Room temperature sintering of polar ZnO nanosheets: II-Mechanism

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Abstract

In a previous work by the authors (A. Fernández-Pérez *et al.*, *Room temperature sintering of polar ZnO nanosheets: I-Evidence, submitted, 2017, DOI: 10.1039/C7CP02306E*) polar ZnO nanosheets were stored at room temperature under different atmospheres and the evolution of their textural and crystal properties during storage was followed. It was found that the specific surface area of the nanosheets drastically decreased during storage, with a loss of up to 75%. The ZnO crystals increased in size mainly through the partial merging of their polar surfaces at the expense of the narrow mesoporosity, in a process triggered by the action of moisture, oxygen and, in their absence, light. In the present work, a set of spectroscopic techniques (FTIR, Raman and XPS) has been used in an attempt to unravel the mechanism behind this spontaneous sintering process. The mechanism starts with the molecular adsorption of water, which takes place on Zn atoms close to oxygen vacancies on the (100) surface, where H₂O dissociates to form two hydroxyl groups and to heal one oxygen vacancy. This process *triggers* the room temperature migration of Zn interstitials towards the outer surface of the polar region. What were previously interstitial Zn atoms now gradually occupy the mesopores, with interstitial oxygen being used to build up the O sublattice until total occupancy of the narrow mesoporosity is achieved.

Keywords: ZnO, polar nanosheets, specific surface area, FTIR, XPS, Raman, mechanism

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Introduction

In the first part of this work [1] it was concluded that polar ZnO nanosheets of high specific surface area ($\sim 120 \text{ m}^2/\text{g}$) lost up to 75% of their specific surface area in about two months during their storage in closed transparent polypropylene vials kept under the light of the laboratory on worktop tables. Loss of surface area occurred in parallel with the growth of nanocrystals, mainly by the partial merging of their polar surfaces at the expense of the small mesopores ($\sim 5 \text{ nm}$ pore size) initially present in the nanosheets. No increase or decrease in weight was detected during the process. Under a gas flow, the highest loss of specific surface after 4 days occurred in moist air (with or without light), $\sim 41\%$; followed by a moist CO_2 -free atmosphere (with or without light and/or oxygen), $\sim 32\%$; then a dry CO_2 -free oxygen-based atmosphere (with or without light), $\sim 21\%$; next a dry inert atmosphere with light, $\sim 15\%$; and finally a dry inert atmosphere in darkness, $\sim 5\%$. In the present work we attempt to relate the changes in specific surface area with variations in surface properties by means of different techniques (TEM, FTIR, Raman and XPS). As with several other properties of ZnO nanostructures, such as photocatalytic activity [2], concentration of defects [3-5], hydroxyl coverage [3, 4], etc., which are related to overall polarity, we will prove in this work that changes in specific surface area during atmospheric storage are also dependent on ZnO polarity. Based on the analytical results obtained, a mechanism for the room temperature sintering of polar ZnO is finally proposed.

Experimental

Samples

The preparation of the samples has been described in the first part of this work [1]. Two samples, denominated ZnO-M and ZnO-P, are analyzed in this work [1]. ZnO-M (stainless steel wire mesh-supported ZnO) consists of eminently polar nanosheets, with a polycrystalline appearance, that are

aligned normal to the wire mesh surface, as shown in Figure 1A in [1]. The (100) non-polar facets of the crystals forming the edges of the nanosheets are preferentially exposed. ZnO-P consists of groups of ZnO nanosheets that were gently scratched from the wire mesh surface with a brush and then disaggregated in a mortar. This material consists of both nanosheets and the more amorphous material connecting the nanosheets with the wire mesh. All this particulate material becomes randomly oriented when deposited on a holder (Figure 1B in [1]), where the (002) polar surfaces of the crystals that form the polar nanosheets are preferentially exposed. After calcination, the samples were subjected to several days of unprotected storage (on open Petri dishes kept under the prevailing light of the laboratory on worktop tables). At given periods of time the surface of the samples was characterized by the following techniques.

Spectroscopic characterization techniques

Transmission Fourier Transform Infrared Spectroscopy (FTIR) spectra of the ZnO-P samples compressed into discs with KBr were recorded from 500 to 4000 cm^{-1} on a Nicolet Magna IR-560 spectrometer fitted with a DTGS KBr absorbance detector. The analyzed regions were deconvolved with the aid of Gaussian functions. Raman spectra from 100 to 700 cm^{-1} were obtained at room temperature (RT) on a T64000 System (Horiba) using as excitation source the 514.53 nm line of an Ar ion laser and excitation times of 30 seconds. All the reported peak areas, positions and widths are the result of Gaussian fitting. Ex-situ X-ray photoelectron spectroscopy (XPS) was carried out on a Specs spectrometer, using Mg-K α or Al-K α (30 eV) radiation emitted from a double anode at 50 W. The binding energies of the resulting spectra were corrected employing the binding energy of adventitious carbon (284.6 eV) in the C1s region. The backgrounds were corrected using Shirley baselines. All the analyzed regions were deconvolved by means of mixed Gaussian-Lorentzian functions (90:10). The quantitative analyses were based on atomic sensitivity factors stored in the CasaXPS database (v2.3.12Dev6).

