Determination of defect content and defect profile in semiconductor heterostructures

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Abstract. In this article we present an overview of the technique to obtain the defects depth profile and width of a deposited layer and multilayer based on positron annihilation spectroscopy. In particular we apply the method to ZnO and ZnO/ZnCdO layers deposited on sapphire substrates. After introducing some terminology we first calculate the trend that the W/S parameters of the Doppler broadening measurements must follow, both in a qualitative and quantitative way. From this point we extend the results to calculate the width and defect profiles in deposited layer samples.

1. Introduction
The actual technology requires high quality and very well characterized semiconductor layers and interfaces for the design of devices for different type of applications. The characterization of ZnO layers grown over sapphire; lead us to develop the way of obtaining further information from W and S parameters.

The physical and chemical properties of ZnO and the progress in crystal growth processes have renewed the interest on this material due to the potentials it presents in different technological fields, particularly in optoelectronic devices working at blue and ultraviolet wavelengths. On the other hand, due to the relative low cost of sapphire substrates, its availability in large area wafers and its transparency up to about 6 μm irradiation wavelength, sapphire is a potential substrate for mass production of ZnO films and it has been largely used for investigating that material. However, the heteroepitaxy of ZnO on sapphire presents several problems due to differences in their chemical nature, structure (wurtzite or corundum), and lattice parameters. Therefore, a necessary step, prior to the technological and practical use of ZnO in optoelectronics, is the knowledge of the ZnO/sapphire interface microstructure in order to control the defects of the deposited films and to improve the quality of the final devices. Even though, defects in ZnO are characterized by different experimental methods, photoluminescence being one of the most relevant, positron annihilation spectroscopy had already shown to be a promising technique for studying the defect structure in ZnO films [1–6].

The study of interfaces by positron annihilation spectroscopy can be performed using slow positron beams. Once one has access to a beam of monoenergetic positrons the most usual
technique to get information of the sample under study is the Doppler broadening of the annihilation peak measured using a Ge detector. We used one monoenergetic slow positron beam, in the 0–40 keV range, of the Laboratory of Physics of the Helsinki Tecnological University. The Ge detector had an energy resolution of 1.24 keV at 511 keV. We used the following energy windows to define the S and W parameters of the annihilation line: \( |E_g - 511 \text{ keV}| < 0.8 \text{ keV} \) \( (p_L/m_0c) \leq 3 \times 10^{-3} \), where \( m_0 \) is the electron mass) for the central S parameter and 2.9 keV \( < |E_g - 511 \text{ keV}| < 7.4 \text{ keV} \) \( (11 \times 10^{-3} \leq p_L/m_0c \leq 29 \times 10^{-3}) \) for the wing W parameter. The absolute values of the parameters are meaningless, because they depend on the widths and positions of the windows. Only the changes of the parameters are important. To facilitate comparisons between various experiments, it is customary to report relative values like \( S/S_{ref} \) and \( W/W_{ref} \), where a good reference is provided by free annihilation in the lattice. These relative values are rather independent of the energy windows and of the small variations in the energy resolutions of different Ge detectors.

The line shape parameters have characteristic values for free positrons in each material, depending on the materials electron momentum distribution. When positrons are trapped, the line shape is characteristic of the trapping defect. For a vacancy-type defect, the density of valence electrons is reduced. This leads to a narrowing of the momentum distribution, which is seen as an increase in \( S \). On the other hand, the localized positron in a vacancy-type defect has less overlap with core electrons than a free positron, leading to a decrease in the core annihilation parameter \( W \).

If the fraction \( \eta_D \) of positrons are trapped and annihilate at a defect \( D \), then the parameters can be expressed as superposition

\[
S = (1 - \eta_D)S_B + \eta_D S_D
\]

\[
W = (1 - \eta_D)W_B + \eta_D W_D
\]

where the subscript \( B \) refers to the free state in the lattice. The changes \( S - S_B \) and \( W - W_B \) are proportional to the trapping fraction \( \eta_D \). A new parameter, called \( R_D \), can be defined if the ratio of the changes are taken into account [7–9]

\[
R_D = |\Delta S/\Delta W| = |(S - S_B)/(W - W_B)| = |(S_D - S_B)/(W_D - W_B)|
\]

which is independent of \( \eta_D \) and thus characteristic of the defect \( D \).

