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Revealing the nature of defects in α-Ag_2WO_4 by positron annihilation lifetime spectroscopy: A joint experimental and theoretical study

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ABSTRACT

Electron-matter coupling is a fascinating way to tune and modify the properties of materials. In this work, we present a study on the formation and nature of vacancy-like defects in α-Ag_2WO_4 samples synthesized in an aqueous or ethanol medium and subsequently submitted to electron beam irradiation at different exposure times. To understand the effects on the geometrical and electronic nature of the generated defects, the data obtained by positron annihilation lifetime spectroscopy were interpreted with the aid of first-principle calculations at the density functional theory level. To complement these results, X-ray diffraction, Raman spectroscopy, photoluminescence emissions and field emission gun scanning electron microscopy techniques were also used. Based on the positron binding energy and the calculated and experimental positron lifetimes, the defect structure of the non-irradiated and irradiated samples was revealed. As a general feature, it was found that the defect structure is more complex for samples synthesized in ethanol than in water. In particular, the results show that all samples contain defects involving Ag vacancies and that the concentration of this type of defect increases with the irradiation time.

Keywords: α-Ag_2WO_4, point defects, positron annihilation lifetime spectroscopy, DFT calculations.

1. INTRODUCTION

The chemical and physical properties of semiconductors are largely determined by the population of defects, which have attracted continuous attention owing to their significant influence on such properties. Due to the similarity to enzymes, the domain where defects appear in the semiconductor structures can be considered active sites in which reactivity takes place and functionality occurs. At concentrations where defects do not interact with each other, they can be represented by individual electronic states isolated within the band of the host material, whose orbital and spin degrees of freedom can be controlled through the use of electromagnetic fields. However, there are still many challenges to be addressed, and further studies are necessary to unveil the nature and effects of the defects in semiconductors [1–3].

In the field of solid materials, the ideal crystal formed by the periodic replication of unit cells does not exist. In reality, crystals are exposed to lattice vibrations, contain defects and have surface and bulk vacancies, impurities and non-stoichiometric compositions [4–7]. For scientists, the management of the presence of defects, which can be associated with a structural and electronic disorder, may enable the creation of new materials with unique, impossible physical properties for well-ordered crystal structures [8–11]. To understand the nature of the defects and their formation and removal mechanisms in semiconductors constitutes a very challenging topic in materials science [11–13].

Positron annihilation lifetime spectroscopy (PALS) is a well-recognized non-destructive nuclear technique to obtain specific information regarding structural and electronic aspects of open volume defects in solids [14]. The advantages of the use of PALS to study defects lie in the fact that positrons are prone to be localized and annihilated in sites with greater electronic density (i.e. more negative) than the average electronic density of the crystal lattice, allowing positron annihilation processes to take place in these sites, which act as positron traps with an associated specific open volume. In particular, PALS

has demonstrated to be a powerful tool to investigate the presence of vacancy-like defects in semiconductors [15,16]. This technique has also been successfully used to obtain information on the defect structure of monocrystalline and polycrystalline semiconductor metal oxides [17–24]. In fact, vacancies in neutral or negative charge states act as efficient positron traps due to the reduced repulsion of positive ions, while positive vacancies do not trap positrons. On the other hand, it is well documented that multiple vacancies or vacancy clusters are even more effective positron traps than single vacancies. In this case, the charge-state dependence is the same as that described for vacancies. Every time an open volume exists in a defect complex, it appears for the positron as a vacancy-like defect, that is, if a negative ion is bound to a vacancy this defect appears as an effective positron trap. It must be said that the effectiveness of this trap depends on the total charge of the vacancy complex. Under this frame, a neutral pair consisting of a negative ion and a positive vacancy also acts as an effective positron trap with the positron localized inside the vacancy [25].

There has been a growing interest in silver tungstate (α-Ag_2WO_4) due to its unique properties with a wide range of applications in the field of environmental remediation, photocatalysis, etc.[26]. α-Ag_2WO_4 has a crystal lattice composed of distorted [WO_6] and [AgO_y] (y= 2, 4, 6, and 7) clusters acting as lattice building blocks, displaying a complex 3D structure. This distinctive structure is responsible for a wide range of technological applications. From an electronic point of view, the top of the valence band (VB) consists of unique hybridized Ag 4*d* and O 2*p* orbitals, which can leave the top position of the VB and narrow down the band gap. The bottom of the conduction band (CB) comprised of delocalized *s* and/or *p* orbitals presents significant dispersity, which means that it possesses high migration efficiency of photogenerated electrons.[27–29]

With the substantial developments of electron microscopes and their beam sources, the use of transmission electron microscopes is no more limited to materials characterization. Recently, different research studies have focused on the effect of electron beam irradiation (EBI) on the generation of defects since more and more related applications have been unveiled.[30–38] Under EBI, energy is transferred from energetic electrons to both electrons and atomic nuclei in the target materials. In this context, our research group has demonstrated that EBI on materials could be employed for advanced fabrication, modification, and functionalization of α-Ag_2WO_4. Its enhanced performance is strongly dependent on the large anisotropy produced by the complex structure of the α-Ag_2WO_4 oxide, which leads to the generation of defects. [27,29,39-55] Therefore, it is necessary a deep knowledge of the structure, nature and concentration of defects at nano- and sub-nanometric scales resulting from the α-Ag_2WO_4 material modification due to EBI for a rational optimization of their properties and the search for new applications. To the best of our knowledge, a systematic investigation on the type of defects and their nature in α-Ag_2WO_4 provoked by EBI has not been conducted yet.

The main goals of the present work are two-fold: (i) to gain a deeper understanding of the formation process and nature of atomic defects in α-Ag_2WO_4 under EBI as a function of the solvent used for the synthesis of the samples, that is, water (WT) and ethanol (AL). The experimental information on these defects was obtained using PALS as well as X-ray diffraction (XRD) with Rietveld refinements, Raman spectroscopy, photoluminescence (PL) emissions, field emission gun scanning electron microscopy (FEG-SEM); and (ii) to understand the fine effects of the geometrical and electronic nature of the generated defects. For this purpose, first-principle calculations at the

density functional theory (DFT) level were performed to complement and rationalize the experimental PALS results.

