Thermal Diffusivity of a Single Crystal Silicon Wafer n-type Doped with Manganese

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Abstract *—The thermoelectric-silicon based material is gaining enormous interest since silicon is abundant and cheap. The thermoelectric materials operate in direct conversion from heat to electrical energy with no mobile parts. This research explores the development of the n-type electrode from the complete thermoelectric assembly by modifying the thermal properties of n-type silicon plates. The manganese (powder 99.9% pure) was diffused into the films in a vacuum chamber and at temperatures between 650˚C to 800˚C for a period of 14 hours. The thermal diffusivity of the films was measured by the flash method using an apparatus LFA 447 NanoFlash from Netzsch. The average thermal diffusivity measured in the films with no manganese is 0.179* cm^2s^{-1}*. This value is consistent with values reported in other research jobs. For the films doped with manganese, the average thermal diffusivity was 0.062* cm^2s^{-1}*. This result reflects a considerable reduction of the thermal diffusivity in silicon films and opens a big window for research developing thermoelectric materials based on conventional materials.*

Key Terms *—Specific Heat, Thermal Conductivity, Thermal Diffusivity, Thermoelectric Material.*

INTRODUCTION

During few decades the interests in found an energy source that fill our power necessities have gained importance. The interest has been focused into finding clean and efficient energy that will change our actual dependence on the fossil fuel. For this the thermo-electrical materials have gained importance and there various research groups doing investigations in this area. The thermo-electrical material is a material that has the capacity to transform waste energy (heat loss) into electrical energy. These materials are used in some devices as computers, optoelectronics and infrared detectors among others [1]. Through the use of these materials, the devices efficiencies have improved. But, the materials have some limitations according with the experts. In order to do this material more efficient an increment in its Seebeck coefficient and as consequence material's figure of merit (ZT) has been suggested [1]. The material used in devices in these days report a ZT approximately equal to 1. This value has remained unchangeable for the last 30 years [1].

One of these materials used as a thermoelectric material is the Silicon (Si), this material present a favorable electrical properties and also high thermal stability [2] although its high thermal conductivity make it low attractive [1]. In order to do this material an attractive thermo-electrical and reduce its thermal conductivity, different interstitial doped have been made. The impurities are boron, arsenic, phosphorous and transition metals (especially, Co, Cr, Cu, Fe, Mn and Ni) [3].

The deposit of a material impurities in other, cause an alteration in the material properties. For Si doped with Mn some researches present the thermo-electric properties such as Seebeck and Resistivity.

This research is focused in determine the thermal diffusivity for Silicon (Si) interstitially doped with manganese (Mn). This parameter could be defined as how quickly a temperature change can be move from one area to another in a material. The thermal conductivity of Mn and Si, are 7.81 $Wm^{-1}K^{-1}$ and 148 $Wm^{-1}K^{-1}$ respectively. It is notable that the manganese thermal conductivity

represents a 5.3 percent of silicon thermal conductivity.

The ZT will be discussed ahead. But is important mentioned its thermal conductivity dependence. Although improve, the ZT has been attached for few decades is estimated by Slack that this number could archive a value of 4[1, 4].

THEORY

Let's take a brief look of different parameters that have relevance in the thermoelectric energy conversion. These parameters are the Seebeck and Peltier effect. As illustrated in Figure 1 [5]. The Seebeck effect was observed at the beginning of 1800s (1821) [5] and is the change in voltage that is proportional to a temperatures gradient. It is represented by Equation (1).

$$S = -\frac{1}{q}\frac{dU/dx}{dT/dx} = \frac{\varepsilon}{dT/dx} \quad (1)$$

where q is the heat flux, U represent the electric potential, T the temperature and ε the electric field.

While, the Peltier effect was observed few year later in 1834 [5] and takes in consideration the head absorbed or rejected in a junction of two dissimilar materials that generate heating or cooling effects, when a current pass. It is represented by Equation (2).

$$J_q = \Pi J_e \quad (2)$$

where Π is the Peltier coefficient, J_q the heat flux and J_q the current density. These two parameters are interrelates as evident in the Peltier coefficient by the Kelvin relation [5]. See Equation (3)

$$\Pi = ST \quad (3)$$

The potential of a power and cooling devices as showed in Figure 2 [1] in order to be a highly efficient thermoelectrically viable depends on the material capacity to acquire a highly Seebeck coefficient and also high electrical conductivity but presenting a low thermal conductivity. This should happen to grow the figure of merit (Z or ZT).

