Low temperature transport of a charge transfer complex nanowire grown with an electric field from vapour phase

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Suspended Cu:TCNQ (Cu-tetracyanoquinodimethane) nanowires have been grown laterally from vapour phase connecting two electrodes ($\sim 1.0\mu$m gap) with and without the presence of external electric field applied between the electrodes during growth. Temperature and bias dependent conductance of these bridged nanowires have been investigated down to 40 K. It has been found that when the nanowire is grown in an electric field, its conductance gets enhanced significantly. The nanowires show a strong non-linear conductance beyond a threshold bias along with a linear conductance at low bias. Below 100 K, the bias dependent non-linear conductance with a threshold, can be fitted to modified Zener tunneling model for charge density wave transport in both types of nanowires, raising the possibility of onset of charge density wave type transport in the Cu:TCNQ nanowires. It has been proposed that the enhancement of the conductance in Cu:TCNQ nanowires when the growth is performed in the presence of electric field occurs due to better charge transfer as well as more ordered arrangements of TCNQ stacks during growth which is enabled by strongly anisotropic polarizability of the TCNQ moiety. This also modifies the parameters related to the non-linear conductance including the threshold value.

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I. INTRODUCTION

Investigations of electronic transport in ultrafine metal and semiconductor nanowires (NWs) have been a topic of considerable current interest. [1–3] Important parameters that determine the transport properties of NW are material composition, growth condition, crystal quality, NW diameter etc. [4, 5] In this paper, we have investigated an interesting possibility whether application of electric field during growth can influence the electrical conductivity of the NW when they are grown from a vapor phase. This question becomes particularly relevant because there are attempts to use electric field assisted growth/alignment as a tool to assemble NWs into large scale circuits. [6–8] Particularly, in the context of semiconductor NWs like Si or carbon nanotube, it has been established that an applied field can produce an alignment field (due to large anisotropy in polarization) that can overcome the randomizing effect of the thermal vibrations. [9–11] In this paper we address the issue whether the applied field, in addition to alignment, can also 'tailor'its properties like the electronic conduction. The work reported here was done in specific context of a charge transfer complex NW for reasons elaborated below. However, it may be seen that this may have a general applicability for growth of NWs of similar such systems. While electric field assisted growth in charge transfer complex have been reported before, [8] mainly to align and make NWs grow as bridges between two electrodes with micron or sub-micron gap. The possibility that such a growth process can actually lead to control/modification of physical properties have not been reported before.

The work reported here was carried out in NWs of the charge transfer complex Cu:TCNQ with average diameters in the range of $\approx$30 nm and length of $\approx 1\mu$m. The NWs were grown from vapor phase as nanobridges between prefabricated electrodes with and without an electric field applied between them. We have investigated the electrical conduction over a wide temperature range (40 K to 300 K) and find that there are substantial differences between wires that are grown with and without an electric field. The NWs show a large component of nonlinear transport beyond a threshold field, which is also strongly temperature dependent. Interestingly, it is found that for T<100 K, the non-linear component of the conduction resembles that of a CDW transport, a phenomena that has not been reported in Cu:TCNQ before. In this temperature range the bias dependent conductance can be well fitted to a modified Zener Tunneling model developed for CDW transport. [12, 13] The applied field during growth also modifies the non-linear component of the conductance including the threshold for the non-linear transport. These aspects have not been reported before in such charge transfer complex NWs like Cu:TCNQ and also raises the possibility of such

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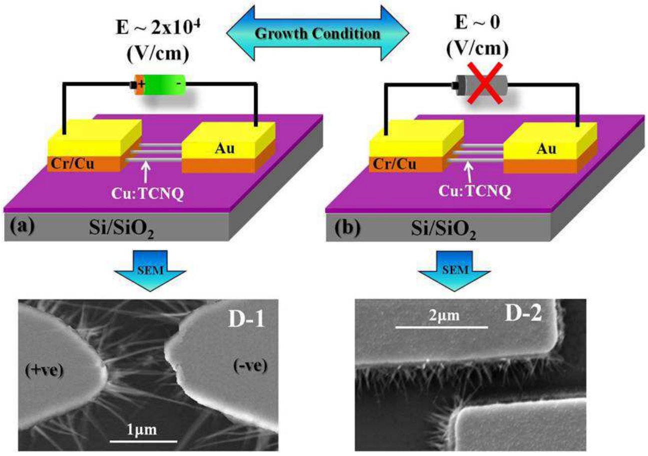

FIG. 1: Schematic of the device for inplane growth of Cu:TCNQ NW within prefabricated pads (a) with and (b) without field. SEM images of Cu:TCNQ NWs corresponding to the growth conditions are represented by arrows.

investigations in other organic charge transfer complexes.
Cu:TCNQ has attracted wide attention both as a system of basic physics interest in context of charge transport in quasi-one dimensional (Q1D) conductors and also because of its application potentials in non volatile electrical memory, [14, 15] humidity sensors [16] and high responsivity photo-detector [17] etc. However, most of the work done on this charge transfer complex material has been concentrated on electrical resistive state switching at and around room tempearure. [14, 15, 18] Investigation of electrical conduction in Cu:TCNQ has been limited to above 100 K before. Its extension below 100 K lead to the observation of the CDW type transport.

In Cu:TCNQ charge (electron) transfer occurs from the donor Cu (that oxidizes to Cu^{+}) to the acceptor TCNQ moiety. In this complex, the structure has an important role to play. Cu:TCNQ can grow into two phases. [19] Phase-I with a distorted tetrahedron of four nitrogen atoms around the metal (Cu) shows higher conductivity. While, in the lower conductivity Phase-II the metal coordination is more tetrahedral. These arrangements alter the packing and orientations of the quinoid ring of TCNQ which in turn affect the conductivity. This makes Cu:TCNQ as an attractive Metal Organic Framework (MOF) system. Growth of Cu:TCNQ crystals from solution by electro-crystallization using different potentials have shown that one may obtain different morphology of the conducting Phase-I Cu:TCNQ. [19] There are interesting report of reducing TCNQ by photochemical reaction leading to formation of metal-TCNQ complexes. [11, 21] Very recently, it has been shown that the change of conductivity of Cu:TCNQ by an applied field (post-synthesis) can be linked to structural changes. [22] The above discussion shows that electric field can act as a tool to alter the structure and electrical properties in Cu:TCNQ. However, it has never been investigated whether application of the electric field during growth, particularly in a vapour phase, can alter its conductivity. The present investigation addresses this particular issue. We also discuss the likely mechanisms that lead to the property modifications.