This paper contains additional three sections. In the Experimental Section below we report the sample synthesis and characterization as well as the computational methods and model systems employed. In section three we present and discuss the obtained results. Finally, the conclusions are summarized in the final section.

2. EXPERIMENTAL SECTION

2.1. Synthesis. The synthesis of α-Ag_2WO_4 samples was performed by the co-precipitation (CP) method in aqueous (WT) and ethanol (AL) media at 70°C. The details and reagents used followed the description made by Foggi et al. [45]. α-Ag_2WO_4 semiconductor powder was cold-pressed at a pressure of ~ 500 MPa into circular pellets with 5 mm in diameter and ~ 1 mm in thickness.

2.2. EBI. To obtain the materials irradiated with electrons, the pellet samples of α-Ag_2WO_4 were placed in a FE-SEM microscope, model Supra 35-VP (Carl Zeiss, Germany), with an acceleration voltage of 30 kV for 3 (WT3, AL3), 6 (WT6, AL6) and 9 (WT9, AL9) min.

2.3. Characterization. The α-Ag_2WO_4 samples were structurally characterized by XRD using a D/Max-2500PC diffractometer (Rigaku, Japan) with CuKα radiation (λ = 1.5406 Å) in the 2θ range between 10°-110°, at a scan speed of 1°min^{-1} in the Rietveld routine. The Rietveld refinements were performed in the General Structure Analysis System (GSAS) program. Micro-Raman spectra were recorded using the iHR550 spectrometer (Horiba Jobin-Yvon, Japan) equipped with a charge-coupled device (CCD) detector and an argon-ion laser (Melles Griot, USA) operating at 514.5 nm with a maximum power of 200 mW, and a fiber microscope. The morphologies, textures and sizes of the

samples obtained were observed with a FEG-SEM microscope (Supra 35-VP, Carl Zeiss, Germany) operated at 10 kV. PL measurements were performed at room temperature (RT) using a 500M Spex spectrometer coupled to a GaAs PMT. A Kimmon He-Cd laser (325 nm line) with laser power up to 40 mW was used as the excitation source.

2.4. PALS. PALS spectra were obtained using a fast-fast spectrometer with a time resolution of 251 ps in a collinear geometry. A 10 μCi-sealed source of ^{22}NaCl deposited onto two thin Kapton foils (7.5-μm thick) sandwiched between two identical samples was used as a positron source. The spectra were acquired at RT, and typical 1.5-2x10^6 counts per spectrum were collected. The lifetime values reported in this work for each sample are at least an average of ten measurements in the same experimental conditions. After subtracting the background and the source contribution, the PALS spectra were analyzed using the LT10 program [56].

2.5. Computational methods and model systems. First-principles calculations at the DFT level were carried out using the Viena *ab initio* simulation package (VASP) version 5.4.4 [57,58]. The semi-local Perdew-Burke-Ernzerhof [59] exchange and the correlation energy functional within the spin-polarized generalized gradient approximation (GGA) formulation were employed. The Kohn-Sham equations were solved using the projector augmented wave (PAW) method [60], employing the following projectors: Ag ($4d^{10}$,$5s^1$), W ($5p^6$,$5d^4$,$6s^2$), and O ($2s^2$,$2p^4$), where the numbers in parentheses represent the valence states. In the calculation, a Gaussian smearing of 0.01 eV was used, and the atoms were allowed to relax until all forces were smaller than 0.01 eV/A on every atom and the equilibrium volume of crystals was obtained by the minimization of stress tensor through a plane wave cut-off of 834 eV and another of 469 eV to optimize

the atomic force. For the Brillouin zone integration, a *k*-mesh of 1×1×2 for stress tensor and atomic force optimizations were employed.

To obtain the theoretical positron lifetimes (τ) for the bulk and vacancy states in the α-Ag_2WO_4 structure, calculations were performed according to Macchi et al. [61]. The positron parameters were calculated using DFT within the so-called standard scheme [62]. The positron wave functions, the parameters τ and the positron binding energy (E_b) were obtained through the Doppler program included in the MIKA package [63], considering as an input parameter the electron density calculated by VASP.

The positron binding energy is defined as the difference between the ground energy E_0 of the delocalized positron and the energy of the positron trapped in the considered defect (E_d):

$$E_b = E_0 - E_d \quad \text{(Eq. 1)}$$

This energy indicates the energy gained for a positron trapped in a specific defect. A positive sign for E_b indicates that the considered defect acts as a positron trapping center.

To get positron parameters, it is necessary to calculate the electron-positron correlation potential. To this end, the local density approximation (LDA) was considered by employing the parameterization proposed by Boronski and Nieminen [64]. Such parameterization was corrected to take into account the incomplete positron screening [62], in which the value of the high-frequency dielectric constant was measured as follows: *ad-hoc* (ε_∞= 17.6).

To model the orthorhombic α-Ag_2WO_4 structure, we used the relaxed cell previously described[65]. A supercell of 672 atoms (2 × 2 × 3 repetitions of the relaxed cell) was used to calculate the positron lifetimes in the different defect states, considering different supercells containing: i) an oxygen monovacancy (V_O); ii) a tungsten monovacancy (V_W

); iii) a silver monovacancy (V_{Ag}); iv) a divacancy constituted by silver and oxygen ($V_{Ag} + V_O$); v) a trivacancy formed by one silver vacancy and two oxygen vacancies ($V_{Ag} + 2V_O$); and finally, a hexavacancy containing two silver and four oxygen vacancies ($2V_{Ag} + 4V_O$). In the present work, different oxygen vacancies were modeled by removing an O atom from the different clusters that are the building blocks of the α-Ag_2WO_4 crystal structure ([WO_6] and [AgO_x] (x = 2, 4, 6 and 7) clusters). The V_W was created by removing a W atom from the [WO_6] cluster located near the center of the supercell. In the case of four non-equivalent V_{Ag} belonging to the different [AgO_x] clusters (x = 2, 4, 6 and 7), an Ag atom at each of the four possible [AgO_x] clusters was removed. Additionally, for each V_{Ag} different vacancies were modeled by removing one or two oxygen atoms that are the nearest neighbors to each V_{Ag} in order to form a divacancy or a trivacancy ($V_{Ag} + V_O$ and $V_{Ag} + 2V_O$, respectively). To form a hexavacancy, two adjacent trivacancies ($V_{Ag} + 2V_O$) were considered.

