PALS Measurements and Ab Initio/DFT Calculations for Positron Traps Identification on Zn-Based Nanopowders

Germán N. Darriba, Marcos Meyer, Mario Rentería and Laura C. Damonte

Departamento de Física and Instituto de Física La Plata (IFLP, CONICET La Plata), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CC 67, 1900 La Plata, Argentina

Positron annihilation lifetime spectroscopy (PALS) was applied to study different positron traps induced by mechanical work and doping with Al atoms in three different Zn-based semiconductors (ZnO, ZnSe and ZnTe). The experimental data were complemented by precise theoretical *ab initio* calculations in the framework of the Density Functional Theory (DFT). In this approach, the equilibrium structures of the doped systems (i.e., final atomic positions) were obtained applying the Full-Potential Augmented Plane Wave plus local orbitals (FP-APW + lo) method, embodied in the WIEN2k code. The Multigrid Instead of the K-spAce (MIKA) program was then used to predict the characteristic semiconductor lifetimes at these equilibrium structures. Also, in order to evaluate the effects produced by the structural relaxations on the lifetime, we predict the annihilation lifetimes for the non-relaxed systems. With the aim to elucidate electronic distortions introduced by the different defects (substitutional Al, Zn vacancies) in the semiconductor, the electronic density of states (DOS) was evaluated. The calculations predict that Al substitutes the Zn atom in the ZnO, ZnTe and ZnSe lattices and a zinc vacancy must appear in order to recover the semiconductor character, as suggest the experimental results. The characteristic positron annihilation lifetimes predicted for the doped samples are compared with those experimentally obtained. This combined experimental and theoretical approach helps us to deeper understand the origin and characteristics of different positrons traps.

SAMPLES PREPARATION:

Milled at a Retsch MM2 horizontal vibratory mill, inside a steel cylinder (8 cm^3) with one steel ball, ball to powder weight ratio of 10:1

Al-doped ZnO: Mixtures of ZnO and Al were prepared to obtain a 5, 10 and 30% at. of aluminum in ZnO, labeled as ZOA_5, ZOA_10, and ZOA_30, respectively, at milling times of 1, 4, and 16 h.

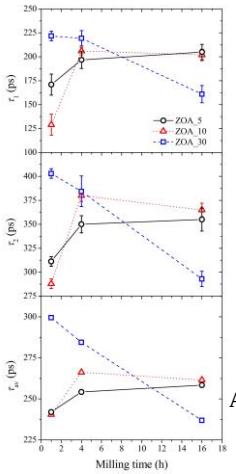
Al-doped ZnSe and ZnTe: Mixtures of ZnSe and ZnTe and Al_2O_3 powders where prepared to obtain 5 at % Al in both compounds, labeled as ZnSe and ZnTe, at milling times of 1, 10 and 30 h. To avoid agglomeration effect on the final product, millings with two surfactants, methanol or $ZnCl_2$, were also done.

CALCULATION DETAILS:

Al-doped ZnO: To simulate the different concentrations of Al impurities and Zn vacancies we used different supercells (SC) containing 2 (2x1x1 SC), 4 (2x2x1 SC), 8 (2x2x2 SC), and 16 (4x2x2 SC) unit cells of ZnO. To simulate the Al-doped ZnO systems we replaced in the 2x1x1, 2x2x1, 2x2x2, and 4x2x2 SCs one Zn atom by an Al one, obtaining 1/4, 1/8, 1/16 and 1/32 cationic dilution, using the notation ZOA(1/4), ZOA(1/8), ZOA(1/16), and ZOA(1/32) for these systems, respectively. Using the 2x2x2 SC and replacing 3 Zn atoms by 3 Al atoms we obtain 3/16 cationic dilution of the Al impurity, called ZOA(3/16). To simulate the Zn vacancies in ZnO we removed one Zn atom in the 2x1x1 SC, 2x2x1 SC, and 2x2x2 SC obtaining 1/4, 1/8, and 1/16 cationic dilution, respectively. And we call these systems as VZn(1/4), VZn(1/8) and VZn(1/16), respectively.

