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## Spin Dependent Processes Measured without a Permanent Magnet

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### Abstract

We review here a novel Hall circuit design that can be incorporated into a working electrode that is used to probe spin-selective charge transfer and charge displacement processes. We describe the general design of a Hall circuit that is based on a semiconductor heterostructure, which forms a shallow two-dimensional electron gas and is used as an electrode. Three different types of spin selective processes have been studied with this device in the past: i) photoinduced charge exchange between quantum dots and the working electrode through chiral molecules. The charge transfer is associated with spin polarization that creates a local magnetization and generates a Hall voltage; ii) charge polarization of chiral molecules by an applied voltage is accompanied by a spin polarization that generates a Hall voltage; and iii) cyclic voltammetry (current-voltage) measurements of electrochemical redox reactions that can be spin-analyzed by the Hall circuit to provide a third dimension (spin) in addition to the well-known current and voltage dimensions. The three works reviewed open new doors into understanding both the spin current and the charge current in electronic materials and electrochemical processes.

Key words: chiral molecules, electron transfer, two dimensional electron gas, semiconductors

## 1. Introduction

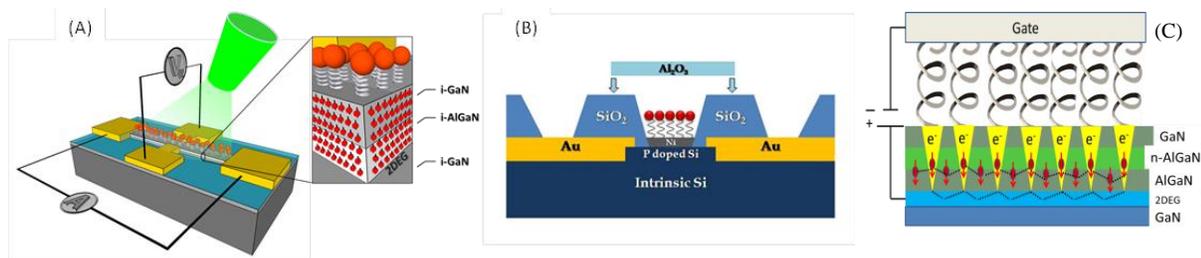
Electron spin plays a fundamentally important role in the structure and transformation of matter, despite the relatively small interaction energies associated with different orientations of an electron spin. The electron spin and Pauli exclusion constrain the electron wavefunction symmetry and profoundly affect the bonding in molecules and materials. Moreover, the effect of the electron spin on chemical transformations is well established,<sup>1,2</sup> particularly in photochemistry<sup>3</sup> and by various magnetic and electrochemical methods.<sup>4,5</sup> Electron spin has also been shown to be important in defining the final product distribution in multi-electron chemical reactions.<sup>6</sup> While X-ray,<sup>7,8</sup> optical<sup>9,10</sup> and electron spin resonance<sup>11,12</sup> are proven spectroscopic ways to probe spin degrees of freedom in molecules or materials, measuring spin currents in electronic materials is often difficult with these methods. Ferromagnets can be used as a spin analyzer;<sup>13</sup> however, it can be difficult to separate the spin effect from the effect of the magnetic field produced by the magnetic material. This issue is of special importance in electrochemistry where the effect of magnetic field of diffusion in electrochemical cells remains controversial.<sup>14,15</sup> Hence, it is understood by now that magnetic fields may have pronounced effect on electrochemical processes, independent from the spin related issues. Therefore, it is of important to develop methods which allows to monitor spin selectivity in chemical or physical processes without the present of magnetic field. Here we review recent works in which a Hall device and chiral molecules were applied for probing spin-selective processes and to induce local magnetization, eliminating the need for a ferromagnetic material. Unlike the spin Hall effect,<sup>16,17</sup> the Hall device provides a real Hall voltage which relates to the total spin polarization at the surface.