II. EXPERIMENTAL

The work was carried out using vapor phase growth. This process gives well defined NWs with much less diameter. Another important advantage for this growth mode is that one can have the growth as a nanobridge that connects two prefabricated contact pads which allows electrical experiments without any post-growth processing or additional lithographic processes for lead attachments.

Fabrication process for nanobridges of Cu:TCNQ join two prefabricated contact pads (electrodes). The tri-layer (Au/Cu/Cr) pads were fabricated using electron beam lithography and lift-off with sequential thermal deposition of a 10 nm Cr (adhesion layer), 50 nm of Cu (growth layer), and 100 nm of Au (protection layer) on oxidized Si wafer with 300 nm of thermal SiO_2. The typical gap between pads was $\sim 1\mu m$ (see Fig. 1 for a schematic and SEM image of a real nanobridge used). The Cu:TCNQ NWs grow by the reaction of TCNQ vapor with the Cu layer in the electrodes via a vapor-solid reaction. [23] TCNQ vapor was created by resistive heating of TCNQ at around 120^{0}C. We made two types of samples. During growth, for one sample an electric field ($E = 2 \times 10^{4}$V/cm) was directly applied between the pads. This sample is marked as D-1. For the other sample no bias was applied during growth. The NWs grown

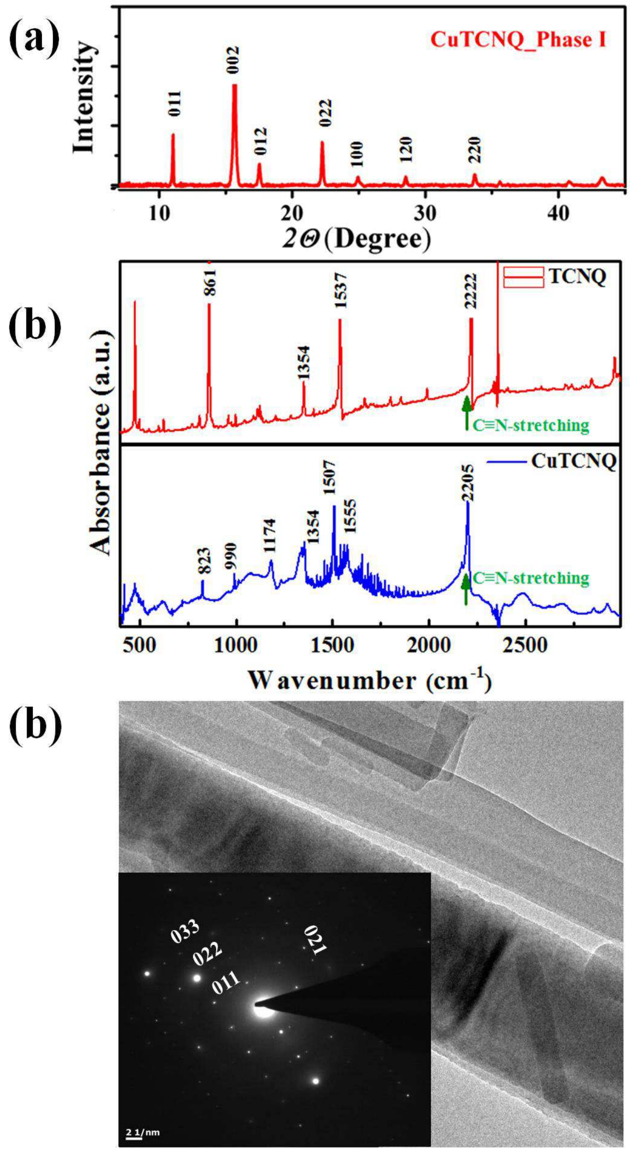

FIG. 2: (Color online)(a) X-ray diffraction patterns of PVD grown NWs. The indexing is as per ICDD data base. (b) FTIR spectra of TCNQ and Cu:TCNQ. Shift in -CN- stretching mode gives the degree of charge transfer Z estimated from ref. [20] (c) TEM image of Cu:TCNQ NW dispersed on a TEM grid. (Inset) Selected area electron diffraction (SAED) pattern of the NW to show its single crystalline nature.

with a zero field is marked as D-2. The NWs grow to bridge the electrodes through the sidewalls of the Cu layer. Generally the growth is stopped as soon as few NWs connect the bridge as determined by finite current between the electrodes. The nanobridges so formed have typically 2-5 NWs of Cu:TCNQ of very similar diameter ($\approx 20-30$ nm) for both the cases, D-1 and D-2. In the NW growth region electrode separation being same ($\sim$1μm) for both the devices length of NWs is assumed to be equal for D-1 and D-2. Fig. 1 (lower frame) shows SEM image of typical nanobridge devices.

