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ELECTRONICALLY CLOAKED NANOPARTICLES

By

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ABSTRACT OF THE THESIS

ELECTRONICALLY CLOAKED NANOPARTICLES

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The concept of electronic cloaking is to design objects invisible to conduction electrons. The approach of electronic cloaking has been recently suggested to design invisible nanoparticle dopants with electronic scattering cross section smaller than 1% of the physical cross section (πa^2) , and therefore to enhance the carrier mobility of bulk materials. The proposed nanoparticles have core-shell structures. The dopants are incorporated inside the core, while the shell layer serves both as a spacer to separate the charge carriers from their parent atoms and as a cloaking shell to minimize the scattering cross section of the electrons from the ionized nanoparticles. Thermoelectric materials are usually highly doped to have enough carrier density. Using invisible dopants could achieve larger thermoelectric power factors by enhancing the electronic mobility. Coreshell nanoparticles show an advantage over one-layer nanoparticles, which are proposed in three-dimensional modulation doping. However designing such nanoparticles is not easy as there are too many parameters to be considered. This thesis first shows an approach to design hollow nanoparticles by applying constrains on variables. In the second part, a simple mapping approach is introduced where one can identify possible core-shell particles by comparing the dimensionless parameters of chosen materials with

provided maps. In both parts of this work, several designs with realistic materials were made and proven to achieve electronic cloaking. Improvement in the thermoelectric power factor compared to the traditional impurity doping method was demonstrated in several cases.

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Chapter 1: Introduction of Thermoelectric

Thermoelectric Materials and Devices

Thermoelectric effects were first reported by Seebeck in 1821. In his experiments, a compass needle was deflected if placed in the vicinity of closed loop, consisting of two dissimilar conductors, when one of the junctions was heated^[1]. The Seebeck effect is described by

$$\Delta V = -S\Delta T \tag{1-1}$$

where ΔV is the voltage generated by the Seebeck effect, S is the Seebeck coefficient and ΔT is the temperature gradient. Thirteen years later, Peltier effect was discovered by Peltier by finding temperature changes in the junction of different conductors with passing electrical current. However, the nature was not rightly explained until 1838 by Lenz. The heat generation rate \dot{Q} by Peltier effect is given by

$$\dot{Q} = (\Pi_A - \Pi_B) I \tag{1-2}$$

where Π_A and Π_B are the Peltier coefficients of different conductors at the junction, *I* is the electrical current. The connection $\Pi = TS$ between the Seebeck and the Peltier effect was explained by Thomson in 1851, who also proposed the Thomson effect, the third effect of thermoelectric effect. The Thomson effect describes a heat production rate \dot{q} by

$$\dot{q} = -\chi J \cdot \nabla T \tag{1-3}$$

where J is the current density and χ is the temperature dependent Thomson coefficient.

Fig. 1-1 shows typical thermoelectric systems. One can use temperature difference to generate electricity by the Seebeck effect as shown in **Fig. 1-1(a)** or achieve the opposite process by the Peltier effect as shown in **Fig. 1-1(b)**.



Figure 1-1. (a) Thermoelectric generator; (b) Thermoelectric cooler

Optimization of Thermoelectric Devices

Given a temperature difference, the term named by power factor is used to describe the ability of one material to generator electrical power. The power factor is given by

$$Power \ factor = \sigma S^2 \tag{1-4}$$

where S is the Seebeck coefficient, and σ is the electrical conductivity. Though materials with higher power factor could generate more energy for given temperature distribution,

high power factor cannot guarantee a high efficiency. The efficiency is tightly related to the thermal property of the system, which can affect the temperature distribution in a thermoelectric system.

The efficiency of a thermoelectric electricity generator is defined by the ratio of energy provided to the load and heat absorbed at the hot junction. The performance of a given material could be described by a dimensionless figure of merit given by

$$ZT = \frac{\sigma S^2 T}{\lambda} \tag{1-5}$$

which includes the Seebeck coefficient S, thermal conductivity λ , electrical conductivity σ and temperature T.

The maximum efficiency of a thermoelectric generator can be estimated by

$$\eta_{max} = \frac{T_H - T_C}{T_H} \cdot \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_C}{T_H}}$$
(1-6)

where T_C and T_H are the cold and hot junction temperature.

For thermoelectric cooler which use electricity to pump heat from cold side to hot side, the maximum coefficient of performance is given by

$$COP_{max} = \frac{T_C}{T_H - T_C} \cdot \frac{\sqrt{1 + ZT} - \frac{T_H}{T_C}}{\sqrt{1 + ZT} + 1}$$
(1-7)

From Eqn. (1-6) and (1-7), an infinite ZT value would maximize η_{max} up to $\frac{T_H - T_C}{T_H}$ and COP_{max} to $\frac{T_C}{T_H - T_C}$, which correspond to a Carnot engine and a Carnot refrigerator respectively.

To optimize the thermoelectric system, there are two directions; 1) optimizing the material properties^[2,3], which is to improve the ZT value; 2) designing a better system.

Semiconductors, ceramics and polymers are usually used as thermoelectric materials. Semiconductors, the most common thermoelectric materials, could have Seebeck coefficients larger than 100 μ V/K. An alloy of Pb_{1-x}Mn_xTe was proved to reach ZT=1.6 at 700K by Pei et al. in 2012.^[4] A summary of the figure of merit ZT value for good thermoelectric materials is given in several review papers^[5,6].

Most of high ZT materials have high ZT only in mid-to-high temperature ranges and are composed of toxic, rare, and heavy elements, and can be melted or oxidized at high temperature in air^[7]. Ceramics have advantages in chemical stability and low cost, and can be used to make more durable devices. Metal oxides (SrTiO₃, CaMnO₃, Ca₃Co₄O₉, In₂O₃), Ti sulfides, and Mn Silicides are some promising thermoelectric material candidates at a temperature range of 300-1200K in air.^[8] Modules of cascade-type and segment-type (**Fig. 1-2**) with several different materials are usually designed to achieve a wide working temperature range.



Figure 1-2. Schematic illustrations of cascade-type thermoelectric modules. (from paper of Koumoto et al.^[8])

Using polymers as thermoelectric materials can also help solve issues such as toxicity and resource shortage. Polymer thermoelectric devices are attracting wide interests due to their flexibility, low-cost and solution processability.^[9,10] Though the thermoelectric properties of conjugated-polymers are currently lower than well-studied inorganic materials,^[11,12] they can be applied to flexible electronics and all-polymer artificial skins.^[13] Though usually higher electrical conductivity leads to lower Seebeck coefficient and higher thermal conductivity, a type of conjugated/ insulating polymer blends with interpenetrating morphology could achieve higher electrical conductivity, lower thermal conductivity without sacrificing the Seebeck coefficient.^[13]

During 1960-1990, thermoelectric industry grew slowly but steadily, mainly because of the merit of application for space activities, labs and medical purposes, where a quiet and reliable equipment is required. The field of thermoelectric witnessed dramatic growth in the last 15 years by introducing the concept of nanostructuring^[5,14]. There are two dominant ideas for low-dimensional materials. Firstly, introduction of nanoscale constituents would introduce quantum-confinement effect to enhance the power factor. The second one is designing internal interfaces in nanostructures to reduce the thermal conductivity more than the electrical conductivity.^[15,16] Recently, these two approaches seems to be combined.^[14] Two reasons were given in Dresselhaus's review paper. At first, the best bulk thermoelectric materials contain nanoscale inclusions^[17]. Secondly, nanocomposites made of low-dimensional materials are now being embedded in host materials^[18], therefore bringing about a lot of interfaces that scatter phonons more effectively than electrons.

