Atomic chain of carbon atoms: Smallest negative differential resistance device

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Abstract. In the present work, we report giant negative differential resistance action in probably the simplest molecular nanoelectronic device comprising of carbon chain placed between two ferromagnetic electrodes named as graphitic carbon nitride (g-C_{3}N_{4}). The negative differential resistance action is spin polarized and only evident at spin down channel. Spin polarized quantum transport studies using Keldysh non-equilibrium Green's function based density functional theory reports very high negative differential resistance over the bias range of ±0.1 V to ±0.3 V. This symmetric negative differential resistance feature has been explained by an analysis of transmission spectrum across the Fermi energy level and Molecular Projected Self-Consistent Hamiltonian states (MPSH) of the system. Role of in-phase and out of phase electron waves in ensuring negative differential resistance feature has been justified through transmission pathways of the system. The simplicity of the molecular system added with robust spin polarized negative differential action added with experimental relevance certainly establishes the uniqueness of the device in respect of modern spintronic research.
1. Introduction

In 1988, after discovery of Giant Magnetoresistance, finding Spintronic devices were started which has become one of the main focuses for the research community because of its high data storage capacity and high-speed data processing [1]. It has combination of three carriers: electronic charge, electronic spin and photon. Besides that, by connecting spin with optics via photon helicity data can be transferred faster which is main requirement for field in Information technology. In the meantime, in the field of spintronic device various electronic transport properties have been originated, including spin filtering action, rectifying action, spin switching effect, negative differential resistance (NDR), magnetoresistance effect [2-6]. Among these various properties NDR behaviours has engrossed attention because its various applications for enhancing the performance of electronic devices.

Saving electricity and thereby reducing power consumption is one of the main focus for the modern research world and to give success to this mission scientists are giving their unsurpassed exertions. In this situation memory device with less power consumption increases demand of those materials showing NDR properties. NDR behaviour can be described as one where with increasing voltage, current decreases, not following ohmic behaviour. This NDR behaviour has been conveyed in a number of literatures. Negative Differential Resistance (NDR) was reported by Guo and their co-workers where doping concentration and edge passivation was changing in doped APNRs devices[7]. Ocal et al. observed NDR behaviour in similar molecules with dissimilar redox performance[8]. Shan et al. also reported NDR action in crossed graphene nanoribbons in a certain bias range[9]. Recently, Carmel et al. illustrates NDR properties in a heavy doping 8APNRs device by either P-type or N-type atoms [10]. Also, Sen et al. in [11-13] a sequence of articles reported NDR behaviour on trimer unit of cis-polyacetylene, fused furan and fused thiophene bi calculating electronic transport properties using nonequilibrium Green’s function (NEGF) method.

Through covalent bonding carbon atoms form a long chain i.e. a carbon family whose chemical as well as theoretical properties were well examined by various experimental and theoretical studies [14]. In 2004, graphene was recognized as one of the most significant carbon allotropes due to its high electron mobility and thermal conductivity [15]. Recently Liu et al. reported NDR behaviour in Carbon chain-based spintronic devices using Keldysh non-equilibrium Green's function methods[16]. Some experimental observation also has been noted e.g. Jin et al. reported that using the electron irradiation in a high-resolution transmission electron microscope a stable carbon atomic chain (CAC) can be possible to achieve from graphene[17]. Lin et al. [18] investigated NDR effect in 1, 4-dibenzyl C_60 and zinc phthalocyanine doped polystyrene amalgam material.

Recently, graphene-based nanomaterial has attracted huge attention due to its potential application in nano electronic device. Husain and their co-workers[19] investigated linear mono atomic carbon chain between zigzag-armchair-zigzag (zz-ac-zz) graphene nanoribbons (GNRs) with multi NDR peaks. Safaeiet al. [20] reported photoelectrochemical water splitting, other emerging applications of g-C_3N_4 in solar cells, electrocatalysts and supercapacitors. Sen et al. [21] reported graphitic carbon nitride (g-C_3N_4) as a half metallic ferromagnet with one spin state in metallic nature and the other spin state in insulating nature with 2.7 eV band gap which consequently increases its potentiality in various application of nano device.

