The Role of Nitrogen in Defect Evolution in Zinc Oxide:

STEM-EELS Nanoscale Investigations

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Abstract

Direct evidence of nitrogen-molecule (N_2) formation after ion-implantation of ZnO has been found in an atomically-resolved STEM-EELS investigation. Taking advantage of the possibility to use multiple detectors simultaneously in aberration-corrected STEM, the detailed correlation between atomic structure and chemical identification is utilized to develop a model explaining the formation and evolution of different defect-types and their interaction with N. In particular, the formation of zinc vacancy (V_{Zn})-clusters filled with N_2 after heat treatment at 650°C was observed, clearly indicating that N has not been stabilized in the O substitutional site, thus limiting p-type doping. Previous results, showing an exceptional thermal stability of vacancy-clusters only for the case of N-doped ZnO are supported. Furthermore, the V_{Zn} - N_2 stabilization leads to suppression of V_{Zn} - Zn_i recombination, hence the highly mobile Zn interstitials preferentially condense on the basal planes promoting formation of extended defects (basal stacking faults, stacking mismatched boundaries). The terminations of these defects provide energetically favourable sites for further N_2 -trapping as a way to reduce local strain fields.

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Point and extended defects, as well as their interaction with dopants, directly influence semiconductor properties hence, identifying different defect-types and understanding their formation and evolution is crucial for mastering semiconductors. The prominent correlation between defects and electrical-optical properties is clearly evident in the case of ZnO, a wide and direct band-gap semiconductor (~ 3.4 eV) with a potential for a variety of next generation solid-state devices in the fields of optoelectronics, quantum technology, spintronics and radiation sensors in harsh environments^{1,2,3}. However, the doping asymmetry, where only n-type conductivity can be readily accomplished, hinders the realization of ZnO devices^{4,5}. Nitrogen (N), has been considered as one of the most promising candidates for p-type doping in ZnO, resulting in intensive studies regarding N-behavior in ZnO^{6,7,8,9,10,11}. However, the results obtained so far are quite contradictory and reliable p-type doping is still challenging. N-doped ZnO has also attracted fundamental interest since it exhibits a remarkable behavior in terms of defect evolution, in comparison to other dopants. In particular, Børseth et al.¹² and Tuomisto et al.¹³ revealed by positron annihilation spectroscopy (PAS) an exceptional stability of Zn vacancy (V_{zn})-clusters for N-doped ZnO. This observation was irrespective of the growth/implantation methods, revealing the generality of the phenomenon. Furthermore, Azarov et al.^{14,15} showed by ion channeling measurements that defects induced by N-implantation into ZnO (Zn interstitial-type defects) exhibit nonlinear thermal evolution trends, demonstrating a dramatic increase in the defect concentration occurring at 650°C (so-called reverse annealing). The exact mechanism for reverse annealing is not yet understood, but the effect occurs exclusively for the N-implants. Hence, it is evident that the defect formation/evolution in ZnO hinges strongly on the implanted species^{12,13,14,16,17}, and detailed nano-structural and chemical defect characterization is of utmost importance to reveal the role of N in the complex defect interplay.

Scanning Transmission Electron Microscopy combined with Electron Energy-Loss Spectroscopy (STEM-EELS) is a unique tool for both imaging and spectroscopy on the atomic scale, giving invaluable insight into the defect interaction and evolution. In the present work, an atomically-resolved STEM-EELS study was performed for the first time on N-implanted wurtzite ZnO single crystals that were heat-treated at 650°C, in order to elucidate the character and interaction of N-related defects. As a result, we propose a model that describes the defect interplay, starting from point defects behavior (interstitials (Zn_i , O_i) and vacancies (V_{zn} , V_o)) promoting the formation of extended defects (V-clusters, stacking faults), and revealing the decisive role of N in defect evolution. The correlation between atomic structure and chemical information on the atomic scale was crucial for the apparent study, hence we took advantage of the possibility to use multiple detectors, in order to obtain simultaneous information through different mechanisms of the electron beam-specimen interactions. In this respect, we performed: a) Simultaneous acquisition of annular bright field (ABF), annular dark field (ADF) and high-angle annular dark field (HAADF) images, providing complementary views of the same region. In particular, ABF is a direct method of visualizing light and heavy elements simultaneously, ADF provides strong diffraction contrast while in HAADF contrast is directly correlated to the atomic number (Z-contrast). b) Simultaneous STEM imaging and EELS on the atomic scale, allowing for correlation between atomic structure and chemical information. Geometric Phase Analysis (GPA) was performed on high resolution STEM images to extract lattice phase maps and for the nanoscale localization of strained regions.