A further illustration of the usefulness of the parameters is given in an \( (W, S) \) plot. Equations 1 and 2 define a segment of a straight line in the \( (W, S) \) plane. The slope of the line is \( R_D \). If there is no trapping (\( \eta_D = 0 \)), the point \( (W_B, S_B) \) represents the free positron state. With saturation trapping (\( \eta_D = 1 \)) we get the point \( (W_D, S_D) \) corresponding to the trapped state. A partial trapping is just an intermediate state of the straight line that is between those two points. Thus any sample, which contains an unknown concentration of the defect \( D \) should have its \( (W, S) \) value on the straight line from \( (W_B, S_B) \) to \( (W_D, S_D) \), provided that no other positron traps are present.

2. Bilayer structures

The ZnO films that triggered our interest in the matter of the paper were grown at atmospheric pressure in a horizontal MOCVD reactor (MR Semicon 102) with a two-inlet configuration, avoiding pre-reactions in the gas phase between the zinc and oxygen precursors: dimethylzinc-triethylamine (DMZn-TEN) and tertiary-butanol (t-butanol). The total nitrogen flow rate through the reaction chamber was kept constant at 5.6 l/min, while the partial pressures of the precursors had a pressure ratio \( R_{V1/II} = 5 \).

Flat sapphire substrates of different orientations \( (1 \, 1 \, 2 \, 0), \, (0 \, 0 \, 0 \, 1), \, (1 \, 0 \, -1 \, 0) \) and \( (1 \, -1 \, 0 \, 2) \) (referred as \( A-, \, C-, \, M-, \, \) and \( R-\) planes, respectively), were used as received. For sapphire
planes \( A \) and \( M \) all experiences were carried out at 420 °C without any prior heat treatment of the substrates. The deposition time was 1000 or 7200 seconds. For \( C \) and \( R \) planes of sapphire another strategy was used too: a growth of a ZnO buffer layer, grown at 350 °C during 4 min (the estimated buffer layer thickness is about 60–70 nm) and a posterior growth at 420 °C. For more details on the MOCVD growth, see [10].

An un-doped single crystal from Eagle Picher, which did not present traps for positrons at room temperature and has a positron lifetime of 170 ps [11], was studied as reference.

Figure 1 shows \( W/S \) plots obtained after \( W \) and \( S \) parameter measurements performed with monoenergetic positrons ranging from 0–40 keV, in the ZnO bulk reference sample and in two ZnO films grown over two different faces of sapphire. In the reference sample (figure 1a) positrons penetrating the sample with the lowest energy have the smallest \( W \) parameter and the largest \( S \) one (bottom right corner of the figure). \( W \) parameter increases and \( S \) parameter decreases as positron implantation energy increases forming a line in the \( W/S \) plot. As in the bulk of the ZnO reference sample there is only one state for positrons, the straight line in the \( W/S \) plot indicates that positrons are annihilating at two states, one corresponding to the ZnO surface and the other to ZnO bulk [12]. The line is quite straight for \( W \) values above 0.75 and \( S \) values below about 1.05. At very low positron implantation energy, where many positrons annihilate in surface states, there is a small deviation related to surface inhomogeneities that may be present in the sample.

As the bulk of the ZnO reference sample has only one positron state, the straight line in the \( W/S \) plot indicates that positrons are annihilating from 2 states one corresponding to annihilations from ZnO surface and the other to ZnO bulk [12]. Increasing positron energy the amount of positrons annihilating from the bulk of ZnO is increasing in respect to the ones annihilating from the surface. Indeed, when positrons are implanted with large energy most of positrons are annihilating from bulk states, and the \((W,S)\) value corresponding to the largest \( W \) and smallest \( S \) is the one corresponding to bulk states (left upper corner in figure 1a). Therefore, the distance between a certain \((W,S)\) point and the one indicated as bulk is related to the positron trapping fraction in bulk state; on the contrary, the distance between that point and the surface point shown in figure 1a is related to the positron trapping fraction at surface state. This is due to the fact that \( S \) and \( W \) parameters corresponding to a particular implantation energy are a linear superposition of positrons annihilating from either of the two possible states [12].

