Thermal conductivity of GeSn alloys: a CMOS candidate for energy harvesting applications

Conductividad térmica de aleaciones de GeSn: Candidato CMOS para aplicaciones de recolección de energía

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Keywords

Thermoelectrics; GeSn; thermal conductivity; 3-omega method; characterization; thin films.

Abstract

The thermal conductivity, κ, of thin GeSn semiconductors with Sn concentration of 12 at.% was studied by the 3-omega method. Accent is put on room temperature characterization where a small lattice conductivity of 4.5W/m-K was extracted. Similar performance was found but using the Raman thermometry optical method indicating the reliability of the measurements and showing GeSn alloys as promising materials for thermoelectric applications.

Palabras clave

Termoeléctrico; GeSn; conductividad térmica; método 3-omega; caracterización; películas delgadas.

Resumen

La conductividad térmica, , the semiconductores delgados de GeSn con concentraciones de Sn del 12% fue estudiada usando el método 3-omega. Especial atención se pone en la caracterización a temperatura ambiente en donde se extrajo una pequeña conductividad de la red de 4.5W/m-K. Un comportamiento similar fue encontrado pero usando el método óptico de Termometría Raman indicando la confiabilidad de las mediciones y mostrando que las aleaciones de GeSn son materiales prometedores para aplicaciones termoeléctricas

Introduction

In thermoelectric materials the conversion between thermal and electrical energy takes place. This process involves heat transport through both electrons and phonons. The efficiency of this process is defined by the figure of merit ZT which relates the thermal conductivity, electrical conductivity, and Seebeck coefficient of the material for a specific temperature. To obtain a high ZT, large Seebeck coefficient and electrical conductivity are required as well as a low thermal conductivity.

$Ge_{1-x}Sn_x$ binary alloys have recently got increasing attention due to their photonic and electronic applications, and its compatibility with the CMOS technology. The thermal conductivity (κ) of this material was only recently investigated for different Sn concentrations by using optical Raman thermometry (~4W/m-K for $Ge_{0.88}Sn_{0.12}$) [1] showing its relevance for thermoelectric applications at room temperature. In this work, a study of the thermal conductivity of GeSn alloys was performed but using the electrical 3-omega method. Layers of different thicknesses and similar Sn concentration.

Experimental methods

Growth, Characterization, and Device Fabrication

The $Ge_{1-x}Sn_x$ layers were grown by chemical vapor deposition (CVD) on a Ge post-deposition annealed (GePDA) buffer on Si(100) wafers. The composition and thickness of the samples were determined by fitting the Rutherford backscattering (RBS) spectrum. A set of 5 samples with similar GePDA (around 350nm) and Sn concentration (~ 12 at.%) with different GeSn thicknesses were chosen for the measurements.

A 200 nm layer of SiO_2 was deposited for electrical isolation on the $Ge_{0.88}Sn_{0.12}$ surface. Afterward, by optical lithography and lift-off a 50nm-Cr/250nm-Au strip was deposited. The metal strip acts simultaneously as heater and thermometer, as shown in the inset in Fig.2. Devices with different dimensions for the heater stripe were fabricated with width (2*b*) and length (*l*) values of 10, 15, 20 µm and 1000, 1500 µm, respectively.

Three-Omega Method

The thermal conductivity can be extracted using the 3ω–method [2]. By applying a current with frequency ω on a conductor (e.g. our heater stripe) the power dissipation generates heat waves with a 2ω oscillatory component. The heat induces a variation of the conductor resistance so that the voltage drop, adding a 3ω oscillatory component. Finally, the temperature oscillation ($\delta T_{2\omega}$) is expressed in terms of both 1ω-voltage ($V_{1\omega}$) and 3ω-voltage ($V_{3\omega}$):

$$\delta T_{2\omega} = \frac{2}{\alpha}\frac{Re(V_{3\omega})}{Re(V_{1\omega})} \tag{1}$$

where α is the temperature coefficient of the heater.

