STORAGE AND TRANSPORT OF ENERGY IN NANOSTRUCTURES

BY

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THESIS

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ABSTRACT

Nanostructures typically exhibit thermo-physical properties that are different from their bulk counterparts. The size dependence of thermo physical properties is attributed to changing energy and mass transport phenomenon with varying length scales. This size dependence can be profitably leveraged to build cheap and efficient energy storage and harvesting systems when the materials are highly abundant. In this thesis, we study two different materials which exhibit favorable properties at lower length scales. In the first case, we study the dependence of particle size on energy storage and Carbon dioxide absorption capability of Calcium oxide particles. We theoretically establish in this work that the CaO nanoparticles achieve higher and faster reaction conversions than the micrometer sized particles. We identify the parameters which contribute to the superior performance of CaO nanoparticles and thereby provide design recommendations to sustain the enhanced performance. In the second case, Silicon, another abundant material, in the form of a nanowire has been experimentally examined as a candidate material for thermoelectric applications to harvest waste heat. We designed and fabricated a device to gauge the thermoelectric figure of merit of nano-structured materials by simultaneous characterization of thermal, electrical and seebeck properties. Using the fabricated device, the silicon nanowires are shown to have a tenfold reduction in thermal conductivity from its bulk value thereby establishing silicon nanowires as a promising thermoelectric material.
To My Parents
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1 INTRODUCTION

According to the estimates of the United States Department of Energy, 83 % of the total energy consumed in the US is obtained from fossil fuels. The operation of a fossil fuel based power plant generates carbon dioxide gas and waste heat as byproducts. Carbon dioxide is a greenhouse gas which causes global warming and the waste heat results in loss of net efficiency of a power generating facility. There is a further loss in the net efficiency of a power plant during the off-peak hours due to lack of proper large scale energy storage methods. Therefore, development of methods to overcome the problems described above bear a huge significance. In this work, we put forth a recommendation to use carbonation reaction of CaO nanoparticles as a method to absorb CO₂ gas and simultaneously store energy. Furthermore, we discuss an experimental methodology to test the usability of various low dimensional materials in thermoelectric devices which could contribute towards harvesting waste heat from power generating facilities.

1.1 Thermochemical energy storage and Carbon dioxide sequestration

Calcination of limestone, an abundant mineral, provides one of the largest heats of reaction at ~1.78 MJ/kg and is an attractive process for thermal energy storage such as in concentrated solar thermal (CSP) power generation. While widely deployed in industrial processes and extensively studied, calcination suffers from poor recycling characteristics [1]. Even though the calcination reaction proceeds to completion, the quality of calcium oxide as a CO₂ sorbent in the reverse reaction declines over repeated calcination-carbonation cycles [1]. Sintering changes the surface texture over multiple cycles, with the formation of macroscopic pores as well as the shrinkage of microscopic pores. Such structural changes are understood to largely dictate the decline by more than 80% over as few as 10 cycles.
Particle size plays a decisive role [2-4] in both calcination and the reverse carbonation processes. In 1974, Barker [5] experimentally showed that using ~10 nm size particles in a powder enhanced reactivity to ~ 93 % with no detectable decline over 30 cycles in a 24 hour period. More recent work [6] has demonstrated high conversion for nanometer-sized CaO particle at much faster rates. Sub-100 nm particle size offers the distinct advantage of short heat (~4 ns) and mass diffusion times (~8 ns for CO$_2$ in CaCO$_3$) as well as reversible structural changes. Further, a micrometer or sub-micrometer scale ordered arrangement of such nanoparticles enables improved control of pore size and avoids problems associated with random pores observed in powders. However, there is significant loss in energy storage density when going from clustered particles to dispersed particles. For 100 nm particles dispersed at 50% areal fraction, the storage per unit area is ~300 J/m$^2$. However, dispersing nanoparticles on a high-surface area micromolded surface (~7x10$^5$ m$^2$/m$^3$) can provide an estimated storage density ~ 0.2 GJ/m$^3$ of system volume, excluding CO$_2$ storage.

While nanoparticles exhibit high conversions over repeated cycles, a theoretical understanding of this process is currently missing in the literature. Variations of the random pore model [7-8] typically seek to explain conversion rates of CaO particles larger than several tens of micrometers. These models cannot be directly applied to study conversion rates of gas-nanoparticle reactions. As the surface area to volume ratio increases with decreasing particle size, the reaction on the outer surface can become comparable to that inside pores. Furthermore, when the particle size becomes comparable to mean free path of the gaseous reactant, the transport of gas from bulk stream to the particle cannot be treated under continuum assumption. These aspects, which are not included in the existing models, could bear an impact on the reaction rate of sub-micrometer sized particles.
In this work, a model to obtain the dependence of conversion of the particle on its size is presented. The model accounts for the reaction on the outer surface apart from the reaction in the pores of the particle. The reaction in the pores is studied by modifying the random pore model and the reaction on the outer surface by using the shrinking core model. The model also includes the impact of the sub-continuum mass diffusion process on the conversion rate of CaO nanoparticles.

1.2 Low dimensional thermoelectric materials: Candidacy of Si nanowires

In order to increase the net efficiency of energy generating facilities, thermoelectric devices are used to harvest waste heat and convert it to electricity. The thermoelectric figure of merit $ZT$ of a material quantifies its usefulness as a thermoelectric material and is given by $ZT = S^2 \sigma / k$; where $S$ is the seebeck coefficient, $\sigma$ is the electrical conductivity and $k$ is the thermal conductivity of the material at temperature $T$.

In this work, a MEMS device [9] which could be used to simultaneously measure thermal conductivity, electrical conductivity and seebeck coefficient of low dimensional structures like nanowires and thin films has been fabricated. The fabricated device can also be loaded into a transmission electron microscopy (TEM) to characterize the crystalline properties and other morphological properties of the material to be tested.

Use of Silicon nanowires as a thermoelectric material has been proposed in recent times. This proposal is based on the experimental results [10,11] in which the thermal conductivity of silicon nanowires has been demonstrated to be ten times lower than its bulk counterpart. Moreover, owing to low mean free path of electrons, the electron transport is expected to remain unaffected as we transition from bulk to nanowire structure in silicon. The reduced thermal conductivity,
unaffected electrical properties and its easy availability makes silicon nanowires a candidate for thermoelectric applications. The thermal conductivity of silicon nanowires has been measured to evaluate its candidacy as a thermoelectric material.
2 CONVERSION TIME CHARACTERISTICS OF CAO NANOPARTICLES

In this chapter, a model to calculate the conversion time characteristics of CaO nanoparticles for various particle sizes is described. Bhatia and Perlmutter [7], in their initial version of random pore model for gas solid reactions, provided an expression for conversion of the solid reactant which takes particle size into account. The expression was derived under an assumption of uniform reaction extent throughout the particle and kinetic control regime on the surface of the particle. This expression cannot be readily used to study the effect of size on the conversion of CaO particles for two reasons. The reaction extent inside the particle is not uniform at all radial positions and the carbonation of CaO reaction is not kinetically controlled. In the model presented in this work, the conversion in the core of the particle is calculated without assuming uniform conversion inside the particle. The reaction on the surface of the particle is separately calculated without assuming kinetic control regime. Finally, the overall conversion is obtained as a superposition of these two models.

