

The Pennsylvania State University

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**ELECTRONIC LOCALIZATION IN 3D SILICON AND PLATINUM METALATTICES
AND MAGNETOELECTRICAL TRANSPORT PROPERTIES OF DIRAC NODAL LINE
SEMIMETAL ZrSiS**

A Dissertation in

Physics

by

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ABSTRACT

This dissertation is composed of two parts. The first part concerns the metalattices, a new type of three-dimensional nanostructured material where we explore the effect of nanoscale geometrical constraint on electron localization in disordered systems. Metalattices are synthesized in late Prof. John Badding's lab by infiltrating self-assembled SiO₂ nanosphere templates using high pressure confined chemical vapor deposition (HPcCVD) technique. Besides a periodicity on 10~100 nm scale, a large surface to volume ratio and geometrical confinement are two major new variables that metalattice structure bring in.

Polycrystalline 30 nm platinum metalattices exhibit weakly localized electrical transport. An anomaly in its temperature-dependent low-field magnetoresistance is found, which bears features characteristic of weak localization effect but not shared by Pt thin films or bulk Pt. We attribute the anomaly to the increased electron-phonon scattering due to large surface to volume ratio in Pt metalattices. Our analysis also reveals that the inhomogeneity introduced by metalattice structure cannot be ignored on the length scales relevant for weak localization in 30 nm Pt metalattices.

We next investigate heavily doped silicon metalattices of three different periodicities (14 nm, 30 nm, and 100 nm) to explore the effect of geometrical constraint. When the characteristic scale becomes smaller and comparable to the Bohr radius of dopants, one would expect stronger electron localization and an increased critical doping level. We did not observe a metallic phase in 100 nm Si metalattices with a carrier density of $3 \times 10^{19} \text{cm}^{-3}$, which is above the critical doping level estimated using Shklovskii's formula for nanocrystal arrays. Our analysis suggests that polycrystallinity in our samples alone cannot explain the absence of metallic phases. We attribute the latter to surface traps on the Si/SiO₂ interface, disorder in the superlattice, and defects or amorphous regions in Si. Future study on high-quality samples is needed to differentiate and

quantify effects due to those variables. Our 14 nm and 30 nm samples show Efros-Shklovskii Variable-range hopping type behavior. The model of multiple co-tunneling gives a satisfactory description of the temperature dependence of zero-bias conductance and current-voltage characteristics, consistent with the theory that multiple co-tunneling is the intergranular transport mechanism in a granular electronic system.

The second part of this dissertation concerns the magnetoelectrical transport properties of Dirac nodal line semimetal (DNLSM) ZrSiS. Single-crystal ZrSiS is obtained by mechanical exfoliation and provides the opportunity to explore the effects of the electronic band structure. The angle-dependent magnetoresistance under two configurations, together with traditional SdH study, provides us with detailed information on the Fermi surface of ZrSiS. We find Shubnikov de-Hass (SdH) oscillations with frequencies consistent with results from recent studies. We also find an unexpected oscillatory component in the detailed angle-dependence of magnetoresistance which is periodic with respect to the inverse of the perpendicular component of the magnetic field, suggesting the quasi-2D nature of the associated electronic states.

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Chapter 1

Electronic localization and transport

Both platinum and silicon metalattice samples studied in this dissertation are inhomogeneously disordered systems. It is therefore prudent to start with a review on electronic localization in a homogeneously disordered system and introduce electrical transport in the weakly and strongly localized regime, respectively. Furthermore, we review how the inhomogeneity of a granular system introduces new properties into the already rich physics of a homogeneously disordered system [7]. As an experimentalist, I aim to present the conceptual framework rather than theoretical formalism.

1.1 Weak localization

1.1.1 Coherent backscattering

The classical picture of diffusion (that is, multiple random scattering) ignores the quantum interference between the wavefunctions scattered by impurities. For a macroscopic system, one observes the ensemble-averaged effect of such quantum interference, which is zero except for self-intersecting scattering paths (**Figure 1-1**). For a particle taking the clockwise and counter-clockwise Feynman paths along such self-intersecting trajectories, it experiences the same potential profile but in inversed time order. When time-reversal symmetry is present, these two Feynman paths interfere constructively, leading to a return probability twice of that in the classical picture. Even after ensemble average (average over different self-intersecting paths), coherent backscattering has a nonzero effect and leads to a quantum correction to electrical conductivity known as weak localization [1].

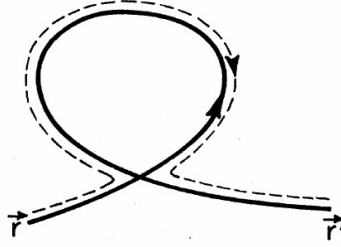


Figure 1-1: A self-intersecting Feynman path for an electron to propagate from $\vec{r}$ to $\vec{r}'$. Propagation along solid and dashed paths can interfere. Adapted from ref [1].

The magnitude of the correction to conductivity due to coherent backscattering can be calculated from first principle. The electrical conductivity can be expressed in the Kubo formula and evaluated using the diagrammatic technique. The result is

$$\sigma_d(L) = \begin{cases} \sigma_0 - \frac{e^2}{\hbar\pi^3} \left(\frac{1}{l} - \frac{1}{L} \right), & \text{for } d = 3 \\ \sigma_0 - \frac{e^2}{\hbar\pi^2} \ln \left(\frac{L}{l} \right), & \text{for } d = 2 \\ \sigma_0 - \frac{e^2}{\hbar\pi} (L - l), & \text{for } d = 1 \end{cases}, \quad (1-1)$$

where L is the length of the system. In one and two dimensions, the conductivity due to backscattering grows as L increases, and perturbation theory fails at sufficiently large length scales. In three dimensions, the leading correction goes as $\frac{1}{L}$, and conventional transport theory is accurate for weak disorder.

Under non-zero temperature, inelastic scattering will destroy the phase coherence needed for quantum interference. The theory of phase-breaking length L_φ and/or time can be complicated, and here we only consider phase-breaking due to inelastic scattering process. The inelastic scattering time increases as temperature decreases. For $L_{Th} = aT^{-p}$, where a is a constant and p is an index depending on the scattering mechanism, dimensionality, etc., the scale-dependent conductivity (eq. 1 – 1) reads [1]

$$\sigma_d(T) = \begin{cases} \sigma_0 + \frac{e^2}{h\pi^3} \frac{1}{a} T^{p/2}, & \text{for } d = 3 \\ \sigma_0 + \frac{p}{2} \frac{e^2}{h\pi^2} \ln\left(\frac{T}{T_0}\right), & \text{for } d = 2 \\ \sigma_0 - \frac{ae^2}{h\pi} T^{-\frac{p}{2}}, & \text{for } d = 1 \end{cases} \quad (1-2)$$

which decreases with decreasing temperature. This is a signature of localization: as temperature decreases, the relevant scale size over which quantum interference is effective increases so that localization behavior is progressively evident. We note that EEI can give a correction to conductivity very similar to that of WL. Luckily, we can still differentiate these two effects, as the EEI effect is relatively insensitive to the magnetic field, while the WL effect gets suppressed easily by a magnetic field (see below) [8].

1.1.2 Magnetoresistance

A magnetic field introduces a magnetic phase shift in the electronic wave function. Under a magnetic field, the electron pair in **Figure 1-4** acquires a phase difference $\Delta\varphi = 2 \int \mathbf{A} \cdot d\mathbf{l}$ after completing the loop in a clockwise and counterclockwise direction. For a loop enclosing flux φ , the phase shift is $\Delta\varphi = \varphi/\varphi_0$, where the magnetic flux quantum $\varphi_0 = hc/2e$. As we increase the magnetic field, the Landau orbit size $L_H = \left(\frac{eH}{hc}\right)^{-1/2}$ decreases. When L_H becomes comparable to the Thouless length L_{Th} , the interference between the clockwise and counterclockwise paths is destructive., and the weak localization effect is suppressed. Thus, the orbital motion leads to negative magnetoresistance (MR) in the weak localization picture [1].

In the presence of spin-orbit scattering, the spin of an individual electron is no longer a good quantum number, but time-reversal symmetry is preserved. Along the two paths in **Figure 1-4**, the spins are rotated in opposite directions. The average overlap between the spins as a result

of this rotation is $-\frac{1}{2}$, because a rotation by 2π of a spin- $\frac{1}{2}$ state basically leads to a sign change. A self-intersecting path and its time-reversed path interfere destructively when spin-orbit scattering is present and leads to a positive MR in the WL picture.

Now we have three length scales, i.e., the flux quantum length L_H , the spin-orbit diffusion length L_{so} , and the Thouless inelastic length L_i . The characteristic fields are defined by the characteristic electron scattering time

$$B_x \tau_x = \frac{\hbar}{4eD}$$

where $x = i, so, s$ for inelastic, spin-orbit, and magnetic spin-flip scattering times respectively.

The characteristic length is related to the characteristic field as:

$$L_x = \sqrt{D\tau_x} = \sqrt{\frac{\hbar}{4eB_x}}$$

A field $B_x = 1T$ corresponds to $L_x \sim 10 \text{ nm}$ and $\tau_x \sim 1 \text{ ps}$ for $D = 1 \text{ cm}^2/\text{s}$ ($\tau_x \sim 0.1 \text{ ps}$ for $D = 10 \text{ cm}^2/\text{s}$). Both positive and negative MR is possible, depending on the relative sizes of the three length scales. In 2D we have [9]

$$\left(\frac{\delta\rho}{\rho^2}\right)_{2D} = -\delta\sigma_{2D} = \frac{e^2}{2\pi^2\hbar} \left\{ \frac{1}{2} f_2\left(\frac{B}{B_\phi}\right) - \frac{3}{2} f_2\left(\frac{B}{B_2}\right) \right\} \quad (1-4)$$

where

$$B_\phi = B_i, \quad B_2 = B_i + \frac{4}{3} B_{so},$$

$$f_2(x) = \psi\left(\frac{1}{2} + \frac{1}{x}\right) + \ln x,$$

$\psi(x)$ is the digamma function. In 3D, the most general expression for the magnetoresistance due to WL that includes spin-orbit scattering, Zeeman splitting, and magnetic impurities is given in eq (2.1) in reference [10]. For systems without magnetic enhancement and with electron diffusivities larger than $2 \text{ cm}^2/\text{s}$, it reads:

$$\left(\frac{\delta\rho}{\rho^2}\right)_{3D} = -\delta\sigma_{3D} = \frac{e^2}{2\pi^2\hbar} \sqrt{\frac{eB}{\hbar}} \left\{ \frac{1}{2} f_3\left(\frac{B}{B_\phi}\right) - \frac{3}{2} f_3\left(\frac{B}{B_2}\right) \right\} \quad (1-5)$$

where

$$\begin{aligned} f_3(x) &= \sum_{n=0}^{\infty} \left\{ 2 \left(n + 1 + \frac{1}{x} \right)^{\frac{1}{2}} - 2 \left(n + \frac{1}{x} \right)^{\frac{1}{2}} - \left(n + \frac{1}{2} + \frac{1}{x} \right)^{-\frac{1}{2}} \right\} \\ &\approx 2 \left[\left(2 + \frac{1}{x} \right)^{\frac{1}{2}} - \left(\frac{1}{x} \right)^{\frac{1}{2}} \right] - \left[\left(\frac{1}{2} + \frac{1}{x} \right)^{-\frac{1}{2}} - \left(\frac{3}{2} + \frac{1}{x} \right)^{-\frac{1}{2}} \right] + \frac{1}{48} \left(2.03 + \frac{1}{x} \right)^{-\frac{3}{2}}. \end{aligned} \quad (1-6)$$

As shown in Ref. [10], for $D = 2 \text{ cm}^2/\text{s}$, **eq.1-6** is in very good agreement with the rigorous result, while for $D = 0.5 \text{ cm}^2/\text{s}$, there are obvious deviations. In **Figure 1-2** we plot the **eq. 1-4** and **eq. 1-5** with $D = 5 \text{ cm}^2/\text{s}$, $\tau_\phi = 100 \text{ ps}$. When $L_\phi > L_{so}$ (i.e., $B_\phi < B_{so}$), the spin-orbit scattering effect dominates and leads to a positive MR under weak magnetic field. Usually L_{so} is a weak function of temperature while L_ϕ decreases rapidly when temperature is raised. When the temperature is high enough that $L_\phi < L_{so}$, inelastic scattering dominates, and MR is negative even for weak magnetic fields. Good agreement between experiment and theory has been found in quench condensed thin film of Mg, Cu, Ag, and Au [11]. In Pd, clear deviations between experiment and theory were observed, likely due to the nearly ferromagnetic behavior of Pd [11]. By fitting the MR to **eq. 1-4** or **eq. 1-5**, one can obtain characteristic field B_χ . Combined with the value of diffusivity D obtained from zero-field conductivity, the characteristic time τ_χ and characteristic length $L_\chi = \sqrt{D\tau_\chi}$ can be calculated. The response to a magnetic field is, therefore, a powerful method to determine characteristic times of the electron system. Under low temperature, L_ϕ can reach submicron, and the corresponding characteristic field B_ϕ can be as small as $10^{-4}T \sim 10^{-3}T$.

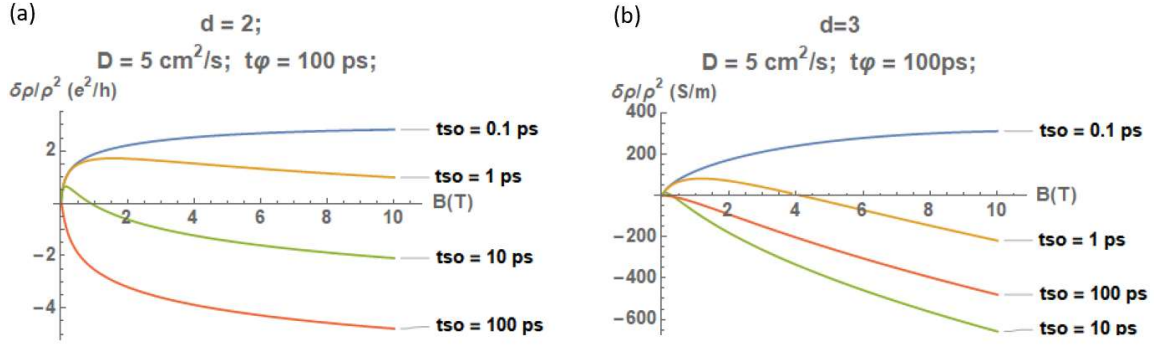


Figure 1-2: Magnetoresistance due to weak localization effect given in the eq. 1-4 for 2D and eq. 1-5 for 3D, respectively. We assume that there is no magnetic impurity ($B_s = 0$) and set $\tau_\phi = 100 \text{ ps}$.

1.2 Anderson Localization

1.2.1 The basic picture

Considered the wave function of a single electron inside a local potential well in a random potential landscape. If this well is much deeper than average, then the wave function of this electron will be localized. Similarly, if the disorder in a potential landscape is strong enough, the zero-order description is that every single electron has its wavefunction localized inside their corresponding local potential well. One can then consider the effect of coupling between different wells as a perturbation. Anderson showed that *such coupling does not produce an extended state from a linear combination of infinitely many localized orbitals*. If we use W to denote the dispersion of the energy associated with each local potential well, and I the coupling between two electrons in nearest-neighboring well, the ratio W/I will be a good measure of how strong the disorder and electron localization is. When W/I is increased (stronger disorder), an initially extended state evolves towards a state localized at some position r_0 . Such a localized state is characterized by an

exponentially decaying envelope wave function $|\psi(r)|\exp(|r - r_0|/\xi)$, where ξ is called the localization length (**Figure 1-3**).

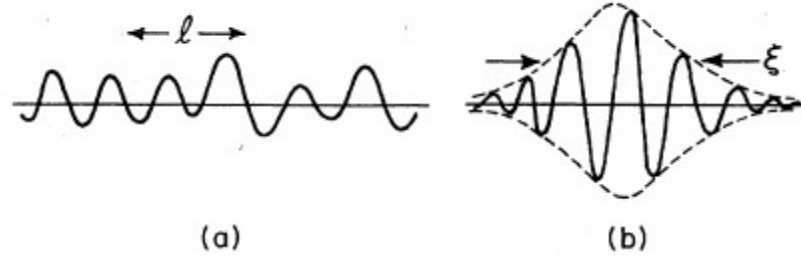


Figure 1-3: Typical wave functions of (a) extended state with mean free path l ; (b) localized state with localization length ξ . Adapted from ref [1].

The Anderson localization leads to insulator-metal transitions [12]. Suppose we start with a crystalline metallic system described by a conduction band (dashed blue line in Figure 1-4) where all states are extended states. When intermediate disorder (i.e. amorphousness) is introduced into the lattice, a band tail with localized states will emerge (shaded regime), while states deeper in the conduction band have a better chance to escape the fate of localization. The energy that divides the localized and extended states is known as the mobility edge E_m . Whether the material is an insulator or a metal depends on the position of the Fermi level E_F (red line) with respect to the mobility edge. If the disorder is strong enough to push E_m above E_F , states near the Fermi level are now localized. In other words, a metal-insulator transition – Anderson transition - occurs as we increase the disorder.

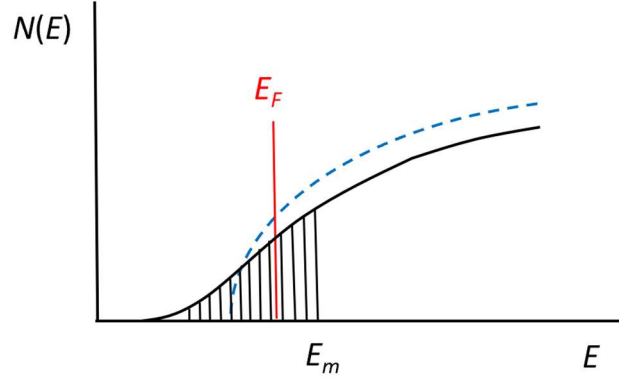


Figure 1-4: Density of states with (black) and without disorder (blue dash line). The shaded area denotes localized states for the case with disorder. If the mobility edge E_m becomes higher than the Fermi level E_F , then an Anderson transition occurs.

1.2.2 Scaling theory of localization

Thouless' hypercube

The basic idea behind the scaling theory of localization is based on Thouless' theoretical framework [13], where he considered building of size $(2L)^d$ in d dimension by putting 2^d cubes of size 2^d together and asked what is the eigenstates of the cube of size $2L$ in terms of those in the initial cubes. The eigenstates of a cube of size $2L$ can be expressed as a linear combination of the eigenstates of the initial cubes. In fact, the eigenstates and eigenenergies of the cube of size $2L$ can be solved by matching the wavefunctions at the boundaries. The degree of hybridization of the wavefunctions in the neighboring cube of size L , as well as the energy shift ΔE , is determined by the coupling (overlap integral of wavefunctions) between neighboring initial cubes and the energy denominator. The energy denominator here is the typical energy difference between two randomly selected basis states, or the spacing between the energy levels in the initial cube: $\delta W \sim (N_0 L^d)^{-1}$,

where N_0 is the density of states in the initial cubes. The quantity here that plays the role of the dimensionless ratio I/W in the last section is $\Delta E/\delta W$, i.e., $\frac{\Delta E}{\delta W} \sim \frac{I}{W}$.

The energy shift ΔE can be estimated from the uncertainty principle as, $\Delta E \approx \frac{\hbar}{\tau}$. If the electron transport inside each initial cube is diffusive, then $\tau = L^2/D$, where D is the diffusion coefficient given by Einstein relation $D = \sigma/e^2 N_0$. We also know that, after sufficient times of this edge-doubling process, one reaches the macroscopic limit where $G(L) = \sigma L^{d-2}$ for $L \rightarrow \infty$. Putting all these relations together, we have

$$\frac{I}{W} \sim \frac{\Delta E}{\delta W} \sim \hbar D N_0 L^{d-2} \sim \frac{\hbar}{e^2} G(L) \equiv g(L).$$

Thus, the dimensionless conductance $g(L)$, a measurable quantity, appears to be the single parameter that controls the nature of the eigenstate as the system doubles in size.

The Ansatz and scaling function

The ansatz behind the scaling theory of localization is that the conductance of a cube after edge-doubling is uniquely determined by the conductance of the initial cube [1]. This statement can be expressed as:

$$\frac{d \ln g}{d \ln L} = \frac{L}{g} \frac{dg}{dL} = \beta(g),$$

where the function $\beta(g)$ is independent of the size L . The unknown function $\beta(g)$ is obtained by interpolating between the $g \gg 1$ and $g \ll 1$ limit. In the limit of $g \gg 1$, that is, $I/W \gg 1$, the system is weakly disordered with weakly localized electronic states, and the classical Boltzmann formula $G(L) = \sigma L^{d-2}$ (Ohm's law) should apply. Therefore, for large conductance we have

$$\lim_{g \rightarrow \infty} \beta(g) = d - 2.$$

In the limit of $g \ll 1$, the electronic state is strongly localized. In this regime, $g(L) = g_0 e^{-L/\xi}$, where ξ is the localization radius. Therefore, for small conductance,

$$\lim_{G \rightarrow 0} \beta(g) = \ln(g/g_0).$$

The function $\beta(G)$ in the perturbative regime has the form

$$\beta(g) = d - 2 - \frac{a}{g},$$

which can be calculated by the diagrammatic technique (not shown here). We will come back to this region in section 1.3. Assuming that the scaling function $\beta(g)$ is smooth and monotonic, the scaling function $\beta(g)$ for $d = 1, 2, 3$ dimensional system is sketched as in Figure 1-5. A positive (negative) scaling function describes a metallic (insulating) system where the conductance of a hypercube increases as its edge is doubled. The arrows in Figure 1-5 show the direction in which $\ln G$ varies when the hypercube's edge is doubled.

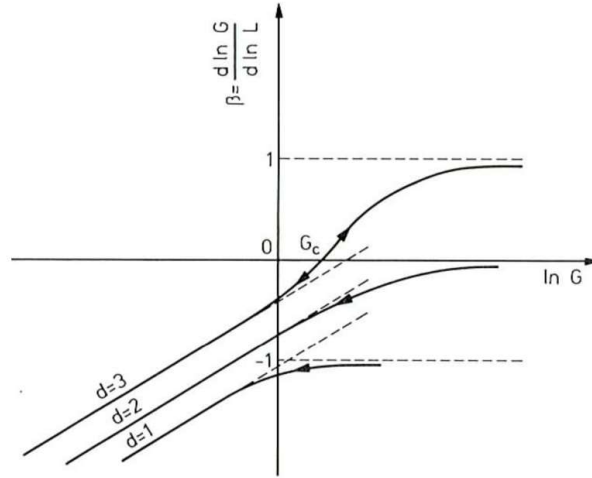


Figure 1-5: Dependence of β on $\ln G$ for $d=1, 2, 3$. Arrows show the direction in which $\ln G$ varies when the hypercube's edge is doubled. Adapted from ref [2].

Consequences of the scaling theory

In three dimensions, $\beta(g)$ starts at a positive value equal to unity for very large g and is negative for very small g (localized regime). At a certain conductance, say g_3 , $\beta(g)$ passes through zero. Let us denote the conductance of a sample at the microscopic cutoff length l is g_0 . If $g_0 > g_3$, then one starts somewhere on the positive part of the $\beta(g)$ curve. On slightly increasing the length scale from l , g increases, and one moves up a little on the $\beta(g)$ curve. Continuing this, at asymptotically large length scales the limit $\beta(g) = 1$ is reached, i.e., the system is an Ohm's law conductor. On the other hand, if $g_0 < g_3$, then one starts somewhere on the negative part of the $\beta(g)$ curve. Increasing the length scale from l decreases g , so that one moves downwards on the scaling curve. At large enough length scales, $\beta(g)$ corresponds to the scaling function for localized states $\lim_{g \rightarrow 0} \beta(g) = \ln(g/g_0)$. Therefore, the scaling theory of localization predicts that a system with conductance $g_0 > g_3$ at the microscopic length scale l is a metal, while one with $g_0 < g_3$ is an insulator. Performing similar analysis, one can see that in 1D and 2D there are no truly metallic states at zero temperature.

Non-zero temperature provides a (thermal) cutoff length for the scaling argument [1]. Suppose the diffusion constant of the electrons is $D = v_F^2 \tau / d$, the inelastic scattering time of the electron is τ_{in} , and the elastic scattering time is τ . If $\tau \ll \tau_{in}$, the electron diffuses a distance

$$L_{Th} = (D\tau_{in})^{1/2}$$

between dephasing inelastic collisions. This is often referred to as the Thouless length. Scale-dependent quantum interference of localization effects are cut off beyond L_{Th} . Thus the $T = 0$ theory with L_{Th} as cutoff describes the localization effect on conductance at a nonzero temperature T . When the size of a system is beyond such a cutoff length L_{Th} , its conductance becomes ohmic, as observed in macroscopic system under finite temperature.

1.3 Hopping conduction

At high temperatures, electrical conduction in semiconductors is dominated by band conduction of intrinsic carriers. This intrinsic carrier concentration decreases very rapidly with temperature due to the large activation energy $\varepsilon_1 = E_g/2$, where E_g is the bandgap. At sufficiently low temperatures, the intrinsic carrier concentration becomes less than the external carrier concentration, which is contributed by impurities. In the latter case, the electrical conduction is dominated by phonon-assisted hopping of electrons in the impurity band (we assume n-type semiconductor in this section). Different from band conduction, hopping conduction concerns localized states, and the overlap of wave functions is as important as the phonons that assist the hopping. This section mainly follows ref. [2].

1.3.1 General description

Interaction with phonons and overlap of the wave functions of localized states give rise to infrequent jumps from one impurity i to another impurity j . It can be shown that the frequency of such transition is $\Gamma_{ij}^0 \propto \exp(-2r_{ij}/a) \exp(-\varepsilon_{ij}/kT)$, where a is the localization radius of states near the Fermi level. The energy difference of the electronic states localized at impurity i and impurity j is

$$\varepsilon_{ij} = 1/2(|\varepsilon_i - \varepsilon_j| + |\varepsilon_i - \mu| + |\varepsilon_j - \mu|),$$

where μ is the Fermi level. Such energy difference is usually of the order of a few millielectronvolts, so the transition usually involves long-wave acoustic phonon. In equilibrium, the transition $i \rightarrow j$ and $j \rightarrow i$ are balanced. Under a weak electric field, however, the forward and

reverse transitions have different probabilities and give rise to a current. Expressing the current in the form of Ohm's law, we get the resistance associated with impurities i and j s:

$$R_{ij} = R_{ij}^0 \exp(\xi_{ij})$$

$$\xi_{ij} = \frac{2r_{ij}}{a} + \frac{\varepsilon_{ij}}{kT}$$

The preexponential factor R_{ij}^0 depends on the strength of electron-phonon interaction as well as the number of phonons available. We note that the factor $\exp(\frac{2r_{ij}}{a})$ arises from the overlap of wavefunctions, while $\exp(\frac{\varepsilon_{ij}}{kT})$ from thermal activation.

The hopping conductivity can be calculated by viewing the system as a random network of resistors R_{ij} connecting donor pairs [14]. Evaluating the electrical conductivity of a random network with an *exponentially wide spectrum* of resistance is the most complicated part of calculating the hopping conductivity [2]. The proper method to deal with such a strongly inhomogeneous medium is based on percolation theory. The effective conductivity's exponential factor, it turns out, is determined by those elements that first create percolation. It can be roughly understood in the following way [12]. Conduction will occur mostly due to the smaller resistances. If the largest resistances are eliminated, the resistance of the whole network is almost unaffected. This process can be continued, going to smaller and smaller resistance until the percolation limit of the network having only resistances smaller than some critical R_0 is reached. Beyond the percolation limit, cutting off more resistances will produce a disconnected (non-percolating) structure. After stopping at R_0 , one may also say that all the resistances that are much smaller than R_0 behave essentially like shorts. Thus, the whole network resistance is to a good approximation determined by the "just percolating" resistance R_0 .