The \( W/S \) plot corresponding to ZnO films grown on sapphire are completely different. They both show a clear cusp. Indeed, at very low implantation energies positrons are annihilating mainly from surface states (bottom right corner in figure 1b). At higher implantation energies the \( W/S \) plot follows a straight line towards a cusp whose maximum depends on the measured film. The cusp position corresponds to a relative maximum (minimum) of the \( W \) parameter (\( S \) parameter) versus implantation energy. At positron implantation energies just above the cusp \((W,S)\) points follow back the previous line, but at further energies the measured values do not follow the previous straight line and they tend toward a new position. The position obtained at the highest implantation energies must correspond to positron annihilation at the bulk of the sapphire. The \( W/S \) plot corresponding to the cusp positions in all the studied ZnO layers fall within a straight line that contains the bulk position measured in the ZnO reference sample and the saturated trapping at Zn vacancies, which has been estimated from simultaneous lifetime and Doppler measurements in electron irradiated single crystal ZnO [11] (see figure 2). It indicates that the same type of defect, the Zn vacancy, is responsible for the trapping at the ZnO films presented here. Moreover, it shows also that all positrons implanted in the sample are annihilating from ZnO layer positron states. We will call “vacancy line” to the line formed by the \((W,S)\) values of the cusps, the \((W,S)\) point of the bulk and the one of the Zn vacancy, which in this particular case represent the linear superposition of positrons annihilating from
Zn vacancy and from ZnO bulk states. It is worth noting, the length between the cusp and the position where \((W, S)\) points leave the straight line depends on the sample, and such points fall within the so called “vacancy line”. It indicates there should exist a profile of Zn vacancy concentration in the studied films, and such a profile varies from sample to sample.

**Figure 1.** \(W/S\) plot of (a) the reference sample and (b) two ZnO layers deposited on sapphire substrate.

\[
(W/S)_{\text{bulk}}\quad \text{Energy}
\]

\[
(W/S)_{\text{surface}}
\]

**Figure 2.** \(W/S\) plot of the cusp positions in all the studied bilayers.

2.1. Implantation profile

In order to obtain further information from \(W/S\) plots like the ones in figure 1b it is necessary to analyze the implantation process. Characteristics such as positron penetration and its implantation depth, positron diffusion length (in the layer and the substrate), and its probability distribution after the diffusion have to be considered. The positron implantation energy and the mean implantation depth of the positron into the sample, \(\langle z \rangle\), are related by the equation

\[
\langle z \rangle = \frac{BE_n^m}{\rho}
\]
where $\rho$ is the material density (5.6 g/cm$^3$ for ZnO) and $n$ and $B$ are 1.6 and $4 \times 10^{-6}$ g/cm$^{-2}$ keV$^{-1.6}$, respectively [12]. Once the positron penetrates into a sample its stopping profile is described by the following Makhovian function

$$I(z) = \frac{2}{z_0^2} e^{-\left(\frac{z}{z_0}\right)^2}$$

where $z_0$ is related to the mean penetration depth by $\langle z \rangle = 0.886z_0$ ([12] and references therein). As figure 3 shows the stopping profile function extends from the surface towards higher penetration values inside the sample. The stopping profile has a long tail, which extends towards larger depths. Indeed, the probability of implantation at depths larger than $2\langle z \rangle$ is small (4.5%). Neglecting the 4.5% area of the implantation profile tail above $2\langle z \rangle$, the resulting function is quasi-symmetrical and centered at the mean penetration depth value $\langle z \rangle$. The maximum penetration depth defined in this way is $2\langle z \rangle$, twice the mean penetration depth. The stopping profile in a ZnO layer deposited on a sapphire substrate is slightly different to that given by equation (5), because both materials have different densities. But, if both materials have similar density values, the shapes of the stopping profiles are qualitatively similar. At high penetration depths the implantation profile will have a slightly longer tail inside the sapphire, since its density is slightly lower than that of ZnO.

Taking into account that from the location where they have been implanted, positrons may diffuse inside the material until they annihilate, we must consider the mean diffusion length ($L_{\text{diff}}$) of the positron in the layer and in the substrate for a correct interpretation of the results. Considering the diffusion equation [12] and using the VEPFIT program [13], we can adjust the variation of the $S$ parameter versus the implantation energy. Fitting the studied samples with VEPFIT gives values of 22 ± 5 nm and 80 ± 10 nm for the positron mean diffusion length in the layer and in the substrate, respectively. The obtained values have to be considered when evaluating the mean penetration depth. When $L_{\text{diff}}$ in the ZnO layer is much smaller than the layer thickness, we can neglect it. As this is the case of the ZnO layers presented in this work, we can consider $2\langle z \rangle$ as the maximum penetration depth for the positrons in the layer.