Discussion of results

Spectroscopic characterization

FTIR in Transmission mode

The ZnO-P sample was characterized via FTIR in Transmission mode at different unprotected storage times. After each analysis the KBr disc was crushed for further storage and the resulting powder was pressed again before the next analysis. The spectra obtained were thoroughly deconvolved in order to assign *exact* wavelength positions to each IR feature. Figure 1 shows the deconvolved spectra corresponding to 10 days of storage (for other storage times refer to the Supplementary Information; Figures S1 to S4). For the ZnO-P sample, the bands and shoulders with maxima located at wavelengths below 600 cm^{-1} (#1, #2 and #3 in Figure 1) were assumed to belong to bulk ZnO vibrations:

- E_2^{high} mode of hexagonal ZnO (Raman active): 430 [6], 437 [7], 443 [8], 448 , 460 and 465 cm^{-1} [9];
- Oxygen deficiency and/or oxygen vacancy (V_O) defect complex in ZnO: 505 cm^{-1} [7];
- $A_1(\text{LO})$ mode (Raman active): 502 cm^{-1} [10];
- Activation of a silent mode: 504 cm^{-1} [8];
- Second order of E_2 modes: 543 cm^{-1} [8];
- $E_1(\text{LO})$ mode (Raman active): $538\text{-}572\text{ cm}^{-1}$ [10].

According to this classification, the #1 band ($455.8 \pm 0.4\text{ cm}^{-1}$) undoubtedly corresponds to the E_2^{high} mode (Raman active), whereas the #2 ($502.5 \pm 4.4\text{ cm}^{-1}$) and #3 ($539.2 \pm 2.7\text{ cm}^{-1}$) bands might have different origins, as indicated above. The broad and poorly defined bands between 750 and 1300 cm^{-1} (#5 to #16) might correspond to hydroxycarbonates originating either from residual hydrozincite, the precursor of ZnO in the preparation method used [11], or, more probably, from aerial exposure

[9, 12-14], including the stretching vibration of C-OH (#15 at 1262 cm^{-1}) [15, 16]. The band at $\sim 1631\text{ cm}^{-1}$ (#22) is attributed to the first overtone of the fundamental stretching mode of -OH [17]. This vibration signals the presence of dissociatively bound H_2O on the surface of the sample [17]. However, the same band in conjunction with the #18 band (1384 cm^{-1}) has also been associated with asymmetrical and symmetrical stretching vibrations of zinc carboxylate, respectively [7]. The #18 band has also been attributed to surface adsorbed CO_2 molecules on ZnO [18]. The very small #28 to #32 FTIR features (2302.8 , 2316.2 , 2333.2 , 2343.0 and 2363.9 cm^{-1} , respectively) are due to CO_2 physisorption [19]. The small bands between 2800 and 3000 cm^{-1} (#33, #34, #35) are associated with the C-H stretching vibrations of alkane groups [7]. The broad absorption band at $\sim 3451\text{ cm}^{-1}$ (#38) has been assigned to the stretching vibration mode of hydroxyl group [17]. This band corresponds to O-H stretching arising from -OH groups bound to ZnO [18]. The small bands at 3455 cm^{-1} [20] and 3497 cm^{-1} [21] should be similarly assigned. The following procedure will be used to resolve the ambiguous assignments referred above.

In FTIR it is assumed that the integrated area of bands ascribed to surface functionalities is proportional to the surface area of the measured sample. As an example, this has been used to estimate the specific surface area of mesoporous silica materials by relating it to the ratio of the integrated area of the band ascribed to surface silanol to the integrated area of the band corresponding to bulk Si-O-Si bonds [22]. However, this technique cannot be applied in our case to track the variation of the specific surface area of the different functionalities with storage time because the area of the Zn-O-Zn bands (those below 600 cm^{-1}) does not appear to be proportional to the total irradiated ZnO weight, since in several revised works [23-25] they show apparently random variations with this parameter. To overcome this problem, we will assume that the surface alkanes (#33 and #34 bands) were produced during the calcination of the hydrozincite precursor and have remained unaltered during unprotected storage. Therefore we can state that the area of these bands is proportional to the total irradiated ZnO weight, and employ the following expression to evaluate a

parameter P which is proportional to the ratio of the surface of a given functionality to the total surface of the sample:

$$\frac{\text{Band area}}{\text{Total surface}} = \frac{\text{Band area}}{W_{\text{ZnO}} \times S_{\text{BET}}} \propto \frac{\text{Band area} \times S_{\text{BET}}^0}{(\text{CH band area}) \times S_{\text{BET}}} = P \quad (1)$$

In this equation *Band area* stands for the integrated area of a given band, W_{ZnO} is the total ZnO weight, S_{BET} and S_{BET}^0 are the specific surface areas of the sample at a given storage time and at time zero [1], respectively, and the *CH band area* is the sum of the integrated areas of the #33 (2859 cm^{-1}) and the #34 (2924 cm^{-1}) bands. Figure 2 shows the variation of P with storage time for the most representative FTIR features included in Figure 1 (the variations of P for all features are to be found in Figure S5). The following conclusions can be extracted from Figure 2:

- CO_2 barely survives as adsorbed species on the ZnO surface (#28 to #32 bands).
- Bands in the range of 750 to 1300 cm^{-1} correspond to a small fraction of hydroxycarbonates quickly formed by exposure to moist air and not to residual hydrozincite. This is suggested by the quasi constancy of parameter P with storage time for the bands in the range 700 to 1300 cm^{-1} , which implies that the hydroxycarbonates rapidly reach equilibrium on the exposed ZnO surface area.
- The #18 band (1384 cm^{-1}) must be attributed to residual carboxylates from hydrozincite calcination (its area varies in a similar way to that of the #33 and #34 alkane bands), whereas the #22 band (1631 cm^{-1}) should be assigned mainly to the first overtone of the fundamental stretching mode of -OH, coming as it does from the dissociatively bound H_2O on the surface of the sample. As observed in Figure 2, parameter P for this band behaves in a similar way to those of the bands for O-H stretching (#38 to #40).
- As expected, parameter P for the alkane bands (#33 and #34), produced from the calcination of the hydrozincite precursor, increases with storage time, as a consequence of the parallel diminution of the specific surface area.

- Parameter P for the #22 and #38 to #40 bands, corresponding to -OH vibrations, diminishes during unprotected storage, which suggests that the amount of surface Zn hydroxides decreases with storage time for the ZnO-P sample. The almost insignificant #39 and #40 bands prove that a minute fraction of hydroxyls are initially formed on the polar surface of ZnO, but follow the same decreasing tendency during storage as the preponderant hydroxyls of the #38 band.

Raman

Raman characterization was performed on the ZnO-P and ZnO-M samples subjected to unprotected storage. The spectra obtained were thoroughly deconvolved to assign the exact Raman shifts to each feature. Figure 3 shows the deconvolved spectra for the ZnO-P sample corresponding to 8 days of storage (for other storage times and samples refer to the Supplementary Information; Figures S6 and S7).

According to the group theory, single-crystalline ZnO has eight sets of optical phonon modes at point Γ in the Brillouin zone, which are classified as $A_1+E_1+2E_2$ modes (Raman active), $2B_1$ modes (Raman silent) and A_1+E_1 modes (infrared active) [26]. The low-wavenumber E_2^{low} mode predominantly involves the vibration of the heavy Zn sublattice, while the high-wavenumber E_2^{high} mode is mainly associated with the vibration of the lighter O sublattice. Moreover, the A_1 and E_1 modes split into transverse-optical (TO) and longitudinal-optical (LO) phonons [27, 28]. In Figure 3, the #3 shoulder, located in the $382.3\text{--}387.1\text{ cm}^{-1}$ range, can be assigned to the $A_1(\text{TO})$ mode of ZnO [26]. The band at $\sim 540\text{ cm}^{-1}$ (#9 peak) has been assigned to second-order scattering of the $E_2^{\text{high}}+E_2^{\text{low}}$ mode [29]. The prominent #1 band, located for all samples and storage times in Raman shifts between 326.5 and 333.5 cm^{-1} , is another second-order scattering mode and its symmetry is predominantly A_1 , with a smaller E_2 component and an even smaller E_1 component [26]. The

frequency of this mode is in good agreement with the difference between the E_2^{high} and E_2^{low} frequencies [26].

The most intense mode identified in the Raman spectra of the ZnO-P and ZnO-M samples (#6 peak, $\sim 438 \text{ cm}^{-1}$) is in good agreement with previously reported values and corresponds to the oxygen vibration mode E_2^{high} of ZnO [30]. A strong peak in the E_2^{high} mode, such as that shown in Figure 3, implies a good crystallinity in the ZnO lattice [31], corroborating the XRD results [1]. As mentioned above, the #1 band in the FTIR spectra (Figure 1) corresponds to this Raman mode. Figure 4A compares the wavelengths of the #1 FTIR band and the frequencies of the #6 Raman peak for sample ZnO-P at different storage times. The observed trend clearly corroborates the FTIR assignment.

Due to its high sensitivity to stress, the E_2^{high} shift is also commonly used to analyze the state of stress of the ZnO films. An increase in the E_2 phonon frequency (blueshift) is ascribed to compressive stress, whereas a decrease in the E_2 phonon frequency (redshift) is ascribed to tensile stress [32]. A redshift in the E_2^{high} frequency could also be attributed to an increase in oxygen vacancies (V_O) [33, 34], but this would be accompanied by a higher intensity of the LO phonon in the A_1 mode, which is around $575\text{--}580 \text{ cm}^{-1}$ [18, 35]. The tensile stress also increases the d-spacing which causes the peaks to shift in the X-Ray diffractogram towards lower 2θ values, whereas the compressive stress decreases the d-spacing, which results in the shifting of peaks towards higher 2θ values in the XRD pattern [17]. Both techniques, Raman and XRD, can therefore be employed jointly to analyze the variation in stress and oxygen defects during unprotected storage. Figures 4B and 4C compare the evolution of the E_2^{high} frequency and the 2θ values during unprotected storage time for ZnO-P (Fig. 4B; 2θ for the (002) XRD peak [1]) and ZnO-M (Fig. 4C; 2θ for the (100) XRD peak [1]). In both of these samples, the initial trends of the parameters are similar; a clear increase in compressive stress during the first two days of storage followed by a marked increase in tensile stress during the following four days. From day 6 the two samples start to differ in behavior. Whereas the trends of the E_2^{high} frequency and 2θ values proceed in parallel for ZnO-M, suggesting

