Observation of charge density wave characteristics in conducting polymer nanowires: Possibility of Wigner crystallization

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We have presented here results of a low temperature transport study of polypyrrole nanowires having low electron densities, which shows characteristics of charge density waves observed in structurally ordered materials. The current-voltage characteristics of all these nanowires show a power-law dependence on voltage and temperature and a "gap" that decreases rapidly as the temperature is increased, confirming the existence of a long-range electron-electron interaction in the nanowires. A switching transition to highly conducting state has been observed above a threshold voltage, which can be tuned by changing the diameters of the nanowires and the temperature. Negative differential resistance and enhancement of noise have been observed above the threshold. These experimental results give evidence in favor of Wigner crystallization in these nanowires.

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I. INTRODUCTION

Possibilities of applications in nanotechnology has triggered extensive research activities to understand charge conduction in quasi-one-dimensional (quasi-1D) conductors such as nanowires and nanotubes where electron-electron interaction (EEI) plays a dominant role. In 1934, Wigner considered the effect of long-range EEI in metals and predicted in a seminal paper[1] the possibility of formation of periodic spatial structures of electrons for very low electron density materials. It has been predicted theoretically that one-dimensional Wigner crystal (1DWC)[2] formation exhibiting the characteristic of a charge density wave (CDW) may occur in nanowires of even structurally disordered materials.[3] The wigner crystal (WC) phase has been observed experimentally in a two-dimensional electron system under an intense magnetic field,[4,5] in surface-state electrons of superfluid helium,[6] in quasi-1D organic charge transfer salt[7] and, recently, in inorganic chain compounds.[8] Although interesting phases such as Lüttinger liquid (LL),[9] which arise due to short-range EEI, have been observed in several one-dimensional (1D) systems,[10–13] the predicted formation of 1DWC in structurally disordered materials[3] has not been observed experimentally. Among various low-dimensional systems, conducting polymer nanowires are easy-to-form quasi-1D systems in the study of EEI as one can tune the carrier concentration of a polymer over several orders of magnitudes by controlling doping concentration, and WC formation has been predicted in conducting polymers.[3,14]

Here, we report results of a low temperature study of polypyrrole nanowires having diameters from 30 to 450 nm. Highly nonlinear current-voltage (I-V) characteristics having $I \propto V^{1+\beta}$ at high V and $I \propto T^{\alpha}V$ at low V were observed. The exponent β is reduced from high values ($\sim 5-7$) with increasing temperature and does not take a value equal to α, in general. A large "gap" voltage (V_G), above which the conductance increases substantially, was observed in the low temperature I-V characteristics. The gap was found to decrease rapidly with increasing temperature and with increasing diameter. The I-V characteristics also show a switching transition to a highly conducting state above a certain threshold voltage $V_{th}(>V_G)$. The threshold field (E_{th}) corresponding to V_{th} was found to depend on the diameter (d) as $E_{th} \propto d^{-4/3}$. Current-driven I-V characteristics show a negative differential resistance (NDR) at low temperatures. An increase in "noise" has been observed in the switched (highly conducting) state. All these experimental results indicate a possibility of Wigner crystal formation in conducting polymer nanowires.

II. EXPERIMENT

A. Sample preparation

Conducting polymer nanowires are quasi-1D systems composed of aligned polymer chains where charge carriers are created by doping. We used a membrane based synthesis technique to grow polymer nanowires.[15] We used a porous polycarbonate membrane of various pore diameters and thicknesses to prepare polypyrrole nanowires. This technique helps us to prepare nearly monodisperse nanowires; details of the synthesis technique has been described elsewhere.[16] The actual diameters of nanowires were characterized from a scanning electron microscopy micrograph and were found to have average values of 30, 50, 70, 110, 350, and 450 nm. The average doping concentration (obtained after an initial doping gradient within a few hundred nanometers) can be systematically reduced by lowering the diameters of the nanowires.[16]

B. Electrical measurements

For electrical measurements, gold pads (2 mm diameter) were sputter deposited on both sides of the membrane to establish parallel connection with $\sim 10^6-10^7$ nanowires (pore density of the membrane $\sim 10^8-10^9/\mathrm{cm}^2$). We have seen that among various contact materials, gold serves as the best contact material and provides less contact resistance.[16] Due to the parallel connection of a large number of nanowires, the maximum current flow through the individual nanowire is very low (less than 10 nA). The room temperature resistance of the individual nanowires (obtained by considering parallel connection of monodisperse nanowires and

dividing the measured resistance with the number of wires) of various diameters are in the range of 10^6–10^9 Ω, which are similar to the previously reported values for various polymer nanowires or nanofibers.[17] As very low current flows through the individual nanowires, the maximum power dissipation in individual nanowires is very low (less than microwatt), and this prevents the the nanowires from burning out.