Figure 3. Shape of the positron implantation profile.
2.2. Determination of the layer thickness

The cusps mean implantation depths for the measured samples range between 70 and 240 nm. Therefore, the maximum penetration depth corresponding to the cusps is, as we will see, smaller that the layer thickness in all the samples. At implantation energy higher than the one corresponding to the cusp, the W/S measured values still lay over the “vacancy line”. The position at which the \((W,S)\) points start to leave the “vacancy line” will be called “abandon point”. In the studied samples the “abandon point” is attained for mean penetration depths between 160 \(\pm\) 30 nm and 440 \(\pm\) 30 nm. Leaving the “vacancy line” indicates that positrons are starting to annihilate from another state, different to the ones that gave the “vacancy line” (delocalized state at ZnO and Zn vacancy). This indicates that for energies larger than the one corresponding to the “abandon point” positrons are annihilating outside the layer too. Taking into account this fact and the shape of the implantation profile (Figure 2), the “abandon point” must correspond to mean penetration depths in the order of half of the sample thickness. Therefore, under these conditions the stopping profile function extends from the surface of the layer up to the interface between the layer and the substrate, see figure 1. For larger energies, positrons cross the interface and start annihilating inside the substrate.

The previous discussion indicates that a simple and non-destructive way for determining the thickness of a layer grown on a substrate consists on determining the “abandon point” in the W/S plot. The thickness of the layer corresponds to twice its mean implantation depth \(2\langle z_{\text{abandon}}\rangle\). Table 1 shows the thickness of the studied samples obtained by two different
Table 1. Layers thickness measured by scanning electron microscopy (SEM) and by the method described in this work.

|        | SEM (nm) | This work (±60 nm) |
|--------|----------|--------------------|
| 540±50 | 540±50   | 480                |
| 410±40 | 410±40   | 480                |
| 450±70 | 450±70   | 480                |
| 860±150| 860±150  | 880                |
| 660±70 | 660±70   | 660                |
| 760±50 | 760±50   | 720                |
| 630±60 | 630±60   | 660                |

methods: the non-destructive method based on determining the abandon point, as introduced in the present work, and a destructive one based in scanning electron microscope images of the cleaved samples. Indeed, there is quite a good agreement between both methods. The proposed criterion yields good results in the studied samples because the positron diffusion is small inside the film. The measured spectra show that the abandon point is well defined in all the studied samples, indicating the very small influence diffusion causes in determining the thickness of the layer.

2.3. Determination of the defect profile

What does indicate the presence of a cusp in ZnO layers grown over sapphire? Between the cusp position and the “abandon point” the W/S curve is directed towards the zinc vacancy value following the “vacancy line”. It indicates, clearly, that the concentration of zinc vacancies close to the interface is significant. At higher energies, the probability of positrons annihilating in the substrate increases and the measured W and S values tend to the annihilation values of sapphire. The distance in the W/S plot between the cusp position and the “abandon point” is proportional to the variation of the zinc vacancy concentration. From figures 1 and 4 it can be inferred that the vacancy concentration is minimum inside the layer at depths lower than one third of the layer thickness and increases up to the interface, that is, for mean penetrations around half of the thickness of the samples.

For mean penetration depths larger than half of the layer thickness the probability that positrons annihilate at the interface and inside the substrate increases, and from this point on the results cannot be easily separated into the different contributions. Moreover, a long positron diffusion length in the substrate might influence the amount of positrons annihilating in the substrate and trapping at interface states. However, taking into account the short positron diffusion length within the layers, only the number of positrons annihilating in the interface would increase. The results can be explained assuming only trapping in the layer and the substrate, so the effect of the interface states is minor in the measured samples.

In figure 4 point C is indicated by an arrow. Point C corresponds to a mean penetration depth of 480 nm, and although this point is outside the straight line (vacancy line), it keeps some information on the annihilation parameters of the layer but with some influence from the substrate. The corresponding mean penetration depth is close to the thickness of the layer, so, 50% of positrons are implanted in the substrate (50 % percentage) and the rest in the layer and it brings information about the annihilation characteristics near the interface. In the following we will analyze this general behavior in order to understand it and to obtain further information.
from these data.

The method we propose for the determination of the defect profile in semiconductor layers grown heteroepitaxially, can be generalized to other hetero(homo)structures if they fulfill the following conditions:

(i) The positron diffusion length is much smaller than the layer thickness.

(ii) The layer has only one defect trapping positrons at the measurement temperature.

(iii) Positron annihilation in the substrate comes from only one state.

The three conditions are not very restrictive and the method could be, thus, employed in many systems.