2.1 Conversion in the core of the particle

In this section, the modified random pore model used to calculate the reaction extent in the core of the particle is described. In this model, it is assumed that the CaO particle is a porous sphere suspended in an environment of carbon dioxide and nitrogen gas mixture at 1 atm pressure with CO$_2$ mole fraction of 0.15. It is further assumed that the gas mixture and the particle are at a constant temperature of 650 C.

As shown in Figure 2.1, the concentration of CO$_2$ drops from $C_b$ in the bulk stream to $C_s$ at the particle surface due to external mass transfer resistance, ER. There is a further reduction in the
CO₂ concentration from $C_s$ to $C$ as it flows through the pores from the surface into the core of the particle. This resistance to the flow due to small pore size is referred to as intra-pellet resistance, IPR. The CO₂ concentration further drops to $C_i$ at the reaction surface due to the product layer resistance PLR encountered while diffusing through the CaCO₃ product layer. The concentrations $C_s$, $C$ and $C_i$ are non-dimensionalized with respect to $C_b$ and the non-dimensionalized quantities are represented as $C_s^*$, $C^*$ and $C_i^*$ respectively.

Figure.2.1: shows the schematic of a CaO nanoparticle suspended in a mixture of CO₂ and N₂ environment at 1000 K. Carbon dioxide gas diffuses into the particle through the pores (white) and the calcium carbonate product layer (grey) to reach the reaction surface of calcium oxide (Black) where the carbonation reaction takes place. Notations used for concentration of CO₂ at various positions with respect to the particle are shown along the horizontal line at the bottom of the figure.

It is assumed that pseudo steady state conditions are prevalent during the carbonation reaction. The assumption implies that the change in concentration of CO₂ at any position over a short period of time is negligible compared to the flow rate of CO₂. Therefore, in a small time interval, the process of CO₂ diffusion and subsequent reaction can be represented by the diffusion-consumption equation as:
\[
\frac{1}{\eta^2} \frac{\partial}{\partial \eta} \left( \eta^2 D^*_e \frac{\partial C^*}{\partial \eta} \right) = \frac{\rho R^2_o}{M D_{eo} C_b} (1 - V_o) \frac{dX(\eta, t)}{dt}
\]  

where \( R_o \) is radius of the particle; \( \eta \) is non-dimensional radial position \( r/R_o \); \( M, \rho \) are molecular weight and density of CaO; \( D_{eo} \) is the intrapellet diffusivity through the pores at the beginning of the reaction; \( D^*_e \) is non-dimensionalized intrapellet diffusivity \( D_e/D_{eo} \) and is a function of time \( t \) and radial position \( \eta \) due to non-uniform change in pore structure across the particle; \( V \) is defined as the volume enclosed by the unreacted CaO pore surface per unit volume in space with \( V_o \) being its initial value; Local conversion \( X(\eta, t) \) is the measure of extent of reaction, defined as the ratio of volume of reactant consumed in a unit volume in space at radial position \( \eta \) in time \( t \) to the volume of reactant available at the beginning of the reaction in a unit volume of space.

The boundary conditions associated with Equation 2.1 are:

\[
\left. \frac{\partial C^*}{\partial \eta} \right|_{\eta=0} = 0
\]

\[
\left. \frac{\partial C^*}{\partial \eta} \right|_{\eta=1} = \frac{Sh(1 - C^*)}{D^*_e}
\]

The first boundary condition Equation 2.2 represents spherical symmetry in the problem, while Equation 2.3 represents external mass transfer resistance to flow of CO\(_2\) from the bulk into the particle. Calculation the CO\(_2\) radial concentration profile over time using Equations 2.1-2.3 enables estimation of overall conversion as a function of time. In the following subsections, formulation of various parameters involved in Equations 2.1-2.3 is described.

2.1.1 Random pore model

The term \( dX/dt \) in Equation 2.1 represents rate of conversion of calcium oxide to calcium carbonate. The rate of conversion is calculated by correlating changes in pore structure to chemical kinetics of the reaction using the random pore model formulated by Bhatia and
Perlmutter [7]. In this section, the key steps and the modifications made to the random pore model are described. The random pore model assumes that pores are cylindrical with size distribution $f(r)$ where $f(r)dr$ is the length of pores with radius in the range $r$ and $r + dr$. By assuming that no pores are formed or destroyed during the reaction, the following equation can be written to balance the number of pores

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial t} \left( f \frac{dr}{dt} \right) = 0 \quad 2.4$$

Assuming that the reaction is of first order with respect to the concentration of CO$_2$ and is proportional to the surface area of the solid reactant (CaO) available, the rate of change of pore radius is given by

$$\frac{dr}{dt} = k(C_i - C_e) \quad 2.5$$

where $k$ is the rate constant of the carbonation reaction, and $C_e$ is the CO$_2$ equilibrium concentration of the carbonation-calcination reaction system. Multiplying Equation 2.5 by unity and integrating over the pore radius from zero to infinity gives the total length of the pores per unit volume of space ($L_E$). Similarly, the surface area ($S_E$) and the volume enclosed ($V_E$) by the unreacted CaO surface in a unit volume of space are obtained by multiplying Equation 5 by $2\pi r$ and $\pi r^2$ respectively and integrating over the pore radius. Allowing for the correction factor $V = 1 - \exp(-V_E)$ to account for pore overlap [12], the corresponding corrected volume $V$ enclosed by the unreacted CaO surface inside the particle is obtained as:

$$V = 1 - (1 - V_0)\exp \left( \frac{-kC_b \int_0^t (C_i^* - C_e^*)dt}{1 - V_0} \right) \left( S_0 + \pi kL_0C_b \int_0^t (C_i^* - C_e^*)dt \right) \quad 2.6$$

where $L_0$, $S_0$ and $V_0$ are the initial values of total length, surface area and volume of the unreacted CaO surface. These parameters appear as constants of integration in the integration of Equation 2.5. The formulation described in this section deviates from the random pore model in
two aspects. In Equation 2.5, the rate is taken to be proportional to \((C_i^* - C_e^*)\) instead of \(C_i^*\) to account for the reversibility of the reaction. Secondly, the term \(C_i^* t\) in the random pore model is replaced by an integral to account for changing value of \(C_i^*\) with time.

Using Eq.6, local conversion \(X\) inside the particle at radial position \(\eta\) and time \(t\) is obtained as

\[
1 - X(\eta, t) = \frac{(1 - V)}{(1 - V_0)}
\]

\[
= \exp\left(\frac{-kC_B \int_0^t (C_i^* - C_e^*)dt}{1 - V_0}. (S_0 + \pi kL_0 C_b \int_0^t (C_i^* - C_e^*)dt)\right)
\]

Differentiating Equation 2.7 with respect to \(t\) provides the local conversion rate \(dX/dt\) as

\[
\frac{dX(\eta, t)}{dt} = \frac{kC_BS_0}{(1 - V_0)} C_i^*(1 - X(\eta, t)) \left(1 + \frac{2\pi kL_0 C_b \int_0^t (C_i^* - C_e^*)dt}{S_0}\right)
\]

2.1.2 Product layer resistance

Equation 2.8 expresses \(dX/dt\) a function of \(C_i^*\), while the left hand side of Equation 2.1 is a function of \(C^*\). Therefore, in order to be able to use \(dX/dt\) from Equation 2.8 in Equation 2.1, \(C_i^*\) has to expressed in terms of \(C^*\). This relation is obtained [8] by analyzing the resistance offered by the CaCO\(_3\) product layer to the flow of CO\(_2\) from the pores to the unreacted CaO surface.

