Temperature dependant thermal and mechanical properties of a metal-phase change layer interface using the time resolved pump probe technique

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Abstract. Time Resolved Pump Probe (TRPP) technique has been implemented to study the thermal and mechanical properties of Ge₂Sb₂Te₅ (GST) film deposited on a silicon substrate. According to the knowledge of the thermal properties of the GST layer, the temperature dependant Thermal Boundary Resistance (TBR) at the metal-GST interface is evaluated. Measuring the acoustic oscillation and more particularly its damping leads to characterize the adhesion at the metal - GST interface. This quantity can be efficiently related to the temperature dependent TBR in the 25°C – 400°C range. The TBR increases with temperature and follows the changes of the crystalline structure of materials. A linear relation between the acoustic reflection coefficient and the logarithm of the thermal boundary resistance is found.

1. Introduction: Phase Change Memory

Phase change materials are extensively studied due to their promising applications in the framework of Phase Change Memory (PCM) or Ovonic Unified Memory [1,2]. PCM functioning involves chalcogenide materials that are allotropic semi conducting elements and alloys belonging to the IV, V and VI group of the periodic classification. They can be reversibly brought from the amorphous to the crystalline state, so that the corresponding different electrical properties between these two states (electrical resistance decreases over 4 decades) can be used for data storage. Ge₂Sb₂Te₅, commonly denoted GST, is one of the most popular chalcogenide alloys [3], since it is stable at room temperature in the amorphous and hexagonal crystalline phases (hcp), and metastable in the face centered cubic phase (fcc) [4,5]. The amorphous/fcc phase transition occurs at 130°C whereas the fcc/hcp one at 350°C. The melting temperature is approximately 600°C. The transformation between crystalline and amorphous phases is reversible: heating the amorphous GST to a temperature slightly above the glass-transition temperature leads to the crystalline phase; subsequent heating to a temperature close to the melting temperature with fast quenching permits retrieving the amorphous phase.

Optimization of the phase change memories operation rests on the knowledge of the thermal properties of the phase change material. The value of specific heat per unit volume of the GST-225, which does not depend on the crystallographic configuration at high temperature, is: \( \rho C_p =1.28 \times 10^6 \) J.K⁻¹.m⁻³. We measured the thermal conductivity of the GST in previous study by using modulated
photothermal radiometry in the $[10^3\text{-}10^5]$ Hz frequency range [8]. This alloy has, according to the crystalline phase, the following densities [6]: 5.87 g.cm$^{-3}$ for the amorphous phase, 6.27 g.cm$^{-3}$ in cubic phase and 6.39 g.cm$^{-3}$ in hexagonal phase. The longitudinal speeds of sound were measured by acoustic picoseconds techniques [7]. The longitudinal velocity is 2.25 nm.ps$^{-1}$, 3.19 nm.ps$^{-1}$ and 3.3 nm.ps$^{-1}$ for amorphous, fcc and hcp crystalline phases respectively. It appears that the thermal resistance at the scale of the GST thickness (some tenth of nanometers) is equivalent to the Thermal Boundary Resistance (TBR) at the interface between contacting layers. This paper aims to measure the TBR at the GST (210 nm)-Al (20 nm) interface from room temperature up to 400°C. It is therefore necessary to generate a short thermal excitation and to carry out the measurement within a sub-nanosecond time range.

2. Experimental procedure

Time Resolved Pump Probe (TRPP) was performed with a picoseconds acoustic experimental setup initially designed to study the acoustic wave propagation phenomena at the picoseconds and nanometer scale [9]. With this technique the response of a material to an ultra short disturbance is determined by measuring the thermally induced variations of the optical reflectivity at the surface. Under the linearity assumption, the relative variation of reflectivity ($\Delta R/R_0$) is proportional to the temperature variation at the surface of the sample. A Ti:sapphire laser produces a 200 fs pulse at 800 nm wavelength with a $f_m=82$ MHz repetition rate. The laser beam is then splitted into 2 separated beams using a polarizing cube. The so-called pump beam heats the surface of the sample. The pump power received by the sample is about 2 mW, the spot having a 20 µm diameter. Before arriving on the sample, the pump beam is differentiated from the probe beam by traversing a non-linear crystal that divides its wavelength by two. The probe beam and the pump beam are both focused at the same location on the surface of the sample. The reflected part of the probe will depend on the surface temperature. A silicon photodiode is used to measure the temperature dependent relative variation of the reflectivity ($\Delta R/R_0$). The probe pulse is shifted temporally compared to the pump by increasing the distance covered by the probe using an optical delay line. This delay line allows us achieving a $T=12.5$ ns time resolution for the recording signal. This signal can be viewed as the impulse response of the sample in a front face configuration. The probe power received by the sample is about 0.12 mW, the spot having a 20 µm diameter. The pump is modulated with an acousto-optics modulator at $f_m=330$ kHz. A Stanford Research SR 830 Lock-In amplifier used this modulation signal as the reference and makes it possible to accurately extract the $\Delta R/R_0$ signal in terms of real and imaginary parts. The signal/noise ratio is improved by carrying out several translations of the delay line. Nevertheless, this repetition will lead also to a cumulative phenomenon on the signal that must be taken into account within the model [10].

