate of 20 Hz. Individual laser pulses can be extracted by a shutter system. The maximum energy for an individual pulse is about 60 mJ. In order to select a specific value of the energy fluence, a set-up with several optical density filters and two adjustable polarizers is used. Since the energy per pulse is a critical parameter for...
the switching process, the energy of each laser pulse applied to the sample is measured using a beam splitter and a power meter. The laser-induced changes of the reflectance of a specific area on the GST film are synchronously monitored by reflecting the light of a continuous-wave diode laser with a wavelength of 635 nm, which is detected using a photodiode and lock-in technique. Since the diameter of the probe beam on the sample surface is about three times smaller than the diameter of the pump beam, the probe beam covers an area of rather constant power density of the pump beam. We distinguish two switching regimes. During the RCP, usually a large number of laser pulses with comparably small values of \( \rho_E \) are applied to the GST film with a small time separation \( \tau_p = 50 \text{ ms} \). In contrast, only a few laser pulses with comparably large values of \( \rho_E \), which are well separated in time by \( \tau_p = 2 \text{ s} \), are used during the AP.

III. RESULTS AND DISCUSSION

We performed a detailed investigation of the re-crystallization process using different values of \( \rho_E \) and observed that the change in the reflectance \( R \) per applied laser pulse as well as the final value of \( R \) depend on the value of \( \rho_E \). Furthermore, if the RCP is completed and the final value of \( R \) is reached, we still observe a small change in \( R \), which appears to be correlated with a small jitter of the energy of the laser pulse and consequently the value of \( \rho_E \). In order to extract more direct information, we re-crystallized the same sample location with different values of \( \rho_E \) and recorded the final normalized reflectance \( R_{\text{final}}/R_C \), where \( R_C \) denotes the measured reflectance of the crystalline phase. Figure 1 shows \( R_{\text{final}}/R_C \) as well as the minimum normalized reflectance \( R_{\text{min}}/R_C \) resulting from an amorphization process as a function of \( \rho_E \). Above \( \rho_E = 10 \text{ mJ/cm}^2 \), \( R_{\text{final}}/R_C \) strongly decreases indicating that the GST film does not fully re-crystallize for these values of \( \rho_E \). The GST film may even be amorphized rather than re-crystallized in this range of \( \rho_E \) values, even though the laser pulses had a much smaller pulse separation than used for the AP.

A similar effect can be observed, after the RCP is nearly completed (\( R_{\text{final}}/R_C \) is reached) and the shutter is kept open so that additional re-crystallization laser pulses are applied.

FIG. 1. Histogram of the final reflectance \( R_{\text{final}}/R_C \) during a RCP (triangles) with \( \tau_p = 50 \text{ ms} \) and minimum reflectance \( R_{\text{min}}/R_C \) during an AP (squares) with \( \tau_p = 2000 \text{ ms} \) versus \( \rho_E \).

FIG. 2. (a) Normalized reflectance \( R/R_C \) and (b) energy fluence \( \rho_E \) versus time after the RCP is nearly completed (\( R_{\text{final}}/R_C \) is reached), demonstrating that both \( R/R_C \) and \( \rho_E \) exhibit small fluctuations. The solid line in (a) represents the average value of \( R/R_C \).

Figures 2(a) and 2(b) show the time dependence of \( R/R_C \) and \( \rho_E \), respectively. These two plots demonstrate that \( R/R_C \) fluctuates due to fluctuations of \( \rho_E \) so that \( R/R_C \) is not exactly constant after the completion of the RCP. We conclude that for values of \( \rho_E \) between 10 and 20 \text{ mJ/cm}^2 both the RCP and the AP can occur. At the same time, the value of \( R_{\text{final}}/R_C \) depends on the value of \( \rho_E \) of the laser pulse last applied. Consequently, there should be a correlation between the value of \( \rho_E \) and the value of the final reflectance.

In order to quantify the correlation between \( \rho_E \) and \( R_{\text{final}}/R_C \), we calculate the correlation coefficient \( \Psi \) for the data shown in Fig. 2 using the following equation:

\[
\Psi = \frac{\sum_{i=1}^{N} [R(t_i) - \bar{R}](\rho_E(t_i) - \bar{\rho}_E)}{\sqrt{\sum_{i=1}^{N} [R(t_i) - \bar{R}]^2 \sum_{i=1}^{N} [(\rho_E(t_i) - \bar{\rho}_E)^2]},
\]

where \( R(t_i) \) and \( \rho_E(t_i) \) denote the normalized reflectance and energy fluence, respectively, at time \( t_i \), while \( \bar{R} \) and \( \bar{\rho}_E \) denote the average values for \( R/R_C \) and \( \rho_E \), respectively. By definition, the values of \( \Psi \) lie between \(-1 \) and \( 1 \), where \( 1 \) indicates correlation, \(-1 \) anti-correlation, and \( 0 \) no correlation. If we calculate \( \Psi \) for the data in Fig. 2, we find \( \Psi = -0.5 \), which indicates partial anti-correlation. Calculating \( \Psi \) for measurements (not shown) with different values of \( \bar{\rho}_E \) and with different spot diameters yields values of \(-0.6 \leq \Psi \leq -0.2 \), indicating that there is a partial anti-correlation between \( R_{\text{final}}/R_C \) and \( \rho_E \) and that the RCP and the AP can occur simultaneously with different weights.