2.3.1. Definitions in the W, S plane  We can divide the W/S curves of all the samples in the W/S plot into three different zones according to the positron implantation (and annihilation) depths into the sample: the layer zone, which corresponds to the “vacancy line” (all positrons annihilate within the layer), the intermediate zone, which starts at the abandon point and extends up to the third zone (positrons annihilate from both, the layer and the substrate), and the third zone, which is representative of the W/S substrate values (most of the positrons annihilate at the substrate). In figure 1b these three zones can be easily distinguished.

The W/S value corresponding to the sapphire substrate can be obtained directly from measurements of the substrate by the other side of the layer sample. On the other hand, all points in the W/S plot are enclosed by three lines, which establish the limits of the W/S plots. These lines are: the “vacancy line”, already defined, the “bulk line”, which runs from the ZnO bulk to the substrate W/S values, and the “saturation line”, which joins the Zn vacancy and the substrate W/S values, see figure 5a.

![Figure 5](image-url)  
Figure 5.  
a) definition of the W/S plane. The inset shows the defect profile \( \eta(z) \) of the layer,  
b) representation of percentage lines, effective constant trapping lines and 2 qualitative positron trends of W/S points.
2.3.2. **W and S annihilation parameters as a function of penetration depth**  
Now, let's analyze the trend of a point, which individual contributions to the W and S parameters will be written as \((W/S)\), for a layer grown over a sapphire substrate (subscript) once it abandons the vacancy line. That is for mean penetration depths larger than approximately the layer half width. The individual contributions to the W and S parameters of a layer with a vacancy profile along the layer thickness and a substrate can be deduced from the next equation:

\[
(W/S)_{\text{total}} = (W/S)_{\text{layer}}[0,d]P_{\text{layer}} + (W/S)_{\text{subst}}[d, D = \infty]P_{\text{subst}}
\]  

(6)

where,

\[
(W/S)_{\text{layer}} = (W/S)_{\text{bulk}}\eta_{\text{eff}}^{\text{bulk}} + (W/S)_{v}\eta_{v}^{\text{eff}}
\]  

(7)

and

\[
\eta_{\text{eff}}^{\text{bulk}} + \eta_{v}^{\text{eff}} = 1
\]  

(8)

\(P_{\text{layer}}\) and \(P_{\text{subst}}\) correspond to the annihilation probability in the layer and the substrate, respectively. \(d\) and \(D\) are the layer and the substrate thicknesses, respectively.

\(\eta_{v}\) is the effective trapping at vacancies. It fulfils a relation similar to the trapping fraction, and allows for non constant trapping fraction:

\[
\eta_{v}^{\text{eff}} = \frac{\int_{0}^{d} \eta_{v}(z)I(z)dz}{\int_{0}^{d} I(z)dz}
\]  

(9)

We can generalize equation (6), that is, the contribution to the experimental W and S values of the sample, \((W/S)_{\text{total}}\), as follows:

\[
(W/S)_{\text{total}} = \int_{0}^{d} (W/S)_{\text{layer}}I(z)dz + \int_{d}^{\infty} (W/S)_{\text{subst}}I(z)dz
\]  

(10)

and,

\[
(W/S)_{\text{layer}} = (W/S)_{\text{bulk}} + [(W/S)_{v} - (W/S)_{\text{bulk}}]\eta_{v}(z)
\]  

(11)

where \(I(z)\) is the implantation profile or probability function along the whole sample, and \(\eta_{\text{bulk}}(z)\) and \(\eta_{v}(z)\) are the bulk and vacancy trapping fractions, respectively.

The ratio \(\eta_{v}/\eta_{\text{bulk}}\) is proportional to the defect concentration \(C(v) = K\eta_{v}/\eta_{\text{bulk}}\), where \(K = N_{\text{at}}\lambda_{b}/\mu\) is the proportionality constant. \(N_{\text{at}}\) is the atom density of the material, \(\lambda_{b}\) the annihilation rate at delocalized states and \(\mu\) the defect specific trapping rate. \(\eta_{v}/\eta_{\text{bulk}}\) is dimensionless and it will be represented by the function \(f(z)\). We can then write

\[
\eta_{v} = f(z)\eta_{\text{bulk}}
\]  

(12)

and taking into account that

\[
\eta_{\text{bulk}}(z) + \eta_{v}(z) = 1
\]  

(13)

The trapping fraction of vacancies is

\[
\eta_{v}(z) = \frac{f(z)}{1 + f(z)}
\]  

(14)

