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Photocurrent enhancement and magnetoresistance in indium phosphide single nanowire by zinc doping

Fernando Maia de Oliveira[1], Ivani Meneses Costa[2], Edson Rafael Cardozo de Oliveira[1], Adenilson José Chiquito[2], Gilmar Eugenio Marques[1] and Marcio Daldin Teodoro[1]

[1] Semiconductor Nanostructures Group, Physics Department, Federal University of São Carlos (UFSCar), CEP 13565-905, CP 676, São Carlos, São Paulo, Brazil

[2] Laboratory of Electronic Transport in Nanostructures (NanO LaB), Physics Department, Federal University of São Carlos (UFSCar), CEP 13565-905, CP 676, São Carlos, São Paulo, Brazil

E-mail: mdaldin@df.ufscar.br

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Abstract

We report the fabrication of intrinsic and Zn-doped InP single nanowire devices by the vapor–liquid–solid and photolithography techniques. Nanowires with a zincblend structure around 100 nm in radius and length at the micrometer scale were readily observed. Electrical measurements of samples containing single nanowires revealed Ohmic and Schottky behavior for the intrinsic and Zn-doped InP devices respectively. The Zn-doped InP device exhibited a thermal and optical dependence with high photosensitivity, whose main conduction mechanism for temperatures ranging from 160 K to 300 K was verified to be variable range hopping, displaying a hopping distance on the order of 240 nm at a low temperature. Strong temperature-dependent positive magnetoresistance was verified for this device.

Keywords: semiconductor, device, nanostructure, nanowire, InP

(Some figures may appear in colour only in the online journal)

1. Introduction

Semiconductor materials have been widely employed in high-efficiency photosensitive systems, mainly as thin films, substrates or nanowires [1]. Most of them are composed of alloys produced by elements of the groups $III-V$, such as indium phosphide (InP), whose inherent presence of a direct bandgap (1.34 eV at 300 K) in the visible–near-infrared (vis–NIR) range guarantees its sensitivity to electronic excitations in the visible range of solar radiation [2]. Allied to the great values of surface-to-volume ratio at the nanometer scale, these remarkable tools are currently being investigated for employment as a new generation of photo-electronic devices [1–5].

In this regard, InP nanowires have been demonstrated to be a class of very promising key materials to be used in photovoltaic systems due to their high photosensitivity [2, 5]. Studies on devices built from semiconductor nanowires and ferromagnetic contacts have demonstrated that both spin and charge can be explored in order to get spintronic functionalities [6]. In addition, the functional features of such nanomaterials can be improved by doping processes, leading to a large number of effects that can be investigated in the scope of electron transport phenomena. Zinc (Zn) has been successfully employed as a natural acceptor impurity for $p-\mathrm{InP}$ doping [7]. In a neutral state, the three deepest electronic levels of Zn atoms are completely filled by electrons, leading the incomplete last fourth level to hold two valence electrons [7]. Furthermore, as with every transition metal, its *d* sublevel undergoes volume shrinkage due to its high occupancy potential, drawing such orbitals nearer to the nucleus. Such aspects promote an electrosphere shielding effect, favoring the loss of two fewer energetic electrons of the outer 4*s* orbital, stabilizing as the cation Zn^{2+}, whose highest energetic sublevel is totally filled by electrons [8]. This process leads to a covalent radius shrinkage, increasing the atomic effective carrier density. Therefore, Zn^{2+} ions act like positive carrier centers of high receptivity, showing electronic acceptor behavior [8]. Zn atom incorporation into crystalline InP occurs through successful interactions between this metal and P atoms. Such interactions lead to covalent bonds that are not totally completed per P atom, and formerly intended to be joined with In atoms generating one pair of holes per acceptor center. The settled substitutions promote $sp^3 - d$ interactions, between localized electrons from the 3*d* metallic orbitals of Zn atoms and holes from the hybrid sp^3 semiconductor orbitals. Such interactions have been reported with great relevance for the role of magnetic characteristics that well up in $III-V$-doped semiconductor nanomaterials [9, 10]. In addition, the reduced nanowire scale leads to an increase of the intensity of the inelastic scattering interactions of electronic carriers, usually related to weak electron localization at low temperatures. Such events promote resistance enhancement, which is visually notable in electric transport measurements under an applied magnetic field [11].

This work describes the preparation of Zn-doped InP single nanowire devices and presents the effects of the temperature and magnetic field to the electrical and optical properties of these devices.

2. Experimental

Pure and Zn-doped InP nanowires were synthesized by the vapor–liquid–solid crystal growth technique, using a three-zone tubular oven at 460 °C, under a He/H_2 (90% helium/10% hydrogen) continuum flux of 30 sccm, at 500 mTorr. In this method, gold seeds in the liquid-phase are the catalysts of the growth process, acting as preferential sites for the adsorption of the vapor-phase and determining the nanowire dimensions. For Au catalyst fabrication, a 2 nm thick gold layer was evaporated onto quartz substrates and annealed at 600 °C, at a pressure of 10 mbar. Then, the InP powder was vaporized by heating it up to 700 °C for 60 min, under a He/H_2 flux of 20 sccm, while the substrates were kept at the growth temperature by the furnace. When the growth process was completed, the precursor heater was turned off, but the gas flux was maintained until the temperature decreased to 100 °C in order to avoid oxidation. Single nanowires were collected from the grown film and deposited over Au/Ti electric contact patterns previously defined by conventional lithography on Si/SiO_2 substrates.

Electrical measurements were performed in order to evaluate the mechanisms underlying the transport properties. For this task, devices were also investigated using light excitation at different power levels as well as magnetic fields in a wide range of temperatures. Each device was electrically connected on top of the $x-y-z$ piezoelectric stages, allowing controllable movement with nanometer precision. The laser beam was focused onto a spot approximately 600 nm in diameter. This system is part of a confocal microscope (Attocube CFMI), whose inspection unit of 50 μm of the field of view allows the laser to be focused right on top of a single nanowire

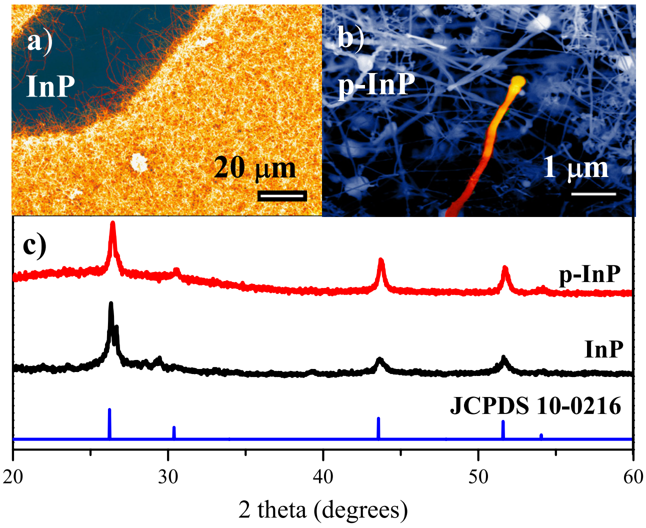

Figure 1. Scanning electron microscopy images of the thin film compound with (a) intrinsic InP and (b) Zn-doped InP, as well as the respective diffractograms (c) in agreement with the standard pattern (JCPDS $10-0216$).

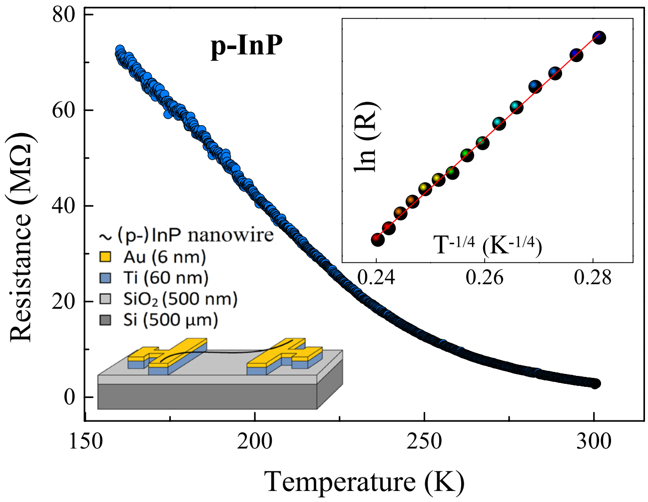

Figure 2. The thermal behavior of electric resistance for a device composed of a single $p-$type InP nanowire in room illumination. A scheme of the device is also depicted.

nanostructure (see inset of figure 5). The microscope was loaded inside a *He* closed cycle cryostat with a superconductor solenoid (Attocube Attodry1000/9T), operating in the range of 4 K to 300 K with the application of a magnetic field in a Faraday geometry. Electrical measurements were performed using a high resistance electrometer (Keithley 6517).

3. Results

After the cooling time, the substrates were covered by a yellow-brown film of nanowires ($50-200$ nm wide and tens of microns long) and microwires (200 nm–40 μm wide and hundreds of microns in length) as observed in figures 1(a) and (b). The grown intrinsic InP and Zn-doped InP were analyzed by scanning electron microscopy (JEOL 6510) as depicted in figures 1(a) and (b). Nanowires around 100 nm

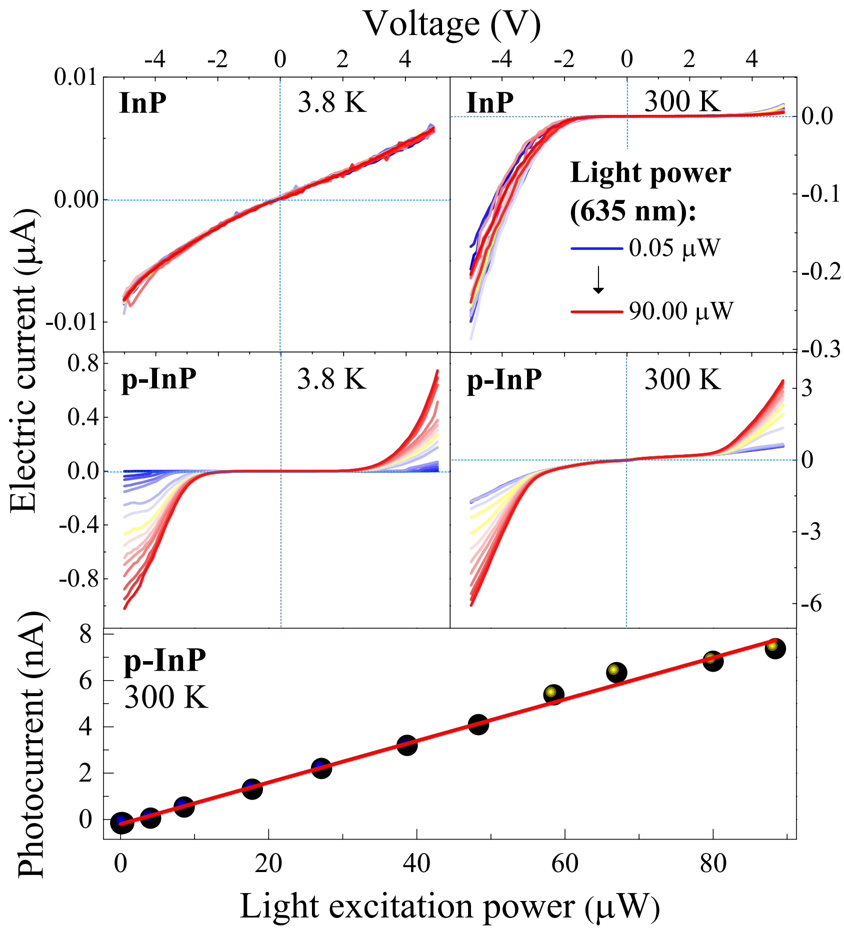

Figure 3. Top panels: the light power dependency of the electric current generated in single nanowire devices of intrinsic InP and Zn-doped InP, at 3.8 K and 300 K. Bottom panel: the photocurrent for a Zn-doped InP single nanowire device at 300 K with no voltage applied for different values of incident light power.

in radius and length at the micrometer scale were readily observed. The crystalline structure was analyzed by x-ray diffraction (Shimadzu, XRD 6100, 40 kV, 30 mA, Cu $K\alpha$ radiation). XRD patterns for different samples (intrinsic InP and Zn-doped InP) are shown in figure 1(c). The diffraction peaks were indexed as a zincblend structure of InP according to the $F{-}43m$ spatial group (JCPDS 10 − 0216) [12].

Typical temperature-dependent semiconductor resistance behavior was observed in our devices, as presented in figure 2: the resistance exponentially decreases as the temperature increases. The observed curve does not follow the simple thermal excitation law for a semiconductor, requiring a more detailed investigation to determine the dominant carrier transport process. Even when nanowires exhibit a crystalline core, any considerable degree of disorder can lead to the localized behavior of carriers, especially near the surfaces [13]. Surface states are well known sources of disorder, randomizing the electron potential inducing localized states at the surface. By taking into account these considerations, the usual thermally excited transport mechanism observed in semiconductor crystals should be replaced by a more complex one, such as variable range hopping (VRH), originally due to Mott and described as [14]

$$R(T) = R_0 \exp\left[\left(\frac{T_0}{T}\right)^p\right], \qquad (1)$$

where R_0 and T_0 are constants and the exponent p is set to 1/4, 1/3 or 1/2 according to the dimensionality of the samples [14]. The fitting of equation (1) to the experimental data leads to a p-value of 1/4 with $R^2 = 0.9976$, which corresponds to a three-dimensional structure [15]. The good agreement between the experimental data and the theoretical values for temperatures ranging from 160 K to 300 K is clearly seen in the inset of figure 2. Considering the density of states at the Fermi level for a three-dimensional material, the calculated hopping distance obtained from the fitting for this temperature range is roughly linear (from 240 nm to 200 nm) and inversely correlated with the temperature. For the p−type InP device, the hopping conduction is related to the hole jumping from occupied acceptor sites to the available empty ones [14]. Previous studies have established the existence of suitable ranges of temperatures that can be employed to measure the electric response of single nanowire devices [15]. Our measurements on the p − InP single nanowire device indicate that the range between 160 K and 300 K was appropriate for defining a model based on the variable range hopping transport of holes. Below 160 K, the sample's response is negligible and above 300 K the effect of thermal excitation becomes predominant [14, 15].

Due to the extremely low values of electric current observed in the complete absence of light for both intrinsic

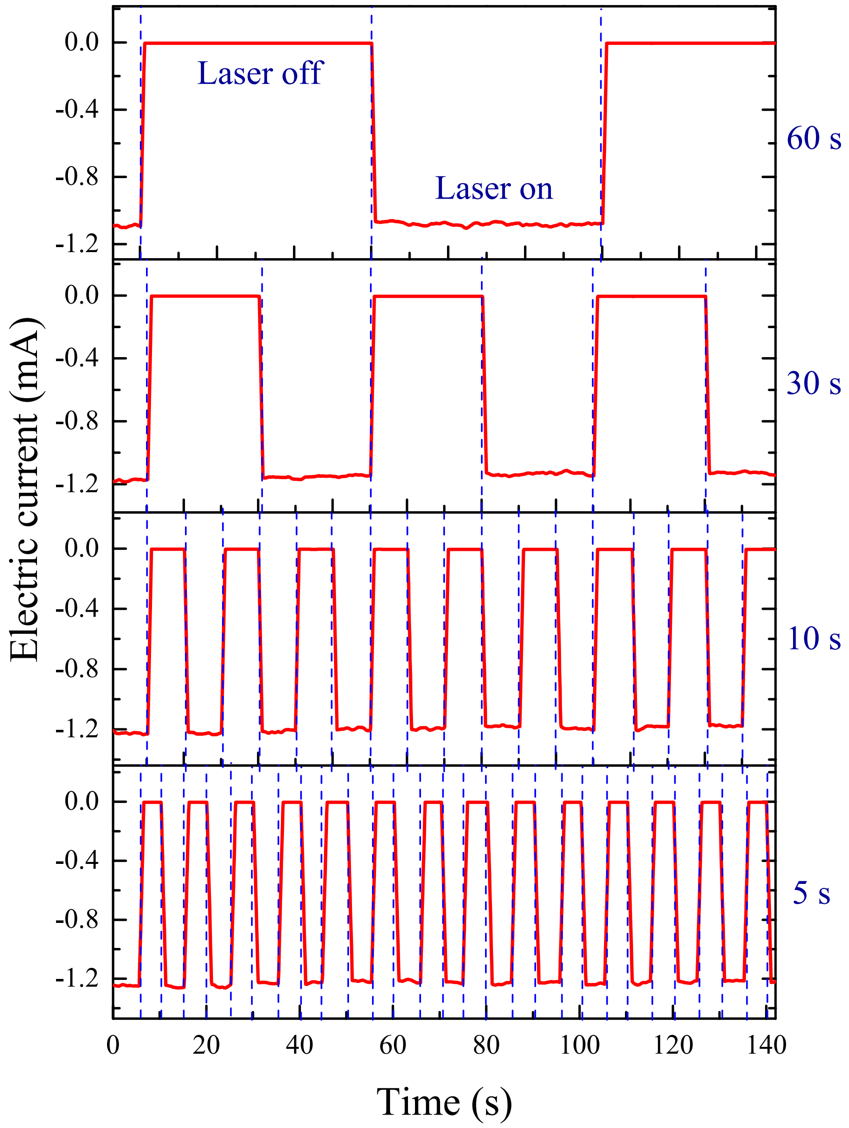

Figure 4. Time-resolved photocurrent for a single $p-$type InP nanowire device at 300 K and different periods of 660 nm light exposition with 67 mW of constant power.

and Zn-doped InP single nanowire devices, all the electric data acquisition was performed under controlled light illumination. In order to evaluate the effects of monochromatic excitation on the transport of carriers in single nanowires (intrinsic InP and Zn-doped InP), electrical measurements were performed under different conditions of light excitation at low (3.8 K) and room (300 K) temperatures, using a laser of 635 nm (1.95 eV). The current–voltage curves observed in figure 3 were obtained for different conditions of light power, ranging from approximately 0.05 μW to 90.00 μW. An Ohmic response was readily observed for the undoped InP device, mainly at low temperatures for all the used light power values. Schottky behavior that is sensitive to light power was verified for the Zn-doped InP device. In this case, two Schottky barriers were perceived for both low and room temperatures; thus the conventional thermionic emission model for Schottky barriers [14] cannot be applied, and a more general analysis based on a back-to-back Schottky model should be used [16]. There are different factors that affect the design of nanostructure-based devices, from structural defects in the nanostructure arising from the growth process itself to those related to the definition of the electrical contacts. The metal–semiconductor interface depends on different factors, such as the structural characteristics of the nanowire surface, the density of the interface states which pin the Fermi level at the surface, as well as the density of impurities at the surface region. These factors lead nanowire devices to show different electric behavior, which varies from Ohmic (the symmetrical linear variation of the electric current according to the applied voltage) to Schottky (asymmetry and no linearity) [16–18].

Linearly dependent behavior between light power and the photogenerated current was verified in the $p-$type InP nanowire device. The results are depicted in figure 3, under different levels of light intensity at 300 K and in the absence of applied voltages. The dependence between excitation power and the resulting photocurrent is associated with the mechanisms that configure the electron–hole pair life cycle [14]. Under very low values of excitation power,

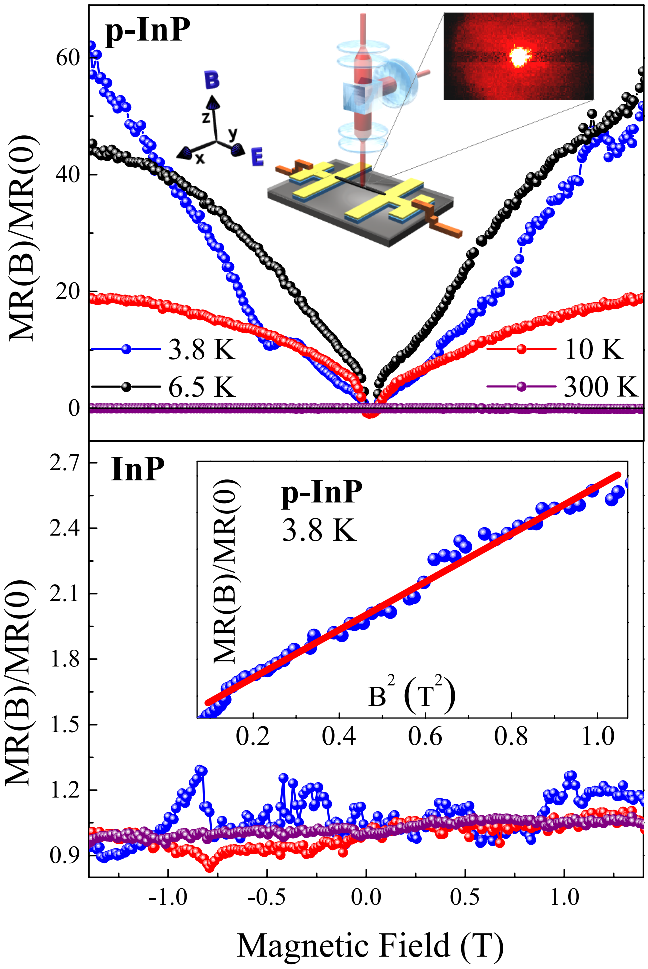

Figure 5. The thermal dependency of transversal magnetoresistance in both intrinsic and Zn-doped InP single nanowire devices, for several magnetic field intensities under 1 μW of 635 nm illumination. The inset at the top represents a simple magnetic measurement setup scheme.

linear behavior is promoted due to the process of pair generation after the absorption of a single photon per generation-recombination cycle. In contrast, in systems where effective electronic excitation is constrained to a metastable intermediate step, with two photons needed per excitonic life cycle, the dependence assumes quadratic behavior. In the case of the $p-$type InP device, linear behavior with $R^2 = 0.9949$ verified in the absence of external fields suggests direct excitation according to the one-photon mechanism [19]. To investigate the stability associated with the photosensitivity of the $p-$type InP nanowire device, time-resolved electrical measurements were performed under visible light excitation. The measurements were accomplished at room temperature applying a 660 nm (1.88 eV) laser operating at a constant power of 67 mW. The incidence of light in the Schottky contacts promotes the generation of photo-induced free carriers that contribute favorably to the conduction in the device, if the photon energy overcomes the Schottky barrier present at the metal–semiconductor interface. This energetic obstacle is related to the metal work function and the semiconductor band gap, as well as the characteristics of the device development [3, 20]. The results for different periods of light exposition are presented in figure 4. A fast response of approximately 1.14 mA s^{-1} of dark-to-photocurrent switching was verified for all the applied times of light exposition. The same result was observed in photo-to-dark current switching, suggesting the absence of distinct intermediate transitions. The device photocurrent reached values of around 1.2 mA representing a maximum external quantum efficiency of approximately 3.4%, defined as the ratio between the number of detected carriers to incident photons. Ratio values in the range of 0.1%–10% are expected in nanowire-based systems due to their high surface-to-volume ratio, which is directly correlated with the probability of nonradiative recombination by surface states [21, 22]. Several factors contribute to the delineation of the photocurrent response of a device, such as carrier concentration, doping level and the effects of external fields. In particular, magnetic field effects are reported to modify the intensity of a photocurrent even in nonmagnetic materials, due to events such as spin–orbit coupling, localized states from defects, additional precessions in the electron–hole spin polarizations and Lorentzian carrier deviations [23–25].

The magnetic dependence of the transport properties of doped and undoped InP single nanowire devices was investigated with magnetoresistance measurements, under continuum light excitation of 635 nm with 1 μW of constant power. The device containing a Zn-doped InP nanowire exhibited an increase in resistance measured under the increment of an applied magnetic field intensity, assuming therefore the positive behavior of magnetoresistance below 10 K, as seen in figure 5. The measurement setup scheme is depicted as an inset in this figure. At room temperature its contribution is negligible as well as that observed for the undoped sample in the whole range of temperatures investigated. At low temperatures the magnetoresistance of the Zn-doped InP device increases following a B^2 dependence, as perceived in the inset of figure 5, and no saturation was observed. The small asymmetry observed in the magnetoresistance curves has been observed in many measurements, but it does not seem to present an apparent relation to the intrinsic magnetic property of the sample, since samples are not expected to keep retaining their magnetic moments. Also, studies have pointed out the induced spin–orbit scattering of electrons between conductive and localized states, which are participants of the orbital hybridization interaction, as an efficient magnetoresistance generator [6].

Several mechanisms can be addressed as responsible for positive magnetoresistance. Being a system presenting some degree of disorder, the localization of electron wavefunctions available for hopping conduction is an important candidate for generating the positive behavior of magnetoresistance [24, 25]. As observed, carrier transport in the Zn-doped InP device is characterized by variable range hopping. The magnetic length, which represents the radial extension of the carrier wavefunction, decreases directly with the intensity of the applied magnetic field [26]. In this case, it presents values on the order of tens of nanometers (a field of 1 T is equivalent to approximately 25 nm of magnetic length), being smaller than the values verified for nanowire width (100 nm) and associated with the verification of positive magnetoresistance. These scale conditions promote three- dimensional conductivity, leading the carrier wavefunctions to be more confined by the magnetic field than by the wire walls. Also, studies have pointed out the induced spin–orbit scattering of electrons between conductive and localized states, which are participants of the orbital hybridization interaction, as an efficient magnetoresistance generator [6, 26]. Since the intensity of an applied magnetic field drives the device current at several orders of amplitude, similar to the that observed in superconducting quantum interference devices (SQUIDs), the thermal dependent magnetoresistance in semiconductor nanowires could be explored for employment in magnetic-thermal sensors [6, 27].

4. Conclusions

We have described the preparation of Zn-doped and undoped InP single nanowire devices by the VLS technique and photolithographic methods. The structural analysis of the nanowire thin films allows the zincblend crystal phase to be identified; the morphology of the grown films was a compound of nanowires and microwires. Ohmic and Schottky behavior were verified in the undoped and Zn-doped single nanowire devices, respectively. The Zn-doped InP device exhibited optically and thermally dependent electrical behavior, whose main conduction mechanism was verified to be variable range hopping at low temperatures. The high photosensitivity of Zn-doped InP presented uniformity for different periods of light exposition, with its photocurrent increasing linearly with the applied light power. A strong and temperature-dependent positive magnetoresistance was also perceived for this device. Such results confirm the applicability of this class of semiconductors as magnetic-thermal sensors, besides their traditional use as high-sensitivity photo-electronic light sensor devices [6, 15, 28].

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ORCID iDs

Fernando Maia de Oliveira https://orcid.org/0000-0003-4272-5416

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