If consider the Figure 2 (a). Current is passed from n-type semiconductor to p-type semiconductor generating Equation (4) a total cooling power,

$$q_c = (S_p - S_n)IT_C - K(T_H - T_C) - \tfrac{1}{2}I^2R \quad (4)$$

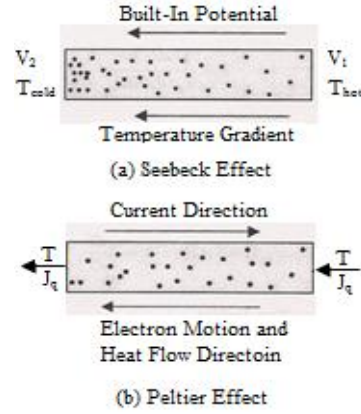


Figure 1
Two basic thermoelectric effects: (a) Seebeck effect, (b) Peltier Effect

where I is the current, T represent the temperature, its subscript indicate cold and hot side of the reservoirs respectively, K is the thermal conductance and R the electrical resistance, That are represented by Equations (5).

$$K = \frac{k_pA_p}{L_p} + \frac{k_nA_n}{L_n} \text{ and } R = \frac{L_p\rho_p}{A_p} + \frac{L_n\rho_n}{A_n} \quad (5)$$

The one-half factors represent half of the Joule heat that returns back to the cool side. The electrical power consumed is represented by Equation (6),

$$W = (S_p - S_n)I(T_H - T_C)I^2R \quad (6)$$

The efficiency in the refrigeration system is described by its coefficient of performance (COP) Equation (6), that is,

$$\phi = \frac{q_c}{W} \quad (7)$$

As the COP is dependent on the current I, for a certain temperature difference, two special case are of interest. The first is determined by solving $dq_c/dI = 0$, generating the Equations (8) and (9), then,

$$I_q = \frac{(S_p - S_n)T_C}{R} \quad (8)$$

$$\phi = \frac{0.5ZT_C{}^2 - (T_H - T_C)}{ZT_HT_C} \quad (9)$$

where Z is the figure of merit with units of $1/T$ in Kelvin and is represented by the Equation (10),

$$Z = \frac{(S_p - S_n)^2}{KR} \quad (10)$$

The figure of merit becomes to be a maximum when the product KR is a minimum, As in Equation (11)

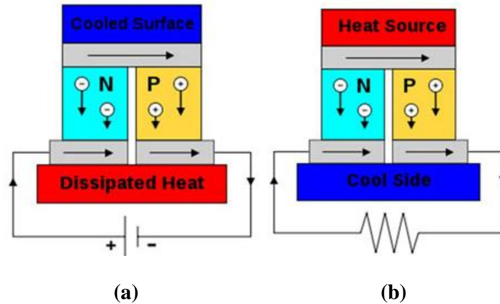
$$Z = \frac{(S_p - S_n)^2}{\left[(k_p\rho_p)^{1/2} + (k_n\rho_n)^{1/2}\right]^2} \quad (11)$$

And the second one is determined by solving $d\phi/dI = 0$, generating the Equations (12) and (13), then,

$$I_\phi = \frac{(S_p - S_n)(T_H - T_C)}{R(\sqrt{1 + ZT_m} + 1)} \quad (12)$$

$$\phi_{max} = \frac{(\sqrt{1 + ZT_m} - (\frac{T_H}{T_C}))T_C}{(T_H - T_C)(\sqrt{1 + ZT_m} + 1)} \quad (13)$$

where T_m is the average temperature. It is clear that ϕ_{max} is proportional to $\sqrt{1 + ZT_m}$, so the COP would approach the Carnot efficiency if Z were to infinity.



(a) (b)

Figure 2

Diagram of Peltier: (a) Refrigeration Mode, (b) Power Generation Mode

These devises are connected in series such as the current flow while the heat flow is in parallel. For the small electrical resistance of each element, these are normally put in series as in the Figure 3 [6] to make the power supplier easier [5].

Therefore, for a material to be a viable thermoelectric material, it should posses a minimum thermo power that is related by the value of Z or ZT [1] (ZT is the dimensionless figure of merit).