The Cu:TCNQ NWs grown by this method consist of more conducting Phase-I Cu:TCNQ, [19] as confirmed by X-ray diffraction(XRD) and Transmission Electron Microscopy (TEM). Generally metal:TCNQ complexes crystallize in Phase-I, when the TCNQ stacks order face to face during growth leading to one dimensional (1D) structure and enhanced conductivity. The data are shown in Fig. 2. From the Fourier Transform Infra Red spectroscopy (FTIR) data and the observed shift in the -CN- stretching band we obtain average charge transfer value (Z) of $\approx$0.5 for the Cu:TCNQ NWs grown by vapor phase. [20]

In the nanobridges since wires are connected to electrodes one can directly make measurements of $I-V$ curves. The

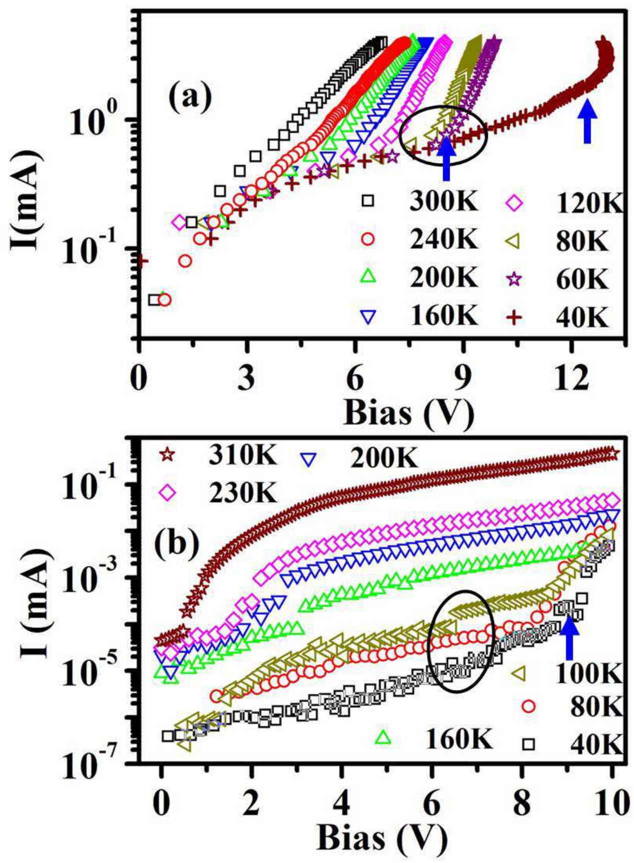

FIG. 3: (Color online) I-V data at different temperatures of NWs grown (a) with field, E$\sim 2\times10^4$ V/cm and (b) without field, E$\sim$ 0 V/cm. The V_{th} for temperatures T $<$ 100 are marked by circles and arrows.

bias dependent conductance $G(V)$ was obtained by differentiating the $I-V$ curves numerically ($G(V) = \frac{dI}{dV}$). The measurements were done using a Source-meter (Keithley SM 2400) in a variable temperature insert in a Closed Cycle Refrigerator down to 40 K. The measurements were performed $\geq$ 40 K temperature because below that temperatures the nanobridges are prone to mechanical failure. The nanobridges withstand thermal cycling reproducibly in the temperature range of 40 K to 300 K.

III. RESULTS

An assortment of the $I-V$ characteristics of both the NW samples were measured over the temperature range 40 to 300 K are shown in Fig. 3. The data are plotted in semi-log scale to accentuate the current in the low bias region. The figure shows that the nature of transport in the two types of NWs are somewhat different. The field grown NWs have higher conductance. The NWs show linear (symmetric) $I-V$ curves at low bias but beyond a threshold voltage V_{th} the $I-V$ curves become strongly non-linear. (Note: The bias V used for measurement is distinct from that used for growth.) The extent of non-linearity is also different in the two types of NWs. The $I-V$ data taken at different temperature show that there is a change in the conductance behaviour below 100 K where it becomes strongly non-linear and the threshold becomes more pronounced (Data highlighted by circles and arrows). We show below that the strongly non-linear behavior may be related to CDW type transport.

The non-linear character of the transport beyond a threshold bias can be seen more clearly in the bias dependence of the conductance (G) as shown in $G-E$ curves shown in Fig. 4, where E is the field ($=\frac{V}{d}$,d = electrode separation). The data shown have been scaled by the number of bridging wires in the nanobridge so that the value of the conductance G represents the conductance value of a single NW. It can be seen from the data that the conductance of the wires grown in presence of the electric field (sample D-1) is larger by at least one order compared to that

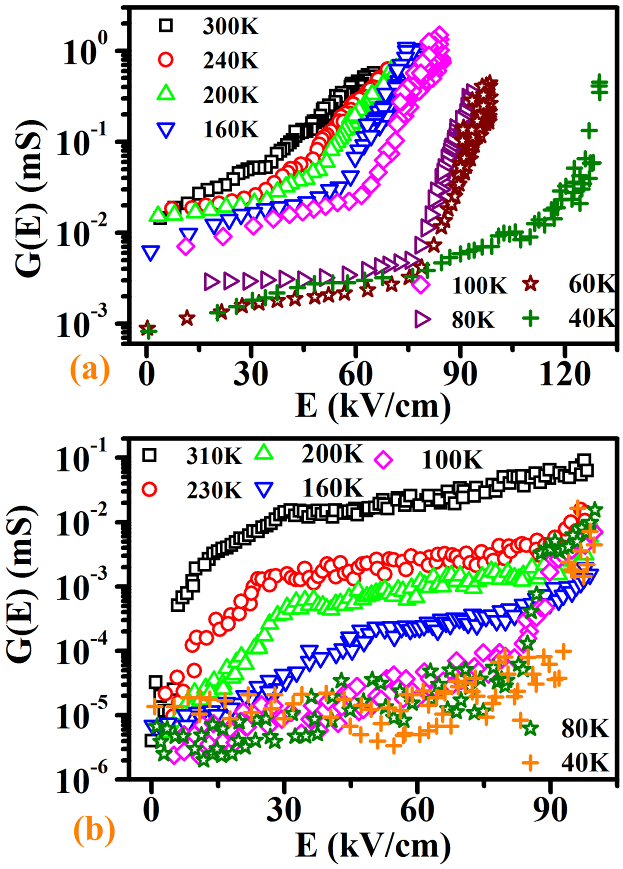

FIG. 4: (Color online) Bias dependent conductance G=dI/dV of NWs grown (a) with and (b) without field. The value of G has been scaled by number of wires to make G the conductance of a single NW.

of NW's grown by the same method but with zero field (sample D-2). The bias dependent G taken at different temperatures also show that the nature of dependence of G on E change for T<100 K. We will discuss this issue in details later on.

