Detection of nitrogen atoms as dopants in a zinc oxide crystal lattice incorporated by the effect of a cooling method in a thin film bilayer scheme

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Abstract. The zinc oxide semiconductor can be directed towards p-type or n-type electrical performance depending on the synthesis conditions and fabrication methods, ranging from chemical, sol gel to physical vapor deposition procedures, or the one used in this work: reactive sputtering. Usually this binary oxide, in thin film form, synthesizes into an n-type semiconductor if is fabricated by means of the reactive sputtering method, using an oxygen-poor atmosphere and specific deposition conditions, already established above. However, due to an accident in the synthesis, it was possible to determine the effect that the typical atmosphere at normal atmospheric pressure with 78% nitrogen had on the expected zinc oxide lattice if was abruptly integrated over the scheme. The verification was done using a scratch angle X-ray diffraction characterization, which evidences the incorporation of nitrogen atoms into the zinc oxide crystal by the widening of the lattice parameters. The experimental arrangement analyzed was a bilayer scheme with a first film of n-type zinc oxide and, on this, a second film of the same oxide but p-type. It was possible to conclude that, apart from the desired diode-like behavior of the bilayer, evidenced by the assembly of the half-wave rectifier, there was also evidence of the incorporation of nitrogen in the crystal lattice in the second layer by the notorious shift of the diffraction peak (101).

1. Introduction
Zinc oxide (ZnO) is found in nature as the mineral zincite and can have additions such as manganese that cause its color to vary from whitish to reddish tones. This binary oxide, after chemical purification, is a white powder and has multiple uses in industry. The most common use is as an additive in industrial materials such as paints, glues, lubricants and even in food due to its non-toxicity [1].

ZnO is a group II-IV semiconductor because oxygen (O) belongs to group IV in the periodic table, and zinc (Zn) to group II. Its crystallization falls into three structures depending on its environmental conditions at the time of synthesis: hexagonal wurtzite, zineblende, only stable if it crystallizes cubic, and a salt rock phase that is metastable because it is produced at very high pressures [2]. The most stable phase is wurtzite and therefore the most found naturally as well as the one expected when synthesizing by reactive sputtering by carrying out this process at low pressures. The lattice parameters of its hexagonal cell are \(a = b = 0.325\) nm, \(c = 0.520\) nm [1,3].

The Pontificia Universidad Javeriana, Bogotá, Colombia, has been working, for some years now, on the synthesis of thin films of binary oxides [4], including ZnO, focused on electrical applications as a
semiconductor element. The crystallization in the form of wurtzite of this oxide has been achieved without any problem when its application was directed to the role of an n-type semiconductor, characteristics that were determined by X-ray diffraction (XRD) and the half-wave corrector test that was implemented for work with this binaries oxides. ZnO behaves as type n due, almost always, to oxygen vacancies in the crystal lattice. By trial and error, it was determined that n-type ZnO was obtained when the reactive atmosphere in the deposition had a partial fraction of oxygen lower than that of the argon used in the process, that is, a relatively oxygen-poor atmosphere.

However, a batch of samples in 2018 produced films with different characteristics than expected. This batch had the particularity of having been generated in two deposition sessions clearly defined in time: the first was the usual deposition with gas mixture conditions that are explained in the experimental methodology below. The second, carried out 2 hours apart and similar in time and under gas mixture conditions, carried out immediately without opening the deposition chamber, had the peculiarity that its cooling was done differently from any other that had been carried out before.

Generally, the deposited films are allowed to cool at low pressure for a couple of hours to later allow the entry of air. Due to an error in the procedure, atmospheric air was allowed to enter the chamber very quickly by opening the emergency gas valve that is connected to the outside. Initially it was thought that the ZnO monolayer was ruined, and another had to be generated for use as an n-type semiconductor. The next procedure for any bilayer generated was the half wave corrector test. This procedure is explained in the methodology of this work, but unintentionally the aforementioned spoiled batch was subjected to this experimental test. Surprisingly this monolayer, which actually turned out to be a bilayer, responded to the electrical test like a half-wave corrector. The explanation of this phenomenon is the reason for this article and will occupy the following paragraphs.

