Sensitive 3-omega measurements on epitaxial thermoelectric thin films

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Abstract. Here we present a work on the development of a sensitive 3-omega instrumentation adapted for the measurement of the thermal conductivity of epitaxial thin films. The experimental setup has been validated by the measurements on an epitaxial germanium nanostructured thin film. This manganese doped germanium matrix contains Ge\(_3\)Mn\(_5\) nanoinclusions having a diameter of 5 to 50 nm, grown by Molecular Beam Epitaxy (MBE). The 3 omega measurements have revealed that the thermal conductivity of GeMn nanostructured thin films can be decreased by a factor of ten as compared to the bulk value.

1. Introduction

With the development of the nanotechnologies, the domain of thermoelectricity has pushed itself to the frontiers of the global research on energy harvesting. For the characterization of the ZT value (figure of merit) of a thermoelectric material, experimental challenges lie in a precise measurement of the thermal conductivity. Efforts are aimed at finding efficient thermoelectric materials under the idea of “electron crystal-phonon glass” material system [1]. The efficiency of a thermoelectric material is characterized by the dimensionless figure of merit (ZT value), which involves the Seebeck coefficient \(S\), electrical conductivity \(\sigma\) and thermal conductivity \(\kappa\) through the formula of:

\[
ZT = \frac{S^2 \sigma T}{\kappa}.
\]  

However, highly accurate measurements of the three concerned factors are required for a straightforward determination of the ZT value. The measurement of thermal conductivity stays the greatest experimental challenge, especially for epitaxial thermal conductive thin films grown on electrical conductive substrates, which are good candidates for potential thermoelectric applications in microelectronics.

The two most developed measurement techniques for thermal conductivity are the 3-omega method [2] and the time-domain thermoreflectance (TDTR) [3]. The TDTR is a pump-probe optical technique, where the time evolution of the surface temperature is measured through temperature-dependent changes in the reflectivity (i.e., the thermoreflectance) [4, 5]. Though the TDTR gives a good spatial resolution, the 3-omega method still shows its advantage in the accuracy of the measurement on thermal resistive thin films [6, 7].
In the work here, we would like to present an advanced experimental instrumentation based on the 3-omega method, developed for highly precise measurements of thermal conductivity of epitaxial semiconductor thin films. The performance of the technique has been confirmed by measurements on a germanium based epitaxial thin film, being a highly promising thermoelectric material. The 3-omega measurements of this thin film contribute to the investigation of the thermoelectric properties of the material, also help us to achieve qualitatively and quantitatively a better understanding of the thermal transport mechanism in nanostructured materials.

2. Experimental methods

2.1. Sample preparation
To investigate the thermal properties of a thin film using the 3-omega method, a transducer metal line acting both as a heater and thermometer is needed to be deposited on the film. In our case it is designed to have a geometry as shown in figure 1. The length of the transducer between the two internal contacts is 2 mm, with its width being 30 µm. The electric current is driven through the two external contacts and the voltage is obtained via the two internal ones. Standard clean room processes like UV lithography and PVD are used to deposit a platinum transducer. Platinum is a common material used for thermometry, it has a temperature coefficient of \( \alpha \approx 0.003 \text{ K}^{-1} \). The thickness of the Pt deposition is 100 nm, so that the transducer gives a resistance of around 100 Ω at RT in formerly described geometry.

For the case of an electrical conductive thin film, an oxide layer is required to electrically isolate the transducer from the sample surface. The aluminium oxide (Al\(_2\)O\(_3\)) is chosen to do the task (figure 2) in our work. Using the technique of ALD (Atomic Layer Deposition) the thickness of Al\(_2\)O\(_3\) thin film is well controlled to be 50 nm, which has been tested previously to sustain a current up to 10 mA.

2.2. Setups for 3-omega measurement
The 3-omega method is about measuring the third harmonic part \( V_{3\omega} \) of the voltage signal detected at the two extremities of the transducer when applying an alternating current (AC) of angular frequency \( \omega \). The frequency dependence of this \( V_{3\omega} \) permits the extraction of the thermal conductivity of the substrate material.