Both the NWs show semiconducting behaviours and the conductance G reduces on cooling. However, the reduction is much stronger for the zero field grown NWs. In case of the field grown sample $D-1$, the reduction on cooling is rather shallow. The limiting low bias conductance G_0 ($G_0 = \frac{dI}{dV}$ for $V \rightarrow 0$) for the zero field grown sample at room temperature is $\approx 5\mu$S so that $\frac{G_0}{e^2/h}$ is $\approx$1/8, signifying that the NW strands are deep into the insulating state justifying a substantial reduction of G_0 on cooling. However, for the NWs grown in field at room temperature the value of $\frac{G_0}{e^2/h}$ is ≤ 1. Thus, the NW strands grown in a field are on the verge of undergoing an insulator-metal transition. The application of a field during growth thus drives the NWs close to the transition boundary.

We have observed resistive state switching with hysteresis in Cu:TCNQ NW at a field of E$\sim 1.4 \times 10^5$ V/cm. Since the phenomenon of switching is not within the scope of the paper, the applied bias voltage has been kept lower than this value for measurement. However, even in relatively lower bias used, a strong dependence of $G(E)$ on bias E can be observed. The onset of non-linearity is distinct from switching with hysteresis. The threshold to non-linear conduction E_{th}, in both the samples are enhanced as the temperature of measurement is reduced. We will do quantitative analysis of the non-linear part of the data later on.

The results presented above clearly show that when an electric field is applied to the NWs during growth, the conductivity of the NWs so grown get strongly modified. The modification occurs in the linear conductance, temperature dependence and also in the non-linear part of the conductance. The experiment establishes the enabling role of the applied electric field during growth. It can thus act as a tool to control the resulting conductance of the NWs. The fact that the experiments were carried out in a nanobridge enabled us to reach conclusion about the conductance change at the level of a single NW. Experiments carried out on a bundle or a film of such NWs would not have allowed us to reach a clean conclusion.

IV. DISCUSSION

A. Analysis of the conductance data with linear and non-linear part

The observed conductance of both the NW samples, contain a linear part (bias independent conductance) and a strong non-linear part when the applied bias crosses a threshold. One of the models that has been proposed for such one-dimensional system is formation of Luttinger liquid where I has a power law dependence on V with $I \propto VT^{\alpha}$ at low bias and $I \propto V^{\beta+1}$ at high bias [24] usually with $\alpha \gg \beta$. There are reports that non-linear conduction in Cu:TCNQ may be following such relation. [24] This was based on data taken over the T range of 330 K to 105 K. [24] On extending the data to lower temperature this does not remain valid. Instead there is a signature of clear threshold for transport and the bias dependent G both the NW samples show behavior that is different from that expected for a Luttinger liquid.

One of the mechanism that can give rise to non-linear transport with a threshold is CDW transport. In a related system of charge transfer complex TTF:TCNQ there is clear signature of CDW transport in bulk single crystals, [25] films, [26, 27] as well as in NWs. [8] In such a system the CDW transport occurs due to Peierls transitions in TTF and TCNQ stacks below 50 K. [28] The NWs of TTF:TCNQ in which such a CDW transport was observed were grown from vapor phase between pre-grown contact pads, as has been done here. [8, 29] Though no CDW type transport or Peierls transition in Cu:TCNQ has been reported till date, we investigated whether the non-linear transport can be described by such a scenario. Since the conductivity of Cu:TCNQ was not measured below 100 K before, it may be the reason that such a phenomena was not observed or reported. Interestingly, there are theoretical studies using Hubbard Model which shows that in Alkali metal TCNQ salts like Na:TCNQ or K:TCNQ the CDW phase can occur due to Peierls transition if the nearest neighbour interaction exceed certain critical value. [illegible]

The transport in the Cu:TCNQ NWs have a linear part G_0 and a bias dependent non-linear part which we write as:

$$G(E) = G_0 + G_1 f(E) \tag{1}$$

Where G_1 is a measure of the weight of non-linear part described by the function $f(E)$. At higher temperatures T> 100 K, in both the samples the functional dependence of $f(E)$ can be described by a power law such that:

$$f(E) = (E - E_{th})^{\gamma} \tag{2}$$

Where both E_{th} as well as γ in both the samples have a shallow rise on cooling with E_{th} and γ values lying in the range 30 - 40 kV/cm and 2.5 - 3 respectively. However, below 100 K, there is a distinct change in the threshold dependent conduction and the bias dependence of G can be better fitted with a modified Zener model developed for CDW transport. [12, 13] For CDW system that shows non-linear transport with threshold the function $f(E)$ can be modelled by modified Zener model [13] as:

$$f(E) = \left(1 - \frac{E_{th}}{E}\right) exp\left(-\frac{E_0}{E}\right) \tag{3}$$

Where E_{th} is the threshold field and E_0 is a scale of field for tunneling across a pinning gap for the CDW.

The fit to the data to Eq. 3 have been shown for the data at 40 K for both the samples in the inset of Fig. 5, where we show the value of the scaled function $\frac{G(E) - G_0}{G_1}$ vs the ratio $\frac{E}{E_0}$. Fig. 5 shows all the data for both the samples below 100 K plotted in the scaled curves. It can be seen that for both the samples, a functional form given by Eq. 3 remains valid.

