In situ backside Raman spectroscopy of zinc oxide nanorods in an atmospheric-pressure dielectric barrier discharge plasma

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Abstract
This work presents in situ backside Raman spectroscopy as a method for the investigation of atmospheric-pressure plasma modification of thin oxide films on metals. By using the backside of a permeable electrode, various contributions from the plasma (UV radiation, electrons, etc.) are blocked, which allows us to solely evaluate the effect of the plasma effluent. This approach is applied to study the influence of different gas mixtures (Ar, Ar/H₂O, and Ar/O₂) on the plasma treatment of zinc oxide nanorod films. The spectral analysis reveals the interaction of the plasma effluent with the zinc sublattice, introducing defects dependent on the plasma gas-phase composition. The in situ measurements show that both the effluent/surface interaction and the resulting defects induce lattice stress in the wurtzite structure. Ex situ Raman measurements demonstrate that the defect stability over time depends on the defect type. The results for the dielectric barrier discharge plasma modification of ZnO-nanostructured thin films indicate that the presented Raman spectroscopic setup is suitable for a variety of systems with a focus on remote plasma modifications.

KEYWORDS
in situ, nanocrystals, plasma treatment, thin films, zinc oxide

1 | INTRODUCTION

Atmospheric-pressure plasma technology is a rapidly advancing field due to its low costs, broad applicability, and high efficiency. Among others, surface treatments by plasma (e.g., surface activation¹,² and sterilization³,⁴) and plasma catalysis (e.g., CO₂ conversion⁵,⁶) and volatile organic compound decomposition⁷,⁸) are of high scientific, economic, and social importance. Thus, various plasma sources and interaction methods are available, ranging from “hot” plasmas for gas-phase reactions (e.g., plasma torches), “cold” plasmas in contact with the sample (e.g., dielectric barrier discharge), or the treatment of the sample using only the plasma effluent (e.g., plasma jets)⁹,¹⁰. In treatments that use the plasma effluent, mainly metastable and long-living
reactive species lead to an impact on the sample, while in situations where the object is in direct contact with the plasma, additional effects such as electron impact, radiation, and interaction with short-lived reactive species have to be considered. The number of simultaneous processes opens the door for synergistic effects within the plasma. \[9,12\] and as a consequence, interaction mechanisms often remain unclear, and the plasma treatment is used as a “black box” tool. This approach leads to a high workload because a broad variety of relevant plasma parameters must be tested (e.g., variations in power, gas composition, and gas flow) without a good understanding of the processes on the surface. By employing in situ characterization techniques, additional knowledge of plasma processes can be gained by identifying intermediates produced during the plasma and investigating time dependencies within the plasma reactions. In this regard, Christensen et al. followed the kinetics of the plasma-induced CO\(_2\) decomposition using in situ Fourier transform infrared spectroscopy (FTIR), identifying CO as the main intermediate.\[5,13\] At a more fundamental study, Budde et al. followed the decomposition of poly(propylene) using in situ FTIR regarding the synergetic effects of Ar ions and UV radiation.\[14\] They found that the combination of UV radiation and Ar ions led to a higher graphitization probability and proposed a decomposition model. Recently, this model was validated in an inductively coupled plasma setup by ellipsometry.\[15\] Thus, the separation of different plasma-related effects can lead to a deeper understanding of the overall plasma process and afterward be transferred to different and more complex plasma setups.

Raman spectroscopy is a powerful tool for the investigation of inorganic oxides, which are interesting materials for various applications such as in electronics, sensors, and energy conversion.\[16–18\] Furthermore, they are often used as heterogeneous catalysts (including plasma catalysis), where the gas/surface interaction plays a major role in the efficiency of the reaction.\[19,20\] In heterogeneous catalysis, the gas has to interact with the catalyst in order to undergo the desired reaction.\[19,20\] Thereby, the adsorption is mainly determined by the local coordination of the atoms and strongly influenced by the defect structure of the catalyst.\[19\] In situ Raman spectroscopy can monitor the surface state during the plasma treatment, leading to a deeper understanding of the surface/plasma interactions.