This $\delta T_{2\omega}$ can also be obtained by modeling a semi-infinite substrate with several thin layers and a finite-width stripe heater as in [2] including the explicit constant value derived in [3]:

$$\delta T_{2\omega} = \frac{P_{2\omega}}{l}\left\{\frac{1}{\pi\kappa}\left[\frac{3}{2} - \gamma - i\frac{\pi}{4} - \frac{1}{2}\ln\left(\frac{2\omega b^2}{D}\right)\right] + \sum \frac{\tau_n}{2b\kappa_n}\right\} \tag{2}$$

where γ is the Euler gamma (γ = 0.5772…), *D* is the thermal diffusivity of the substrate, τ is the thickness of the thin layers, and *P* is the input power.

The first term corresponds to the temperature variation $\delta T_{2\omega}$ in the substrate while the sum of terms represents each of the thin layers. This theoretical equation leads to the so-called differential 3ω-method, which is basically the subtraction of measurements to take the Si substrate and Ge buffer out of the final calculation. In this case, the δT_A of a Si/GePDA/SiO_2 is subtracted from the δT_B of a Si/GePDA/GeSn/SiO_2 to isolate the GeSn δT_{diff} of interest and finally calculate the value of interest:

$$\delta T_{diff} = \delta T_B - \delta T_A = \frac{P_{2\omega}\,\tau_{GeSn}}{2lb\kappa_{GeSn}} \tag{3}$$

Finally, equating δT in (1) and (2) leads to,

$$V_{3\omega} = \alpha\frac{V_{1\omega}^3}{\sqrt{2}lR}\left\{\frac{1}{\pi\kappa}\left[\frac{3}{2} - \gamma - i\frac{\pi}{4} - \frac{1}{2}\ln\left(\frac{2\omega b^2}{D}\right)\right] + \sum \frac{\tau_n}{2b\kappa_n}\right\} \tag{4}$$

A lock-in amplifier supplies the 1ω AC voltage using one of the two pairs of the device contacts and the other two are used for measuring the 3rd harmonic component of the input voltage frequency that corresponds to the $V_{3\omega}$ (see inset in Fig. 2). Three measurements were made on the samples: frequency scan, voltage scan, and resistance. For the frequency scan measurement ω is variated at a fixed $V_{1\omega}$. For the voltage scan measurement, the $V_{1\omega}$ is variated at fixed ω. In both $V_{3\omega}$ is extracted. Finally, for the resistance measurement $V_{1\omega}$ is variated at a certain ω and the current is measured.

Results

Fig.1a clearly shows the linear dependency with ln(ω) for the in-phase component and a constant behavior for the out-of-phase component of $V_{3\omega,}$ as is expected according to equation (4). Also, as a validation of the method the $V_{1\omega}$ was variated from 0 to 5V at 1KHz (voltage scan measurement) to show the cubic dependency between $V_{3\omega}$ and $V_{1\omega}$. In Fig.1b this dependency is shown by fitting the natural logarithm of both voltages resulting in a value of ~3.17.

The temperature coefficient of resistance for the stripe, α in (1), was obtained by increasing the temperature from 50K to 350K and fitting the resistance at different temperatures for a linear approximation of the value. Using two different devices a value of ~0.00224 K^{-1} at 300K was obtained as shown in Fig.1c. The validated 3ω method was then used to extract the thermal conductivity of GeSn layers with different thicknesses.