The electrical measurements were carried out using a Keithley 2400 source meter, a Keithley 2000 multimeter, or an Agilent 34420A nanovoltmeter in a pseudo-four-probe configuration. Measurements were done in a two-probe configuration for a very high resistive sample using a Keithley 6517A electrometer. Voltage was supplied using the source of the electrometer, and the current flowing through the sample was measured. Before each measurement, instrument performances were checked using a standard resistance of different values (up to 100 GΩ). The consistency of the results were checked by repeated measurements, by changing the contact material, and by changing the scan speed of the bias voltage or current. For a very high resistive sample, noise in the measured current has been reduced by averaging over 30 data points and giving sufficient delay (≥60 s) before taking data at each bias step. Differential conductance values (dI/dV) were obtained by numerically differentiating the I-V curves and were verified by lock-in measurements. A lock-in measurement of dI/dV vs V was done by using an Agilent 33220A function generator, an SR 830 lock-in amplifier, and a current amplifier (Ithaco 1212 or SR 570). A small sinusoidal ac voltage (20 mV peak to peak) of 17 Hz has been added to a dc bias and supplied to the nanowire samples. All the measurements were done in an Oxford cryostat under a liquid helium environment over the temperature range of 1.7–300 K. The sample temperature was controlled using a Lakeshore 340 temperature controller, a heater, and a calibrated temperature sensor (cernox) placed on the sample holder. All the instruments were interfaced with a computer via the GPIB interface. The LABVIEW (National Instruments Corp., Austin, TX) software has been used for data acquisition.

III. RESULTS AND DISCUSSION

The conductance vs voltage and dI/dV vs voltage data of various nanowires [refer to Figs. 1(a) and 1(b)] show the existence of gap voltage (V_G). We have measured the value of V_G by noting the change of slope from the conductance vs voltage data for different diameter nanowires, as shown in Fig. 1(b). V_G was found to be inversely proportional to the diameter (d) of the nanowires [refer to the inset in Fig. 1(b)]. It is to be noted that the zero-bias current and, hence, the conductance below the V_G increase with the temperature and diameter of nanowires. The gap was found to reduce rapidly with the increase in temperature and vanishes at a relatively high temperature that depends on the wire diameter.

The strong temperature dependence of the gap is a signature of electron-electron interaction[18,19] and has been observed earlier in chains of graphitized carbon nanoparticle.[20] The temperature and diameter dependence of the gap in our

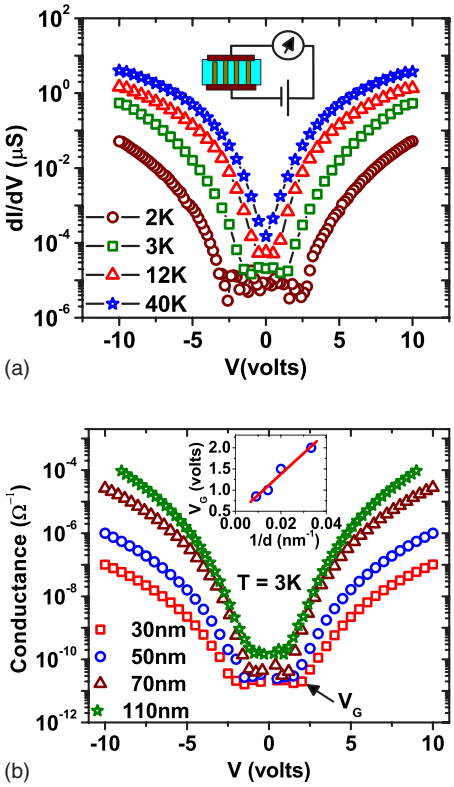

FIG. 1. (Color online) (a) Differential conductance (dI/dV) is plotted as a function of bias voltage (V) for a 30 nm diameter nanowire at various temperatures. Schematic diagram of the two-probe measurement configuration is shown in the inset. (b) Conductance vs voltage plot for four different diameter nanowires at T=3 K. A gap voltage (V_G) for 30 nm diameter nanowire has been indicated by an arrow. V_G has been plotted as a function of inverse diameter (d) in the inset.