In this work, we concentrate on zinc oxide (ZnO), which is a material of wide interest as stable, low toxic semiconductor.\[16\] In particular, the synthesis of diverse ZnO nanostructures has attracted great attention due to their tunability both in shape and properties, enabling application in nanodevices, for example, as field-effect transistor\[21\] or as adhesion-promoting particles in hybrid films.\[22\] In nanostructures, crystallinity is of great importance, determining the growth direction and overall properties of the material.\[23,24\] Crystalline ZnO exhibits a wurtzite structure, belonging to the P6\(_3\)mc space group.\[25\] In this case, the irreducible representation of the zone-center optical phonons (\(\Gamma_{\text{opt}}\)) is given by \(\Gamma_{\text{opt}} = A_1 + E_1 + 2E_2 + 2B_1\),\[25,26\] where \(A_1\) and \(E_1\) are the polar modes, split due to the polarity-induced macroscopic electric field in longitudinal optical (LO) and transversal optical (TO) modes, and both \(E_2\) (\(E_2^{\text{low}}\) and \(E_2^{\text{high}}\)) are nonpolar modes. These modes are Raman active, whereas the \(B_1\) modes are silent. Additionally, multi-phonon features such as combinations and overtones can lead to further peaks present in the ZnO Raman spectra (e.g., \(E_2^{\text{high}} + E_2^{\text{low}}\)). Plasma treatments have shown to be able to improve the electrical properties of ZnO thin films,\[27\] the adhesive properties of ZnO nanowires,\[28\] and even the corrosion properties of ZnO nanorods (ZnO-NRs).\[29\] It is understood that defects are introduced by the plasma, which in turn changes the semiconducting properties of the film.\[27,30\] Therefore, if the type and density of specific defects can be modified, the functional properties can be tuned to the respective application.\[29\]

In our previous studies on ZnMgAl alloys, the plasma gas composition was seen to play a central role in determining the nature of the plasma/surface interaction. When using argon as main working gas, the addition of either water or oxygen led to the identification of different surface reaction mechanisms. In particular, pure Ar plasma converted native carboxylates to carbonates, Ar/O\(_2\) gas mixtures showed mainly the oxidation of the surface, and an Ar/H\(_2\)O mixture showed a combination of both effects. These changes had a high impact on the adsorption of adhesives and self-assembled monolayers, where the addition of oxygen and especially water increased the adhesion properties of the surface.\[31,32\]

In this work, we present a novel setup that allows us to perform in situ Raman spectroscopy on the back-side of a gas permeable electrode. The setup geometry limits the plasma/surface interaction to the plasma effluent, thus allowing to determine the impact of long-living plasma-produced species on the surface. The method was successfully applied to the plasma treatment of ZnO-NR films as function of the plasma gas composition (Ar, Ar/H\(_2\)O, and Ar/O\(_2\)) gas mixtures).
2 | EXPERIMENTAL

2.1 | Novel plasma reactor for in situ characterization of the surface modifications due to the plasma effluent

A plasma reactor was developed to investigate the surface changes at the backside of a permeable electrode in real-time in situ conditions using Raman spectroscopy. The schematic of the setup is displayed in Figure 1. The gases (Linde, Germany) had a purity of 99.999%, and the flow was controlled by respective mass flow controllers (red-y-compact, Vögtin Instruments, Swiss) to produce three different plasma gas mixtures: (1) Ar + 5% H2O (Ar/H2O), (2) Ar + 5% O2 (Ar/O2), and (3) pure Ar. The flow ratios necessary to obtain the 5% volume fractions of H2O or O2 were adjusted by determination of the total water or oxygen contents using either a humidity sensor (UTF75, Sensor-Tec, Germany) or a lambda probe (BA 4510, Bühler, Germany). The total gas flow was kept constant at 2 L/min. The high-voltage electrode, consisting of an 18-mm-diameter copper disk topped by a 20-mm Al2O3 ceramic disk of 3-cm thickness as a dielectric barrier, was embedded in a poly(ether ether ketone) housing. The high voltage was produced by a G2000 high-voltage generator (Redline, Germany) and was set to 5.3 kV for all plasma gas mixtures using a frequency of 35 kHz. The novel approach of this setup is the use of a gas permeable electrode, which can be monitored at the backside using Raman spectroscopy. The electrode is coated with the material under investigation (here electrochemically deposited ZnO-NRs), so that the substrate/plasma effluent interaction can be investigated in situ and in real time. In this work, a stainless steel mesh (Type 304, 400 mesh, 0.001" diameter wire, Plano GmbH, Germany) was used as the electrode, offering a high gas permeability combined with high conductivity. The mesh is coated with ZnO-NRs (see Section 2.3) and mounted at a distance of 1 mm to the dielectric barrier. The gas is introduced to the plasma from the side and is then directed through the mesh.