1.3.2 Variable range hopping

When the temperature is sufficiently low, only resistances having very small values of ϵ_{ij} will contribute to conduction [15]. The reason is that the typical resistance between neighboring impurities can become larger than those connecting some remote impurities whose energy levels happen to be very close to the Fermi level. Assuming that within a narrow energy range $-\epsilon_0 < \epsilon < \epsilon_0$, the density of state is a constant $g(\epsilon) = g(\mu)$, and $N(\epsilon_0) = 2g(\mu)\epsilon_0$ states contributes to hopping conduction. One example of such density of states is that around the Fermi level in amorphous semiconductors. According to the last section, the resistivity can be written as

$$\rho = \rho_0 \exp\left(\frac{1}{N^{1/3}(\epsilon_0)a} + \frac{\epsilon_0}{kT}\right) = \rho_0 \exp\left(\frac{1}{[g(\mu)\epsilon_0]^{1/3}a} + \frac{\epsilon_0}{kT}\right),$$

where a is the localization radius of states near the Fermi level. Under very low temperature, states in the narrow band $-\epsilon_0 < \epsilon < \epsilon_0$ become very rare and their decreasing overlap becomes important. Because of the competition between the overlap and the activation, the resistivity has a sharp minimum at $\epsilon_0(T) \equiv \frac{(kT)^{3/4}}{[g(\mu)a^3]^{1/4}}$, which is called the optimal bandwidth. The corresponding resistivity is

$$\rho(T) = \rho_0 \exp\left[(T_0/T)^{1/4}\right],$$

where the characteristic temperature is

$$T_0 = \frac{\beta}{kg(\mu)a^3}$$

This is the law of Mott variable-range hopping in 3D. The coefficient β can be determined from a rigorous derivation based on the percolation method. As the temperature is lowered, the optimal bandwidth grows as $T^{-1/4}$. The typical hopping length

$$\bar{r} \sim [g(\mu)\epsilon_0]^{-1/3} \sim a (T_0/T)^{1/4}$$

also grows as $T^{-1/4}$, hence the term “variable-range hopping” (VRH). Generally, the term VRH refers to the temperature dependence of the form

$$\rho(T) = \rho_0 \exp[(T_0/T)^p], \text{ where } 0 < p < 1 \quad (1-7)$$

The value of p depends on the behavior of the density of states $g(\varepsilon)$ near the Fermi level. For example, Mott-VRH hopping in 2D has $p = 1/3$. For $g(\varepsilon) = g' \left(\frac{|\varepsilon - \mu|}{\varepsilon'} \right)^n$ with $n > 0$, the density of states vanishes at the Fermi level. With similar derivation, one can show that to $p = \frac{n+1}{n+4}$. An important case is $n = 2$, which can result from Coulomb interaction between localized states in the immediate vicinity of the Fermi level. At the presence of such a Coulomb gap, VRH at sufficiently low temperature obey **eq.1-7** with $p = 1/2$, known as Efros-Shklovskii variable-range hopping (ES-VRH). In the following, we discuss how the long-range Coulomb interaction leads to a gap in the density of states (DOS) around the Fermi level.

1.3.3 Coulomb gap in the density of states

In a lightly doped semiconductor, its impurity band contains three classes of sites: (1) positively charged donors which have donated their electrons to acceptors, (2) neutral donors, and (3) negatively charged acceptors that have accepted an extra electron from donors (). We use n_k to denote the occupation number for donor k : $n_k = 0$ for ionized donors and $n_k = 1$ for neutral donors. At zero temperature, one can obtain the distribution of electrons $\{n_k\}$ by seeking the unconditional minimum of the functional $\tilde{H} = H - \mu \sum_k^{do} n_k$, where H is the electrostatic energy and μ is the Fermi level. This is a complicated many-body problem, and the only feasible way to minimize $\tilde{H}$ in the absence of a small parameter is the following. This approach works for low, intermediate and high levels of compensation alike. One first minimizes $\tilde{H}$ with respect to one

arbitrary occupation number n_k , then with respect to a simultaneous variation of two occupation numbers, etc. Good convergence of Such a method has shown good convergence [16].

We denote the single-electron energy for each site k as $\tilde{\epsilon}_k$, measured from the Fermi level μ . As expected, minimizing with respect to one single n_k simply leads to $n_k = 0$ for $\tilde{\epsilon}_k > 0$ (occupied states below the Fermi level) and $n_k = 1$ for $\tilde{\epsilon}_k < 0$ (empty state above the Fermi level). Next, we seek to minimize $\tilde{H}$ by transferring one electron from an occupied site i to an empty site j . When we create one such electron-hole pair, we pay the interaction energy between these two localized states. Nevertheless, we can lower the total energy if $\Delta_i^j = \tilde{\epsilon}_j - \tilde{\epsilon}_i - e^2/\kappa r_{ij} < 0$, where κ is the dielectric constant of the system. In other words, it is required that

$$\Delta_i^j = \tilde{\epsilon}_j - \tilde{\epsilon}_i - e^2/\kappa r_{ij} > 0$$

for configuration $\{n_k\}$ in equilibrium. This is the condition that gives rise to the Coulomb gap. Consider one occupied state below the Fermi level with $\tilde{\epsilon}_i = -\tilde{\epsilon}/2$, and one empty state above the Fermi level with $\tilde{\epsilon}_j = \tilde{\epsilon}/2$. The inequality above requires $r_{ij} > e^2/\kappa\tilde{\epsilon}$, which is a restriction on the concentration of ionized donors. In 3D, the corresponding DOS is

$$g(\tilde{\epsilon}) = \frac{\alpha_3 \tilde{\epsilon}^2 \kappa^3}{e^6}$$

where α_3 is a numerical coefficient. We note that the Coulomb gap exists for localized states only. Metals don't have a "Coulomb gap", only a minimum of DOS at the Fermi level.

The only energy scale here is the interaction energy at the average distance between impurities, and the above equation is the only possible combination of the energy and the effective electron charge $e/\sqrt{\kappa}$ which has the correct dimensionality. The above argument is valid when bare DOS g_0 is large compared to $g(\tilde{\epsilon})$. For the case where $g_0 = \text{const}$, the width of the Coulomb gap is $\Delta = \frac{e^3 g_0^{1/2}}{\kappa^{3/2}}$.

1.4 Granular electronic system

Granular system includes a large range of material from quench-condensed metal film to self-assembled NC array. Granularity introduces new effects upon already rich physics in disordered systems. One long-standing puzzle, also relevant to this thesis, is that the ES-VRH type temperature-dependent conductivity across many different granular systems, either irregular or periodic (as least nominally so). Important understandings are achieved recently, but open questions remain. This section is mainly based on reference [7] and the model therein. The authors assume that electron motion inside each grain is diffusive and that an electron spends some time τ_0 inside a grain before it tunnels to a neighboring grain. The diameter of the grain is a . By definition of granular systems, the intragranular conductance g_0 , is larger than the intergranular conductance g .

1.4.1 Physical quantities characterizing granular systems

One expects a granular system to exhibit a metal-insulator transition (Mott transition for periodic array at $T=0$) at $g \sim 1$ (in the unit of $e^2/\hbar$). When $g \gtrsim 1$, a sample exhibits metallic behavior and grains are strongly coupled together. Electrons effectively screen out the on-site Coulomb interactions. When $g \lesssim 1$, a sample exhibits insulating behavior and electrons are localized in the grains.

We denote the mean distance between the energy levels as δ . For metal particles of the size of several nanometers, the parameter δ is typically of the order of several kelvins. If we take individual grain as the starting point of Thouless' scaling idea and define that energy shift of a level

inside one grain due to intergranular coupling as Γ , then similar to the argument in section 1.1, we have

$$\Gamma = g\delta.$$

In the limit of large conductance, this level-shifting Γ is larger than the energy spacing δ , and the discreteness of the levels within a grain becomes irrelevant. The time an electron spends inside a grain is $\tau_0 = \Gamma^{-1}$. Note that it is different from the time it takes for an electron to transverse a grain, which is inversed proportional to the Thouless energy for a single grain

$$E_{Th} = g_0\delta.$$

The effective diffusion constant (over large distance) is $D_{eff} = g\delta a^2$, again different from that for a single grain $D_0 = g_0\delta a^2$.

For insulating granular array, another important parameter is the single-grain Coulomb energy E_c . In this regime, electrons are localized in the grains and the charge of each grain is quantized. The on-site Coulomb interaction is not fully screened. For a strictly periodic array, E_c leads to simply-activated behavior [7,17].

1.4.2 Transport properties in a metallic granular system

In the classical regime (high enough temperature), the conductivity of a metallic granular array can be described by the Drude model $\sigma = 2e^2 g a^{2-d}$. As in homogeneously disordered metals, electron-electron interaction (EEL) and quantum interference lead to corrections to the Drude conductivity under low temperature. The correction due to quantum interference is

$$\frac{\delta\sigma_{WL}}{\sigma_0} = \begin{cases} -\frac{1}{4\pi^2 g} \ln(\tau_\phi \Gamma) & \text{for } 2D \\ -\frac{1}{2\pi g} (\tau_\phi \Gamma)^{\frac{1}{2}} & \text{for } 1D \end{cases}$$

Which is similar to the case of a homogeneously disordered system (**eq. 1-2**). The correction due to EEI has two parts. Denoting the corrections coming from the high and low energies with respect to Γ as $\delta\sigma_1$ and $\delta\sigma_2$, the results are:

$$\frac{\delta\sigma_1}{\sigma_0} = -\frac{1}{2\pi dg} \ln \left[\frac{gE_c}{\max(T, \Gamma)} \right]$$

$$\frac{\delta\sigma_2}{\sigma_0} = \begin{cases} \frac{\alpha}{12\pi^2 g} \sqrt{\frac{T}{\Gamma}}, & d = 3 \\ -\frac{1}{4\pi^2 g} \ln \frac{T}{\Gamma}, & d = 2 \\ -\frac{\beta}{4\pi g} \sqrt{\frac{\Gamma}{T}}, & d = 1 \end{cases}$$

The low-energy part is $\delta\sigma_2$ essentially the same as the EEI correction for a homogeneously disordered system and describes large-scale behavior. Intuitively, one would expect the granular metal model to be reduced to an effective disordered medium on distances much larger than a . The high-energy part $\delta\sigma_1$ is unique to granular systems and has no counterpart in the homogeneously disordered system.

1.4.3 Hopping conductivity in an insulating granular system

Consider a periodic granular array made of nanocrystals (NCs) or quantum dots where the interdot coupling is weak. Under low temperature, such a system is an exemplary Mott insulator, and the electrical transport mechanism is hopping between grains. At the limit of very weak intergrain coupling, the Mott gap is simply the Coulomb charging energy of the grain. Many NC arrays, either disordered or (nominally) periodic, show ES-VRH type hopping, which is puzzling as one would expect a simply activated behavior for periodic arrays. Understanding this question is achieved recently by Beloborodov *et al* [7]. There are two crucial ingredients of the hopping

conductivity: a) finite DOS in the vicinity of the Fermi level, and b) the ability to hop on distances larger than a single grain. In a realistic system, the electrostatic disorder due to charged defects leads to a finite density of states (DOS) at the Fermi level, which is further modified by the long-range Coulomb interaction and gives rise to ES-VRH [7,17]. Such DOS has been explicitly shown in computer simulation for NC arrays [18].

The mechanism for long-distance hopping over several grains, they propose, is multiple cotunneling, which is simultaneous tunneling of electrons via virtual states in intermediate grains. Depending on the temperature and applied bias, cotunneling can be either elastic or inelastic. When an electron-hole pair is created in the intermediate grain, the co-tunneling event is inelastic. Otherwise, it's an elastic cotunneling event (**Figure 1-6**). Both elastic and inelastic co-tunneling processes lead to ES-VRH type temperature dependence of zero-bias conductance, but only inelastic co-tunneling gives rise to non-linear current-voltage (I - V) characteristics under low bias [19–21]. For inelastic multiple cotunneling through $j = N - 1$ junctions in a row, the current is shown to be

$$I_{in} \sim V \left(\frac{g_T}{h/e^2} \right)^j \left[\frac{(eV/N)^2 + (k_B T)^2}{E_c^2} \right]^{j-1}$$

where g_T is the tunnel conductance of a single junction [20]. At low temperature such that $k_B T \ll \frac{eV}{N} < E_c$, the asymptotic form of I - V characteristic is a power law $I_{in} \sim V^{2j-1}$. For elevated temperature $\frac{eV}{N} \ll k_B T < E_c$, the asymptotic I - V characteristic returns linear. Such current-voltage characteristic is observed in gold nanocrystal arrays [21,22] (**Figure 1-7**).



Figure 1-6: Schematics of elastic and inelastic cotunneling. Adapted from [7].

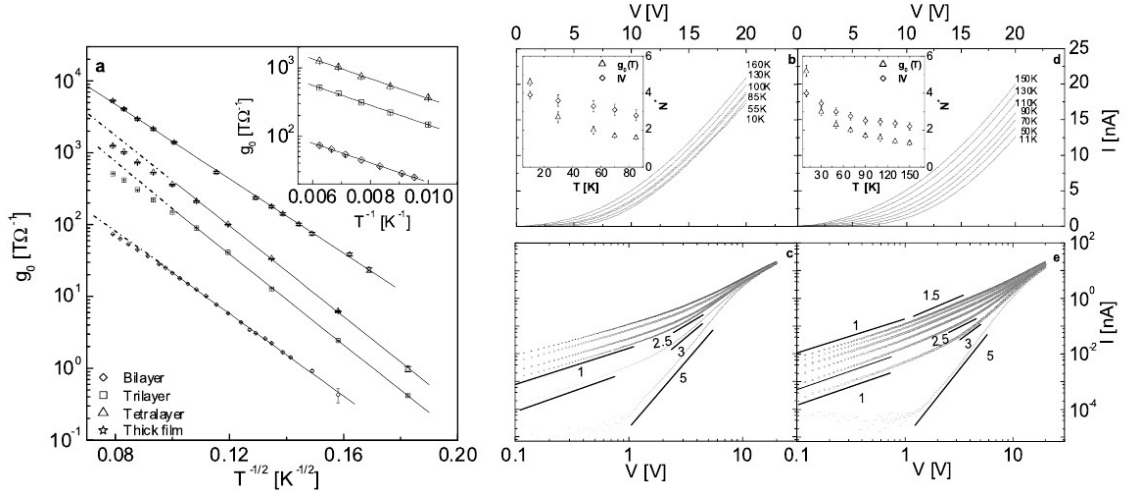


Figure 1-8: Electrical transport in gold nanocrystal arrays [22]. The zero-bias conductance shows ES-VRH type behavior. The current-voltage characteristics are explained by the multiple co-tunneling theory.

1.4.4 Metal-insulator transition in NC arrays

A criterion for IMT in touching NC arrays, analogous to the Mott criterion for bulk doped semiconductor, is given by Shklovskii *et al.* For the MIT approaching from the metallic side, the argument is as the following. At MIT, electronic transport is limited by the contact (facet) between NCs. The NC themselves are metallic, and we describe it with a Fermi wave vector $k_F = \left(\frac{3\pi^2}{g}n\right)^{1/3}$. NCs touch each other through the small facet of radius ρ . For the case of $k_F\rho \gg 1$, the conductance through such a circular constriction is given by

$$G = \frac{e^2}{4\pi^2\hbar} k_F^2 \pi \rho^2$$

in quasiclassical theory. Equating this to the conductance quantum $G_m \equiv \frac{e^2}{\pi\hbar}$, we obtain that the criterion for the MIT in touching NC arrays:

$$k_F\rho \simeq 2.$$

Shklovskii *et al* also considered the IMT from the insulating side and obtained the same result. Crudely speaking, this condition requires electron wave packets to be small enough to pass through the contact facet, a stronger condition than the bulk case (**Figure 1-8**). For example, for arrays made of Si NC with a diameter $d = 8 \text{ nm}$, this criterion gives a critical doping concentration of $n_c \approx 5 \times 10^{20} \text{ cm}^{-3}$, two orders of magnitude higher than that in the bulk as given by Mott criterion $n_M = 3 \times 10^{18} \text{ cm}^{-3}$.

The above description gives a good estimate of the critical concentration if the Fermi energy is a good estimate for the energy of the top shell. This is true for $d \gg a_B$, where the NC has a random energy spectrum filled up to $\epsilon_F = \hbar^2 k_F^2 / 2m^*$ owing to the random potential of donors. In the opposite quantum-confined case $d \ll a_B$, the spectrum in a NC is better described by energy shells (n, l) separated by gap $\Delta \sim 20\hbar^2 / m^* d^2$, as the random potential of donors is not strong enough to lift the degeneracy due to spherical symmetry.

Three-dimensional nanocrystal (NC) arrays can be viewed as the inversed structure of metalattices. Like NC arrays, we expect that the geometrical constraint in metalattices will lead to physical properties different from those in the bulk form. In self-assembled NC arrays, there is a tunnel barrier between neighboring NCs, which doesn't exist for metalattices. In chapter 4 we will discuss the consequence of the inversed fcc structure for heavily doped silicon metalattices.

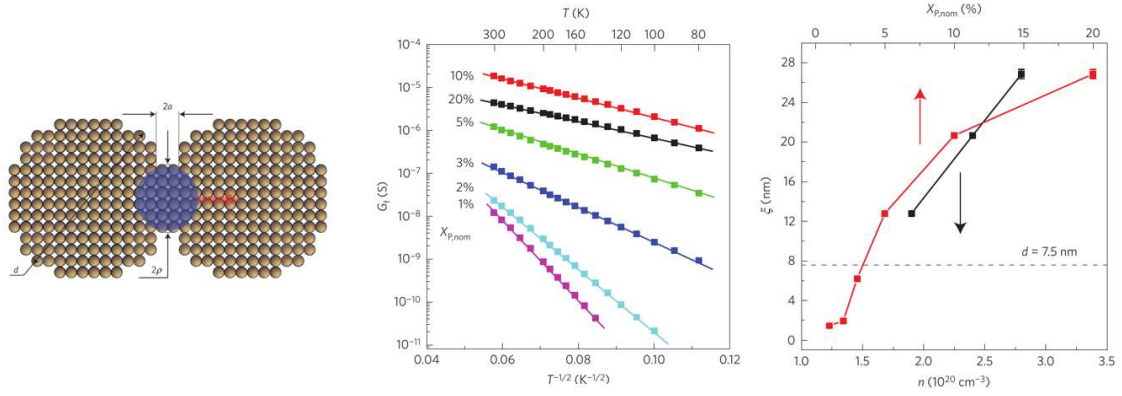


Figure 1-8: Insulator-metal transition in heavily doped silicon nanocrystal arrays [23].

Chapter 2

Experimental background

As metalattices are a new type of material, it is prudent to give a brief introduction to its preparation, even though it is carried out not by the author but by her collaborators. The recipes of device fabrication developed by the author are then detailed for both metalattices and single-crystal ZrSiS. Those recipes can be optimized in the future if needed, particularly for Si metalattices. Whereas the material synthesis and device fabrication of metalattices have not been covered by the previous study, the low-temperature electrical measurement techniques are standard. Several technical details, however, should be properly dealt with to ensure accurate experimental results.

2.1 Metalattice preparation

Templates of metalattices used in this dissertation are self-assembled SiO₂ nanosphere colloidal crystals of face-centered-cubic structure. First, monodisperse silica nanospheres with diameters of 30 - 125 nm are synthesized suspended in a colloidal solution [1-4]. The nanospheres were then self-assembled into close-packed templates by a previously described vertical deposition method with tightly controlled temperature and humidity [4]. The templates were then heated to 600 °C to remove the organic capping groups prior to metalattice deposition.

The key technique for metalattice infiltration is high pressure confined chemical vapor (or fluid) deposition (HPcCVD / HPcCFD), which is realized in late Prof. John Badding's group and explained in Appendix 1. Spatial confinement was used to increase the tendency for heterogeneous surface nucleation and the growth relative to homogenous nucleation [19]. Spatial confinement on top of the template was found to be critical to the suppression of homogenous reaction and the

formation of a (blocking) metal coating on top of the template. The lateral size of the metalattice film is limited only by the size of the reactor, which is on the mm scale.

To prepare Pt metalattices, we adapted a metallization chemistry involving (1,5-cyclooctadiene)dimethyl platinum (II) as a Pt precursor pre-dissolved in supercritical CO₂ with a mixture of 20% H₂ in He as a reducing agent [25]. The temperature for both the precursor dissolution and the deposition reaction was 70 °C. Under all three confinement conditions (Fig. A1-2 in Appendix 1), Pt was well infiltrated into the interstitial voids, forming well-connected metalattices. We successfully synthesized Pt metalattices using templates of silica nanospheres with diameters ranging from 30 to 125 nm. A Pt overlayer co-deposited on top of the metalattice during the Pt nanocasting was removed by reactive ion etching (RIE) before the SEM images were collected. Within a detection limit of 1-2%, no carbon impurities often found in other preparative routes to 3D nanomaterials were detected by XPS in our Pt metalattices (Fig. A1-3). The continuous Pt overlay film was removed afterward, but the SiO₂ spheres were left in this metamaterial of Pt. Further detail of Pt metalattices synthesis can be found in Appendix 1.

Amorphous silicon metalattices are synthesized by HPcCVD using 1- 10% silane in helium (by partial pressure) at 400 °C with total pressure of 20-35 MPa. We successfully synthesized Si metalattices using templates of silica nanospheres with diameters ranging from 14 nm to hundreds of nm. The as-deposited amorphous silicon metalattices are further annealed thermally at 800 - 850°C to polycrystalline Si metalattices. Further information on the poly-Si metalattice structure with respect to annealing condition can be found in Appendix 1. Prior to high-resolution TEM and TEM tomography study, dopant distribution study by secondary ion mass spectroscopy (SIMS) and electrical transport study, silica colloidal template was removed using hydrofluoric acid followed by drying in acetone (Appendix 1). Anisotropic plasma etching using chlorine radicals was used

for silicon over-layer removal. Further details on structural and chemical characterization can be found in Ref. [26].

2.2 Device fabrication

2.2.1 Metalattices

Electrical transport devices used in this dissertation are all prepared by lithographic techniques. For metalattices, we first use an optical microscope to identify ordered regions where the template has as few defects as possible. Electrical transport devices are then fabricated in such areas using two rounds of photolithography in Penn State Nanofab. For Si metalattices, an extra annealing step is needed afterward for making electrical contact.

- (1) The first round of lithography defines an etching mask to protect such a mesa (**Figure 2-1** a, b). The recipe is the same for Pt and Si metalattices. As the metalattices to be removed is relatively thick (varies from 100 nm to 1 μm depending on the sample), photoresist MEGAPOSITTM SPRTM 955 is used to form a thick etch mask. We follow the instruction in the datasheet of SPR 955 for resist spin, exposure and develop.
- (2) Reactive ion etching (RIE) is used to remove the unprotected film (**Figure 2-1** c). For Pt metalattices which are grown on a silicon substrate, a mixture of Ar (40 sccm), Cl₂ (20 sccm) and CF₄ (15 sccm) is used to chemically etch the SiO₂ template and physically mill away Pt metalattices. For Si metalattices grown on a quartz substrate, CF₄ is used in RIE. Scanning electron microscopy (SEM) and the optical microscope was used to check the complete removal of the unprotected area. For silicon metalattices, this is performed on a sacrificial sample to calibrate the etching rate. For the devices used on electrical transport

study, SEM is avoided as it can cause damages to the electrical properties of silicon nanostructure.

- (3) The remaining etching mask is then stripped with MicroChemTM Remover PG. A gentle oxygen plasma RIE is used to remove any possible photoresist residue (**Figure 2-1 d**).
- (4) The second round of lithography fabricates electrical devices on the metalattice mesa isolated in the first step. As the metalattices to be contacted with is thick, we use the so-called “cap-on bilayer lift-off process” for a good lift-off result. A bilayer photoresist stack is used, where the under layer is NANOTM PMGI SF 11 and the top layer is SPR 3012. The top layer resist is imaged and becomes a mask for the exposure of the PMGI film. The develop rate of the PMGI in the exposed portion is enhanced so the amount of undercut is reduced in the unexposed regime. The PMGI layer is selectively developed with PMGI 101 developer, which does not further develop the imaging resist layer. Technical processing details can be found in the respective datasheet of photoresists.
- (5) Metallization. For Pt metalattices, which is chemically stable and electrical very conductive, there are many choices for the metal used for electrodes, and we used cost-effective aluminum (200 nm) with a titanium underlayer (10 nm) to promote adhesion. For phosphorous doped Si metalattices, we choose platinum as an electrode material as platinum forms silicide and promotes electrical coupling. Before the metallization of silicon metalattices, a 10-sec buffered oxide etching is used to remove the native oxide so that electrical contact to silicon can be made. A mild argon RIE is used to clean the contact area before Pt deposition. One common problem for physical vapor deposition of platinum is film peeling due to the large difference between the surface energy of platinum and the substrate (quartz in our case), The deposition temperature is set to 5 °C to promote the adhesion of platinum to the substrate. During the deposition, the sample is tilted by 45 degrees with respect to the metal source (**Figure 2-1 e**) so that continuous film can be

formed along the sidewall of the sample. This is necessary as the deposited metal film must be much thinner than the bilayer resist stack for the “lift-off” process to work, while a thin film deposited perpendicular to the substrate wouldn’t cover the sidewall of the sample.

- (6) “Lift-off” the remaining resist (with the undesired metal film on top) using a heated bath ($\sim 50^{\circ}\text{C}$) of MicroChemTM Remover PG. An acetone bath can also be used to remove the majority of the PMGI film prior to the Remover PG bath. Sonication is strictly avoided as it can result in the loss of the metal lattices and the electrodes. An optical image of a final metalattice device is shown in **Figure 2-1 f**.
- (7) For silicon metallattices, the electrical contact is annealed in a tube furnace with an inert atmosphere (argon) at 375°C for 30 minutes. We ramp the temperature slowly ($1^{\circ}\text{C}/\text{min}$) to avoid cracking of the templates [26]. We store the silicon metallattices under vacuum to avoid oxidization.

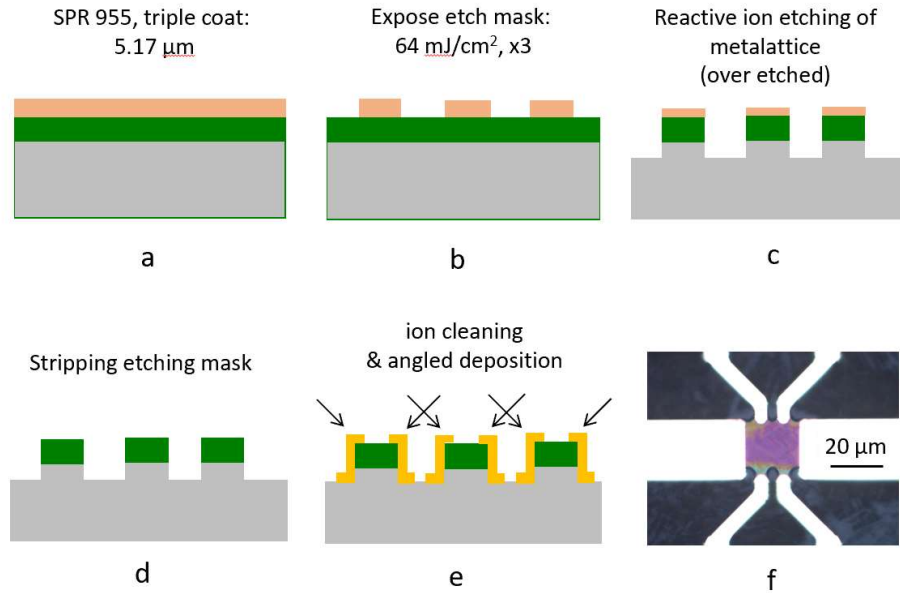


Figure 2-1: Metalattice device fabrication process (a-e) and an optical image of an electrical transport device on Si metalattice on a quartz substrate (f). The details of the second round of lithography (steps between (d) and (e)) are omitted. In (f), the bright parts are metal electrodes, the purple area is a mesa of Si metalattices, and the dark area is a quartz substrate.

2.2.2 single-crystal ZrSiS

For ZrSiS (Chapter 5), we use mechanical exfoliation to obtain ZrSiS flakes about a hundred nanometers in thickness onto a silicon wafer with 300 nm thermally grown SiO₂. The top side of the wafer was mechanically polished to provide a smooth surface for exfoliation and further processing. As the yield of exfoliation depends on the van der Waals force between the exfoliated ZrSiS crystal and the SiO₂ surface, it is necessary to clean the substrate prior to exfoliation. A 10-minute immersion in Cyantek Nanostrip is effective in removing surface contaminants; the details of the cleaning procedure can be found in Ref [27]. Electrical contact is then made using Ti/Au following step (4) to step (6) described in the last section. We have also measured bulk ZrSiS crystal with electric contact made by silver epoxy (data not shown), but the data is not as clean as exfoliated flakes, likely because exfoliated flakes are of higher quality and can possibly be a single crystal.