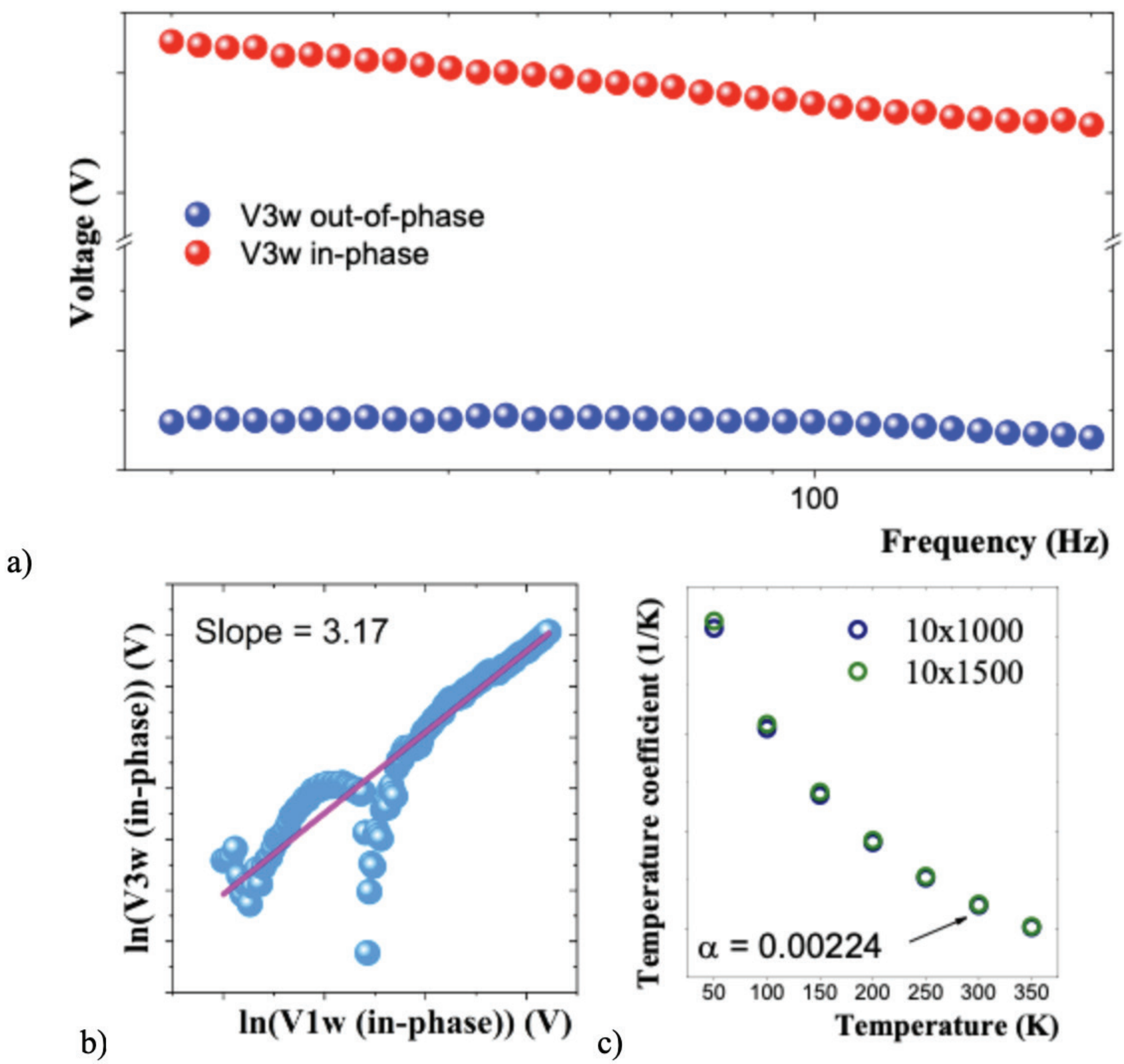

Figure 1. a) Real and imaginary parts of the $V_{3\omega}$ as a function of frequency, b) The cubic dependency of the $V_{3\omega}$ with the $V_{1\omega}$ is shown by linearly fitting the logarithm of both values. c) Temperature coefficient (α) at different temperatures for two devices with different stripe geometries (2*b* x *l*)

Fig.2 shows a thermal conductivity for different GeSn thicknesses. For thinner samples (40nm) the lower thermal conductivity value is associated with the increase of the phonon scattering at the $Ge_{0.88}Sn_{0.12}$ / Ge PDA interface and possibly due to very high compressive strain in the GeSn lattice. After a certain thickness, above the critical thickness for strain relaxation, the conductivity is almost constant. However, the defect density in the thin Ge PDA (350 nm) can contribute to increased scattering and lower the k. For this reason a very thick GeSn layer (700 nm) grown on high-quality 1500 nm Ge substrate was measured to confirm the results. Sets of devices for every sample were measured showing the same behavior. While the layers are not intentionally doped (~ p-type $1x10^{17}cm^{-3}$) it allows us to neglect the electrons contribution to the thermal conductivity. The measured κ represents the GeSn lattice thermal conductivity.