2.2 | Equipment and methods

To confirm the successful application of the ZnO-NR on the steel mesh, field emission scanning electron microscopy (FE-SEM) was performed using a “NEON 40” FE-SEM (Carl Zeiss SMT AG, Oberkochen, Germany). The images were acquired at low acceleration voltages of <2 kV at a base pressure of below 10⁻⁶ bar using a Schottky Field Emitting Cathode.

The plasma reactor was coupled to an “InVia Renishaw Raman microscope” (Renishaw, Gloucestershire, UK), using a 532-nm YAG-Laser, a 50× objective, an 1800-L/mm grating, and a CCD detector. The plasma reactor was moveable to position the sample so that the microscope was focused on a mesh strand as indicated in Figure 1. During the in situ measurements, the position was kept constant. The measurements after the in situ measurement (called in the following “ex situ” measurements) were performed at different spots (at least three) on the mesh. The laser power used for all measurements was determined at the end of the objective by a calibrated USB photodiode (DIN EN ISO 9001, THORLABS, Germany) to

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**FIGURE 1** Schematic of the plasma reactor allowing in situ Raman spectroscopy on surfaces in contact with the plasma effluent for different plasma gas mixtures by using a coated mesh as gas permeable electrode. A field emission scanning electron microscopy (FE-SEM) image of the ZnO nanorod-coated mesh is presented at the right side, with the focus point for the Raman measurement marked with a red dot [Colour figure can be viewed at wileyonlinelibrary.com]
be 1.24 mW (10% set in software). The Raman spectrometer was calibrated using the peak position of 520.0 cm$^{-1}$ ($\pm 0.5$ cm$^{-1}$) of a reference silicon wafer. The recording time was set for the ex situ measurements to 10 s with 15 accumulations and for the in situ measurements to 5 s with six accumulations, resulting in an in situ recording time of 30 s. Thereby, 20 measurements were recorded before, 20 measurements during, and 20 measurements after the plasma, leading to 30 min recording time in total. The focus was automatically adjusted by a focus tracker between each measurement. To compare the in situ and ex situ measurements, the resulting Raman spectra were normalized to the $E_2^{\text{high}}$ at 437 cm$^{-1}$ without further corrections.

### 2.3 Coating of the mesh with ZnO-NR films

ZnO-NRs were grown on stainless steel mesh by cathodic electrodeposition in a three-electrode setup as already described elsewhere.$^{[33]}$ First, the mesh was cleaned in an ultrasonic bath of (sequentially) tetrahydrofuran, isopropanol, and ethanol. Afterward, the ZnO-NR deposition was carried out in an aqueous solution of 0.01 M hexamethylenetetramine and 0.01 M Zn(NO$_3$)$_2$$\cdot$6H$_2$O. The mesh was clamped into the preheated electrolyte solution ($T = 80 \pm 2^\circ$C), and a constant current density of $-1$ mA/cm$^2$ was applied for 900 s (the current density refers to the mesh size immersed into the solution). Electrochemistry was performed using a Reference 600 potentiostat (Gamry Instruments). A cylindrical tube (stainless steel) was used as a counter electrode to provide a homogenous electric field over the complete mesh. The reference electrode was a KCl-saturated Ag/AgCl electrode connected to the solution using a salt bridge (0.1 M NaNO$_3$ aqueous solution) to inhibit the heating of the electrode. After the deposition was finished, the samples were immediately taken out of the electrolyte, rinsed with ultrapure water (ultra-clear TWF, SG Water, Hamburg, Germany), and dried with clean compressed air.

The successful deposition was confirmed by FE-SEM images as seen in Figure S1, showing a typical NR structure with a width of 150 $\pm$ 50 nm. FE-SEM cross-sectional analysis (Figure S1c) revealed a complete coverage of the steel surface and an average NR length of 657.5 $\pm$ 108 nm.