A thin layer of product develops over the reaction surface as the reaction progresses and adds a resistance to the flow of CO\(_2\) to the CaO reaction surface. Assuming that the product layer thickness \(\Delta\) is small, growth of the product layer can be expressed as

\[
\Delta = ZkC_B \int_0^t (C_i^* - C_e^*)dt
\]

Balancing the CO\(_2\) diffusion rate through the product layer and the rate of consumption of CO\(_2\) at the CaCO\(_3\)-CaO interface gives:
where $D_p$ is the diffusion coefficient of CO$_2$ through the calcium carbonate product layer [13,14]. Eliminating $\Delta$ from Equation 2.9 and 2.10, the concentration of CO$_2$ at the reaction surface $C_i^*$ is related to the concentration of CO$_2$ in the pores $C^*$. For the calculations in this work, the value for $D_p$ is obtained from the value of apparent product layer diffusivity extracted by Bhatia and Perlmutter [Bhatia Lime].

### 2.1.3 Intrapellet Resistance

The term $D_e^*$ in Equation 2.1 represents intrapellet resistance to the flow of CO$_2$ into the particle through pores. Since the molar volume of CaCO$_3$ is greater than the molar volume of CaO, dimensions of the pores decrease as the reaction progresses resulting in lowering intrapellet diffusivity. The ratio of molar volume of the product formed to that of reactant is denoted as $Z$. For the carbonation of CaO, the value of $Z$ is 2.16.

The initial intrapellet diffusivity $D_{e0}$ at the beginning of the reaction is defined as

$$D_{e0} = \frac{1}{D_M} + \frac{1}{D_K}$$  \hspace{1cm} 2.11

where $D_M$ is molecular diffusivity of CO$_2$ and $D_K$ is the Knudsen diffusivity of CO$_2$ through the pores (8). The non-dimensional change in intrapellet diffusivity through the pores can be related to porosity $\varepsilon(\eta,t)$ as (8):

$$D_e^*(\eta,t) = \frac{D_e(\eta,t)}{D_{e0}} = \frac{\varepsilon(\varepsilon_0)}{\varepsilon_0 \gamma(\varepsilon)}$$  \hspace{1cm} 2.12

where $\gamma(\varepsilon)$ is tortuosity which varies as $1/\varepsilon$ according to Wakao and Smith model [15].

The change in porosity can be, in turn, related to the local conversion, $X$ using the relation

$$\varepsilon^*(\eta,t) = \frac{\varepsilon}{\varepsilon_0} = 1 - \frac{(Z - 1)(1 - \varepsilon_0)X(\eta,t)}{\varepsilon_0}$$  \hspace{1cm} 2.13
Equations 2.11, 2.12 and 2.13 together give the change in intrapellet diffusivity $D_e^*$ in terms of the local conversion, $X$ as:

$$D_e^*(\eta, t) = \left(1 - \frac{(Z - 1)(1 - \varepsilon_0)X(\eta, t)}{\varepsilon_0}\right)^2$$ \hspace{1cm} 2.14

2.1.4 External mass transfer resistance

In a gas-nanoparticle reaction, the mean free path of the gas is comparable to size of the particle. This aspect is quantified by Knudsen number defined as $Kn = \lambda/2R_o$ where $2R_o$ is particle radius and $\lambda$ is the mean free path of the gas given by $1/\sqrt{2}\pi nd^2$ where $d$ is collision diameter and $n$ is number of molecules per unit volume [16]. Estimation of the Sherwood number in the continuum regime ($Kn < 0.01$) and in the free molecular regime ($Kn > 10$) is well established. However, for the particle size of interest (50 nm to 1 $\mu m$), $Kn$ falls in the transition regime where $0.01 < Kn < 10$. To obtain the effective Sherwood number in the transition regime, several approaches [17-21] have been suggested in the literature. Fuchs and Sutugin [22] proposed an interpolation formula obtained by flux matching method. In their method, they assume a fictitious sphere at a radial distance of several mean free paths from the surface of the particle. The flow is assumed to be governed entirely by diffusion beyond this sphere and by the kinetic theory formulations between the sphere and the particle surface. By matching the mole flux at the interface of these regions, they proposed an expression for the ratio of mole flux in transition regime $n_{tr}^*$ to that in the continuum regime $n_{con}^*$. In this calculation we use the improved Fuchs-Sutugin interpolation formula suggested by Loyalka [23]

$$\frac{n_{tr}^*}{n_{con}^*} = \left(1 + Kn \frac{\sqrt{\pi} \frac{4}{3} Kn + 1.0161}{\frac{4}{3} Kn + 1}\right)^{-1}$$ \hspace{1cm} 2.15

In continuum regime, the mole flux to a sphere from the surrounding gas is given by
From Equations 2.15 and 2.16, the effective external mass transfer coefficient is obtained as

\[ n_{con}^* = 4\pi R_0 D_m (C_b - C_s) \quad 2.16 \]

The convective mass transfer coefficient provides the effective Sherwood number required in Equation 2.3 as \( Sh = k_m R_0 / D_e \). The effective Sherwood number is plotted as a function of Knudsen number in Figure 2.2. As the radius of the particle decreases, the Knudsen number increases and the flow of CO\(_2\) transitions from the continuum regime \((Kn < 0.01)\) through the transition regime \((0.01 < Kn < 10)\) to the free molecular regime \((Kn > 0.01)\). It can be observed from Figure 2.2 that with decreasing particle size, the effective Sherwood number decreases. The effect of the reducing Sherwood number is discussed in the results section.
2.2 Reaction on external surface:

The total surface area of unreacted CaO in the pores decreases with decreasing particle size. As the radius of the particle decreases, the area on the external surface of the particles approaches the value of the unreacted CaO surface area in the pores. Therefore, neglecting the reaction on the outer surface of the particle could lead to underestimation of the total conversion. In their earlier version of random pore model [7] for gas solid reactions, Bhatia and Perlmutter suggested an expression for calculating the overall conversion in a generalized gas solid as

Figure 2.2: The variation of effective Sherwood number with Knudsen number. The Knudsen number is defined as the ratio of mean free path of the gas mixture and the size of the particle.
\[ 1 - X(t) = \frac{(1 - V)}{(1 - V_0)} \left(1 - \frac{kC_b t}{R_0}\right)^3 \] 2.18

The first term in Equation 2.18 represents conversion in the core of the particle and is assumed to be uniform throughout the particle. The second term represents the reaction on the outer surface of the particle and assumes that the reaction proceeds under kinetic control regime. However, for the Carbonation of CaO, the product layer diffusion may significantly affect the reaction rate on the surface of the particle. In order to address this issue, a model which takes into account all possible resistances involved in the reaction is used. The reaction extent on the outer surface of the particle is calculated by using the shrinking core model under pseudo steady state assumption [24].

Figure 2.3: shows schematic of a sector in the cross section of the particle for two different models. In the model represented by figure 2.3a, chemical reaction on the external conversion is neglected. In the model represented by figure 2.3b, conversion on the external surface of the particle is taken into account in addition to the conversion inside the particle.