As a first approach, a further relaxation of the defective structures was not taken into account for all calculations. Besides, all defect states were considered in their neutral states. It is worth mentioning that for different semiconductors the calculated positron lifetimes for defects in the negative charge states are always slightly shorter (between ~2% and ~8%, depending on the considered negative charge state) than those determined for the same semiconductor containing defects in its neutral states [66,67].

3. RESULTS AND DISCUSSION

3.1. X-Ray Diffraction. XRD analysis was performed in order to understand the structural order/disorder of the materials at long range (periodicity and organization) in relation to the solvent (WT and AL) used and its subsequent modification by EBI. **Fig. SI-1** (see Supporting Information) shows the corresponding XRD patterns. According to

the analysis of the results, all samples correspond to α-Ag_2WO_4 with orthorhombic structure and *Pn*2*n* space group, which is in accordance with the crystallographic record No. 248969[68] in the *Inorganic Crystal Structure Database* (ICSD). All samples have well-defined peaks, which are associated with a high degree of long-range order. No additional peaks were observed, demonstrating that the pure α-Ag_2WO_4 phase was obtained in both solvents and also after modification by EBI.

The lattice parameters (*a*, *b* and *c*) as well as the cell volume (v), full width at half maximum (FWHM) and reliability parameters (R_{wp}, R_p, χ^2) was obtained by Rietveld refinements and are shown in **Figure SI-2** and **Table SI-1**. The reliability parameters obtained in the Rietveld refinement indicate that the results have a high degree of quality. It was observed that for the samples synthesized in WT or AL and subjected to EBI, there was an increase in the values of the lattice parameters and unit cell volume. These changes can be directly related to the FWHM of the main α-Ag_2WO_4 diffraction peak (231) at 2θ = 32°. According to **Table SI-1**, the FWHM increases with the EBI time, causing the appearance of a more disordered system.[39]

3.2. Micro-Raman Spectroscopy. According to our group's theory, the orthorhombic α-Ag_2WO_4 structure belongs to the C_{2v}^{10} symmetry group, which has 21 active Raman modes from the decomposition point Γ = ($6A_{1g}$ + $5A_{2g}$ + $5B_{1g}$ + $5B_{2g}$). Although all 21 modes are active in Raman, in this case only 9 of them can be observed (see **Fig. SI-3**) due to the overlapping of some modes as well as the high degree of disorder of the systems at short range. Previous results [44] point out that the vibrational modes located at 106 and 317 cm^{-1} are related to [AgO_x] clusters (x = 2, 4, 6, and 7), while the vibrational modes located between 600 and 1000 cm^{-1} refer to the O-W-O bending angles and W-O stretching bonds of the [WO_6] clusters [28].

3.3. Field Emission Gun Scanning Electron Microscopy. The morphologies, particle sizes and textures of all prepared pellet samples of α-Ag_2WO_4 (WT and AL) were investigated by FE-SEM, and the results are presented in **Fig. SI-4**. It was observed that both WT (**Fig. SI-4(A)**) and AL (**Fig. SI-4(B)**) samples have rod-like morphology with hexagonal shape and (001), (010) and (101) exposed surfaces. From the analysis of the results (see **Fig. SI-5),** the average length and width of the rods of the WT sample are 0.37 ± 0.13 and 0.13 ± 0.10 μm, respectively, while for the AL sample the corresponding values are 0.66 ± 0.17 and 0.27 ± 0.13 μm.

Fig. 1 shows the behavior of the WT (**Figs. 1(A)** to **1(D)**) and AL (**Figs. 1(E)** to 1**(H)**) pellets under EBI at voltage of 30 kV for 0, 3, 6 and 9 min. We noted that the exposure to the electron beam generates the delocalized growth of some metallic Ag particles on the surface of α-Ag_2WO_4. This phenomenon was reported in previous studies, and it is due to the reduction of the Ag^+ cation at both [AgO_2] and [AgO_4] clusters, thus generating Ag metal nanoparticles on the semiconductor surface[28,29,46,48,50,69,70].

<**Figure 1**>

Figure 1. FE-SEM of WT samples irradiated for **(A)** 0, **(B)** 3, **(C)** 6 and **(D)** 9 min, and AL samples irradiated for **(E)** 0, **(F)** 3, **(G)** 6 and **(H)** 9 min.

3.4. Photoluminescence

PL measurements provide important information about the structural defects in the crystal lattice. **Fig. SI-6** exhibits the PL spectra of α-Ag_2WO_4 samples at room temperature with laser excitation at 325 nm. The behavior of the PL spectra is associated with multiphonon processes, where the relaxation of electron momentum occurs by several paths with the participation of various energy intermediate states

within the forbidden band gap region [71–73]. The spectra arise from the octahedral [WO_6] and [AgO_x] (x = 2, 4, 6 and 7) clusters, with maximum emission centered in the blue-green region at 449 nm[28,45,65,74]. The luminescence mechanism of these materials is assigned to the charge transfer within the [WO_6] clusters, from the 2*p* orbital of O atom and 4*d* orbital of Ag atom of the VB to the 5*d* orbital of the W atom of the CB. Moreover, it is known that a modified crystal lattice, i.e. a lattice with increased structural defect density, also favors the emission in the blue-green region, which is more energetic.[28,75] In particular, the PL emissions can be associated with the electronic transitions from the $^1A_1$ ground state to the $^1T_2$ excited state corresponding to the octahedral [WO_6] cluster [73,76]. In order to understand the PL behavior of all samples, the PL spectra were deconvoluted to investigate the contributions of the individual components using a Voigt function and considering the peak positions and their respective areas, as seen in **Fig. SI-6**. For all samples, the spectra were decomposed into two components centered at 450 and 490 nm, contributing to the blue and green colors of the visible spectrum, respectively (see **Fig. 2**).

<**Figure 2**>

Figure 2. Percentages of PL deconvolution components for samples located at **(A)** 450 and **(B)** 490 nm as a function of EBI time.

