Metal-Insulator transitions in epitaxial $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films grown using hybrid molecular beam epitaxy

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Abstract

Growth of epitaxial $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films using hybrid molecular beam epitaxy and stability of thin films in oxygen rich atmospheres at elevated temperatures are investigated. Only Sr-rich films with $x > 0.95$ were stable at such conditions. GdTiO_3 is a ferrimagnetic Mott insulator while SrTiO_3 is a diamagnetic band insulator. The metal-insulator transition occurs by electron doping of SrTiO_3 (Gd-doped SrTiO_3) or hole doping of GdTiO_3 (Sr-doped GdTiO_3). The latter is investigated in more detail. It is shown that the insulating state, even in undoped GdTiO_3 , is dominated by small polaron hopping, which transitions to metallic, Fermi-liquid-type conduction with large amounts of Sr alloying. The metal-insulator transition is also accompanied by transition from n -type to p -type conduction. Furthermore, ferrimagnetism persists into the metallic phase. The results show that the insulating phase is stabilized even for large amounts of Sr doping by polaron formation, and that the transition to the metallic phase occurs via a continuous first order transition and a two phase region.

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1. Introduction

Rare earth titanates ($RTiO_3$, where R is a trivalent rare earth ion) are prototypical Mott insulators [1-3]. The properties of these materials are controlled, to a large extent, by oxygen octahedral tilts in the crystal structure, which is derived from the cubic perovskite but orthorhombically distorted [4, 5]. The tilts depend on the rare earth ion size, and increase systematically from La to Y. Metal-insulator transitions can be induced by doping (alloying), for example by substituting divalent Sr on the trivalent R -site (“hole doping”) [6].

$GdTiO_3$ is one of the rare earth titanates with a highly distorted perovskite structure ($a = 5.4031 \text{ \AA}$, $b = 5.7009 \text{ \AA}$, and $c = 7.6739 \text{ \AA}$) [5], and becomes ferrimagnetic below a Curie temperature of $\sim 30 \text{ K}$ [3, 7]. Hole-doping with Sr produces a metal-insulator transition near the composition of $Gd_{0.8}Sr_{0.2}TiO_3$ [8]. This transition is the main focus of this work. A second metal-insulator transition is expected at high Sr concentrations (Sr-content $\gg$ Gd-content). Such concentrations can be viewed as lightly doped $SrTiO_3$. $SrTiO_3$ is a band insulator with diamagnetic properties and an ideal perovskite structure ($a = 3.905 \text{ \AA}$) [9]. Upon doping with trivalent Gd, electrons are donated into the conduction band, derived from Ti d -orbital states, resulting in n -type conduction. Considering the whole range of $Gd_{1-x}Sr_xTiO_3$, a transition from p -type to n -type behavior and suppression of the ferrimagnetism are expected. Such a trend has been observed in bulk $La_{1-x}Sr_xTiO_3$ [10] and $Y_{1-x}Ca_xTiO_3$ [11] compounds.

Growth of high quality thin films of $Gd_{1-x}Sr_xTiO_3$ is of great importance for the study of the underlying physics of the metal-insulator transition [6, 10-14], study and control of magnetism [15], and development of electronic devices through formation of heterostructures and control of the charge density of a two-dimensional electron gas [16, 17]. This work

documents the conditions for the growth of stoichiometric $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ ($0 \leq x \leq 1$) thin films using hybrid molecular beam epitaxy. Furthermore, the influence of Sr content (x) on the electrical and magnetic properties is discussed.

2. Experimental Procedure

$\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films were grown on (001) surfaces of SrTiO_3 and $(\text{La}_{0.3}\text{Sr}_{0.7})(\text{Al}_{0.65}\text{Ta}_{0.35})\text{O}_3$ (LSAT) substrates. Similar to SrTiO_3 , LSAT has a cubic perovskite structure with a lattice parameter of $7.72 \text{ \AA}$ [18]. (001) surface of LSAT is closely lattice matched to the (110) surface of GdTiO_3 and imposes a compressive in-plane stress [19]. Gd-rich films ($x < 0.5$) were grown on LSAT substrates, while Sr-rich films were grown on SrTiO_3 substrates.

Films were grown by hybrid molecular beam epitaxy (Veeco MBE GEN 930 system), with titanium tetra isopropoxide (TTIP, Sigma-Aldrich 99.999%) as the titanium and oxygen source. Gd and Sr were evaporated from solid sources (AMES Lab, 99.99% Gd and Sigma-Aldrich, 99.95% Sr). For Sr-rich compositions ($0.7 < x < 1$), the deposition approach was closely matched that for stoichiometric growth of SrTiO_3 [20, 21]. For Gd-rich compositions ($0 < x < 0.5$), the growth conditions were similar to those described elsewhere for the growth of stoichiometric GdTiO_3 [19]. All films were grown at a substrate temperature of $900 \text{ }^\circ\text{C}$. For the growth of Sr-rich films, an oxygen plasma source was used ($\sim 5 \times 10^{-6}$ Torr equivalent to $\sim 7 \times 10^{-4}$ Pa), while for the growth of Gd-rich films, oxygen was only supplied by the TTIP. For Sr-rich films, the growth window was mapped for different Gd concentrations by changing the ratio of A-site cations (Gd+Sr) to B-site cations (Ti). This ratio was changed by keeping the Sr and Gd fluxes constant and varying the TTIP flux. Gd-rich films were grown based on the growth

window of GdTiO_3 with different Sr fluxes (Sr cell temperature varied between 325 °C, 350 °C, and 375 °C). The growth details of Gd-rich samples can be found in Refs. [16, 19].

Sr-rich films with $x > 0.95$ were annealed after growth in oxygen at 800 °C for 30 seconds to ensure oxygen stoichiometry of the films and SrTiO_3 substrates. However, films with $x < 0.95$ exhibited structural changes during the oxygen anneal (discussed in section 3.2). Therefore, $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ films with $x < 0.95$ were grown on LSAT substrates (which does not reduce appreciably and therefore does not require an oxygen anneal) for electrical transport studies.

In-situ reflection high-energy electron diffraction (RHEED) and X-ray diffraction (XRD, Phillips PANalytical X'Pert MRD Pro thin film diffractometer equipped with a duMond–Hart–Partels Ge(440) incident beam monochromator and Cu $K\alpha$ X-ray source) were used for structural characterization. The XRD data were acquired using 2θ - ω scans. The amount of Sr to Gd content in each film was determined by Rutherford backscattering spectroscopy (RBS at Arizona State University) for Sr-rich films and X-ray photoelectron spectroscopy for Gd-rich films, as reported in Ref. [16] (The measured compositions for different Sr cell temperatures are as follows: $\text{Gd}_{0.96}\text{Sr}_{0.04}\text{TiO}_3$ for a Sr cell temperature of 325 °C, $\text{Gd}_{0.87}\text{Sr}_{0.13}\text{TiO}_3$ for 350 °C, and $\text{Gd}_{0.56}\text{Sr}_{0.44}\text{TiO}_3$ for 375 °C). For RBS measurements, thin films were grown on sapphire (Al_2O_3) substrates and the amount of elemental Sr, Gd, Ti, and O were measured.

Electrical properties were measured using a Physical Property Measurement System (Quantum Design PPMS). Metallic samples were measured using a four-point probe (Van-der Pauw geometry) while insulating samples were measured using a two-point probe geometry. Ohmic contacts were 300 nm-Au/50 nm-Ti for Gd-rich and 300 nm-Au/20 nm-Ni/40 nm-Al for

Sr-rich films, respectively, where Au is the top layer. Magnetic properties were measured using a Magnetic Property Measurement System (Quantum Design MPMS). To correct for the magnetic contribution of substrate and a 350 nm-thick Ta backing layer, each sample was measured twice: once with the film as-grown and the second time after the film was removed by dry etching in a reactive ion etching chamber. The magnetization of the thin film was estimated as the difference between the two magnetization measurements. All low-temperature measurements were performed at temperatures between 300 K and 2 K.