nanowires can only be explained by considering a "pinned" collective state[3] where the pinning strength increases with decreasing diameter. This is consistent with the fact that the observed voltage required for the switching transition also increases with decreasing diameter. In a previous study, the existence of a collective behavior was predicted in these nanowires as a non-Curie-type temperature dependence of the static dielectric constant[16] was observed. Here, dipoles (formed by a dopant counter ion) interact among each other via a Coulomb interaction and produce a collective pinning.[3] The observed characteristics of V_G here is consistent with the Wigner crystal formation, which is pinned by the impurity.[3,5,6]

Above the voltage V_G, I-V characteristics of all nanowires show a power-law behavior—a known characteristic of 1D conductors. In contrast to conventional three-dimensional (3D) materials, 1D conductors exhibit fascinating transport properties due to the power-law dependence of tunneling density of states, which can be parametrized as $dI/dV \propto T^{\alpha}$ and $\propto V^{\beta}$ for low bias ($V \ll k_B T/e$) and high bias ($V \gg k_B T/e$) conditions, respectively.[9] In Fig. 2(a) we have shown representative data that show an $R \propto T^{-\alpha}$ behavior. In this figure, we have also plotted the same data as $\log(R)$ vs $T^{-1/4}$ to show that variable range hopping (VRH) can also

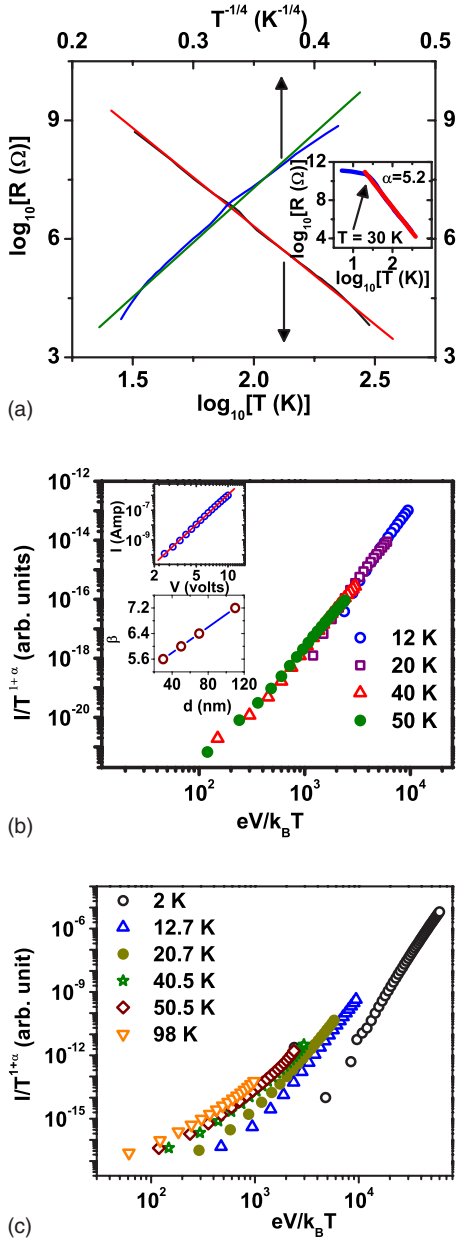

FIG. 2. (Color online) (a) Resistance (R) vs temperature (T) data for 50 nm diameter nanowire. The upper arrow indicates the plot of $\log_{10} R$ as a function of $T^{-1/4}$ and its linear fit. The lower arrow indicates a double-logarithmic plot of R as a function of T and its fit by a power law $R(T) \propto T^{-5.2}$. The power-law dependence of R-T data for 30 nm diameter nanowire has been shown in the inset. (b) $I/T^{1+\alpha}$ is plotted against eV/k_BT, where $\alpha=5.2$ for 30 nm nanowire for four different temperatures. I-V data for 30 nm diameter nanowire at $T=3$ K is plotted in a double logarithmic scale in the upper inset. The data are fitted (solid line) by the power law $I \propto V^{1+\beta}$, with $\beta=5.6$. The plot of β determined at $T=3$ K is shown as a function of diameter d in the lower inset (continuous lines are guides to the eye). (c) Plot of $I/T^{1+\alpha}$ vs eV/k_BT for 70 nm diameter nanowire that shows deviation from the LL theory.