2. Materials and methods
The laboratory has an unbalanced magnetron sputtering equipment that is composed of a Pfeiffer HI Cube vacuum pump, a stainless-steel chamber and glass chamber. Within this experimental setup are located the anode and the cathode facing each other at a distance that can be 4 cm. The cathode is a target zinc with a purity of 99.99% and a diameter of 7.62 cm and the anode there is a substrate holder where the thin film grows. The vacuum system is composed of a turbo-molecular pump with cold cathode and full range sensors. The pressure control system is given by a dosing tank where it is mixed with gases through partial pressures in order to have an environment of 70% argon (Ar), 30% gaseous oxygen (O2) for this deposition.

The electrical system used for sputtering magnetron comprises, in addition to the facing electrodes, an unbalanced magnet behind the target that produces a magnetic field of 0.01 T to 0.1 T, an Advance Energy MDX 1.5K source that produces a maximum voltage of 1 KV and transformer for supplying 120 V alternating current (ac). The process is controlled manually, where the working pressure inside the chamber is established and subsequently the voltage, power and current are determined to carry out the discharge, during a time of 10 minutes-12 minutes and measurement of the behavior of the current is made, and the voltage at this time.

In the magnetron sputtering technique, the zinc target is pulverized by means of a discharge of 100 W. Variables such as partial pressure (P1), supplied power (W) and distance between the electrodes (4 cm) are monitored during discharge. The partial gas mixture (percentage of support gas, in this case Ar, and percentage of reactive gas, in this case O2) was kept constant throughout the 10 minutes-12 minutes of making the ZnO films. The response of the 140 V voltage and the 4 mA current was observed. The temperature on the substrate holder was also monitored during and after the growth of the coating to have a controlled cooling that prevents the detachment of the thin film.

The maximum allowable power density for the target according to [1] due to the nature of the metallic target, allowing a maximum power density of 9 W/cm². On the other hand, the values given for the percentage of the amount of O2 during the deposition are taken as a basis the values managed by different authors [5,6].
2.1. Generation of experimental samples
The bilayer type scheme was generated using the Zinc target and the reactive atmosphere with the mixture of gases described above on copper substrates in the form of cylinders, 1 cm in diameter and 1 cm high, prepared metallographically. The synthesis steps of the scheme were:

2.1.1. First layer deposition. Already with the working vacuum level, after the action of the turbomolecular pump, the reactive sputtering process is carried out for 10 minutes-12 minutes.

2.1.2. First cooling. The film deposited in the vacuum chamber is allowed to rest for 2 hours, taking care to keep all the gas access valves closed.

2.1.3. Second layer deposition. The sputtering process is activated again at the same time as the gas access valves are opened, maintaining the deposition for a further 10 minutes-12 minutes.

2.1.4. Final cooling. As soon as the time determined for the second deposition is reached, air from the atmosphere is allowed to enter by opening the emergency valve and it is left to rest for one more hour.

2.2. Characterization equipment
Two techniques were used to characterize these coating schemes, XRD and the half-wave rectifier assembly. XRD was used to determine the presence of nitrogen in the crystal lattice, reproducing results already established by other authors [7-9] and the corrector to demonstrate its diode-like behavior.

2.2.1. X-ray diffractometer. Each layer was characterized in terms of chemical composition and crystallinity through the grazing angle technique for thin film using a Diffractometer model Panalitical Xpert PRO owned by the “Instituto de Ciencia y Tecnología de Materiales” from the Universidad Pedagógica y Tecnológica de Colombia, Tunja, Colombia, using the HighScore Plus software.