In recent years, a new aspect regarding the role of the electron spin in chemistry was found; and it is related to the spin-selective electron transport through chiral molecules, known as the chiral induced spin selectivity (CISS) effect.<sup>18,19</sup> As an electron moves, either ballistically or by tunneling, through chiral electrostatic potential of a molecule, an effective magnetic field is generated in the rest frame of the electron. This field can be viewed as resulting from the centripetal force acting on the electron in curved motion. The effective magnetic field acts on the electron spin.<sup>20</sup> The effect takes place as long for coherent transport, this means molecules of length of 1-2 nm. However, for longer molecules the electron transport is assumed to take place by multiple coherent steps, hence for each such step the CISS effect will be relevant, as indeed

observed in DNA.<sup>21</sup> The CISS effect is strong enough that helical molecules have been shown to act as highly efficient spin filters; i.e., transmitting one preferred spin direction with a selectivity of up to 60%. The selectivity is known to depend on the sign of the electric field acting across the molecule, on the chirality of the enantiomer being used as a spin filter, and on the direction of motion of the electron.<sup>21-25</sup> In addition to transmission through molecules, it was recently shown that charge reorganization within a chiral molecule is accompanied by an electron spin polarization.<sup>26</sup>

When electrical current flows in a material between two electrodes, a magnetic field applied perpendicular to the direction of current flow induces an electric potential that is perpendicular both to the current and the magnetic field directions. This long-known phenomenon is called the Hall effect,<sup>27</sup> and it has played important practical and fundamental roles in understanding the electronic properties of semiconductors.<sup>28,29</sup> Figure 1A shows a schematic diagram of a Hall circuit that is based on a semiconductor AlGaIn/GaN heterostructure, which forms a two-dimensional electron gas (2DEG) between the semiconductor layers. The structure is designed to produce a shallow 2DEG that is less than 30nm below the top surface; and it is in electrical contact with source and drain electrodes on each end, which defines the length of the source/drain current's channel. In addition, metal electrodes (Hall electrodes) are located on the other two sides of the source/drain current channel, allowing one to probe any induced voltage which may arise upon application of a magnetic field. This circuit is sensitive to magnetic field strengths as small as  $10^{-3}$  T and can be calibrated using a simple permanent magnet of known field strength. We have also made Hall probe circuits of this type using AlGaAs/GaAs heterostructures and with silicon material (see Figure 1B).

If a monolayer of chiral molecules are self-assembled on the surface of the device and an electrical potential is applied across the molecular layer (i.e., between the tail of the molecules and the 2DEG), then it generates a magnetization that acts on the source/drain current to generate a potential between the Hall electrodes, referred to as the Hall potential (Fig. 1C). The potential which acts across the molecules is applied either by photoexcitation of nanoparticles that are attached to the chiral molecules<sup>30</sup> or by placing the electrode into an electrochemical cell and applying a voltage across the monolayer film.<sup>26</sup> It is important to appreciate that the magnetization is due to the 2DEG mediated exchange interaction between the injected spins, as described in section 5.

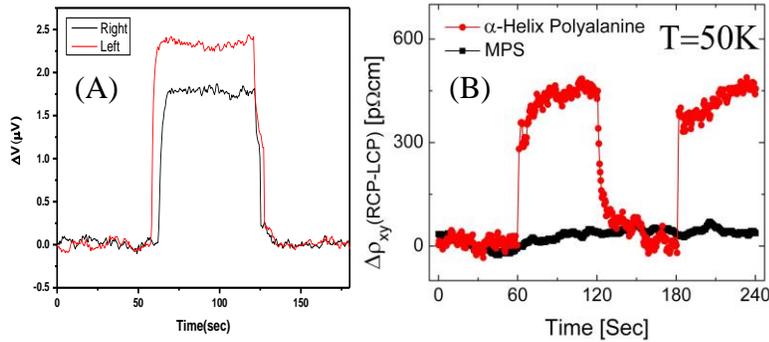


**Figure 1:** A) Schematic structure of a GaN-based Hall circuit. A two-dimensional electron gas is formed between the AlGaN layer and the GaN layer underneath it. Current flows between two electrodes and the Hall voltage is measured between the transverse set of electrodes. This image also shows nanoparticles (NPs) attached to the substrate through chiral molecules (shown as coils) adsorbed on top of the conductive channel. B) Schematic cross section of a Si-based Hall sensor. A thin (blue) *p*-doped Si layer located between two gold (yellow) electrodes. The thin Ni layer is represented in gray and the adsorbed chiral molecules with the InAs NP on top are shown in red. C) Illustration of our suggested model for the electronic states inside the GaN/AlGaN-chiral molecules hybrid device. Electronic states from the molecules hybridize with states in a narrow impurity band in the semiconductor indicated by the yellow triangle. As a consequence of the CISS effect, these states form effective Ising spins that interact through a ferromagnetic RKKY interaction mediated by the nearby 2DEG. The extent of hybridization depends on the potential applied on the molecules, either by electric field or by photoexcitation. Here it is represented as a “gate”. Figure 1A is adapted with permission.<sup>30</sup> Copyright 2016 Nature.