Nanostructuring of semiconductors is widely applied to commercial products such as high electron mobility transistors and lasers because of electron wave effects and quantum confinement. However, up to now the primary benefit of nanostructuring for thermoelectric materials has been the effect on thermal properties, rather than electronic properties.^[5]

One approach of improving ZT is by modulation doping via increasing the electron mobility^[19]. Modulation doping is firstly proposed by Dingle and Störmer in 1970s, the latter of whom was awarded the Nobel Prize in Physics 1998. Modulation doping gained Störmer a permanent position at Bell Labs.^[20] Modulation-doped heterostructures are materials containing nonuniform distributions of dopant atoms and embodying heterostructures to guide carriers and separate them from impurities.^[21] The first modulation doped heterostructures were MBE-grown GaAs-Al_xGa_{1-x}As superlattices

with modulated silicon doping.^[22] This technology has been applied to thin film devices to optimize electron transport in the in-plane direction. The modulation doped structure usually have 3 main parts, an undoped layer as channel for electrons, a doping layer to provide enough carriers, and an undoped layer as an insulation between ionized dopants and the channel. By this design, there is less impurity scattering for carriers travelling in the in-plane direction and could improve electron mobility while providing enough conduction carriers.

Recently the concept of modulation doping was applied to bulk nanocomposite thermoelectric materials.^[23] In that work, a small part of silicon nanograins are doped and mixed with undoped SiGe host nanograins. Then the mixture of grains is pressed to produce a bulk material. The interfaces are separated by about 20nm and carriers could flow through the device given that the screening length is 5-10nm. For the demonstrated case, the power factor was improved by 40% when compared with uniformly doped host, as shown by **Fig. 1-3**. This improvement is mainly by enhancing electron mobility and the thermal conductivity was increased. Thermal conductivity enhancement from larger electrical conductivity is inevitable, but other parts from lattice thermal conductivity could be reduced by methods such as adding alloys into materials. Modulation doping is most useful at low temperatures since 1) phonon scattering is the main scattering mechanism at a high temperature; 2) most of impurities stay unionized at low temperature.^[19]



Figure 1-3. Demonstration of enhanced power factor using the modulationdoping technique. Left: power factor of a p-type modulation-doped sample, $(Si_{80}Ge_{20})_{70}(Si_{100}B_5)_{30}$ (black squares), compared to the uniformly alloyed single-phase nanocomposite sample $Si_{86}Ge_{14}B_{1.5}$ (red filled circles) and to the p-type SiGe bulk alloy used in RTGs for space power missions (solid line). Right: schematic view showing the modulation doping scheme. Impurities are incorporated only inside nanoparticles. (from Dr. Mona Zebarjadi's recent paper^[19])

Chapter 2: Electronic Cloaking and Anti-resonant Scattering

Electronic Cloaking

Modern materials design has enabled us to tune materials properties and design materials with unprecedented characteristics, which cannot be found in nature. The introduction of metamaterials has paved the way for an entirely new venue in future technologies.

A key advance in metamaterial design is the cloaking concept, i.e. design of objects invisible to a particular range of waves. This concept has been transposed to different fields to realize materials with extreme properties and to design new devices. Electromagnetic or optical cloaking was proved possible by using transformation-optics method^[24,25] and scattering cancellation via homogeneous and isotropic shells^[26].

The nature of transformation optics is that a coordinate transformation in Maxwell equations is equivalent to a mapping between material properties distributions in two spaces.^[27] The transformation could be expressed by conformal mapping^[24], which connects virtual space and physical space in two dimensions. More details about conformal mapping are explained by Box 1 of Dr. Huanyang Chen's paper^[28]. This theory has been applied to devices such as invisible cloaks^[24,25], carpet cloaks^[29,30], field concentrators^[31] and rotators^[32]. As for acoustic cloaking, it has unique features and is not analogous to electromagnetic cloaking^[33]. Cloaking materials must have subwavelength scale structure. In principle, acoustic wavelengths, much larger than optical wavelengths, make the design of acoustic cloaking easier. It has been shown that acoustical parameters in the cloak should be anisotropic to achieve acoustic

cloaking.^[34,35] Recently, experiments were done to demonstrate thermal cloaking in a copper plate^[36] and thermally conductive sealant^[37].

In analogy to the examples above, electronic cloaking^[38–42] could be used for quantum sensing^[40]. The theory of transformation optics requires anisotropic properties, together with the truth that effective mass and/or potential is variant is space, make the application of transformation optics hard for electronic cloaking.^[39] Zebarjadi et al. introduced the idea of electronic cloaking based on scattering cancellation with the promise of designing advanced semiconductors with extremely high electrical conductivities^[39] and enhanced thermoelectric properties^[38]. Using 2D electronic cloaking, they proposed new 2D devices^[43] such as filters, sensors and switches.

In the work done by Liao et al.^[39], partial wave method was used to calculate the scattering cross section by a finite spherically symmetric potential. The governing formula is given by

$$\sigma = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \delta_l \tag{2-1}$$

here δ_l is the phase shift of the *l*th partial wave, k is the wave number. The total scattering cross section is a summation of all the partial waves, however the contribution of high order one is low and could be negligible. The strategy is to make scattering of the first two partial waves relatively small and reach an almost zero total scattering. By analyzing the function of potential barrier and well, they concluded that a combination of a barrier and a well produced by core-shell nanoparticle is the key to achieve the goal

above. At specific electron energy range, a total scattering cross section less than 0.01% could be realized with proper artificial core-shell nanoparticle design.

Application of Anti-resonant Scattering to Thermoelectric Materials

Semiconductor materials are usually doped with a high concentration of external impurity atoms to provide the required level of conduction carrier (electrons/holes) densities for a good electronic performance. The electrical conductivity, σ of a material is proportional to the product of the charge carrier density and its mobility ($\sigma = ne\mu$). Carrier mobility, μ , characterizes how fast conduction carriers move through a solid-state material. It depends on the interaction potential of the scattering centers with the conduction carriers and therefore could be manipulated by using the freedom of design and engineering the interaction potential of the scattering centers. By cloaking the carrier donating centers, carrier mobility could be significantly improved^[23].

Carrier mobility is a key material parameter in determining the performance of semiconductor-based devices such as transistors, LEDs, solar cells, thermoelectric, etc.^[44–46] Increased charge carrier mobility for many applications is desired for enabling an increase in the electrical conductivity of semiconductor devices, and almost always leads to better device performances with other parameters being equal. The approaches of scattering cross section cancellation^[39] and transportation optics^[42] were proved to improve carrier mobility.

A good thermoelectric material needs large Seebeck coefficient, electrical conductivity, and small thermal conductivity per discussed in the first chapter. The concept of electronic cloaking was applied to optimize thermoelectric materials.^[38] Different from using resonant carrier scattering to improve thermoelectric power factor,^[47] Zebarjadi et al. used anti-resonant scattering method. A cartoon of the core-shell nanoparticle is shown in Fig. 2-1. The calculation results are shown in Fig. 2-2. By this approach, electrical conductivity could be improved for lower scattering cross section for conduction carriers. It is known that the Seebeck coefficient could be enhanced when there are sharp features in the differential conductivity, $\sigma(\varepsilon) = q^2 \tau(\varepsilon) v^2(\varepsilon) DOS(\varepsilon)$, with respect to electron energy, ε .^[14,48] Introducing cloaking windows could result in sharp features in the relaxation times, $\tau(\varepsilon)$, and therefore in the differential conductivity and could enhance the Seebeck coefficient as discussed in an earlier publication.^[38] In addition, potentially, electronically cloaked dopants can lower the thermal conductivity since they are not invisible to phonons. For example, in the case of electronically cloaked core-shell nanoparticles, if the combination of core, shell and host materials is chosen to have large acoustic mismatch, they could scatter phonons significantly. This is not in conflict with nanoparticles being transparent to electrons. Therefore, incorporation of invisible nanoparticle dopants could potentially improve all the three thermoelectric parameters simultaneously.