2.3 Electrical transport measurement

Temperature control between 400 K and 2 K is realized using Quantum Design Physical Property Measurement System (PPMS). Even though the commercial PPMS system includes a set of measurement electronics, we bypass that in favor of our custom low-noise measurement system for both high resistance and low resistance measurements, as some of our voltage measurements are performed near the theoretical limit (see below) (**Figure 2-2**). The four-point configuration is used to eliminate contact resistance and measurement electrode resistance. In this section, we explain the why and how of our high resistance and low resistance measurement. Other details,

including wiring nanostructure to measurement electronics, protecting samples from electrostatic discharge, data acquisition, can be found in Ref [27] .

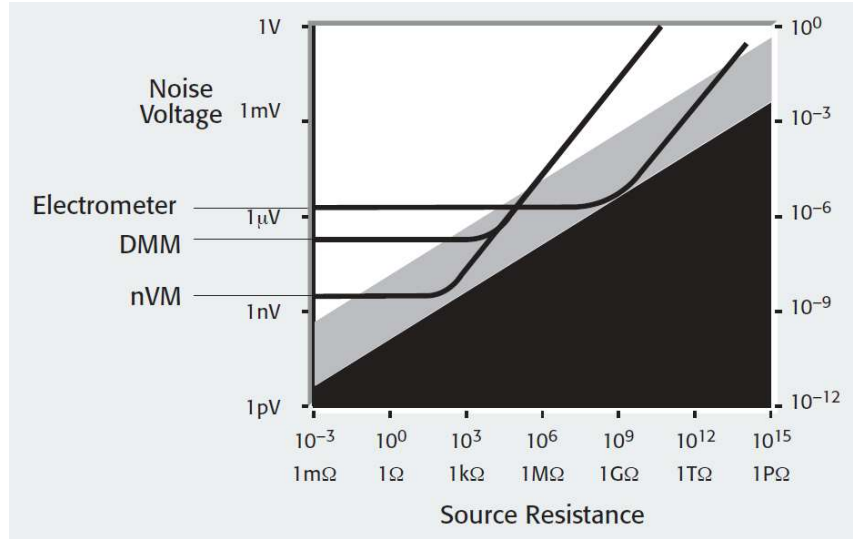


Figure 2-2: Limits of voltage measurements at various source resistances for typical digital multimeter (DMM), nano voltmeter (nVM) and electrometer. The white area is within theoretical limits, grey near theoretical limits, and the dark area is prohibited by noise. Adapted from [3]

2.3.1 Low resistance measurement

The theoretical limit of resolution in an electrical measurement is defined by Johnson noise. Johnson noise is generated by the resistance present in the circuit due to the thermal motion of charge carriers at nonzero temperature. The voltage noise is proportional to the square root of the resistance, bandwidth, and absolute temperature [3]. In our experiment on the magnetoresistance in Pt metal lattices under low temperature, the resistance is about $1\sim 10 \Omega$ with an MR at the order of 0.01% under a magnetic field of 9T. Under a bias current at the order of $1 \mu\text{A}$, it requires a resolution of $\sim 1 \text{nV}$ in voltage measurement, which should be achieved by using a nano voltmeter rather than a typical digital voltmeter. In our four-point measurement, we use the Keithley Model 6221 AC and DC current source featuring sub-pico ampere resolution and Keithley Model 2182

Nanovoltmeter featuring nanovolt resolution. Such a setup can reliably measure superconducting states in a superconductor under transition temperature.

A voltmeter also has a nonzero offset voltage due to thermoelectric EMF and offsets in the voltmeter input circuit. The thermoelectric EMF is generated when different parts of a circuit are at different temperatures and when conductors made of dissimilar materials are joined together. The effect of thermoelectric EMF should be minimized by allowing test equipment to warm up and reach thermal equilibrium at a constant ambient temperature. The thermoelectric EMF, as well as the internal offset of a voltmeter, can be canceled by reversing sources. Reversing the direction of measuring current also cancels the effect of zero drift in internal offset and the effect of device heating on the measured voltage. Making measurements between a fixed source current and a zero current also accounts for the effect of offset voltage, but not device heating.

2.3.2 High resistance measurement

Under low temperature, 14 nm and 30 nm Si metalattices are highly resistive. Below 10 K, the resistance of the devices used in our study is in the giga-ohm range. We note that a resistance above 100 G Ω is usually regarded as an open circuit. When measuring such high resistance, measurement errors can result from electrostatic interference as the charge does not dissipate quickly enough in response to the changes of charge distribution in the environment. Electrostatic shielding can be achieved by placing the device under test in a simple metal box. For measurements performed in PPMS, the Dewar serves as a shield to our devices.

Measurements from voltage sources with high internal resistance are subject to loading errors from the meter input resistance. A practical voltmeter has a finite input resistance which makes the measured voltage smaller than the source voltage. The input impedance of the voltmeter must be at least 100 times greater than the unknown resistance in order to avoid loading errors. A nonzero input bias current that flows through a practical voltmeter also causes loading errors. We

use Keithley 6430 which has an ultrahigh input impedance ($10^{16} \Omega$) for four-point measurements on 30 nm and 14 nm silicon metalattices under low temperature. If a van der Pauw (VdP) measurement is needed, we use a low current source Keithley 6221 which has sub-picoamp current resolution and performs differential measurement with a voltmeter. It can be achieved by using an electrometer like Keithley 6430 which has a built-in unitary gain buffer, or by customizing a voltmeter like Keithley 2182 by adding an operational amplifier with low input bias current or low offset voltage. Figure 2-3 shows an electronics setup for 4-point VdP measurement on high resistance samples, where triax cables are represented by a double blue line and regular coax cables by a single black line. The triax output of Keithley 6221 is connected to row 1 (R1) of the switch matrix. Row 2 (R2) of the switch matrix is connected to “Low” banana plug in the rear of Keithley 6221. When setting the triax configuration of Keithley 6221, choose “guard” for inner-shield and “float” for output-low.

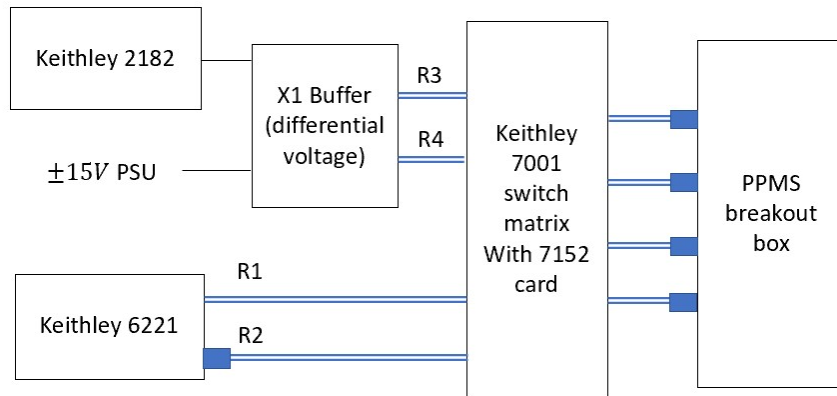


Figure 2-3: Electronics setup for 4-point Van der Pauw measurements on high resistance samples.

Another major source of error is leakage current generated by high resistance paths between low current conductors and nearby voltage sources. To reduce leakage currents, one should choose good quality insulators (and keep them clean) and reducing humidity. Guarding should also be used to reduce leakage current. A guard is a conductor connected to a low impedance

point in the circuit that is nearly at the same potential as the high impedance lead being guarded. For example, the resistor being measured in **Figure 2-4** is supported by two insulators mounted in a metal test fixture. The guard puts the top of the right insulator at almost the same potential as the bottom, so no significant current will flow through it and the current measured by the ammeter is from the device under test as desired. In our measurement setup, it can be achieved by connecting the ground of the PPMS Dewar with the ground of Keithley 6430 using 2-wire sensing. Another example of guarding involves the leakage resistance of a coax cable, which can be eliminated by using a triax cable guarded by a source-measure unit (SMU) (**Figure 2-5**). Cable guard is necessary when testing high-impedance devices ($> 1\text{G}\Omega$). Details on setting a cable guard can be found in Ref. [28].

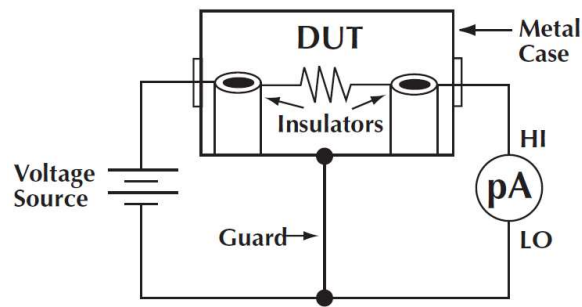


Figure 2-4: Guarding to reduce leakage currents. Adapted from Ref. [3]

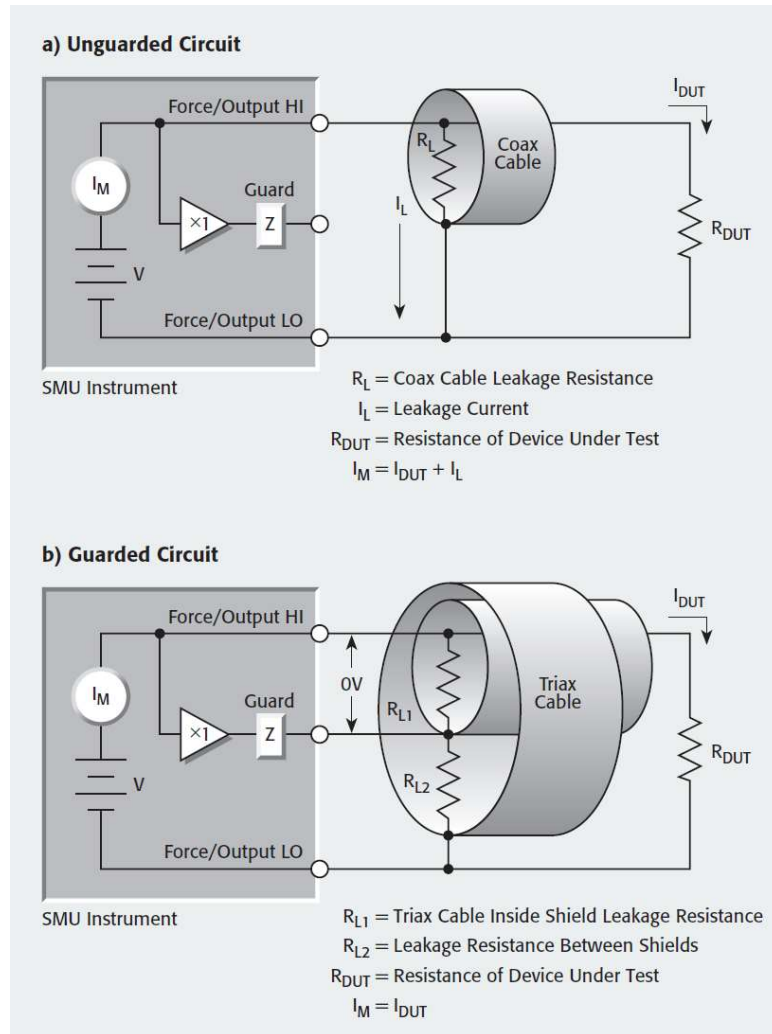


Figure 2-5: Guarding to the leakage resistance of a cable with a source-measure unit. Adapted from Ref. [3]

2.3.3 Horizontal Rotator Option in PPMS

Angle-dependent magnetoresistance measurement on ZrSiS flakes is carried out using the PPMS Rotator option. The operation is simple and well explained in the PPMS Horizontal Rotator Option Manual, but we wish to note a few details. First, to ensure accurate reading of angle, one should always follow either clockwise or counterclockwise direction when using the rotator to avoid errors from mechanical backlash. Second, the rotator is a considerable thermal load for the

cryostat, and one must use the thermometer on the rotator sample holder (rather than that at the bottom of the sample chamber) to read and control and temperature of the sample. To use our own electronics for electrical transport measurement while controlling the temperature through PPMS Model 6000 controller, a home-built adaptor was used to connect the rotator thermometer to the four-pin Lemo connector at P2 port on Model 6000 via our home-made breakout box.

Chapter 3

Quantum Transport in 30nm Platinum Metalattices

3.1 Introduction

Platinum is a late transition metal with large spin-orbit coupling, large electron-phonon coupling and is nearly ferromagnetic. Nanostructure platinum has shown properties markedly different from its bulk form. Most relevant to this chapter, it has been shown that the surface of Pt can modify its properties. For example, superconductivity has been discovered in compact platinum powder with grain size in the micron range or below [29,30]. Theoretical calculations show that the reason is the harmful spin fluctuation contribution to the intragrain pairing interaction is strongly reduced by spin-orbit scattering [31]. However, few works exist for electrical transport of nanostructured Pt in 3D, often because samples are not suitable for transport measurements [32–35]. Here we report electrical transport in 3D Pt metalattices where low-field magnetoresistance shows an anomaly in low-temperature range and discuss how this is related to the nanoscale geometrical constraint in metalattices. The work presented in this chapter also appears in a paper I co-authored (accepted by Physical Review Material). I also added some discussion on relevant length scales (Section 3.5) that is not presented in that paper.

3.2 Structural and chemical characterization

Metalattices are three-dimensional nanomaterials formed in the voids of a template of close-packed nanospheres with a diameter below 100 nm. The SiO₂ nanospheres self-assemble into well-ordered face-centered-cubic (fcc) close-packed structure by Dr. Jennifer Russell and Pratibha Mahale in Prof. Mallouk's group from Penn State. They synthesized monodisperse silica nanospheres with diameters of 30 - 125 nm suspended in a colloidal solution [24]. A previously

described vertical deposition method with tightly controlled temperature and humidity was used to assemble the template [24]. The templates were then heated to 600 °C to remove the organic capping groups prior to confined supercritical fluid chemical deposition of Pt. **Figure 3-1** shows the template made of 30 nm diameter nanospheres. We will use the diameter of the nanosphere to denote the metalattices infiltrated into such a template.

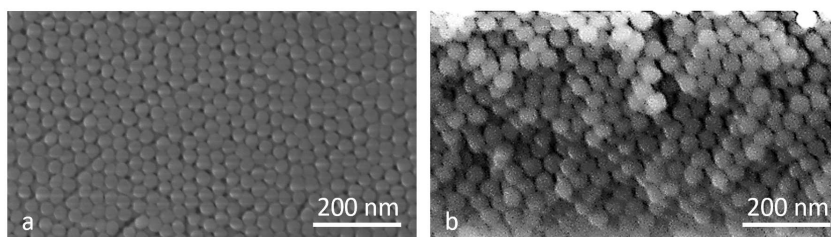


Figure 3-1: Template formed by self-assembled silica nanospheres. Scanning electron microscope (SEM) images of a template assembled from 30 nm silica nanospheres. (a) top view. (b) cross-section view.

The Pt metalattices are synthesized by Dr. Yunzhi Liu and Andrew Glaid from Prof. John Badding's group in Penn State. The infiltration of voids in the close-packed silica nanosphere template by high-pressure confined chemical fluid deposition (HPcCFD) is similar to HPcCVD introduced in Chapter 2. To prepare Pt metalattices, the metallization chemistry adopted involves (1,5-cyclooctadiene)dimethyl platinum (II) as a Pt precursor pre-dissolved in supercritical CO₂ with a mixture of 20% H₂ in He as a reducing agent [25]. The temperature for both the precursor dissolution and the deposition reaction was 70 °C. More discussion on the metallization chemistry can be found in ref. [24]. Pt metalattices were successfully synthesized using templates of silica nanospheres with diameters ranging from 30 to 125 nm. The lateral size of the metalattice film is limited only by the size of the reactor, which is on the mm scale. A Pt overlayer co-deposited on top of the metalattice during the Pt nanocasting was removed by reactive ion etching (RIE) before

the SEM images were collected. The SiO₂ spheres were left inside the sample, as they are insulating and have no effect on the electrical transport properties.

Metalattices can conceptually be divided into meta-atoms, the interstitial void space of the SiO₂ template, and meta-bonds the thin channels connecting the tetrahedral and octahedral voids, which are referred to as octahedral sites (OS) and tetrahedral sites (TS), respectively (**Figure 3-2**). **Table 3-1** shows the typical length scales in metalattices of different periodicity. A remarkable feature of metalattices is the ordering of their meta-atoms. The sizes, the shapes, and chemical composition of the meta-atoms and meta-bonds are uniform over a length scale on the order of millimeters, owing to the void-free infiltration of metal or semiconductor into the parent silica nanosphere lattice. The meta-atoms are thus correlated over a large distance relative to their size, similar to the correlation of atoms in crystalline solids. [24]

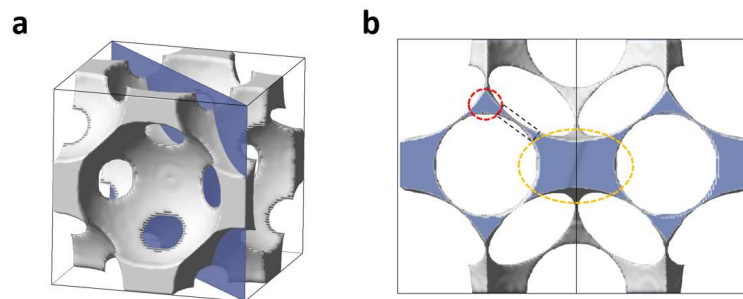


Figure 3-2: (a) 3D schematic showing a plane (purple) along $[1\ 1\ 0]$ direction cutting the metalattice structure (grey). (b) Metalattice sliced by the purple plane facing $[1\ 1\ 0]$ direction. A tetrahedral site is marked by a circle with a red dash line, an octahedral site by a circle with dashed orange line, and a meta-bond with a rectangle with dashed black line. For tetrahedral (octahedral) sites, one out of four (two out of eight) legs are cut away by the purple plane. The radius of the silica nanosphere is set to be 7% larger than its actual value to emphasize the shape of tetrahedral and octahedral sites.

Table 3-1: Length scales in metalattices of different periodicity.

metalattices	OS linear size (nm)	TS linear size (nm)	Thinnest part of metabond (nm)	Distance between neighboring OS and TS (nm)	Distance between two neighboring OS or TS (nm)
14 nm	6	3	1.1	9	12
30 nm	13	7	2.3	18	26
60 nm	26	14	4.6	36	52
100 nm	43	23	7.7	60	87

A metalattice is not only an ordered, pervasively connected nanomaterial but is also interweaved by a surface with a large area. For the face-centered cubic (fcc) template, each unit cell hosts four SiO_2 spheres of diameter d . The lattice constant of the unit cell is $L = \sqrt{2}d$. The surface area is $4\pi d^2$ for each unit cell, while the volume for the inverse fcc structure is $L^3 - \frac{2}{3}\pi d^3 = 0.73d^3$. Therefore, the surface area to volume ratio of the inversed opal structure (metalattices) is $4\pi/0.73 = 17.2/d$, higher than that of the fcc templates ($s = 6/d$). It increases quickly as we shrink the size of the SiO_2 used in the templates, even though the porosity remains a constant (74% for inversed fcc structure).

In **Figure 3-3**, we show scanning electron microscopy (SEM) images of the top surface and the side view of three different Pt metalattices, where the diameter of silica nanospheres used in the template is 30 nm, 75 nm and 125 nm, respectively. The size of nanospheres is checked under SEM and shows a standard deviation of up to 5 nm. In images of 30 and 75 nm metalattices, occasional intergrowth and dislocations in the crystal of silica nanosphere can be seen. The 125 nm metalattice, however, appears to be free from such lattice imperfections within the field of view. The cross-sectional images of the Pt filled template indicate that Pt is infiltrated into the template from the top to the bottom, with the thickness of the metalattices up to 1 μm .

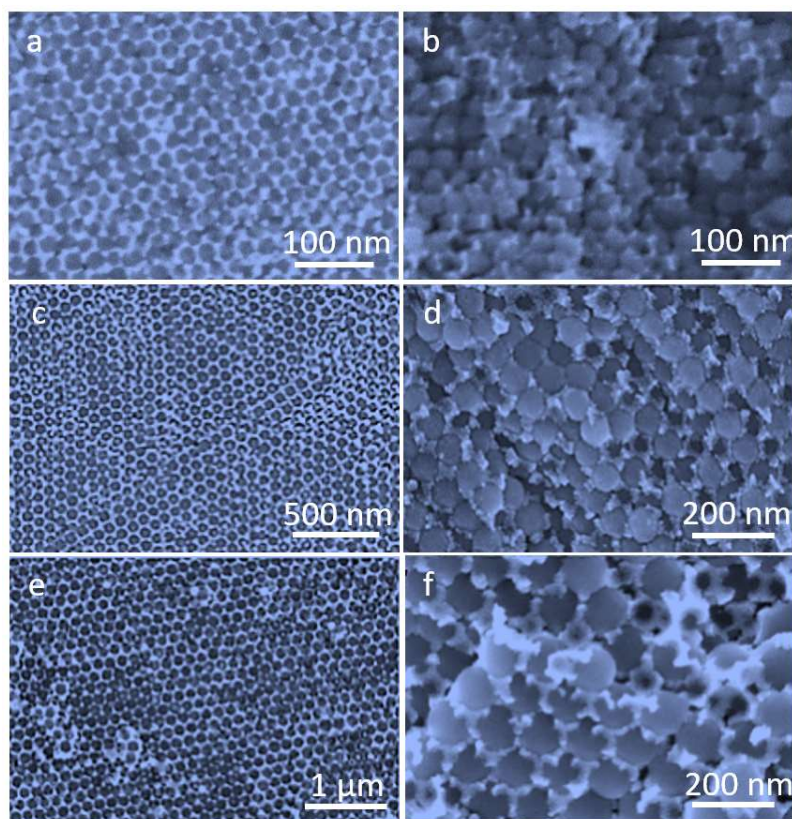


Figure 3-3: Preparation of metallattices of Pt with a varying periodicity. Scanning electron microscope (SEM) images for 30 nm (a, b), 75 nm (c, d), and 125 nm (e, f) Pt metallattices, showing the top and cross-section view, respectively. All images were taken on samples with silica nanospheres left inside the samples.

Selected area electron diffraction (SAED) reveals that the as-deposited metallattices consist of polycrystalline Pt (**Figure 3-4(a)**). Scanning transmission electron microscopy (STEM) and high-angle annular dark-field (HAADF) imaging (**Figure 3-4 (b)**) showed an inversed face-centered cubic structure. **Figure. 3-4 (c)** is the Energy-dispersive X-ray spectroscopy (EDS) mapping of Pt of the area shown in Figure 3-2 (b) and confirms the chemical composition of the network. Careful inspection of the high-resolution TEM (HRTEM) images of a 30 nm Pt metalattice revealed parallel lattice fringes from crystalline grains (data not shown) of a size in the range of 5 - 10 nm. High angle annular dark-field (HAADF) STEM image of the cross-section of a 30 nm Pt metalattice over a large length scale (**Figure 3-4(d)**) suggests long-range alignment of

meta-atoms and their good connectivity. Data from HAADF-STEM tomographic studies (**Figure 2-4 (e)**) show that the Pt metalattice prepared by infiltrating a template of 30 nm silica nanospheres is nearly void-free. The meta-atoms at tetrahedral (TS) and octahedral (OS) sites possess sizes and shapes as expected in filled interconnected clusters. The linear sizes of the meta-atoms are roughly 7 nm for tetrahedral and 13 nm for octahedral sites. The bowtie-shaped meta-bonds have a thickness of roughly 2 nm in the thinnest part. The distance between two neighboring octahedral and that between two tetrahedral sites are both 26 nm, and the octahedral and tetrahedral sites are separated by 18 nm. The occasionally broken meta-bonds seen in **Figure 2-4 (e)** were likely artifacts introduced by the high-energy focused ion beam preparation of this ultrathin sample.

3.3 Temperature-dependent resistivity under zero magnetic field

Metalattices of Pt prepared with a template of 30 nm silica nanospheres are measured down to 2 K in Physical Property Measurement System (PPMS) by Quantum Design. Our measurements reveal metallic behavior in the temperature dependence of the sample resistance. The nominal values of resistivity of the two samples at 2 K were 280 $\mu\Omega$ cm for Sample 1 and 550 $\mu\Omega$ cm for Sample 2, with a residual resistance ratio (RRR) of 1.77 and 1.16, respectively (**Figure 3-5 (a)**). To account for the volume of the template made of SiO₂ spheres, we introduce a scaling factor α to calculate the effective length L' , width W' , thickness t' , resistivity ρ' , etc., of the Pt metalattice. Assuming void-free infiltration, the volume of the Pt metalattice will be 26% of the nominal value. Therefore, $\alpha = 0.26^{-1/3} = 0.638$, and $L' = \alpha L, W' = \alpha W, t' = \alpha t, \rho' = \alpha \rho$, where L, W, t, ρ are the nominal length, width, thickness, and resistivity of the sample, respectively. The scaled resistivities are 179 $\mu\Omega$ cm and 351 $\mu\Omega$ cm. Using the carrier density of the bulk single crystal Pt [36] and the scaled resistivities, we obtain the mean-free path to be 2.23 nm and 1.44 nm for Sample 1 and 2, respectively.

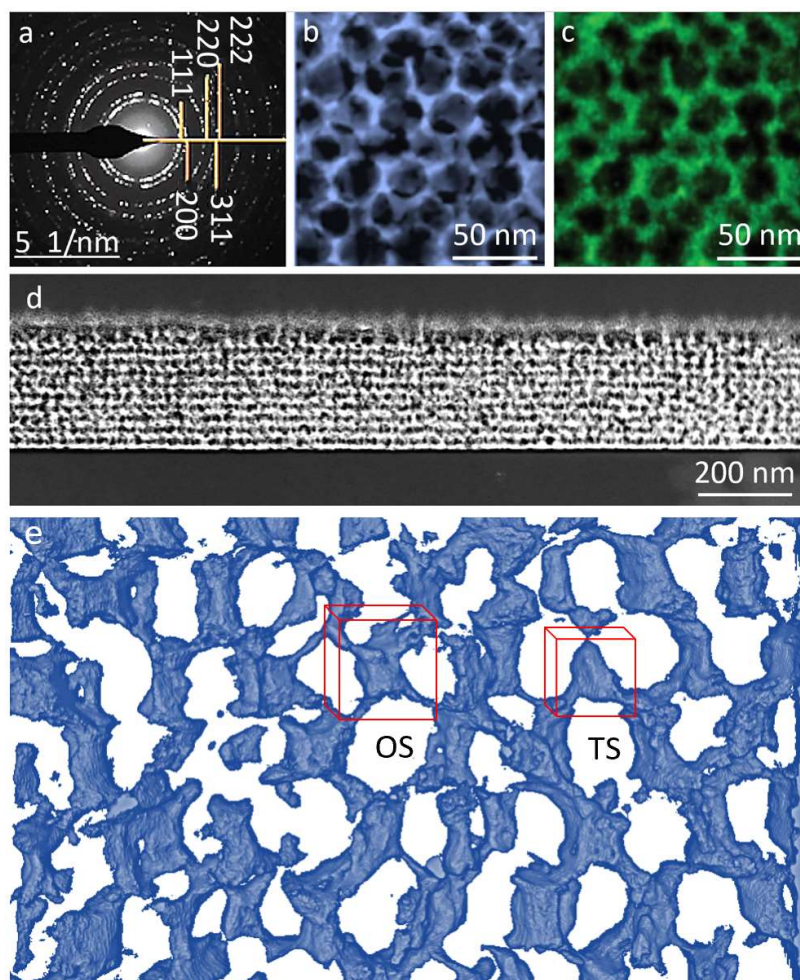


Figure 3-4: Characterization of 30 nm Pt metalattices. (a) Electron diffraction pattern from transmission microscope (TEM) studies showing that Pt metalattice is polycrystalline. (b) High angle annular dark-field (HAADF) STEM image of the cross-section of the Pt metalattice. (c) Energy-dispersive X-ray Spectroscopy (EDS) image showing uniform Pt composition in the same area as in (b). (d) Cross-sectional TEM shows that Pt metalattice is well ordered over a length scale of 1 μm . (e) HAADF-STEM tomography image of a Pt metalattice, tilted to show the 3D shape of octahedral and tetrahedral site (TS) and octahedral sites (OS). The defects seen in this image were likely introduced by the high-energy focused ion beam preparation of the ultrathin sample for this study.