that they are mainly affected by the evolution of stress, in the case of ZnO-P the 2θ values exhibit an increasing trend while the E_2^{high} frequency values show the opposite tendency, indicating a continuous increase in the V_O of the sample.

The intensity of the small #2 band, in the $355\text{-}363\text{ cm}^{-1}$ range, may be related to the amount of surface Zn(OH)_2 [36, 37]. The weak #8 band detected at $\sim 483\text{ cm}^{-1}$ is associated with ZnO and exhibits A_1 symmetry (LA overtones) [26]. The area of this band might also be influenced by a very small contribution of Zn(OH)_2 [38], much lower than in the case of the area of the #2 band. The fraction of the #2 band, evaluated as the ratio of its integrated area to the total integrated area of the Raman spectrum in the $300\text{-}600\text{ cm}^{-1}$ range (Fig. 3), evolves during storage as shown in Figure 4D; the amount of surface Zn(OH)_2 decreases continuously in the case of ZnO-P, in congruence with the FTIR results, but increases for the ZnO-M sample.

The band at $\sim 560\text{ cm}^{-1}$ (peak #10) is associated with the presence of Zn interstitials (I_{Zn}) [39]. Figure 4E shows that the #10 band fraction increases with storage time for the ZnO-P sample up to ~ 10 days' storage time and then experiences a clear decrease. On the other hand, in the case of the ZnO-M sample the #10 band fraction experiences a continuous decrease during storage. These trends suggest the transport of I_{Zn} from the non-polar areas to the polar areas of ZnO, where it is progressively incorporated into the Zn sublattice, which explains the maximum corresponding to the ZnO-P trend.

The #11 band is a wide peak located at $578.9 \pm 1.6\text{ cm}^{-1}$ (the average for samples ZnO-P and ZnO-M at all the storage times analyzed). This value lies between 574 cm^{-1} and 584 cm^{-1} , Raman shifts that correspond to the $A_1(\text{LO})$ and $E_1(\text{LO})$ modes of ZnO, respectively [26], signifying that the #11 band is produced by both modes and is indicative of the presence of oxygen vacancies [18]. As can be observed in Figure 4F, the fraction of the #11 peak, related to the amount of V_O , increases slightly with storage time for the ZnO-P sample. This result is congruent with the above discussion of the evolution of E_2^{high} frequency for ZnO-P. On the other hand, the #11 peak fraction decreases during

storage for the non-polar ZnO-M sample. Oxygen vacancy defects in non-polar nanowires have already been reported to have been heavily reduced by long-term exposure to air at RT [40].

XPS

XPS analyses were performed on the ZnO-P and ZnO-M samples for three different unprotected storage times (0, 5 and 45 days) using both Mg-K α and Al-K α sources. The Al-K α source allows a slightly deeper layer of the sample to be analyzed than the Mg-K α source. Calculation of the sampling depth is no easy task [41, 42]; following the criterion of the so-called *universal curve* for elements [41], the resulting sampling depths are, on average for the C1s, O1s and Zn2p_{3/2} electrons, around 3 or around 4 nm, using the Mg-K α or the Al-K α source, respectively. On the other hand, following the criterion used by Seah and Dench [42] for inorganic compounds, the average sampling depths increase to around 7 or around 9 nm, with the Mg-K α or the Al-K α source, respectively. In any case both criteria are based on experimental data which show a high level of scattering. Nevertheless, with the information provided by both sources it is possible to perform a rough depth profile analysis, although the depth values are only approximate. Figure 5 shows XPS plots for regions C1s, O1s, Zn2p_{3/2} and Zn2p_{1/2} corresponding to the fresh ZnO-P sample (storage time = 0). The plots for all the samples and storage times are included in the Supplementary Information (Figures S8 to S11). The XPS results for all regions, samples and storage times are listed in Table 1 (the results obtained with Mg-K α source are in the shadowed cells for purposes of clarity). As can be observed in Figure 5 the C1s region can be deconvolved into four peaks at ~282.2, 284.6, 286.3 and 288.0 eV (Mg-K α source). The peak at around 282.2 eV is usually associated to metallic carbides [43-45]. However, there is no sound explanation for the presence of carbides on the ZnO surface. Reassigning this peak to adventitious carbon (284.6 eV) would cause an unacceptable shift in the binding energies of the other spectral regions of more than 2 eV with respect to the literature values. The presence of this peak might therefore have been the result of a charging effect [46], that also