Linear conductance G_0 for the whole temperature range (300 K - 40 K) is shown in Fig. 6. The parameters of the fit namely G_1, E_{th} and E_0 are shown in Fig. 7 as a function of temperature (below 100 K). A number of observations can be noted from Fig. 7, that reflect both the similarity and differences between the two NW samples. It is also interesting that in both the samples, the non-linear conduction (with threshold) for ≤100 K, can be described by the Eq. 3. Though there is a qualitative similarity between the parameters of the non-linear conduction in the two

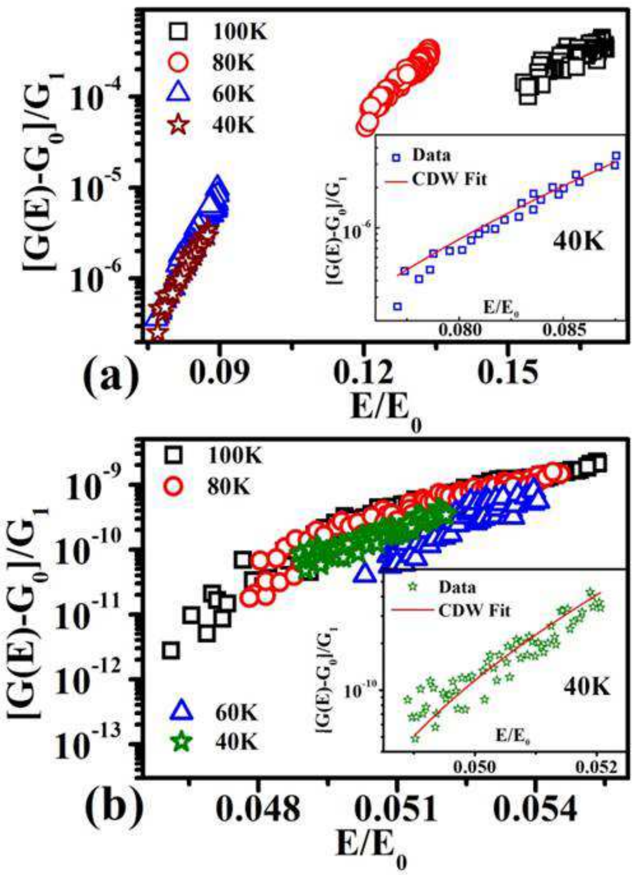

FIG. 5: (Color online) The non-linear part of conductance for the NWs grown (a) with and (b) without field as different temperatures fitted to the modified Zener tunneling relation. Inset in (a) and (b) indicates the CDW fit at 40 K.

samples, there are important quantitative differences between the two set of parameters belonging to the two samples. It need to be emphasized that though the non-linear conduction in both the samples follow Eq. 3 which is associated with CDW transition, we are not in a position to firmly claim that the non-linear conduction so observed indeed originate from CDW related phenomena. However, there does exist a possibility, as discussed before, of a Peierls transition in the TCNQ stacks in Cu:TCNQ leading to formation of CDW. This, however, would need independent support from temperature dependent structural data.

B. Linear conductance and the temperature dependent resistivity

The values of the field independent conductance G_0 differ significantly in the two samples. This is shown in Fig. 6(a). Near room temperature the field grown wires (D-1) have a conductance that is about one order more than that of the zero field grown NWs (D-2), as stated before. However, due to steep temperature dependence of the more insulating NWs in D-2, G_0 of the two differ by nearly 2 orders at 100 K. There are also certain qualitative observations that can be seen in the temperature dependences of G_0 of the two NW samples. The initial G_0 decreases from 300 K down to 250 K region for both the samples, although steeper for the zero field grown NW. However, there is a temperature independent plateau in both the samples below 220 K region down to about 125 K where they again show a gradual decrease on cooling. From the conductance G_0 we obtain the resistivity ($\rho = \frac{A}{G_0 l}$, A=area, l=length of NW). We find that ρ shows activated behavior following a variable range hopping (VRH) relation for a disordered 1D system [24, 31, 32] for the temperature range down to 200 K as:

$$\rho(T) = \rho_0 + exp\left(\frac{T_0}{T}\right)^{1/n} \quad (4)$$

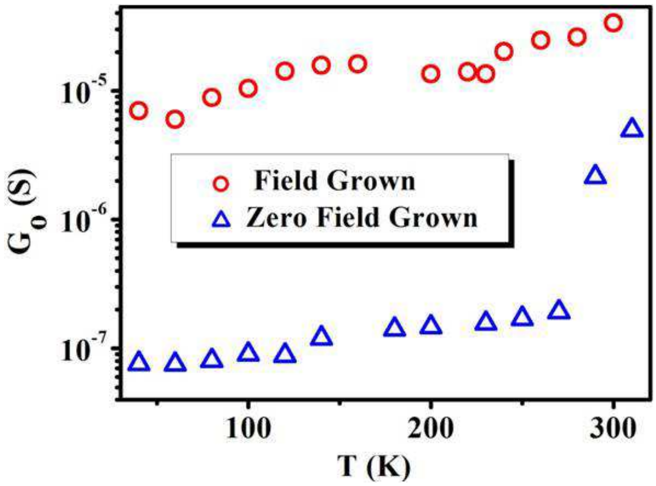

FIG. 6: (Color online) Temperature dependence of the linear conductance G_0 (calculated from the slope of linear region of $I-V$) for field grown and zero field grown NW.

Where T_0 is the energy scale for the hopping and the exponent $n = d + 1$, d being the dimensionality. For 1D system like the one being investigated expected n=2. The value of T_0 is related to the inverse localization length (α) and the width of distribution of site energies ($\pm\Delta$) so that $T_0 \sim \frac{a\alpha\Delta}{k_B}$, a being the interatomic distance. The fit parameters are given in Table I. For both the samples, the VRH eqn holds above 200 K and it deviates from this below this temperature. In the high temperature region where the VRH equation holds, the value of T_0 reduce from 6300 K (≈ 520 meV) in D-2 to around 1625 K (≈ 135 meV) in D-1. The reduction of the value of T_0 in the field grown sample points to reduction in disorder. Reduction of the disorder will enhance the localization length so that α decreases. The reduction of disorder will also decrease the spread Δ. Both these factor will lead to decrease in T_0. The inference we can obtain from the data is that on application of the electric field during growth, the order in the TCNQ is enhanced. We will see below that it likely arises from increasing the order in stacking of the TCNQ.

TABLE I: Fitted parameters for VRH model.