give a reasonable fit. We found that for low bias data, VRH gives a better fit,[16] but power law gives a better fit for the data taken at a higher bias. This type of bias dependent R-T behavior has been discussed earlier in the context of "dirty" LL theory.[21] In the inset in Fig. 2(a), we have plotted resistivity data (measured with 1 V bias) against temperature in a log-log scale for a 30 nm diameter nanowire and have fitted it to show that power-law dependence ($R \propto T^{-\alpha}$, with $\alpha=5.2$) remains valid above 30 K. Due to the presence of V_G below 30 K, the resistance for this bias becomes nearly temperature independent, as observed in other polymer nanowires.[17] For a 30 nm diameter nanowire taking $\alpha=5.2$ and plotting $I/T^{1+\alpha}$ versus $eV/(k_BT)$, various I-V curves of different temperatures collapse on a master curve [Fig. 2(b)]. A clean LL state predicts $\alpha=\beta$ and scaling of I-V curves of different temperatures to such a master curve.[9,22] For a higher diameter nanowire, the scaling was not good, and one such representative data has been shown for 70 nm diameter nanowires in Fig. 2(c). The observed R-T behavior above ~30 K, its bias dependence, and the scaling behavior of different temperature I-V characteristics of various diameter nanowire suggest that the LL state can describe some features of the high temperature ($T>30$ K) electronic transport properties of the nanowires. The LL behavior has been observed previously in polymer nanofibers in the above temperature range with $\alpha \sim 2.2$–7.2 and $\beta \sim 2$–5.7.[17] A similar power-law behavior has been observed in other 1D systems such as carbon nanotubes ($\alpha, \beta \sim 0.36$) (Ref. 10) and nanowires of InSb ($\alpha \sim 2$–7, $\beta \sim 2$–6),[13] $NbSe_3$ ($\alpha \sim 1$–3, $\beta \sim 1.7$–2.7),[23] and MoSe ($\alpha \sim 0.6$–6.6, $\beta \sim 0.32$–4.9).[24]

At low temperature (<30 K), for almost all of the nanowires, the I-V characteristics of different temperatures could not be collapsed to a single master curve. From the I-V data, we get $\beta=5.6$ at $T=3$ K for a 30 nm diameter nanowire [refer to the upper inset in Fig. 2(b)], and for other diameter nanowires, this value goes up to 7.2 at 3 K [refer to the lower inset in Fig. 2(b)]. The α value obtained from the high temperature (>30 K) and/or high bias R-T data is not equal to β in general[25] for most of the nanowires at low temperatures. The β values were found to decrease with increasing temperature. For a quasi-1D system, the LL theory predicts a decrease of β with increasing diameter, but our experimental results show an increasing β value with increasing diameter [refer to the lower inset in Fig. 2(b)] at a low temperature (3 K). The presence of V_G, absence of a single master curve, and unequal exponents α and β in these wires show that the LL theory is not applicable in describing the electronic properties of these nanowires in the low temperature regime. Below, we will show that the Wigner crystal state, which shows the characteristics of the charge density wave, can satisfactorily explain the low temperature experimental observations.

For a quasi-1D system, the strength of, Coulomb correlation is defined as $r_s=a/(2a_B)$, where a is the average distance between electrons and a_B is the effective Bohr radius. Low doped polymer nanowires with a quasi-1D nature and low electron density ($r_s \gg 1$) are potential candidates to form a Wigner crystal that can exhibit characteristics of a charge density wave state.[2,3,14,17,26] For weakly pinned Wigner crystals, tunneling density of states shows a power-law behavior with the applied bias,[27] and the exponent ranges from ~3 to 6.[28,29] It has been shown[28] that for 1DWC with increasing pinning strength, β should decrease. The variation of V_G