Below we describe three different studies: a light induced magnetization effect,<sup>30</sup> electric field-induced charge polarization accompanied by spin polarization,<sup>26</sup> and magnetless spin-dependent electrochemistry.<sup>31</sup>

## 2. Light-induced magnetization

Light can be used to generate a spin-polarized photopotential across a molecular film, and a magnetization which is generated by a spin-polarized charge distribution can be measured by using the Hall circuit shown in Fig. 1A. For these studies a self-assembled monolayer of SHCH<sub>2</sub>CH<sub>2</sub>CO- $\{Ala-Aib\}_5$ -COOH oligopeptides was adsorbed on the source/drain channel, via their COOH functional groups, and CdSe nanoparticles (NPs) were attached to the exposed end of the monolayer film, via their thiol groups. Upon excitation of the CdSe NPs with 514 nm light and 2.3 mW average power, a photopotential is generated between the outer NP layer and the substrate. Under steady-state illumination this photopotential is maintained through a balance of photogeneration, exchange, and recombination currents. By applying a constant current of 10  $\mu$ A in the source/drain channel of the Hall device, any imbalance in the spin population of electrons accumulated on the GaN surface can be sensed by measuring the Hall voltage between the electrodes that are located perpendicular to the source/drain channel. Figure 2 shows the Hall voltage signal that is measured at room temperature for CdSe NPs linked to the GaN device via chiral linkers.



**Figure 2:** (A) Hall voltage measurements at 300 K for CdSe NPs that are tethered to a GaN surface via an alpha-helical peptide, as shown in Fig. 1A. “Right” and “Left” refer to excitation with clockwise or counterclockwise circular polarized light. (B) Results obtained with the device shown in Fig. 1B. Absolute Hall response as a function of time is shown by subtracting the two circular polarizations. Subtracting the left-circular polarization from the right-circular polarization the Hall signal under illumination is compared to the dark signal. The red curve shows the Hall response using polyalanine to linked to the InAs nanoparticles while the black curve (MPS) shows the case of achiral linker molecules. Adapted with permission.<sup>30</sup> Copyright 2016 Nature.

The device presented in Fig 1A is unique because it allows, in principle, a high spin polarization without a significant charge polarization. Therefore, high magnetizations can be achieved by the accumulation of spins onto the device without encountering the difficulty of Coulomb repulsion, which arises when spin-polarizing a medium by injecting spin-polarized electrons. In this sense, the device is analogous to a spin-torque transfer device.<sup>32</sup> Using a calibration curve, we can estimate the effective magnetic field that would be required, for obtaining the same Hall voltage from an ordinary Hall measurement, to vary between several Gauss to almost 100 Gauss.

In a related experiment, a silicon based device (Fig. 1B) was used to demonstrate the creation of a local optical magnetization via the CISS effect.<sup>33</sup> In this experiment, L-polyalanine molecules as well achiral 3-mercaptopropyl-trimethoxysilane (MPS) molecules were used to link an InAs NP to the 5 nm thick Ni layer, which was selected to achieve maximal perpendicular magnetization – ultrathin Ni films break into domains that allow for perpendicular magnetization. The ambient temperature magnetization was evaluated by calculating the Hall coefficient knowing the Si channel density of charges and was estimated to be around 100G. All measurements were done at ambient conditions and room temperature.

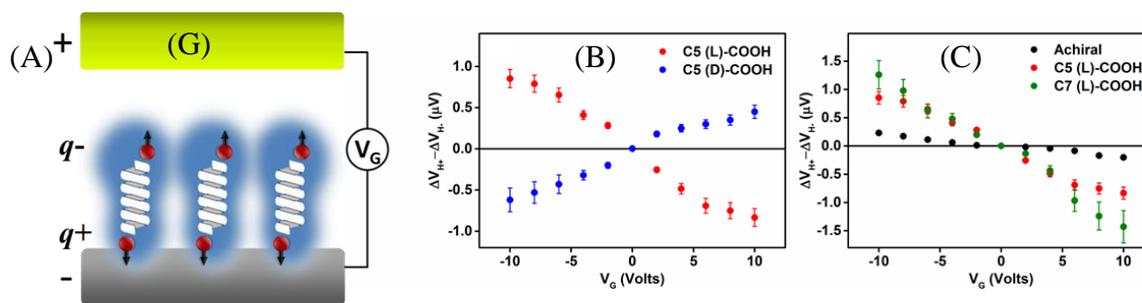
Figure 2B presents the absolute Hall response for excitation of InAs nanoparticles with two circular light polarizations, right circularly-polarized (RCP) and left circularly-polarized (LCP). Because the chiral linkers act as a spin filter, via the CISS effect, only one kind of spin is