The measured sample was formed by 210 nm thick amorphous GST layer, deposited by sputtering on a Si (100) substrate covered with a 100 nm thick thermal SiO$_2$ layer. The GST layer is capped with a 20 nm thick Al layer. The sample is heated using a turntable LINKAM TS 1000 furnace under inert atmosphere (Ar) between 20 and 400°C.

3. Heat transfer model

Previous work [9] based on the two temperature model has demonstrated that the electron-phonon thermalization in the Al is reached close to $\tau=10$ psec. Time greater than 10 ps are therefore necessary in order to apply the Fourier’s law for the GST/Al system. The GST layer behaves as a semi infinite medium between two successive pulses. The size of the laser spot being larger than the heat penetration depth at the modulation of the pump, the heat transfer is considered one-dimensional. No heat loss is assumed on the front face of the sample and the temperature is imposed by the furnace on the rear face. Figure 1 presents the model in a synthetic form by using the thermal impedances schema.
The repetition rate of the pump is taken into account in the model since the temperature does not have time to go back to its initial value when the next pulse arrives, i.e. the cumulative thermal effect. In agreement with the reference [11], the normalized measured signal related to the real part of the lock-in is then:

\[
S(\tau) = \sum_{k=-\infty}^{\infty} \theta_{Al} \left( i2\pi \left( \frac{k}{T} + f_m \right) \right) \exp \left( \frac{i2\pi k \tau}{T} \right)
\]

where \( \tau \) varies from 0 to \( T \).

4. Results and discussion
The estimated TBR at the Al/GST interface are reported on figure 2 (The estimated values at Au (30 nm)-GST interface is also reported). The Levenberg - Marquardt algorithm based on measurements made up to 6 ns on the 25- 400°C temperature range is used to estimate TBR.

The values of the TBR increase strongly with temperature and thus number of crystals at GST/metal interface. As represented in figure 3, SEM measurement beyond 250°C showed a dissociation of the Al layer. This observation agrees with the high value of TBR starting from 250°C. A degradation of the aluminium film is also observed at 400°C that can explain the fast decrease in the TBR value. Indeed, we observed the Al layer collapsed of the GST layers at this temperature. Calculation with Diffuse Mismatch Model [11] of TBR of Al/GST interfaces is about \( 10^{-10} - 10^{-9} \) K.m².W⁻¹ for fcc phase. By focusing on the short times (0-50ps), an acoustic wave is observed (see...
Fig. 4). The period of this oscillation (+-10 ps) corresponds to the first acoustic resonance of the 20 nm aluminium top layer. The attenuation of these vibrations decreases with temperature.

The acoustic reflection is $|R_e| = \exp\left(-\alpha_{\text{exp}} / f_{\text{exp}}\right)$ where $\alpha_{\text{exp}}$ is the wave attenuation and $f_{\text{exp}}$ is the measured frequency of the acoustic wave (as reported in figure 4). As presented in figure 5, a linear relation between the thermal boundary resistance and the acoustic reflection coefficient is found and is related to the phonon flux transmitted across the interface. A comparable result is obtained for Au on GST but it is more difficult to quantify. However, such a result demonstrates that the TBR can be directly related with the adhesion force. To analyze the acoustic damping results, the Al and GST could be considered as two elastic layers connected by massless springs at the interface or could be connected by a layer of inter-diffusion of element between Al and GST layers [12].

However the standard deviation of estimated TBR and acoustic reflection coefficient is about 20%. It means that these values need to be improved by making new experiments with better accuracy. In addition, the links between acoustic wave and TBR measurements need to be understood, in particular by studying the evolution of interface structure with chemical and structural analysis.

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