2.2.2. Half wave corrector. In this setup, the Rigol DG1022 signal generator was set to a triangular output with a low frequency of 10 Hz and connected in series to a measured resistance of 98.5 Ω and to the bottom of the cylindrical specimen, in such a way that the diode formed by a bilayer was polarized directly in that direction, assuming the copper substrate as a conductor. The Rigol DS1102E oscilloscope used channel 1 to measure generator voltage and channel 2 to monitor current over the probe. The dual display mode was chosen, and the values were exported to a data file that was later plotted and analyzed.

3. Results and discussion
When analyzing the phenomenon of a double zinc deposition behaving as a p-n semiconductor bilayer, the difference between each deposition was weighed. Obviously, the difference was the cooling of each layer. While the first film was allowed to settle at a low pressure and with the reactive atmosphere of O and Ar, the second one underwent a rapid depressurization when atmospheric air at 18 °C entered the deposition chamber. Since the air has 78% nitrogen, it was suspected that this element somehow affected the crystal lattice of ZnO. A qualitative way to detect the presence of nitrogen in the crystal lattice is the XRD as done by Kumari, et al. [7]. In this work they focus on the shift of the diffraction peak (101) as a function of doping in zinc oxide nanoparticles.

On the other hand, the electrical behavior of the bilayer was evidenced with a half-wave rectifier assembly implemented in the “Pontificia Universidad Javeriana, Bogotá”, Colombia. In the work of Li [9] it is determined that the p-type doping effect is thermodynamically unstable and returns to n-type behavior after a certain time, around a few days. The bilayers obtained were immediately characterized with the half-wave corrector scheme and therefore there was no opportunity to establish whether the nitrogen subsequently left the crystal lattice.
The deposition of this bilayer raises concerns about how n-type and p-type materials integrate in the diode deplexion zone. An indication of how it can be visualized is in [10], where the mechanisms of multilayer deposition by reactive sputtering are reviewed.

3.1. X-ray diffractograms

The experimental samples of ZnO layers under the slow cooling conditions were more abundant than those produced in the bilayer batch that was abruptly cooled by atmospheric air. The comparison of the diffractograms can be seen in Figure 1. and they are identical in most of the cases except for some that were contaminated for one reason or another. The diffractograms of the second layer, which were made already mounted on the first, did not show significant differences at the global level, but following the work of Kumari, et al. [7] showed slight differences in the peak (101) indicating a broadening in the network parameter due to the shift of this peak.

Unlike Kumari, et al. [7], the work of Barnes, et al. [5] speculates on an effect of nitrogen on the ZnO crystal both of broadening and contraction of the lattice parameter. Associates the effect of residual nitrogen and the combination of oxygen vacancies. In this work this effect was not considered and the entire phenomenon of N embedding in the network is attributed as a dopant.

To show the XRD θ 2θ patterns, the range from 30° to 55° was chosen, where the peaks were expected at 31.61, 34.31, 36.11, 47.41 that correspond to the planes (100), (002), (101) and (102). The other lines, corresponding to greater angles, were not so visible and in some cases, they were not noticeable in the diffractograms. The semi-quantitative analysis made by the HighScore Plus software did not show traces of nitrogen compounds or residual nitrogen and determined crystallization type hexagonal wurtzite space group P63mc. To determine the shift of the peak (101), a zoom was made to the data for angles between 35.9° and 36.5°.

The work of Kumari, et al. [7] establishes a shift of the peak (101) for doping of ZnO nanoparticles of around 0.05° when there are percentages of nitrogen greater than 1%, and this is precisely what is observed when comparing the diffractograms of the two ZnO films. The shift is to the right because the atomic radius of nitrogen is greater than that of oxygen and therefore its replacement in the crystal lattice causes the lattice parameters to increase slightly [10]. However, this work reports a practically equal shift for doping greater than 1%, a fact that determines the presence of nitrogen, but not its percentage in the crystal lattice.

