Characterization of defects in neutron-irradiated SnO_2 using positron annihilation technique

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Abstract. In this work the two-component density functional theory is employed in the modelling of defects in neutron-irradiated SnO_2. Since defects are localized, the local density approximation (LDA) is utilized. Although LDA gives a good approximation of electron-positron annihilation momentum density at high momentum electron states, it does not consider the variational nature of the electron density. This has an unintended consequence of having over estimated annihilation rates or lower positron lifetimes compared to experimental values. This deficiency in LDA is corrected by using the generalized gradient approximation (GGA) which considers the variation nature of electron density. The accumulation of annihilation spectrum using coincidence setup, is utilized to allow for the determination of annihilation parameters, S and W. The experimentally obtained S-parameter values 0.370812 for unirradiated and 0.374281 for neutron-irradiated SnO_2 suggests and increase in the defect density. Two positron lifetimes 240 ps and 263 ps for bulk and defect respectively were obtained in the framework of the generalized gradient approximation (GGA). The average positron lifetime of 252 ps suggests that neutron-irradiation caused a displacement damage or open volume vacancies in the material.

1. Introduction

Tin oxide (SnO_2) of space group $P4_2/mnm$ has drawn much attention due to its application in transparent electrodes [1], electron magnetic shielding [2] as well as n-type thin film transistors [3] and in gas sensing [4,5]. Recently, tin oxide is being reviewed as a component in advanced nuclear fuel designs [6]. Therefore, the radiation impact on such a material has, to a less extent, been exploited using other techniques and to even a lesser extent using positron annihilation technique (PAT). Radiation, especially moderate to fast neutron, is bound to cause spatial damage in the target material. PAT is a sensitive and non-destructive tool [7-10] for studying the density of defects as well as their nature following the damage caused by the radiation. Irradiation of materials with neutrons introduce several defects such as vacancies, vacancy clusters, voids, and other types of defects.

In this work, we investigate the defects in pelletized SnO_2 caused by the bombardment of neutrons from Americium-beryllium (AmBe) of activity 300 Gbq. The experimentally obtained Doppler broadening of the annihilation line, which is characterized by the S-parameter, shall serve as a measure of a positron-electron annihilation momentum density at annihilation sites as well as in the bulk. We further extend our study to the annihilation rates due to positron annihilating with core and valence electrons of tin and oxygen atoms using the local density approximation (LDA) as well as the generalized gradient approximation (GGA).

2. Experiment

Powder SnO_2 was pelletized to a diameter of 0.8 cm and thickness of 0.4 cm using a pelletizer at the University of Witwatersrand. X-ray diffraction (XRD) was used to ascertain if there was no structural deformation during the powder compression into pellets. XRD used is a Bruker D8 equipped with Goebel Mirror. The diffractometer utilized Cu-Kα radiation. Rietvield refinements were carried out using TOPAS 4.2. Figure 1 shows the arrangement used during the irradiation of the sample. XRD was also used to check if any structural damage occurred after irradiation.

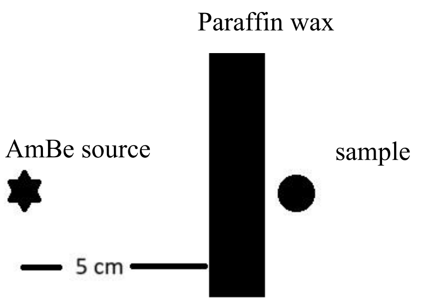

Figure 1. The AmBe neutron source – paraffin wax – sample arrangement. This arrangement was employed for irradiation purpose.

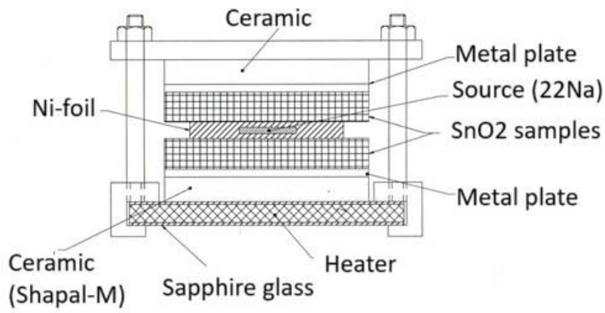

Figure 2. Sandwich arrangement in which ^{22}Na is placed between two equal irradiated sample. This is the source-sample arrangement for Doppler broadening experiment