As the reaction proceeds on the particle surface, the external unreacted CaO surface recedes in the radial direction from \( R_O \) to \( R_i(t) \) in time \( t \). Furthermore, since the ratio of molar volume \((Z)\) of CaCO\(_3\) to that of CaO is greater than 1, the overall particle radius increases to \( R_s(t) \) as indicated in Figure 3b. The CO\(_2\) concentration drops from \( C_b \) in the bulk stream to \( C_s \) at the external surface of the particle as it diffuses to the particle surface. The CO\(_2\) concentration
further drops to \( C_i \) as it flows through the product layer of thickness \( R_s(t) - R_i(t) \). The overall resistance to the flow of CO\(_2\) at time \( t \), \( H_{ex} \) is (15)

\[
H_{ex} = \frac{1}{4\pi} \left( \frac{1}{k_m R_o^2} + \frac{1}{D_p} \left( \frac{1}{R_i(t)} - \frac{1}{R_s(t)} \right) + \frac{M}{k_p R_i(t)^2} \right) \tag{2.19}
\]

The three terms in Equation 20 are the external mass transfer resistance, product layer diffusion resistance to the flow from the external surface at \( R_s(t) \) to CaO-CaCO\(_3\) interface at \( R_i(t) \), and the carbonation reaction resistance respectively. In this model, it is assumed that the product layer diffusivity \( D_p \) is constant at a given temperature and that the concentration of CO\(_2\) varies linearly across the product layer. Equation 2.19 is used to obtain the number of moles of CO\(_2\) consumed from time \( t \) to \( t + dt \) as \( \frac{(C_b - C_e)}{H_{ex}} \). Stoichiometry considerations provide the rate of change of radial position of the CaCO\(_3\)-CaO interface as

\[
\frac{C_b - C_e}{H_{ex}} = \frac{\rho}{M} \left. d \left( \frac{4\pi R^3}{3} \right) \right|_{R_i} = 4\pi R_i(t)^2 \frac{dR_i(t)}{dt} \tag{2.20}
\]

Furthermore, from the definition of \( Z \), the ratio of molar volume of CaCO\(_3\) to CaO

\[
\frac{4}{3} \pi (R_s(t)^3 - R_i(t)^3) = Z \frac{4}{3} \pi (R_o^3 - R_i(t)^3) \tag{2.21}
\]

By differentiating equation 2.21 with respect to time, the rate of change of the external surface radius \( R_s \) as a function of rate of change of the CaCO\(_3\)-CaO interface position is obtained.

\[
R_s(t)^2 \frac{dR_s(t)}{dt} = (1 - Z)R_i(t)^2 \frac{dR_i(t)}{dt} \tag{2.22}
\]

Equations 2.20 and 2.22 can be used to obtain the values of \( R_s(t + dt) \) and \( R_i(t + dt) \) after a time step of duration \( dt \).

### 2.3 Numerical Methodology
In this section, the steps followed to calculate overall conversion of a particle are described. The procedure employed to calculate the conversion in the core of the particle as a function of time is described below. To calculate the conversion in the core of the particle, Equations 2.1-2.3 are discretized using the control volume method to obtain a set of linear equations in $C^*(\eta, t)$, the CO$_2$ concentration in pores at radial position $\eta$ and time $t$. In the discretization step [25], the $C_i^*(\eta, t)$ factor outside of the integral in Equation 8 is expressed in terms of $C^*(\eta, t)$ using Equations 2.9 and 2.10. The rest of the terms are obtained by using the values at time $t$-dt using the formulae given in section 2.1. The linear equations in $C^*(\eta, t)$ are solved using the tridiagonal matrix algorithm to obtain concentration profiles $C^*(\eta, t)$ across the particle radius as a function of time $t$. Using Equations 2.9 and 2.10, the concentration profile at the reaction surface in the pores $C_i^*(\eta, t)$ is obtained from the concentration profile $C^*(\eta, t)$. Using $C_i^*(\eta, t)$ the local conversion $X(\eta, t)$, the intraparticle diffusivity parameter $D_e^*$ and the product layer thickness $\Delta$ are obtained and are further used for calculation of $C^*(\eta, t + dt)$ and $X(\eta, t + dt)$ in the next time step.

To account for the conversion on the outer surface of the particle, the radial position of the CaO-CaCO$_3$ reaction surface is calculated at all times. This is obtained by straight forward integration of $dR_l/dt$ from Equation 2.20.

Once the conversion profile $X(\eta, t)$ and radial position of the outer reaction surface $R_l(t)$ are obtained at all times, the overall conversion is calculated by using Equation 2.22. Since all the CaO beyond $R_l(t)$ is converted, the fraction of unreacted volume of CaO left over within this radius is calculated and its supplementary value is taken as the overall conversion.

\[
1 - \overline{X(t)} = 3 \int_{\eta=0}^{R_l(t)/R_0} (1 - X(\eta, t))\eta^2 d\eta \quad 2.23
\]
To validate the discretization and calculation methodology, the results of the computation with the result obtained by using orthogonal collocation technique [8] are compared. The parameters for this particular computation have been changed to the values used by Bhatia and Perlmutter in their publication. The matching result presented in Figure 2.4 shows the validity of the discretization and calculation methodology.

![Graph](image)

Figure 2.4: shows the comparison between the result obtained by numerical calculation (solid line) and the result obtained by Bhatia and Perlmutter by using orthogonal collocation technique (square markers).

### 2.4 Results

In this section, the changes in conversion time characteristics of an isolated Calcium Oxide particle as we transition from sub-millimeter to sub-micrometer particle size regime are
presented. This transition is analyzed by individually weighing in the significance of various parameters at different particle sizes.

As discussed in section 2.1, the mean free path of the gas mixture becomes comparable to the particle size as the transition from micrometer to nanometer sized particles is made. It is further shown in Figure 2.2 that the effective Sherwood number decreases with decreasing particle size. The reduced Sherwood number manifests as increased external mass transfer resistance to the flow of CO2 from bulk to the surface of the particle. However, the decreasing effective Sherwood number showed no effect on the conversion characteristics of the particles even at very small radii. In Figure 2.5, a comparison of the external mass transfer resistance, the product layer diffusion resistance and the reaction resistance for reaction on the external surface of a particle of radius 50 nm is shown. It can be clearly seen from the figure that the product layer diffusion resistance and the reaction resistance are the only competing resistances. The external mass transfer resistance is orders of magnitude smaller than the product layer diffusion and the reaction resistance. Therefore, the transition from micrometer sized particles to nanometer sized particles is not accompanied by loss in conversion due to increased external mass transfer resistance.
Figure 2.5: shows the comparison between various resistances that are involved in the reaction on the outer surface of an isolated 50nm particle. The external mass transfer resistance shown in the inset is orders of magnitude smaller than the product layer and reaction resistances.

In Figure 2.6, the effect of intraparticle resistance on the conversion time characteristics for three particle sizes is shown. The solid lines in the figure are obtained by taking the initial intraparticle diffusivity \( D_{eo} \) to be infinity. Under this assumption, the concentration of CO\(_2\) and therefore the local conversion are uniform throughout the particle. However, the smaller particles react faster owing to the reaction on the external surface which is discussed later in this section.

The dotted lines in Figure 2.6 are calculated by using the value of intraparticle diffusivity obtained from Equation 2.14. It can be seen from the figure that the particles of size 5 \( \mu \text{m} \) do not reach complete conversion. Due to the finite value of intraparticle diffusivity, the CO\(_2\) concentration and the conversion rate reduce as we move into the particle. As the reaction
progresses, the intraparticle diffusivity decreases rapidly at the outer portions of the particle due to higher CO$_2$ concentrations. This turns off the flow of CO$_2$ to the inner regions of the particle thereby leading to incomplete conversions.