Figure 2-1. Cartoon of the nanoparticle. The dashed line is from band offset and the solid line shows the potential profile after considering charge transfer. (adapted from the work of Zebarjadi et al.^[38])



Figure 2-2. Thermoelectric properties calculated for GaAs at temperature T = 50 K. Four different types of dopants are plotted: regular impurities (imp), traditional nanoparticles (npt), and two different core-shell structured nanoparticles (np1 and np2). Here the properties of np1 and np2 were manually tuned. (from the work of Zebarjadi et al.^[38])

Chapter 3: Combinatorial Approach to Identify Electronically Cloaked Hollow Nanoparticles

The possibility of designing core-shell nanoparticles which are "invisible" to the conduction electrons has been demonstrated as introduced in last chapter. A total scattering cross section smaller than 0.01% of the physical cross section was demonstrated by artificially adjusting the parameters of barrier and the well in a core-shell geometry. In this part, we aim to extend the developed concept and find realistic materials combinations that satisfy the cloaking criteria. We report designs of hollow nanoparticles, which could be used to realize the cloaking concept in III-V semiconductor host matrices. Such particles could be used in advanced materials design to enhance and tune the electrical and the thermoelectric properties of a given host matrix. This work may also contribute to defect engineering by coating defect sites with a proper cloaking layer.

For semiconductors, the external impurity atoms used for doping act as scattering centers and randomize the motion of conduction carriers, thus limiting their mobility. In our previous study, we demonstrated that it is possible to replace conventional dopants with invisible dopants^[38]. In order to realize this goal, we added all the dopants inside spherical nanoparticles, and then designed a cloaking cover around the nanoparticles to make them invisible to the conduction electrons. The nanoparticles used, therefore, had core-shell structure. These nanoparticles were artificial as their band-offsets (between core and shell and between shell and host) and effective masses were tuned numerically to satisfy the cloaking conditions, i.e. the scattering cross section was small enough to be considered negligible. For real materials, band offsets and effective masses are set by the nature of the material and might not be consistent with adjusted parameters. Therefore, the designed nanoparticles in the previous work might not correspond to any realistic material. By using artificial nanoparticles, an order of magnitude increase in the electrical conductivity and consequently, the thermoelectric power factor of GaAs at low temperatures was demonstrated. In addition, it was speculated that the nanoparticles might reduce the thermal conductivity^[49], if materials with large acoustic mismatch is used for the core-shell.

The question is the possibility of designing realistic core-shell nanoparticles with real material properties as the input and investigate their effectiveness on improving the electrical conductivity and enhancing the Seebeck coefficient of a given host matrix, which is the focus of this chapter.

This chapter is organized in the following manner: a combinatorial search algorithm is proposed to obtain proper material characteristics that may achieve electron cloaking. Then the results for several host matrices are reported. Finally, a complete optimization is reported for one of the materials combinations.

Methodology

The cross section of scattered waves by a spherically symmetric potential is calculated by the partial wave method^[50]. The total cross section of electrons with a specific incident energy is given as **Eqn. 2-1**, $\sigma = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) sin^2 \delta_l$, where δ_l is the phase shift of the l^{th} partial wave and $k = \frac{\sqrt{2m_0E}}{\hbar}$ is the wave number. m_0 is the effective mass of the host matrix and *E* is the energy of electron.^[39]

The phase shifts of higher-order partial waves are small and could be neglected if their angular momentums, l is larger than ka (l>ka), where a is the outer radius of the nanoparticle.^[50] Thus, a negligible total scattering cross section could be achieved by eliminating scattering cross section of the first two partial waves and using ka values close to or less than one.

To reduce the number of variables and simplify the search, we use hollow nanoparticles whose core is a vacuum. Today, many different hollow nanoparticles such as PbTe^[51], gold^[52], Cu₂O, ZnS, ZnO, and many others were fabricated successfully^[53], making the choice of hollow nanoparticle possible. In this work, we only consider such hollow nanoparticles as shown in **Fig. 3-1**. In this figure, *a* and *a_c* are the radii of the core and the shell. *m_{core}*, *m_{shell}*, *m_{host}* are the effective mass for vacuum, shell and host material respectively. *E_{c,host}* and *E_{c,shell}* are the conduction levels of host and shell. ΔE_{c1} and ΔE_{c2} is the band offset of the core-shell and the shell-host. We assume that the bands are aligned according to the Anderson's rule.



Figure 3-1. Structure of hollow nanoparticle

We used a combinatorial approach to find proper materials combinations. For an efficient search, we started from a rough scan, which ignores charge transfer and band bending. For a given host material and targeted hollow nanoparticles, the only relevant parameters which may affect the scattering cross section are electron incident energy (*E*), core size (*a_c*), shell size (*a*), the shell layer's effective mass (*m_{shell}*) and the band-offset between the shell and the host (ΔE_{c2}).

Small nanoparticles correspond to smaller ka values, which corresponds to faster decay of high-order partial wave terms in **Eqn. 2-1**. For a small size nanoparticle, there is a better chance of having negligible high-order partial waves. However a_c and a cannot be too small for practical purposes. We set $a_c=1$ nm and $a=2\sim3$ nm for our rough scan. If we do not see a cloaking point for such small particles, the chances of observing cloaking for larger particles would be small, as reflected by the trend of **Fig. 3-2**.



Figure 3-2. The effect of shell properties on the normalized scattering cross section (%) contours. The scattering cross section is calculated for Ga_{0.2}In_{0.8}As (as the host matrix) with a fixed electron energy E=150meV. The size of the vacuum core is also fixed at $a_c=1$ nm. We then scan the possible effective masses and band offsets for the shell to identify proper shells. (a) a=20Å, (b) a=22Å, (c) a=24Å, (d) a=26Å.

For thermoelectric applications, heavily doped semiconductors are used and the optimum Fermi level (the Fermi level corresponding to the optimum power factor) is known for a given thermoelectric material. For example GaAs optimum Fermi level at room temperature is around 63meV above the conduction band edge, which is calculated from optimum carrier density^[54]. Since only electrons in the Fermi window contribute to the transport, the electron incident energy should be set only to values close to the optimum Fermi level.

Setting all of the parameters as described above, we only need to scan for the two remaining parameters, which are ΔE_{c2} and m_{shell} . It is then feasible to plot the scattering cross section versus these two parameters and set upper and lower bounds for them. Once the ranges are determined, one can look up a materials database and find proper shell materials whose effective masses and band-offsets with the host matrix falls in the determined range.

Our criteria for selecting the parameters range is when electron-nanoparticle scattering cross section less than 1% of the physical cross section (πa^2) is achieved. We refer to this region as the *cloaking region*. After obtaining a proper shell material from the rough search, we further optimize the size and the doping density of the embedded hollow nanoparticles in the given host matrix.