Figure 1a presents a low-magnification ADF-STEM image with an overlay of the N-implanted profile calculated by the Transport of Ions in Matter (TRIM) code¹⁸. The diffraction contrast of the ADF image reveals that the average depth of the implanted zone is close to 120 nm from the surface, which is in agreement with the TRIM calculations and the maximum ion concentration is expected approximately at ~ 80 nm from the surface. Figures 1b and 1c present high resolution ADF-STEM and HAADF-STEM images respectively, that were recorded simultaneously, illustrating the defect formation in the area close to the maximum ion concentration.

The ADF image provides strong diffraction contrast, hence the localization of extended defects is easily detectable. In addition to the extended defects, at the corresponding HAADF image we observe the formation of nano-sized areas exhibiting darker contrast. Accounting that HAADF is a pure Z-contrast image, formed by scattering from heavy elements (in our case Zn), these dark nano-sized areas can be indicative of volumes with lower atomic density (e.g. vacancy-clusters) or/and clustering of light elements.

Figure 1. (a) Low-magnification ADF-STEM image with an overlay of the N-implanted profile calculated by the TRIM code. Both imaging and TRIM data are in agreement revealing an implanted area of ~120 nm, with the maximum ion concentration at ~80 nm from the surface. (b) ADF-STEM and (c) HAADF-STEM images recorded simultaneously, close to the maximum ion concentration region. Extended defects are easily detectable in the ADF image due to strong diffraction contrast while the HAADF Z-contrast image additionally reveals the existence of nano-sized cluster-like defects with lower atomic density.

(i) Extended defects

Formation of basal stacking faults (BSFs) was found to dominate the N-implanted region. The wurtzite (WZ) structure is described by the stacking of close-packed double layers of (0001) planes (basal planes) and the perfect stacking sequence along the [0001] direction is ABABAB, where each letter corresponds to a Zn-O bilayer. Figures 2a and 2b show an atomically-resolved ADF image recorded from the middle part of a BSF, allowing for simultaneous direct visualization of heavy and light elements. The Zn-O dumbbells are resolved and a BSF of I_1 -type was identified, characterized by one violation of the stacking rule, changing the stacking sequence according to ABABCBCB. These stacking faults introduce one cubic structural unit in the stacking sequence (Figure 2c). Their average lateral extension after the annealing process is up to 20 nm and they can be formed due to agglomeration of self-interstitial atoms (Zn_i , O_i) into the basal planes, since they were found to be of interstitial-type due to the insertion of an extra half-plane (Figures 2d-2e). They are usually bounded by Frank-Shockley dislocations with Burgers vectors $b = 1/6 \langle 02\bar{2}3 \rangle = 1/2 \langle 0001 \rangle + 1/3 \langle 01\bar{1}0 \rangle$ (components)¹⁹. The $1/3 \langle 0001 \rangle$ Burgers vector component alters the stacking sequence of the perfect WZ crystal, while the $1/3 \langle 01\bar{1}0 \rangle$ causes a slip of the upper part of the ZnO crystal with respect to the lower part as we cross the BSF (Figures 2f-2g)²⁰. Note that basal stacking faults are the most common ones in wurtzite materials, and Wang et al.²¹ have also suggested that interstitials condense on the basal plane.