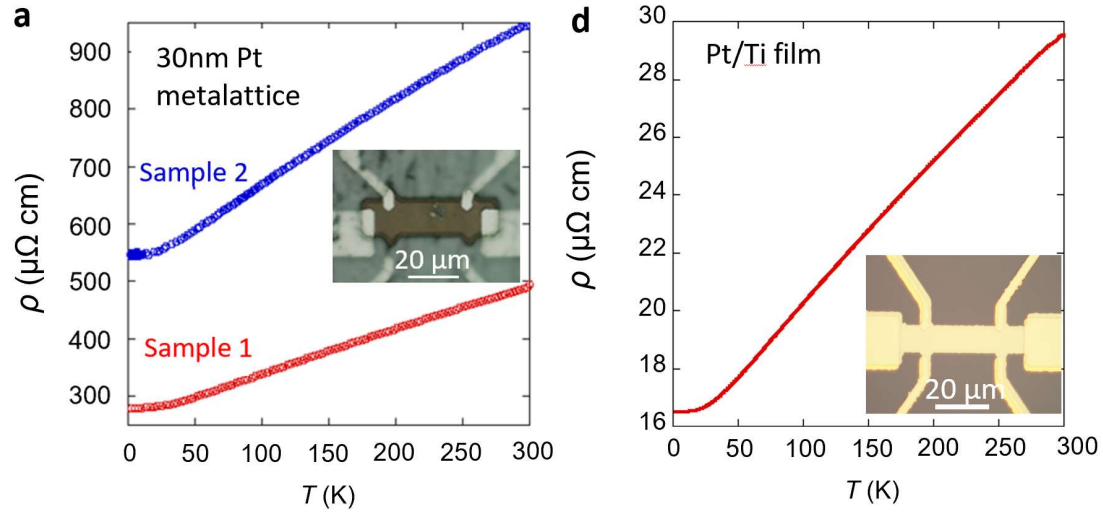


Figure 3-5: (a) Temperature dependence of the resistivity of 30 nm Pt metalattices. The inset shows an optical image of a sample. (d) Temperature dependence of the resistivity of a planar film of Pt. A 5-nm-thick Ti underlay was used to promote adhesion. The substrate is Si with 300 nm thermally grown SiO₂. The inset shows an optical image of the device.

As discussed before, the grain size in Pt metalattice observed in HRTEM is 5~10 nm. To study what effect such polycrystallinity has on the Pt metalattice, a control sample of Pt film with a similar grain size is needed. We prepare a 10 nm platinum film on a 5 nm titanium underlayer (to promote adhesion) using e-gun evaporation at room temperature. We chose the thickness to be 10 nm, as an average of the size of the octahedral and tetrahedral sites. The SEM image of our control sample (**Figure 3-6**) shows that the effective grain size in our control sample is 10 - 20 nm, slightly larger than that in 30 nm Pt metalattices. The residual resistance ratio (RRR) value of this Pt film, 1.7, is very close to that of the Pt metalattice (**Figure 3-5 (b)**). The resistivity of the 10 nm Pt film is more than one order of magnitude lower than in 30 nm metalattice. Such differences likely result from the geometric constraint of the metalattice structure rather than polycrystallinity.

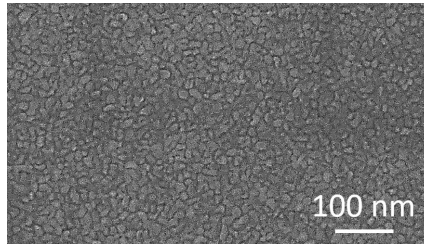


Figure 3-6: Presence of grains in the Pt film control sample. SEM image of the top view of the control sample, a 10 nm thick Pt film grown on SiO₂/Si substrate with a 5-nm-thick titanium underlay by e-gun evaporation. The effective grain size is seen to be 10 - 20 nm.

3.4 Magnetoresistance

Under a magnetic field perpendicular to the plane of the metallic film, the magnetoresistance according to classical Boltzmann transport theory is quadratic under low field and saturates at a very high magnetic field [37], as seen in bulk Pt [38]. **Figure 3-7** shows the MR of Pt metalattices under a magnetic field perpendicular to the plane of the metalattice film. Below roughly 20 K, the magnetoresistance depends linearly on the magnetic field down to 1 T, decreasing in magnitude as the temperature is raised. Above 30 K, the conventional quadratic field dependence in MR returns. The control sample shows very similar behavior under the perpendicular magnetic field in the field dependence, the temperature dependence, and the magnitude MR. However, its longitudinal MR shares the same characteristics, suggesting a non-orbital origin. The mechanism of such background MR is unclear to us, but we can conclude that it does not originate from the nanoscale geometrical constraint or the large surface to area ratio which are unique to the metalattices. We observe an interesting low-field anomaly in Pt metalattices but not the control sample, which is discussed below.

3.4.1 Low-field anomaly in magnetoresistance

From 2 K to 20 K, the low-field MR is positive, as one may expect for a material with large spin-orbit coupling like Pt. Within a small temperature window from 20 to 28 K, an unexpected negative low-field MR emerges (**Figure 3- 7(b)**). The amplitude of negative magnetoresistivity was found to be around 2.5×10^{-3} , 3.6×10^{-3} , and $1.8 \times 10^{-3} \mu\Omega \text{ cm}$ at 1 T at 22, 24, and 26 K, corresponding to a magnetoconductivity of 11, 17, and 5.5 S m^{-1} , respectively, after taking into account the sample volume reduction from the template with a maximum amplitude around 24 K. As the temperature is further raised, the low-field MR return positive. The disappearance of the negative MR below 1T happens around the same temperature as the background (high field) MR transitions from being linear to being quadratic. We observe such behavior in both Pt metalattice samples we study (**Figure 3-7 (c, d)**). Measurements on Sample 2 were not done at as many temperatures as Sample 1, and we will use data from Sample 1 in further discussion.

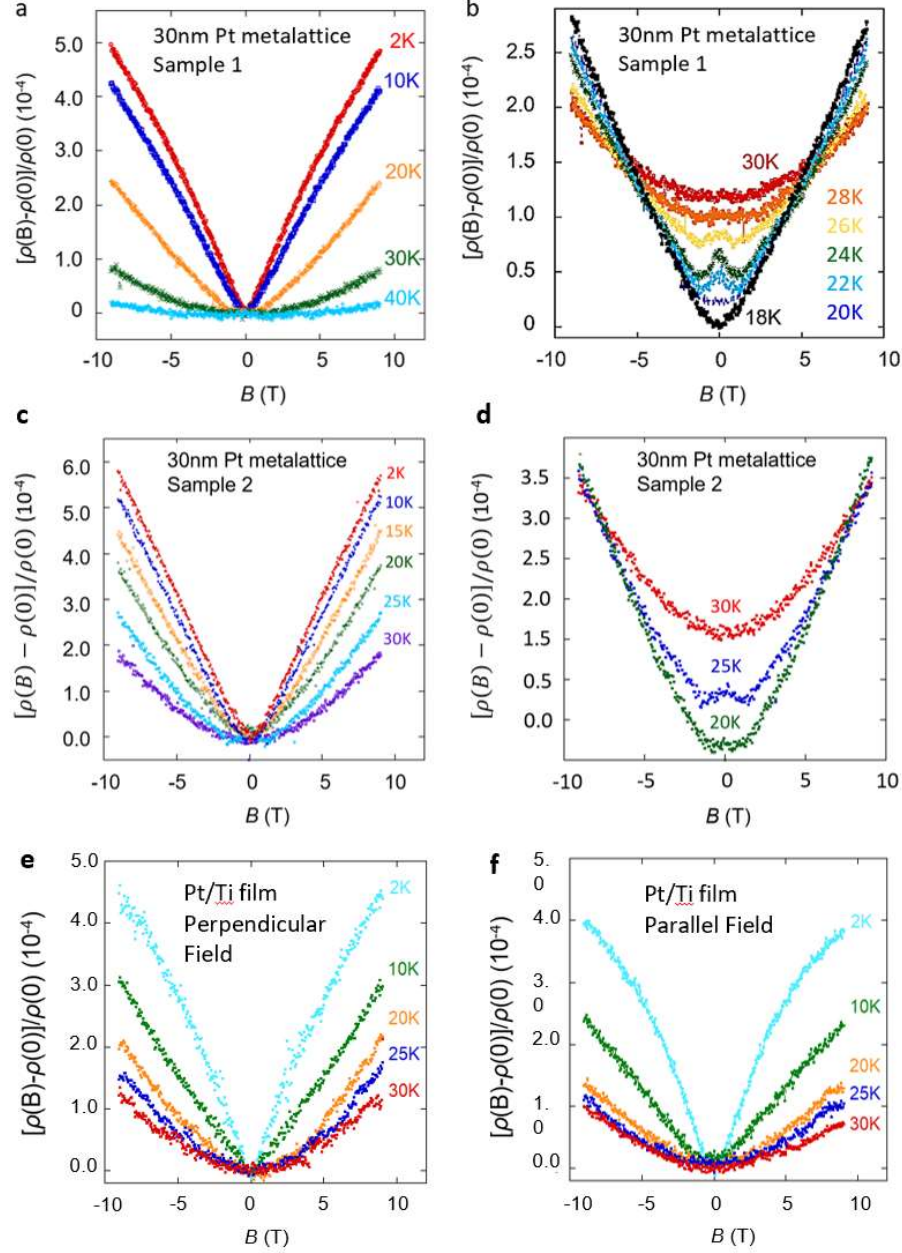


Figure 3-7: Temperature-dependent magnetoresistance in Pt metalattices and control sample. (a) The normalized values of magnetoresistance (MR) at fixed temperatures below 20 K for Sample 1 and 2 are shown in (a) and (c), respectively. Detailed behavior of MR in Sample 1 between 18 and 30 K is shown in (b). The temperatures for the curves from top to bottom are $T = 30, 28, 26, 24, 22, 20$ and 18 K. All curves except that obtained at 18 K were shifted vertically for clarity. MR of Sample 2 at the same temperature is shown in (d). Figure (e) and (f) show the MR of the control sample, Pt film. The magnetic field is perpendicular to the measurement current and the plane of the film in (e), and parallel in (f).

To the best of our knowledge, there are physical mechanisms that can lead to negative magnetoresistance: Kondo impurities [39] and ferromagnetism [40], and weak localization effect. We performed a general survey scan in XPS and observed no iron (Fe) impurities with a detection limit of ~ 0.2 atom%. Therefore, Kondo effect is unlikely the origin of the observed negative MR in Pt metalattice. While superparamagnetism has been observed in small Pt nanoclusters [32], we see no evidence of ferromagnetic order from our superconducting quantum interference device (SQUID) study in Pt metalattices. We conclude that ferromagnetic order is not the origin of negative MR in Pt metalattices either. As explained in Section 1.3, the effects of weak localization can lead to negative MR in the low magnetic field range. The inelastic scattering (here we only consider electron-phonon scattering) contributes to a negative MR with a characteristic length L_φ . The spin-orbit coupling contributes a positive MR with a characteristic length L_{SO} . The ferromagnetic fluctuation contributes a negative MR characterized by L_{MF} . Whether the observed MR is positive or negative depends on the relative size of the three parameters L_{SO} , L_φ and L_{MF} .

3.4.2 Comparing to 3D WL theory

The expression of MR due to weak localization effect in 3D is given in Ref [10]. Importantly, however, all existing theories are formulated for homogeneously disordered systems, while metalattices are distinctly inhomogeneous. The large surface to volume ratio potentially leads to the dominance of surface scattering, which is not included in existing theories. The ordered structure featuring strong and specific nanoscale geometrical constraints are expected to have an effect on the WL/WAL not found in a homogeneous system. For example, the spin-orbital length is found to be 12 nm in 1D Pt wire [28], comparable to the lateral size of meta-atoms (13 nm / 7 nm) or the length of meta-bonds (18 nm between octahedral and tetrahedral sites) in 30 nm

metalattices. Nevertheless, one may view the metalattices as an effective medium and expect existing theories to give a reasonable description. In the following, we compare our experimental results to the 3D WL/WAL theory in ref [10].

We focus on data at 24 K, where the anomaly is most distinct. We fit the MR data in the $|B| > 1$ T range to a superposition of quadratic and linear function of $|B|$ (**Figure 3-8 (a)**). Such a background MR due to classical effect is subtracted, and the remaining component is plotted in **Figure 3-8 (b)**. We choose a diffusion coefficient $D = 10 \text{ cm}^2/\text{s}$, a value typical for metals. The spin-orbit and electron-phonon dephasing times are chosen as $\tau_{so} = 100 \text{ ps}$ and $\tau_{\phi} = 10 \text{ ps}$, respectively. We will comment on the selection of these two values in the next section. The resulting theoretical curve (blue line in **Figure 3-8 (b)**) is in reasonable agreement with our experimental data below 5 T. Under a high magnetic field, the weak localization effect is expected to be suppressed. The correction in MR is about $600 \text{ S} \cdot \text{m}^{-1}$, in reasonable agreement with the value calculated from 3D weak localization formula [10]. The deviation in the field dependence of MR could result from the inhomogeneity or the spatial variation in the diffusion coefficient in metalattices.

The unexpected low-field MR in the 20 – 28 K range suggests an enhanced electron-phonon scattering due to metalattice structure. As mentioned before, the spin-orbit scattering at the vast rough surface is expected to suppress the ferromagnetic fluctuation. Therefore, the ferromagnetic fluctuation is unlikely the origin of the observed negative MR. In the experiment, the magnitude of the ferromagnetic fluctuation usually can be accessed from longitudinal MR for which one applies a magnetic field along the direction of the current. In metalattices, however, the current paths are limited by the nanostructure and cannot be aligned throughout the sample. The large surface to volume ratio means a higher contribution from spin-orbit scattering, which would contribute a positive MR. It suggests that the enhancement of electron-phonon scattering is strong enough to compensate for the negative MR due to spin-orbit scattering.

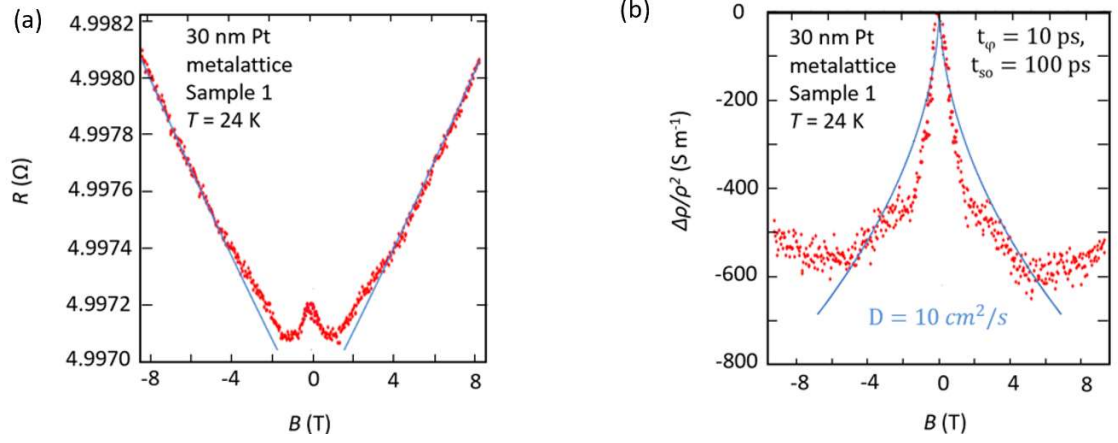


Figure 3-8. Fitting of Magnetoresistance in 30 nm Pt metalattices (a) Fitting a linear and quadratic (in $|B|$) background to MR in 30 nm Pt metalattices at 24 K. (b) MR in 30 nm Pt metalattices at 24 K after background subtraction. The blue curve is the theoretical result of the WL/WAL theory in 3D. For the theoretical calculation of the MR using the formula in Ref. 25, the diffusion coefficient is set to 10 cm²/s and the spin-orbit and electron-phonon dephasing times are 100 and 10 ps, respectively.

3.5 Further discussion on typical length scales

As pointed out in chapter 1, at the presence of spin-orbit scattering, one normally expects some positive MR under low field but only negative MR when the temperature is lowered. One may question why we cannot fit the positive MR in metalattices under low temperature to existing 3D WL formula. We think this does not exclude WL as the mechanism behind the unexpected MR behavior in Pt metalattices because the existing formula does not account for the inhomogeneity and surface scattering in Pt metalattices. In this section, we analyze why 30 nm metalattices are inhomogeneous in the length scales relevant to the weak localization effect. As the characteristic inelastic length changes with temperature, it's possible that the electrons effectively “see” different nanoscale structures under different temperatures. We also comment on our choice of spin-orbit scattering time used in the last section.

The diffusion constant D of metal typically $1\sim 10\text{ cm}^2/\text{s}$. For the sake of argument, let us take $D = 7\text{ cm}^2/\text{s}$. Since $B_x\tau_x = \frac{\hbar}{4eD}$ ($x = \varphi, so$ for inelastic and spin-orbit scattering, respectively), a characteristic time $\tau_x = 100\text{ ps}$ corresponds to a characteristic field $B_x = 2.3 \times 10^{-3}\text{ T}$ and a characteristic length scale $L_x = 0.27\text{ }\mu\text{m}$. Such a length is at the order of ten times the distance between tetrahedral (TS) and octahedral sites (OS), which is 26 nm for 30 nm metal lattices, long enough to complete a loop around a SiO_2 sphere ($\text{TS} \rightarrow \text{OS} \rightarrow \text{TS} \rightarrow \text{OS} \rightarrow \text{TS} \rightarrow \text{OS}$, for example), so electrons circling a SiO_2 sphere in clockwise and counterclockwise direction are phase coherent and can interfere with each other (**Figure 3-9**). When $\tau_x = 10\text{ ps}$, which corresponds to $B_x = 0.015\text{ T}$ and $L_x = 85\text{ nm}$, electrons lose their phase coherence before completing a loop around a SiO_2 sphere, but can still interfere when traveling through three metabonds. When $\tau_x = 1\text{ ps}$, which corresponds to $B_x = 0.15\text{ T}$ and $L_x = 31\text{ nm}$, electrons can barely maintain their phase coherence when traveling through one metabond. When $\tau_x = 0.1\text{ ps}$, which corresponds to $B_x = 2.3 \times 10^{-4}\text{ T}$ and $L_x = 8.5\text{ nm}$, only trajectories within one meta-atom can interfere (TS is about 7 nm and OS is about 13 nm).

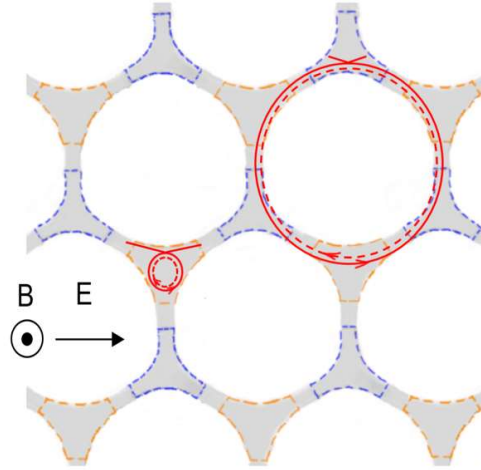


Figure 3-9. Relevant interference path in Pt metal lattices projected on the (111) plane is different when the characteristic lengths of weak localization take different values. The clockwise path (solid red line) interferes with its time-reversed counterpart (dashed red line, counterclockwise) when the time-reversal symmetry is preserved. Blue and orange dashed line label tetrahedral and octahedral sites, respectively.

The inelastic characteristic time τ_ϕ in metals under low temperature drops quickly when the temperature is raised with a typical form $\tau_\phi \sim T^{-\alpha}$, where α around 2 seems common but take different values in different materials [11]. In the disordered thin metal film, the typical value τ_ϕ around liquid helium temperature is at the order of 100 ps, which will drop to the order of 1~10 ps when temperature is raised to around 30 K. Our choice $\tau_\phi = 10$ ps is not far from the mark. Furthermore, under the lowest temperature that we measure (2 K), it's likely that inelastic scattering contributes to WL for trajectories as large as those circling a SiO₂ sphere, but under ~ 25 K only for trajectories within a meta-atom. We therefore expect inhomogeneity of metalattices to be important for WL and that its effect may change when the temperature is raised.

The spin-orbit scattering time, by contrast, is usually insensitive to temperature. The spin-orbit characteristic field B_{so} known to be proportional to Z^4 , where Z is the atomic number ($Z=78$). Some known values in the literature include $B_{so} = 0.54$ T for Mg ($Z=12$) [42] and $B_{so} \sim 0.003$ T Ag ($Z=47$) [43]. For bulk platinum, we estimate it to be at the order of 10^{-4} T or 0.1 ps using the Z^4 rule. This is much smaller than what we chose in the last section. We note that the use of a 5-nm-thick titanium underlayer should only reduce the overall spin-orbital coupling of the system because it has a small Z value compared to platinum. Further study is needed to examine if the large τ_{so} can be explained by the enhanced spin-orbit scattering due to the vast rough surface. A spin-orbit characteristic length of $L_{so} \sim 8$ nm ($\tau_{so} \sim 0.1$ ps) would suggest that the spin-orbit scattering contributes to weak (anti)localization in Pt metalattices only for electron motions roughly within one meta-atom, while with $L_{so} \sim 270$ nm ($\tau_{so} \sim 100$ ps), the nanostructure of 30 nm metalattices will modify the WL contributed by spin-orbit scattering.

Chapter 4

Heavily Doped Nanocrystalline Silicon Metalattices

4.1 Introduction

In semiconductor nanostructure, one expects effects from quantum confinement when the Bohr radius of a dopant is comparable to the characteristic length scale of the nanostructure. For example, the bandgap in a semiconductor nanocrystal can be tuned by its diameter [44]. In 30 nm silicon metalattices, electron energy loss spectroscopy (EELS) has shown blue shifts in the Si $L_{2,3}$ edge energy in octahedral sites, tetrahedral sites and metabond that are consistent with first-principle calculation [26], confirming spatial modulation of quantum confinement even at the presence of polycrystallinity. Here we investigate the effect of the nanoscale geometrical constraint in metalattice on electrical transport properties. For silicon nanocrystal arrays, which is the inverse structure of metalattices, Shklovskii *et. al.* have proposed a theoretical formula for the critical doping level of metal-insulator transition that suggests a much higher critical doping level than bulk doped silicon [23]. In search of enhanced critical doping level in silicon metalattices, we focus on heavily doped samples. Three different templates, made of silica nanospheres 14 nm, 30 nm, and 100 nm in diameter, are used to study size effect. We will show that metalattices with smaller periodicity indeed show more localized behavior compared to the reference silicon film deposited using the same recipe. We will discuss how it is related to polycrystallinity, the surface to volume ratio, and disorder in the superlattice, but future study is needed to understand these effects quantitatively. We will also show that the temperature dependence of zero-bias conductance supports the theory of multiple co-tunneling as the origin of Efros-Shklovskii variable range hopping in granular electronic systems.

4.2 Structural and chemical characterization

Silicon metalattices are synthesized by HPcCVD technique with 1-10% silane (SiH_4) in helium (by partial pressure) at 400°C under a total pressure of 20 – 35 MPa. All silica colloidal crystal templates used in this study are in face-centered cubic crystal packing. To introduce phosphorous dopants, phosphine is added to the gas mixture to deposit n-Si materials. All samples (metalattices and the reference HPcCVD Si thin film) used in this study are deposited at 400°C using the same PH_3/SiH_4 gas ratio during the HPcCVD process. Details of the synthesis process can be found in ref. [26]. The as-deposited amorphous silicon metalattices are annealed at $800 - 850^\circ\text{C}$ in a nitrogen environment. The silicon overlayer is removed by chlorine reactive etching without damaging the underlying metalattices. The structural integrity of Si metalattices is confirmed by SEM (**Figure 4-1**) and TEM studies. Further details on structural and chemical characterization of intrinsic silicon metalattices can be found in ref. [26]. Here we present our study on the dopant distribution in the silicon metalattices, which is not discussed in Yan's thesis.

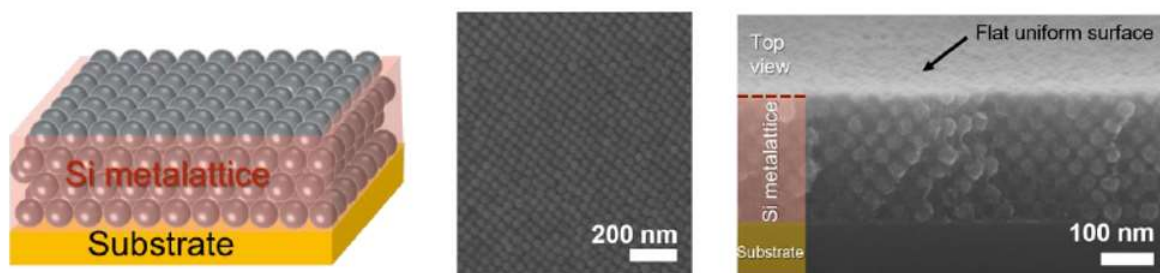


Figure 4-1: Schematic and FESEM images of as-received silicon metalattices. Left: Schematic of targeted etching results, where only the top layer is removed and the metalattices is intact. Middle: FESEM top view of Si metalattices after RIE. Right: Cross-section FESEM view of 30 nm Si metalattice after RIE. A uniform surface with colloidal crystal morphology is obtained. Courtesy of Dr. Hiu Yan Cheng.

4.2.1 Chemical doping level

Nanoscale geometrical constraint imposes new challenges for introducing and characterizing dopants, and one should not assume a uniform distribution of dopants without experimental confirmation. Growth kinetics, rather than thermodynamics, may be the governing factor of dopant distribution, as seen in doped semiconductor nanocrystals. Indeed, this is how dopants can be incorporated inside NCs at all since purely thermodynamic consideration leads to a self-purification model where all dopants will diffuse to the surface of NCs. Using atom probe tomography (APT), we find that the phosphorous atoms distribute uniformly inside the metalattices (data not shown). Dopant segregation common in Si nanostructure is not observed. Secondary ion mass spectroscopy (SIMS) finds a chemical doping level of $1.1 \times 10^{21}/\text{cm}^3$ in 30 nm Si metalattices and co-deposited Si film (Figure 4-2), and $1.0 \times 10^{21}/\text{cm}^3$ in 100 nm Si metalattices. Before SIMS, the template is etched out to eliminate errors from phosphorous atoms that may have diffused into the SiO_2 matrix. Within the detection limit, we do not observe variation in dopant density inside 30 nm Si metalattices and 100 nm Si metalattice, with a doping level close to that in the co-deposited silicon film. The doping level obtained here, however, includes electrically inactive dopants. As mentioned before, grain boundaries act as traps for both dopants and electrons [45]. The vast Si/ SiO_2 interface can also host trap states deep inside the bandgap and leads to an increase in carrier trapping and scattering [46]. Therefore, we expect the electrical active doping level to be lower than what SIMS indicates.

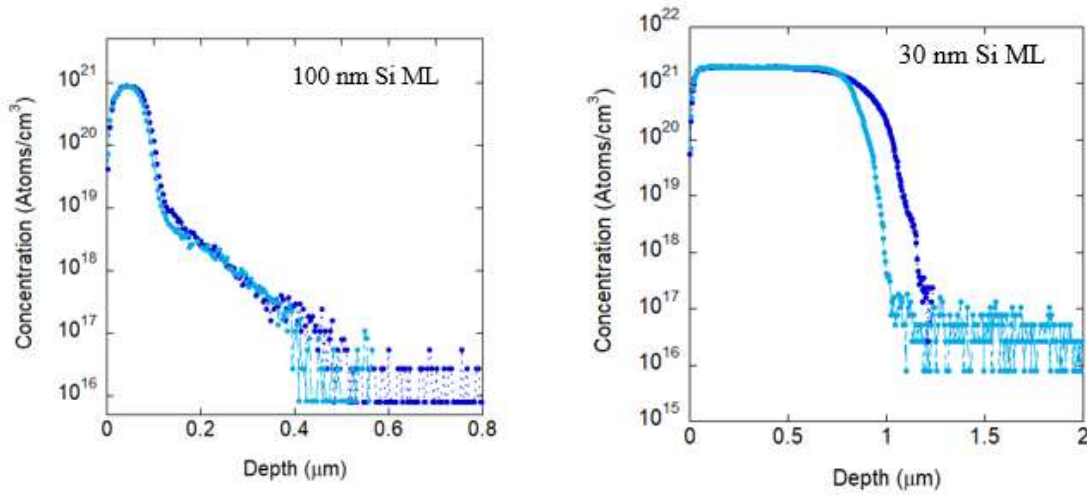


Figure 4-2. The dopant concentration in silicon metalattices on a silicon wafer with thermally grown SiO_2 surface revealed by secondary ion mass spectroscopy. The 100 nm Si metalattice is about 100 nm thick (one layer), while the 30 nm Si metalattice is 1 μm thick (about 30 layers). The chemical doping level is $1.0 \times 10^{21}/\text{cm}^3$ and $1.1 \times 10^{21}/\text{cm}^3$ in 100 nm and 30 nm Si metalattices, respectively.

4.2.2 Transmission electron microscopy

The grain size of a polycrystalline semiconductor is known to significantly affect its electrical properties. The crystallinity of our Si metalattice samples is probed using the first order A_{1g} c-Si peak at 520 cm^{-1} [26]. It is found that the full crystallization temperature of HPcCVD Si metalattices on a quartz substrate is above 750 C, which is much higher than that for the co-deposited film (650 C). Besides Raman spectroscopy, high-resolution transmission electron microscopy (HRTEM) is used to also investigate the crystallite growth inside metalattices. **Figure 4-3** shows a representative image of a 30 nm Si metalattices, where crystallites ($5 \times 4 \text{ nm}$) smaller than the size of the meta-atom site (7 nm and 13 nm) can be grown at an annealing temperature of 850 °C. Smaller crystallites from 1-3 nm in length can also be seen surrounding the larger crystals. Nano-crystallites with different crystal orientations are observed. As discussed in Appendix 2, grain boundaries make the electrical properties of polysilicon very different from monocrystalline

silicon, although the difference is small for carrier density above $10^{20} / \text{cm}^3$. Later in this chapter we will see that how the grain boundaries in silicon metalattices affect the carrier density we determined from the Hall effect for different samples.

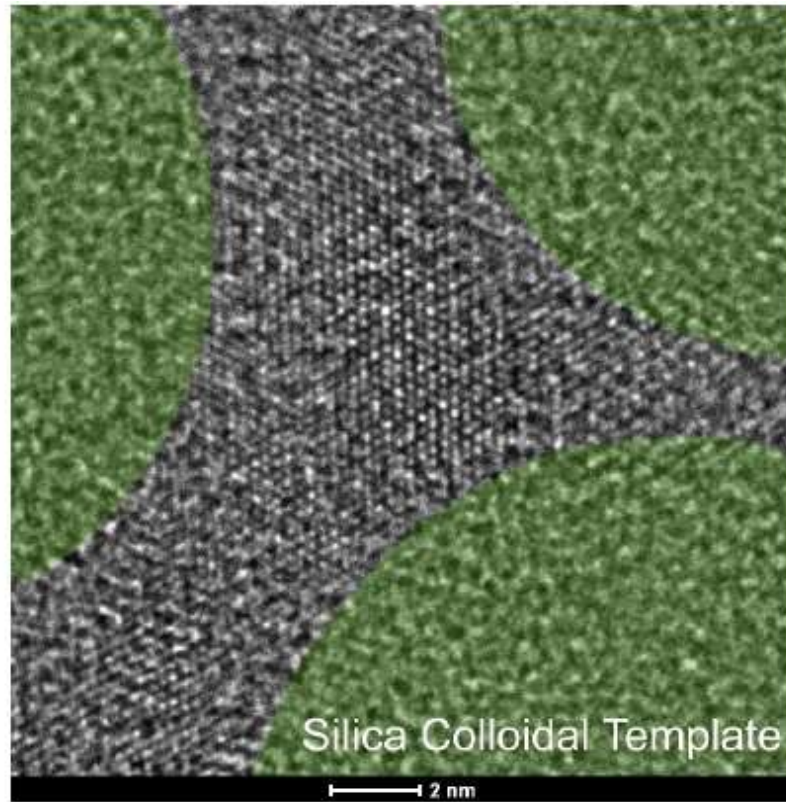


Figure 4-3. High-Resolution transmission electron microscopy image of a 30 nm silicon metalattices after thermal annealing at 850 °C. TEM credit: Dr. Shih-Ying Yu.

4.3 Carrier density from the Hall effect

As stated in the last section, the doping level determined from chemical characterization does not necessarily represent the electrically active doping level and should be measured by the Hall effect. In §4.3.1 we show that the carrier density revealed by the Hall effect in the control sample is one order of magnitude smaller than the chemical doping level revealed by SIMS. We attribute this to the polycrystalline nature of the film. We will also show that the longitudinal

transport in the control sample is consistent with such a carrier density. In §4.3.2 we present our numerical study on the Hall effect in inversed fcc structure. Based on the numerical result, in §4.3.3 we calculate the carrier density given by Hall effect in Si metalattices.

4.3.1 Co-deposited polycrystalline Si film

Figure 4-4b shows the Hall effect measured in the co-deposited Si film control sample at 300 K, which indicates a charge carrier density of $n_H = 1.2 \times 10^{20}/cm^3$. This is an order of magnitude smaller than the chemical doping level measured by SIMS, meaning that about 90% of the dopants are electrically inactive, likely trapped in the numerous grain boundaries in this nanocrystalline silicon film. As introduced in chapter one, the critical doping level for bulk silicon is $3.74 \times 10^{18}/cm^3$ [47], and we expect the co-deposited silicon film to be metallic. Indeed, the Hall effect shows no temperature dependence, characteristic of extended electronic states. The longitudinal transport properties of the co-deposited Si film also confirm such metallic nature. Its resistivity (**Figure 4-4 a**) drops slightly from $1.95 m\Omega \cdot cm$ at 300K to $1.63 m\Omega \cdot cm$ at 2K, suggesting that charge carrier scattering is dominated by defects rather than phonons. Combined with the Hall effect, the mobility of the Si film at 300K is calculated to be $11.9 cm^2/(V \cdot s)$, which is consistent with values reported in literature for heavily doped polysilicon at the doping level of $n_H = 1.2 \times 10^{20}/cm^3$. The magnetoresistance (MR) at low temperature is negative and characteristic of weak localization in weakly disordered metallic systems (**Figure 4-4 c**). When the temperature is raised, such a quantum interference effect is suppressed and the classical quadratic MR appears.

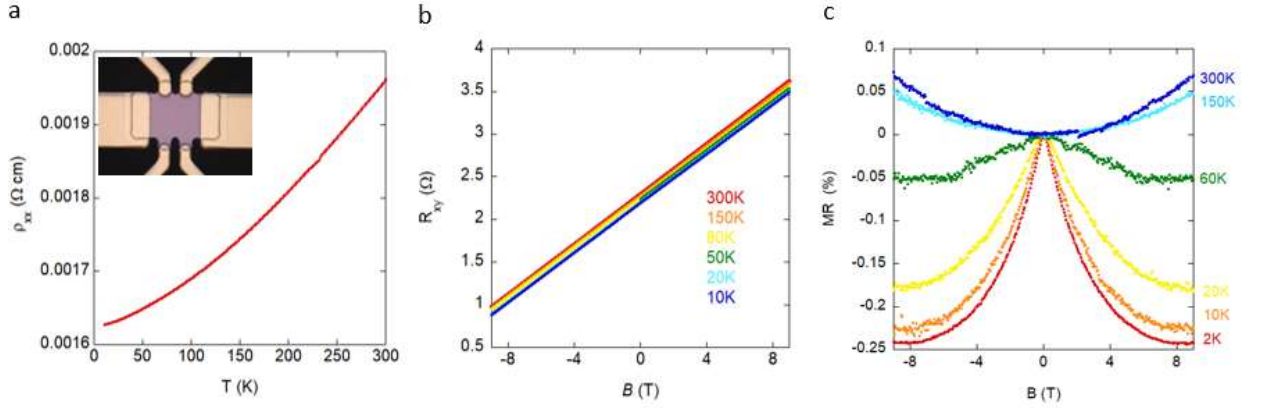


Figure 4-4. Electrical transport in the co-deposited polycrystalline heavily doped silicon film. (a) The temperature-dependent resistivity shows metallic behavior. The inset shows an optical image of the electrical transport device made of the silicon film. (b) The Hall effect of the co-deposited silicon film indicates a carrier density of $n_H = 1.2 \times 10^{20}/\text{cm}^3$ and show no temperature dependence. (c) The magnetoresistance (MR) under different temperature.

4.3.2 Hall effect in the inversed fcc structure

As we explained in Appendix 2, one must be cautious about the interpretation of the Hall effect in a multiply connected 3D structure. Using the method described there, we carry out a numerical study of Hall voltage for the inversed face-centered cubic structure and a solid block of the same dimensions. As in the experiment, the magnetic field is perpendicular to $[111]$ direction of the fcc lattice, which is along the z -axis (**Figure 4-5a**). Current is sourced along the x -axis, and the position of Hall voltage probes can be seen in the view in x - z planes. We also study the same structure of different porosity by keeping the lattice constant the same but decreasing the size of SiO_2 spheres by scaling the radius of SiO_2 sphere by a factor of p . **Figure 4-5 b** shows that the Hall voltage is almost unchanged as the porosity decreases and essentially is determined by the carrier density as if it were a continuous block, at least for the small dimensionless magnetic field range (β) simulated here. The nominal carrier density inferred from the measured Hall voltage is almost the same as the carrier density of the underlying material. The porosity, however, does have

an impact on the potential landscape (**Figure 4-5 c-f**), as different geometry imposes different boundary conditions for the corresponding partial differential equations.

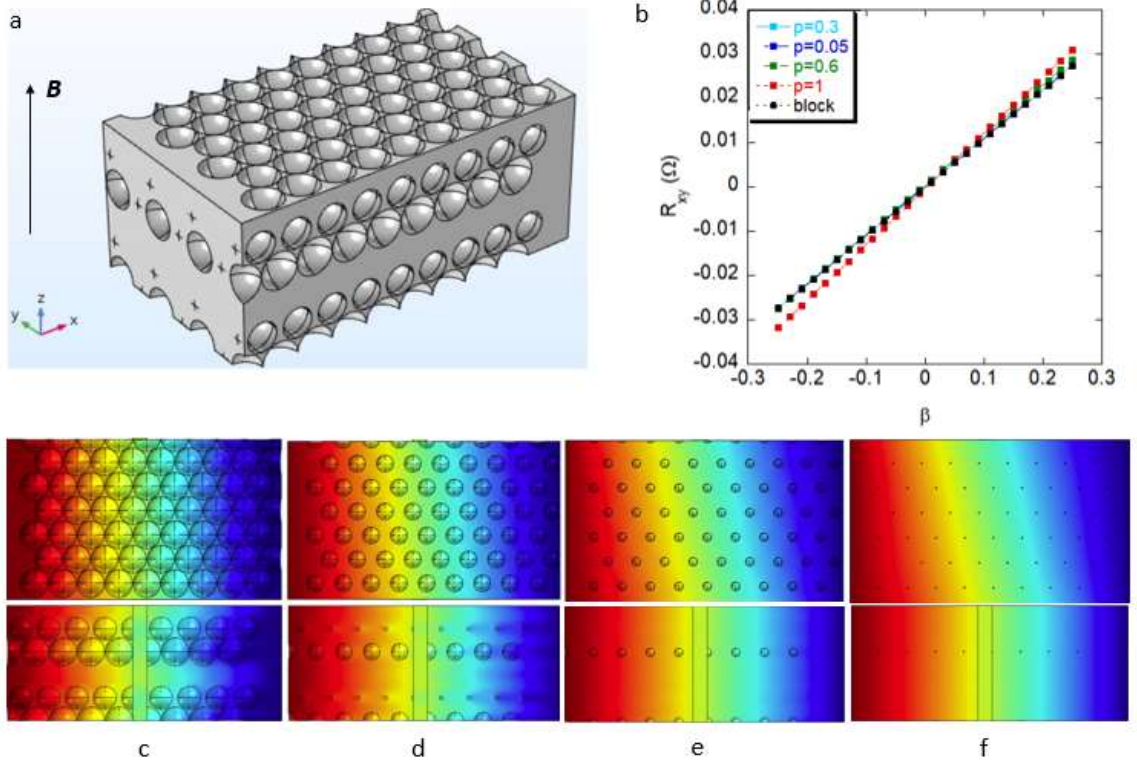


Figure 4-5. Numerical simulation of Hall effect in metalattices of different porosity. (a) The simulated sample, as in the experiment, is cut perpendicular to the $[111]$ direction of the fcc lattice and contains six layers of SiO₂ spheres (ABCABC stacking). A solid block of the same dimension is also simulated. (b) The simulated Hall resistance as a function of the dimensionless magnetic field range (β), as we change the porosity of the metalattice by scaling the radius of SiO₂ by a factor of p . (c)-(f) shows the electrical potential on the $[111]$ surface and $[010]$ surface for $p = 1, 0.6, 0.3$ and 0.05 , respectively. The position of the Hall probes is also shown in plots for $[010]$ surface.

4.3.3 Polycrystalline Si metalattices

Figure 4-6 shows the Hall effect in silicon metalattices at 300 K. The result from the co-deposited Si film is also shown as a reference. Based on the numerical simulation from the last section, we obtain the charge carrier density for 30nm Si metalattices and 100nm Si metalattices to be $3.5 \times 10^{18}/\text{cm}^3$ and $2.8 \times 10^{19}/\text{cm}^3$. We note that the numerical simulation does not take the

surface effect into account since it assumes that the conductivity tensor is the same everywhere. In 100 nm Si metalattices, we see no temperature dependence in the Hall effect between 300 K and 2 K (data not shown), which is characteristic of delocalized states. As the samples become more resistive, the noise in the Hall signal due to longitudinal MR also increases. For 30 nm Si metalattices under low temperature and for 14 nm Si metalattice even under 300 K, we are unable to detect the Hall effect for 14nm Si metalattices due to high background resistance.

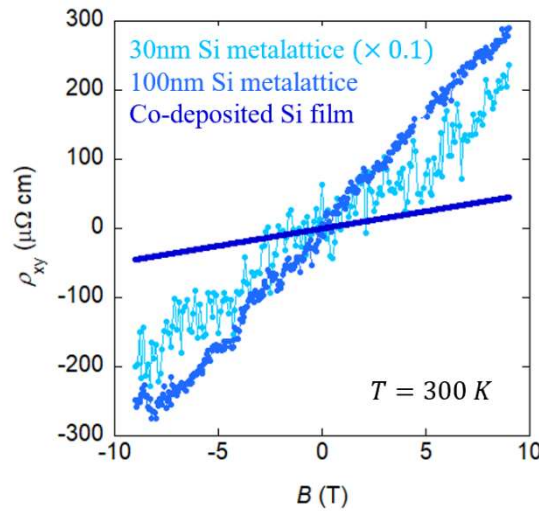


Figure 4-6. Experimental result of the Hall resistivity at 300 K in co-deposited Si film, 100 nm Si metalattice and 30 nm Si metalattices (scaled by a factor of 0.1). The carrier density in 30 nm and 100 nm Si metalattices are $3.5 \times 10^{18}/\text{cm}^3$ and $2.8 \times 10^{19}/\text{cm}^3$, respectively.

To get a crude sense of whether such doping level is high for metalattices, we can use Shklovskii's theory formulated for touching nanocrystal arrays as a qualitative reference [23,48]. As introduced in Chapter One, the IMT for nanocrystal arrays occurs at $n_c \rho^3 \simeq 0.3g$, where ρ is the radius of the neck connecting two nanocrystals, and g is the number of equivalent minima in the conduction band. Colloquially speaking, this criterion demands the carrier density for each grain to be high enough so that the wave packet can go through the neck quasi-classically without the assistance of phonons. Obviously, this criterion can only serve as an estimate for metalattices, which have the inversed nanostructure of touching NC arrays. With higher surface to volume ratio

and two types of meta-atoms, metalattices likely have higher critical doping level compared to monodispersed NC arrays. The thinnest part a wave packet must go through is that of the meta-bond, which is 7.7nm for 100nm metalattices. Using $\rho = 3.5\text{nm}$, we get an estimate for critical concentration to be $n_c = 5.3 \times 10^{18}/\text{cm}^3$, only slightly larger than the critical concentration for bulk silicon. The value $n_c = 5.3 \times 10^{18}/\text{cm}^3$ is lower than the measured carrier density in 100 nm Si metalattices, so we expect the 100 nm Si metalattices to be close to the IMT. For 30nm Si metalattices, the same reasoning leads to $n_c = 2.0 \times 10^{20}/\text{cm}^3$, much higher than that revealed by the Hall effect. In fact, the carrier density in 30 nm Si metalattices measured from Hall effect is even a little lower than the critical doping level for bulk silicon, and the nano-crystallinity will probably localize all carriers, as we will discuss in the next section.

We note that the carrier density of 100 nm Si metalattice measured from Hall effect is much smaller than that in the reference polysilicon film. For high doping level as that in 100 nm Si metalattices ($\sim 3 \times 10^{19}/\text{cm}^3$), the resistivity of polysilicon is a weak function of grain size (see next section), suggesting that the large Si/SiO₂ interface hosts considerable number of traps for carriers. As the surface to volume ratio is inversely proportional to the diameter of the SiO₂ spheres (d), we assume that the carrier density for Si metalattices (n_d) is

$$n_d = n_0 - \frac{a}{d}$$

where n_0 is the carrier density of the reference film and where a is a constant. Therefore, from $n_{100\text{ nm}} = 2.8 \times 10^{19}\text{cm}^{-3}$ and $n_0 = 1.2 \times 10^{20}\text{cm}^{-3}$, one would expect that carrier density in 30 nm Si metalattice to be about $n_{30\text{ nm}} \sim 8.4 \times 10^{18}\text{cm}^{-3}$. At such doping level, however, the depletion width around the grain boundary becomes comparable to the average grain size in 30 nm Si metalattices (6 nm). At this case, the inhomogeneity of the carrier density in a polysilicon cannot be ignored, and in Hall measurement one would obtain a carrier density smaller than the doping

level in the bulk. It can explain the smaller value of doping level ($3.5 \times 10^{18}/cm^3$) measured from the Hall effect in 30 nm Si metalattices. The small grain size compared to the depletion width at certain doping level has further effect on the resistivity of polysilicon metalattice, as we will discuss in the next section.

4.4 Effect of template size on the resistivity

The temperature-dependent zero-bias (ohmic) nominal resistivity $\rho(T)$ is shown in **Figure 4-7**. Data from the co-deposited silicon film is also shown as a comparison. The metalattices show insulating behavior (negative $d\rho/dT$) and very high resistivity, reaching $2.08 \Omega \cdot cm$, $30.6 \Omega \cdot cm$, and $82.4 \Omega \cdot cm$ at 300K in 100nm, 30nm and 14nm Si metalattices, respectively. What's the effect of template size on the resistivity of Si metalattices? More precisely, how do such values compare to the resistivity of (continuous) polysilicon with the corresponding carrier density and similar grain size? First, we note that **Figure 4-7** shows the nominal resistivity calculated with the nominal dimension of the sample. To account for the geometry, it should be multiplied by a scaling factor, which is calculated numerically using the same method of our simulation of Hall effect (see Appendix 4, with a trivial $\beta=0$). The resistivity of metalattices labeled in **Figure 4-8** is scaled by such a factor.

As discussed in the appendix, one can calculate the resistivity of a polysilicon sample for a certain grain size and doping level given the three grain boundary parameters - the width δ , and mobility shoulder Δ' and band tail Δ . Therefore, we need to know the carrier density and grain size of the polysilicon film to be compared with. The average grain size in 30 nm Si metalattices has been determined from Raman spectroscopy (6 nm). If we assume that the average grain size in metalattices is proportional to the periodicity of the template, the average grain size in 100 nm Si

metalattices is about 20 nm. The doping level determined from the Hall effect may be smaller due to polycrystallinity induced inhomogeneity. However, one can still make semi-quantitative discussion, as we show in the following.

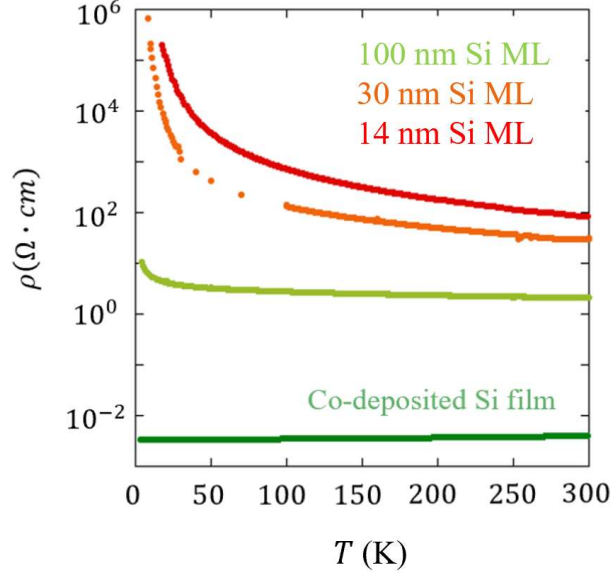


Figure 4-7: Temperature dependence of zero-bias resistivity in 14 nm, 30 nm, 100 nm Si metalattices and the co-deposited film. The resistivity for metalattices reported here is the nominal value, that is, calculated using their nominal dimensions.

At the doping level of $N_A = 3 \times \frac{10^{19}}{\text{cm}^3}$, as that revealed by Hall effect in 100 nm Si metalattices, one obtains the resistivity of grain boundary to be around $0.1 \Omega \cdot \text{cm}$ and depletion width $W \lesssim 1 \text{ nm}$. Comparing the depletion width to the average grain size ($\sim 20 \text{ nm}$), we can see that the depletion due to grain boundary in 100 nm Si metalattice is small compared to the grain size, so we expect the carrier density measured by the Hall effect to be very close to the doping level. In **Figure 4-8**, we compare the resistivity of 100 nm Si metalattice with the resistivity for polysilicon with a doping level of $3 \times \frac{10^{19}}{\text{cm}^3}$ and different grain sizes L at 300 K as calculated in **Ref. [6]**. When the grain size L is about 10 nm, $\frac{\delta}{L} \sim 0.1$, the depletion length W is small compared to L so that the grain and grain boundary have a comparable contribution to the resistivity of the grain. Still, it seems that the resistivity of 100 nm Si metalattices is about one order of magnitude

higher than polysilicon film with comparable grain size and doping level $n_1 = 3 \times \frac{10^{19}}{\text{cm}^3}$. We argue that the extra resistivity originates from the Si/SiO₂ interface. The property of states on Si/SiO₂ interface is a nontrivial question that depends on the preparation, and we do not attempt to explain the microscopic origin of the extra resistivity due to Si/SiO₂ interface. From a purely phenomenological point of view, we assume that the resistivity of silicon metalattice is a weighted average of bulk resistivity ρ_1 for a continuous film with the same carrier density n_1 and grain size L_2 and interface resistivity ρ_S : $\rho_{100 \text{ nm ML}} = a \rho_1 + \frac{b}{100 \text{ nm}} \rho_S$ where a, b are constants, and the weight of interface resistivity is inversely proportional to periodicity of the template. The first term describes the effect of grain size, while the second term describes the effect of Si/SiO₂ interface. We assume that the interface resistivity ρ_S is a weak function of the doping level n_1 , which itself depends on the periodicity of the template.

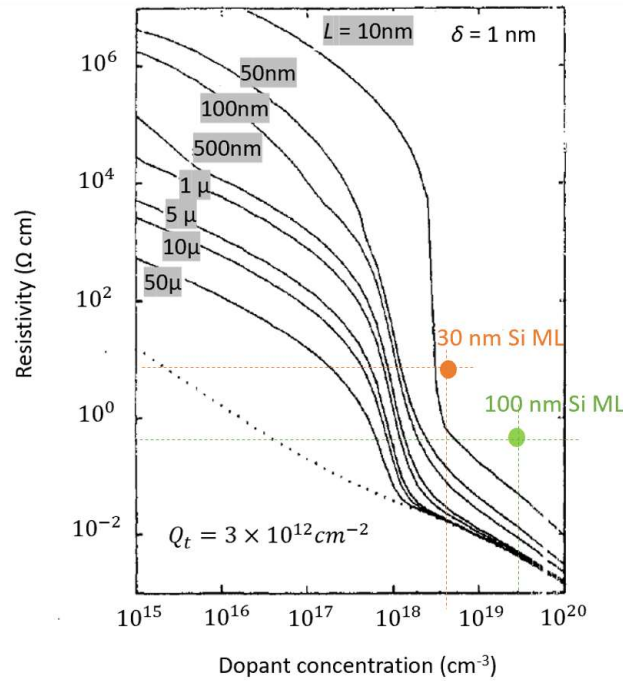


Figure 4-8. Compare the “distributed circuit” resistivity and dopant concentration for 30 nm Si metalattices and 100 nm Si metalattice with the resistivity for polysilicon with different grain size L at 300 K as calculated in Ref. [6]. Dashed line: resistivity for a single crystal.

In the last section, we estimated that the doping level of 30 nm Si metalattices is $8.4 \times 10^{18}/\text{cm}^3$. The depletion width around a grain boundary is about 3 nm for doping level $3.5 \times 10^{18}/\text{cm}^3$ and about 1 nm for $2.8 \times 10^{19}/\text{cm}^3$ (as in 100 nm Si metalattices). Therefore, the depletion due to grain boundary in 30 nm Si metalattice is comparable to the grain size, and some small grains may be fully depleted. For 14 nm Si metalattices, while Hall data will be needed to discuss the depletion due to grain boundaries, it is likely that many grains metalattices are fully depleted, as it has smaller average grain size and expected to have lower carrier density compared to 30 nm Si metalattices. Like 100 nm Si metalattices, we assume that $\rho_{30\text{ nm } ML} = a \rho_2 + \frac{b}{30\text{ nm}} \rho_S = a \rho_2 + \frac{10}{3} (\rho_{100\text{ nm } ML} - a \rho_1) = \frac{10}{3} \rho_{100\text{ nm}} + a(\rho_2 - \frac{10}{3} \rho_1)$ where ρ_2 is the bulk resistivity for a continuous film with carrier density n_2 and grain size L_2 . Unfortunately, without knowing the carrier density n_2 and the constant a , we are unable to make further quantitative discussion on the resistivity of 30 nm Si metalattices.

4.5 Variable-range hopping like behavior

4.5.1 Zero-bias conductance

We find that the zero-bias conductance in metalattices is well described by ES-VRH law $G_0 = A \exp [-(T_{ES}/T)^{\frac{1}{2}}]$ (**Figure 4-9**). The characteristic temperature T_{ES} is determined by the electron localization length ξ and the dielectric constant ϵ_r through $T_{ES} = C e^2 / \epsilon_r k_B \xi$, where k_B is the Boltzmann constant, $C \approx 9.6$ is a numerical coefficient. The effective dielectric constant of metalattices is estimated by Maxwell-Garnett formula $\epsilon_r = 5.26$. From T_{ES} obtained by fitting experimental data (**Table 4-1**), it follows that the localization length for the 14nm and 30nm Si metalattices 6nm and 9nm, respectively, comparable to the size of the octahedral site (6nm and

13nm). For the VRH hopping picture to be self-consistent, the typical hopping length should be larger than the localization length, which we discuss below.