By getting inspiration from above studies here we have placed a carbon atomic chain (CAC) between two graphitic carbon nitride (g-C_3N_4) electrodes where CAC is quasi one-dimensional (1-D) acting as a tunnelling barrier between these two electrodes. Using non-equilibrium Green function’s (NEGF) method tied with density functional theory quantum spin transport characteristics has been calculated and corresponding current voltage characteristics shows NDR effect within a certain bias range -1.0 V to +1.0 V. Observed result has been explained by analysing Transmission spectra, Transmission pathways and MPSH states which establishes our anticipated device as a potential device for future application.
2. Computational Details

In this theoretical investigation the first step was to optimize unit cell of $g$-C$_4$N$_3$ with help of Gaussian16 suite of programme with hybrid B3LYP functional coupled with density functional theory [22,23]. Using that optimized unit cell two $g$-C$_4$N$_3$ electrodes were designed and a 1-D CAC was sandwiched between them and re-optimized the system using ATK2019.12 [24] program. All quantum transport calculations were done with the help of Perdew-Burke-Ernzerhof (PBE) [25] type GGA functional and DZP basis set; with core electrons labelled by norm-conserving Troullier–Martins pseudopotentials [26]. For self-consistent field (SCF) analysis 100 k points in the direction of transport were used with 150 Ry cut off energy. Current for Up spin and Down spin channel are estimated using Landuer and Büttiker formula [27-29] as given below:

$$I_{\sigma}(V) = \frac{e}{\hbar} \int_{\mu_L}^{\mu_R} T_{\sigma}(E, V_b) [f_L(E - \mu_L) - f_R(E - \mu_R)] dE \quad (1)$$

Here, $T_{\sigma}(E, V)$ signifies the spin-dependent transmission coefficient and $f_{L/(R)}$ denotes the Fermi function of the left and right electrode and can be represented as

$$f_{L/(R)}(E) = \frac{1}{1 + \exp((E - \mu_{L/(R)})/kT)}.$$

$\mu_{L/(R)}$, $k$ and $T$ have their conventional denotation as chemical potential of electrodes, Boltzmann constant and temperature, respectively. The chemical potential is further well defined as $\mu_{L/(R)} = E_F \pm eV/2$, where $E_F$ is the Fermi energy of the electrode(s).

3. Results and Discussions

An optimized structure of two probe system $g$-C$_4$N$_3$-CAC-$g$-C$_4$N$_3$ is represented by figure 1 where the electrodes are in ferromagnetic state which is more stable than the antiferromagnetic state, reported by Du et al. [29]. Now coupling between half metallic electrode and molecular system plays a decisive role in electron transport which is major part of a molecular device.
3.1 Current – Voltage (I-V) Characteristics: Negative differential resistance (NDR) action

In this present study we have observed current(I)-voltage(V) characteristics within a bias range from -1.0 V to +1.0 V, given by figure 2. The figure clearly illustrates that when voltage increases current also increases initially up to -0.1 V and +0.1 V for down spin channel. After that current decreases abruptly though voltage increases which is definition of NDR action. But no significant current can be observed for up spin channel. The figure shows two sharp NDR peaks at both positive bias (+0.1V) and negative bias (-0.1V) though the magnitude of peak at positive bias is less than the negative bias. The observed result has been further explained through transmission spectra.

3.2 Analysis of transmission spectrum at zero bias

To analyse the origin of NDR effect transmission spectra at ±0.1V have been observed which is shown by figure 3 which quite clearly portrays that at the Fermi level the value of transmission coefficient is quite higher at +0.1V than -0.1V for down spin channel. But no significant value can be observed for up spin channel. Therefore, the dominance of down spin channel over up spin channel and decrease of current with increasing voltage (NDR effect) is fully clarified by observed results of transmission spectrum.