Fig. 3-2 shows the total electron-nanoparticle scattering cross section at incident energy E=150meV versus m_{shell} and ΔE_{c2} . The host material is Ga0.2In0.8As; the outer radius of the shell is increased slowly from Fig. 3-2 (a) to (d). The bright region in Fig. 3-2, which corresponds to scattering cross section less than 1% of the physical cross section, is the cloaking region. From these results we can determine that the value of proper m_{shell} is generally around 0~0.1m0 (m0 is the mass of electron), and ΔE_{c2} is around -0.2eV~0eV for Ga0.2In0.8As being the host matrix. We refer to this range of values as cloaking range of each parameter. The cloaking region becomes smaller, and moves towards the coordinate's origin as the nanoparticle size increases. That is, cloaking range of m_{shell} and

 ΔE_{c2} shrinks and shifts to smaller values for larger nanoparticles. With a fixed shell thickness as shown in **Fig. 3-3**, the cloaking region also decreases, and the *m*_{shell} cloaking range shrinks as electron incident energy increases. However, ΔE_{c2} cloaking range does not change greatly with increasing *E*. Note that this is merely our numerical results observation and we do not have a clear explanation for these trends.



Figure 3-3. The effect of electron energy on normalized scattering cross section (%) for fixed host material and nanoparticle geometric structure. Ga_{0.2}In_{0.8}As is taken as the host matrix and the outer radius of the shell is fixed at a=22Å. (a) E=50meV, (b) E=100meV, (c) E=150meV, (d) E=200meV.

Once this initial scan is performed and the cloaking ranges for each parameter is determined, we can choose proper shell materials for the given host. As an example, for the chosen materials here, Ga0.2In0.8As (**Fig. 3-2(a)**), we can see that InAs and alloys of Ga0.06In0.94As fall in the cloaking region. Using InAs as the shell and Ga0.2In0.8As as the

host, 'cloaking' can be achieved. Furthermore, a slight diffusion of Ga from the host matrix to the shell layer (up to 6%) would not affect the results significantly.

In the next step, we will further optimize the size and the doping density of the selected materials (i.e. InAs/ Ga_{0.2}In_{0.8}As).

As shown in **Fig. 3-4**, the cloaking range of a and E is decreasing when a_c is increasing. For a small shell thickness, the total scattering cross section increases with increasing E, while for larger thicknesses, the total cross section first decreases and then rises with increasing E, that is there is an anti-resonance dip in the scattering cross section. For a smaller a_c , the E cloaking range is larger, creating more choices for the corresponding Fermi level. Also by comparing (a)-(d) in **Fig. 3-4**, we find that a similar shell thickness is required for different core sizes. With similar 'good' shell thicknesses, the scattering cross section dip is found at a smaller energy value for a larger core.



Figure 3-4. Effect of nanoparticle sizes on the normalized scattering cross section (%) for a specific materials combination: InAs is taken as the shell and Ga_{0.2}In_{0.8}As as the host matrix. The radii of the core is set to (a) a_c =10Å, (b) a_c =15Å, (c) a_c =20Å, (d) a_c =25Å. We have scanned a large class of materials including GaAs, InAs, InP and their alloys such as Ga_xIn_{1-x}As to find realistic material combinations. Results for some of the other host materials are shown in **Fig. 3-5**. For InAs, GaAs and InP, the optimum Fermi level is about 67meV^[54], 63meV^[54], 30meV^[54] respectively, which were calculated from optimum carrier density at 300K. Points in each graph show some of the possible shell materials identified for that particular host matrix. Among these points, the lattice constant of GaInSb doesn't match well with GaAs. There still exits great chance to find other proper shells by considering more materials and lowering the temperature, which would increase the range of proper parameters and make it easier to find matched materials.



Figure 3-5. Normalized scattering cross section (%) for (a) GaAs, (b) InAs, (c) InP. $a=10\text{\AA}$ and $a_c=20\text{\AA}$ are set for these calculations.

Application to Thermoelectric Materials

After finding the proper shell/host combination as described above, we take one of the optimal combinations to calculate the actual scattering cross section, including charge transfer from the doped shell layer to the host. For the first nanoparticle (np1), the radius of the core is 1.5nm and the radius of the total nanoparticle is 2.7nm. For np2, the radii of the core and the shell are 3.5nm and 5.0nm respectively. These sizes are obtained from **Fig. 3-4**. Ga0.2In0.8As is taken as the host and InAs is the shell material of the nanoparticle, while the core is vacuum. The material's parameters are reported in the Appendix. For GaInAs, we consider alloy, polar optical phonons, acoustic phonons and impurity scatterings^[55] in addition to nanoparticle scattering and we use Matthiessen rule to calculate the total scattering rate. We use linearized transport integrals^[56] to calculate the thermoelectric transport coefficients including the Seebeck coefficient, electrical conductivity and finally the thermoelectric power factor. Using the parameters reported in the Tab. 3-1, we were able to reproduce the electron mobility values reported in the literature for GaInAs (see Fig. 3-6). Each nanoparticle is assumed to donate one electron to the host matrix (Z=1) and different densities of nanoparticle produce different doping densities $(1 \times 10^{13} \sim 2 \times 10^{17} \text{ cm}^{-3})$. The potential profile for np2 is shown in **Fig. 3-7**, from which we can see a lower potential both at the core and at the shell than that without charge transfer. After considering the charge transfer, 'cloaking' can still be achieved, as shown is Fig. 3-8. The minimal total cross section at the dip is less than 1% of the

physical cross section. Both np1 and np2 show a scattering dip, but the corresponding electron energy is very different. All the PWs contribute to the total cross section, while the phase shifts of higher orders PWs are relatively small if ka is less than 1, making the summation in **Eqn. 2-1** converge fast^[50]. Since np2 has a larger size (*a*) compared to np1, it requires a smaller electron energy to achieve a similar ka value. Therefore, the corresponding energies and the energy dip of np2 is shifted to smaller values compared to np1 (see **Fig. 3-8**).

Table 3-1. Property of materials

	1 5			
Material	Electron effective mass	Electron affinity(eV)		
InAs ^[57]	0.023	4.9		
Ga _x In _{1-x} As ^[57]	(0.023+0.037x+0.003x ²)	(4.9-0.83x)		
InP ^[57]	0.08	4.38		
GaAs ^[57]	0.063	4.07		
Electron Mobility (cm ² /V•s)	Katoda - Katoda - Chattopadhyay - 1.0E22 - 5.0E22 - 0.4 0. x in Ga_ln _{1-x}	6 0.8 1.0 As		

Figure 3-6. Electron mobility VS x for Ga_xIn_{1-x}As. "Katoda" refers the experiment data with carrier density in the range of $1.0 \times 10^{22} \sim 5.0 \times 10^{22}$ m⁻³, "Chattopadhyay" shows the numerical result with carrier density set at 4.0×10^{22} m⁻³, " 1.0×10^{22} " and " 5.0×10^{22} " show our calculation results using n= 1.0×10^{22} m⁻³ and n= 5.0×10^{22} m⁻³ respectively. All the data is for room temperature. This figure shows the comparison among our calculation results and data from other groups^[58,59]. Our results consist well with other's data, proving that the host property of Ga_xIn_{1-x}As used for calculation is credible.



Figure 3-7. Potential profile as a function of position in radial direction for np2 after considering carrier. The dashed line labeled 'actual potential' shows the actual potential with consideration of charge transfer. The radius of the core is 3.5nm and the outer radius of the shell is 5.0nm. Only one electron is doped per nanoparticle. Ga0.2In0.8As is taken as the host and InAs as the shell material of the nanoparticle while the core is vacuum.



Figure 3-8. Scattering cross section for np1 and np2 as a function of electron energy. Both the minimum scattering cross sections are less than 1%, illustrating the achievement of invisibility of the nanoparticle.