After the deconvolution process, the contribution of the band centered at 450 nm slightly decreases, while the band centered at 490 nm increases. This can be related to structural defects (shallow defects) of the band located at shorter wavelengths and vacancy defects (deep defects) of the band at longer wavelengths, revealing an increase in the number of vacancies as a function of EBI exposure time. Besides that, it was

observed that the increased number of defects is more pronounced in the AL than the WT synthesized samples.

3.5. PALS Measurements

From the spectra decomposition, several lifetime components could be obtained, being each of them characterized by a lifetime τ_i and having an associated intensity I_i. The state *i* can be delocalized in the crystal lattice (bulk state), or localized at different defect sites in which positrons become trapped and annihilated. In this last case, the value of the positron lifetime reflects the size of the open volume associated with the defect in which positrons are annihilated. Increased lifetime values indicate that positrons become trapped in bigger open volumes.

All PALS spectra obtained in the present work were satisfactorily fitted considering three lifetime components. Initially, a free constraint fitting analysis showed the presence of an almost constant long-lived lifetime, τ_3=1800±100 ps, usually assigned to the ortho-Positronium (o-Ps) annihilation via the pick-off process. Then, a second analysis was carried out fixing this component at 1800 ps. As a result, a small value of intensity associated with τ_3 (I_3 < 2%) was obtained, indicating that the powder compression process used to fabricate the pellets was good enough to produce well-compacted samples. It is worth mentioning that this long lifetime component related to the small value of I_3 was not considered for further discussions. I_1 and I_2 were then normalized to 100%.

On the other hand, α-Ag_2WO_4 microcrystals present a particle size higher than the typical positron diffusion length, L_+~100 nm, in solids.[14] In this scenario, it was assumed that almost all positrons are annihilating in defects located inside the grains (*i.e.* intragranular defects). Values of the positron lifetime parameters obtained from the

decomposition of the PALS spectra measured on samples synthesized in WT and AL solvents are reported in **Tables 1** and **2**, respectively.

Table 1. Values of positron lifetimes and their associated intensities obtained from the decomposition of PALS spectra for α-Ag_2WO_4 microcrystalline WT samples irradiated and non-irradiated at different times.

<**Table 1**>

Table 2. Values of positron lifetimes and their associated intensities obtained from the decomposition of PALS spectra for α-Ag_2WO_4 microcrystalline AL samples irradiated and non-irradiated at different times.

<**Table 2**>

First-principles calculations are extremely useful for the interpretation and rationalization of the experimental results of PALS measurements. The calculated positron lifetimes and the corresponding binding energies of the supercell containing different vacancy-like defects are presented in **Table 3**.

Table 3. Values of positron lifetimes, τ, and binding energy, E_b, for different positron defect states in the α-Ag_2WO_4 structure.

<**Table 3**>

From the analysis of the calculated E_b values reported in **Table 3**, we can infer that independently of the type of cluster from which one oxygen atom was extracted, V_O can hardly trap positrons even in its neutral charge state. This behavior is due to the

delocalization of the positron wavefunction. This effect can be seen in **Fig. 3(A)**, where it is possible to visualize a positron wavefunction isodensity plot calculated for V_O created between two clusters (one [WO_6] and one [AgO_4]). On the contrary, cation vacancies such as V_W and V_{Ag} act as effective positron traps, which is in good agreement with the results reported in the literature for semiconducting oxides.[15,17,18] The cationic vacancy V_W is not a deep positron trap since its binding energy is small when compared to that calculated for d V_{Ag} in different cluster structures, that is, ~0.1 eV *versus* ~0.6 eV. In **Table 3**, it can also be seen that the positron lifetime for V_W = 178 ps is barely 4% higher than that calculated for the α-Ag_2WO_4 bulk of the supercell (τ_b = 172 ps). This behavior can be attributed to a weak localization of the positron wavefunction in the defect, according to the isodensity plot in **Fig. 3(B)**. As observed, the positron wavefunction is mostly localized in the interstitial space near the missing W atom. In the case of the cationic vacancy V_{Ag}, remarkable changes in the calculated positron parameters are not sensed, except for the V_{Ag} at the [AgO_6] cluster. In particular, when an Ag atom is extracted from an [AgO_2] cluster, there is a strong increase in the positron lifetime with respect to τ_b, resulting in a calculated positron lifetime approximately 33% higher than τ_b and a positron binding energy of 0.6 eV. If V_{Ag} occurs at the [AgO_7] or [AgO_4] cluster, the corresponding τ and E_b values are slightly smaller than those obtained for the same vacancy created in an [AgO_2] cluster. Conversely, for a V_{Ag} created in an [AgO_6] cluster, more significant changes in the positron parameters can be obtained, which are reflected in a strong localization of the positron wavefunction within the empty space left by the missing Ag atom. As an example, **Figs. 3(C)** and **3(D)**, display positron wavefunction isodensity plots calculated for the monovacancy states characteristic of a V_{Ag} created inside [AgO_4] and [AgO_2] clusters, respectively.

<Figure 3>

Figure 3. Positron wavefunction isodensities calculated for monovacancy states: **(A)** a V_O created between one [WO_6] and one [AgO_4] clusters; **(B)** a V_W created inside a [WO_6] cluster; **(C)** a V_{Ag} formed inside an [AgO_4] cluster; and **(D)** a V_{Ag} created within an [AgO_2] cluster. The positron isodensities are represented by three surface contours, which correspond to 70%, 50% and 30% of the maximum positron density. For the sake of clarity, only the participating clusters are shown in the figures. W atoms are represented in red, Ag atoms in blue and O atoms in dark gray. Missing atoms related to the different monovacancies are labeled.

On the other hand, when oxygen vacancies are aggregated to a V_{Ag} to form different Ag-O vacancy complexes (*i.e.*, one V_{Ag} complex with one or more oxygen vacancies), the related positron lifetimes are higher than those calculated for the positron annihilated in a V_{Ag} (~10% and ~ 20% for Ag-O divacancy and Ag-O trivacancy, respectively), meaning that these complexes are deeper positron traps. **Figs. 4(A)**, **4(B)** and **4(C)** display positron wavefunction isodensity plots calculated for the vacancy complexes representing a $V_{Ag} + V_O$ divacancy created inside an [AgO_2] cluster, a $V_{Ag} + 2V_O$ trivacancy corresponding to the whole missing [AgO_2] cluster, and a $V_{Ag} + 2V_O$ trivacancy formed inside an [AgO_4] cluster, respectively. In the case of V_{Ag}, the positron wavefunction is strongly localized inside the Ag vacancy and the corresponding positron wave function isodensities are slightly affected by the presence of V_O. Finally, important changes in the positron parameters regarding the $2V_{Ag} + 4V_O$ hexavacancy were observed. We could note that the presence of a second d V_{Ag} reduces the positron lifetime and the corresponding $E_b$values, strongly modifying the positron wavefunction,

according to the isodensity plot presented in **Fig. 4(D)**, where it is possible to see the positron localized between two Ag vacancies.