Figure 2. Calculated current(I)-voltage(V) characteristics in 2D nanostructure of g-C₄N₃-CAC-g-C₄N₃

Figure 3. Transmission spectrum(a.u.) in 2D nanostructure of g-C₄N₃-CAC-g-C₄N₃ obtained at ±0.1V
3.3 Analysis of Transmission Pathways

In this study, the observed NDR effect has also been primarily explained by transmission pathways with pictographic representation which shows the influence of local bond to the net transmission coefficient. Also, how the current for both up and down spin channel is affected by quantum interference of electron, that is also possible to explain. Here figure 4 depicts transmission pathways for both up and down spin channel at ±0.1V. In this figure different arrows with different colour indicate different direction of current i.e., current at different phases. Three colours denote three phases: blue colour signifies zero phase, green colour signifies π/2 phase and red colour is for π phase. Now from the condition of constructive and destructive interference it can be clearly said that for zero phase constructive interference occurs and for π/2 and π phase destructive interference occurs. Now figure 4 clearly illustrates that negligible current is flowing in case of up spin channel whereas a significant number of blue arrows are present for down spin channel at both positive and negative bias. But interestingly the number of blue arrows in down spin channel is lesser at -0.1 V compared to +0.1 V, implies larger current for down spin channel at +0.1 V than -0.1 V which is in validation with figure 2.

![Transmission Pathways](image)

**Figure 4. Transmission pathways in 2D nanostructure of g-C₄N₃-CAC-g-C₄N₃ obtained at ±0.1V**

3.4 Analysis of Molecular Projected Self-Consistent Hamiltonian (MPSH)

Finally, to give the molecular level explanation we have examined molecular projected self-consistent Hamiltonian (MPSH) states of g-C₄N₃-CAC-g-C₄N₃ at representative finite bias ±0.1V which is shown in figure 5. Due to L-C-R interaction MPSH states formed and the specific matrix form for each eigen state called MPSH state is given as:

\[
\begin{bmatrix}
H_L + \Sigma_L & V_L & 0 \\
V_L^\dagger & H_C & V_R \\
0 & V_R^\dagger & H_R + \Sigma_R
\end{bmatrix}
\]

Where L, R and C signifies to left electrode, right electrode and central region of the two-probe system. Here, \(H_L, H_R\) and \(H_C\) are the Hamiltonian matrices in the left electrode (L), right electrode (R), contact region (C), respectively, and the interaction potentials between L-C and L-R regions are categorized by \(V_L\) and \(V_R\), respectively. A close inspection at figure 5 clearly manifest presence of no electron charge density over the molecules in up spin channel at±0.1V whereas electron charge density is delocalized over molecules and electrodes in down spin channel. But the delocalization is lesser at -0.1 V than at +0.1 V which provides larger current at +0.1V than -0.1V at down spin channel which at the end mollifies I-V characteristics in figure 2.
Fig. 5 MPSH states in 2D nanostructure of g-C4N3-CAC-g-C4N3 obtained at ±0.1V

4. Conclusions

To conclude, our quantum transport studies on g-C4N3-CAC-g-C4N3 quite clearly establishes tunnel barrier created by carbon atomic chain is sufficient to create smallest negative differential resistance devices with high degree of NDR action over the bias range of ±0.1V to ±0.3V. The NDR response is spin selective and makes the device unique in respect of spintronics applications as well as the smallest spin polarized NDR device. Observed, NDR action has been critically examined by a number of theoretical analyses and highly consistent over all types of analysis. The deep down transmission coefficients at spin down channel around 0.1 eV and its subsequent fall up to 0.3 eV is in corroboration with the observed result. Presence of transmission pathways in spin down channel and highly delocalized MPSH states in spin down channel provides sufficient explanation of the observed results. Finally, the spin polarized negative differential resistance makes the device potentially useful a source of pure spin current and if realized experimentally we believe it would open up new directions in spintronics research.

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