### 3 RESULTS AND DISCUSSION

#### 3.1 Real-time in situ Raman spectroscopy

In Figure 2a, the normalized spectra (to $E_2^{\text{high}}$ at 437 cm$^{-1}$) collected in situ before, during, and after the plasma treatment using Ar/H$_2$O as plasma gas are displayed as contour map. The black areas indicate low intensity, whereas bright green areas illustrate high intensities of the respective Raman spectra. The x axis shows the time in seconds, where the plasma was switched on at 0 s and off after 600 s. Figure 2b presents the evolution of the intensity of selected peaks determined from the contour plot. Figure 2c displays the averaged spectra over 600 s before, during, and after the plasma, respectively.

The Raman spectra of the untreated ZnO-NR ($\approx 600$ to 0 s, Figure 2c) exhibited characteristic peaks for the ZnO wurtzite structure. The spectra were fitted to obtain the respective peak contributions (Figure S2). The results of the fits are presented in Table S1 and are summarized in Table 1. While the Raman peaks associated with the crystal lattice of ZnO are well established, peaks related to defects are quite diverse and often controversial. For instance, Khachadorian et al. showed the high diversity of different defect modes by calculating the phonon density of states for isolated Zn and O vacancies and interstitial Zn using density-functional theory (DFT) studies, where a large number of related phonon branches around 300 cm$^{-1}$ and between 450 and 520 cm$^{-1}$ were found.$^{[37]}$ Interestingly, the surface optical (SO) phonon mode (located at 555 cm$^{-1}$) related to defects such as disorderly arranged areas and grain boundaries was observed in the spectra.$^{[34,41,42]}$ Additionally, the positions of the $E_2^{\text{low}}$ and $E_2^{\text{high}}$ are redshifted and broadened (Table S1), indicating a defect-rich structure of the deposited ZnO-NRs.$^{[25]}$

During the plasma treatment using Ar/H$_2$O, new narrow peaks appeared at 594, 797, 848, 951, and 1092 cm$^{-1}$ immediately after the plasma was turned on: the five narrow peaks displayed a high intensity during an additional measurement (not shown here) in which the power of the Raman laser was reduced to zero while focusing on a gap of the net. Therefore, these peaks are assigned to plasma emissions which were gathered as stray light of the plasma emission. This is in agreement with the temporal development of the peaks (displayed in detail in Figure 2b for the peak centered at 950 cm$^{-1}$), which immediately disappeared as soon as the plasma was turned off. Besides, an increase in the $E_2^{\text{low}}$ peak (at 97 cm$^{-1}$), the $E_2^{\text{low}}$ asymmetric tail (132 cm$^{-1}$ to 300 cm$^{-1}$), and at 555 cm$^{-1}$ (SO phonon vibration mode) was seen: the $E_2^{\text{low}}$ vibration is dominated by the Zn atoms (in comparison with the $E_2^{\text{high}}$ (437 cm$^{-1}$), which is dominated by the oxygen atoms of the ZnO lattice), whereas the $E_2^{\text{low}}$ asymmetric tail is associated to lattice stress or displacement.$^{[25,26]}$ In the case of the SO phonon mode, Zeng et al. assigned its appearance to the loss of the long-range periodicity (and thus the symmetry) at the
FIGURE 2  In situ contour profile of the normalized (to $E_2^{\text{high}}$ at 437 cm$^{-1}$) Raman spectra during the Ar/H$_2$O plasma treatment. Spectra were recorded continuously 600 s before, during, and after the plasma treatment, where the plasma treatment started at 0 s. (a) Time-resolved contour map of the Raman spectra. (b) Time-resolved peak evolution of chosen peak intensities. (c) Normalized, averaged spectra over the complete time before, during, and after the plasma [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 1  Peak position and their respective assignment found in the Raman spectra before and after the respective plasma treatments