Since the \( V_{3\omega} \) voltage is 1000 times smaller than the first harmonic voltage \( V_{1\omega} \), it cannot be measured without the help of an active electronic setup increasing the \( V_{3\omega}/V_{1\omega} \) ratio. Two solutions are used in most of the cases. One is based on electronic techniques in a geometry of “differential bridge” \([2, 3, 6]\), and another one by using the structure of Wheatstone bridge \([8, 9]\). Here in our case, we have designed our own device based on the idea of a differential bridge; the overall electrical circuit of the setup is shown in figure 3. The variable resistance of the device \( R_{\text{ref}} \) is highly precise to 0.001 Ω, and highly stable with temperature.
The sample is pasted by a resist to the sample holder of a calorimeter, after the micro-bonding, the holder is mounted inside a cryostat, closed, pumped and connected, ready for the measurement. The cryostat ensures a large range of temperature environment from the temperature of liquid helium up to 400K.

3. Modelling of 3-omega method for thin films and strategy of measurement

3.1. The 3-omega method for thin film

According to the principles of 3-omega method, for the case of a narrow transducer metal line on the surface of an infinite half-volume substrate, an approximation of the temperature oscillation at the sample surface can be deduced [2] if the width of the line is largely small comparing to the thermal penetration depth (low frequency range), and the thickness of the transducer is negligible. The realisation of the first condition strongly depends on the frequency range used for measurement. As a general trend, the frequency range is distinguished by two regimes, the high frequency regime and the low one, by comparing the width \( b \) of the transducer metal line to the thermal penetration depth \( \mu \) into the related sample substrate. The thermal penetration depth is defined by:

\[
\mu = \left( \frac{D}{\omega} \right)^{-1}
\]

where \( D \) is the thermal diffusivity of the substrate material below the transducer. For the need of the approximation of the surface temperature oscillation, the frequency regimes are defined by:

Low frequency regime: \( \mu >> 2b \)

High frequency regime: \( \mu << 2b \)

The second condition can easily be satisfied because usual substrates are generally much thicker (~500 µm) than the transducer line (~100 nm). In the low frequency regime the temperature oscillation at the sample surface can thus be approximated by:

\[
\Delta T = \frac{P_i}{\pi \cdot k_0} \left( -\frac{1}{2} \ln \frac{\omega}{\Omega} + \eta - i \frac{\pi}{4} \right)
\]

(\( P_i = \frac{R_i I^2}{l} \)) (4)
where $P$ is the linear heat dissipation with $R$, the electric resistance, $l$ the applied AC current and $l$ the length of the transducer, the thermal angular frequency $\alpha = 4\pi f$, where $f$ is the electric frequency of the AC current; $\Omega = \frac{k_0}{\rho C b^2}$ with $k_0$ the thermal conductivity of the substrate, $\rho$ the density, $C$ the specific heat, $b$ the half width of the transducer and $\eta = 0.92$.

Via the relation between the real part of the temperature oscillation and the real part of the $V_{3\omega}$ signal shown in equation (4), the thermal conductivity of the sample substrate $k_0$ can be calculated through the equation:

$$V_{3\omega\text{anph.}} = \frac{1}{2} R l \alpha \Delta T_{\text{real}}$$

$$k_0 = - \frac{\alpha \cdot R^2 \cdot l^3}{4 \cdot \pi \cdot l} \left( \frac{dV_{3\omega\text{anph.}}}{d \ln \omega} \right)^{-1} = - \frac{1}{2 \cdot \pi \cdot l} \left[ \frac{d \left( \frac{\Delta T_{\text{real}}}{P} \right)}{d \ln \omega} \right]^{-1}$$

where $\frac{d \left( \frac{\Delta T_{\text{real}}}{P} \right)}{d \ln \omega}$ can be obtained through a linear fit of the curve $\frac{\Delta T_{\text{real}}}{P} (\ln \omega)$ within the concerned frequency zone.