The \((W/S)_{\text{total}}\) can be written as:

\[
(W/S)_{\text{total}} = (W/S)_{\text{subst}} \times e^{-\left(\frac{d}{\lambda_{0}}\right)^{2}} + (W/S)_{\text{bulk}} \left(1 - e^{-\left(\frac{d}{\lambda_{0}}\right)^{2}}\right) + \int_{0}^{d} [(W/S)_{v} - (W/S)_{\text{bulk}}] \left[\frac{f(z)}{1 + f(z)}\right] I(z)dz
\]  

(15)
where $I(z)$ is [14]:

$$I(z) = \begin{cases} 
\frac{2z}{z_0^2} e^{-\left(\frac{z}{z_0}\right)^2} & ; \ z < d \\
\frac{2}{z_1} \left[ \frac{d + \frac{\eta}{\rho_1}(z-d)}{z_0} \right] e^{-\left[ \frac{d + \frac{\eta}{\rho_1}(z-d)}{z_0} \right]^2} & ; \ z > d 
\end{cases} \tag{16}$$

In the particular case of ZnO, $z_0 = 40/\rho_0/0.886E^{1.6}$ and $z_1 = 40/\rho_1/0.886E^{1.6}$. $\rho_0$ and $\rho_1$ are the densities of the layer and the substrate, respectively. It depends on the density of the material and the energy of positrons like a Makhovian function.

If the density of the substrate is much larger than the layer one, most positrons will preferentially annihilate in the layer, independently of their energy. On the other side, if the density of the substrate is much lower than the layer one, positrons with enough energy will enter easily into the substrate and the penetration depth will get largely increased. In the following we will consider that the densities of layer and substrate are similar and, therefore, the probability distribution in the substrate will be similar to the layer one. In the analysis above we have estimated the expression for $I(z)$ in a simple way, but a more exact expression could be obtained from experimental measurements or Monte-Carlo calculations.

### 2.3.3. W/S curve behaviour for energies larger than the one of the “abandon point”

We can obtain the behavior of $W/S$ points easily for positron energies larger than the one of the “abandon point”, assuming $\eta_0 = constant$. Such a constant corresponds to a layer with a constant defect concentration profile along its thickness. In this case $f(z) = f(0) = constant$, and the $W$ and $S$ parameters can be easily calculated.

In this case equation (15) becomes:

$$(W/S)_{total} = e^{-\left(\frac{\eta}{\rho_0}\right)^2} (W/S)_{sub} + \left(1 - e^{-\left(\frac{\eta}{\rho_0}\right)^2}\right) [(W/S)_{bulk\eta_{bulk}} + (W/S)_{\eta_{v}}] \tag{17}$$

$$(W/S)_{total} = e^{-\left(\frac{\eta}{\rho_0}\right)^2} (W/S)_{sub} + \left[1 - e^{-\left(\frac{\eta}{\rho_0}\right)^2}\right] (W/S)_{layer} \tag{18}$$

$$(W/S)_{total} = (1 - P_0)(W/S)_{sub} + P_0(W/S)_{layer} \tag{19}$$

where $P_0$ is the probability of the positron to annihilate inside the layer. $P_0$ is obtained integrating the probability $I(z)$ from 0 to the entire layer thickness. Its value depends on the layer thickness, the densities of the layer and the substrate, and the positron implantation energy.

$$P_0 = 1 - e^{-\left(\frac{\eta}{\rho_0}\right)^2} \tag{20}$$

In this case, equation (19) defines a straight line joining the vacancy line with $(W/S)_{sub}$. Other values of $\eta_0$ give other straight lines joining $(W/S)_{sub}$ value with the corresponding $\eta_v$ that is located on the vacancy line. Any of such lines, corresponds to constant defect profile density along the sample thickness. Let’s take a value for $f(0)$ which leads to a value of 0.5 for $\eta_0$ in equation (14). For this case, the $W/S$ value will follow a line as the straight line $M$ in figure 5b [15]. Therefore, we can define constant trapping fraction lines ($\eta^{eff}$), which join points with the same effective trapping fraction. They extend between the “vacancy line” and the substrate value.

On the other hand, the analyses above allows to define and draw parallel lines to the “vacancy line” in figure 5b, too. Each line corresponds to a mix of the layer and substrate $W$ and $S$ parameters in different proportions, that is, for different mean penetration depths or $P_0$. So we can draw for instance, the called “50% line” in figure 5b. Assuming that the $W/S$ values, for the
annihilation of positrons which penetrate twice the width of the layer sample, can be obtained as approximately a contribution of 50% of the \(W/S\) parameters of the film plus another 50% contribution of the \(W/S\) parameters of the substrate, equation (16).