Synthesis Condition	Fitted Parameters	
	ρ_0 (Ω−cm)	T_0 (K)
Field grown	$\sim 1.05 \times 10^{-3}$	$\sim$ 1626
Zero field grown	$\sim 6.69 \times 10^{-7}$	$\sim$ 6300

C. Parameters of non-linear conductance with threshold

The non-linear part of the conductance, whose weight we measure by G_1, show strong rise on cooling. The parameters for fit to the modified Zener model (Eq. 3) E_0 and E_{th} both show an enhancement on cooling. For the zero field grown sample (D-2), G_1 changes by nearly one order on cooling from 100 K to 40 K tending to a temperature independent value at lower T. In the same region, the G_1 for the field grown NWs (D-1) changes steeply by around 2 orders. Interestingly, the value of G_1 for D-1 stays smaller than that of D-2, which is opposite to what has been seen for G_0 which is distinctly higher for the field grown sample D-1.

The existence of a distinct threshold field is seen in both the samples and E_{th} enhances on cooling. Interestingly the value of E_{th} for the samples are very close. Enhancement of E_{th} on cooling has been observed in other systems also that show CDW type transition. [8] The parameter E_0 also increase on cooling for both the samples, more steeply for the field grown sample. For the zero-field grown sample E_0 is larger and has a relatively shallow T dependence.

It will be worthwhile to compare the parameters E_0 and E_{th} seen for the Cu:TCNQ with those observed in NWs of a system like TTF:TCNQ that are known to show Peierls transitions. The value of the ratio $\left(\frac{E_0}{E_{th}}\right)$ is an

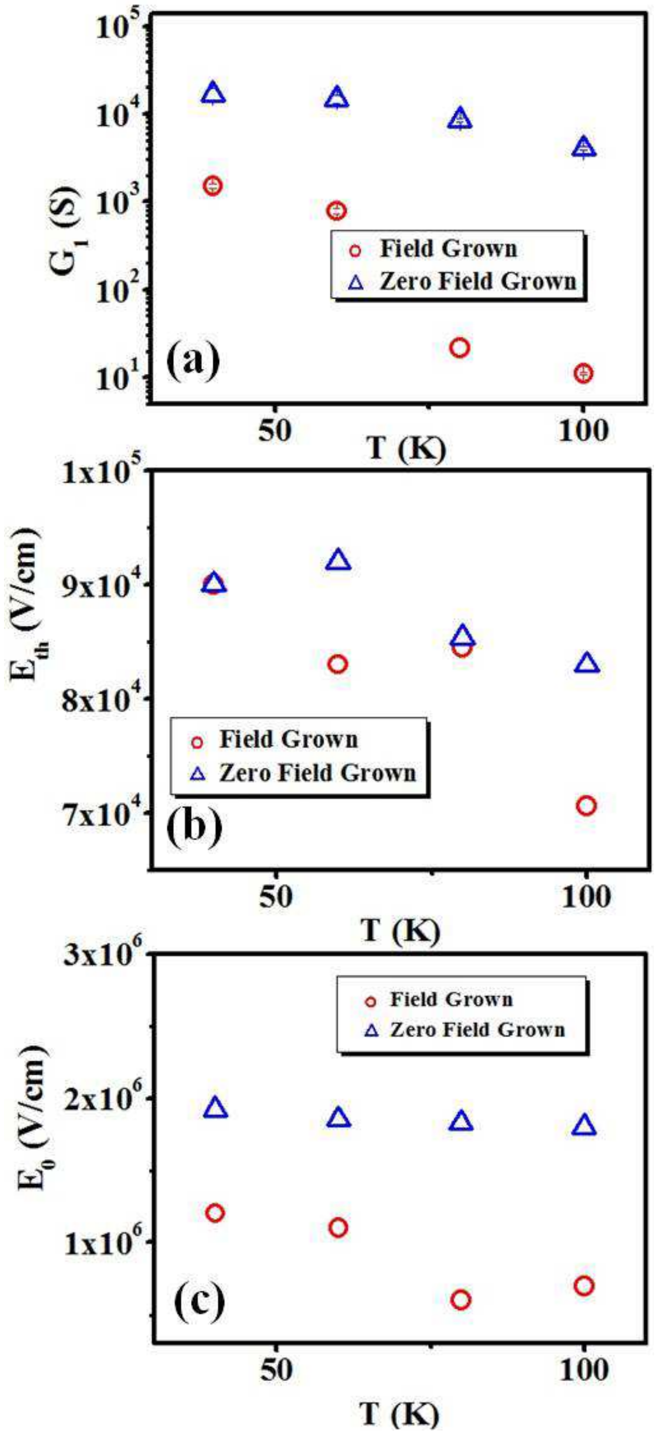

FIG. 7: (Color online) Temperature dependence of the parameters (a) G_1, (b) E_{th} and (c) E_0 as obtained from the fit to modified Zener tunneling relation as shown in Fig. 5.

important parameter and gives the ratio of the tunneling length L_t to the coherenece length of the CDW system ξ_0 so that $\left(\frac{E_0}{E_{th}} = \frac{L_t}{\xi_0}\right)$. The value of the ratio is around ≈ 2-5 for clean CDW systems like $NbSe_3$. [33] For NWs like TTF:TCNQ is ≈ 10 at low temperatures. For the field grown Cu:TCNQ NWs, at 40 K the ratio is 10 while it is ≈20 for the zero field grown NWs. The fields $E_0 \sim \xi_0^{-1}$ and $E_{th} \sim L_t^{-1}$. Since for both the NWs E_{th} are nearly same, the larger value of the ratio for the zero-field grown sample most likely arises due to smaller coherence length ξ_0.

The coherence length ξ_0 is $\propto E_g^{-1}$ where E_g is the pinning gap of the CDW. The application of the field, if it leads to better alignment of the TCNQ stacks can lead to reduction of E_g and hence an enhancement of ξ_0 and a smaller E_0. The smaller value of the field E_0 in the field grown sample, thus may justified within the frame work of a CDW transport.

To conclude this part we observe, whatsoever, be the origin of the strong non-linearity, it is present in both samples but it is affected by the field applied during growth. The strong non-linearity appears to follow the transport behavior of a CDW system .