| Wavenumber | Assignment$^{[25,26,34–36]}$ | Appear in |
|------------|------------------------------|-----------|
| 97 cm$^{-1}$ | $E_2^{\text{low}}$ | All |
| 132–300 cm$^{-1}$ (117, 165, and 250 cm$^{-1}$) | $E_2^{\text{low}, \text{tail}}$ | All |
| 203 cm$^{-1}$ | $2E_2^{\text{low}}$ | All |
| 330 cm$^{-1}$ | $E_2^{\text{high}} - E_2^{\text{low}}$ | All |
| 376 cm$^{-1}$ | $A_1^{\text{(TO)}}$ | All |
| 415 cm$^{-1}$ | $E_1^{\text{(TO)}}$ | All |
| 437 cm$^{-1}$ | $E_2^{\text{high}}$ | All |
| 473 cm$^{-1}$ | 2LA, phonon branches$^{[37]}$ and Zn$^{[37]}$ | All |
| 557 cm$^{-1}$ | SO phonon mode$^{[34]}$ | All |
| 580 cm$^{-1}$ | $A_1^{\text{(LO)}}$ and $E_2^{\text{(LO)}}$$^{[38–40]}$ | Ar/O$_2$ plasma |
| 670 cm$^{-1}$ | TA + LO | All |
| 594, 797, 848, 951, and 1092 cm$^{-1}$ | plasma emissions | Ar/H$_2$O plasma |
| 1100 cm$^{-1}$ | 2$A_1^{\text{(LO)}}, 2L_0$, and 2$E_1^{\text{(LO)}}$ | All |
surface which they confirmed by high-resolution transmission electron microscopy (HRTEM) measurements.\[34,42] Thus, additional TEM measurements were conducted before and after the Ar/H₂O plasma treatment. The results are presented in Figures S8–S10 and showed no major change in the crystal phase but a roughening of the surface after the Ar/H₂O plasma treatment. This roughening most likely caused the symmetry loss at the surface and gave rise to the SO phonon mode. This process induced stress in the lattice due to the creation of interfacial defects in agreement with the results of Mondal et al.\[41] SO phonon mode, $E_{2}^{\text{low}}$, and the $E_{2}^{\text{low}}$ asymmetric tail were continuously and simultaneously increased over the complete 600-s plasma treatment, showing their direct correlation. After the plasma was turned off, these changes slowly decreased.

The in situ measurement of the plasma treatment using Ar/O₂ is displayed in Figure 3. Here, a new peak located at 580 cm⁻¹ rapidly rose during the plasma “on” time. This peak position is associated with the closely located $A_{1}(\text{LO})$ and $E_{1}(\text{LO})$ modes.\[38–40] Thereby, the $E_{1}(\text{LO})$ is very sensitive to oxygen-related defects, such as $V_{O}$.\[38,41] The new peak was accompanied by a simultaneous rise in the $E_{2}^{\text{low}}$ (97 cm⁻¹) and slightly the $E_{2}^{\text{low}}$ asymmetric tail (132–300 cm⁻¹) as already seen during the Ar/H₂O plasma. It has to be noted that although oxygen-related defects are created, the interaction of the plasma effluent is based on the Zn atoms ($E_{2}^{\text{low}}$) rather than the O atoms ($E_{2}^{\text{high}}$). The fast rise within the first 100-s plasma treatment was followed by a steady behavior during the rest of the plasma treatment. Afterwards, the asymmetric tail immediately dropped, whereas the $A_{1}(\text{LO})/E_{1}(\text{LO})$ peak and the $E_{2}^{\text{low}}$ slowly decreased. Thus, the small lattice stress is caused by the plasma effluent and not by the created defects. This supports an assignment of the peak at 580 cm⁻¹ as oxygen vacancy, because, contrary to interfacial defects, oxygen vacancies lead to a relaxation of the surrounding lattice.\[43] In comparison, the in situ measurement using pure Ar (Figure S3) showed no defect formation during the plasma treatment. Only the signal corresponding to $E_{2}^{\text{low}}$ increased slightly during the plasma “on” time and relaxed immediately when the plasma was turned off. Corresponding X-ray photoelectron spectroscopy (XPS)

![In situ contour profile of the normalized (to $E_{2}^{\text{high}}$ at 437 cm⁻¹) Raman spectra during the Ar/O₂ plasma treatment. Spectra were recorded continuously 600 s before, during, and after the plasma treatment, where the plasma treatment started at 0 s. (a) Time-resolved contour map of the Raman spectra. (b) Time-resolved peak evolution of chosen peak intensities. (c) Normalized, averaged spectra over the complete time before, during, and after the plasma](https://wileyonlinelibrary.com)
measurements (Supporting Information) directly after the plasma treatment showed no significant changes in the surface adsorbates (Figure S5) and zinc (Figure S7). Only minor changes were seen in the oxygen after the Ar/O₂ plasma treatment, which was assigned to oxygen adsorbed at oxygen vacancies (Figure S6).