Other different lines, for different values of the probability of the positron in the film, \(P_0\), can be drawn parallel to the “vacancy line” as in figure 5b. We will call them the hundred percent or \(P_0\) lines (%lines). The \(\eta^{eff}\) trapping fraction line is the one connecting the trapping fraction value at the vacancy line and the \((W/S)\) substrate value. The effective trapping fraction in a particular point of each hundred percent line is given by the point where the above line cuts the corresponding hundred percent line.

### 2.3.4. Non constant defect profiles

In heterostructures due to the interface the defect concentration profile is not constant. Indeed, it usually increases towards the interface. We can qualitatively predict the \(W/S\) behavior or trend for this case using the hundred percent lines.

In this situation once the \((W/S)\) point abandons the “vacancy line”, at mean penetration depths from the sample half width to approximately the width of the sample, the point will descend to higher trapping fraction values along each “% line” in figure 5b. At the same time it moves towards the \(W/S\) point representative of the sapphire substrate. This will happen for mean penetration depths up to the layer width 50% line in figure 5b, because at that mean penetration the maximum of the positron implantation profile is located at the interface. For higher mean penetration depths the substrate influence will increase and the \(W/S\) point will move along a straight line towards the \(W/S\) value of sapphire. In this case we can expect a trend with two lines of different slopes \((N\) line in figure 5b) in the \(W/S\) plot. The first line of the above trend connects the abandon point and the point in the 50% line. The second line connects the 50% line point and the \(W/S\) value of the substrate.

We can deduce the defect concentration profile of a particular layer by a pair of values \((P_0, \eta^{eff})\) in the \(W/S\) plot. For any experimental point, the \(\eta^{eff}\) value and its associated \(P_0\) value can be calculated and, using these values, the defect profile can be approximately obtained.

We can perform the analysis of the \(W/S\) plot for a varying defect concentration distribution, for what we only need to know the vacancy concentration \(f(z)\) or the trapping fraction \(\eta_v\) as a function of the sample depth. Using equation (15) we can calculate the evolution of the \(W/S\) parameters versus implantation energy. We need only to solve the integral of equation (15) for the appropriate values of \(f(z)\). The equation can be solved numerically for any distribution of zinc vacancies.

Considering the previous discussion we can also calculate the variation of the trapping fraction \(\eta_v\) along the sample fitting equation (15) to the experimental variation of the \(W\) and \(S\) parameters for different penetration depths [16].

### 2.4. Three layers structures

We can extend easily the equations obtained in the case of two layers for samples composed by two layers plus one substrate. In this case the two layers equation (6) becomes

\[
(W/S)_{total} = (W/S)_{layer_1}[0,d_1]P_{layer_1} + (W/S)_{layer_2}[d_1,d_2]P_{layer_2} + (W/S)_{subst}[d_2,D = \infty]P_{subst}
\]

where,

\[
(W/S)_{layer_i} = (W/S)_{bulk_i}\eta^{eff}_{bulk_i} + (W/S)_v\eta^{eff}_{v_i}
\]

and

\[
\eta^{eff}_{bulk_i} + \eta^{eff}_{v_i} = 1
\]
In this case an equation for $\eta_{v_i}^{eff}$ can be obtained equivalent to equation (9),

$$\eta_{v_i}^{eff} = \frac{\int_{d_{i-1}}^{d_i} \eta_{v_i}(z)I(z)dz}{\int_{d_{i-1}}^{d_i} I(z)dz} \tag{24}$$

where $i = 1, 2$ and $d_0 = 0$. Following a similar discussion than in the case for two layers a similar function as the one described in equation (15) can be obtained. So,

$$(W/S)_{total} = (W/S)_{subst} \times e^{-\left(\frac{d}{\eta_i} \right)^2} + (W/S)_{bulk1}(1 - e^{-\left(\frac{d}{\eta_i} \right)^2}) + (W/S)_{bulk2}(e^{-\left(\frac{d}{\eta_i} \right)^2} - e^{-\left(\frac{d}{\eta_i} \right)^2} + \int_{d_1}^{d_2} ([W/S]_{v_1} - (W/S)_{bulk1}) \left[ \frac{f_1(z)}{1 + f_1(z)} \right] I(z)dz + \int_{d_1}^{d_2} ([W/S]_{v_2} - (W/S)_{bulk2}) \left[ \frac{f_2(z)}{1 + f_2(z)} \right] I(z)dz \tag{25}$$

As in the case of a bilayer, we can first obtain the behavior of $(W/S)$ points assuming $\eta_{v_1}$ and $\eta_{v_2}$ constants, that is, considering that the two layers have constant defect concentration profile along their thicknesses (constants $f_1(z)$ and $f_2(z)$). In that case equation (19) becomes

$$(W/S)_{total} = [1 - (P_1 + P_2)](W/S)_{subst} + P_1(W/S)_{layer1} + P_2(W/S)_{layer2} \tag{26}$$

where $P_1$ and $P_2$ are the probabilities of positron to annihilate inside layer 1 and layer 2 respectively.