For modeling the measured time dependence of the reflectance, we combine a rate equation formalism with a two-dimensional model of the GST film. We divide the measurement area into \( N \) small independent units. Every unit can either be amorphous or crystalline. The reflectance of an amorphous unit is \( R_a = R_{\text{min}} \), while for a crystallized unit the reflectance \( R_c \) is assumed to be 1. The measured reflectance \( R \) corresponds to the sum over all the reflectances \( R_i \) of each independent unit of the whole measurement area. Thus,
where \( n_c \) and \( n_a \) denote the number of crystalline and amorphous units, respectively. The degree of crystallization \( C \) can be defined as \( C = n_c/N \), while the degree of amorphization \( A \) becomes \( 1 - C = A = n_a/N \) due to the constraint \( C + A = 1 \). To relate the measured reflectance \( R \) to the degree of crystallization, we use Eq. (2) and the definition of \( q \) to obtain

\[
C = \frac{R - R_a}{R_c - R_a} = \frac{R - R_{\text{min}}}{1 - R_{\text{min}}}. \tag{3}
\]

The RCP always occurs within an amorphous area and can be described by a rate \( W_{c \rightarrow a} \), while the AP occurs within a re- crystallized area with a rate \( W_{a \rightarrow c} \). Thus, the time derivative of the degree of crystallization becomes

\[
\frac{dC(t)}{dt} = \frac{W_{a \rightarrow c}}{W_c} A(t) - \frac{W_{c \rightarrow a}}{W_a} C(t)
\]

Using with the initial condition \( C(t = 0) = C_0 \) and the abbreviation \( W = W_{a \rightarrow c} + W_{c \rightarrow a} \), the solution of Eq. (4) is

\[
C(t) = \frac{W_{a \rightarrow c}}{W} [1 - \exp(-Wt)] + C_0 \exp(-Wt). \tag{5}
\]

For long times, i.e., \( t \rightarrow \infty \), the solution tends to

\[
C(t \rightarrow \infty) = \frac{W_{a \rightarrow c}}{W}.
\tag{6}
\]

Since \( C(t) \) is related to the measured reflectance \( R(t) \) through Eq. (3), we can use Eq. (6) to determine \( W_{a \rightarrow c}/W \) from the measured quantities \( R_{\text{final}} \) and \( R_{\text{min}} \). The rates \( W_{a \rightarrow c} \) and \( W_{c \rightarrow a} \) are also expected to depend on \( \rho_E \), because Fig. 2 and the evaluation of Eq. (1) suggest a partial anti-correlation between \( \rho_E \) and \( R \).

To determine the dependence of the rates \( W_{a \rightarrow c} \) and \( W_{c \rightarrow a} \) on \( \rho_E \), we measured \( R(t) \) as well as \( R_{\text{min}} \) and calculated \( C(t) \) from these using Eq. (3). To prevent a thermal correlation between the laser pulses, the time between two laser pulses was set to \( \tau_p = 2 \, \text{s} \). To obtain a clearly measurable reflectance change, we chose appropriate values of \( \rho_E \). Figures 3(a) and 3(b) show the time dependence of the measured \( C \) (triangles) and \( \rho_E \), respectively. We performed several switching cycles with different average values of \( \rho_E \). For each switching cycle, we fitted \( C(t) \) over a time range for the RCP indicated by the dotted vertical lines in Fig. 3(a) and for the AP indicated by the dashed vertical lines in Fig. 3(a) using Eq. (5). For one particular RCP, the experimental data (triangles) and the fit (solid line) to Eq. (5) are enlarged in the inset of Fig. 3(a). For a complete switching cycle containing a RCP and an AP, this procedure results in two values of \( W_{a \rightarrow c} \) and two values of \( W_{c \rightarrow a} \). Note that in Eq. (5) \( W \) is an abbreviation for \( W_{a \rightarrow c} + W_{c \rightarrow a} \). All values of \( W_{a \rightarrow c} \) and \( W_{c \rightarrow a} \) obtained in this way are shown in Figs. 4(a) and 4(b), respectively, as a function of \( \rho_E \), which is averaged over the corresponding switching process, i.e., AP or RCP. Figure 4 clearly demonstrates that both rates exhibit an exponential dependence on \( \rho_E \). In order to describe this dependence, the following exponential function has been fitted to rates \( W_{a \rightarrow c} \) and \( W_{c \rightarrow a} \):

\[
W(\rho) = W_0 + W_A \exp \left( \frac{\rho_E}{W_p} \right), \tag{7}
\]

where \( W_0, W_A, \) and \( W_p \) denote fit parameters, which are summarized for both rates \( W_{a \rightarrow c} \) and \( W_{c \rightarrow a} \) in Table I and the corresponding fits are displayed in Fig. 4 as solid lines.

In order to test the quality of the model, \( C(t) \) in Fig. 3(a) was calculated using Eqs. (3) and (5) with \( W_{a \rightarrow c} \) and \( W_{c \rightarrow a} \) determined for each actual value of \( \rho_E \) using the parameters \( W_0, W_A, \) and \( W_p \) from Table I. As a starting condition, we used \( C(t = 0) = 1 \). Although in some cases the calculated values of \( C(t) \) are considerably smaller than the measured
ones, the comparison between the measured and calculated values of $C(t)$ in Fig. 3(a) demonstrates that the applied model qualitatively reproduces the measured $C(t)$. This observation suggests that the AP and RCP can be indeed described by a rate equation model, where the switching rates depend on the energy fluence of the laser pulse.

IV. SUMMARY

We optically amorphized and re-crystallized a MBE-grown GST film with laser pulses of 60 ps duration. The reflectivity data can be qualitative described by a rate equation model, which takes the amorphization process and the re-crystallization process simultaneously into account. The switching rates are assumed to depend on the energy fluence. From the obtained results, we conclude that in principle the AP and RCP can occur for any value of $\rho_E$, but with different switching rates. In order to predict a certain degree of crystallization for a particular value of the energy fluence, the presented model needs to be refined.

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