Our thin film of interest (thickness $t_1$) is generally deposited on a very thick substrate (Si or Ge or other). As illustrated in figure 4, as long as $t_1$ is largely small comparing to the width $2b$ of the transducer, the heat transport is considered to be one-dimensional across the film and the heat flux conserved.

![Figure 4](image-url)

**Figure 4.** Schematic illustration of a sample substrate with a thin film deposited on top (in red) that needs to be measured.

This approximation brings a shift in the real part of the surface temperature oscillation:

$$\Delta T = \frac{P}{\pi \cdot k_0} \left( - \frac{1}{2} \ln \frac{\omega}{\Omega} + \eta - i \frac{\pi}{4} \right) + \frac{P \cdot R'}{2b}$$

Or

$$\frac{\Delta T_{\text{real}}}{P} = \frac{1}{\pi \cdot l \cdot k_0} \left( - \frac{1}{2} \ln \frac{\omega}{\Omega} + \eta \right) + \frac{R'}{2bl}$$

$$\Delta \left( \frac{\Delta T_{\text{real}}}{P} \right) = \frac{R'}{2bl}$$

where the thin film represents itself only as a thermal barrier resistance $R'$ for the heat flux, which is directly related with its thickness and thermal conductivity through:
\[ R' = \frac{f_1}{k_1} + R_c \]  

where \( R_c \) is the effective thermal resistance of interfaces, being the total interface thermal resistance of the thin film involved sample minus the total one for the case of the sample substrate.

3.2. Measurement strategy

Following the above model, measurements need to be carried out on two sets of samples to extract the thermal conductivity of an electrical conductive thin film, as illustrated in figure 5. It is the \( \Delta T \) shift between them that will give the thermal conductivity of the layer of interest.

As a test of the method, the thermal conductivity of an Al\(_2\)O\(_3\) thin film is investigated using the model and the experimental modus operandi explained above. Measurements are carried out on samples of an Al\(_2\)O\(_3\) thin film (50 nm) on top of a GaAs substrate (electrical resistive), and of the GaAs substrate alone as a reference sample. The thermal conductivity of the Al\(_2\)O\(_3\) thin film is found to be around 0.8 Wm\(^{-1}\)K\(^{-1}\) (considering \( R_c \) to have a value of \( 10^{-8} \) Km\(^2\)W\(^{-1}\) as an approximation [10]), showing a nice coherence with published relative works [11].

Further tests have been done on an epitaxial thin film, based on a well crystallized and highly doped germanium matrix, and containing spherical Ge\(_2\)Mn\(_5\) nano-inclusions [12, 13]. The nano-inclusions are randomly distributed in the matrix having a diameter of 5 to 50 nm depending on the epitaxial conditions, e.g. the concentration of Mn, growing temperature, annealing temperature and etc. These Ge:Mn thin films are grown on germanium substrate with a thickness of 100 to 300 nm in the general cases.

According to the sample geometries and the structural properties of Ge:Mn thin films, some approximations are considered for the determination of the effective thermal resistance of interfaces for the sample pair. As the thin film of Ge:Mn is grown by molecular beam epitaxy on the Ge substrate using MBE, the germanium matrix of Ge:Mn thin film is well crystallized as its Ge substrate, thus the interface thermal resistance between Al\(_2\)O\(_3\) and Ge is considered to be equal to the one between Al\(_2\)O\(_3\) and Ge:Mn:

\[ R_{Al_2O_3/Ge} \cong R_{Al_2O_3/MnGe} \]  

The effective interface thermal resistance \( R_c \) can then be calculated via:

\[ R_c = (R_{Pt/Al_2O_3} + R_{Al_2O_3/MnGe} + R_{MnGe/Ge}) - (R_{Pt/Al_2O_3} + R_{Al_2O_3/Ge}) = R_{MnGe/Ge} \]  

and the interface thermal resistance between the epitaxial Ge:Mn and Ge (\( R_{GeMn/Ge} \)) is relatively very small down to the order of \( 10^{-9} \) Km\(^2\)W\(^{-1}\) [14, 15]. The \( R_c \) can then be determined to be:

\[ R_c \approx 10^{-9} \,(K \cdot m^2 \cdot W^{-1}) \]  