It can be further seen from Figure 2.6 that there is no adverse effect of finite intraparticle diffusivity on the conversion time characteristics of 50 nm and 100nm. The concentration drop of CO$_2$ in the nanometer sized particles is very small leading to more complete reactions. Therefore, the intraparticle diffusion resistance works adversely on the ultimate conversion of the micrometer sized particles and shows no such affect for the sub-micrometer sized particles.

Figure 2.6: Conversion time characteristics for isolated CaO particles of radius 50nm, 100nm and 5 µm with finite (dotted lines) and infinite (solid lines) intraparticle diffusivity.
Figure 2.7: shows the difference in the times taken to reach half conversion with and without accounting for the reaction on the external surface of the particle.

In Figure 2.7, the difference in times taken to reach half conversion with and without inclusion of the reaction on the outer surface is shown. The particle of radius 50 nm reaches half conversion 68.5 seconds faster when the reaction on the outer surface is taken into account. On the other hand, for the particle with radius of a micrometer, the time difference to reach half conversion is 4 seconds. Therefore, for the particles of smaller radius, the reaction on the external surface can be leveraged to obtain faster conversions. However, the factors which reduce the external surface area such as sintering of nanoparticles could lead to reduction in the ultimate conversion of the nanoparticles. It is therefore advisable to use the CaO nanoparticles separated on a scaffold to obtain higher and faster conversions.
3 THERMAL CONDUCTIVITY MEASUREMENT OF A SINGLE SILICON NANOWIRE

3.1 Device Fabrication

The thermal conductivity of a nanowire is measured by placing the nanowire across two suspended membranes that at different temperatures and measuring the heat flow through the wire from one membrane to the other [9]. In this section, the process flow employed to fabricate a device to measure the thermal conductivity of a nanowire is described. The measurement devices are fabricated at wafer scale. A 300 \( \mu \)m thick double polished silicon wafer is used for the fabrication of measurement devices. The fabrication starts with deposition of 150 nm of PECVD silicon nitride on one side of the wafer and 300 nm on the other side. The side with 150 nm nitride is referred to as the front side and the other side as the backside of the wafer. The 150 nm thick nitride on the front side serves as a protective layer to prevent any damage to the front side while processing the back side. It is to be noted that for the deposition of silicon nitride using PECVD, only mixed frequency mode has been used throughout this work to minimize the stress in nitride films.

On the backside of the wafer, a 10 nm film of Aluminum, yellow in Figure 3.1, is deposited using an e-beam evaporator followed by a 100 nm thick film of PECVD silicon nitride. After the deposition of silicon nitride, a 1.2 \( \mu \)m thick film of photo-resist AZ 5214E (PR) is spun on the backside of the wafer using a high speed spinner. A HMDS primer is spun before spinning the PR to improve adhesion of PR to the nitride surface. Using optical lithography, square windows of dimensions 700 X 700 \( \mu \)m are patterned in the PR film on the backside. The square patterns in the PR film are transferred to the nitride film using CH\(_4\) Freon RIE anisotropicetch. The RIE
etching process is typically carried out for longer than required times to make sure that the nitride film in the windows is completely etched and Aluminum underneath is exposed.

After etching the nitride film through the windows, the wafer is dipped in 20 % by weight KOH solution at 80 C. The exposed Aluminum gets consumed by KOH instantly and the window pattern is transferred to aluminum film as shown in Figure 3.1 a. The wafer is cleaned and dried thoroughly using DI water and a hot plate at 110 C, followed by another round of CH₄ Freon RIE etching to transfer the window pattern to the 300nm nitride film. The nitride film is again over-etched in this step to ensure that the silicon on the backside of the wafer is exposed as shown in Figure 3.1 b.

The wafer is not dipped in 20 wt % KOH solution to etch about 75 nm of silicon on the backside of the wafer. This etching step is timed carefully to prevent silicon over-etching in which case the windows patterns in the wafer could propagate and break the entire wafer.

Figure 3.1: Fabrication on the backside of the wafer. Silicon is represented in gray, Aluminum in yellow and silicon nitride in blue. The opening on the bottom side of the wafer are square patterns of size 700 μm X 700 μm
Before beginning the fabrication on the front side of the wafer, the 150 nm protective nitride film is removed using 10:1 BOE solution. This step is typically overdone to ensure complete removal of nitride film on the front side. To prevent damage to the nitride film on the backside during the BOE etch, a film of PR is spun on the backside of the wafer before beginning the BOE etching and is removed using acetone and PR stripper after the BOE etch. To ensure complete removal of PR, an additional step of O$_2$ plasma cleaning is performed every time a PR film is removed using acetone or PR stripper. Residues of PR get exposed to high temperatures in subsequent fabrication steps and stick to the surface. It is highly difficult to remove the PR residues after they are exposed to high temperatures. Therefore, whenever a film PR is to be removed, it is important to ensure its complete removal.

After the cleaning step, a 300 nm PECVD film is deposited on the front side of the wafer followed by deposition of 3 nm of Titanium and 30 nm Platinum film using an e-beam evaporator. The 3 nm titanium film is used to promote adhesion of Pt film to the nitride film and the nitride film acts as an insulator between the metal films and silicon underneath. The schematic of the wafer at this stage is shown in Figure 3.2a.

A film of silicon nitride of thickness 50 nm is deposited on top of the platinum film and a layer of PR is spun on the top of the nitride film using HMDS as an adhesion promoter. Using optical lithography process, the device pattern comprising of two serpentine coils of width 1 μm and twelve beams each of width 2 μm is made in the PR film. The windows patterned on the backside of the wafer are aligned with the symmetric center of the device pattern on the front side using infrared mode in the aligner. In the infrared mode, IR radiation is incident on the backside of the wafer mounted on the aligner chuck.
Figure 3.2: Schematic of the measurement device at various stages of fabrication. Platinum film shown in 3.2a is patterned to obtain the coil and beam structure shown in Figure 3.2b. The coil and the beam structure is wrapped in silicon nitride as shown in Figure 3.2c. The silicon nitride wrapped around platinum is selectively etched to expose contact pads and electrodes as shown in Figure 3.2d.
The window patterns transmitted using the IR radiation is used to align the windows with the center of the device pattern.

The pattern in the PR film is then transferred to the Pt film in the subsequent steps. It is desirable to have thinner Platinum serpentine coil width to increase the electrical resistance of the serpentine coil and to thereby increase the joule heating when a fixed current is passed through it. To achieve this purpose, the serpentine coil pattern in the PR film is thinned down from 1 \( \mu \text{m} \) to nearly 500-700 nm by using O\(_2\) plasma etching.

The thinned down patterns in the PR are transferred to the 50 nm nitride film using the CH\(_4\) Freon plasma RIE and to the platinum film using Argon plasma ion milling process. The 50 nm nitride film acting as an etch mask in the Argon plasma ion process needs to be removed in later steps to expose the platinum. However, silicon nitride films on exposure to Argon plasma become hard to etch using Freon plasma RIE etch. To overcome this problem, the wafer is dipped in a 10:1 BOE solution for a short time to etch off the 50 nm nitride film left on the Pt pattern. The patterned pt film is shown in Figure 3.2b.

A nitride film of thickness 300 nm is deposited on the front side thereby sandwiching the patterned Pt film in between two nitride films with a combined thickness of 600 nm. Using optical lithography followed by Freon plasma RIE etch, the 600 nm thick nitride is patterned as shown in the Figure 3.2c. Using another round of optical lithography and Freon plasma RIE etch, platinum is selectively exposed in certain regions of the device as shown in the Figure 3.2d. The square regions of exposed platinum are called the contact pads. The purpose of the contact pads is to electrically connect the device to various instruments like current source, lock-in amplifiers
etc. The regions of exposed platinum at the center of the device are called the electrodes and their purpose is to make thermal/electrical contact with the nanowire sample to be measured.