slightly affected the Zn2p region (Figure 5). The most intense peak in the C1s region is considered to be adventitious (graphitic) carbon, and by convention it is placed at 284.6 eV. The peak at 286.3 eV corresponds to C-OH bonds [47, 48] and the peak at 288.0 eV to C=O bonds [47-49]. The large amount of carbon on the surface of the samples (over 20% according to Table 1) is somewhat anomalous. The majority of this carbon belongs to adventitious or graphitic carbon, which is often arbitrarily assumed to be produced by such secondary causes as contamination from the oil pump (which does not form a part of our equipment). This is why not everybody agrees on its use as a reference [50]. We will therefore not attempt to draw any conclusion from the amounts of adventitious carbon and will focus on the variation in the concentration of the C-OH and C=O species. As can be observed in Figure 5 and Table 1, these species are mainly located on the external surface, since the amount detected using the Mg-K α source is much greater than that detected by means of the Al-K α source. Furthermore, the concentration of C-OH diminishes and that of C=O increases slightly during unprotected storage in the case of the ZnO-M sample (Table 1), whereas these concentrations behave more randomly for the ZnO-P sample. This suggests that they do not belong to inefficiently calcined hydrozincite (as in that case their concentration would increase towards the interior of the sample and with storage time, due to the decrease in specific surface area) but mainly to hydroxycarbonates rapidly formed by exposure to moist air. This result is consistent with the conclusions obtained from the FTIR analysis (the #7 to #17 bands in Figure 2). The rapid formation of these carbonaceous species rules out their participation in the mechanism of slow ZnO sintering, reinforcing the idea that the slightly accelerating effect of aerial CO₂ and water on the loss of specific surface area might be due to the acidity supplied by CO₂, as reported in [1].

The O1s region for both samples at all storage times has been deconvolved into three peaks. The first peak, O1s-I in Figure 5, at 529.8 eV, is ascribed to Zn-O bonds in an environment of complete oxidation in the wurtzite ZnO crystal [51-54]. The O1s-II peak at 531.3 eV includes the oxygen linked to carbon as C=O, which is commonly observed at ~531.5 eV [55-57], and the O δ^- ions ($\delta < 2$)

in the oxygen-deficient regions within the ZnO matrix (Zn-O links surrounded by oxygen vacancies), which display binding energies between ~530.8 eV [53, 54] and ~531.5 eV [58, 59]. Once corrected to take into account the C=O contribution (evaluated from the corresponding peak in the C1s region), the remaining area of the O1s-II peak is proportional to the amount of V_O in the ZnO matrix. The O1s-III peak at 532.1 eV includes the oxygen linked to carbon as C-OH, whose binding energy usually has values of over 532 eV [57, 60]. Once the contribution of the C-OH bonds has been discounted, the remaining area of the O1s-III peak is related to Zn-OH links originating from the dissociative chemisorption of water [51, 53, 61-64].

As can be observed in Figure 5, the Zn2p_{3/2} and Zn2p_{1/2} regions can both be deconvolved into three peaks. The first peak at 1018.7 eV or 1041.6 eV, for Zn2p_{3/2} or Zn2p_{1/2}, respectively (Mg-K α source) is ascribed to a not very significant charging effect. When the Mg-K α source is employed, the second peak in both regions (Zn2p_{3/2}-I and Zn2p_{1/2}-I in Figure 5) appears at 1020.95 $\pm$ 0.03 and 1044.04 $\pm$ 0.03 eV, respectively. The energy separation between these peaks (23.09 eV) is typical for divalent Zn (note in Table 1 that this separation decreases to 22.95 eV when the Al-K α source is employed). These results are in agreement with the standard data for pure ZnO [65-67].

Zn(OH)₂, whose presence was detected in the O1s region as part of the O1s-III peak, has been reported to show a peak at a binding energy of 1.1 eV above that of the ZnO peak in the Zn2p_{3/2} region [68]. In the present work, the Zn2p_{3/2}-II peak is ascribed to Zn(OH)₂, showing a difference in binding energy with respect to Zn2p_{3/2}-I somewhere in the 1.1-2.1 eV range (1022.0-1022.9 eV binding energy range). A similar range of variation (1021.8-1022.7 eV) has been reported by Kayaci *et al.* [69] in reference to the NIST XPS database values (<http://srdata.nist.gov/xps/>). Analogous differences were found for the peaks in the Zn2p_{1/2} region (Table 1). It can be seen that the (Zn2p_{3/2}-II)-(Zn2p_{3/2}-I) binding energy difference is inversely related to the relative amount of surface Zn(OH)₂ (Figure S12 in the Supplementary Information).