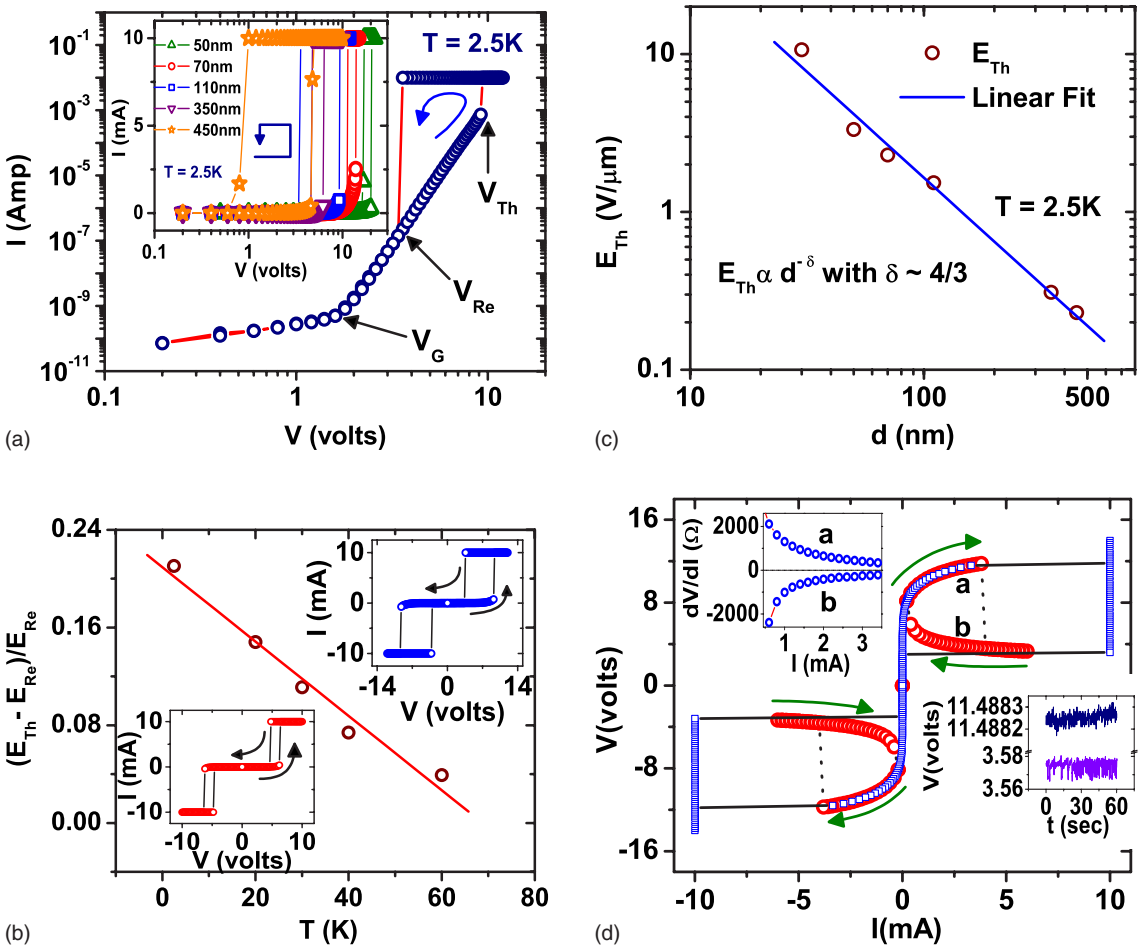

FIG. 3. (Color online) (a) Voltage biased I-V characteristics of 110 nm diameter nanowire at T=2.5 K, showing the gap and switching transition, the same for various diameter nanowires shown in the inset. (b) Hysteresis $(E_{th}-E_{Re})/E_{Re}$ is plotted against temperature for 70 nm diameter nanowire. Upper and lower insets show voltage driven I-V characteristics of 110 and 350 nm diameter nanowires, respectively, at 2.5 K; arrows indicate the direction of voltage scan. (c) Threshold field (E_{th}) is plotted as a function of diameter (symbol) for various nanowires at 2.5 K. The data are fitted (solid line) by the power law $E_{th} \propto d^{-\delta}$ with $\delta \sim 4/3$. (d) A comparison between voltage biased (square) and current biased (circle) I-V measurements of 450 nm diameter nanowire at 1.7 K (arrows indicate the direction of scan). In the lower inset, fluctuations in the voltage have been shown for 3 mA (upper curve) and 4 mA (lower curve) bias currents (note the different scales used). The upper inset shows NDR in the switched state [indicated by (b)].

with d [refer to the inset in Fig. 1(b)] clearly indicates that pinning strength increases[19] with decreasing diameter. Hence, our observation of the reduction in β value with decreasing diameter of nanowires is consistent with the 1DWC model. Moreover, higher values of the exponents observed here also indicate that 1DWC has been formed in our nanowires.