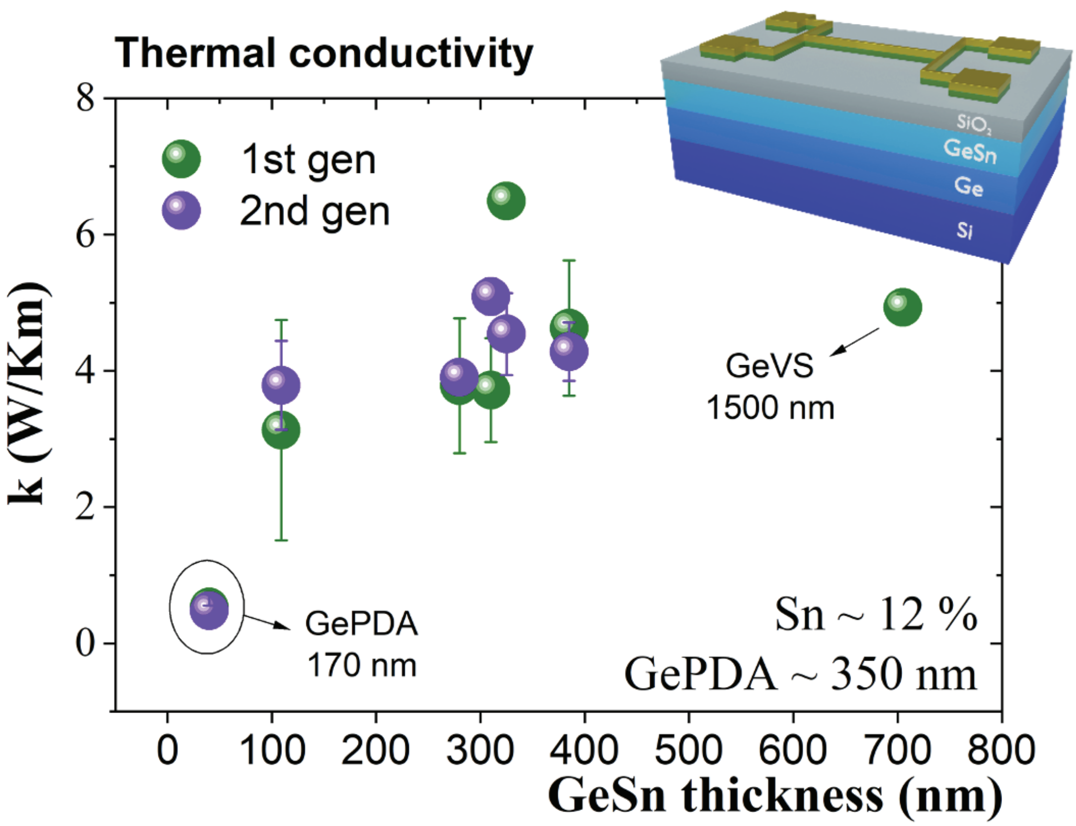

Figure 2. Thermal conductivity for different GeSn layer thicknesses for two generations of measurements.

Conclusions

The electrical 3ω-method was used to extract the κ of $Ge_{0.88}Sn_{0.12}$ alloys at different thicknesses. A constant behavior was shown for thicknesses above 100nm. The constant tendency spreads near a very low value of 4W/m-K, in agreement with previously published data [1] for the same Sn concentration. As outlook, samples with different Sn concentrations will be presented to confirm the decrease of the with the Sn content. New devices are being prepared to measure also the Seebeck coefficient.

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Introduction

In thermoelectric materials the conversion between thermal and electrical energy takes place. The efficiency of this process is defined by the figure of merit ZT which relates the thermal conductivity (κ), electrical conductivity (σ), and Seebeck coefficient (S) of the material for a specific temperature. To obtain a high ZT, large S and σ are required as well as a low κ.

$$ZT = \frac{\sigma S^2}{\kappa} T$$

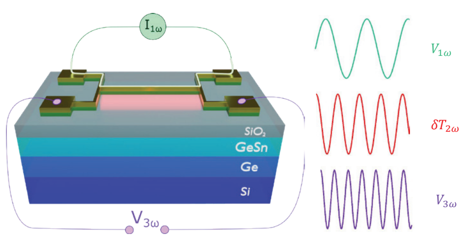
Figure of merit

GeSn sample grown by CVD.
Si subs. + Ge buffer (PDA) + GeSn

$Ge_{1-x}Sn_x$ binary alloys are novel group IV semiconductors fully compatible with Si-based technology which are promising candidates for thermoelectric applications at room temperature.

For this work, the thermal conductivity of thin GeSn (~12% Sn) layers was measured by the electrical 3ω-method to demonstrate that for such Sn concentrations the κ significatively decreases compared to that of pure Ge (~64 W/Km).