The device structure with platinum patterns wrapped in silicon nitride rests on the silicon substrate at this stage. By using 20 wt% KOH solution at 75 C, the silicon underneath the device structure is etched away thereby suspending the device. During the KOH etch to suspend the membranes, the silicon exposed through the windows on the backside of the wafer is also etched. At the end of the KOH etch step, the membranes are suspended and a through hole is formed in the substrate. The purpose of the through hole is to enable transmission electron microscopy imaging of any sample that is placed in between the membranes. Figure 3.3 shows SEM images of the measurement devices at various magnifications at the end of the fabrication steps discussed so far.

![SEM images of measurement devices at various magnifications](image)

Figure 3.3 (cont. on next page)
Figure 3.3 (cont. on next page)
Figure 3.3: SEM images of the fabricated measurement devices. The images are presented in the increasing order of magnification. The SEM image in Figure 3.3a shows the three devices on a silicon chip. The contact pads (white squares) and the through hole are easily discernible. A magnified version of the through hole made for TEM purposes can be seen in Figure 3.3b. Figure 3.3 c shows the heating and sensing membranes across which a nanowire is to be placed. Figure 3.3 d shows the exposed platinum electrodes on which the tips of nanowires are to be welded.

It can be seen in Figure 3.3c that there are two serpentine Pt coils each wrapped in silicon nitride membranes. The membrane on the left is referred to as the heating membrane and the one on the right is referred to as the sensing side. The heating and sensing membranes are each connected to the rest of the substrate by means of six beams. The length of the beams is designed to be over 400 μm to increase the thermal resistance of the beams thereby ensuring thermal isolation of the membranes. In other words, when a sample is placed in thermal contact across the membranes, an insignificant amount of heat flows through the beams to the sensing side compared to the heat flow through the sample.
As mentioned previously, the devices are fabricated at a wafer scale. After the fabrication, the wafer is diced into pieces of 1 cm X 1 cm by using a dicing saw. To prevent contamination to the devices from the tap water used in dicing saw equipment, a layer of PR is spun on the wafer and is removed after the dicing process using a PR stripper and O₂ plasma de-scum.

Arrays of silicon nanowires are synthesized on wafer scale using electro-less etching method. To transfer the nanowires to the fabricated devices, the nanowire arrays are scratched off the substrate and spread over a glass slide using a razor blade. The glass slide is then brought into contact with a silicon chip with suspended devices on it. Each 1 square cm chip has 18 suspended devices. One of these devices is often found to have a nanowire across the membranes. The nanowire is then welded to the platinum electrodes at the edges of the membranes. The welding is done by using platinum metal in a Focused ion beam chamber. The SEM image of the nanowire welded to platinum electrodes of a device is shown in Figure 3.4.

![SEM image of nanowire welded to electrodes](image)

Figure 3.4 (cont. on next page)
3.2 Measurement Principle

In this section, the principle used to measure the thermal conductivity of a nanowire is described. In Figure 3.6, the schematic of the measurement device with a nanowire across its membranes is shown. To measure thermal conductivity of a nanowire, a temperature gradient must be applied...
across the nanowire. This is done by passing DC current through the Pt coil in the heating membrane. The part of the platinum pattern through which the DC current is passed is marked in red in the Figure 3.6. The DC current generates joule heat in two beams and the serpentine coil in the heating membrane. The heat generated in each of the two beams is denoted as $Q_L$ and the heat generated in the coil is denoted as $Q_C$. It is assumed that half of the heat generated in the beams flows to the heating membrane and the other half flows to the substrate.

As a result, the amount of heat available in the heating membrane is $Q_C + 2*(Q_L/2)$. A steady state “thermal circuit” showing the flow of this heat from the heating membrane to the substrate through various pathways is shown in Figure 3.7. The entire heating membrane is assumed to be at a uniform temperature $T_H$ as shown in figure 3.6. Out of $Q_C + Q_L$, $Q_{nw}$ is assumed to flow through the nanowire to the sensing membrane and then through the beams on the sensing side to the substrate. The conductance of the nanowire, denoted as $G_{nw}$ in Figures 3.6 and 3.7, also includes the thermal conductance of the silicon Pt interface. As a result of the heat flow $Q_{nw}$, the temperature of the sensing membrane rises to $T_S$. The remaining heat $Q_C + Q_L - Q_{nw}$ flows through six beams on the heating side to the substrate which acts as a heat sink at a set bath temperature of $T_O$. The combined thermal conductance of six beams on each side is denoted as $G_b$ in Figure 3.7.
Figure 3.6: Schematic of a measurement device with nanowire placed across the membranes. DC current is passed through the Pt film highlighted in red. $Q_C$ is the heat generated in the coil and $Q_L$ is the heat generated in each of the beams. It is assumed to half of $Q_L$ flows to the substrate and the other half flows into the membrane.

Figure 3.7: Thermal circuit of the measurement device with a nanowire. $1/G_b$ is the thermal resistance of six beams on either side of the device. $1/G_{nw}$ is the combined thermal resistance of the nanowire and the platinum silicon interface. $T_H$, $T_S$ and $T_O$ are the temperatures of the heating membrane, sensing membrane and the substrate respectively.

From the thermal circuit shown in Figure 3.7, the thermal conductance of the nanowire is obtained as described below. By using the Fourier law of heat conduction under steady state conditions, we get
Combining Equations 3.1 and 3.2, we get

\[ G_b = \frac{Q_H + Q_L}{(T_H - T_O) + (T_S - T_O)} \]  

3.4

Once the value of \( G_b \) is obtained, the thermal conductance of the nanowire \( G_{nw} \) is obtained using Equation 3.3 as

\[ G_{nw} = G_b \frac{(T_S - T_O)}{(T_H - T_S)} \]  

3.5

### 3.3 Instrumentation

From Equations 3.4 and 3.5, it is quite apparent that we need to measure \( T_H, T_S \), and \( Q_C + Q_L \) to obtain the thermal conductance and thereby the thermal conductivity of the nanowire. To measure the above mentioned quantities, a variety of instruments are connected to the fabricated device. In this section, the instrumentation that comprises the measurement setup and their purpose is described. The measurement setup comprises of five SR-830 lock-in amplifiers, a Keithley DC current source and two 20 MΩ high precision resistors [26]. The instruments are connected to the nanowire bearing device as shown in the schematic Figure 3.8.
Figure 3.8: Schematic of the measurement set-up. The measurement setup comprises of five lock-in amplifiers, a DC current source and two high precision resistors connected to the device as shown in the figure.

An SR-830 lock-in amplifier has two functionalities. It has an internal oscillator which can output sinusoidal signals with amplitude of 0 to 5 V and frequency in the range of 1 mHz to 102.4 kHz. Secondly, it can isolate a signal of one particular set frequency from any noisy signal and output the voltage/current value of the isolated signal. The frequency of the signal to be isolated/generated can be directly programmed or can be input to the lock-in amplifier by sending a sinusoidal signal at the desired frequency through its reference port. The function of current source and the high precision resistors is self explanatory.