Fig. 3-9(a) shows the power factor improvement using a hollow nanoparticle. As can be seen, anti-resonance nanoparticles can improve the thermoelectric power factor significantly. The peaks of the power factor for np1 and np2 have an improvement of 45%, as compared to the host doped with uniform impurity. We can also see from **Fig. 3-9(b)** that np1 and np2 show a conductivity which is several times larger than the impurity-doped sample, which is expected since the scattering rates are much lower when conventional dopants are replaced by the designed hollow nanoparticles. The Seebeck coefficient is slightly decreased for the hollow nanoparticle embedded sample (**Fig. 3-9(c)**). An increase is expected in the Seebeck coefficient as a result of introducing sharp features in relaxation times and therefore in the differential conductivity.^[60] However, it

should be noted that after replacing conventional dopants with the designed hollow nanoparticles, the scattering is dominated by the background phonon and alloy scattering in the Fermi window and therefore the scattering dip does not enhance the Seebeck coefficient. **Fig. 3-10** shows important scattering rates versus energy in the host matrix. The alloy scattering rate is the dominant scattering rate in the hollow nanoparticle doped sample. Thus, the power factor does not vary significantly when the nanoparticle size is changed. The optimum Fermi levels for np1, np2 and the impurity doped sample are all found at about 5meV, as shown in **Fig. 3-8(a)**. The scattering dip is found at around 20meV for np1 and at around 160meV for np2; the former is closer to the optimum Fermi level. However, due to the background scatterings, the power factor, mobility and Seebeck coefficient appear similar for np1 and np2, as shown in **Fig. 3-9**.





Figure 3-9. Comparison of the power factor for different samples. The line labeled by 'imp' shows the uniform impurity doped sample.



Figure 3-10. Momentum scattering rates of different kinds for Ga_{0.2}In_{0.8}As at 50K. "phonon" refers to the electron scattering by polar optical and acoustic phonons. "impurity" is calculated at the optimum Fermi level using a traditional ionized impurity-doped sample. 'np2' shows the scattering rate by nanoparticle (np2) at the optimum Fermi level. Scattering by alloy in np2 sample is also plotted.

These results are very encouraging since they are not nanoparticle parameter sensitive and therefore the enhancement is observable even if there is randomness to some degree in the nanoparticle sizes.

The main role of the designed nanoparticles is to minimize the doping scattering rates. The hollow nanoparticle doping method shows a significant advantage over that of uniform doping method. This type of doping is most effective in samples where doping scattering rates are the dominant scattering mechanisms and the other rates are negligible. To demonstrate the importance of background scattering, we performed calculations, using Gao₁Ino_{.9}As as the host, leaving other parameters unchanged. The results show an over 80% improvement of a maximum power factor by substituting the impurity with hollow nanoparticles, as shown in **Fig. 3-11**. According to the analysis for Ga0.2In0.8As, alloy scattering plays a major role. For Ga0.1In0.9As, there is less alloy scattering than for Ga0.2In0.8As, emphasizing the importance of the background scattering, which can be seen by comparing **Fig. 3-10** and **Fig. 3-12**.



Figure 3-11. Power factor vs Fermi energy using Ga0.1In0.9As as the host. The np3 has the same core-shell structure as np2. The "imp1" shows the results for uniform doped sample.



Figure 3-12. Momentum scattering rates of different kinds for Ga_{0.1}In_{0.9}As at 50K. "phonon" refers to the electron scattering by polar optical and acoustic phonons. Black solid line "np3" shows the scattering rate by nanoparticle (np3). Red solid line refers to alloy scattering.

Summary

From this work, we can conclude that the concept of anti-resonant nanoparticle renders the enhancement of electrical conductivity and the power factor possible. In this work, we have identified several possible hollow nanoparticles/host material combinations including InAs/InGaAs, InP/GaInAs. The material of the host matrix and nanoparticle is not limited to those shown in this work. We introduced a simple combinational search method to identify proper shell/host combinations. There exists a great chance to find other and even much better material combinations. The advantage of anti-resonant nanoparticles is much more significant for samples where doping scattering is the dominant scattering mechanism and the other background scatterings are weak. The strategy developed here may be expanded to improve the design of semiconductor materials with better electronic and thermoelectric properties, which can be applied in many different fields.

Chapter 4: Dimensionless Mapping to Identify Electronically Cloaked Non-hollow Nanoparticles

The main difficulty of designing electronically cloaked nanoparticles is the fact that the created potential upon coating is not tunable and is determined by the band alignment of the chosen materials for the core, the shell and the host as well as the charge distribution in these layers. To find proper combinations of materials, one needs to probe a large class of materials combinations and layer sizes. This approach is time-consuming and impractical. Here we introduce a simple mapping method to identify possible combinations by comparing the dimensionless parameters of the chosen materials with the provided maps and without any transport calculations. Using this approach, we have identified several combinations of core, shell and host materials for which electronic cloaking is achievable. We have optimized the size and doping level of some of these materials combinations to maximize their thermoelectric power factor. Compared to traditional impurity-doped samples, up to 14.50 times improvement in the thermoelectric power factor was observed at T=77K.

Design of objects invisible to electrons of specific energy is attractive for many applications such as electronic filters, switches, high mobility materials and fast response devices.^[39-41,43,61-67] Recently, it has been proposed that cloaking could be used to design invisible dopants to reduce the ionized impurity scattering rates and to enhance the electron mobility.^[39] Core-shell structures that are following the shape of the Fermi surface are useful for such designs. For example when the Fermi surface is spherical

(parabolic band structure), spherical core-shell particles could be used wherein the size and the band offsets are tuned to lower the electron-nanoparticle scattering cross section to values as low as 1% of the physical cross section, πa^2 , in a narrow energy window (cloaking window). Here *a* is the nanoparticle radius. When such nanoparticles are used as dopants, and when the cloaking window and the Fermi window are tuned to overlap, significant improvement in the electron mobility could be achieved compared to the conventional doping especially at low temperatures wherein impurity scattering is the dominant scattering.^[38]

A core-shell structure is made of two co-centered step-function potentials. Different combinations of well-barrier, barrier-well, well-well or barrier-barrier could be used to observe cloaking states, which would be discussed later in this chapter. One can theoretically tune the sizes, potentials and effective masses of the barriers and wells to minimize the electron-nanoparticle scattering cross section. The problem comes from the fact that in materials design, these potentials are not tunable and they are set by the band-offset and the details of charge transfer between the three layers. This makes the search for proper combinations of the three materials, a time consuming and expensive task as there are too many parameters involved in the search. Even for the simplest parabolic band structure, conductivity effective mass, electron affinity, work function, the size of each layer, the temperature and the nanoparticle volume fraction are the determining parameters for the electron-nanoparticle scattering rates. This makes the problem a function of 13 parameters and therefore one needs to search a huge parameter space to identify proper materials combinations.

In a recent paper, we applied restrictions to these parameters to narrow down the search.¹² To lower the number of involved parameters, we excluded one material and confined our search to hollow nanoparticles wherein the core is fixed to vacuum. Using a combinatorial search algorithm, we were able to identify several combinations of hollow nanoparticles and host materials for which cloaking is possible. Obviously, hollow nanoparticles are difficult to synthesize and there is a need to identify filled core-shell structures. In this work, we develop a new search method to identify embedded core-shell nanoparticles to improve mobility and thermoelectric properties of certain host materials.