accumulated on the surface of the sensor, creating an effective magnetic field that is measured by the Hall voltage it induces. A localized magnetization is evident for chiral molecules (red line), however no magnetization is measured for MPS achiral linker molecules (black line).

The experiments described above demonstrate that one can inject a spin into semiconductors or ferromagnets through chiral monomolecular films, without the need for a permanent magnetic layer; and the magnetization can be quantified via the Hall effect.

### 3. Electric field induced spin and charge polarization in chiral molecules

Noncovalent interactions between molecules are ubiquitous in Nature, and they necessarily involve charge redistribution of the molecular electron clouds. More specifically noncovalent interactions between chiral biomolecules can play a key role in many biological processes. The Hall probe method is sensitive enough to measure the spin polarization that accompanies charge redistribution in a monomolecular film of chiral molecules.<sup>26</sup> In this case, the electrode with an embedded Hall circuit was placed in an electrochemical cell and a voltage was applied between it and a counter/gate electrode (see Fig 5). This voltage generates an electric field across the molecular layer and causes their electron clouds to redistribute the charge. For a film of chiral molecules, this charging current is spin-polarized and a Hall voltage is generated between the transverse electrodes.



**Figure 3:** (A) The experimental setup in which a Hall device, coated with a self-assembled organic monolayer, is placed in solution with a counter (or gate) electrode and an inert electrolyte. When an electric potential  $V_G$  is applied between the gate electrode (G) and the device, the ionic solution is polarized so that an electric field acts on the adsorbed molecules. As a result, the molecules are polarized, due to charge reorganization (partial charges  $q+$  and  $q-$ ), and this induces a charge displacement in the surface region of the device. Because the charge polarization is accompanied by spin polarization (red balls with black arrows), a magnetic field is created that acts on the electrons flowing between the source and drain electrodes in the semiconductor device. The Hall potential  $V_H$ , which is formed as a result of the spin magnetization, can be measured as a function of  $V_G$ . When an electric field is applied on a chiral molecule ( $V_G$ ) it induces charge reorganization in the molecule, resulting in spin polarization. Gate voltage ( $V_G$ ) dependent Hall measurements conducted on devices coated with different oligopeptides. (B) When the adsorbed layer is either L-SHCH<sub>2</sub>CH<sub>2</sub>CO- $\{Ala-Aib\}_5$ -COOH (red) or D-SHCH<sub>2</sub>CH<sub>2</sub>CO- $\{Ala-Aib\}_5$ -COOH (blue). (C) The dependence of the Hall voltage on  $V_G$  is shown for monolayer films of achiral 11-mercapto-undecanoic acid (black), chiral L-SHCH<sub>2</sub>CH<sub>2</sub>CO- $\{Ala-Aib\}_5$ -COOH (red), and chiral L-SHCH<sub>2</sub>CH<sub>2</sub>CO- $\{Ala-Aib\}_7$ -COOH (green). Adapted with permission.<sup>26</sup> Copyright 2017, The National Academy of Sciences of the United States of America

To measure the spin polarization that accompanies the charge polarization in chiral molecules, a monomolecular film of the molecules was adsorbed onto the GaN surface of the Hall device/working electrode (see Fig. 3) and then the Hall device was placed into a buffered electrolyte solution. Upon application of a voltage between the working electrode and a counter-electrode (G), an electrostatic field is generated across the molecular film, inner part of an electrical double layer, and a charge polarization is induced. If this charge polarization is accompanied by spin polarization, then a Hall voltage develops. The electric field induced spin polarization was studied for two chiral L-oligopeptides of different length, a chiral D-oligopeptide, and an achiral molecule as a control.