D. Suggested scenario for effect of applied electric field during growth leading to change in conductivity of nanowire

In Cu:TCNQ there are two distinct factors (likely interdependent) that can alter its conductivity. First is the alignment in stacking of the TCNQ molecules and second is the degree of charge transfer (Z). It is thus likely that any modification of one or both of the above will lead to a change in the conductivity of the charge transfer complex. The applied electric field during growth can affect both the processes. Based on this we propose the following likely scenario for our observation that the growth of the Cu:TCNQ NW in an electric field enhances its conductivity.
The growth model of Cu:TCNQ from vapor phase has not been worked out in details. In the vapor phase growth the length grows in time following a time dependence that originates from diffusion of ionic species (Length, $l \propto \sqrt{t}$), while the diameter does not change after initial growth period. This diameter constrained growth is very similar to growth in solution where Anodized Alumina Oxide (AAO) templates have been used to limit lateral growth. [34] In both the growth processes two phenomena are involved after the initial nucleation phase. (See the schematic in Fig. 8). There is diffusion of Cu^{+1} ions from the Cu electrode though the growing wire to the open growth face. There is also diffusion of electrons from the Cu electrode (due to redox potential) to the top growing surface, leading to oxidation of the arriving TCNQ molecules to $TCNQ^{-1}$, which then reacts with the diffusing Cu^{+1} ions to make the Cu:TCNQ. The efficiency of the process (ionic diffusion, as well as electron transport from Cu side to growth face) would determine the extent of the charge transfer Z. Application of an electric field during growth process will enhance the Cu ions migrate from Cu electrode to the NW tip, thus facilitating the extent of charge transfer and Z enhances. In general the Cu:TCNQ NW grown have $Z \approx 0.5 - 0.6$. We have shown a small increment in Z using such materials as Graphitic Oxide can lead an enhancement in conductivity by an order of magnitude. [35] Thus an enhanced Z, enabled by the applied electric field during growth can increase the conductivity in the field grown wire substantially as observed.

The conductivity of the grown nanowire would also critically depend on the alignment of the TCNQ stacks in the NWs. As the NW grows from the vapor phase with arrival of TCNQ molecules, the successive molecules due to randomization by thermal forces may not have proper alignment. This lack of proper alignment would lead to improper arrangements of TCNQ stacks which will lead to lower conduction even if the grown wires have predominantly Phase-I. Application of the electric field, due to highly anisotropic polarizability α (as in TCNQ molecule) can lead to a torque that will align the arriving TCNQ molecules leading to proper stackings. Such a polarization anisotropy induced alignment has been observed in aligned growth of carbon nanotubes from the vapour phase in presence of an applied field. The polarization anisotropy driven torque overcomes the randomizing effect of the thermal field leading to ordered growth. [36] In Cu:TCNQ, the field driven enhancement in the order of stacking of TCNQ will enhance the conductivity and will also increase the coherence length ξ_0 for the CDW phase. We do observe in our experiment that NWs grown in an electric field shows larger ξ_0 and thus lower threshold field E_{th}. The scenario suggested above, though qualitative, can explain the observation that field applied during growth can indeed change the conductivity of the NW.

V. CONCLUSION

In conclusion, we have shown that application of electric field during vapor phase growth can be a viable tool to enhance/modify the conductivity of NWs. The electrical conductance of the NWs (measured) down to 40 K shows a strong non-linear conductance which has a well defined threshold for T $\leq$ 100 K. The non-linear conductance was found to follow a modified Zener tunneling model proposed for CDW transport. Such an observation was not made

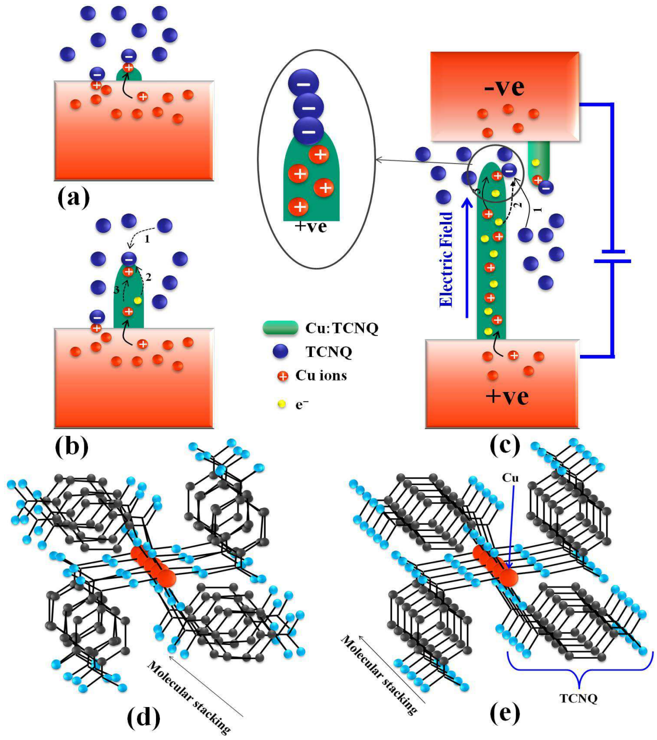

FIG. 8: (Color online) Schematic of Cu:TCNQ NW growth under externally applied field. (a) Nucleation of the ions, (b) NW growth and (c) accelerated nucleation process under field. Stacking of the Cu:TCNQ molecules during growth (d) without field and (e) with field. Field growth NW are having better $\pi - \pi$ stacking of the TCNQ molecules.

before in Cu:TCNQ and opens up the possibility of new investigation of CDW in this system.

The application of the field during growth enhances significantly the conductance and for a single NW grown in field the conductance is close to $\frac{e^2}{h}$, the boundary of insulator-metal transition. The parameters of the non-linear conductance also change when the wire is grown in an electric field.

We proposed a scenario for the field growth condition where the applied field helps diffusion of Cu^{+} ions from Cu to the growing face leading to enhanced charge transfer which results in enhanced conductivity. The field applied during growth has been proposed to improve the stacking of the TCNQ moiety leading to enhancement of conductance and also change in parameters of the non-linear conduction. Though the experiment has been done in context of a charge transfer complex NW, the concept may have applicability in growth of other semiconducting NWs.