<**Figure 4**>

Figure 4. Positron wavefunction isodensities calculated for vacancy complexes: **(A)** a $V_{Ag} + V_O$ divacancy created inside an [AgO_2] cluster; **(B)** a $V_{Ag} + 2V_O$ trivacancy corresponding to the whole missing [AgO_2] cluster; **(C)** a $V_{Ag} + 2V_O$ trivacancy formed inside an [AgO_4] cluster; and **(D)** a $2V_{Ag} + 4V_O$ hexavacancy created between an [AgO_2] cluster and a neighboring [AgO_7] cluster. The positron isodensities are represented by three surface contours, which correspond to 70%, 50% and 30% of the maximum positron density within the contour. For the sake of clarity, only the participating clusters are shown in the figures. W atoms are represented in red, Ag atoms in blue and O atoms in dark gray. Missing atoms related to the different monovacancies forming the vacancy complexes are labeled.

Based on the lifetime values obtained by first-principles calculations, the experimental results reported in **Tables 1 and 2** can be rationalized as follows:

- <u>For the WT samples:</u> The shortest lifetime τ_1 is always lower than the calculated τ_b. In such a case, τ_1 must be considered as a reduced bulk lifetime due to positron annihilation in intragranular defects characterized by the second lifetime component. Therefore, the relevant information linked to vacancy-like defects can be obtained from τ_2 and I_2. For the non-irradiated sample, τ_2 = 274±2 ps and I_2 ~73%. Taking into account the calculated positron lifetimes reported in **Table 3**, the experimental τ_2 value can be interpreted as the result of positron annihilations in Ag-O vacancy complexes. Specifically, positron traps have a size distribution around a mean value equivalent to

that formed by two oxygen vacancies surrounding one silver vacancy ($V_{Ag} + 2V_O$). Besides, the elevated I_2 value indicates a high concentration of this kind of defect in the non-irradiated sample. When the EBI exposure time increases, the τ_2 values decrease from 274 to 263 ps, while the associated I_2 values increase from ~73% to ~80%. The change in the positron lifetime can be assigned to a progressive decrease in the concentration of Ag-O vacancy complexes (greater than $V_{Ag} + 2V_O$) with a consequent increase in the concentration of a smaller type of vacancies such as V_{Ag} and $V_{Ag} + V_O$. It is worth mentioning that the I_2 increases reflect an increment of the total concentration of defects related to silver vacancies.

- For the AL samples: The interpretation of the experimental positron lifetimes reported in **Table 2** requires a different sequence when compared with the results obtained for the irradiated and non-irradiated WT samples. First, all τ_2 and I_2 values are respectively higher and lower than those obtained for the WT samples. Regarding the τ_2 experimental value, it is higher than the maximum theoretical lifetime calculated for the different defect states listed in **Table 3**. As a consequence, it must be assumed that positrons are annihilated in vacancy complexes (VC) containing Ag vacancies (*Ag-VC*) with an associated open volume larger than that of a $2V_{Ag} + 4V_O$ hexavacancy. In order to obtain higher theoretical positron lifetimes, it is necessary to build more complex structures of vacancy clusters that should be associated with real defects. For our calculations, we tried to avoid building defects that could be hardly interpreted in terms of a feasible defect structure. On the other hand, increased EBI exposure times decrease the systematic τ_2, which in turn is correlated with a strong increase of I_2. This behavior could be interpreted as a progressive decrease in the VC concentration with a consequent increase in the concentration of Ag-O vacancy complexes having an equivalent mean size between a $V_{Ag} + 2V_O$ trivacancy and a $2V_{Ag} + 4V_O$ hexavacancy.

As it can be seen in **Table 2**, when the irradiation times increase, the τ_1 and I_1 values systematically decrease from ~219 to ~178 ps and from ~61% to ~25%, respectively.

To simplify the interpretation of the PALS results obtained for the AL samples, the data obtained by measuring the samples submitted to the maximum EBI time (9 min) are firstly presented and discussed. At this irradiation time, the experimental τ_1 value is, within the error bars, equal to the calculated lifetime τ_b, and its associated intensity is non-negligible (I_1~25%). Consequently, it can be concluded that a shorter lifetime is an average positron lifetime, resulting from the contributions of the reduced bulk positron lifetime and those coming from positron annihilations in V_{Ag}. Thus, in terms of the theoretical positron lifetimes reported in **Table 3**, by decreasing the EBI exposure times the τ_1 tends to increase, which can be mainly assigned to a significant and systematic increase in positron annihilability in V_{Ag}.

4. CONCLUSIONS

Information on the type and concentration of defects and the localization of their electronic levels in the semiconductor oxides is critical to design materials with specific characteristics to be used in different technological applications. In particular, it is essential to understand the changes in the structural defects at nano- and sub-nanometric scales as a consequence of the modification of materials due to EBI.

A detailed analysis based on the results obtained by positron annihilation lifetime spectroscopy together with the theoretical positron lifetime values calculated using first-principle calculations at the DFT level made it possible to establish the nature of vacancy-like defects in both pure α-Ag_2WO_4 samples and those submitted to EBI. The PL measurements revealed that the increase of EBI exposure time induces a progressive change in the defect structure from shallow vacancy defects to deep ones.