#### **4. Magnetless spin-dependent electrochemistry**

The Hall device can also be used to monitor the spin-dependence of electrochemical processes. Electrodes coated with chiral molecules have been used in the past for enantioselective electrochemistry studies, mainly aimed at developing enantioselective electrochemical sensors.<sup>34-39</sup> The enantioselectivity of chiral electrodes has been assumed to arise from stereospecific interactions of a chiral film coating<sup>40</sup> on the electrode's surface with the two enantiomers of a chiral molecule in the solution. This assumption is almost certainly true when one observes both redox potential shifts and changes in the faradaic current; however, one can also observe changes in the faradaic current without a redox potential shift. In this latter situation, the enantioselectivity could involve an electronic term that relates to the electrons' correlation energy; hence, it is affected by the electrons' spin.<sup>41</sup>

By using a working electrode that possesses an embedded Hall probe, one can perform “three-dimensional (3D) spin-electrochemistry”;<sup>31</sup> monitoring the charge current, the voltage, and the spin polarization current simultaneously, *in operando*. The Hall device is similar to the one described in Figure 1; however, it now serves two purposes: it is the working electrode as in a conventional electrochemical cell and, simultaneously, it measures the spin polarization of the current. A cyclic voltammetry measurement can be conducted by varying the voltage between the GaN working electrode and a counter electrode, and the Hall potential can be monitored by the embedded circuit. The Hall potential originates from the spin-polarized electron current that flows into (or out from) the GaN layer in a spin-selective faradaic process.

This experimental method eliminates the need to use magnetic electrodes or apply a magnetic field for studying the spin-dependent effects in electrochemistry. This is beneficial as external magnetic fields can introduce various effects that may influence the electrochemical process, even if there is no spin-dependent reaction.<sup>42-46</sup> In addition, it directly correlates the electrochemical process at various potentials and the spin selectivity as expressed by the magnitude of the Hall potential.

## **5. How the Hall device detects the spins?**

Based on time dependent Hall signal studies, on microwave absorption studied, and magnetic measurements performed using superconducting quantum interference device (SQUID), we concluded that when spin polarized electrons are injected into III-V heterostructures (like AlGn/GaN or AlGaAs/GaAs) that contain two dimensional electron gas (2DEG) layer, the semiconductor becomes ferromagnetic. Namely it gets magnetized, even at room temperature, with magnetization direction that depends on the direction of the polarization of the injected spins.<sup>47</sup> Figure 1C presents schematically the proposed mechanism. When the concentration of the injected spins is high enough, a strong exchange interaction due to 2DEG and via the RKKY mechanism<sup>48,49,50</sup> induces a magnetic state that survives as long as the spin concentration is high. The magnetization is therefore enhanced by the 2DEG. Indeed when structures that not contain 2DEG were studied no significant magnetic field could be measured. Hence it is important to appreciate that the measured magnetization is not simply due to the spin polarization, but it results from the injection of spin polarized electrons in the proximity of the 2DEG.

## **6. Conclusions**

The electron's spin attracts much attention recently because of possible applications in the field of spintronics.<sup>20</sup> However, the electron's spin is essential for the existing of matter. While classical electrostatics forbid the formation of a stable system in which two electrons are located in the same volume, this becomes possible by the correlation term introduced by quantum mechanics. Namely, two electrons can occupy the same orbital if they have the opposite spins.<sup>51</sup> This is indeed what requires for the formation of chemical bond. Hence, formation of bonds and selectivity in chemistry can be controlled by controlling the spins of the electrons that are involved in the bond formation.<sup>1,52</sup> Studying spin dependent processes in Chemistry involves usually the application of either quite sophisticated optical methods, with typically low sensitivity, or magnetic fields. When one applies magnetic fields, they may create various

unwanted effects, especially when electron transfer processes are involved, since the magnetic field can interact with the electrons. Hence performing spin dependent studies without magnetic field or without optical elements is highly desirable. This review described several studies in which spin selective processes were monitored by using a modified working electrode that has an embedded Hall circuit; thus, it was not necessary to use a permanent magnetic layer or an external magnetic field. The spin polarized electron current was generated by the CISS effect, as electrons are passed through chiral molecules or reorganize within a chiral molecule. Hence the methodology allows one to perform spin-dependent electrochemical redox reactions without the need to apply magnetic field, reducing the possibility for additional artefacts. The method describes can also be applied for producing magnetic fields at sub-micron dimensions, where today very large magnets have to be used. Finally, it allows also to perform relatively fast switching of magnetic field, at least at MHz frequency and perhaps even faster. All this can be done at room temperature, either in ambient or in solutions. Therefore the methods described provide new tools for studying spin dependent processes both in Chemical and Biology related applications.

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TOC:

