

STUDY OF ELECTROLUMINESCENT DIODES OF $\text{GaAs}_{1-x}\text{P}_x$ USING CONDUCTANCE SPECTROSCOPY

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Abstract

Electroluminescent diodes (LEDs) based on $\text{GaAs}_{1-x}\text{P}_x$ ($0 \leq x \leq 1$) materials are widely used for commercial signage. The present report provides a characterization of electrical properties of this material. We have used admittance spectroscopy at ambient temperature to achieve our objective. Measurements were carried out by considering bias voltage and frequency, varying in 0.25V – 2V and 20Hz – 1MHz ranges respectively. In order to study the role of the Arsenic-Phosphorus substitution, samples with three different Phosphorus content have been investigated; $x = 0.4, 0.63$ and 1 . We have established that the dc-electrical conductance decreases, whilst the characteristic threshold voltage increases, with increasing substitution ratio for the whole range of bias voltage. This general trend is thought to be caused by a change in the charge transfer mechanism due to the disorder introduced in the structure as Arsenic atoms sites are gradually replaced by new generated Phosphorus atoms sites ($\text{As} - \text{Ga} - \text{As} \rightarrow \text{As} - \text{Ga} - \text{P}$). Our results have shown that both frequency and substitution ratio variations alters the conduction response for bias voltage values lower than the threshold voltage value. In fact, it has been found that dc-conductance is independent of the frequency whilst ac-one increases according to the universal Jonscher's power law ($\alpha A\omega^s$). In fact, for bias voltage values, exceeding the threshold voltage value, conductance curves show clearly a remarkable series of crossovers that would explained by transitions from semiconducting to metallic behavior. This phenomenon is more pronounced when x ratio reaches lower values. It is then established that conductance process is simply in agreement with the hopping model.

Keywords

Electroluminescent diodes, Gallium arsenide phosphide, GaAsP, Admittance spectroscopy, Hopping

1. Introduction

Light emitting diodes (LEDs) widely used for lightening last decades belong to the new family of Solid State Lighting (SSL) devices [1]. The latter are opposed to the traditional sources as the light emission is not performed by means of electrical filament or a gaseous fuel lightening but uses a solid-phase-based electronic chip. The change to Solid state lighting is indeed concomitant to several advantages as reported elsewhere [2 and referencetherein].

Therefore, the use of the ternary alloys made of the $\text{GaAs}_{1-x}\text{P}_x$ ($0 \leq x \leq 1$) semiconducting materials is of main interest as their bandgap E_g can be set to produce light from the near infrared to the visible regions ($1.42 \text{ eV} \leq E_g \leq 2.3 \text{ eV}$). In fact, this can be achieved as the bandgap can be shifted with increasing Arsenic-Phosphorus substitution ratio [3]. Furthermore, the current conductance has been reported to show 'Optical bowing' phenomena [4] which is characterized by a declination parameter b as given by the following equation:

$$E_g(x) = (1 - x) E_g(GaAs) + x E_g(GaP) - bx(1 - x)$$

Most of the experimental results has indicate that the **b**-parameter is found to be in the **0.175 – 0.21 eV** range [5, 6, 7].

Unlike other materials that crystallize in the hexagonal wurtzite-like structure (**α -ZnS**) such as **GaAs**- and **GaP**-based nanowires (NWS), the bulk materials generally crystallize in cubic zinc-blend-like structure (**β -ZnS**). According to the obtained structure, the material may exhibit different optical and electrical properties, such as that the quantum yield, the carrier lifetime, and the carrier mobility. This sensivity can be also dependent on the nature and concentrations of dopants [8].

We aim in this work to study the interplay between electrical properties – chemical substitution of LEDs devices made of **GaAs_{1-x}P_x** (**0 ≤ x ≤ 1**). In order to achieve this objective, we have used admittance spectroscopy measurements. Our results are discussed in the view to suggest a model to understand the conduction behavior and explain the mechanism of the electrical conductivity of these materials, and thereby provide experimental evidence on the correlation between substitution ratio **x** and conductance response **G**.

Complex semiconductors have a dispersion of the dielectric constant and conductivity that was attributed to intergranular capacity as sometimes called Maxwell-Wagner effect [9-10]. Maxwell-Wagner effect can be represented mathematically by similar relationship to Debye dispersion formula [11] as given here by the series resistivity:

$$\rho_N = \rho^\infty + \frac{\rho^0 - \rho^\infty}{1 + \tau^2 \omega^2}$$

Where **ρ^0** and **ρ^∞** indicate resistivity at zero and infinite values of frequency, respectively. **τ** is the time constant. **ω** is the angular frequency.

2. Experimental

The measurement bench used to characterize our samples is composed mainly of an RLC-meter (**LCR – 8000G**) operating in the frequency range from **20Hz** to **1MHz**. The level of the excitation voltage can be set between **1mV** and **2V** with the possibility to super-impose dc voltages. The whole system is fully controlled by a computer via a **GPIB-card (IEEE 488** interface). The program used for data acquisition has been developed by our care.

3. Results and Discussion

In order to carry out this part, we had to overcome some difficult tasks as the spatial and spectral distributions which greatly differ from one LED to another. Thus, the bias voltage values taken at different excitation may be placed in different response zones as respect to the characteristic voltage threshold values of each LED at which photons are emitted. The threshold values are noted **$V_{ts}^{x=0.4}$** , **$V_{ts}^{x=0.63}$** and **$V_{ts}^{x=1}$** for **GaAs_{0.6}P_{0.4}**, **GaAs_{0.27}P_{0.63}** and **GaP**, respectively. These values are first determined in the section **A** whilst the conduction measurements are subject of section **B**.

3.1 Study of luminous intensity of the LEDs:

The study of the I - V characteristic is important to understand the mechanism of conductivity behavior of our samples as explained earlier.

The direct current through the junction is given by the following formula [12]:

$$j_d = j_s e^{eV/kT} + j_{gr} \quad (1)$$

Where j_s and j_{gr} are saturation and recombination current, respectively. The latter can be written:

$$j_{gr} = \frac{en_i}{2\tau_m} W_{eff} e^{eV/2kT} \quad (2)$$

Where W_{eff} is the effective width of the depletion region. n_i is the intrinsic carrier density. τ_m is relaxation time of the moment.

Figure 1 shows the curves indicating the change of the current I across $\text{GaAs}_{0.6}\text{P}_{0.4}$, $\text{GaAs}_{0.27}\text{P}_{0.63}$ and GaP samples when excited with a bias voltage V . We can see in this figure that the current I across the samples remains unchanged until a given value specific to each curve/sample, then starts to increase rapidly as bias voltage increases. This behavior concerns all samples and it is indeed expected by equation 1 and 2. One can be therefore able to distinguish two separate zones for each sample as regard to its characteristic threshold voltage.

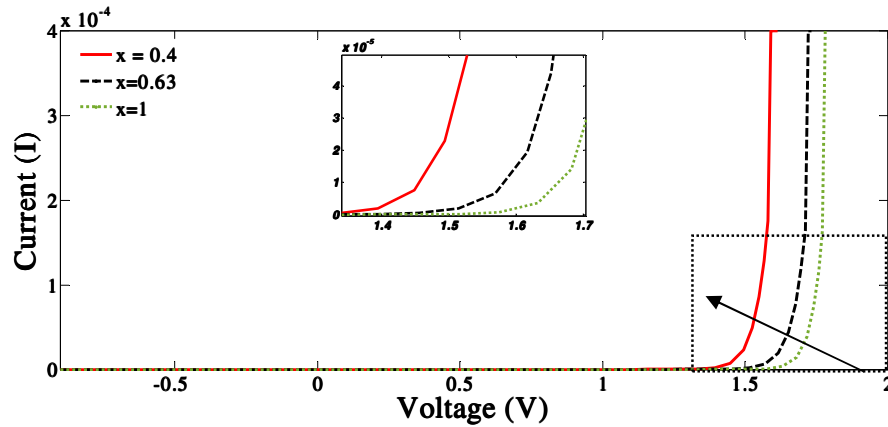


Figure 1: Current-voltage characteristic of $\text{aAs}_{0.6}\text{P}_{0.4}$, $\text{GaAs}_{0.27}\text{P}_{0.63}$, and GaP samples.

The constant regime concerns the so called “blocking or state-off zone” for bias voltage V values lower than the threshold value (*i. e.* $V < V_{ts}^x$). The second concerns the so called “passing or state-on zone” for $V > V_{ts}^x$.

We note that the value of the threshold voltage V_{ts} of the samples increases as the substitution ratio x increases. Table 1 summarizes the extracted values of the threshold V_{ts} for different nominal phosphorus concentration x in the samples. Also, one can see the consequent emitting

light color according to the above changes. As increasing the bias potential, the external field created by the RLC-Meter opposes the internal field of the PN junction. As soon as the external field exceeds the internal field, a current controlling is established through the space charge region of the junction, which results in a rapid rise in current and conductance.

Table 1: Different features of the $\text{GaAs}_{0.6}\text{P}_{0.4}$, $\text{GaAs}_{0.27}\text{P}_{0.63}$ and GaP samples.

Phosphorus Content x	0.4	0.63	1
Nominal Elements Concentrations	$\text{GaAs}_{0.6}\text{P}_{0.4}$	$\text{GaAs}_{0.27}\text{P}_{0.63}$	GaP
Threshold Voltage value (Volts)	1.337	1.457	1.575
LED's Emitting Color	Red	Yellow	Green

According to the band theory, the reduction observed in conduction can be caused an enlarging of the bandwidth. In fact, the later becomes higher when Phosphorus content x decreases from **0** to **1** in the mixed crystal system $\text{GaAs}_{1-x}\text{P}_x$ [15-17] as expressed by the following equation:

$$E_g(\text{eV}) = 1.424 + 1.150x + 0.176x^2 \quad \text{at } 300\text{K}.$$

The gap becomes therefore important with higher Phosphorus content x which leads to the reduction of conduction. Moreover, high mobility is due also to the fact that $\text{GaAs}_{0.6}\text{P}_{0.4}$ has a direct gap which is not the case for the other samples ($x = \mathbf{0, 63}$ and $\mathbf{1}$).

3.2 Conductivity Analysis

3.2.1 Polarization with a voltage lower than the threshold voltages:

This part provides separately the conductance response of the samples to an electrical field-time dependent of magnitude ranging from **0.25** to **1 V**; $V < V_{ts}^{x=0.4}$, $V < V_{ts}^{x=0.63}$ and $V < V_{ts}^{x=1}$. All measurements have been done at room temperature and excitation frequencies ranging from **20Hz** to **1MHz**. Figure 2 shows the conductance, noted G , variation as function of logarithmic frequency variation below the threshold voltage value corresponding of each LED; **a-GaP** ($x = 1$), **b-GaAs_{0.27}P_{0.63}**, and **c-GaAs_{0.6}P_{0.4}**.

The conductance of all our samples can be therefore separated into two *dc*- and *ac*-conductance terms as shown in the following equation:

$$G(\omega) = G_{DC} + G_{AC}$$

One can remark that, the conductance for all alloys remains unchanged at low frequencies, lower than $\sim 10^5 \text{Hz}$. This regime corresponds to the *dc*-conductance response part, noted G_{dc} . One can see in this zone an abrupt increase of the conductance response when bias voltage is set to **1V**. This 'jump' decreases as the substitution ration x decreases to become insignificant when the **As** to **P** atoms substitution is total (**GaP**; $x = 1$). This trend is further studied in the next part and it has been observed also for the G_{ac} response obtained for frequencies higher than $\sim 10^5 \text{Hz}$. In this frequency domain, conductance curves show a parabolic-like increase. This dispersion region concerns the *ac*-conductance response part, noted G_{ac} , and can be described by the universal power law; $G_{AC} = G_{DC} + A\omega^n$ where ω is the angular frequency and n is an exponent [13].

In fact, the spectrum indicates that there is a superposition of different transport mechanisms on the high frequency range, this behavior is known by 'Frequency hopping' and it indicates

that different types of hopping and charge carriers are involved in the transport. Conduction is usually due to the small polaron mechanism SPH [14].

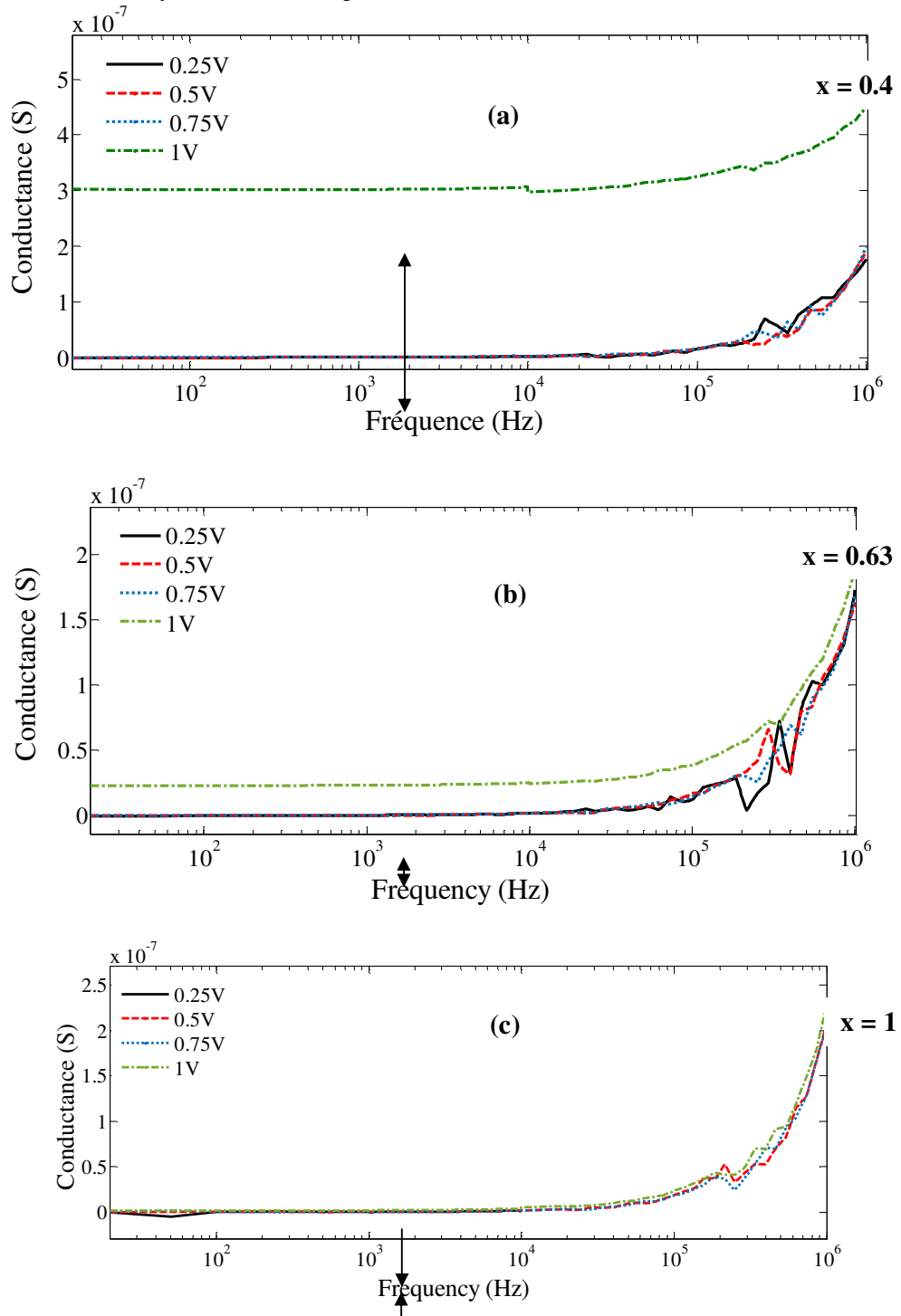


Figure 2: Conductance response as a function of the excitation frequency under different bias voltage values (0.25V, 0.5V, 0.75V, 1V) of a- $\text{GaAs}_{0.6}\text{P}_{0.4}$ (a), b- $\text{GaAs}_{0.27}\text{P}_{0.63}$ (b), and c- GaP ($x = 1$) samples.

3.2.2 Polarization with bias voltages lower and higher than the threshold voltages:

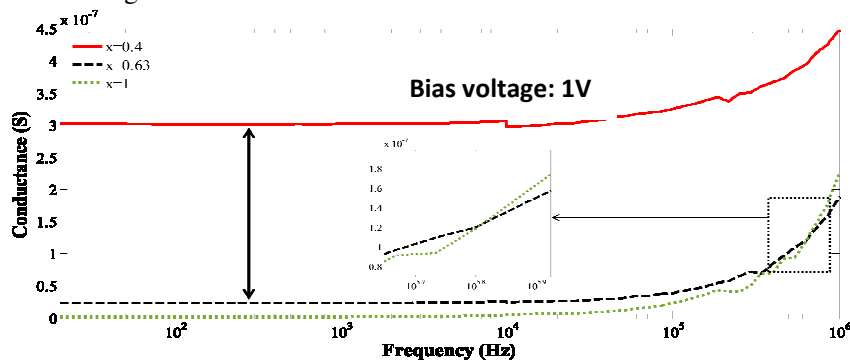
In the seek of understanding the abrupt change of conductance response seen in the previous part, we have reproduce in figure 3-a the curves taken at bias voltage of **1 V** lower than the characteristic threshold voltage values (i.e. $V < V_{ts}^{x=0,4} < V_{ts}^{x=0,63} < V_{ts}^{x=1}$). For comparison, we this series complete with a new series of measurements performed at bias voltage of **2 V** (i.e. $V > V_{ts}^{x=0,4} > V_{ts}^{x=0,63} > V_{ts}^{x=1}$). This later series are displayed in figure 3-b. Figure 3-a shows that the ‘jump’ appears also when the Phosphorus content x changes. In fact, the conductance G is found to decrease with increasing x . Also, the change is more important for lower values of x . Moreover, we can see in figure 3-a that the conductance of the sample with $x = 1$ exceeds that with $x = 0.63$ at high frequencies. At 10^6 Hz the conductance G_{ac} reaches the maximum values of $\sim 1.9 \cdot 10^{-7} \text{ S}$ and $\sim 2.3 \cdot 10^{-7} \text{ S}$ for those samples, respectively. This reverse may indicates that in the high frequency the process of conduction becomes higher for phosphorus-doped systems.

Figure 3-b shows a new complex behavior of the conductance response as compared to the one observed for the first series. We suggest to discuss this behavior in three ditinctive reagions:

- For low frequency values (i.e. $20 \text{ Hz} \leq f \leq 2 \cdot 10^2 \text{ Hz}$): we notice a quantitative increase in the conductance response G with increasing substitution ratio x . All curves present quatitavely the same behavior as the one seen above and we have explained by the power law $G(\omega) = A\omega^n$ valid for high frequency regimes. This may be indicative of the presence of the hopping conduction process.

- For medium frequency values (i.e. $2 \cdot 10^2 \text{ Hz} < f < 2 \cdot 10^5 \text{ Hz}$): conductance response G remain merely constant for all the three LEDs. Quantitavely, one can see that the conductance response is found to take as usual the highest value and decreases with decreasing values of x . This result confirms again the influence of the sensivity of the conduction to an increase of x . The curves starts to decrease with frequency at different values ($x = 0,4$ at 10^5 , $x = 0,63$ at $\sim 6 \cdot 10^4$ and $x = 1$ at $\sim 10^4$) which may indicate a metallic behavior in this range due to the presence of the relaxation phenomenon in the system. The displacement of the crosseover points to high frequency is concomitant to a decrease of x and indicates a sensivity to the excitation frequency.

- For high frequency values (i.e. $f > 2 \times 10^5 \text{ Hz}$): conductance response curves continue their decrease except of the sample with the highest value of phosphorus content x ($x = 1$). Indeed the latter increases and even exceeds the sample with $x = 0.63$. This reverse confirms the trend observed for the conductance in the same condition and bias voltage value of **1 V**. This indicative that the diode with higher x value tends to recover its semiconductor behavior.



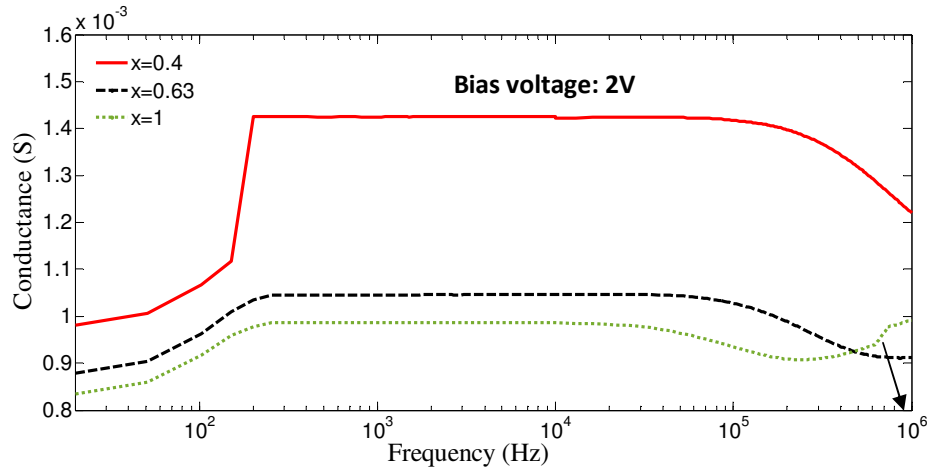


Figure 3: Variation of the conductance with the frequency at bias voltage of a-1V and b-2V for $\text{GaAs}_{0.6}\text{P}_{0.4}$, $\text{GaAs}_{0.27}\text{P}_{0.63}$, et GaP ($x = 1$) samples. Inset of a- and arrow in b- indicate the point at which the conductance response of the two samples are reserved.

The electrical properties depend strongly on the nature of the dopant and its contents. In fact, as the electronic configuration of As is $4s^2 4p^3$ and of P is $3s^2 3p^3$, the decrease of the atomic radius, $R_{\text{P}}(\text{Å}) < R_{\text{As}}(\text{Å})$ is concomitant to an increase of the ionization energy and electronegativity ($\chi(\text{P}) = 2.19$ and ($\text{As}) = 2.18$ at Pauling scale). Thus the replacement of As by P causes a depletion in the number of the charge carriers responsible of the conduction. This change removes the metallicity character and causes the system to behave as a semiconductor.

4. Conclusion

To study the effect of the phosphorus concentration x on the electrical properties of LEDs made of $\text{GaAs}_{1-x}\text{P}_x$ with $x = 0.4$, $x = 0.63$ and $x = 1$ was investigated by means of conductance spectroscopy over a wide frequency range and at different bias voltages. We can argue that the substitution of the Arsenic- by Phosphorus-atoms in this system alters significantly its electrical conductance. Particularly, Phosphorus atoms makes the conductance response less sensitive to the bias voltage excitation and more sensitive to high frequency values.

Below the threshold voltage value, all samples exhibit a semiconducting behavior. ac -conductance is governed by the of Jonscher's power law $G(\omega) = A\omega^n$. This indicates that the conduction process occurs by charge carriers hopping. Above the threshold voltage value, the conductance response of the LEDs shows a change to the metallic behavior. The latter is more pronounced when for the sample with the lower phosphorus concentration for which more metallic characteristics are shown.