3. Results and Discussion

3.1. Growth Window

Measurement of the out-of-plane lattice parameter as a function of the TTIP/Sr beam equivalent pressure (BEP) ratio reveals the growth window for SrTiO_3 , in which the lattice parameter is constant and equal to that of bulk SrTiO_3 [20]. A similar method was used to map the growth window of Sr-rich films. Figure 1(a) shows the XRD patterns of $\text{Gd}_{0.028}\text{Sr}_{0.972}\text{TiO}_3$ at different TTIP/Sr BEP ratios. The out-of-plane lattice parameters calculated from XRD data [Fig. 1(a)] as a function of the TTIP/Sr BEP ratio is shown in Fig. 1(b). Off-stoichiometric compounds show an increase in the out-of-plane lattice parameter, which is similar to SrTiO_3 thin films [20]. Therefore, a growth window exists for the growth of stoichiometric $\text{Gd}_{0.028}\text{Sr}_{0.972}\text{TiO}_3$ films, but it is narrower than that of SrTiO_3 films.

Figure 2 summarizes the growth window for $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ films with various Gd contents up to 17% ($x = 0.83$). The growth window becomes narrower as the Gd content increases, which indicates increasing difficulties in the growth of stoichiometric, Gd-rich $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films. For Gd concentrations above 30% ($x < 0.70$) no growth window could be detected while an

oxygen plasma source is used. Therefore, only TTIP was used as a source of oxygen for the growth of Gd-rich samples, similar to the growth conditions of GdTiO₃.

High resolution XRD and corresponding RHEED patterns for 150 nm-thick stoichiometric, Sr-rich Gd_{1-x}Sr_xTiO₃ films on SrTiO₃ substrates are shown in Fig. 3(a). A film peak shift to higher 2θ angles (lower out-of-plane lattice parameters) was observed as the Gd content increased, which is expected due to the smaller lattice parameters of GdTiO₃ compared to SrTiO₃. Figure 3(b) shows the XRD and corresponding RHEED patterns of 20 nm-thick stoichiometric, Gd-rich films ($x < 0.5$). The difference in thin film peak positions for different Gd concentrations are not apparent (due to the small film thickness, and hence broad film peaks), and therefore an accurate measure of the out-of-plane lattice parameters is not achievable. Streaky RHEED patterns and XRD data indicate phase pure and stoichiometric growth conditions for these alloys.

3.2. Film Stability

Stabilization of GdTiO₃ requires reducing conditions; an oxygen-rich atmosphere promotes stabilization of the pyrochlore phase (Gd₂Ti₂O₇). SrTiO₃ however, requires oxidizing conditions for oxygen-stoichiometry. In the growth conditions of this study (even in the presence of oxygen-plasma) the SrTiO₃ substrate reduces and becomes metallic. To remove the oxygen vacancies, samples were oxygen annealed at elevated temperatures. To study the effect of this treatment on the stability of Gd_{1-x}Sr_xTiO₃ films, samples with different Gd contents were annealed at 800 °C for 30 seconds in a rapid thermal annealing (RTA) furnace under a flow of one atmosphere of oxygen. Figure 4 shows the XRD plots before and after this treatment. No change in thin films with very low Gd concentrations ($x > 0.95$) can be observed. However,

samples with higher Gd concentrations ($x < 0.95$) exhibit a film peak shift after the treatment, and samples with even higher Gd content ($x = 0.167$) show a structural change. Therefore, this study indicates that films with Sr concentrations lower than $x = 0.95$ are incompatible with oxygen annealing and undergo structural change. To avoid the oxygen annealing step, films with $x < 0.945$ were grown hetero-epitaxially on LSAT substrates, which do not contribute to electrical transport measurements, even when subjected to the reducing conditions during film growth.

3.3. Electrical and Magnetic Properties

Figure 5 shows the magnetic properties of the $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ films. At temperatures above 50 K, all films show paramagnetic behavior. Due to the combination of instrumental error for weak magnetic signals and the subtraction of the large substrate diamagnetic and Ta backing layer paramagnetic responses, the error in the paramagnetic regime can be on the order of the magnetization. The Curie temperature and the coercivity are not affected by these errors. As can be seen from Fig. 5, the GdTiO_3 film becomes ferrimagnetic below 30 K, similar to bulk GdTiO_3 [3]. Both the Curie temperature and the magnetization decrease monotonically with increasing amounts of Sr substitution.

Electrical resistivity and the inverse of the Hall coefficient for $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films are shown in Figs. 6(a) and (b), respectively. Figure 6(a) shows that the films with low Sr concentrations ($x < 0.2$) are insulating, while films with higher Sr concentration are all metallic. A metal-insulator transition composition of about $x = 0.20$ -0.35 can be estimated, which is in close agreement with polycrystalline $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ ($x = 0.20$) reported in literature [8]. The Hall resistance was linear as a function of magnetic field. Figure 6(b) shows temperature dependent

$(t.q.R_H)^{-1}$ for different metallic compositions, where t is the film thickness, q is the electron charge, and R_H is the 2D Hall coefficient. All metallic thin films were n -type. For a material containing only one type of carrier, $(t.q.R_H)^{-1}$ corresponds to the 3D carrier density, n . At room temperature the mobility of all carriers, even if they reside in multiple bands with different effective mass, is limited by phonon scattering, so this gives a reasonable estimate of n . As mentioned earlier, the samples with $x < 0.945$ were grown on LSAT substrates to avoid oxygen annealing at elevated temperatures. Therefore, it can be argued that oxygen vacancies in such films might contribute to the electrical transport. Hall effect measurements of an 80 nm SrTiO_3 film grown on LSAT in the absence of oxygen plasma showed a room-temperature carrier density of about $n_{\text{ov}} = 4 \times 10^{18} \text{ cm}^{-3}$. Compared to the carrier densities obtained from $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ ($x < 0.945$), n_{ov} is several orders of magnitude lower than those generated by chemical substitutions, and hence is negligible. Furthermore, carriers due to oxygen vacancies are highly temperature dependent and their density, n_{ov} , show a significant drop at low temperatures. Carrier densities for different compositions shown in Fig. 6(b), n , exhibit only a small temperature dependence, supporting the earlier argument about negligible effect of n_{ov} .

A summary of electrical and magnetic properties from Figs. 5 and 6 is presented in Fig. 7. Figure 7(a) shows the room temperature electrical resistivity versus x , which exhibits a minimum at $x \approx 0.7$. The metal-insulator transition occurs between $0.2 < x < 0.35$, similar to bulk $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ [8]. The estimated carrier density at 2 K and room temperature are shown in Fig. 7(b). The carrier density increases linearly with Gd content, but starts to deviate near the metal-insulator transition, similar to what has been observed for $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$ [6]. The high resistance of the insulating $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ films ($x < 0.2$) made Hall measurements inconclusive. Insulating films showed positive Seebeck coefficients, while the Seebeck coefficient was negative for

metallic films (see ref. [16]). A cross-over from p -type to n -type behavior is commonly observed in doped $RTiO_3$ at the metal-insulator transition [10].

Figure 7(b) also shows the ferrimagnetic Curie temperature (T_c), which decreases with an increasing amount of Sr. T_c is lowest for the $Gd_{0.56}Sr_{0.44}TiO_3$ film (~ 3 K). The observation of a ferrimagnetic metal in the $Gd_{1-x}Sr_xTiO_3$ system is surprising. For example, prior studies of ferromagnetic bulk $Y_{1-x}Ca_xTiO_3$ indicate the disappearance of ferromagnetism prior to reaching the metal-insulator transition [11]. One possible explanation for the stabilization of the ferrimagnetic phase is film strain, and another is that the film is composed of both ferromagnetic-insulating and paramagnetic-metallic domains. Based on the analysis discussed below, the second explanation seems more likely.