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[1] L. Ma, J. Wang, J. Yip, and F. Ding, *J. Phys. Chem. Lett.*, 2014, **5**, 1192-1197.
[2] A. Roy , T. Pandey , N. Ravishankar , and A. K. Singh, *J. Phys. Chem. C*, 2014, **118**, 18676.
[3] C. Wang, Yongjie Hu, Charles M. Lieber and S. Sun, *J. Am. Chem. Soc.*, 2008, **130**, 8902.
[4] C. Durkan and M.E. Wallend, *Phy. Rev. B*, 2000, **61**, 14215.

[5] A. Bid, A. Bora, and A. K. Raychaudhuri, *Phy. Rev. B*, 2006, **74**, 035426.
[6] Peter A. Smith, Christopher D. Nordquist, Thomas N. Jackson, Theresa S. Mayer, Benjamin R. Martin, Jeremiah Mbindyo, and Thomas E. Mallouk, *Appl. Phys. Lett.*, 2000, **77**, 1399.
[7] D. Gates, *Nature Nanotechnology*, 2010, **5**, 484.
[8] T Phanindra Sai and A K Raychaudhuri, *Nanotechnology*, 2010, **21**, 045703.
[9] J. E. Fischer, W. Zhou, J. Vavro, M. C. Llaguno, C. Guthy, R. Haggenmueller, M. J. Casavant, D. E. Walters and R. E. Smalley, *J. Appl. Phys.*, 2003, **93**, 2157.
[10] T-In Jeon, K-Ju Kim, C. Kang, S-Jae Oh, J-Hiuk Son, K. Hyeok An, D. Jae Bae, and Young Hee Lee, *Appl. Phys. Lett.*, 2002, **80**, 3403.
[11] Chuan Zhao, Alan M Bond, *J. Am. Chem. Soc.*, 2009, **131**, 4279-4287.
[12] J Bardeen, *Phys. Rev. Lett.*, 1979, **42**, 1498.
[13] J Bardeen, *Phys. Rev. Lett.*, 1980, **45**, 1978.
[14] R. S. Potemeber, T. O. Poehler, *Appl. Phys. Lett.*, 1979, **34**, 405.
[15] R. Müller, S. Jonge, K.Myny, D.J.Wouters, J.Genoe, P.Heremans, *Solid State Electron.*, 2006, **50**,601.
[16] K. Wang, X. Qian, L. Zhang, Y. Li, and H. Liu, *ACS Appl. Mater. Interfaces*, 2013, **5**, 5825.
[17] R. Basori, K. Das, P. Kumar, K. S. Narayan, A. K. Raychaudhuri, *Optics Express*, 2014, **2**,4944.
[18] J. Billen, S. Steudel, R. Müller, J. Genoe, and P. Heremans, *Appl. Phys. Lett.*, 2007, **91**, 263507.
[19] R. A. Heintz, H. Zhao, X. Ouyang, G. Grandinetti, J. Cowen, and K. R. Dunbar, *Inorg. Chem.*, 1999, **38**, 144.
[20] J. S. Chappell, A. N. Bloch, W. A. Bryden, M. Maxfield, T. O. Poelher and D. O. Cowan, *J. Am. Chem. Soc.*, 1981, **103**, 2442.
[21] Anthony P. O'Mullane, Nigel Fay, Ayman Nafady, and Alan M. Bond, *J. Am. Chem. Soc.*, 2007, **129**, 2066.
[22] C. A. Fernandez, P. C. Martin, T. Schaef, M. E. Bowden, P. K. Thallapally, L. Dang, W. Xu, X. Chen , B. P. McGrail *Scientific Report*, 2014, **4**, 06114.
[23] Z. Zhou, R. Jin, G. Eres, A. Subedi, and D. Mandrus, *Appl. Phys. Lett.*, 2006, **89**, 133124.
[24] Z. Zhou, K. Xiao, R. Jin, D. Mandrus, Jing Tao, D. B. Geohegan, and S. Pennycook, *Appl. Phys. Lett.*, 2007, **90**, 1931151.
[25] M J Cohen and A J Heeger, *Phys. Rev. B*, 1977, **16**, 688.
[26] R. Springell, R. C. C. Ward, J. Bouchet, J. Chivall, D. Wermeille, P. S. Normile, S. Langridge, S. W. Zochowski, and G. H. Lander, *Phys. Rev. B*, 2014, **89**, 245101.
[27] P. Goli , J. Khan , D. Wickramaratne , Roger K. Lake , and Alexander A. Balandin, *Nano Lett.*, 2012, **12**, 5941.
[28] V. Solovyeva and M. Huth, *Synth. Met.*, 2011, **161**, 976.
[29] T Phanindra Sai and A K Raychaudhuri, *Mater. Res.Soc. Symp. Proc.*, 2008, **1058**, JJ05-03.
[30] M. Kumar, Benjamin J. Topham, R. Yu, Quoc B. D. Ha, and Zoltan G. Soos, *J. Chem. Phys.*, 2011, **134**, 234304.
[31] A. N. Bloch, R. B. Weisman, and C. M. Varma, *Phys. Rev. Lett.*, 1972, **28**, 753.
[32] M. M. Fogler, S. V. Malinin, and T. Nattermann, *Phys. Rev. Lett.*, 2006, **97**, 096601.
[33] L Sneddon, M C Cross and D S Fisher, *Phys. Rev. Lett.*, 1982, **49**, 292.
[34] H-X. Ji, J-S. Hu, Y-G. Guo, W-G. Song, and L-J. Wan, *Adv. Mater.*, 2008, **20**, 4879-4882.
[35] R. Basori and A. K. Raychaudhuri, Accepted in *IEEE Explore Conference Proceeding*, 2014.
[36] Y. Avigal and R. Kalish, *Phys. Lett.*, 2001, **78**, 2291.