The main conclusions of the present work can be summarized as follows: i) for non-irradiated α-Ag_2WO_4 samples synthesized in water, the defects are mainly composed of a high concentration of Ag-O vacancy complexes with a mean size equivalent to a trivacancy formed by two V_O surrounding one Ag vacancy; (ii) the defects in the non-irradiated α-Ag_2WO_4 samples synthesized in ethanol mainly comprise an Ag vacancy complemented with a non-negligible concentration of vacancy clusters containing three or more V_{Ag}; (iii) in the irradiated samples synthesized in water, we observed that an increase of the EBI exposure times causes a larger progressive decrease in the concentration of Ag-O vacancy complexes than a trivacancy with concomitant increase in the concentration of V_{Ag} and Ag-O divacancies. In addition, a slight increase in the total concentration of defects related to V_{Ag} was detected. In these samples, the irradiation induced the formation of new small Ag-related defects; finally, (iv) for the irradiated samples synthesized in ethanol, the increase of irradiation times induces a progressive decrease in the concentration of vacancy clusters containing Ag vacancies with concomitant formation of an important number of Ag-O vacancy complexes bigger than a $V_{Ag} + 2V_O$ trivacancy.

The present results have provided a complete defect structural description of pure α-Ag_2WO_4 semiconductor under EBI that would contribute to the better control of its tunable response. It is not only related to the formation of quantum dots, which confine the electrons at the Ag vacancy centers, but also provides unambiguous physical meaning on the nature of defects generated by EBI. The knowledge gained by this study can allow engineers to incorporate new functionalities into Ag_2WO_4-based semiconductor devices.

CONFLITS OF INTEREST

There are no conflicts to declare.

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FIGURES AND TABLES

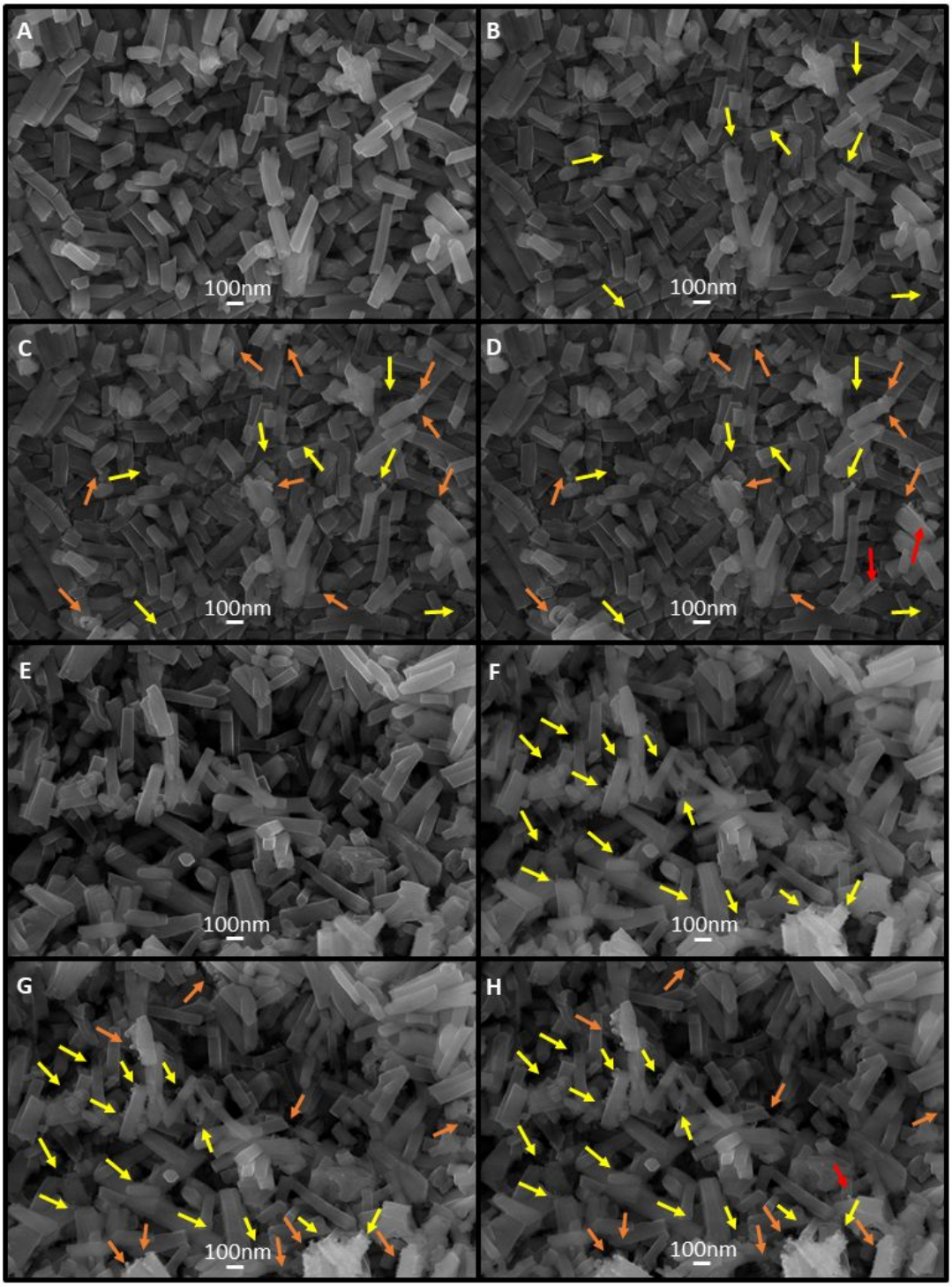

Figure 1. FE-SEM of WT samples irradiated for **(A)** 0, **(B)** 3, **(C)** 6 and **(D)** 9 min, and AL samples irradiated for **(E)** 0, **(F)** 3, **(G)** 6 and **(H)** 9 min.