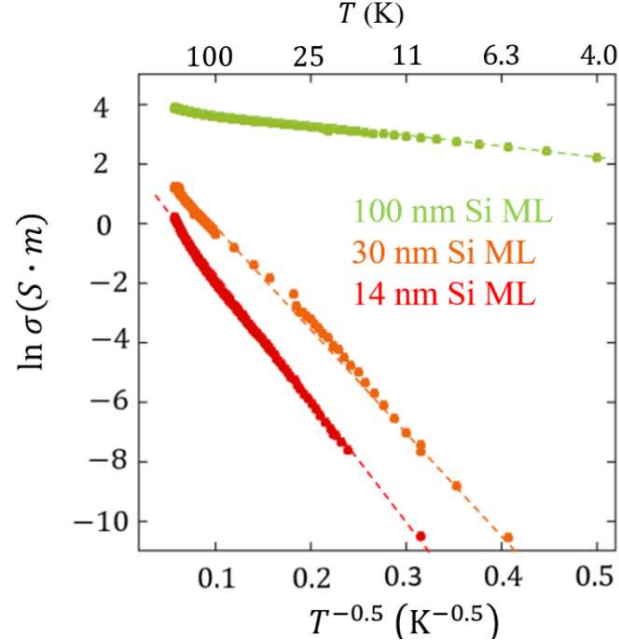


Figure 4-9: Zero-bias conductance of metalattices shows Efros-Shklovskii-VRH behavior.

Table 4-1: Efros-Shklovskii Variable-range hopping type behavior in heavily doped silicon metalattices.

Metalattice	T_{ES} (K)	ξ (nm)	E_0 (V/m)	$E_{0,exp}$ (V/m)	n_c ($10^{18}/\text{cm}^3$)	n_{Hall} ($10^{18}/\text{cm}^3$)
100 nm	11	810	6.42×10^2	9.13×10^3	5.28×10^{18}	7.62×10^{19}
30 nm	1.1×10^3	9	5.78×10^6	2.15×10^6	1.98×10^{20}	1.68×10^{19}
14 nm	1.6×10^3	6	1.26×10^7	1.38×10^7	1.95×10^{21}	-

The typical hopping length in ES-VRH is given by $r^* = \xi \sqrt{T_{ES}/CT}$. For 100 nm Si metalattice, the typical hopping length at 10 K is close to its localization length, consistent with the expectation that 100 nm Si metalattice is approaching IMT. For 30nm Si metalattice at $T = 10K$, the localization length obtained above gives $r^* \approx 30nm$, 1.6 times of the distance between a tetrahedral and its nearest octahedral sites (18nm). We note that in a metalattices made from a

template with a face-center-cubic structure, a tetrahedral (octahedral) site and its nearest tetrahedral (octahedral) neighbor is not connected by the meta-bond; an electron in an octahedral site must go through a tetrahedral to get to the nearest octahedral site. A typical hopping length of 30nm suggests that electron transport involves one to two hopping between meta-atoms. For 14nm Si metalattices at 10K, the typical hopping length is $r^* \approx 24nm$, suggesting that hopping transport typically involves three meta-atoms. At about $T = 100K$, similar analyses indicate that an electron at one meta-atom hops to only the nearest meta-atoms for both 14nm and 30nm Si metalattices. Therefore, above 100K, electrical transport is no longer described by variable range hopping. This is consistent with the deviation of zero-bias conductivity from the $T^{-1/2}$ law above 100K.

4.5.2 Field-driven regime

Under high voltage bias, ES-VRH picture predicts a temperature-independent conductance $G = A \exp \left[-(E_0/E)^2 \right]$, where the characteristic field E_0 is determined by T_{ES} through $E_0 = \frac{k_B T_{ES}}{2e\xi} \propto \frac{T_{ES}^2}{\varepsilon_r}$ [7,49,50]. In **Figure 4-10** we present such analysis. In each plot, the plateau in a low bias region describes the temperature-dependent ohmic conductance, while the linear portion under high bias describes the field-driven behavior and is essentially temperature independent. For 14 nm Si metalattice, the data at 2K are presented separately in **Figure 4-10 d** because they are obtained in a cool-down different from that in **Figure 4-10a**, which introduces error due to sample oxidization and thermal cycling. Assuming $\varepsilon_r = 5.26$, we obtain $E_{0,exp} = 1.38 \times 10^7 V/m$ by fitting the field-driven conductance in **Figure 4-10 d**. This is in good agreement with that predicted by T_{ES} and ξ obtained from the zero-bias conductance, $E_0 = 1.26 \times 10^7 V/m$. For 30nm Si metalattice at 2K, we obtain an experimental value $E_{0,exp} = 2.15 \times 10^6 V/m$, which again agrees well with that inferred from zero-bias conductance $E_0 = 5.78 \times 10^6 V/m$ (**Table 4-1**).

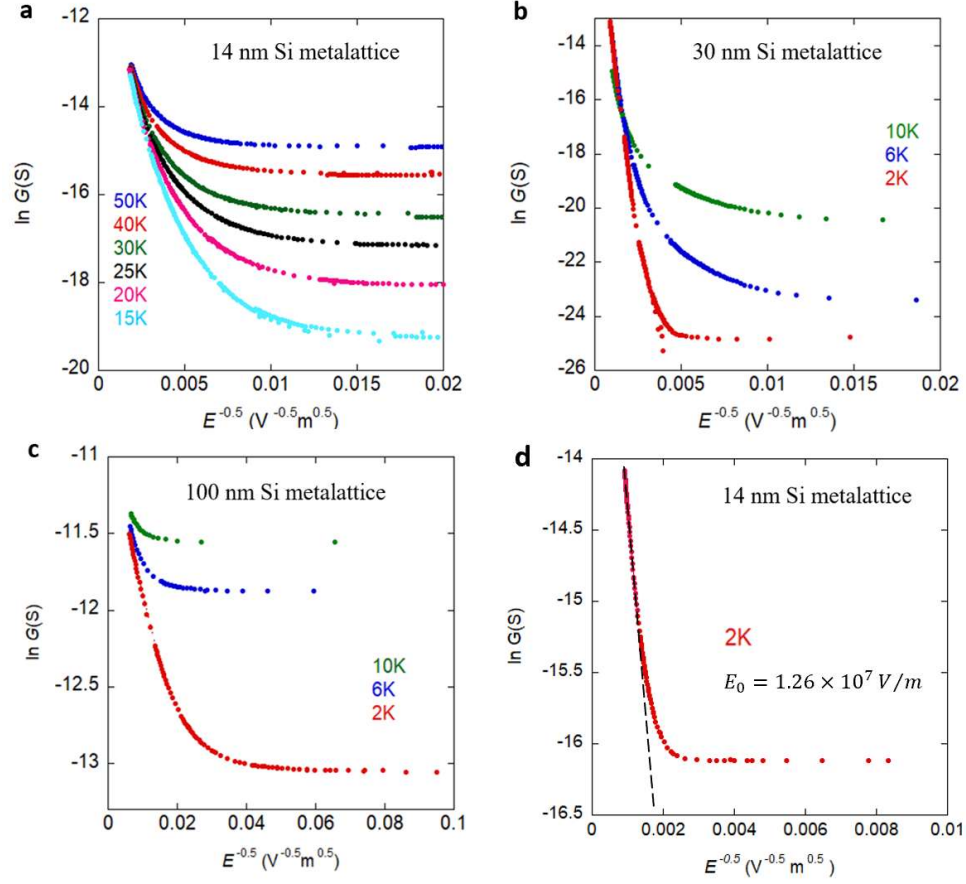


Figure 4-10. Field-driven behavior in longitudinal resistances of Si metallattices. (a) The conductance of 14 nm Si metalattice below 50 K. The plateau in the low bias region describes the temperature-dependent ohmic conductance. Under high bias, the conductance is described by $G = A \exp \left[-(E_0/E)^{\frac{1}{2}} \right]$ and has little temperature dependence, typical for ES-VRH under the electric field-driven limit. (b) The conductance of 30 nm Si metalattice at 2 K, 6 K and 10 K. (c) Conductance of 100 nm Si metalattice at 2 K, 6 K, and 10 K. It shows weaker field-driven behavior and correspondingly lower electric field threshold comparing to 30 nm Si metalattice. (d) The conductance of 14 nm Si metalattice at 2 K.

For 100nm Si metalattice at 2K, however, the experimental value $E_{0,exp} = 9.13 \times 10^3 V/m$ is more than 10 times larger than that inferred from the ohmic region, $E_0 = 6.42 \times 10^2 V/m$. Its localization length is also unusually large compared to its characteristic length scale. A large localization length implies that multiple meta-atoms are strongly coupled together, which is typical when a system comes close to the insulator to metal transition (IMT). In fact, using the

experimental value $E_{0,exp}$ and T_{ES} , we obtain a localization length of $52nm$, comparable to the octahedral site in $100nm$ Si metalattice ($43nm$), and a dielectric constant 8.2, consistent with stronger screening as a system approaches IMT.

We note that the nonlinear behavior under high bias is unlikely a result of self-heating. We ramp the current slowly to ensure that equilibrium is reached. No hysteresis in forward-backward scanning of the I - V characteristics is observed. All I - V characteristics are symmetric with respect to the origin. The temperature difference across the single-crystal quartz substrate with a thickness l ($\sim 10^{-3} m$) can be estimated by $\Delta T = Pl/\kappa S$, where P is the thermal power ($< 10^{-4} W$), κ is the thermal conductivity of single-crystal quartz ($\sim 10 W/m \cdot K$), and S is the area of the electrodes for one Si metalattice device ($\sim 2.5 \times 10^{-7} m^2$). Hence $\Delta T \sim 1 K$, a negligible value for the temperature above 10 K. The quantitative agreement between zero-bias conductance and field-driven conductance also confirms that the non-linear I - V characteristics under intermediate and high bias are intrinsic properties of Si metalattices. We also note that this nonlinearity is not due to electrical contact effect, because similar nonlinearity is observed in different device geometries with different channel lengths.

4.6 Analysis using the co-tunneling picture

The original variable-range hopping picture is developed for lightly doped semiconductors to explain the stretched exponential form of temperature-dependent conductivity. The ES- type temperature dependence results from optimizations of hopping between dopants when VRH electron-electron interaction is not negligible [51]. The observation of ES-VRH type behavior in metalattices and other granular electronic systems is puzzling [7] because geometrical constraints, such as meta-bonds in metalattices and the neck between two touching NCs, would modify

available hopping paths considerably. Beloborodov et al proposed the theory of multiple cotunneling to explain the intergranular electron hopping in an insulating granular system [7,19]. Multiple cotunneling is simultaneous tunneling of electrons via virtual states in intermediate grains. The geometrical constraints on the hopping path, imposed by intergranular junctions (meta-bonds), were modeled phenomenologically by z (the coordination number of grain in NC lattice) and g (intergranular conductance). It is argued that, in inelastic multiple cotunneling, the energy difference of the initial and final states should take the form of Coulomb interaction due to charging of grains [7]. An optimization between such Coulomb energy and probability of associated multiple cotunneling leads to ES-VRH type conductivity in the ohmic region. Depending on the temperature and applied bias, cotunneling can be either elastic or inelastic. When an electron-hole pair is created in the intermediate grain, the co-tunneling event is inelastic. Otherwise, it's an elastic cotunneling event.

4.6.1 Current-voltage characteristics

Both elastic and inelastic co-tunneling processes lead to ES-VRH type temperature dependence of zero-bias conductance, but only inelastic co-tunneling gives rise to non-linear current-voltage (I - V) characteristics under low bias [19–21]. For inelastic multiple cotunneling through $j = N - 1$ junctions in a row, the current is shown to be

$$I_{in} \sim V \left(\frac{g_T}{h/e^2} \right)^j \left[\frac{(eV/N)^2 + (k_B T)^2}{E_c^2} \right]^{j-1} \quad (4-1)$$

where g_T is the tunnel conductance of a single junction [20]. At low temperature such that $k_B T \ll \frac{eV}{N} < E_c$, the asymptotic form of I - V characteristic is a power law $I_{in} \sim V^{2j-1}$. For elevated temperature $\frac{eV}{N} \ll k_B T < E_c$, the asymptotic I - V characteristic returns linear. Eq. (4-1) is originally theorized and observed for a linear array of identical normal-metal small junctions. It

also gives a good description for gold NC solids from bilayer to thick films, where the organic ligands coating NC form tunnel barriers for electrons in each NC.

Figure 4-11 presents temperature-dependent I - V characteristics of different metalattice samples in the relevant temperature range. We estimate the charging energy E_c for a single meta-atom with lateral size D by $E_c = e^2/\epsilon_r D$, the charging energy of a nanosphere with diameter D . For octahedral sites in 100 nm Si metalattices, the charging energy is ~ 6.5 meV (~ 75 K). At 2 K, we observe $j = 5$ in 30 nm Si metalattices (**Figure 4-11 b**) and $j = 1.5$ in 100 nm Si metalattices (**Figure 4-11 c**), suggesting that the number of meta-bonds involved in multiple cotunneling is larger in 30 nm Si metalattices than in 100 nm Si metalattices. Similarly, the temperature needed for multiple cotunneling involving j junctions (meta-bonds) is higher for metalattices of smaller periodicity. For example, 14 nm Si metalattice shows $j = 3$ at 15 K (**Figure 4-11 a**), while 30 nm Si metalattice shows $j = 3$ for 6 K (data not shown).

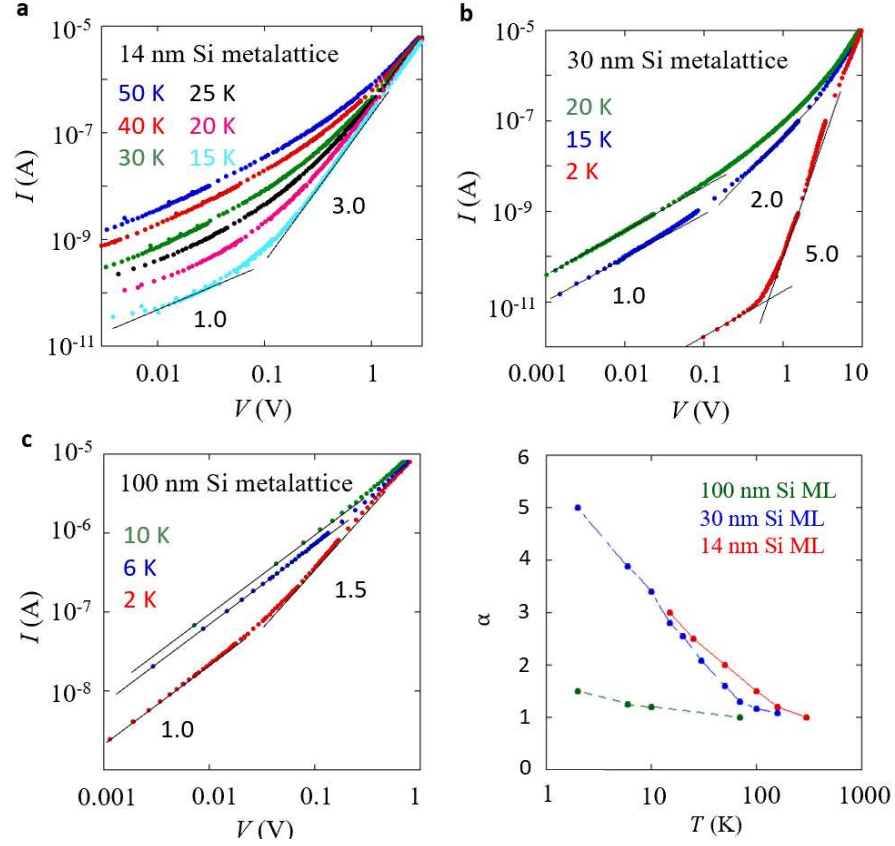


Figure 4-11: Current-voltage (I - V) characteristics of various Si metallattices. (a, b, c) Double-log plots of I - V characteristics in 14 nm, 30 nm and 100 nm Si metallattices, respectively. Solid lines are guides to the eye, emphasizing $I \sim V^\alpha$ law as inelastic cotunneling theory predicts under low temperature. The exact value of α is labeled next to each line. Towards zero-bias, one return to ohmic behavior $\alpha = 1$. (d) The index α in power-law $I \sim V^\alpha$ in different metallattices.

4.6.2 Temperature dependence in the zero-bias limit

Equation (1) also gives prediction on the temperature dependence of zero-bias conductance G_0 . Curiously, to the best of our knowledge, this prediction has not been examined in NC arrays, even though eq. (1) is used to discuss the I - V characteristics therein. In the $V \rightarrow 0$ limit, $\frac{eV}{N} \ll k_B T$, expansion of eq. (1) gives $G_0 \sim g_T T^\nu$, i.e. $\ln G_0 = \nu \ln T + \text{const}$, with $\nu = 2(j - 1)$. It turns out that linear dependence of $\ln T$ on $\ln G_0$ is observed in all metallattices studied, with a decreasing ν as the temperature is raised (**Figure 4-12**). Two temperature ranges can be identified for each metallattices. Below ~ 20 K, 30 nm and 14 nm Si metallattices both show zero-bias conductance

$G_0 \sim T^5$. Above ~ 50 K, $G_0 \sim T^\nu$ in 30 nm and 14 nm Si metalattices are best fit by different exponents (1.5 and 2.0, respectively). We believe the index ν is still related to the number of junctions (meta-bonds) the hopping involves, even though the exact relation needs to be revised for metalattices. As the temperature is raised, the typical hopping length decreases, resulting in smaller index ν . The 100 nm Si metalattices, show $\nu = 1.0$ below ~ 10 K and some fractional ν above 10 K. The physical meaning of a fractional ν is not clear to us. We note that the upper bound for conductance through a meta-bond, calculated using the size of octahedral sites in 100 nm metalattices ($a = 43$ nm) at 300 K, is $G_0 = \frac{a}{\rho_0} = 4.3 \mu S$, smaller than the conductance quantum $77 \mu S$. Therefore, metalattices samples studied here are in the strongly localized regime, and we do not expect $\ln G_0 \sim \nu \ln T$ to originate from a correction due to interaction effect, as in weakly localized granular systems [7].

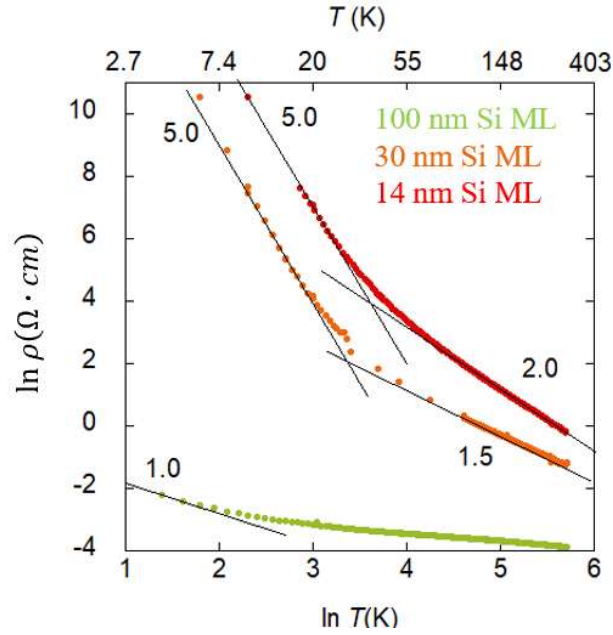


Figure 4-12: zero-bias conductance analyzed with eq. (4-1). Below ~ 20 K, 30 nm and 14 nm Si metalattices both show zero-bias conductance $G_0 \sim T^5$. Above ~ 50 K, $G_0 \sim T^\nu$ in 30 nm and 14 nm Si metalattices are best fit by different exponents (1.5 and 2.0, respectively). The 100 nm Si metalattices, show $\nu = 1.0$ below ~ 10 K and some fractional ν above 10 K.

It's interesting to observe that both stretched exponential and power-law fit the zero-bias conductance in heavily doped nanocrystalline Si metalattices equally well. This is mathematically allowed, as the power-law can result from a combination of exponentials. If cotunneling theory indeed gives rise to ES-VRH conduction, the difference between two fitting formulas should be superficial. In this sense, our observation supports the argument that multiple co-tunneling accounts for the intergranular electron hopping in ES-VRH conduction of granular electrical system [7]. However, one may argue that the theory of co-tunneling is not expected to describe metalattices, as in metalattices there is not tunneling junction as that in nanocrystal arrays. The model for electrical transport in Si metalattices, and the relation between co-tunneling and ES-VRH picture, needs future study on both experimental and theoretical front.

Chapter 5

Magnetoelectrical transport properties of ZrSiS flakes

Topological nodal-line semimetal (TNLSM) is a new class of quantum material featuring Dirac band crossing along a line (loop) in the Brillouin zone. Recent first-principle and ARPES studies prove ZrSiS as a TNLSM, and magneto-electric transport and various quantum oscillations measurements have been carried out to study its Fermi surface and possible consequence of the Dirac nodal line. Here we report systematic magneto-electric transport measurement on exfoliated ZrSiS crystal. The results of SdH oscillations agree with previous reports, while angular magnetoresistance shows unexpected fine oscillations. We uncover the periodicity for the latter, which resembles that from a two-dimensional electronic state. These results call for further investigation of the 2D- Dirac bands in ZrSiS.

5.1 Introduction

Topological semimetal (TSM) is a new class of topological quantum matter that recently attracts interest from both theoretical and experimental points of view. In contrast to topological insulators, they feature band crossing in the bulk (rather than surface) and therefore host 3D (instead of 2D) Dirac/Weyl fermions. In topological Dirac semimetals (DSM), such band crossing is protected by both time-reversal symmetry and inversion symmetry, as in the case of Na_3Bi [52,53] and Cd_3As_2 [54–57]. If one of these symmetries are broken, those (3D) Dirac fermions evolve into Weyl fermions [58–60]. The most recent development in this field is the discovery of topological nodal line semimetal (TNLSM), where the band crossing along a (continuous) line in the Brillouin zone (BZ) is protected by non-symmorphic symmetry from perturbations like spin-orbit coupling [61,62]. ZrSiS has been shown to be a TNLSM by first-principal and ARPES studies [63–66]. It has two types of Dirac cones: the first type is close to the Fermi level (FL) and forms a

nodal loop in the $k_x - k_y$ plane, while the second type is about 0.5eV below FL and sits along k_z ($R - X, A - M$) line of Brillouin zone (BZ) (**Figure 5-1 b**). The latter is generated by silicon square lattice and protected by non-symmorphic symmetry. Magneto-electrical transport measurements have been carried out in attempt to study the consequences of the Dirac nodal line (DNL) [67–71].

Magnetoresistance (MR) measurements have been a useful tool to probe the electronic properties of metallic material. One of the most popular ways to determine Fermi surface (FS) morphology is by measuring Shubnikov-de Haas (SdH) oscillations, which show up in longitudinal resistivity ρ_{xx} as the Landau levels are moved through the Fermi energy when the strength of the magnetic field is varied [72,73]

$$\rho_{xx} = \rho_0[1 + A(B, T)\cos 2\pi(B_F/B - \delta + \gamma)]$$

Here, $1/B_F$ is the SdH frequency and is proportional to the area of the extremal orbit of the Fermi surface. The phase shift δ takes the value of $\delta = 0$ (for a 2D system) or $\delta = \pm 1/8$ (for a 3D system), and γ is related to the Berry phase Φ_B via $|\gamma - \delta| = |1/2 - \Phi_B/2\pi - \delta|$. Similar quantum oscillations due to Landau level quantization also show up in magnetization and thermoelectric power. In ZrSiS, such quantum oscillations have revealed both 3D and 2D Dirac cones [69,74,75] and non-trivial Berry phase. The 2D Dirac cones are found under a magnetic field along the c -axis with a frequency of 240T and a phase $|\gamma - \delta|$ of 0, although when the magnetic field tilts, the frequency appears to deviate from true 2D electronic states [69,74].

The “classical” behavior of MR (those not originating from the Landau level quantization) also reflects the electronic properties of a material. Semimetals with almost compensated electron and hole pockets give rise to large non-saturating MR quadratic in the field strength [76], while DSM and WSM can show linear and negative MR [77,78]. The angle dependence of magnetoresistance (AMR) – which is surveyed by tilting the magnetic field with fixed magnitude - reflects the symmetry and shape of FS. For instance, the three interchangeable Dirac valleys in bismuth give rise to six-fold symmetric in-plane AMR under a low magnetic field, while when

polarization is induced under a high magnetic field, such symmetry is lost. In ZrSiS, a four-fold symmetric, butterfly-shaped AMR is observed [69,79,80], while a two-fold symmetric AMR is seen in ZrSiTe [80]. It indicates the FS of ZrSiS is more 3D-like (while ZrSiTe is more 2D-like), but its implication on the shape of FS needs further investigation.

We carry out both SdH and AMR measurements on electrical transport devices of ZrSiS defined by photolithography. Flakes of ZrSiS down to about 200nm in thickness are obtained by mechanical exfoliation. The cleavage plane is between sulfur atoms of the zig-zag shaped Zr-Si plane (Fig. 1(a)). With mild ion cleaning on the exfoliated flakes prior to deposition, good electrical contact can be made with Ti/Au electrodes. Low-temperature electrical transport measurements are carried out in Quantum Design Physical Property Measurement System with 9T magnets. We survey the behavior of MR under different field configurations, while the measurement current is kept in the *ab* plane of the ZrSiS crystal. The inset of **Figure 5-2** (a) depicts Configuration A, where the field rotates from parallel to the current ($\theta = 0^\circ$) to parallel to the *c*-axis of the crystal ($\theta = 90^\circ$). Here the angle θ is that between the current and the magnetic field. The inset of **Figure 5-2** (b) depicts Configuration B, where the field is rotated from in-plane to out-of-plane but kept perpendicular to the current throughout the process.

5.2 Results

First, we examine the zero-field resistivity of a ZrSiS flake (which is equivalent to $\theta = 0^\circ$) in the 9-T temperature-dependent resistivity in **Figure 5-1** (d). Fig. 1 shows results from sample #3, which has a thickness of 766nm, a residual resistance ratio (RRR) of 62 and a resistivity of $87 \text{ n}\Omega \cdot \text{cm}$ at 2K. We present in Fig. 1(d) its temperature dependence of MR when a 9T magnetic field is along different orientation in Configuration A. When cooled down from 300K, the sample shows decreasing MR until an upturn sets in the range of 70K~120K, depending on the value of θ .

We attribute this field-induced upturn behavior to extremely large MR under low temperature, since ZrSiS is a near-compensated semimetal [68,74]. When cooled down further to below 20K, depending on θ , the sample shows either metallic (e.g., $\theta = 90^\circ, 60^\circ$) or insulating (e.g., $\theta = 75^\circ, 45^\circ$) behavior. Such angle dependence is quantitatively different from what is reported in Ref. [19], where, for instance, the metallic-like behavior is observed for $\theta = 90^\circ$ and $\theta = 60^\circ$. We note that, however, the angle dependence we observe here is in accordance with the appearance of peaks or valleys in SdH oscillations as well as AMR (see supplemental information for a detailed discussion). Therefore, we attribute the apparent angle-dependent metal- or insulator-like behavior to Landau level quantization.

The MR as a function of the strength of the magnetic field under Configuration A (at 2K) is shown in **Figure 5-2 (a)**. We observe a large positive background (reaching 7000% under a 9T field at $\theta = 90^\circ$), which can be well fitted by a quartic function $MR = c_0 + c_1 \cdot H^2 + c_2 \cdot H^4$ (the odd orders in the polynomials are found to have very little weight). A large quadratic MR is consistent with a near compensated semimetal and has been reported in ZrSiS before [68–70,74] (Appendix 3). After subtracting such a background, we perform Fourier transform to examine the frequency of SdH oscillations under different field orientations, getting results (data not shown) consistent with [69]. Such a measurement under Configuration B (**Figure 5-2 (b)**) seems to be a less effective way to extract frequencies of SdH oscillations, as the oscillations have smaller weights compared to the background under most angles.