As indicated in Table 1, the sampling region of the polar ZnO-P sample exhibits a clear oxygen excess (the O/Zn values corrected for the presence of oxygen-containing carbon species are in the range of 1.6-1.8 for the first 5 days, increasing up to 3.9 after 45 days!), which does not occur in the non-polar ZnO-M sample (the O/Zn ratio in the non-polar region experiences a slight increase from 0.9 to 1.1 after 45 days of unprotected storage, associated in part with the parallel diminution of oxygen vacancies and the increase in surface hydroxyls). As the non-carbonaceous oxygenated species (region O1s) are ZnO (both in an oxidized environment or surrounded by oxygen vacancies) together with a small fraction of $\text{Zn}(\text{OH})_2$, such a high oxygen excess in ZnO-P cannot have originated from chemisorbed oxygen or the small amount of surface hydroxides, but must have originated from either a deficiency in Zn in lattice positions (Zn vacancies, V_{Zn}) or an excess of oxygen interstitials (I_{O}), both of these impurities having an acceptor character [54]. I_{O} are sometimes identified in the O1s-II peak of the O1s region, together with V_{O} defects [70] and on other occasions in the O1s-III peak, together with chemisorbed oxygen or water [71, 72]. Were the Raman information to be considered semi-quantitative, then the amount of oxygen vacancies in the ZnO-M sample at zero time storage would have to be higher than that of the ZnO-P sample (Figure 4F), contradicting the results of the XPS analyses using an Al-K α source (Table 1). In that case, part of the O1s-II peak could be associated to I_{O} , especially in the case of the sample stored during 45 days, almost 20% of whose non-carbonaceous species are either V_{O} or I_{O} . However, this amount of I_{O} would not be enough to explain the high oxygen excess observed in the ZnO-P sample. Therefore, the oxygen excess on the surface of the polar ZnO-P sample must be the result of both a moderate presence of oxygen interstitials and a high concentration of zinc vacancies. Hence, the non-polar region of ZnO has more I_{Zn} (donor type) than the polar region, whereas the polar region has more V_{Zn} (acceptor type) than the non-polar region. If we consider both the Raman (Figure 4E) and XPS results together, then it appears that unprotected storage provokes the diffusion of I_{Zn} from the non-polar to the polar region, this process compensating for the parallel increment in Zn vacancies in the

polar region during the first ~10 days (Figure 4E), during which a more or less constant O/Zn ratio of under 2 is maintained (Table 1). However, once the I_{Zn} amount becomes negligible in the polar region, at times of over 30 days (Figure 4E) the O/Zn ratio shoots up to values of over 3 (Table 1) due to the constant appearance of fresh V_{Zn} in this area and the presence of some I_O .

As can be deduced from Table 1 from the values obtained from the different sources (i.e., different sampling depths), oxygen vacancies are more concentrated within the bulk of the crystals than on their surface (except in the case of the ZnO-P sample after 45 days), although the presence of oxygen interstitials might be amplifying this effect, as pointed out above. The number of oxygen vacancies increases with storage time in the polar region and decreases slightly in the non-polar region, as confirmed by Raman analysis (Figure 4F).

Finally, surface $Zn(OH)_2$ is initially present in low amounts both on the polar surface (ZnO-P; 3.8%) and on the non-polar surface (ZnO-M; 1.6%), in reasonable agreement with the Raman results (Figure 4D), which rules out the possible contribution of I_O to the O1s-III peak. During unprotected storage, more surface zinc hydroxides are formed on the non-polar surface (up to 3.6% at 45 days) while they clearly decrease on the polar surface, in agreement with results of the FTIR (Figure 2; #38 band) and Raman (Figure 4D) analyses. It is well known that water dissociates in oxygen vacancies both on polar [73] and on non-polar [4] ZnO surfaces. The opposing trends of the oxygen vacancies and the $Zn(OH)_2$ amounts with storage time (Figures 4D and 4F) might therefore signify that $Zn(OH)_2$ on the polar surfaces is progressively decreasing, leaving oxygen vacancies on the surface, while the less significant presence of $Zn(OH)_2$ on the non-polar surfaces is gradually increasing by a mechanism of dissociative water adsorption on the oxygen vacancies.

Proposed mechanism of specific surface area loss during storage

On the basis of the results obtained in the previous sections and in the first part of this work [1], a mechanism for the loss of specific surface area in polar ZnO will now be proposed. A simplified diagrammatic representation of the mechanism (only the action of water is considered for oxygen vacancy healing) is shown in Figure 6. According to the variation in specific surface area obtained under different atmospheres (Figure 7 in [1]), the presence of moisture or oxygen or, in their absence, light is needed to *trigger* the surface area loss mechanism. From the different surface area losses depicted in the figure, it can be seen that the presence of water: a) provokes a faster reduction in specific surface area than oxygen and b) *does not need the simultaneous presence of O_2 to provoke surface area loss*. The spectroscopic results suggest that molecular adsorption of water takes place on Zn atoms close to oxygen vacancies on the (100) surface, where it dissociates to form two hydroxyl groups, thereby healing the oxygen vacancy (Figure 6). This spontaneous reaction, which is both supported [74] and refuted [75] by first principle DFT calculations, is the logical conclusion of this study. The storage-induced increase in surface hydroxyls and decrease in oxygen vacancies on the (100) surface is supported by the Raman (Figures 4D and 4F) and XPS (Table 1) results. The healing of oxygen vacancies can also be achieved slowly by aerial oxygen [40], proving that the sintering mechanism can also occur in the absence of water (Figure 7 in [1]). We propose that the energy released by oxygen vacancy healing in the non-polar region (which is essentially a process of surface oxidation), by the action of moisture or, more slowly, by aerial oxygen, *triggers* the room temperature migration of Zn interstitials towards the polar region (Figure 6). Illuminating the sample in an inert atmosphere also provokes a certain degree of surface area loss (Figure 7 in [1]). In this case, energy from the irradiated photons might be sufficient to cause the migration of I_{Zn} , though at a much slower rate. Zn interstitials become mobile at temperatures as low as 90-130 K [76] across grain boundaries (as occurs during the degradation of ZnO varistors [77-79]) both via *interstitial* or *interstitialcy* mechanisms [76]. These defects are known to be the predominant ionic defects at varying zinc and oxygen partial pressures [77] together with oxygen vacancies [80, 81]. They are