This chapter is organized in the following manner: first, we describe the way to calculate scattering cross section and explain the new search method to identify proper materials combinations for electronic cloaking. We use a small material database to test the feasibility of the proposed mapping method. Finally, two sets of identified materials combinations are optimized and the effect of nanoparticle doping on their thermoelectric properties is discussed.

Methodology

We follow the same method as discussed in our previous published paper and use partial wave method^[50] to calculate scattering cross section of electron waves from spherical core-shell nanoparticles.^[39] The total scattering cross section of an electron with incident energy, ε , from a core-shell nanoparticle, ignoring charge transfer, is given as^[39]

$$\frac{\sigma}{\pi a^2} = \frac{4}{(ka)^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \delta_l \tag{4-1}$$

$$\delta_{l} = \arctan(\frac{kaj_{l}'(ka) - \gamma_{l}\alpha j_{l}(ka)}{kan_{l}'(ka) - \gamma_{l}an_{l}(ka)})$$
(4-2)

 $\gamma_{l}a = \frac{m_{h}}{m_{s}} \frac{(\beta a)^{2} j_{l}(\alpha a_{c}) n_{l}^{\prime}(\beta a_{c}) j_{l}^{\prime}(\beta a) - \frac{m_{s}}{m_{c}} [\alpha a\beta a j_{l}^{\prime}(\beta a) j_{l}^{\prime}(\alpha a_{c}) n_{l}(\beta a_{c}) + \alpha a\beta a j_{l}(\beta a_{c}) j_{l}^{\prime}(\alpha a_{c}) n_{l}^{\prime}(\beta a)] - \beta^{2} a^{2} j_{l}(\alpha a_{c}) j_{l}^{\prime}(\beta a_{c}) n_{l}^{\prime}(\beta a)}{\beta a j_{l}(\alpha a_{c}) n_{l}^{\prime}(\beta a) j_{l}(\alpha a_{c}) n_{l}(\beta a) j_{l}^{\prime}(\alpha a_{c}) n_{l}(\beta a_{c}) + \alpha a j_{l}(\beta a_{c}) j_{l}^{\prime}(\alpha a_{c}) n_{l}(\beta a)] - \beta a j_{l}(\alpha a_{c}) j_{l}^{\prime}(\beta a_{c}) n_{l}^{\prime}(\beta a)}$

We use the same terminology as used in **Ref. 39**. **Eqn. 4(1)-(3)** are slightly modified to make them dimensionless. Here, δ_l is the phase shift of the l^{th} partial wave, $k = \frac{\sqrt{2m_h\varepsilon}}{\hbar}$, $\alpha = \frac{\sqrt{2m_c(\varepsilon - V_c)}}{\hbar}$ and $\beta = \frac{\sqrt{2m_s(\varepsilon - V_s)}}{\hbar}$ are wave numbers in the host, core and shell regions respectively. a_c is the core radius and a is the nanoparticle radius. V_c and V_s are the potentials of the core and shell relative to the host respectively. m_h , m_c and m_s are the effective masses of the host matrix, core and shell materials respectively.

By making the equations dimensionless, we note that the scattering cross section is only a function of 6 independent parameters namely αa , βa , ka, $\frac{a_c}{a}$, $\frac{m_h}{m_s}$, and $\frac{m_s}{m_c}$. So instead of 13 parameters, now we only need to scan for six! Note that we ignored charge transfer at this step. We also note that $\frac{a_c}{a}$ is the only parameter, which is controllable for a given set of materials, and it is not a material parameter. The other parameters depend on the chosen materials properties. Therefore we choose the following strategy.

We fix the last two parameters, $\frac{m_h}{m_s}$ and $\frac{m_s}{m_c}$ and we develop a map which we will explain shortly for the rest of the parameters. We prepare a set of maps for different discrete mass ratios, for example, 0.5, 1, 1.5, 2, 3 and 5. Then for a given materials combination, we select a map with the closest mass ratios. At this stage, with a good certainty and with limited calculations, we can decide whether or not the chosen combination will have cloaking windows, by positioning the dimensionless parameters of the materials combination in the map and identifying the overlapping regions. The approach is only possible since the results are not too sensitive to the mass ratios and small changes in the mass ratios do not result in extreme changes in the scattering cross section.

To form such maps, we loop over αa , βa and ka for given mass ratios. Each of these parameters will be one axis of the map. For given αa , βa and ka, we scan $\frac{a_c}{a}$ ratio and calculate the scattering cross section using **Eqn. 4-(1-3)**. We accept the combination of αa , βa and ka if the relative scattering cross section $\frac{\sigma}{\pi a^2}$ is less than 1% for any reasonable $\frac{a_c}{a}$ ratio. These combinations are saved in a matrix and the information of $\frac{a_c}{a}$ is also saved for later use. After developing the maps, for a given combination of real materials for core, shell and host, as soon as we decide on the energy, α , β and k are known and therefore (αa , βa , ka) will be a line in the map (with varying a). If the line crosses the saved matrix points, then there is chance of observing cloaking states and if not, cloaking is not possible.

To exclude extremely small nanoparticles, we do not include nanoparticle sizes (core radius and shell thickness) smaller than 1nm. At locations wherein the line of $(\alpha a, \beta a, ka)$ overlaps the map, we further check the radius of core and the thickness of shell to make sure that they are reasonably large.

Six mass ratio values (0.5, 1, 1.5, 2, 3, 5) of $\frac{m_s}{m_c}$ and $\frac{m_h}{m_s}$ are considered to form 36 sets of maps in total. **Fig. 4-1** demonstrates the two dimensional projection of some of the maps created for the mass ratios of 1 and 5. The values of α and β are either pure real or pure imaginary. The imaginary part in the map indicates that the energy of the electron is lower than the potential of the corresponding layer and therefore the electrons are tunneling.



Figure 4-1. General dimensionless maps: βa and αa solutions for which the total scattering cross section of the electron-nanoparticle is smaller than 1% of the physical

cross section. βa and αa are either pure real or pure imaginary, both cases are plotted here. (a) βa and αa solutions for ka = 1 and $\frac{m_h}{m_s} = \frac{m_s}{m_c} = 1$, are plotted using red dots. This plot is then broken down to the corresponding $\frac{a_c}{a}$ values. For example black color refers to obtained solutions when $\frac{a_c}{a}$ ratio is set equal to 0.75, and so on. Other plots: Blue dots represent the general map for (b) $\frac{m_h}{m_s}$, and $\frac{m_c}{m_s} = 1$, (c) $\frac{m_h}{m_s} = 1$ and $\frac{m_s}{m_c} = 5$, and d) $\frac{m_h}{m_s} =$ 5, $\frac{m_s}{m_c} = 1$. In these plots all ka values are scanned. These are in fact 3D plots wherein ka is the z-axis. Here we simply show the projection on a 2D plot. The solutions are then broken down to different planes corresponding to different ka values as indicated in the legend. In figure (d), solutions for ka = 1, 2 and 3 are not plotted as there is no satisfied point in those regions.

An interesting observation from these maps is that even in the case of barrier-barrier twostep potential, cloaking is possible. However in most cases, the corresponding *ka* values are small (*ka* <0.5). Another remark is to note that for certain set of parameters, the cloaking is achievable regardless of the value of αa . For example, in **Fig. 4-1(b)**, when *ka* is around 2 and βa is around 1, cloaking is achievable for any arbitrary value of αa . This makes the choice of the proper material for the core an easy choice. In such cases, the only relevant parameter for the host is its effective mass.