Figure 2. (a) High-resolution ABF-STEM image of a BSF of I_1 -type and (b) the corresponding enlarged colored image. The Zn-O dumbbells are easily resolved, revealing a change in the stacking sequence according to ABABCBCB. (c) Structural model of the I_1 -BSFs showing the insertion of one cubic layer in the wurtzite structure. (d) Overlap of HAADF image and the corresponding ϵ_{yy} strain map, acquired from the left termination of the BSF, (e) the corresponding overlap of the ϵ_{yy} strain map and Bragg filtering image with g_{0002} . The insertion of an extra half plane is illustrated, indicating that the BSF is of interstitial-type. (f) Overlap of HAADF image and the $g_{1\bar{1}00}$ phase map and (g) the corresponding phase profile showing a phase change ~ 2 rad across the I_1 -BSF, consistent with the in-plane shift of the crystal equal to $1/3 [1\bar{1}00]$.

Extrinsic basal stacking faults (E-BSFs) exhibiting smaller lateral extension (~ 5 nm) were also observed. The E-BSF is described by a stacking sequence according to ABABCABAB (Figures 3a and 3b) and introduces three cubic structural units in the wurtzite structure (Figure 3c). Similar to the I_1 -BSFs, they are formed by the precipitation of self-interstitial atoms (Zn_i , O_i) on the basal plane, since they were also found to be of interstitial-type due to insertion of extra half-planes (Figures 3d and 3e). They are bounded by Frank dislocations with Burgers vectors $b = 1/2\langle 0001 \rangle$, so no slip is caused of the upper part of the ZnO crystal with respect to the lower part (Figures 3f and 3g)²⁰. However, these faults require higher energy for their formation than the I_1 -BSFs, taking into account that the formation energy is almost proportional to the number of the inserted cubic layers²². This justifies the fact that we always observe them in smaller lateral extensions.

Figure 3. (a) High-resolution ABF-STEM image of a BSF of E-type and (b) the corresponding enlarged colored image. The Zn-O dumbbells are easily resolved, revealing a change in the stacking sequence according to ABABCBAB. (c) Structural model of the E-BSFs showing the insertion of three cubic layers in the wurtzite structure. (d) High resolution ADF image and (e) the corresponding ε_{yy} strain map overlapped with the Bragg filtering image with g_{0002} . The insertion of extra half-planes is illustrated, indicating the interstitial nature of the defect. (f) Overlap of HAADF image and $g_{1\bar{1}00}$ phase map and (g) the corresponding phase profile showing no phase change across the E-BSF, indicating zero in-plane shift.

Another extended defect-type observed is the stacking mismatched boundary (SMB), characterized by the ‘double’ positioned monolayers of Zn (Figure 4). SMBs are prismatic stacking faults (PSFs) on the $(1\bar{2}10)$ plane (proposed by Amelinckx)²³ and they exhibit an average lateral extension close to 20 nm. SMBs act as connections between two I_1 -BSFs lying on different basal planes (also shown by Knoll et al.²⁴). The I_1 -type BSFs frequently appear in pairs separated by 2–3 unit cells along the c -axis after which the original stacking sequence is restored. This arrangement is energetically favorable, as the strain fields at one side of each BSF can overlap and cancel.

Figure 4. High-resolution STEM images of a stacking mismatched boundary formed by a prismatic stacking fault on the $(1\bar{2}10)$ plane. In the ABF image on the left (a) the Zn-O dumbbells are resolved, while the HAADF image on the right (b) shows the position of the Zn atomic columns.

(ii) V-cluster stabilization by N_2

In addition to the extended defects (Figure 1b), the corresponding HAADF image (Figure 1c) reveals the formation of nano-sized areas exhibiting darker contrast. This is indicative of reduced atomic mass density, indicating that vacancy clusters or/and clustering of light elements are formed.