also known to diffuse faster than oxygen vacancies [69] with rather low energy barriers (0.5-1 eV) at low temperature [82, 83]. On reaching the polar region, the Zn interstitials do not occupy the Zn vacancies. Instead, they emerge on the $(00\bar{1})$ surface where they can (a) displace terminal hydroxylated Zn atoms of the O-terminated polar plane, causing the release of a water molecule and the concomitant formation of an oxygen vacancy, (b) displace terminal non-hydroxylated atoms or (c) simply jump over terminal oxygen atoms. These formerly interstitial Zn atoms then gradually occupy the mesopores (Figure 5 in [1]), causing the Zn sublattice to expand (Figure 6), and the specific surface area of the material to diminish. This process continues until the narrow mesoporosity of the nanosheets completely disappears. At the same time interstitial oxygen serves to build up the O sublattice; the presence of I_O defects has been proved by XPS and there is no other source of oxygen in an inert atmosphere, under which the ZnO sample also experiences a certain surface area loss when it is irradiated by the lab light [1]. In the expanded lattice there is an abundance of Zn vacancies, as proved by XPS (Table 1). We assume that this process occurs on an O-terminated polar plane, because hydroxyls on this plane are known to be much less stable than hydroxyls on a Zn-terminated polar plane [84]. The storage-induced decrease in hydroxyls on the $(00\bar{1})$ plane is supported by the FTIR (bands #22, #38, #39 and #40 in Figure 2), Raman (Figure 4D) and XPS (Table 1) analyses, whereas the increase in oxygen vacancies is backed by the Raman (Figure 4F) and XPS (Table 1) analyses. While the amount of Zn interstitials in the non-polar region continuously decreases (Figure 4E), the Zn interstitials in the polar region initially increase due to their diffusion from the non-polar region, but they soon start to decrease (Figure 4E) due to their incorporation into the newly formed Zn sublattice that occupies the mesopores. The decrease in Zn interstitials, together with the potential diminution of oxygen interstitials in the bulk, contributes to an increase in crystallinity [1]. The loss of polar surface area also explains the decrease in I_{002}/I_{100} observed by XRD for ZnO-P (Figure 2B in [1]). A final point worth noting is that the diminution of

Zn interstitials accompanied by the increase in Zn vacancies during the process can be expected to diminish the donor character of the n-type ZnO semiconductor.

Conclusions

The mechanism of room temperature sintering of polar ZnO nanosheets starts with the molecular adsorption of water, which takes place on Zn atoms close to oxygen vacancies on the (100) surface, where it dissociates to form two hydroxyl groups, thereby healing one oxygen vacancy. It is proposed that the energy released by oxygen vacancy healing on the non-polar region, performed either by the action of moisture or, more slowly, by aerial oxygen, *triggers* the room temperature migration of Zn interstitials towards the polar region. On reaching the polar region, the Zn interstitials show up on the (00 $\bar{1}$) surface where, among other actions, they can displace terminal hydroxylated Zn atoms on the O-terminated polar plane. The formerly interstitial Zn atoms gradually occupy the mesopores, while at the same time interstitial oxygen serves to construct the O sublattice, until the narrow mesoporosity in the nanosheets completely disappears.

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Captions to figures

Figure 1. Deconvolution of FTIR spectra for ZnO-P after 10 days of unprotected storage.

Figure 2. Variation of parameter P (equation (1)) with storage time for the ZnO-P sample previously subjected to unprotected storage (type and position of the FTIR features inside the plots. Band assignments in Figure 1).

Figure 3. Deconvolution of Raman spectra for ZnO-P after 8 days of unprotected storage.

Figure 4. A) Comparison of the wavelengths of the #1 FTIR band with the frequencies of the #6 Raman peak for sample ZnO-P at different storage times; B) Evolution of the E_2^{high} frequency and 2θ ((002) peak) values with unprotected storage time for ZnO-P; C) Evolution of the E_2^{high} frequency and 2θ ((100) peak) values with unprotected storage time for ZnO-M; Evolution of the fraction of the #2 (D), #10 (E) and #11 (F) Raman bands with unprotected storage time for ZnO-P and ZnO-M.