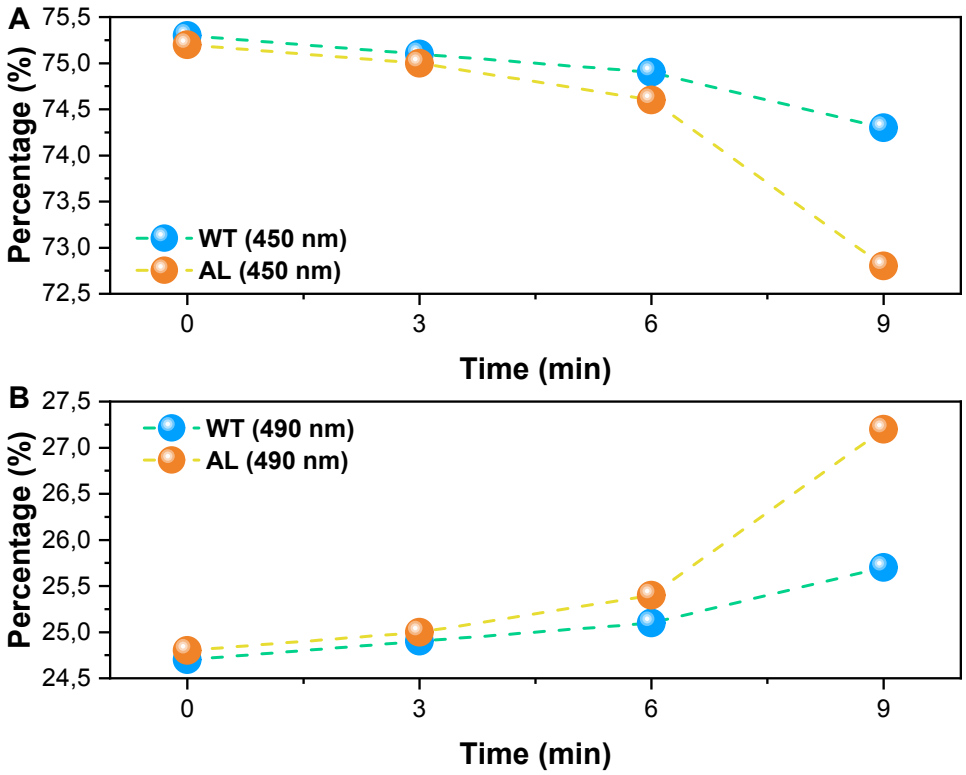

Figure 2. Percentages of PL deconvolution components for samples located at **(A)** 450 and **(B)** 490 nm as a function of EBI time.

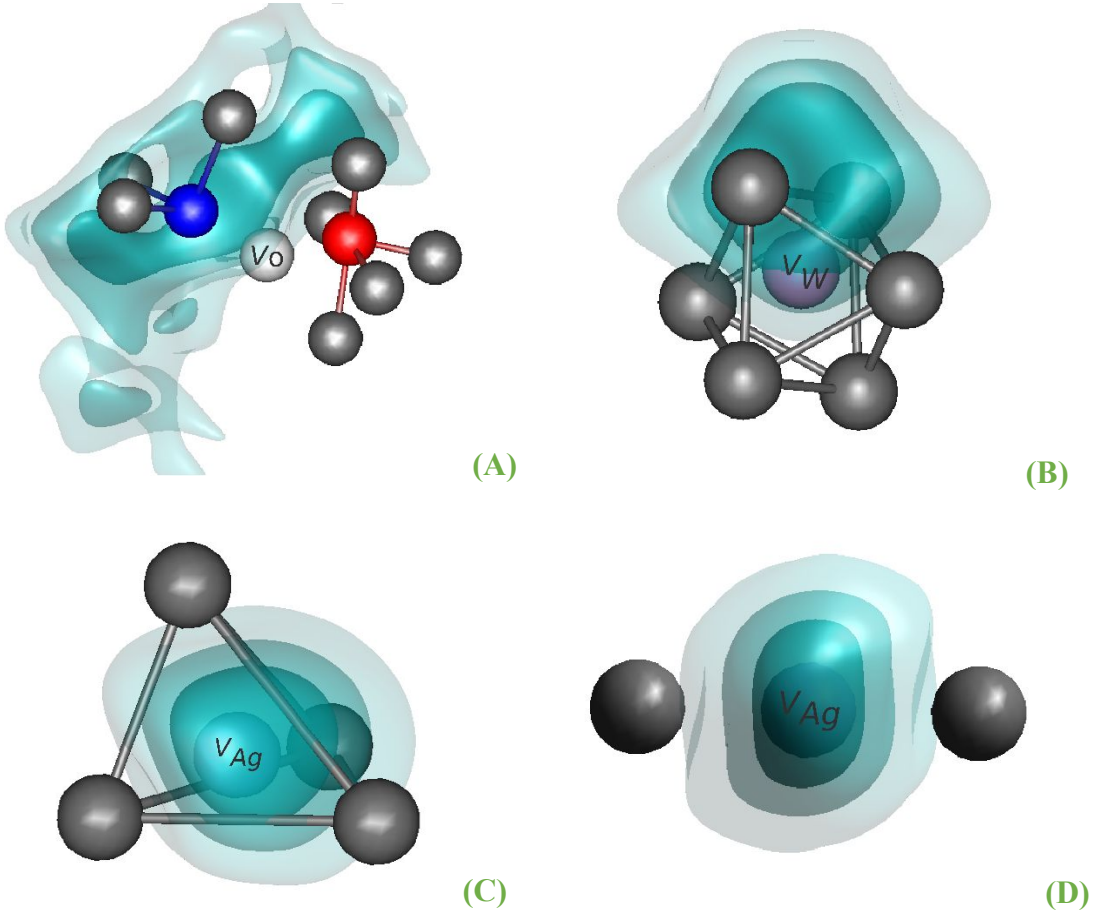

Figure 3. Positron wavefunction isodensities calculated for monovacancy states: **(A)** a V_O created between one [WO_6] and one [AgO_4] clusters; **(B)** a V_W created inside a [WO_6] cluster; **(C)** a V_{Ag} formed inside an [AgO_4] cluster; and **(D)** a V_{Ag} created within an [AgO_2] cluster. The positron isodensities are represented by three surface contours, which correspond to 70%, 50% and 30% of the maximum positron density. For the sake of clarity, only the participating clusters are shown in the figures. W atoms are represented in red, Ag atoms in blue and O atoms in dark gray. Missing atoms related to the different monovacancies are labeled.