Materials and Methods

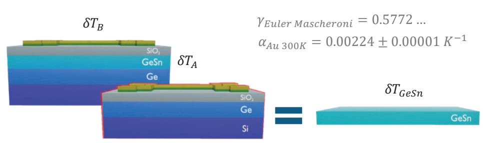


$$\underbrace{\delta T_{2\omega} = \frac{2\,Re(V_{3\omega})}{\alpha\,Re(V_{1\omega})}}_{\text{Experimental}}$$

$2b$: stripe width
l: stripe length
ω: frequency
D: subs. thickness
τ: thin layer thickness
P: applied power

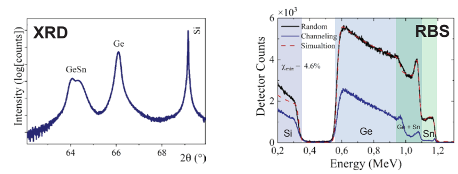
$$\delta T_{2\omega} = \underbrace{\frac{P_{2\omega}}{l}\left\{\overbrace{\frac{1}{\pi\kappa}\left[\frac{3}{2} - \gamma + i\frac{\pi}{4} - \frac{1}{2}\ln\left(\frac{2\omega b^2}{D}\right)\right]}^{\text{Substrate}} + \overbrace{\sum \frac{\tau_n}{2b\kappa_n}}^{\text{Thin layers}}\right\}}_{\text{Theoretical}}$$

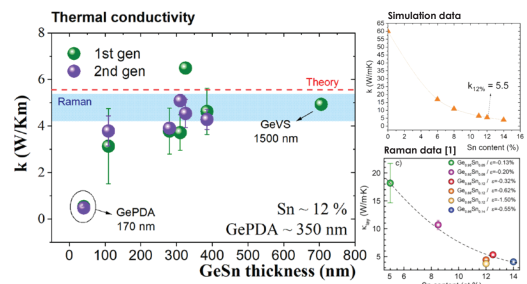
$\gamma_{Euler\ Mascheroni} = 0.5772\ldots$
$\alpha_{Au\ 300K} = 0.00224 \pm 0.00001\ K^{-1}$



$$\delta T_{GeSn} = \delta T_B - \delta T_A = \frac{P_{2\omega}}{l}\left\{\frac{\tau_{GeSn}}{2b\kappa_{GeSn}}\right\}$$

Results and Discussion



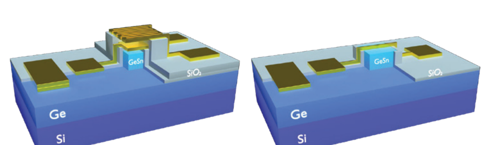


1. "Thermoelectric Efficiency of Epitaxial GeSn Alloys for Integrated Si-Based Applications: Assessing the Lattice Thermal Conductivity by Raman Thermometry", D. Spirito, N. von den Driesch, C. L. Manganelli, M. H. Zoellner, A. A. Corley-Wiciak, Z. Ikonic, T. Stoica, D. Grützmacher, D. Buca, and G. Capellini, ACS Applied Energy Materials 2021 4 (7), 7385-7392 https://pubs.acs.org/doi/10.1021/acsaem.1c01576

For thinner samples (40nm), the low thermal conductivity value is associated with the increase of the phonon scattering at the GeSn/Ge(PDA) interface and possibly due to very high compressive strain in the GeSn lattice. After a certain thickness, above the critical thickness for strain relaxation, the conductivity is almost constant. However, the defect density in the thin Ge(PDA) (350 nm) can also contribute to increase the scattering and decrease the κ. For this reason, a very thick GeSn layer (700 nm) grown on high-quality 1500 nm Ge substrate was measured to confirm the results

Conclusions / Next Steps

The electrical 3ω-method was used to extract the κ of GeSn (~12% Sn) alloys at different thicknesses. A constant behavior was shown for thicknesses above 100nm. The constant tendency spreads near a very low value of 4 W/Km, in agreement with previously published data [1] for the same Sn concentration. As outlook, samples with different Sn concentrations will be presented to confirm the decrease of the κ with the Sn content. New devices are being prepared to measure also the Seebeck coefficient and electrical conductivity.



S and κ device
σ device

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