In order to investigate this, atomic scale STEM-EELS was performed on these regions. Figure 5a shows an ADF-STEM intensity map across a nano-sized dark area, close to the maximum ion concentration region. The corresponding relative thickness map shows a clear reduction in the effective thickness (Figure 5b) correlated to a local Zn-depletion, indicating the existence of a nano-sized V_{Zn} -cluster. In addition, the corresponding N-K intensity EELS map (Figure 5c) reveals a N-rich region. The EELS spectra (Figure 5d) show that (1) nitrogen is localized exactly inside the V_{Zn} -cluster, while in the surrounding area the N-K signal disappears abruptly, indicating an almost pure ZnO ‘matrix’. Moreover, the shape and the energy position of the N-K edge indicate the formation of molecular nitrogen (N_2), -as shown in Figure 5e, where spectra from monochromated STEM-EELS are compared to reference spectra of gaseous N_2 and GaN-. Hence, the formation of N_2 -filled nano-voids (V_{Zn} - N_2 clusters) is identified. In general, they appear to be randomly distributed in the implanted region however, a more careful inspection reveals that they are typically formed in the vicinity of the extended defects. Figure 5f reveals the formation of a void at the termination of a basal stacking fault. In particular, the cores of partial edge dislocations that bound the BSFs can act as strong sinks for dopants, accommodating local strain fields (Figures 5 g-i).

Figure 5. (a) ADF-STEM intensity map across a nano-void and the corresponding (b) relative thickness map and (c) N-K intensity EELS map. A clear drop in ADF intensity and thickness are indicative of a Zn-depleted area (V_{Zn} – cluster). (d) The corresponding EELS-spectra acquired from the area (1) inside and (2) outside the V_{Zn} – cluster. N-K signal is detected only inside the V_{Zn} – cluster and disappears abruptly outside it. (e) The shapes of the N-K peaks are clearly illustrated, where monochromated spectra from: our experiment from the N-implanted ZnO sample, N_2 reference²⁵ and our experiment from a GaN reference sample are compared. Hence, the formation of a V_{Zn} - N_2 cluster surrounded by an almost pure ZnO matrix is identified. (f) Bright field TEM image under two-beam conditions with $g1\bar{1}00$ revealing a nano-cluster localization at the termination of a basal stacking fault, (g)-(i) ABF-STEM image and the corresponding GPA strain maps, showing local strain fields associated with the partial edge dislocations bounding the BSFs. The cores of dislocations can act as strong sinks of dopants accommodating the local strain fields.

Our experimental STEM-EELS results are in agreement with previous theoretical/experimental studies and go further in terms of the comprehensive nanostructural picture regarding the N-behavior in ZnO. According to calculations of Nickel and Gluba²⁶, the O site is energetically unfavorable for the localization of N_2 . Furthermore, first-principles calculations by Lambrecht and Boonchun²⁷ showed that N_2 may occupy a V_{Zn} . Photo-Electron Paramagnetic Resonance (EPR) measurements by Philipps et al.²⁸ indicated that the N_2 acceptor level is even deeper than N_O and N_2 may exist as a molecule in interstitial locations or voids. Soudi et al.²⁹ observed N-related complexes in MBE-grown ZnO nanowires performing Raman spectroscopy. N_2 molecule was observed by X-ray absorption experiments in the annealing process of MBE-grown ZnO:N by Fons et al.³⁰, proposing that annealing caused the formation of N_2 bubbles.

In order to understand the formation mechanism of N_2 in the N-implanted samples, it is worth noting that the nitrogen is introduced in the form of ionized N^+ and after implantation N is expected to be placed either in an interstitial position (N_i) or substitutional position (N_O) in the oxygen sub-lattice. However, according to our STEM-EELS results, signals revealing Zn-N bonds were not observed. This indicates that N taking a substitutional O position (N_O) is not a stable configuration. It has been previously reported that the low p-type

doping efficiency of N in ZnO could be attributed to the instability of N_O due to the unfavorable local chemical environment (Fons et al.³⁰). DFT calculations by Gao et al.³¹ indicated that the existence of O_i plays a decisive role in N_O deactivation and formation of N_2 . In particular, N_O would be easily kicked out to an interstitial site (N_i) by O_i , due to their attractive interaction. Furthermore, their calculations showed that the N_i - N_i binding energy is large due to the large strength of the $N\equiv N$ triple bond, hence the total energy drops dramatically once two N_i bind together to form N_2 .