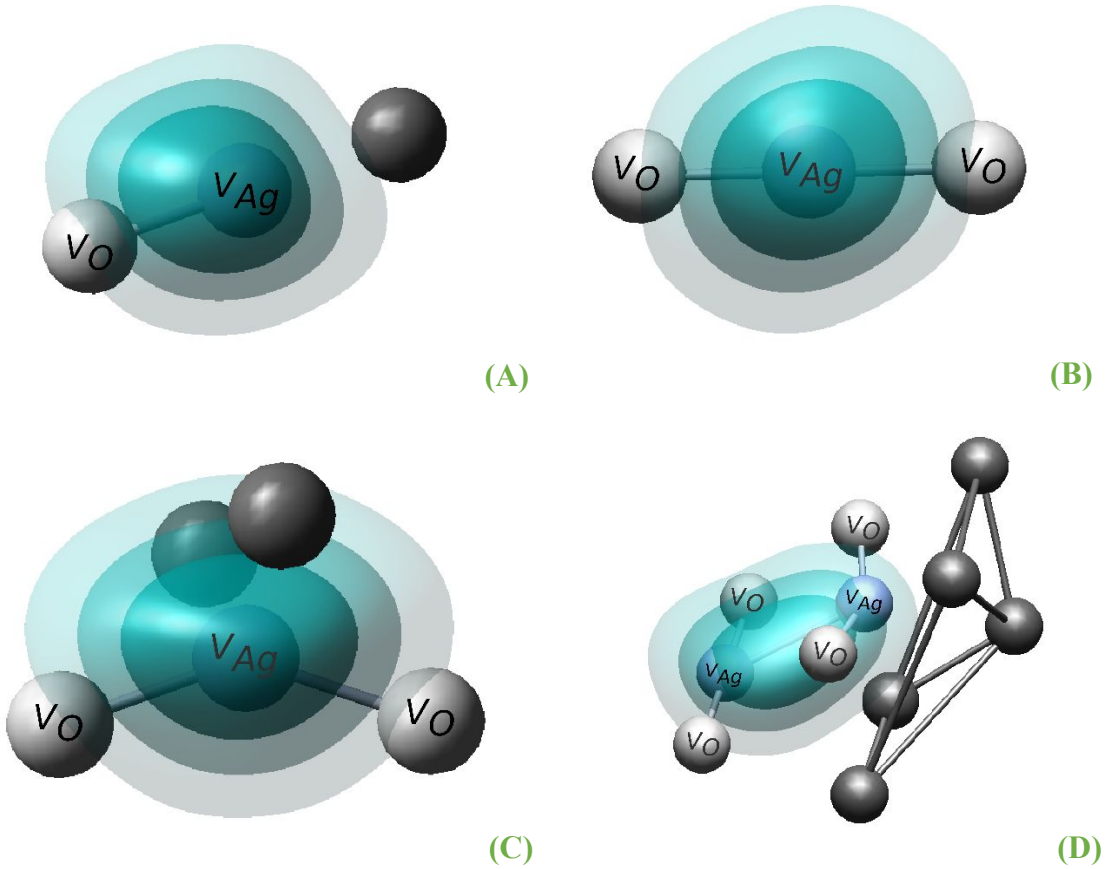

Figure 4. Positron wavefunction isodensities calculated for vacancy complexes: **(A)** a $V_{Ag} + V_O$ divacancy created inside an [AgO_2] cluster; **(B)** a $V_{Ag} + 2V_O$ trivacancy corresponding to the whole missing [AgO_2] cluster; **(C)** a $V_{Ag} + 2V_O$ trivacancy formed inside an [AgO_4] cluster; and **(D)** a $2V_{Ag} + 4V_O$ hexavacancy created between an [AgO_2] cluster and a neighboring [AgO_7] cluster. The positron isodensities are represented by three surface contours, which correspond to 70%, 50% and 30% of the maximum positron density within the contour. For the sake of clarity, only the participating clusters are shown in the figures. W atoms are represented in red, Ag atoms in blue and O atoms in dark gray. Missing atoms related to the different monovacancies forming the vacancy complexes are labeled.

Table 1. Values of positron lifetimes and their associated intensities obtained from the decomposition of PALS spectra for α-Ag_2WO_4 microcrystalline WT samples irradiated and non-irradiated at different times.

Irradiation time (min)	τ_1 *(ps)*	I_1 *(%)*	τ_2 *(ps)*	I_2 *(%)*
0	172 ± 1	24.7 ± 0.5	274 ± 2	72.6 ± 0.5
3	156 ± 3	24.9 ± 0.5	274 ± 2	75.1 ± 0.5
6	154 ± 2	21.0 ± 0.5	271 ± 1	79.0 ± 0.5
9	141 ± 1	20.0 ± 0.5	263 ± 1	80.0 ± 0.5

Table 2. Values of positron lifetimes and their associated intensities obtained from the decomposition of PALS spectra for α-Ag_2WO_4 microcrystalline AL samples irradiated and non-irradiated at different times.

Irradiation time (min)	τ_1 *(ps)*	I_1 *(%)*	τ_2 *(ps)*	I_2 *(%)*
0	222.1 ± 0.6	61.4 ± 0.5	345 ± 2	38.6 ± 0.5
3	214.4 ± 0.5	50.8 ± 0.5	324 ± 2	49.2 ± 0.5
6	204.4 ± 0.5	39.0 ± 0.5	299 ± 1	61.0 ± 0.5
9	182.7 ± 0.5	24.8 ± 0.5	286 ± 1	75.2 ± 0.5

Table 3. Values of positron lifetimes, τ, and binding energy, E_b, for different positron defect states in the α-Ag_2WO_4 structure.

Cluster	***Defect state***	***τ (ps)***	E_b ***(eV)***
bulk	-	172	-
[WO_6], [AgO_x] (x = 2, 4, 6 and 7)	V_O	173	~ 0
[WO_6]	V_W	178	0.1
[AgO_2]	V_{Ag}	230	0.6
	$V_{Ag} + V_O$	255	0.8
	$V_{Ag} + 2V_O$	275	1.0
[AgO_4]	V_{Ag}	225	0.6
	$V_{Ag} + V_O$	250	0.8
	$V_{Ag} + 2V_O$	265	0.9
[AgO_6]	V_{Ag}	204	0.4
	$V_{Ag} + V_O$	223	0.5
	$V_{Ag} + 2V_O$	239	0.7
[AgO_7]	V_{Ag}	227	0.6
	$V_{Ag} + V_O$	250	0.8
	$V_{Ag} + 2V_O$	264	0.9
-	$2V_{Ag} + 4V_O$	311	1.2

TOC