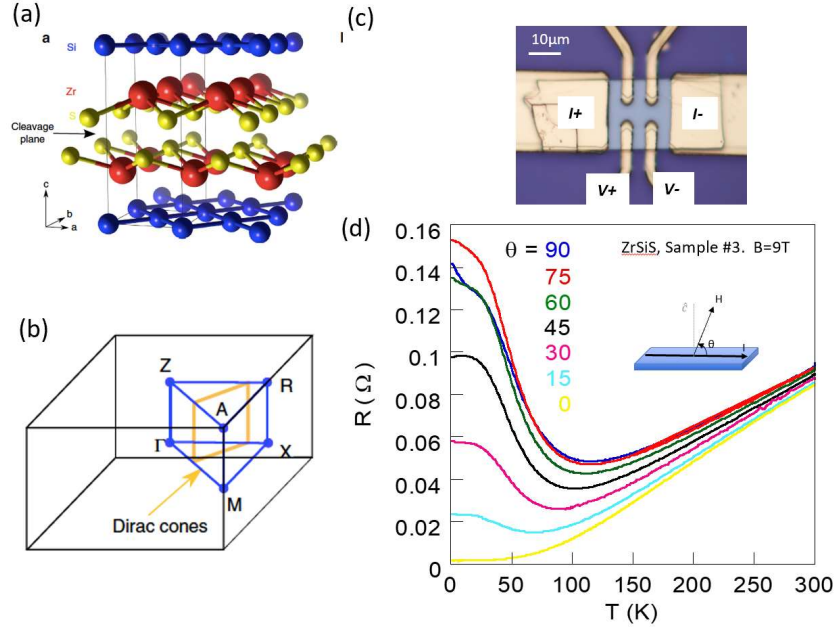


Figure 5-1: (a) crystal structure of ZrSiS (b) the Brillouin zone of ZrSiS (c) Optical image (top-down) of sample #3 (d) Temperature dependence of magnetoresistance under different field orientation with respect to crystal axis. The up-turning that sets in around 80K is due to extremely large magnetoresistance under low temperatures. Depending on the field orientation, the low-temperature behavior (below 20K) can be either metallic-like ($\theta = 90, 60$) or insulator-like ($\theta = 75, 45$), in accordance with the appearance of peak or valley in SdH oscillations (see supplemental information).

Although the SdH frequencies and their angle dependence agree well with exiting reports, the AMR we observe shows different and more detailed features. Under Configuration A, the AMR is two-fold symmetric (**Figure 5-2 (c)**), while under Configuration B, a four-fold symmetric component is also clearly present (**Figure 5-2 (d)**). In reference [69], however, the two configurations show very similar AMR with four-fold symmetry and maximums at $45^\circ, 135^\circ, 225^\circ$, and 315° . We note that a two-fold symmetric AMR under configuration A is consistent with a more 2D-like Fermi surface since the Lorentz component would be two-fold symmetric. On top of this global symmetry, the AMR also exhibits fine features, as evident in Fig. 2(e)(f), which are conventional plots of Fig. 2(c)(d) in the $0^\circ \sim 90^\circ$ range. Those fine features are absent in [19], and we discuss their possible origin in the following.

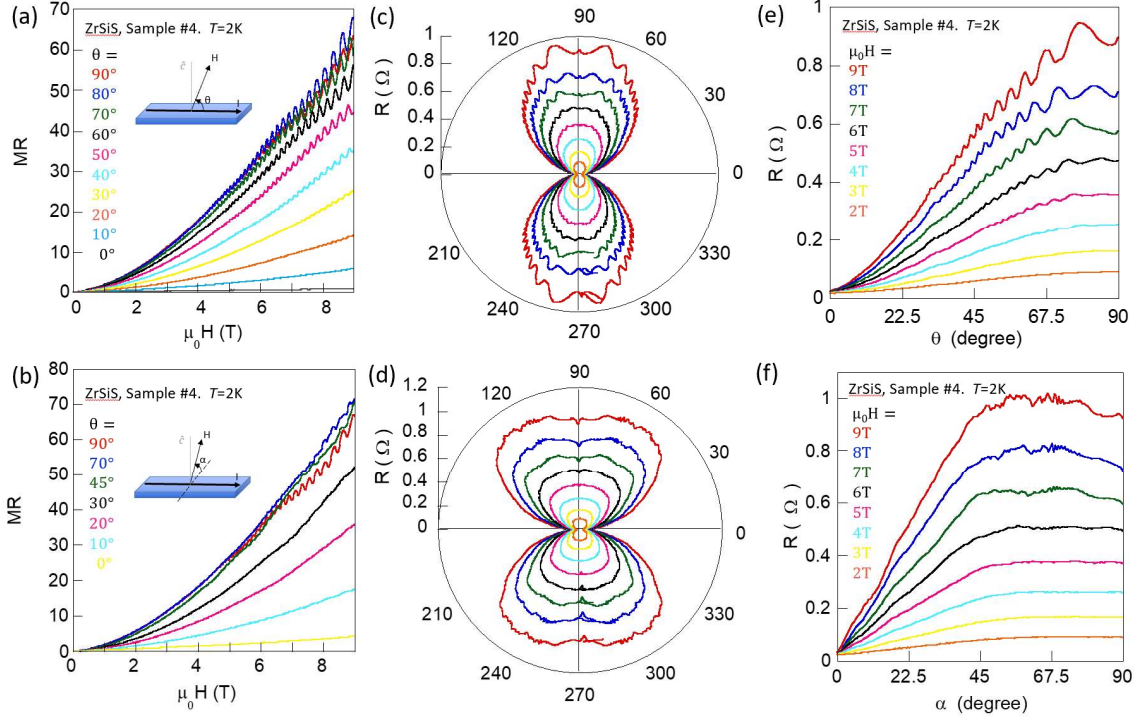


Figure 5-2: Shubnikov de Haas (SdH) quantum oscillation and angle-dependent magnetoresistance (AMR) in ZrSiS. The insets in (a) and (b) describe two corresponding magnetic field configurations (see text). (a)-(b): Under a magnetic field with a fixed direction, clear SdH oscillation can be observed on top of a large quartic background. (c)-(f): AMR shows different patterns under two configurations.

5.3 Discussion

Let's first consider the dependence of MR on FS in the semiclassical description of electron dynamics (Appendix 3). For non-magnetic material, the magneto-conductivity is expressed in Shockley-Chambers formula as an integral over cross-sections of the FS perpendicular to the magnetic field [81]

$$\sigma_{\alpha\beta} = \frac{1}{4\pi^2} \frac{e^2}{\hbar^2} \int dk_H \frac{m_H^* \tau}{2\pi} \int_0^{2\pi} d\phi' \int_0^{2\pi} v_\alpha(\phi) v_\beta(\phi - \phi') e^{-\phi'/\omega_H \tau} d\phi$$

Where k_H is the component of crystal momentum along the direction of the magnetic field, m_H and ω_H are effective cyclotron mass and cyclotron frequency, respectively, and v_α , v_β are

components of Fermi velocity. As the magnetic field tilts, the shape of those 2D-slices of FS shifts, and hence the magnetoresistance is angle-dependent. To the best of our knowledge, in semiclassical theory, AMR oscillations (AMRO) with certain periodicity are only seen in layered metals— for instance, Sr_2RuO_4 . For them, AMRO arises as a result of the gentle warping of the Fermi surfaces along the k_z direction [82]. The Fermi surface corrugates so little that it fits in between two adjacent Landau tubes, so the extremal orbit treatment that gives rise to SdH oscillations is inappropriate. Instead of periodicity in $1/B_z = 1/B\cos\theta$, such AMRO manifest itself in the interlayer conductivity as oscillations with a periodicity in $\tan\theta = B_y/B_z$, where B_y is the in-plane field. The AMRO we observe in R_{xx} of ZrSiS does not have such periodicity.

In search of hints of the origin of AMRO in ZrSiS, we examine its temperature dependence. **Figure 5-3 (a)** presents the AMR between 2K and 18K under a 9-T magnetic field in Configuration A. The smooth background (which is two-fold symmetric in a polar plot) stays almost unchanged, while the oscillatory part gradually weakens with increasing temperature and becomes hardly discernable at 18K. We note that a very similar trend shows up in the temperature dependence of SdH oscillations (**Figure 5-3(d)**), which suggests that these two phenomena may have the same origin - Landau level quantization. In fact, the AMRO appears to be periodic (**Figure 5-3 (b)(c)**) when we plot the oscillatory part in **Figure 5-3(a)** against $1/B_\perp$, the inverse of the perpendicular component of the magnetic field (see supplemental material for background subtraction). **Figure 5-3 (c)** is a replot of **Figure 5-3 (b)** on a different scale to show detailed oscillations. The SdH oscillations are plotted in the same fashion (**Figure 5-3 (e)(f)**) for comparison. To confirm that AMRO is periodic in terms of $1/B_\perp$, we also survey the field dependence of AMRO 2K (**Figure 5-4**). The result confirms that, when the field strength is varied, the AMRO remains periodic with respect to $1/B_\perp$. The oscillation frequency has no noticeable

change (Figure 5-4 (a)) and is found to be $B_F = F_0 = 156T$, which is not seen in our SdH oscillations.

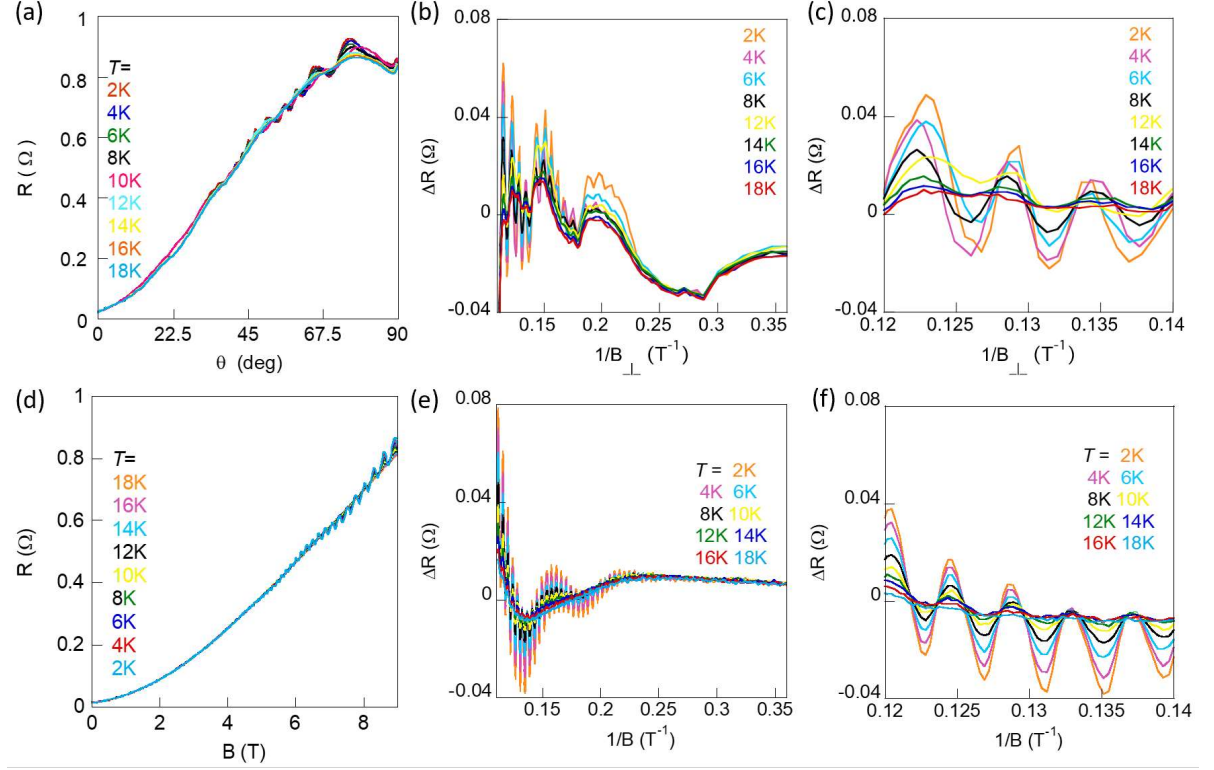


Figure 5-3: Temperature dependence of AMR and SdH oscillations under the 9T field in configuration A. (a) AMR in the temperature range of 2K ~ 18K. (b) After subtracting the background, AMR shows clear periodic oscillation (AMRO) with respect to the inverse of the perpendicular component of the magnetic field. The quick oscillations sit on top of a slower oscillation. (c) Same plot as (b) but on a different scale to show the details of the quick oscillation, which almost die out at 18K. (d) Magnetoresistance in the temperature range of 2K ~ 18K, with the magnetic field parallel to the c-axis of the crystal. (e)(f) SdH oscillations in two different scales and they also die out around 18K. The frequency of SdH oscillations and AMRO are clearly different (c)(f).

Before proposing a possible explanation for this periodic AMRO, let's consider standard SdH oscillations first. As mentioned before, under a magnetic field with a fixed direction, for a strictly 2D system, the frequency B_F reflects the projection of the area of FS perpendicular to that field, while for the 3D system, it reflects the extremal area of FS perpendicular to the field. Generally speaking, for a 3D Fermi surface, both B_F and m (which determines the oscillation

amplitude $A(B, T)$ depend on the direction of the field. Hence, when studying the SdH oscillations, one usually keeps the direction fixed while changing the strength of the field. The exception is made for 2D systems – for instance, 2DEG in n-type inverted silicon surfaces [83]. There, since only the perpendicular component of the field (relative to the Fermi surface) matters for a 2D system, SdH oscillations show up when the field is tilted. We therefore propose that this 156T oscillations in AMRO may originate from a two-dimensional band in ZrSiS. Indeed, previous SdH oscillation measurement [69] observed an oscillation frequency of 154T with $B \parallel c$, although its corresponding Fermi pocket remains to be identified.

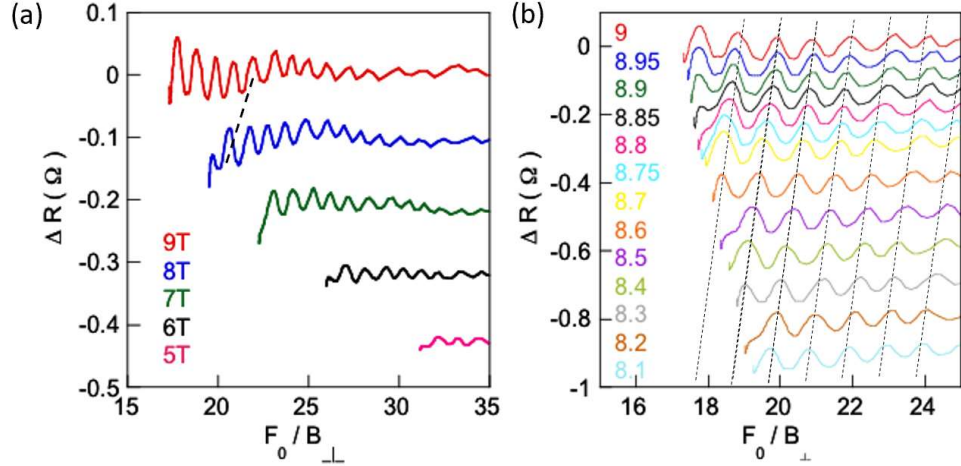


Figure 5-4: AMRO under Configuration A, as a function of the perpendicular component of the magnetic field. Here we normalize the x -axis with the frequency of AMRO, which is found by FFT to be $F_0 = 156T$. (a) AMRO under $B = 9, 8, 7, 6, 5T$. Note that different from SdH measurements, what is varied for each curve is the direction of the magnetic field rather than its magnitude. (b) AMRO under $B = 9T \sim 8T$, here the step size is small to show the apparent “phase shift” of AMRO oscillations (dashed line).

We also observe an apparent phase shift when the field strength is varied (see dashed lines in **Figure 5-4 (b)**). For example, the peak around $F_0/B_{\perp} = 22$ in the 9T curve shifts to around $F_0/B_{\perp} = 21$ in the 8T curve. One apparent deduction from it is a shift in $|\gamma - \delta|$, or equivalently, the Berry phase. However, it can also just be an effect of the small variation in the period – for

example, the last two peaks in 9T-curve in **Figure 5-4(b)** seem to shift away from the dashed line.

This could be related to the slower oscillation which one can see in **Figure 5-3 (b)**.

Chapter 6

Conclusion and future directions

The first part of this dissertation, dedicated to electrical transport properties of platinum and silicon metalattices, showed the nanoscale geometrical constraint can have considerable effects on electron localization. For metal metalattices, where the geometrical constraint is not strong enough to expect the effects of quantum confinement, the large surface area to volume ratio can still lead to properties not seen in the bulk, as seen in polycrystalline 30 nm platinum metalattices. Those samples exhibit weakly localized electrical with an anomaly in its temperature-dependent low-field magnetoresistance that is not observed in reference Pt film. Our analysis using the weak localization framework suggests an enhanced electron-phonon scattering at the presence of a large surface area to volume ratio. We argued that the discrepancy between our data and existing weak localization theory does not disqualify the latter as the mechanism behind the MR anomaly, as existing theories do not take the inhomogeneity of metalattice into consideration. To test our interpretation, it will be interesting to carry out parallel studies in Pt metalattices with a different periodicity which has a different surface area to volume ratio as well as a different constraint on self-intersecting scattering paths. Modifying the Pt/SiO₂ interface can also provide information on the role surface scattering in weak localization in Pt metalattices. To make a quantitative comparison to theory, we will also need weak localization theory or simulation formulated for metalattice structure.

Effects due to quantum confinement are expected in semiconductor metalattices when the Bohr radius of dopants is comparable to the characteristic length scale of metalattices. Inspired by previous studies in semiconductor nanocrystal arrays, we searched for a higher critical doping level in metalattices of smaller periodicity. Specifically, we carried out electrical transport studies in 14 nm, 30 nm and 100 nm phosphorous doped Si metalattices deposited with the same PH₃/SiH₄ gas

ratio. All of our Si metalattice samples are insulating, with the 14 nm and 30 nm samples showing Efros-Shklovskii Variable-range hopping (ES-VRH) type behavior, while the co-deposited silicon film shows metallic behavior as expected. The model of multiple co-tunneling also gives a satisfactory description of the temperature dependence of zero-bias conductance and current-voltage characteristics, consistent with the theory that multiple co-tunneling is the intergranular transport mechanism in a granular electronic system. In 14 nm and 30 nm Si metalattices, the power-law of temperature-dependent zero-bias conductance shows a clear transition in the index around 30 K, which is consistent with a change in the number of meta-atoms involved in the multiple cotunneling process.

While more localized behavior is indeed observed in smaller metalattices, the interpretation of the mechanism of the localization is complicated by several other variables, albeit unintended, including the change in average grain size, distribution of grain size, and area of Si/SiO₂ interface, disorder in superlattices and amorphous region inside Si metalattices. Electrostatic gating, which sweeps the Fermi level without introducing those extra variables into a device, is highly desirable as a future experiment. A more detailed survey on different periodicities would also help, as one may be able to extract the contribution from classical geometrical effect to see the effect of quantum confinement. To see the effect of the nanoscale inversed fcc structure on the electronic structure of metalattices, one will need a much larger grain size than current samples. Impurity levels in tetrahedral sites are expected to be deeper than octahedral sites, and electrons may prefer to hop from an octahedral site to another octahedral site rather than its nearest neighbor (a tetrahedral site), which is further away but requires less energy.

While the first part of this dissertation concerns disordered electronic systems, in the second part we aim at effects from single-crystal band structure and Fermi surface. We show that ZrSiS, a recently discovered Dirac nodal line semimetal (DNLSM), exhibits complex quantum properties in magneto-transport measurements. The single-crystal ZrSiS flakes, obtained by

mechanical exfoliation, are above 100 nm in thickness and is usually considered bulk samples. In conventional Shubnikov-de Haas oscillation, we observed frequencies as well as their angle dependence consistent with results from recent studies. Unlike previous studies, however, we also uncover an unexpected periodicity in the oscillatory component in angular magnetoresistance (AMRO). The anisotropy of the Fermi surface in the semiclassical Boltzmann theory does not give rise to such an oscillation in MR periodic that resembles SdH from a 2D Fermi pocket. Future experiments are needed to explore the origin of the AMRO. If it is a surface effect, whether due to the distinct surface states in DNLSM or surface depletion as in narrow-band semiconductor or other semimetal, one should see an increase in the weight of this oscillatory component as the thickness of the flake is reduced.

A.1 Further details on metalattice preparation

Chemical vapor deposition (CVD) is a fundamental technique to produce a high-quality, uniform, conformal coating of various solid materials over a large area. In typical CVD, the substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit. By-products and excess reactants are then removed by gas flow through the reaction chamber. A wide range of materials, including metal, semiconductor, dielectrics and polymer, can be deposited by CVD [84]. However, conventional CVD operates under low pressure (from vacuum to 1atm), which limits its use in micro- and nano-scale structures [85] due to the large mean free path (MFP).

According to kinetic theory of gases, the mean free path is determined by

$$l = \frac{k_B T}{\sqrt{2} \pi P d^2}$$

where k_B is the Boltzman's constant, T is the temperature of gas molecule, P is the pressure of the gas, and d is the kinetic diameter of the gas molecule. In conventional CVD, the operating pressure is low (from vacuum to 1atm), which translates to a MFP of hundreds of nanometers. When the typical pore size is close or less than the MFP, conformal coating inside porous structure becomes challenging due to insufficient mass transport of reactants. Material growth inside micro- or nano-pores is slow compared to that on outer surface and will be prohibited once the outer surface is coated. High pressure reduces the MFP of gas molecules, enabling sufficient mass transport into small pores and therefore conformal coating inside micro- and nano-pores. For example, high pressure CVD (HPCVD) has been used to fabricate optical fiber in silica capillaries with various semiconductors, including silicon [86–90], germanium [91] and zinc selenite [92–94].

High pressure increases the rate of gas molecule collision and the rate of precursor decomposition [93], which can be used to the advantage of thin film deposition. For example,

high pressure CVD enables the deposition hydrogenated amorphous silicon (a-Si:H) under low enough temperature which is required for hydrogen passivation of the dangling bonds in a-Si [86,87,90,95]. However, if the open volume inside the reactor is too large, reactant gas molecules would have enough time to decompose and form particles before they land onto a surface, promoting gas phase nucleation (homogeneous growth). In other words, the surface area to volume ratio (SAV) needs to be large enough to favor thin film deposition inside a reactor. To deposit a uniform thin film onto a planar substrate, all open dimensions inside the reactor need to be limited. This is achieved by inserting a thin spacer made of stainless steel in between two substrates. The role of high pressure and special confinement is summarized in Figure A-1. Further details on the equipment set up and deposition chemistry can be found in ref [26] and [96].

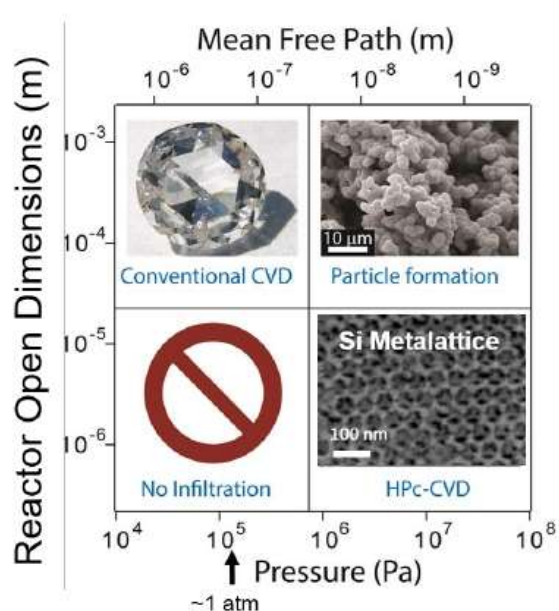


Figure A-1: Pressure, mean free path (MFP) and reactor open dimension in nano-templates infiltration. Conventional CVD uses low pressure (top left) where the MFP of gas molecules is large and cannot infiltrate into small pores (bottom left). When pressure is raised without reactor modification, homogeneous reaction dominates to yield particle formation (top right). When high pressure (35 – 70 MPa) is combined with reactor open dimension confinement, infiltration into small pores is possible (Bottom right). Adapted from Ref [26].

Pt metalattices are deposited by Dr. Yunzhi Liu and Andrew Glaid using high pressure confined supercritical fluid chemical deposition (HPcCFD) technique. We used 99.999% purity H_2 for the precursor reduction (mixed with 99.999% purity He) and 4.0 instrument grade CO_2 as a supercritical solvent, all from Praxair. A high-pressure reservoir to serve as the source the of H_2/He mixture, a reactor and associated high pressure lines for filling, evacuating, and purging, was custom built using commercial parts from High Pressure Equipment Company and Swagelok; the details can be found in Ref. 1. The hydrogen was charged into the reservoir to ~ 10 MPa using a Newport Scientific two-stage 207 MPa diaphragm pump. The reservoir was then charged with ~ 48 MPa He, making a H_2/He gas mixture with 20% H_2 concentration. We deposited Pt metal into the silica nanosphere templates to form metalattices in a batch reactor. The spacer between the two pieces of silica sphere template film on the silicon wafer determined the reactor space confinement. 0.036 g (dimethylcyclooctadiene) Pt was loaded into the reactor in a high purity argon Vacuum Atmospheres glovebox, charged with liquid CO_2 using a custom-built manual pump to pressures in the range of 10 to 13 MPa, and then wrapped with heating tape and heated at $70^\circ C$ for 4 hours to ensure dissolution and infiltration of the precursor. Next, the high pressure H_2/He gas mixture from the reservoir was added to initiate the reaction, and at the same time the heating tape was turned off, and the furnace was kept at the same temperature. The reaction proceeded for 5 hours, the reactor was cooled, the high-pressure gas was released, and finally the reactor was evacuated. Removal of the Pt coating was done using a ULVAC NE-550 inductively coupled plasma (ICP) etching system (Ar, O_2 and Cl_2).

A.2 Resistivity of heavily doped polycrystalline silicon

Polycrystalline silicon has electrical properties very different from monocrystalline silicon due to grain boundaries, a complex structure usually consisting of a few atomic layers. To understand the contribution to conduction due to grain boundary, the early approach is to view grain boundary as a trapping and scattering center in the thermionic emission – thermionic field emission – thermionic field emission scattering model [4,97]. However, to account for experimental result, this model contains a scaling parameter that have no obvious physical meaning. More importantly, the theory of thermionic emission is based on the assumption that thermal equilibrium is established at the plane that determines the emission, in this case the edge of depletion width, and that carriers are taken to be free particles in the depletion region. It was later proposed that the grain boundary itself should be modeled as a conduction channel with its own transport properties in addition to the trapping characteristics [6]. The temperature dependence of the resistivity is explained in terms of conduction channels inherent in the amorphous grain boundary. It has been shown that the conduction channel model fits experimental results better than the trapping - thermionic emission model [6,98]. We follow the conduction channel model in this dissertation.

In the conduction-channel model, single-crystal grains are in equilibrium with amorphous grain boundaries, and the density of states in the grain boundary is modeled to be an exponential band tail. **Figure A-2** shows the energy band diagram of a unit cell of the degenerate p-type polysilicon. The length of the grain is L , and the width of the depletion region in the grain is W . The amorphous grain boundary is characterized by the width δ , the band tail Δ , the mobility shoulder Δ' and the density of defect states Q_t . The resistivity of the polysilicon (ρ) is given by the resistivity of the grain (ρ_g) in series with the resistivity of the grain boundary (ρ_{gb}), and the barrier (ρ_B):

$$\rho = \left(1 - \frac{2W+\delta}{L}\right) \times \rho_g + \left(\frac{\delta}{L}\right) \times \rho_{gb} + \left(\frac{2W}{L}\right) \times \rho_B \quad (2-1)$$

The resistivity of the grain is the same as single-crystal silicon $\rho_g = 1/q\mu_c p_c$, where μ_c is the hole mobility and p_c the hole concentration in single-crystal silicon. For degenerately doped silicon with dopant concentration N_A , we assume complete ionization and $p_c = N_A$. We also ignore the third term on the above equation as ρ_B is small due to negligible barrier height in the doping concentration range around 10^{19} cm^{-3} .

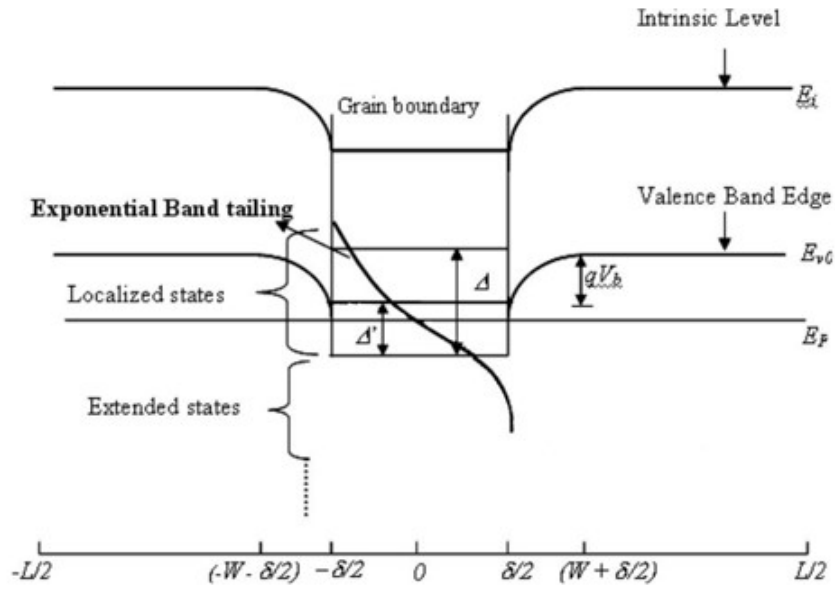


Figure A-2. Energy band diagram of a unit cell of the degenerate p-type polysilicon. Adapted from Ref [98] with minor revision.