An analysis of the $Gd_{1-x}Sr_xTiO_3$ temperature dependent DC resistivity is presented in Fig. 8. For $x > 0.35$ the films are metallic and the temperature dependence of the resistivity can be described by the Fermi-liquid expression, $\rho(T) = \rho_0 + AT^2$, where ρ is resistivity and T is temperature [Fig. 8(a)]. This indicates that electron-electron scattering is the dominant scattering mechanism, even to fairly high temperatures. Figure 8(b) shows the temperature coefficient (A) as a function of the room temperature carrier concentration. In general, the A -coefficient decreases with increase in carrier concentration [22], and such behavior was observed away from the metal-insulator transition. As the transition is approached, an increase in the A -coefficient was observed which indicates mass enhancement due to electron correlation effects. This behavior is predicted by Mott-Hubbard theory [23] and has been observed for other $R_{1-x}A_xTiO_3$ compounds as the metal-insulator transition is approached from the metallic side [6, 24].

For $x < 0.2$ the samples show insulating behavior. When fit to an Arrhenius equation, the resistivity versus temperature yields an activation energy of 0.14 eV for GdTiO_3 , which is similar to that of other $RTiO_3$ single-crystals [25], but much lower than the Mott-Hubbard gap measured by optical conductivity (0.5-0.7 eV) [25, 26]. The most likely mechanism giving rise to such small activation energy is thermally-activated small polaron hopping, which has also been suggested in literature [3]. The conditions for the formation of small polarons are a narrow conduction band and strong electron-phonon coupling. The bandwidth of the $RTiO_3$ becomes narrower as the lattice distortion increases (from $R = \text{La}$ to $R = \text{Yb}$) [3, 5]. Furthermore, electron-phonon interaction is greatly enhanced in distorted perovskites. In $RTiO_3$ the polaron size decreases with the decrease in rare earth ionic radius from ten unit cells in LaTiO_3 to small polaron size in GdTiO_3 [3]. Therefore, the temperature dependent resistivity data for all insulating samples were analyzed using small polaron hopping [27, 28]:

$$\rho(T) = CT \exp\left(\frac{T_0}{T}\right), \quad (1)$$

where C is a temperature independent constant and T_0 is the characteristic temperature.

Figure 8(c) shows ρ/T as a function of $1/T$ for insulating compositions of $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ ($0 \leq x < 0.35$). Dashed lines indicate high temperature resistivity data fits to Eq. (1). Activation energies for small polaron hopping were calculated as 0.17 eV for GdTiO_3 , 0.14 eV for $\text{Gd}_{0.96}\text{Sr}_{0.04}\text{TiO}_3$, and 0.12 eV for $\text{Gd}_{0.87}\text{Sr}_{0.13}\text{TiO}_3$, showing a decrease in activation energy with an increase in Sr-content. Decreasing activation energy suggests shrinkage of the polaron gap. Deviation from linearity at low temperatures can be explained either by transition to variable range hopping [29-32] or proximity to $\theta/2$ (where θ is the Debye temperature) [33, 34].

However, due to the limited range of available data, a detailed analysis cannot be performed and thus, a clear conclusion about the cause of the deviation from linearity cannot be made.

To better understand the metal-insulator transition, it can be argued that composition fluctuations of all length scales exist in a solid solution [35]. Near the metal-insulator transition, composition fluctuations can form metallic domains due to shrinkage of the polaron gap and an increase in the size of polarons surrounded by insulating regions. Metallic conduction throughout the sample would be the result of coalescence of metallic domains, which can also explain the persistence of ferrimagnetism in the metallic phase.