The sample was irradiated for 24 hours with neutron in the energy range from 0.223 MeV to 2,3 MeV. The irradiated samples and the positron source were organized in a standard sandwich arrangement as shown in Figure 2. The activity of the ^{22}Na source, whose decay scheme shown in Figure 3, was 15 µCi. This arrangement was maintained at an average pressure of about 2×10^{-6} Torr. The circuit diagram used for the annihilation spectrum measurement is shown in Figure 4. A positron emitted from ^{22}Na rapidly thermalizes and diffuse until it finds a vacancy where it annihilates with low momentum electron, producing a pair of gammas (511 keV) in opposite directions. These two photons were detected by a high-purity germanium (HPGe) with resolution of 1.27 keV (FWHM) at photopeak of 511 keV.

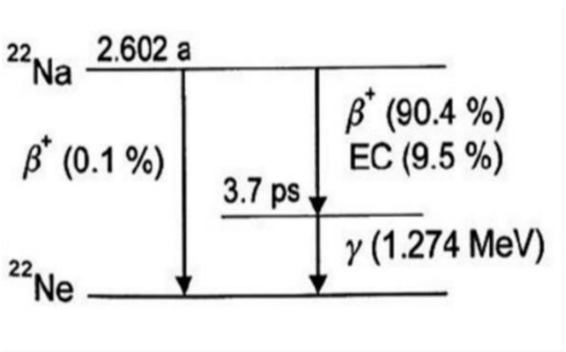

Figure 3. The decay scheme of ^{22}Na to ^{22}Ne. The decay is accompanied by the emission of 1275 keV gamma which is a start signal in positron lifetime measurements.

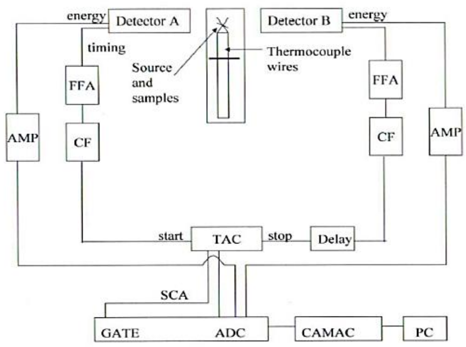

Figure 4. Circuit diagram for both Doppler broadening and lifetime measurements

3. Results and discussion

X-ray diffraction confirmed the absence of structural damage after pressing tin oxide powder into pellets. The XRD pattern is shown in Figure 5.

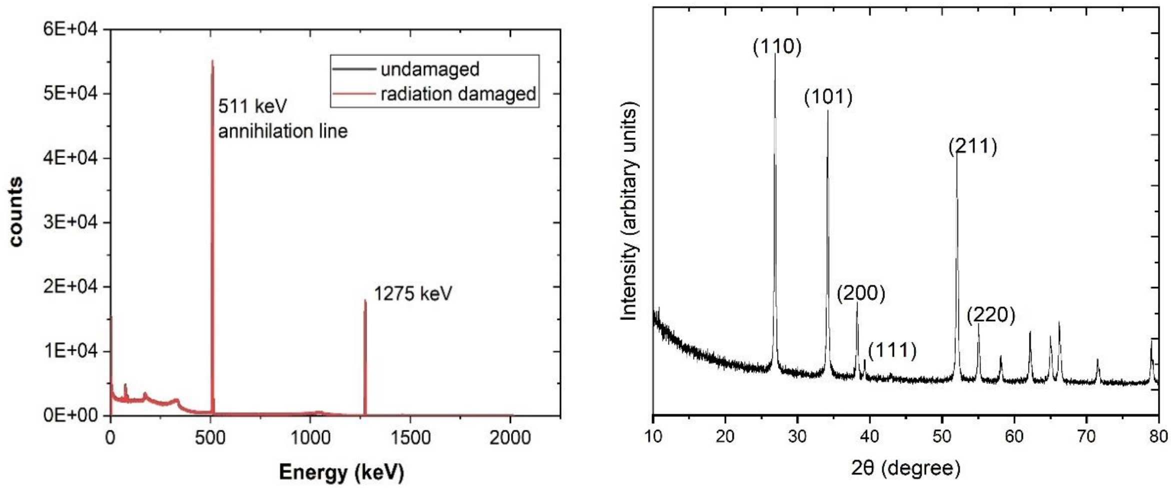

Figure 5: (*left*) Annihilation spectra for unirradiated and irradiated SnO_2 samples. (*right)* XRD confirmation of the structure of SnO_2 after irradiation.