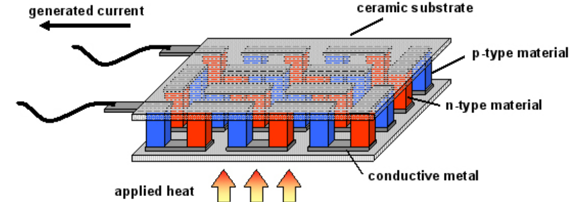


Figure 3

Actual thermoelectric device

Reviewing the Equation (11) a manner to grow this parameter is reducing the material thermal conductivity which is governed by the heat flow.

The term of heat flow was given mathematically by Fourier and is the rate of a volume gain or lost heat energy. The heat gained in a volume element is described mathematically as follow; see Equation (14),

$$\frac{\partial Q}{\partial t} = \frac{\partial}{\partial t}\int CT\rho dV \quad (14)$$

where C is the specific heat per unit mass at constant pressure (C is assumed to be constant), T is the change in temperature, and ρ is the density of the differential volume element.

The heat gained per second by the volume V must also be equal to the rate at which heat is conducted through its surface area $\vec{S}$. The heat conducted per second through a surface element $d\vec{S}$ is proportional to the component of the temperature gradient, grad T (or ∇T), normal to the surface. This conducted heat is also proportional to the magnitude of the area element $d\vec{S}$ [6]

$$\frac{\partial Q}{\partial t} = \int k\nabla T . d\vec{S} \quad (15)$$

This equation is generally considered to be the defining equation of the thermal conductivity k .

Equation (15) can be rewritten in terms of a volume integral by use of Gauss's theorem, which states that the surface integral for a vector is the volume integral for the divergence of this vector. In

this case the vector is $k\nabla T$, and Equation (16) becomes

$$\frac{\partial Q}{\partial t} = \int \nabla . k\nabla T dV \quad (16)$$

Equation (14) and (16)

$$\frac{\partial}{\partial t}\int CT\rho dV = \int \nabla . k\nabla T dV \quad (17)$$

Then, See Equation (18)

$$C\rho\frac{\partial T}{\partial t} = \nabla . k\nabla T \quad (18)$$

In one-dimensional case with no lateral heat loss and k constant, becomes to be Equation (19),

$$C\rho\frac{\partial T}{\partial t} = k\frac{\partial^2 T}{\partial x^2} \quad (19)$$

If an experimental sample exchange head with its surrounding, additional terms (see Equation (20)) in the heat equation should be needed to take this into account

$$C\rho\frac{\partial T}{\partial t} = k\frac{\partial^2 T}{\partial x^2} + Q_I + Q_M \quad (20)$$

Where Q_I represent an initial heat exchange, which may depend upon x, but independent of *t*. Q_M is an additional heat exchange that occurs when a small heater has been intentionally turned on to establish a non-steady-state condition whose characteristic will be used to determine the thermal properties of the sample. Because of the linearity of the differential equation, Q_I and Q_M produce independent temperatures T_I and T_M. Therefore, Q_I establishes an initial steady-state temperature distribution T_I in the sample which satisfies the steady-state equation [6] Equation (21),

$$k\frac{\partial^2 T_I}{\partial x^2} + Q_I = 0 \quad (21)$$

Subtracting Equation (21) from the right side of Equation (20), and $C\rho\partial T_I/\partial t = 0$ from the left side of Equation (20), we have the Equation (22)

$$C\rho\frac{\partial}{\partial t}(T - T_I) = k\frac{\partial^2}{\partial x^2}(T - T_I) + Q_M \quad (22)$$

The one dimensional equation for heat flow, with heat losses, may then be written as fallow, Equation (23)

$$\frac{\partial\theta}{\partial t} = D\frac{\partial^2\theta}{\partial x^2} + \mu\theta \quad (23)$$

Where $\theta = T - T_I$ represent the transient temperature change in the sample and heat losses have been considered to be proportional to θ with a constant of proportionality μ. Where variable $D$is represented by Equation (24)

$$D = \frac{k}{C\rho} \quad (24)$$

Was first called thermal diffusivity by Lord Kelvin [6].