Finally, an exciting observation is that even for relatively large ka values ($ka \sim 5$), cloaking is possible. This is very important since it indicates that one can observe cloaking for large size particles. Later on we show that for one of the identified combinations, the radius of nanoparticle could reach to 10nm. The cancellation of the first two partial waves technique developed in our first publication relies highly on the fact that higher order partial waves could be ignored only when ka is less than or equal to 1.⁴⁰ When developing these maps, we calculate total scattering cross section and we include all higher order partial waves (until the sum converges), yet it can be seen that for

relatively large *ka* values, cloaking is possible. In fact cloaking could be achieved when the 0^{th} order partial wave gives nearly zero scattering cross section and the contribution from the higher-order partial waves is relatively small, as shown in **Fig. 4-3(a)**. In this example, the minima of the scattering cross section of the 0^{th} and 1^{st} order partial waves do not overlap. However, at the minimum of the 0^{th} one, the contribution from the higher order partial waves is negligible, making the minimum of the total scattering cross section reach values less than 0.2% of the physical cross section. We can conclude that to achieve extremely small scattering cross sections, none of the previously thought conditions are necessary. In other words, the co-existence of barrier and well, the overlap of the first two minima, and small ka values (less than or close to one) are not required and the phase-space of observing cloaking is much larger than what was believed previously.

To test the feasibility of the method mentioned above, we form a materials database as shown in **Tab. 4-1**. The database includes 15 materials. These materials could be used for core-shell-host combinations. Combinations of A-A-A are not allowed but A-B-A combinations are allowed. More over for each set of A-B-C or A-B-A we can use n-type or p-type doping. If only considering material combinations of same type, there will be $15 \times 14 \times 15 \times 2=6300$ different combinations to test.

Name	Hole Effective	Electron	Eg	Electron	Lattice
	Mass (m ₀)	Effective Mass	(eV)	Affinity	Constant
		(m_0)		(eV)	(Å)
Ge ^[57]	0.33	0.119	0.66	4.0	5.658
Si ^[57]	0.49	0.26	1.12	4.05	5.431
GaAs ^[57]	0.51	0.063	1.424	4.07	5.65325
GaP ^[57]	0.79	0.3	2.26	3.8	5.4505
InAs ^[57]	0.41	0.023	0.354	4.9	6.0583
InP ^[57]	0.6	0.08	1.344	4.38	5.8687
AlAs ^[57]	0.75 ^[69]	0.262 ^[69]	2.168	3.5	5.6611
GaN $(\beta)^{[57]}$	1.3	0.13	3.2	4.1	4.52
GaN $(\alpha)^{[57]}$	1.4	0.2	3.39	4.1	5.186
Ga0.51In0.49P ^[70]	0.7	0.088	1.849	4.1	5.653
$Ga_{0.47}In_{0.53}As^{[57]}$	0.45	0.041	0.74	4.5	5.8687
PbTe	0.024@4K ^[71]	0.035@4K ^[71]	0.3 ^[72]	4.6 ^[72]	6.462 ^[73]
PbS	0.083 ^[71]	0.087 ^[71]	0.42 ^[73]	4.6 ^[74]	5.936 ^[73]
CdTe ^[75]	0.8	0.09	1.49	4.28 ^[76]	6.482
ZnTe	0.68 ^[77]	0.12 ^[78]	2.35 ^[73]	3.53 ^[76]	6.1 ^[75]

 Table 4-1. Material data base (Most of data @300K)

Maps with closest mass ratios are adopted for each materials combination. In this process, several selection rules were enforced. First, only nanoparticles with core radius larger than 1 nm and shell thickness larger than 1 nm were accepted. Second, only adjacent layers with lattice mismatch less than 5% were allowed. Finally, for each materials combination, a proper energy range was identified for the host matrix to be close to the optimum Fermi level (the Fermi level at which the thermoelectric power

factor of bulk host reaches its maximum). Then intersection of the $(\alpha a, \beta a, ka)$ lines and the relevant maps were investigated to identify cloaking points.

Using the process described above, the original 6300 combinations were narrowed down to 14 combinations, which satisfied all of the search criteria enforced. These fourteen good combinations are listed in **Tab. 4-2**. All of the 14 identified combinations were tested later with their exact mass values. All combinations could satisfy the size criteria and have minimal relative scattering cross section less than 3% and majority of them could reach below 1%. Note that this is not guaranteed in the first filtering processes since only maps with the closest mass ratios (and not the exact mass ratios) are chosen and therefore mass ratios in the first scan are not exact. Also note that one cannot afford to form an infinite number of maps with all possible mass ratios. So there is a tradeoff between the accuracy of the filtering and the cost of the calculations. The main advantage of the method is that the maps could be calculated once and saved as a database for permanent use.

Index	Туре	Host	Core	Shell
1	n	GaAs	InP	Ge
2	n	Gao.47Ino.53As	InAs	InP
3	n	GaAs	PbS	Ge
4	n	GaN(a)	Ge	Si
5	n	GaN(a)	GaN(α)	Si
6	n	GaN(a)	Ga0.51In0.49P	Si
7	n	Ga0.51In0.49P	InP	Ge
8	n	Ga0.51In0.49P	Ga0.47In0.53As	Ge
9	n	Ga0.51In0.49P	PbS	Ge
10	n	Ga0.51In0.49P	GaN(α)	Si
11	n	GaAs	Ga0.47In0.53As	Ge
12	n	Gao.47Ino.53As	PbS	InP
13	р	InAs	InAs	Gao.47Ino.53As
14	р	Gao.47Ino.53As	Gao.47Ino.53As	InAs

 Table 4-2. Good Combination

Application to Thermoelectric Materials

The screening process described above does not consider charge transfer between core, shell and host materials. The main purpose of the nanoparticles in the context of thermoelectric materials is to dope the host matrix. Therefore the effect of charge transfer from nanoparticles to the host matrix cannot be ignored. In the next step, one needs to calculate the effect of charge transfer in the identified combinations. Finally optimization



of the nanoparticle size, doping level and volume fraction is required to optimize the thermoelectric properties of the designed core-shell nanoparticle doped host materials.

Figure 4-2. a, c) The total scattering cross section relative to the physical scattering cross section and the contribution from the first 4 partial waves without considering charge transfer (Solid lines). The dashed line shows the total scattering cross section after considering charge transfer. c, d) Nanoparticle potentials: The black solid lines show the 2-step potential without considering the charge transfer and the magenta dashed ones show the potential with consideration of charge transfer. Parameters for (a, b): calculated for combination 1 (GaAs-InP-Ge). The radius of nanoparticle is a = 4.5 nm, and the radius of core is $a_c = 1.5 nm$. When charge transfer is accounted for, the doping density is $3 \times 10^{22} m^{-3}$ corresponding to 1 electron per nanoparticle. Parameters for (b, d): calculated for combination 2 (Ga_{0.47}In_{0.53}As - InAs- InP). The outer radius of nanoparticle is a = 4.4 nm, and the radius of core is $a_c = 2 nm$. When charge transfer is accounted for, the doping density of nanoparticle is n = 4.4 nm, and the radius of core is $a_c = 2 nm$. When charge transfer is accounted for, the doping density of nanoparticle is $n = 2 \times 10^{22} m^{-3}$ corresponding to 1 electron per nanoparticle.

We have performed partial optimization for two of the identified combinations, namely combination 1: GaAs, InP, Ge and 2: Ga0.47In0.53As, InAs, InP in the order of host, core and shell. The total scattering cross section for the optimized nanoparticle doped matrix made out of combination 1 is shown in **Fig. 4-2**(a), and was discussed in the methodology section. The same cross section is also calculated for combination 2 and is shown in **Fig. 4-2**(c). As could be seen, there is a large difference in the scattering cross section, with and without charge transfer. In both tested cases, the net effect of considering charge transfer is to shift the cloaking window to smaller energies.