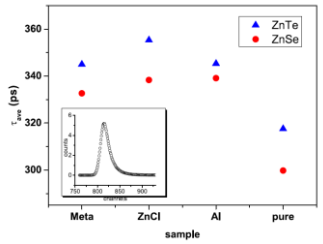
Al-doped ZnSe and ZnTe: To simulate the different concentrations (1/4, 1/8, 1/16 and 1/32) of Al impurities and Zn vacancies we used the unit cell and a 2x2x2 supercell (SC) containing 4 unit cells of ZnSe (ZnSe_AlxZn) or ZnTe (ZnTe_AlxZn).For 1/4 dilution of the Al impurity we replace 1 Zn atom for 1 Al in the unit cell. For the 1/8, 1/16 and 1/32 dilutions we replace 4, 2 and 1 Zn atoms for 4, 2 and 1 Al atoms in the 2x2x2 SC,respectively. Also, we performed calculations replacing one Se atom by one Al atom in ZnSe (ZnSe_AlxSe) and replacing one Te atom by one Al atom in ZnTe (ZnTe_AlxTe). The same criteria but removing Zn atoms instead of replacing by Al atoms, obtaining ZnSe_VZn and ZnTe_VZn. When we generate Zn vacancies in Al-doped systems we call this as ZnSe_AlxZn+ VZn and ZnTe_AlxZn+ VZn

PALS RESULTS



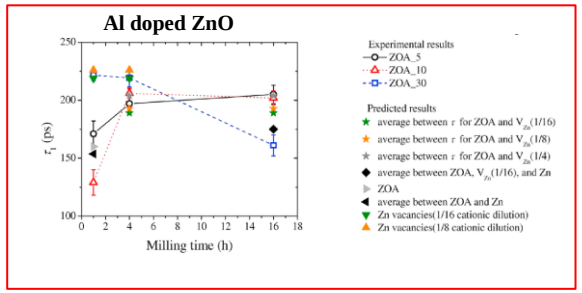
Al doped ZnO

Al doped ZnSe and ZnTe



COMPARISON BETWEEN *Ab Initio* and EXPERIMENTAL RESULTS

Al doped ZnO



CALCULATIONS RESULTS:

Al doped ZnO

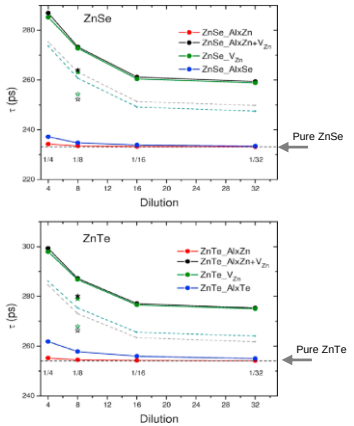
Al-doped	τ(ps) unrelaxed structures	τ(ps) relaxed structures
ZOA (1/32)	158.8	158.6
ZOA (1/16)	158.9	158.0
ZOA (1/8)	159.3	159.8
ZOA (3/16)	159.6	160.4
ZOA (1/4)	159.9	160.5

Does not depend on the substitution of Al by Zn, neither does it depend on the concentration of Al.
τ (ZnO)calc.=158.5 ps ; τ (ZnO)exp.=158.5 ps

Zn Vacancies	τ(ps) unrelaxed structures	τ(ps) relaxed structures
VZn (1/16)	208.9	218.9
VZn (1/8)	215.5	226.8
VZn (1/4)	235.0	248.2

It depends on the concentration of Zn vacancies

Al doped ZnSe and ZnTe



The dotted curves correspond to τ values predicted at relaxed systems
The star correspond to τ values predicted for different Zn vacancies distributions, the closed (open) stars correspond to unrelaxed (relaxed) systems.

SUMMARY and CONCLUSIONS

- ❖ In all Al- doped semiconductors, the positron lifetime is strongly affected by the electronic and the structural distortions introduced by Zn vacancies while it remains practically unperturbed by those introduced by substitutional Al atoms.
- ❖ For Al-doped ZnO and Zn vacancies in ZnO we predicted from first principles the appearance of extended single donor level located at the bottom of the conduction band and a localized double acceptor level located in the top of the valence band, respectively.
- ❖ Shallow positron traps like Se and Te interstitial are suggested to contribute to the first lifetime component.
- ❖The variation in defect dilution confirmed the agglomeration of positron traps that leads to an increase in the second lifetime component.
- ❖ The overall experimental results lead us to conclude that all samples contain great number of defects with sizes larger than a divacancy.
- ❖ PALS measurements combined with state-of-the-art theoretical positron lifetime predictions can give a deeper insight into the different defect complexes and their influence in the structural and electrical properties of doped semiconductors.

EDUCACIÓN PÚBLICA Y GRATUITA

UNIVERSIDAD NACIONAL DE LA PLATA

I F L P CONICET U N L P