The positron-electron annihilation spectra for unirradiated and irradiated samples are shown in Figure 5. The measure of the density of defects is the S-parameter which is defined as the ratio of the total counts in the centroid (around 511 keV) to the total counts under the annihilation curve. Expanded view for both annihilation curves are shown in Figure 6. Table 1 shows the calculated S-parameters. The calculated annihilation rates using generalized gradient approximation show two lifetime components. The bulk positron lifetime τ_b component for positrons annihilating in a defect-free region. The second component τd refers to the positron lifetime for positrons annihilating with electrons at defect sites. Table 2 shows both lifetime components as well as the average positron lifetime.

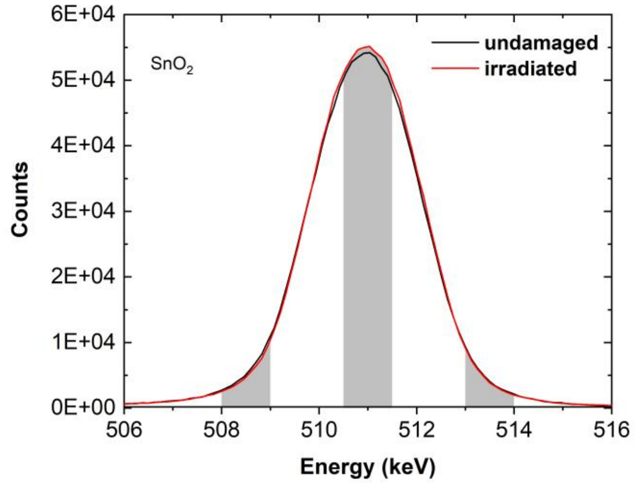

Figure 7. The peak of neutron-irradiated annihilation peak is more pronounced than that of the unirradiated annihilation peak.

	Unirradiated SnO_2	irradiated SnO_2
Centroid area	469999	478720
Total area	1267485	1279038
S-parameter	0.370612	0.374281
W-parameter	0.036882	0.033784

Table 1. The calculated S- and W- parameters from the annihilation curve with its centroid around 511 keV

	LDA	GGA
Bulk	220 ps	241 ps
Defect	246 ps	263 ps
Average	233 ps	252 ps

Table 2. The calculated positron lifetime components using local density approximation (LDA) as well as the generalized gradient approximation (GGA)

The positron lifetime components are derived from the electron-positron annihilation rate given by equation 1 [11-16],

$$\lambda = \pi r_o^2 c \int n_+(r) n_-(r) \gamma(n_-(r)) dr \qquad (1)$$

where r_o is the classical electron radius, n_+ and n_- are the positron and electron densities respectively. γ is the enhancement factor.

Using local density approximation (LDA) the annihilation rates are overestimated especially for low momentum electron-positron annihilations. Figure 7 shows the comparison between LDA and the generalized gradient approximation (GGA) which consider the variational nature of charge density. Table 2 is derived from these values of annihilation rates from core states to defect sites as well as in the bulk.

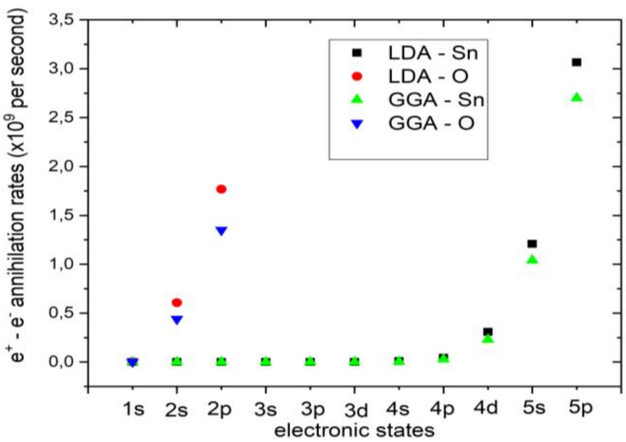

Figure 7. Comparison of positron-electron annihilation rates in individual atoms (Sn and O). The annihilation rates are small in core states but increases with low momentum electrons