![Figure 5. Schematic illustration of the sample geometries for the 3-omega measurement of an electrical conductive thin film.](#)
4. Experimental results

The 3-omega measurements have been carried out on n-type Ge substrate and Ge:Mn thin films grown on the same n-type doped Ge substrate. The thin film is 240 nm thick, with the concentration of manganese 6%. As for our samples concerning a germanium substrate \(D = 3.6 \times 10^{-5} \text{ m}^2\text{s}^{-1}\) being around 0.35 mm thick, based on the calculation of \(\mu\) as shown in table 1, the frequency range for our 3-omega measurements is chosen to be between 100 Hz and 1000 Hz. Data of \(V_{3\omega}\) signals as a function of frequency from the sample and the reference Ge (n-type) substrate, at different temperature, are gathered and treated. The curves of \(\frac{\Delta T_{\text{real}}}{P}\) as a function of \(\ln \omega\) for cases at different temperatures are plotted in figure 6.

| \(f\) (Hz) | 100 | 1000 |
|----------|-----|------|
| \(\mu\) (\(\mu m\)) | 169 | 54 |

**Table 1.** Thermal penetration depth into the Ge substrate at frequency 100 Hz and 1000 Hz.

![Graph showing \(\Delta T_{\text{real}}\) as a function of \(\ln \omega\) for different temperatures.]

**Figure 6.** Signals of \(\frac{\Delta T_{\text{real}}}{P}\) as a function of \(\ln \omega\) at four different temperatures (260K, 280K, 300K and 320K) measured from Ge:Mn film on Ge substrate.

With the slope from a linear fit of the curves, the conductivity of the Ge substrate (below the thin films in the Ge:Mn sample) can be calculated. The same treatment has also been done for signals from reference substrate sample, and the results for the bulk thermal conductivity from both samples are presented in table 2. The differences between these two set of measurement is a good indication on the absolute error (accuracy) made on the measurement of \(k\). This error in accuracy can be estimated to be around 5%.
Table 2. Results of the thermal conductivity of Ge (n-type) substrate as a function of temperature for the two different sets of sample: bare Ge and Ge/Ge:Mn.

| T (K) | 260 | 280 | 300 | 320 |
|-------|-----|-----|-----|-----|
| Ge    | 74.7| 64.8| 58.4| 56.7|
| Ge:Mn sample | 81.2| 70.1| 60.6| 57.7|

At a given temperature, the comparison of the curves $\frac{\Delta T_{real}}{P}$ from the two samples reveals a clear shift as shown in figure 7, from the curve of reference sample to the Ge:Mn sample. At 320K in the figure, based on the shift of a value of 0.75, the thermal conductivity of the Ge:Mn thin film is calculated to be 5.5 (±1) Wm⁻¹K⁻¹. This remarkable reduction of the thermal conductivity as compared to the bulk Ge substrate is currently attributed to the nanostructuring occurring in the GeMn layer. Extensive measurements are in progress to fully understand the influence of this nanostructuring on the thermal properties of GeMn thin films.

Figure 7. Comparison of the curves $\frac{\Delta T_{real}}{P}$ from Ge:Mn sample and the Ge reference substrate sample at 320K.

5. Conclusions
Based on the 3-omega method, we have developed a sensitive instrumentation for the characterisation of thermal properties of thin films. The measurements of the thermal conductivity have been successfully performed on an epitaxial nanostructured germanium thin film. The results have revealed a remarkably reduced thermal conductivity of this thin film by a factor of 10 at 320K, compared to the value for bulk Ge substrate (60W/mK).
To properly understand the physics of the involved phonon scattering mechanism introduced by the nanostructures, the 3-omega measurements will be continued on different samples of the Ge:Mn thin film with further investigations into the influence of the nano-inclusions (size and spatial distribution) on the thermal property: i.e. the Mn concentration, the diameter and dispersion of the inclusion. Further experiments will also be carried out in parallel for a complete characterisation of the thermoelectric properties of the thin film, including the measurements of the electrical conductivity, the Seebeck coefficient, and finally the determination of the ZT value.

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