Figure 5. Deconvolution of the XPS spectra in the C1s (Mg-K α and Al-K α sources), O1s, Zn2p_{3/2} and Zn2p_{1/2} (Mg-K α source) regions for ZnO-P after 0 days of unprotected storage.

Figure 6. Mechanism of specific surface area loss proposed for polar ZnO in a moist atmosphere.

Tables

Table 1. XPS results for ZnO-P and ZnO-M at 0, 5 and 45 days of unprotected storage time

Sample	ZnO-P						ZnO-M					
Storage time	0 days		5 days		45 days		0 days		5 days		45 days	
XPS source	Mg-K α	Al-K α	Mg-K α	Al-K α	Mg-K α	Al-K α	Mg-K α	Al-K α	Mg-K α	Al-K α	Mg-K α	Al-K α
%C	33.2	13.4	30.7	11.4	37.9	30.4	24.5	14.9	20.4	11.7	21.4	13.9
%C-C (284.6 eV)	22.0	9.6	18.9	9.0	28.0	23.6	15.8	12.0	12.5	9.0	13.1	10.4
%C-OH (286.3 eV)	2.0	1.2	1.2	0.4	2.2	1.7	2.3	1.3	1.2	0.9	0.7	0.7
%C=O (288.0 eV)	9.2	2.7	10.5	2.0	7.7	5.1	6.4	1.7	6.7	1.7	7.7	2.8
Binding energies (eV)												
O1s-I	529.7	529.9	529.7	529.8	529.7	529.9	529.8	529.7	529.8	529.8	529.8	529.8
O1s-II	531.2	531.4	531.2	531.3	531.2	531.4	531.3	531.2	531.3	531.3	531.3	531.3
O1s-III	532.0	532.1	532.2	532.1	531.8	532.1	532.0	532.0	532.0	532.1	532.0	532.1
Zn2p3/2-I	1020.9	1020.7	1020.9	1020.7	1021.0	1020.9	1021.0	1020.7	1021.0	1020.7	1020.9	1020.7
Zn2p3/2-II	1022.0	1022.1	1022.2	1022.7	1022.6	1022.9	1022.9	1022.8	1022.4	1022.7	1022.3	1022.4
Zn2p1/2-I	1044.0	1043.7	1044.0	1043.7	1044.1	1043.8	1044.1	1043.6	1044.0	1043.7	1044.0	1043.7
Zn2p1/2-II	1045.2	1045.3	1045.2	1045.9	1045.5	1045.9	1045.9	1045.8	1045.3	1045.7	1045.2	1045.5
Carbon-free composition (%)												
%O	62.8	61.8	64.2	61.4	79.7	74.7	48.5	50.2	48.9	49.7	52.4	51.7
Zn-O (O1s-I)	54.4	40.9	51.9	41.3	57.8	56.2	43.4	38.7	41.6	38.5	45.2	41.3
V _O [+I _O ? ^(a)] (O1s-II)	0.8	14.7	6.5	17.5	19.8	17.0	2.0	8.9	1.5	7.6	0.0	4.8
Zn-OH (O1s-III)	7.5	6.1	5.8	2.5	2.0	1.5	3.1	2.6	5.8	3.6	7.2	5.7
%Zn	37.2	38.2	35.8	38.6	20.3	25.3	51.5	49.8	51.1	50.3	47.6	48.3
ZnO (Zn2p3/2-I)	33.5	35.1	32.9	37.4	19.3	24.6	49.9	48.5	48.2	48.5	44.0	45.4
Zn(OH) ₂ (Zn2p3/2-II)	3.8	3.1	2.9	1.3	1.0	0.7	1.6	1.3	2.9	1.8	3.6	2.8
O / Zn ^(b)	1.69	1.62	1.79	1.59	3.91	2.95	0.94	1.01	0.96	0.99	1.10	1.07
V _O / O ^(c)	0.01	0.24	0.10	0.29	0.25	0.23	0.04	0.18	0.03	0.15	0.00	0.09
OH / O ^(d)	0.12	0.10	0.09	0.04	0.03	0.02	0.06	0.05	0.12	0.07	0.14	0.11
Zn(OH) ₂ / Zn ^(e)	0.101	0.081	0.080	0.033	0.051	0.029	0.030	0.026	0.057	0.036	0.075	0.058

^(a) The potential contribution of I_O to the O1s-II peak is discussed under the XPS epigraph of the *Discussion of results* section;

^(b) [(O1s-I)+(O1s-II)+(O1s-III)]/[(Zn2p3/2-I)+(Zn2p3/2-II)];

^(c) (O1s-II)/[(O1s-I)+(O1s-II)+(O1s-III)];

^(d) (O1s-III)/[(O1s-I)+(O1s-II)+(O1s-III)];

^(e) (Zn2p1/2-II)/[(Zn2p3/2-I)+(Zn2p3/2-II)]

Figures

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6