Furthermore, our STEM-EELS investigation revealing localization of N_2 at V_{Zn} -clusters, explains results previously reported by Børseth et al.¹² and Tuomisto et al.¹³. In particular, they detected by PAS the formation of V_{Zn} -clusters in N-doped ZnO. These vacancy-clusters with an open volume larger than that of a Zn monovacancy already exist in the as-implanted ZnO and after heat treatment at 600°C they start to grow in size. Interestingly, they showed that V_{Zn} -clusters exhibit an exceptional thermal stability even at higher temperatures, which is not typically observed for other dopants. According to our results, the thermal stability could be associated with the localization of N_2 molecules in the V_{Zn} -clusters, possibly reducing strain due to local lattice distortion. It is worth noting that with PAS it is not possible to directly detect V_O , but it is highly likely that the V-clusters observed by PAS and STEM are also a combination of both V_{Zn} and V_O .

Our results, showing N_2 -filled V_{Zn} -clusters, also explain the formation of the extended basal stacking faults. The stabilization of V_{Zn} -clusters by N_2 suppresses the V_{Zn} - Zn_i recombination, which results initially in a high Zn_i concentration in the implanted region. The resulting local strain in addition to the high Zn_i mobility even at room temperature can easily lead to migration of Zn_i , that preferentially condense on the (0001) basal planes, resulting in formation of interstitial BSFs (insertion of extra planes). It is essential to emphasize that the BSFs formation needs the precipitation of a complete Zn-O bilayer, meaning that in addition to agglomeration of Zn_i , also O_i should diffuse at the same time. Further diffusion of interstitial point defects into the basal plane gradually increases the BSF size leading to a partial strain saturation.

Regarding the formation energies of BSFs in ZnO, calculations by Yanfa Yan et al.²² showed that in general all BSFs exhibit low formation energies, -comparable to what is observed in GaN-. This indicates that they can form easily through kinetics in ZnO. The BSFs of I_1 -type that are dominant in our case, are energetically favorable compared to other BSF-types. E-BSFs are less energetically favorable, justifying the fact that we always observe them in smaller lateral extensions. As the E-BSFs grow in size, the excess stacking fault energy can only be partially reduced by changing the loop structure from E-type to I_1 -type. This can happen by the nucleation of a partial dislocation $b = 1/3\langle 01\bar{1}0 \rangle$ that shears the E-BSF into I_1 -BSF (dissociation of Frank loop into Frank-Shockley)³². This implies that part of the I_1 -BSFs that we observe can be the result of E-BSFs dissociation.

Finally, the terminations of the extended defects that we observed (BSFs and SMBs), can provide energetically favorable sites for further N_2 localization. In particular, the cores of partial edge dislocations that bound the SFs can act as strong sinks of dopants, accommodating the local strain fields³³.

Figure 6. Model describing defect evolution in N-implanted ZnO.

In conclusion, through a comprehensive nanostructural and chemical investigation we have elucidated the behavior of nitrogen into a ZnO host matrix and described a model regarding the defect evolution (Figure 6). Our EELS results show direct evidence for the formation of N_2 molecules, thereby supporting previous reports on the low stability of N substitution on O sites. Furthermore, we propose that V_{Zn} -clusters are stabilized by the presence of N_2 , resulting in an exceptional thermal stability compared to the situation with other dopants, and leading to a suppression of V_{Zn} - Zn_i recombination. Thus the highly mobile Zn interstitials can easily migrate and form interstitial-type extended defects. In particular, Zn_i preferentially condenses on the basal planes, resulting in the formation of basal stacking faults that grow in size leading to strain saturation. The dominant BSF-type is the energetically favorable I_1 -type terminated by stacking mismatched boundaries or Frank-Shockley dislocations, which again provide energetically favorable sites for further N_2 -trapping as a way to reduce local strain fields.

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Supporting Information Available:

Experimental methods employed; Ion-implantation process, Monte Carlo simulations using the TRIM code, (Scanning) Transmission Electron Microscopy ((S)TEM), Electron Energy-Loss Spectroscopy (EELS), Geometric Phase Analysis (GPA), TEM sample preparation, sample thickness evaluation by low-loss EELS.

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