A constant DC current in the range of 0 to 4 μA is applied across the terminals B_H and E_H using the Keithley current source. This DC current generates joule heating in the two beams and the coil through which it flows. As described in the thermal circuit in the previous section, the heat generated flows to the substrate at set temperature T_0 through the nanowire and the twelve beams. As a result, the temperatures of the heating and sensing membranes rise from the set bath
temperature $T_O$ to $T_H$ and $T_S$ respectively. Due to increased temperature of the membranes, the electrical resistance of the platinum coils also increases from base resistance $R_{H0}$ and $R_{S0}$ to $R_H$ and $R_S$ respectively. $R_{H0}$ and $R_{S0}$ are the resistances of the platinum coils in heating and sensing membranes when no DC current is applied.

By exploiting the linear correlation of Pt coil resistance to the membrane temperature, the temperature rise $T_H$ and $T_S$ are obtained by measuring the resistances $R_H$ and $R_S$ respectively. After the DC current is applied and the steady state is achieved, the platinum coil resistances are measured by passing a small additional AC current (~250 nA) through each of the coils and measuring the corresponding voltage difference $V_{AC}$ across the coil.

The resistance of the platinum coil in the heating membrane $R_H$ is measured as follows. The sine output from the lock-in amplifier-1 is set to an amplitude of 5 V and frequency $f_1$ and is applied across the series connection of a 20 M$\Omega$ high precision resistor and the platinum line between the terminals $B_H$ and $E_H$. The resulting AC current $I_{AC}$ at the set frequency $f_1$ is measured by Lock-in amplifier-1. The purpose of the 20 M$\Omega$ high precision resistor is to make the resulting ac current very small thereby reducing its joule heating contribution.

The sine output from lock-in amplifier-1 is also connected to the frequency reference input port of lock-in amplifier-2. Now, using the lock-in amplifier-2, the voltage $V_{AC}$ at frequency $f_1$ is measured across the terminals $A_H$ and $D_H$. Using $V_{AC}$ and $I_{AC}$, the resistance of the platinum coil is obtained using Ohm’s law as $V_{AC}/I_{AC}$. In a similar fashion, to measure the resistance $R_S$ of the platinum coil in the sensing membrane, Lock-in amplifier-3 is used at frequency $f_2$ to generate and measure AC current across terminals $B_S$ and $E_S$ and Lock-in amplifier-4 is used to measure corresponding AC voltage.
To measure the quantity $Q_C+Q_L$ required in Equation 3.4, a fifth lock-in amplifier is used on the heating side. Lock-in amplifier-5 takes its frequency reference from Lock-in amplifier-1 and measures the combined resistance $R_C$ of the coil and 1 beam across the terminals A$_H$ and E$_H$. By simply using the expression for joule heating, the quantity $Q_C+Q_L$ is obtained as

$$Q_C + Q_L = R_C l_{DC}^2$$

\[3.6\]

### 3.4 Data analysis and Results

In this section, the method of analyzing the data from the instruments to obtain the thermal conductivity of the nanowire at any temperature $T$ is described.

The DC current from the Keithley current source is varied from -4 $\mu$A to 4 $\mu$A in steps of 0.05 $\mu$A. At each DC current step, a wait time of 1.5 second is allowed for the heat flow to reach a steady state. Under the steady state conditions, the coil resistances $R_H$ and $R_S$, the combined beam and coil resistance $R_C$, and the heat quantity $Q_C+Q_L$ are measured as described in the previous section. The $R_H$ and $R_S$ values are plotted as a function of applied DC current as shown in Figure 3.9.
Figure 3.9: Change in resistance of the platinum coil in the heating and sensing membranes at one particular bath temperature.

The parabolic nature of the curve is expected for the following reason. The resistance of the coil varies linearly with temperature which in turn varies linearly with the heat generated in the coil. However, the heat generated in the coil varies as the square of the DC current applied. As a result, the resistances of the platinum coils $R_H$ and $R_S$ have a parabolic relationship with the applied DC current $I_{DC}$.

This measurement is repeated at various bath temperatures $T_O$ from 10 K to 300 K. The bath temperature is varied by using Liquid He and a PID temperature controller. At each bath temperature $T_O$, the resistance values of the platinum coils $R_H$ and $R_S$ at zero DC current are
taken as the base resistances $R_{H0}$ and $R_{S0}$ that temperature. The base resistance values at each bath temperature are plotted to obtain $R$ vs. $T$ calibration plots as shown in Figure 3.10.

Figure 3.10: Resistance of the platinum coil in the heating and sensing coil as a function of temperature. The plot shown is used as a calibration plot to obtain the temperature rise of the membranes from the measured change in resistances in Figure 3.9.

Using the resistance and temperature data, the value of $dR/dT$ at each temperature is obtained for both heating and sensing membranes. The dependence of $dR/dT$ is shown as a function of bath temperature in Figure 3.11. The temperature rise in the heating and sensing membranes $T_H$ and $T_S$ is estimated at each DC current step using the expression

$$T_H = T_O + \frac{dR_{H0}}{dt} \Delta R_H$$

3.7
Figure 3.11: Temperature coefficient of resistance of the platinum coil in the heating and the sensing membranes as a function of temperature. The value of $dR/dt$ at each bath temperature is obtained from the calibration plot in Figure 3.10 using central differencing method.

Further, the quantity $Q_C+Q_L$ at each DC current step is obtained using Equation 3.6 and is plotted against the sum of temperature rise in both membranes, $(T_H-T_O) + (T_S-T_O)$ as shown in Figure 3.12. This plot is expected to be linear because the values along both the coordinates vary as a square of applied DC current $I_{DC}$. It follows from Equation 3.4 that the slope of this linear plot gives us the combined thermal conductance of six beams on each side.
Figure 3.12: Heat generated in the platinum coil and a beam on the heating side plotted as a function of sum of temperature rise in the heating and the sensing side. The slope of the linear fit, shown in red, gives the combined thermal conductance $G_b$ of six beams on each side.

Now, using Equation 3.5, the thermal conductance of the nanowire is obtained as the slope of the linear fit of $G_b\cdot(T_S-T_O)$ as a function of temperature difference across the nanowire $T_H-T_S$. The thermal conductivity of the nanowire is then obtained from the thermal conductance by using

$$k_{nw} = G_{nw}L/A$$

where $L$ and $A$ are the length and cross sectional area of the nanowire which are obtained by SEM and TEM imaging of the nanowire. The data analysis described so far is done for each bath temperature $T_O$ to calculate the thermal conductivity at all temperatures. The thermal conductivity of a silicon nanowire as a function of temperature is shown in Figure 3.13.
Figure 3.13: Thermal conductivity of a single silicon nanowire as a function of temperature.

It can be seen from Figure 3.13 that the thermal conductivity of a single silicon nanowire is over ten times smaller than the thermal conductivity of bulk silicon (~150 W/mK). However, further measurement of electrical and Seebeck coefficient needs to be done to establish silicon nanowire as a formidable candidate for thermoelectric applications.
4 SUMMARY AND CONCLUSIONS

A theoretical model has been developed to calculate the conversion time characteristics of carbonation reaction of CaO nanoparticles. The model is developed by modifying the random pore model and superposing it with the shrinking core model. The conversion time characteristics calculated for various particle sizes suggest that the CaO particles enable higher and faster absorption and energy storage when the particle size is less than a micrometer. The faster conversion is attributed to increasing contribution of the reaction on the external surface of the particle towards total conversion. The external surface area reducing factors such as sintering of nanoparticles reduce the absorption and storage capability of CaO nanoparticles over repeated cycles. Therefore, it is advisable to use CaO nanoparticles dispersed on a scaffolding structure which can prevent loss of external surface area in order to obtain sustainable CO₂ absorption and energy storage capabilities.