The average positron lifetime of 252 ps suggests a vacancy-type defect which is a displacement damage due to the collisions of neutrons with lattice atoms. The cross-section of neutrons with tin is about 124 mb which is not large for any transmutation doping to take place. The concentration of defects, C_v, due to neutron irradiation is given by equation 2 [17],

$$C_v = \frac{N_{at}}{\mu_v \tau_b} \frac{\tau_{av} - \tau_b}{\tau_v - \tau_{av}} \tag{2}$$

where N_{at} is the atomic density of SnO_2, and μ_v is the specific trapping coefficient. τ_{av}, τ_b and τ_v are the average, bulk and vacancy positron lifetimes respectively.

4. Conclusion

The positron annihilation technique which characterizes defects in neutron-irradiated tin oxide in the energy range from 0.223 MeV to 2.23 MeV show that the positrons annihilate at open volume vacancies as well as in the bulk. The change in the S-parameter from 0.370812 (unirradiated SnO_2) to 0.374281 for neutron-irradiated sample clearly shows that the neutrons, in the suitable energy range, can cause displacement damage or vacancies in the sample. The average positron lifetime of 252 ps at in the framework of the generalized gradient approximation clearly indicates the presence open volume vacancy or point defects.

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References

[1] F. Mei, R. Li and T. Yuan, *Tin oxide materials – synthesis, properties and applications,* Elsevier, Chapter 20, pp 579-597, 2020.

[2] J. Huang, B.S. Yan, C.Y. Chen and W.T. Lo, "Ceramic materials for electronic applications," *Ceramic International,* vol 27, no. 3, pp 363-365, 2001

[3] K.J. Saji and A.P. Reena Mary, *ECS Journal of Solid State Science and Technology*, vol 4, no. 9, pp Q101-Q104, 2023

[4] N.A. Pandit and T. Ahmad, "Tin-oxide based hybrid nanostructures for efficient gas sensing," *Molecules,* vol. 27, no. 20, p.7038, 2022

[5] J.F. Mcleer, P.T. Mosely, J.O.W. Norris, D.E. Williams, P. Taylor and B.C. Tofield, *Materials Chemistry and Physics,* vol. 17, no. 6, pp 577-583, 1987

[6] I. Kim, F. Khatkhatay, L. Jiao, G. Swadeney, J. Cole, J. Gan and H. Wang, *Journal of Nuclear Materials, vol.* A20, no 1-3, pp. 143-148, 2012

[7] D.T. Peterson and J.G. Byrne, *Material Science Engineering,* vol. A, no. 110, pp.L27-L29, 1989

[8] M. Yamawaki et. al, *Japan Journal of Applied Physics,* vol. 59, pp 066502-1 – 066502-4, 2020

[9] C. Tobi, Z. Homonnay and K. Suvegh, *Radioanalytical and Nuclear Chemistry,* vol. 332, pp. 2741-2747, 2023

[10] I. Prochazka, *Material Structure,* vol. 8, no. 2, pp. 55-60, 2001

[11] K. Itawa, R. Greaves, T.J. Murphy, M.D. Tinkle and C.M. Surko, *Physical Review A,* vol. A, no. 51, pp. 473, 1995

[12] F. Tuomisto and I. Makkonen, *Rev. Mod. Phys.,* vol. 85, pp. 1583, 2013

[13] J. Slotte et. al., "Direct observations of the vacancy and its annealing in germanium," *Physical Review B,* vol. 83, no. 23, pp. 235212-1 – 235212-5, 2011

[14] C.S. Sundar, *Bulletin of Material Science,* vol. 17, no. 7, pp. 1215-1232, 1994

[15] Y. Dong et. al., *Physical Review B,* vol. 109, pp 104104, 2024

[16] F. Selim, *Material Characterization,* Elsevier*,* vol. 174, pp. 110952, 2024.

[17] X. Hu et.al., *Physical Review B,* vol. 95, pp. 104103, 2017