At low temperatures, all the nanowires show a switching transition to a highly conducting state above a certain threshold voltage $V_{th}(>V_G)$. For a fixed temperature, we did not observe any switching transition when the bias voltage is kept ~1 mV below V_{th} for a long time. The sharp threshold indicates a collective phenomena,[30–32] and the transition is not due to field heating. In Fig. 3(a) and in its inset, we have shown representative switching transitions for the nanowires measured at 2.5 K. All the nanowires showed hysteresis in the switching transition, which is independent of the bias scan speed (thus removing any possibility of a capacitive effect). The nanowires could switch back to the low conducting state only when the applied voltage is reduced to a value V_{Re} $(|V_{th}|>|V_{Re}|>|V_G|)$. With decreasing temperature, the hysteresis, defined as $(E_{th}-E_{Re})/E_{Re}$ (E_{Re} is the field corresponding to V_{Re}), increases [refer to Fig. 3(b)]—this behavior is consistent with that observed in switching CDW.[30–33] It has been shown theoretically that the formation of 1DWC is equivalent to having $4k_F$ CDW in a system.[2,3] The sliding state of this pinned CDW can explain the field induced switching transition observed here. The presence of V_G and V_{th} is also consistent with two thresholds observed in semiconducting CDW systems.[33]

Depending on the pinning strength, a pinned CDW become nonconducting below a certain threshold field. When an applied dc field is strong enough to overcome the pinning energy, the CDW depins and a sliding motion starts to give rise to a switching transition.[30–33] When the CDW is confined in two directions as in the nanowires, phase deformations occur along the length of the nanowires. In this situation, pinning of CDW is one dimensional and the threshold field is

expected to be proportional to $d^{-4/3}$.[34] The plot of E_{th} vs d shown in Fig. 3(c) confirms this dependence in our nanowires. The change in E_{th} with d is obviously not due to surface pinning as that would have given us $E_{th} \propto d^{-1}$. It has been also observed previously in a study of $NbSe_3$ samples that surface pinning can be excluded for highly resistive samples $(R/L > 1\ \Omega/\mu\text{m})$.[34] We measured current-driven I-V characteristics to investigate the nature of a switched state in these nanowires. The measurements [Fig. 3(d) and its upper inset] exhibit a NDR. This type of behavior has been observed in a sliding CDW state[33,35] and is expected in 1DWC. The comparison between voltage driven and current-driven I-V characteristics has been shown in Fig. 3(d), and this shows the uniqueness of the threshold field for both types of measurements. We have also observed a large fluctuation in the measured voltage in the switched state [refer to the lower inset in Fig. 3(d)], which gives a strong evidence of sliding motion above E_{th};[33] a similar increase in noise has been observed previously in a two-dimensional Wigner crystal.[4]

IV. CONCLUSION

The results presented here show that the I-V characteristics of all the nanowires have three distinct regions [refer to Fig. 3(a)]. Below V_G, current is very small and that increases with temperature and diameter. Between V_G and V_{th}, power-law characteristics of a 1D transport is observed. Above V_{th}, a switching transition is observed which exhibits hysteresis, $d^{-4/3}$ scaling, NDR, and noise enhancement. All these findings confirm the formation of 1DWC, which is expected to exhibit characteristics of CDW, in our nanowire. Although power-law-dependent I-V characteristics can be explained by other models such as the Lüttinger liquid[9] and environmental Coulomb blockade (ECB),[36] these theories cannot explain the observed switching transition and related phenomena reported here. Moreover, the LL theory is clearly inconsistent with observed V_G and the reduction of β with decreasing diameter [refer to the inset in Fig. 2(b)] observed at low temperatures. In addition, we could not get an expected collapse to a master curve[22] for higher diameter nanowires. The ECB theory can account for V_G, but it predicts an increase in β with increasing environmental impedance. In our case though, the resistance of the nanowires decreases with increasing diameter and β increases. In conclusion, all our experimental findings show that a one-dimensional Wigner crystal has been formed at low temperatures in nanowires of a structurally disordered material such as a conducting polymer.

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