Let’s analyze qualitatively the above equation that corresponds to constant vacancy concentration profile in the two layers. If $P_1 \gg P_2$ and $P_1$ close to one, equation (26) yields the vacancy line of the first layer. If $P_1 \ll P_2$ and $P_2$ close to one, equation (26) yields the vacancy line for layer two. When $P_1$ very small and $P_{subst} \simeq 1 - P_2$ the equation yields a line that goes from the vacancy line of the second layer to the $W/S$ value of the substrate. However, due to the relation between $P_1$ and $P_2$ the abandon points corresponding to the different lines are not as acute as in the bilayer case.

In the following we present in figure 6 the $W$ and $S$ parameters obtained after monoenergetic positrons implantation in a three layer formed by ZnCdO/ZnO/Al$_2$O$_3$ and we give a preliminary discussion of the results. The thin films were deposited on $R$–plane sapphire substrates. A relatively thick ZnO buffer layer (of about 800 nm, estimated from growing conditions) was deposited prior to ZnCdO alloy growth. The ZnO buffer was grown at 376 °C (see [17] for more details).

Figure 6a presents $W$ and $S$ parameters versus positron implantation energy and its corresponding $W/S$ plot, figure 6b. The $W/S$ plot shows four straight lines with different slopes for monoenergetic positrons in the range 0–40 keV. At low positron energies, most of positrons annihilate from surface states of ZnO:Cd(4.5%) layer (bottom right corner). Increasing energy $(W/S)$ points follow a straight line towards a position where there is a relative large concentration of points with relatively similar $W$ and $S$ parameters. Those points correspond to the plateau of $W$ and $S$ parameters versus implantation energy observed in figure 6a, which ends at about 1.1 μm penetration depth. However, increasing positron energy, a new slope change occurs for positron penetrations up to 1.8 μm. From this point a short straight line runs up to positron penetration depths of 2.7 μm. After, this point and for larger positron penetration depths $(W/S)$ points follow another straight line that it is clearly directed toward $(W/S)$ values of sapphire (not shown in the figure). Following the previous discussion, it is clear that the straight line running between 1.8 μm and 2.7 μm penetration depths must correspond to positron annihilation preferentially happening at the ZnO buffer, indicating that 2.7 μm corresponds to the “abandon
Figure 6. (a) W and S parameters versus positron implantation energy for a heterostructure formed by two ZnO layers deposited over a sapphire substrate and (b) its corresponding \( W/S \) plot.

point” between annihilations in the two layers and the substrate. Therefore, \( (W/S) \) points that run between surface and 1.8 \( \mu \)m positron penetration depths must correspond to \( W \) and \( S \) parameters of the overlayer of ZnCdO. However, the \( W/S \) plot indicates clearly the presence of two straight lines in such region and the piling up of many points for positron implantation energies in the range 5–15 keV. This behaviour suggest that Cd content along the layer is not uniforme. Indeed, from the surface to 1.1 \( \mu \)m depths Cd content uniformity is indirectly deduced for the piling up of \( (W/S) \) points corresponding to implantation energies in the range 5–15 keV. It indicates that the presence of Cd induces the presence of positron traps, which trap positrons preferentially for penetration depts upto 1.1 \( \mu \)m; however, for larger penetration depths, closer to the ZnCdO/ZnO the Cd induced defects decrease; which suggest the lower Cd presence in the neighbourhood of the ZnO/ZnCdO interface.

3. Conclusions
We have presented a method to analyze \( W/S \) plots of Doppler broadening data obtained with slow positron beams. A detailed analysis of the method for a system formed by a semiconductor layer over a substrate has been presented. The method allows to determine easily and nondestructively the thickness of the layer. The method allows to perform quantitative determinations of the defect profile inside the layer, too. The method can be extended to heterostructures formed by several semiconductor layers over a substrate. In this work a preliminary extension of the method for heterostructures having two different layers over a substrate has been presented.

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