4. Conclusion

Gd_{1-x}Sr_xTiO₃ thin films grown by hybrid molecular beam epitaxy, were shown to exhibit a metal-insulator transition, accompanied by a *p*-type to *n*-type transition for compositions around $0.2 < x < 0.35$. Gd-rich compositions ($x > 0.5$) were grown based on the growth conditions of stoichiometric GdTiO₃ (no supply of additional oxygen), while Sr- rich films were grown based on the growth conditions of stoichiometric SrTiO₃ (using oxygen plasma source). Stoichiometric growth conditions were determined by reflection high-energy electron diffraction and X-ray diffraction. The resistivity and Hall coefficient demonstrate the influence of chemical composition over the complete range of x in Gd_{1-x}Sr_xTiO₃, from low carrier density Gd- doped SrTiO₃ and metallic, high carrier density Gd_{0.56}Sr_{0.44}TiO₃ to insulating GdTiO₃. Persistence of ferrimagnetism in metallic phase was observed which can be explained by existence of paramagnetic metallic and ferrimagnetic metallic domains close to the metal-insulator transition.

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Figure Captions:

Figure 1. (a) High resolution XRD data for 150 nm $\text{Gd}_{0.028}\text{Sr}_{0.972}\text{TiO}_3$ at different TTIP/Sr BEP ratios, and (b) out-of plane lattice parameters calculated from XRD data as a function of TTIP/Sr flux ratio. The shaded area shows the growth window.

Figure 2. Evolution of the growth window as a function of Gd content ($1-x$) in $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ films. The markers represent limits of the stoichiometric condition determined using similar analysis presented in Fig. 1. To construct this plot, a compound with out-of-plane lattice parameter deviation of more than 0.05% is considered off-stoichiometry.

Figure 3. XRD and corresponding RHEED patterns for stoichiometric (a) 150 nm Sr-rich $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ ($x = 0.993, 0.945, 0.872$, and 0.715) grown on SrTiO_3 substrates, and (b) 20 nm Gd-rich $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ films ($x = 0.44, 0.13$, and 0.04) grown on LSAT substrates.

Figure 4. High resolution XRD of 150 nm $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films with different Gd content grown on SrTiO_3 substrates (a) before and (b) after oxygen anneal at 800 °C for 30 seconds.

Figure 5. (a) Magnetic susceptibility as a function of temperature for GdTiO_3 and $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ ($x < 0.5$) films measured in field cooled mode under a constant magnetic field of 0.01 T. Arrows show the Curie temperature for each film. (b) Magnetization as a function of magnetic field at 2 K for GdTiO_3 and insulating $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ films, in the magnetic field range of ± 0.5 T.

Figure 6. Temperature dependent (a) electrical resistivity and (b) inversed Hall coefficient (corresponding to carrier density assuming single carrier model) for $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ films.

Figure 7. (a) Room temperature electrical resistivity as a function of Gd content for $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ films. The dotted line is a guide to the eye. The resistivity exhibits a minimum at about 30% Gd. (b) Inversed Hall coefficient (at room temperature and 2 K, and linear fit to the 2 K data represented as a dashed line) and Curie temperature as a function of Gd content for $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ films. The dashed line at $x = 0.2$ indicates the metal-insulator transition phase boundary. The shaded area represents the ferrimagnetic phase.

Figure 8. (a) Resistivity as a function of T^2 for metallic $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films. Dashed lines represent fits to the Fermi liquid equation. (b) Temperature coefficient, A , as a function of room temperature inverse Hall coefficient $(tqR_H)^{-1}$ for the Fermi liquid fits presented in part (a). Note, not all the $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ samples are shown in part (a). (c) Temperature dependent resistivity of the insulating $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ samples presented as ρ/T versus $1/T$. The dashed lines show fits to the small polaron hopping expression, Eq. (1).

Fig 1

(a)

(b)

Fig 2

Fig 3

(a)

(b)

Fig 4

Fig 5

Fig 6

Fig 7

Fig 8