The conduction in grain boundary is dominated by diffusion and hopping processes. Suppose there are p_{ext} carriers in the extended states and they move by diffusive motion with mobility μ_{ext} , and there are p_{hop} carriers below the mobility shoulders and they move by thermally assisted hopping with mobility μ_{hop} . Typically, at 300 K one has [6]

$$\mu_{ext} \sim 10 \text{ cm}^2/\text{Vs} \quad \text{and} \quad \mu_{hop} \sim 0.1 \text{ cm}^2/\text{Vs}.$$

The effective mobility of the grain boundary is $\mu_{gb} = \frac{p_{ext}}{p_{gb}}\mu_{ext} + (1 - \frac{p_{ext}}{p_{gb}})\mu_{ext}$. The resistivity of the grain boundary

$$\rho_{gb} = \frac{1}{q\mu_{gb}p_{gb}} = \frac{1}{q(\mu_{ext}p_{ext} + \mu_{hop}p_{ho})}$$

is determined by the concentration of extended and localized carriers (p_{ext} and p_{hop}), which in turn are determined by the parameters describing grain boundary (δ , Δ , Δ' and the trap density Q_t).

The barrier height is

$$V_b = \frac{qN_a W^2}{2\varepsilon_0 \varepsilon_{Si}}$$

where N_a is the doping level. The depletion width is determined from the charge neutrality condition

$$W = \frac{Q_t + \delta \cdot p_{gb}}{2N_a},$$

which is determined by the carrier density p_{gb} from the charge neutrality condition. By requiring that the carrier density p_{gb} gives self-consistent value through the W and V_b , one can numerically calculate the Fermi level and hence all other parameters including W , V_b , p_{gb} , μ_{gb} , and ρ_{gb} . The mobility shows a minimum around a critical doping level at which the depletion region around a grain boundary extends right through the grain and the barrier height V_b reaches its maximum. Below such doping level, the traps inside the grain boundary consumes all the carriers, while above doping level, the depletion region only extend partially through the grains. The role of V_b in this model is to lower the mobility shoulder and to reduce the number of holes in the extended state conduction mode. For not too high doping level, Boltzmann distribution can be used when calculating the number of holes in the extended state and the localized states in the grain boundary, and the comparison between the conduction channel theory and experimental results is given in

Figure A-3 which is adapted from Ref. [6]. At high doping level (above 10^{19}cm^{-3}), Ref. [98] showed that using the Fermi-Dirac distribution gives better result.

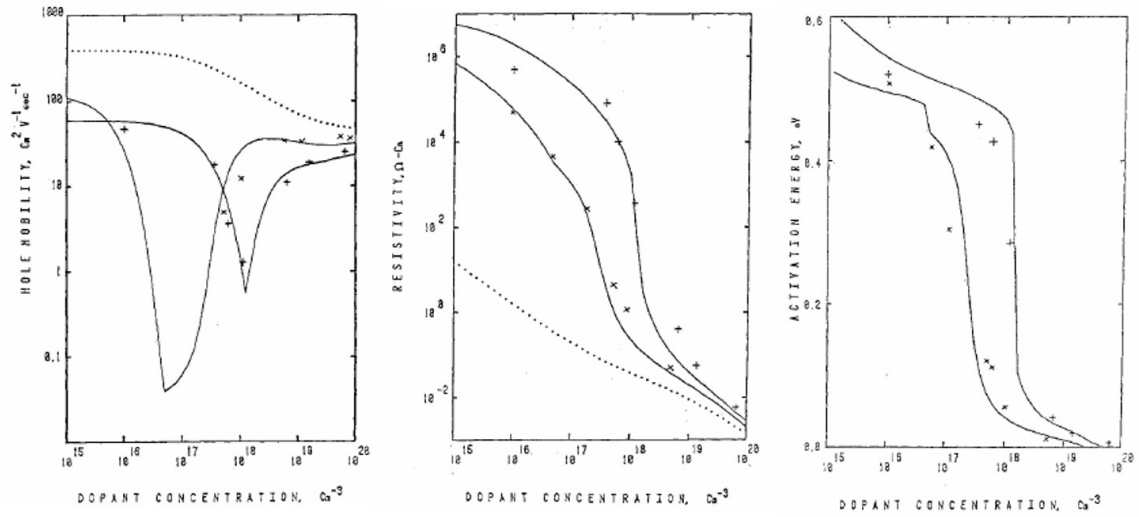


Figure A-3. Mobility, resistivity and activation energy verses doping concentration in boron-implanted poly-Si. The solid lines are theoretical results calculated using the conduction channel model for poly-Si. The dashed lines are theoretical results for single-crystal silicon. Experimental data are obtained from B-implanted poly-Si where the measured average grain size is 25 nm (+) [4] and 200 nm (×) [5] in diameter respectively. Adapted from Ref [6].

A.3 Magnetoresistance in metals

Magnetoresistance (MR), the increase in the electrical resistance of a metal or semiconductor when subject to a magnetic field, provides information of the shape and connectivity of the Fermi surface. Many interesting features in MR can be explained by simple drift velocity model (Drude model), which we describe first in this section. The standard geometry for measuring MR is the following: a long thin wire is directly along the x axis, and a dc electric field E_x is established in the wire by means of an external power supply. A uniform magnetic field B_z is applied along the z axis, thus normal to the axis of the wire.

Consider a Fermi gas of electrons with an approximately spherical Fermi surface. The conductivity is $\sigma_0 = ne^2\tau/m^*$, where n is the number density of electrons, m^* their effective mass, and τ the relaxation time. A magnetic field can have a significant effect on the conductivity if it is strong enough to bend the trajectory of electrons appreciably during a free path. The cyclotron frequency is $\omega_c = eB/m^*$. Combining the above two equations, we have the mean angle turned between collisions

$$\beta \equiv \omega_c \tau = B\sigma_0/ne.$$

Unless $\beta > 1$, no great MR effect can be expected. For $\beta \ll 1$, the magnetic field increase the resistance by an additive term proportional to B^2 , as a term linear in B is not permitted by the symmetry of the system with respect to the sign of the magnetic field. For $\beta \gg 1$, the transverse MR of a crystal may generally do one of the three quite different things [76]:

- (a) The resistance saturates under high magnetic field for all orientations of the crystal axes relative to the measurement axes. It happens for closed orbit except for compensated materials.
- (b) The resistance does not saturate up to the highest field studied for all crystal orientations. This happens for compensated materials, that is, the number of electrons equals that of holes.

(c) The resistance saturates in some crystal directions, but not saturate in other crystal directions. This behavior is also exhibited as an extraordinary anisotropy of the resistance in a magnetic field. It happens for Fermi surfaces with open orbits in certain directions.

A.3.1 Drift velocity model

For single carrier-type isotropic effective mass and constant relaxation time, in the steady state, the equation of motion of the drift velocity for carriers having isotropic mass is

$$m^* \mathbf{v} = e\tau(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (5-1)$$

$$v_x = \mu E_x + \beta v_y; \quad v_y = \mu E_y - \beta v_x; \quad v_z = \mu E_z.$$

Solve for v_x, v_y we get

$$v_x = \frac{\mu}{1 + \beta^2} (E_x + \beta E_y); \quad v_y = \frac{\mu}{1 + \beta^2} (E_y - \beta E_x)$$

For $\mathbf{B} \parallel \hat{\mathbf{z}}$, the conductivity and resistivity tensor defined by $j_\alpha = \sigma_{\alpha\beta} E_\beta$ (Einstein summation rule applies) and $\boldsymbol{\rho} = \boldsymbol{\sigma}^{-1}$, are

$$\boldsymbol{\sigma} = \frac{ne\mu}{1 + \beta^2} \begin{pmatrix} 1 & \beta & 0 \\ -\beta & 1 & 0 \\ 0 & 0 & 1 + \beta^2 \end{pmatrix} \quad (5-2)$$

$$\text{and } \boldsymbol{\rho} = \frac{1}{ne\mu} \begin{pmatrix} 1 & -\beta & 0 \\ \beta & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

In the standard geometry, the boundary condition permit current flow only in the x direction, $j_y = j_z = 0$, therefore $E_y = \beta E_x$, $E_z = 0$, and $j_x = \frac{ne\mu}{1 + \beta^2} (E_x + \beta E_y) = ne\mu E_x$, which is independent of the magnetic field. Therefore, in standard geometry, there is no MR for single carrier-type isotropic effective mass and constant relaxation time, as the Hall electric field just balances the Lorentz force of the magnetic field. In the high magnetic field limit $\beta \gg 1$, we have

$$\boldsymbol{\sigma} \approx ne\mu \begin{pmatrix} \beta^{-2} & \beta^{-1} & 0 \\ -\beta^{-1} & \beta^{-2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (5-3)$$

A.3.2 Compensated metal

A simple extension of the drift velocity model is to introduce a second carrier type. An important practical situation is the high magnetic field behavior of a system with both electrons (m_1, τ_1, n_1) and holes (m_2, τ_2, n_2) . The equation of motion for two types of carriers are

$$\mathbf{v}_1 = \left(\frac{e\tau_1}{m_1}\right)(\mathbf{E} + \mathbf{v}_1 \times \mathbf{B}); \quad \mathbf{v}_2 = -\left(\frac{e\tau_2}{m_2}\right)(\mathbf{E} + \mathbf{v}_2 \times \mathbf{B}).$$

Under high magnetic field such that $|\omega_{c1}|\tau_1 \gg 1$ and $|\omega_{c2}|\tau_2 \gg 1$, the term on the left hand side of above two equations can be neglected, and we have

$$E_x + v_{1y}B = 0; \quad E_x + v_{2y}B = 0,$$

Thus $j_y \equiv n_1 e v_{1y} - n_2 e v_{2y} = (n_2 - n_1) \frac{e E_x}{B}$, whence $\sigma_{yx} = (n_2 - n_1) \frac{e}{B}$. If there are equal numbers of holes and electrons, $\sigma_{yx} = 0$, then there is no Hall voltage in high field limit, $E_y = 0$.

The resistivity becomes simply $1/\sigma_{xx}$,

$$\sigma_{xx} \cong \frac{n|e|}{B^2} \left(\frac{1}{|\mu_1|} + \frac{1}{|\mu_2|} \right); \quad \rho_{xx} = \sigma_{xx}^{-1} \propto B^2$$

where $n = n_1 = n_2$. Therefore, the transverse magnetoresistance does not saturate for all orientations if there are equal numbers of holes and electrons.

A.3.3 Open orbits

So far, we have assumed that electrons move on cyclotron orbits (closed orbits). This, however, may not be true in a real metal when the magnetic field is applied in certain direction with respect to the crystal axis. For carriers on a real Fermi surface, the equation of motion should be expressed in the $\mathbf{k}$ space, and the effect of a magnetic field on an electron states is given by:

$$\hbar \dot{\mathbf{k}}_n = e \mathbf{v}_n \times \mathbf{B} \quad (5-4)$$

where

$$\mathbf{v}_n = \frac{1}{\hbar} \nabla_{\mathbf{k}} E_n(\mathbf{k}) \quad (5-5)$$

Here n denote the band the carrier belongs to. This means that the electron moves in orbits defined by the intersection of the Fermi surface a plane normal to the direction of the magnetic field. In the repeated Brillouin zone scheme, it is possible to have open orbit. Consider, for example, the Fermi surface of copper, which touches the boundary of the reduced Brillouin zone (Figure A-4).

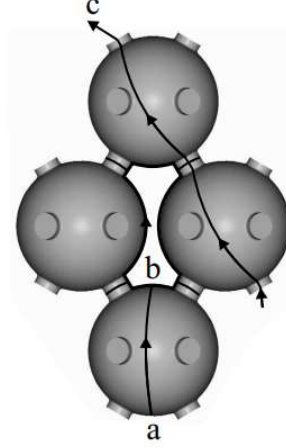


Figure A-4: Three different types of orbits on the Fermi surface of copper. a: a (closed) electron orbit; b: a hole orbit of dog's bone shape; c: open orbit. Adapted from Ref [99].

In strong magnetic fields, an open orbit carries current essentially only in a single direction in the plan normal to the magnetic field. Suppose that for a given crystal orientation there are open orbits parallel to k_x ; in real space these orbits carry current parallel to the y axis. The strength of the magnetic field does not affect the average carrier velocity v_y on the orbit. It only affects the rate k_x at which the open orbit is traversed in k space. Thus, *the open orbit cannot be saturated by the field.* We can associate a conductivity as equal to $ne\mu s$, where s is a constant. In the high field, instead of Eq. 5-3 we have

$$\sigma \approx ne\mu \begin{pmatrix} \beta^{-2} & \beta^{-1} & 0 \\ -\beta^{-1} & s & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (5-6)$$

With Eq.5-6 we obtain $j_y = 0$ when $E_y = \frac{E_x}{s\xi}$, thus $j_x \approx ne\mu(\beta^{-2}E_x + \beta^{-1}E_y) = ne\mu\left(1 + \frac{1}{s}\right)\beta^{-2}E_x$, and the effective resistivity is

$$\rho \approx \frac{\beta^2}{ne\mu} \frac{s}{s+1} \propto B^2$$

which does not saturate. If the crystal is oriented so that the open orbit carries current in the x direction, then

$$\sigma \approx ne\mu \begin{pmatrix} s & \beta^{-1} & 0 \\ -\beta^{-1} & \beta^{-2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

And $j_y = 0$ if $E_y = \beta E_x$, so that

$$j_x \approx ne\mu(s+1)E_x.$$

For this orientation the MR saturates. If the open orbit runs in a general direction in the xy plane, the conductivity tensor in the $\beta \gg 1$ limit is

$$\sigma \approx ne\mu \begin{pmatrix} s_1 & \beta^{-1} & 0 \\ -\beta^{-1} & s_2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

This gives $j_y = 0$ if $E_y = E_x/\beta s_2$, so that

$$j_x \approx ne\mu \left(s_1 + \frac{1}{\xi^2 s_2} \right) E_x \rightarrow ne\mu s_1 E_x.$$

Thus, the MR saturates except when the open orbit carries current almost precisely parallel to the y direction.

A.3.4 Shockley-Chambers formula

So far, we have explained the three cases of general behavior of MR in metals qualitatively using the rather simple drift velocity model and open orbits. The quantitative behavior of MR of a metal depends on both its Fermi surface and the defects in a specific sample. Within semiclassical Boltzmann approximation, the magneto-conductivity for an arbitrary FS can be calculated [81,99].

When $\omega_H \tau > 1$, it is simpler to derive the transport properties from the Boltzmann equation expressed in terms of the variables $(E(k), k_H, \phi)$, which are defined as follows:

- i) Energy $E(k)$, which stays constant in a magnetic field.
- ii) Component k_H , the component of k along the direction of the magnetic field, which also stays constant.
- iii) A phase variable defined as an integral round the cyclotron orbit: $\phi = \omega_H \frac{c\hbar}{eH} \int \frac{dk}{v_\perp}$
where ω_H is the cyclotron frequency.

Under this coordinate system, the universal formula for magneto-conductivity is the Shockley tube-integral formula, which is an integral over cross-sections of the FS perpendicular to the magnetic field [81], As the magnetic field tilts, the shape of those 2D-slices of FS shifts, and hence the magnetoresistance is in general angle-dependent. In the limit of $\omega_H \tau \gg 1$, the above formula can be further simplified as:

$$\sigma_{\alpha\beta} = \frac{1}{4\pi^3} \frac{e^2}{\hbar^2} \int dk_H \frac{m_H^* \tau}{2\pi} \int_0^{2\pi} d\phi' \int_0^{2\pi} v_\alpha(\phi) v_\beta(\phi - \phi') e^{-\phi'/\omega_H \tau} d\phi \quad (5-7)$$

where k_H is the component of crystal momentum along the direction of the magnetic field, m_H is effective cyclotron mass, τ is the relaxation time, and v_α, v_β are components of Fermi velocity. The velocities, cyclotron mass and cyclotron frequency depend on k_H .

In Eq. (5-7), only the factor $e^{-\phi'/\omega_H \tau}$ depends on the magnetic field. As the range of ϕ' is limited, one can expand the factor $e^{-\phi'/\omega_H \tau}$ in powers of $\phi'/\omega_H \tau$ and obtain a series expansion of the conductivity tensor in powers of B^{-1} . Within such relaxation-time approximation, it is possible to calculate the MR from first principle [100,101]. Such study has been done for ZrSiS very recently, and I'll discuss it later in the chapter. It can be shown that Eq. (5-7) gives the general form of the conductivity tensor in the high fields as:

$$\boldsymbol{\sigma} \approx \begin{pmatrix} a\beta^{-2} & d\beta^{-1} & e\beta^{-1} \\ -b\beta^{-1} & b\beta^{-2} & f\beta^{-1} \\ -e\beta^{-1} & -f\beta^{-1} & c \end{pmatrix}$$

where the coefficients a, b, c, d, e, f are non-zero and independent of $\mathbf{B}$. By inverting the conductivity matrix, we obtain the transverse resistivity

$$\rho_{xx} = \frac{1}{\Delta} (bc + f^2) \beta^{-2} = \frac{(bc + f^2) \beta^{-2}}{(cd^2) \beta^{-2} + (abc + af^2 + be^2 + f^2) \beta^{-4}} \rightarrow \frac{bc + f^2}{cd^2} + O(\beta^{-1})$$

Therefore, the transverse resistivity saturates at high fields. Now we have qualitatively explained the MR in metals that generally falls in three categories using semiclassical theory.

A.4 Numerical Simulation of Hall effect in Arbitrary Multiply Connected Structure

The textbook presentation of the classical Hall effect is usually for the case where the current $\mathbf{I} = I\hat{\mathbf{x}}$ is injected into a rectangle slab of (homogeneous) material of thickness t subject to a perpendicular magnetic field $\mathbf{B} = B\hat{\mathbf{z}}$. In this special case (**Figure A-5 a**), the carrier density can be determined by measuring the transverse voltage U_{xy} as $n = \frac{1}{R_H e} = \frac{tBI}{U_{xy}e}$. When we carve a homogeneous block of doped silicon with carrier density n_0 into a block of metalattice and perform such a Hall measurement, a naïve guess will be that the measured carrier density n is n_0 scaled by the volume fraction of the metalattices (for example, $n = n_0/0.26$ for metalattices of inversed fcc structure). However, this is incorrect. The mistake is easier to see in the so called “Hall bar with a hole” geometry in 2D.

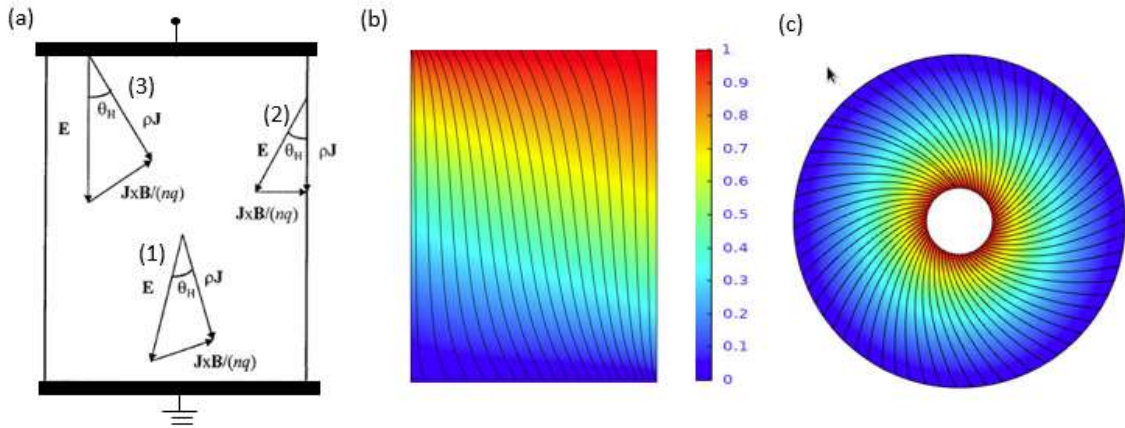


Figure A-5: Hall effect in standard Hall-bar geometry and Corbino geometry. The relation between the local current density and electric field is depicted in (a). The upper extended contact is set to a nonzero potential, while the lower contact is grounded. The numerical simulation for such geometry is shown in (b), while the color map corresponds to the potential, and the black line shows current streamline. In Corbino geometry (c), the inner rim is set to a constant voltage while the outer rim is grounded). The electric field is forced along the radial direction, and the non-zero Hall angle dictates that the current streamline to be skewed and travel longer distance when a magnetic field is turned on. In (b) and (c) the parameter $\beta = 0.5$.

Following **Ref.** [102], we can perform numerical calculation of the effective Hall voltage for arbitrary singly or multiply connected geometry using finite element method (FEM). The electric current module of the commercial software package COMSOL Multiphysics is used. The calculation is performed by solving the continuity equation

$$\nabla \cdot (\boldsymbol{\sigma} \nabla \phi) = 0$$

with the conductivity tensor $\boldsymbol{\sigma} = \boldsymbol{\rho}^{-1}$,

$$\boldsymbol{\rho} = \rho_0 \begin{pmatrix} 1 & \beta & 0 \\ -\beta & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

where the dimensionless magnetic field

$$\beta = \omega_c \tau = \tan \theta_H,$$

The Hall angle θ_H affects the boundary conditions with which the electrostatic potential is solved. If the current direction is predetermined, as in the usual Hall bar geometry far away from the electrical contact or at a floated boundary, the current is parallel to the edge (**Figure A-5 a (2)**), which dictates the electric field to have a nonzero component perpendicular to the boundary. If the electric field direction is predetermined, as at the extended electrical contact of a standard Hall bar, the current is tilted to maintain the Hall angle with respect to the electric field (**Figure A-5 a (3)**). For simple geometry like the standard Hall bar or a disk, analytical solution of the electrical potential can be obtained, even though they may not be the partial differential equation problems with standard boundary condition [103]. For arbitrary geometry, the relevant boundary condition problem will be solved numerically.

In **Figure A-5 b** and **c** we present the numerical results in standard Hall-bar geometry and Corbino geometry with parameter $\beta = 0.5$. In Corbino geometry (that is, the inner rim is set to a constant voltage while the outer rim is grounded), the electric field has zero azimuthal component, and the current is forced to rotate and travel longer distance, leading to higher resistance under a

magnetic field. **Figure A-6** compares the Hall effect in a standard Hall bar and the “Hall bar with a hole” with point current source. Such configuration (and many more) is also studied in **Ref.** [104]. In this particular case, the anti-Hall bar has an area about five times smaller than the Hall bar, but otherwise has the same material properties. Suppose these two different samples are put inside black boxes and measured under the same configuration. The Hall voltage an experimentalist will pick up turns out to be quite similar, that is, the two samples have similar nominal Hall coefficient and carrier density n . If she assumes that the nominal carrier density calculated from effective Hall voltage is a (scalar) average over the entire area, she would conclude that the second sample (anti-Hall bar) is made of a material with a much higher carrier concentration $n_0 = 5n$. In the contrary, we know that these two samples are made from the same material! Similar result can be obtained for an array made of such doubly connected elements (**Figure A-7**). The Hall voltage does not seem to depend on the lattice geometry, but different lattice (geometry) does have an impact on the potential landscape, as they impose different boundary conditions.

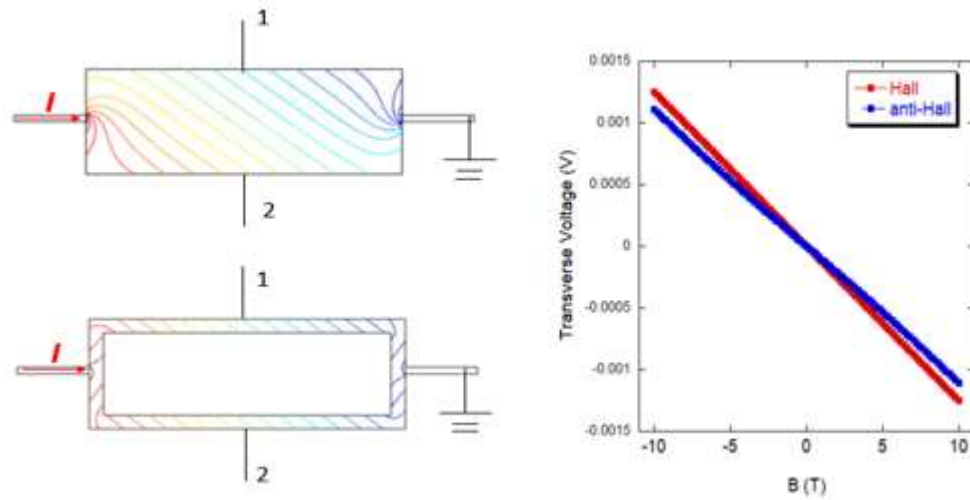


Figure A-6: Hall effect in standard Hall-bar geometry and in the “anti-Hall bar” (Hall bar with a hole). The two samples are made of the same material and are subject to the same measurement configuration. The Hall voltage is picked up between probe 1 and 2. We also sketch the equal potential line in colors.

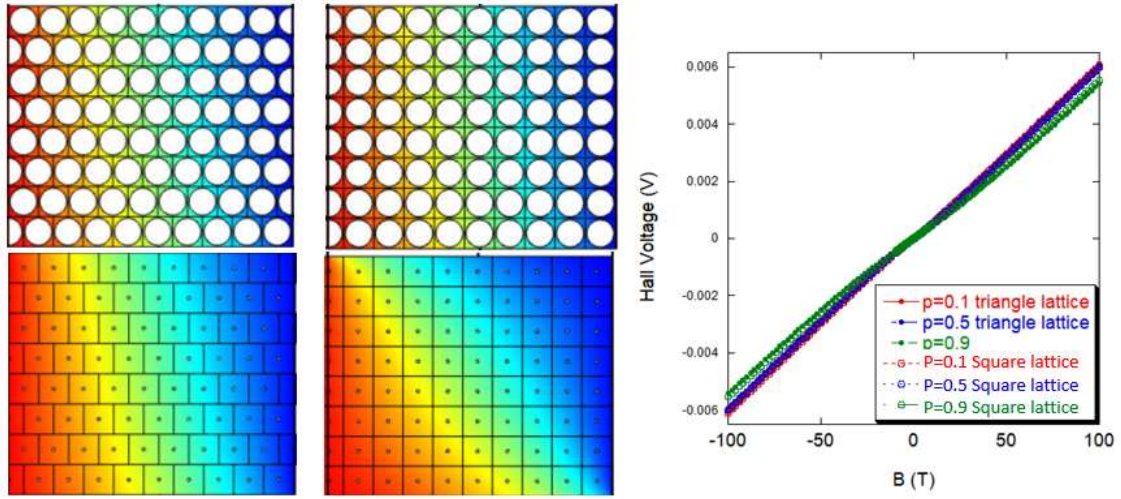


Figure A-7: Hall effect in a lattice made of doubly connected elements. The two samples are made of the same material and subject to the same measurement setup.

A general expression of the effective Hall tensor for a 3D metamaterial is given in **Ref. [102]**. The effective Hall tensor for an arbitrary geometry is a weighted volume average of the microscopic Hall tensor of the structure **Ref. [102]**, where the weights are determined by the matrix-valued current density. Given certain 3D structure, one can even see a sign reversal in the effective Hall tensor, which means that one in principle could obtain an effective p-type material from purely n-type semiconductor molded into certain geometry. However, such extreme case does not happen for inversed fcc structure, as we presented in Chapter 4.

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Selected Publications

Y. Chen *et. al.*, “Quantum Transport in Three-Dimensional Metalattices of Platinum Featuring an Unprecedentedly Large Surface Area to Volume Ratio”, accepted by *Physical Review Materials*.