EXPERIMENTAL DIFFUSIVITY DETERMINATION THEORY

The determination of the thermal diffusivity could be possible without reference standards required. Using the flash method. But, is recommendable the use of reference material to verify the results. Standard test method is available for this procedure.

This method consists in imparting a high intensity radiant energy flash to a sample for one side with short duration. This flash energy is absorbed by the sample while for the other sample side the temperature increment with respect to the time is recorded. The thermal diffusivity is then calculated using the sample thickness and the time that took to reach certain percentage of its maximum temperature value. Figure 4 present a schematic diagram of the apparatus for measuring D by flash method. This technique could be employed to a variety of small sample size, materials and a wide range of temperature ranging from about 75 up to 2800˚K [7]

This analysis comes from Equation (25)

$$T(x,t) = \frac{1}{L}\int_0^L T(x,0)dx$$

$$+\frac{2}{L}\sum_{n=1}^{\infty} exp\left(\frac{-n^2\pi^2 Dt}{L^2}\right) cos\frac{n\pi x}{L} \times$$

$$\int_0^L T(x,0)\, cos\frac{n\pi x}{L} dx \qquad (25)$$

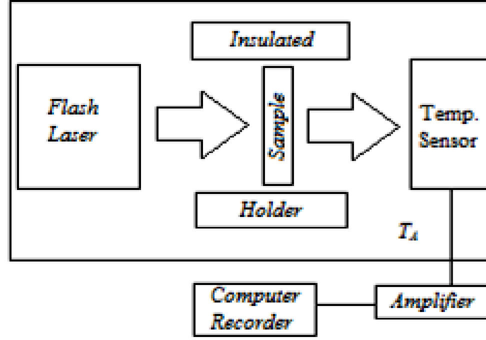


Figure 4
Apparatus Diagram

As the sample has a uniform small thickness L with an initial temperature T, and the pulse energy is uniformly absorbed in a small depth l instantaneously. The boundary conditions at these instants are,

$$T(x,0) = \frac{Q}{C\rho l} \qquad 0 < x < l$$

$$T(x,0) = 0 \qquad l < x < L \qquad (26)$$

Using these conditions presented in Equation (26) the Equation (27) becomes

$$T(x,t) = \frac{Q}{C\rho L}[1 + 2\sum_{n=1}^{\infty} cos\frac{n\pi x}{L}\frac{sin(n\pi l/L)}{(n\pi l/L)}$$

$$exp\left(\frac{-n^2\pi^2}{L^2}Dt\right)] \qquad (27)$$

As the thickness L is small then l is very small and the expression $sin(n\pi l/L) \cong n\pi l/L$. Then the back temperature when $x = L$ is

$$T(x,t) = \frac{Q}{C\rho L}[1 + 2\sum_{n=1}^{\infty}(-1)^n$$

$$exp\left(\frac{-n^2\pi^2}{L^2}Dt\right)] \qquad (28)$$

With the use of two normalized parameters in Equation (28) (dimensionless) this equations become Equation (29),

$$T' = 1 + 2\sum_{n=1}^{\infty}(-1)^n exp(-n^2 t') \qquad (29)$$

Parker was the first person employing this method to determine the thermal diffusivity [6]. As presented in Figure 5 [6] he Suggested two equations in which D could be determinate, the first using the time to archive its half maximum temperature (Half-Time) Equation (30) and the second when is not possible the first suggestion an extrapolation occurs see Equation (31).

$$D = 0.1388L^2/t_{1/2} \qquad (30)$$

And

$$D = 0.0486L^2/t_x \qquad (31)$$

Where $t_{1/2}$half-rise time and t_x is the time axis intercept extrapolation for the straight portion.

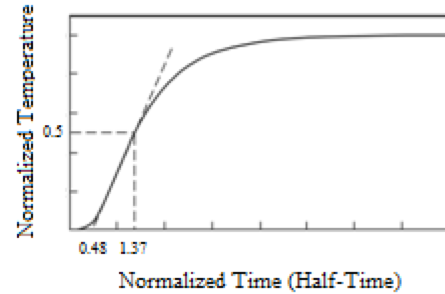


Figure 5
Dimensionless Temperature Profile

SAMPLE DEVELOPMENT

The material of interest is Si as mentioned before. This is available in wafer with a diameter of 3 inch and a thickness of 0.5 mm approximately. From this Si wafer was cut six samples to be doped. The cut was generated with a diamond knife. The dimensions of these samples are 10 mm by 10 mm. This size is necessary to hold the samples in the equipment.

In order to dope this material interstitially a table of graphite was machined. The table dimensions are of 4 inches long by 2 inches wide

and 0.75 of thickness. From the thickness side in direction to the wide were made 5 holes with a drill 11/32 inches diameters to put ceramics tubes that works as an isolator between the tungsten resistance and the graphite table. Then, two hole of 0.5 inch were done to support the table above other ceramic table that also worked as an isolator. Over the graphite table was generated a dent of 1 mm deep, 24 mm long by 11 mm wide to put the samples and manganese.

As the idea was to put the manganese powder between two samples of silicon to be interstitially doped, over the graphite table prepared at vacuum chamber, was also machined other block of graphite with dimensions of 2.0 inches long by 1 inch wide using the same thickness. For this block was also made a dent of approximately 0.4 mm deep. The intention was to confine the materials under certain pressure.

After that a resistant of tungsten was prepared using a tungsten wire of 0.02 inch diameters. This resistance was made using a stainless steel rod in a lathe at 22 rpm to prepare the coil. The mandrel diameter is 0.185 inches and there approximately 40 turns per inch. Basically were prepared five resistances in series (continuously) with 45 turns per resistance and leaving a space of 0.375 inches between them. This space was necessary to turn it through each ceramic pipe. Then, the resistances were added to the five ceramics pipe with an inside diameter of 0.250 inch mentioned before. At each resistant end, 8 inches of tungsten wire were left to connect the power.

With the components ready and armed onto the chamber area as presented in Figure 6, the samples of Si were cleaned and two of them putted over the graphite table. Over this samples were spread 0.5 mm of powder manganese (99.9%) and then other two samples were collocated over to complete the layer-by-layer. The block of graphite was putted over in order to hold the layer-by-layer in its area.

Then, the chamber cap was collocated in its place to close the system and turned on the vacuum pump. When the vacuum reached pressures fewer than 20 Torr a mass flow rate amount of hydrogen was inserted constantly in the chamber. This amount of hydrogen prevents the tungsten oxidation.

After establishes this condition the potentiometer was turned on. To reach the temperature desire, the power was incremented 1 ampere each 15 minute, if the temperature presents almost steady-state conditions. The samples were doped for a period of 12 hours with temperatures over 650℃. Then, an increment in the temperature using the process mentioned before was done to archive temperatures of 800℃ for two hours.

Finally an abrupt change in the temperatures turning the potentiometer power off and incrementing the hydrogen mass flow rate was done, to conclude the samples preparation. These were cleaned into a solution of one part of hydrochloric acid, two parts of nitric acid and three parts of water for an hour.

Figure 6
Graphite Table Assembly

DISCUSSION

The characterization of the samples to determinate its thermal diffusivity was done using LFA 447 NanoFlash equipment, that apply the flash method principles. Although, the samples placed in the layer-by-layer top, did not bring results as expected. Maybe a cause of this is its low exposure to the interstitial diffusion. Since the resistance was only in the lower area and the atoms migration to an interstitial empty position could be easier in that way. The bottom samples prepared reflect a

dramatically reduction in its thermal diffusivity, when this is compared with the silicon thermal diffusivity.

For the single crystal silicon wafer not doped the average thermal diffusivity reported by this method was 0.179 cm^2s^{-1} that is consistent with values reported previously for silicon wafers [8]. And for the single crystal silicon wafer sample doped with manganese, the average thermal diffusivity was 0.062 cm^2s^{-1}. This result reflects a considerable reduction of this parameter.

SUMMARIES

Since the Si was doped interstitially with Mn and the interstitial atoms are smaller. The Si density theoretically remains basically the same after the process, and the specific heat capacity is function of the density, which means the parameter highly impacted during the process was the thermal conductivity. Using this theatrical asseveration. The value of thermal conductivity for the materials not doped and doped become to be 2.918 $Wm^{-1}K^{-1}$ and 1.01 $Wm^{-1}K^{-1}$ respectively. Assuming this as true, the material thermal conductivity was reduced in a 65 percents of its initial value. In the actuality this parameter represents an issue for its influence in the figure of merit and its role affecting the thermoelectric performance.

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