![Figure 1](image-url)
3.2. Half wave rectifier testing
The property of the p-n type joint in the coating scheme was evidenced by this assembly. Needle-type electrical contact was used to avoid ruining the film and the copper substrate served as a conductive element to close the circuit. All the schemes were deposited on cylindrical copper specimens. The voltage of the source was compared against the current of the circuit and the voltage in which the bilayer was in active mode was obtained. Values that varied between 1.8 V to 2.0 V were obtained for the bilayers that did not show insulating or resistive behavior. Due to the instability of the circuit, the results were recorded by means of the oscilloscope used in a .dat file and a complete oscillation was used to demonstrate the desired behavior.

Figure 2 shows one of the graphs obtained for a particular scheme. The peak-to-peak voltage of the triangular signal (in blue) is 7 V and with the current values (in red), when it enters active mode, the threshold voltage can be calculated simply by drawing a vertical line when the current it stops being zero and crosses voltage. In this case, the threshold voltage of the scheme gives approximately 1.9 V and a maximum current of a little more than 50 mA at the peak of the signal.

In other works, apart from XRD, more characterization techniques such as: Raman spectroscopy, X-ray fluorescence, thermogravimetry and electron microscopy are integrated [11,12], which broaden the vision of this phenomenon and it would be advisable to implement it for future work.

4. Conclusions
The behavior observed as a p-n junction in an apparent zinc oxide monolayer, after applying it in a half-wave corrector assembly, led to the conclusion that there were two types of zinc oxide films in the same cover scheme.

X-ray diffractometry determined the presence of nitrogen in the crystal lattice of the second layer. This led to the conclusion that the cooling of the two zinc oxide layers was carried out differently. The abrupt change in pressure and temperature in the newly deposited and hot second layer caused nitrogen to join the network and thus a kind of doping was achieved to generate a p-type semiconductor. This doping according to X-ray diffraction is above 1% due to the shift of the peak (101) and must have been conditioned by the difference in the temperature and pressure of the deposition chamber with respect to the laboratory environment (18 °C, 0.74 Atm).

The first layer deposited, whose pressure and temperature conditions were not changed during cooling, achieved the usual result of a type n layer.
References

[1] Jagadish C, Pearton S J 2006 Zinc Oxide Bulk, Thin Films and Nanostructures: Processing, Properties, and Applications (Amsterdam: Elsevier Science)

[2] Segura A, Sans J A 2003 Appl. Phys. Lett. 83(2) 278

[3] Ellmer K, Klein A, Rech B 2008 Magnetron sputtering of ZnO films Transparent Conductive Zinc Oxide: Basics and Applications in Thin Film Solar Cells (Berlin: Springer-Verlag Berlin Heidelberg) Chapter 5

[4] Blanco J, Salas Y, Jiménez C, Pineda Y, Bustamante A 2017 Journal of Physics: Conference Series 935(1) 012017:1

[5] Barnes T M, Olson K, Wolden C A 2005 Appl. Phys. Lett. 86(11) 112112

[6] Chen J Y, Zhang H T, Chen Q, Husian F, Cherng J S 2020 Vacuum 180 109576

[7] Kumari R, Sahai A, Goswami N 2015 Progress in Natural Science: Materials International 25(4) 300

[8] Pathak T K, Kumar V, Purohit L P 2015 Physica E: Low-dimensional Systems and Nanostructures 74 551

[9] Li S X Z 2003 Nitrogen Doped Zinc Oxide Thin Film (Berkeley: University of California)

[10] Zhang S B, Wei S H, Zunger A 2001 Physical Review B 63(7) 075205

[11] Theys B, Sallet V, Jomard F, Lusson A, Rommeluère J F, Teukam Z 2002 J. Appl. Phys 91(6) 3922

[12] Oba F, Nishitani S R, Isotani S, Adachi H, Tanaka I 2001 J. Appl. Phys 90(2) 824