Thermoelectric devices made of various kinds of materials can be used to harvest waste heat. An experimental methodology to characterize the thermoelectric figure of merit of low dimensional structures is put forth. The candidacy of silicon nanowire as a thermoelectric material has been partially established by demonstrating the reduction in thermal conductivity as we transition from bulk to nanowire structure.

Future experimental work should be focused on establishing favorable electrical conductivity and Seebeck coefficient of silicon nanowires. A further study on the effect of surface texture on the thermoelectric figure of merit needs to be studied. In parallel, several other materials in their low dimensional form needs to be studied.
APPENDIX

Further details of the single nanowire measurement device fabrication process are presented in the table below:

<table>
<thead>
<tr>
<th>Process</th>
<th>Name</th>
<th>Description</th>
<th>Additional details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preparation</td>
<td>Cleaning</td>
<td>Hot Acid Bath or Acetone/Methanol 1' 5'@150C</td>
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</tr>
<tr>
<td></td>
<td>Dehydration bake</td>
<td></td>
<td></td>
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<tr>
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<td>Stress measurement</td>
<td>First curvature scan</td>
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<td>Nitride</td>
<td>Nitride deposition</td>
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<td>CHA evaporation</td>
<td>Ti deposition</td>
<td>deposit 10 nm Titanium on back side</td>
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<tr>
<td>STS PECVD</td>
<td>Nitride deposition</td>
<td>50nm on backside</td>
<td>19 min for 300 nm</td>
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<td>30s @ 6000 rpm backside</td>
<td>TEM backside window patterning</td>
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<td>AZ 5214 30s@6000 rpm (1000 rpm dispense, 1000 rpm/s ramp)</td>
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<tr>
<td></td>
<td>Soft bake</td>
<td>2'@110C</td>
<td>Mask4</td>
</tr>
<tr>
<td></td>
<td>Exposure</td>
<td>12s (HC)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Development</td>
<td>MF319/ 1.5 min / DI water rinse</td>
<td>DI water wash only</td>
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<td>Hard bake</td>
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<td></td>
<td>O2 Descum</td>
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<td>Ti O2 Plasma</td>
<td>Transfer the pattern from PR to 50nm nitride layer</td>
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<td>Etch nitride</td>
<td>Transfer pattern from 50nm SiNx to Ti</td>
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<td>Patten Ti</td>
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<td>KOH wet etching</td>
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<td>Remove front side nitride while protecting backside with PR</td>
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<td>- Si wafer</td>
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<td>Exposure</td>
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</tr>
<tr>
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<td>Development</td>
<td>MF319/ 1.5 min / DI water rinse</td>
<td>DI water wash only</td>
</tr>
<tr>
<td>O2 Descum</td>
<td>Hard bake</td>
<td>2'@110C</td>
<td>~10nm/min</td>
</tr>
<tr>
<td></td>
<td>TI O2 Plasma</td>
<td>~25' (until remaining PR of exposed area is gone)</td>
<td></td>
</tr>
<tr>
<td>PlasmaLab Freon RIE Nitride</td>
<td>Nitride RIE etching</td>
<td>50nm nitride patterning (?' w/ Process 4 (CF4) ~ ??nm/min, Use D2)</td>
<td>PR etch rate:~30nm/min</td>
</tr>
<tr>
<td>PR removal</td>
<td>PR removal</td>
<td>Acetone/methanol/DI water 5' &amp; Aleg 355@70C for 10'</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TI O2 Plasma</td>
<td>30'</td>
<td></td>
</tr>
<tr>
<td>Ar Ion Milling</td>
<td>PlasmaLab Master RIE</td>
<td>Ar 10%/Pressure &lt;30mT/RF 90% (~300W) for 35min</td>
<td>Nitride etch rate: 0.3nm/min</td>
</tr>
<tr>
<td>Plasmalab Freon RIE Nitride</td>
<td>Nitride RIE etching</td>
<td>Nitride mask removal</td>
<td></td>
</tr>
<tr>
<td>STS PECVD Nitride</td>
<td>EtchDep/Predep (If necessary)</td>
<td></td>
<td>~40min</td>
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</table>

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<table>
<thead>
<tr>
<th>Nitride deposition - Si wafer</th>
<th>300nm nitride deposition (17' @ MF ~ 175 Å/min)</th>
<th>Use dummy wafer pieces (D1,D3)</th>
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<tbody>
<tr>
<td>Stress measurement</td>
<td>Nitride stress measurement</td>
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</tr>
<tr>
<td>Photolithography (Quintel)</td>
<td>HMDS 30s @ 5000 rpm</td>
<td>Nitride structure patterning ~1.4µm</td>
</tr>
<tr>
<td></td>
<td>PR coat AZ 5214 30s@5000 rpm (1000 rpm dispense, 1000 rpm/s ramp)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Soft bake 2'@110C</td>
<td></td>
</tr>
<tr>
<td>Exposure</td>
<td>15s (HC)</td>
<td>Mask2</td>
</tr>
<tr>
<td>Development</td>
<td>MF319/ 50-60&quot; / DI water rinse</td>
<td>DI water wash only</td>
</tr>
<tr>
<td>Hard bake</td>
<td>2'@110C</td>
<td></td>
</tr>
<tr>
<td>O2 Descum</td>
<td>TI O2 Plasma 5'</td>
<td></td>
</tr>
<tr>
<td>PlasmaLab Freon RIE</td>
<td>Nitride RIE etching 600nm nitride patterning (22' w/ Process 4 (CF4) ~ 30nm/min, Use D1)</td>
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<tr>
<td>PR removal</td>
<td>PR removal Acetone/methanol/DI water 5' &amp; Aleg 355@70C for 10'</td>
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</tr>
<tr>
<td>TI O2 Plasma</td>
<td>30'</td>
<td></td>
</tr>
<tr>
<td>Photolithography (Quintel)</td>
<td>HMDS 30s @ 5000 rpm</td>
<td>Windows patterning</td>
</tr>
<tr>
<td></td>
<td>PR coat AZ 5214 30s@5000 rpm (1000 rpm dispense, 1000 rpm/s ramp)</td>
<td>~1.2µm</td>
</tr>
<tr>
<td></td>
<td>Soft bake 2'@110C</td>
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<tr>
<td>Exposure</td>
<td>20s (HC)</td>
<td>Mask3</td>
</tr>
<tr>
<td>Development</td>
<td>MF319/ 50-60&quot; / DI water rinse</td>
<td>DI water wash only</td>
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<tr>
<td>O2 Descum</td>
<td>Hard bake 2'@110C</td>
<td></td>
</tr>
<tr>
<td>PlasmaLab Freon RIE</td>
<td>Nitride RIE etching 300nm nitride patterning (11' w/ Process 4 (CF4) ~ 30nm/min, Use D3)</td>
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</table>

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<table>
<thead>
<tr>
<th>Dicing</th>
<th>Dicing saw</th>
<th>PR removal</th>
<th>Acetone/methanol/DI water 5' &amp; Aleg 355@70C for 10'</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR removal</td>
<td>PR removal</td>
<td>Tl O2 Plasma</td>
<td>30'</td>
</tr>
<tr>
<td>Structure release</td>
<td>KOH etch</td>
<td>Structure release</td>
<td>KOH etch</td>
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REFERENCES