For the optimized nanoparticle size, the Fermi level is modified by changing the doping density. The thermoelectric power factor (σS^2) is then calculated for each Fermi level using the Matthiessen's rule and **Eqn. 4-(4-6)** and is compared to that of conventional impurity doping.

$$\sigma = e^2 \int_{-\infty}^{+\infty} d\varepsilon \left(-\frac{\partial f_0}{\partial \varepsilon} \right) \sigma(\varepsilon)$$
(4-4)

$$S = \frac{1}{Te} \left[\frac{\int_{-\infty}^{+\infty} d\varepsilon \left(-\frac{\partial f_0}{\partial \varepsilon} \right) \sigma(\varepsilon)(\varepsilon - \varepsilon_f)}{\int_{-\infty}^{+\infty} d\varepsilon \left(-\frac{\partial f_0}{\partial \varepsilon} \right) \sigma(\varepsilon)} \right]$$
(4-5)

$$\sigma(\varepsilon) = g(\varepsilon)v(\varepsilon)^2\tau(\varepsilon) \tag{4-6}$$

here $\sigma(\varepsilon)$ is the differential conductivity, $g(\varepsilon)$ is the density of states and $v(\varepsilon)$ is the group velocity, and f_0 is the Fermi Dirac function.

For combination 1, the electrical conductivity could be greatly improved by using nanoparticle dopant at high Fermi levels, corresponding to large doping densities (see

Fig. 4-3(a). For low doping density, the scattering is dominated by other scattering mechanism, namely background phonon, as was discussed in **Ref. 68**. By using core-shell nanoparticle doping, the Seebeck coefficient decreases slightly. The net improvement in the thermoelectric power factor is about 1450%, which is the result of improved mobility (see **Fig. 4-3**(c)).

The second combination in **Tab. 2** is also tested and optimized. The optimized potential profile with and without charge transfer is shown in **Fig. 4-2**(d). **Fig. 4-2**(c) shows that after considering charge transfer, the minimum scattering cross section is smaller and shifts to lower energies. **Fig. 4-4** shows the thermoelectric properties comparison between nanoparticle doping and uniform impurity doping. Similar to what was observed for combination 1, the electrical conductivity is increased and the Seebeck coefficient is slightly decreased. The maximum power factor is improved by 18% by using nanoparticle doping. The improvement of electrical conductivity is much lower than combination 1. This is because the alloy scattering plays a great role for combination 2, while there is no alloy scattering in the host material (GaAs) of combination 1.



Figure 4-3. Comparison of electrical conductivity, Seebeck coefficient and power factor for different doping methods. The blue curve is GaAs doped with invisible nanoparticle

dopants (combination 1 in Table 2). The geometry of the designed nanoparticles is described in **Fig. 2**. The red curve labeled by 'impurity' refers to conventional uniform impurity doping of the host matrix (GaAs).

The reduction in the Seebeck coefficient in both cases could be explained by the enhancement in the electrical conductivity, which increases the denominator of Eqn. 4-5. Fig. 4-5 compares electronic band structure contribution $(h(\varepsilon) = e^2 \left(-\frac{\partial f_0}{\partial \varepsilon}\right)g(\varepsilon)v(\varepsilon)^2)$, the relaxation times ($\tau(\varepsilon)$), and the differential conductivity ($h(\varepsilon)\tau(\varepsilon) = e^2 \left(-\frac{\partial f_0}{\partial \varepsilon}\right)\sigma(\varepsilon)$) for Ga_{0.47}In_{0.53}As host matrix doped with invisible dopants (combination 2) and conventional dopants (single impurity). In both cases the carrier density is $n = 2 \times 10^{22} m^{-3}$ corresponding to a Fermi level of -0.52 meV. As could be seen in Fig. 4-5(a), the slope of the relaxation times increased significantly, however, its absolute value also increased significantly which increases the electrical conductivity and reduces the Seebeck coefficient. This is also reflected in Fig. 4-5(c). Another explanation is the fact that the peak value of $h(\varepsilon)\tau(\varepsilon) = e^2 \left(-\frac{\partial f_0}{\partial \varepsilon}\right)\sigma(\varepsilon)$ shifts to energies closer to the Fermi level, resulting in lower Seebeck coefficients.^[60] Enhancement in the Seebeck coefficient is possible for cloaking windows designed at larger higher energies.^[38]



Figure 4-4. Comparison of electrical conductivity, Seebeck and power factor for different doping method. The blue curves is for combination 2 in **Tab. 4-2** and the geometry is described in **Fig. 4-2**. The curve labeled by 'impurity' refers to conventional



uniform impurity doping and the curve labeled by 'nanoparticle' means material doped by core-shell nanoparticles.

Figure 4-5. a) Comparison of $\tau(\varepsilon)$; b) Curve of $h(\varepsilon)$; c) Curve of $h(\varepsilon)\tau(\varepsilon)$. The curve labeled by 'impurity' refers to conventional impurity doping and the curve labeled by 'nanoparticle' means material doped by core-shell nanoparticles.

Summary

In this chapter, a new search algorithm is proposed to identify possible combinations of core-shell-host materials to achieve electronic cloaking. A set of maps based on dimensionless parameters was formed to screen out good materials combinations. Using the maps we showed that the phase space for achieving electronic cloaking is much larger than what was previously thought and it is possible to design much larger invisible nanoparticles (radius > 10 nm). For any given combination of materials, one can simply compare the materials dimensionless parameters with the provided maps to check if the cloaking is possible. Using a simple database, we checked and demonstrated the efficiency of this method. We narrowed down the original 6400 combinations to 14 optimistic combinations. Two of these combinations were optimized with respect to their nanoparticle sizes and their doping density. We showed that by using nanoparticle doping instead of conventional uniform impurity doping, the electrical conductivity and the power factor could be significantly improved. The strategy described in this work could help researchers design semiconductor materials with better thermoelectric and electrical properties.

Chapter 5: Summary and Future Work

In this thesis, new approaches to design hollow and filled core-shell structured nanoparticle that could achieve electronic cloaking are presented. We started by introducing the thermoelectric materials and devices. We then discussed methods of improving thermoelectric properties. One optimistic method is using electronic cloaking to design invisible dopants. In the first main part of this thesis, a combinational methodology is proposed to simplify the process of designing hollow nanoparticles for electronic cloaking. The core is set to be vacuum in order to decrease the number of total variables involved. Several nanoparticles that could achieve electronic cloaking are designed and optimized for thermoelectric materials doping. With invisible hollow nanoparticles as dopants, the electrical conductivity is improved greatly, while there is a little decrease in Seebeck coefficient. Therefore the power factor is improved significantly.

In the second part, a new method to design filled core-shell nanoparticles rather than hollow ones is presented. Several dimensionless variables are used. This method uses a set of maps to identify proper designs. A material database is used to prove the feasibility. Several nanoparticle dopants are designed and used in thermoelectric materials. The power factor could be increased by over ten times for host material without alloy using invisible dopants. Seebeck coefficient of samples with the designed nanoparticle dopants is a slightly smaller than traditional impurity doped samples. The reason is analyzed and the situation with larger Seebeck is described. Some of the future works include: 1) studying the effect of nanoparticle dopants on the thermal conductivity. By using large mismatch at the interface of nanoparticle and host, the thermal conductivity should decrease in theory; 2) experimentally validating the enhancement of thermoelectric properties through core-shell nanoparticles dopants.

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