Taking all results into account, we conclude that all plasma gas mixtures produced a measurable interaction with the zinc sublattice (visible by the increased \(E_{2}^{\text{low}}\)), but only the addition of oxygen-containing components (O₂ or H₂O) led to the formation of defects. It has to be kept in mind that due to the backside geometry, only the plasma effluent (long-time stable reactive species) could interact with the ZnO-NRs. Pure atmospheric-pressure Ar plasma effluents are known to contain various meta-stable excited Ar species.[44] Both Ar/H₂O and Ar/O₂ plasmas contain additional oxidizing species in the plasma effluent, but these species are different in both cases: while Ar/H₂O plasma discharges are known to mainly produce reactive OH radicals and H₂O₂,[45] Ar/O₂ plasma discharges generate activated O and O₃.[30]

### 3.2 Raman spectroscopy at an expanded timescale

In order to determine the long-term stability of the plasma-induced defects, the results gathered in situ were compared with ex situ Raman measurements performed directly after the plasma treatment and after 1-month storage in vacuo. The time dependence of the peak ratios (including the in situ results presented beforehand) is shown in Figure 4. The error bars are based on at least three samples which were measured at multiple spots (except for the in situ measurements) on the same mesh. Figure 4 illustrates the difference of the measurements in situ compared with measurements after the plasma: already 600 s after the plasma has been switched off (corresponding to \(t = 1200\) s in Figure 4), a decrease in nearly all peak ratios is visible. Especially the stress induced by the plasma and the increase in the \(E_{2}^{\text{low}}\) due to the pure Ar plasma treatment is only detectable during and shortly after the plasma treatment. This emphasizes the benefit of in situ measurements and their contribution to the knowledge of plasma effluent/surface interfaces. Different behaviors were seen depending on both the plasma gas mixture and the investigated normalized intensities: For the Ar/O₂ plasma-treated ZnO-NR, all plasma-induced changes immediately started to relax after the plasma was switched off (compare with Figure 3). Within the 600 s, after the plasma is switched off (in situ), the stress and defects were seen to relax quite fast. No permanent change induced by the plasma could be detected on the treated surfaces after 1 month. In comparison, the plasma treatment using Ar/H₂O led to highly stable defects even after 1 month. The lattice stress measured ex situ stayed at a higher level compared with the untreated sample, although not as high as seen during the plasma. Thus, both the defects themself and the plasma effluent/surface interaction caused stress in the material. Pure Ar plasma showed no plasma effluent-induced changes except for the already discussed increase in the \(E_{2}^{\text{low}}\) during the plasma treatment during the in

![Comparison of in situ (the value at the end of the plasma treatment and the end of the in situ measurements were taken and are indicated by a black frame) and ex situ measurements after the plasma for different plasma-induced changes in the ZnO nanorod (NR). The plasma duration is indicated by a violet band. The peak ratios (all normalized to \(E_{2}^{\text{high}}\) at 437 cm\(^{-1}\)) are shown for (a) defect peak (located at 555 cm\(^{-1}\) for Ar and Ar/H₂O and 580 cm\(^{-1}\) for Ar/O₂), (b) Zn lattice vibration correlated to the \(E_{2}^{\text{low}}\) at 97 cm\(^{-1}\), and (c) the lattice stress associated to the \(E_{2}^{\text{low}}\) asymmetric tail from 132–300 cm\(^{-1}\) [Colour figure can be viewed at wileyonlinelibrary.com](image)
situ measurements. Despite this, a small increase in the $E_2^{low}$ asymmetric tail and the SO phonon mode was visible in the ex situ measurements. These are attributed to not homogeneously distribute residual humidity.[31]

4 | CONCLUSION

It could be shown that the backside in situ Raman spectroscopic analysis allowed for the study of plasma effluent-induced changes on ZnO-NRs. In particular, the modification of the ZnO-NR surface-near region as a function of different plasma gas mixtures was evaluated. The plasma treatment using pure Ar led to minor interactions with the Zn sublattice, whereas Ar/O$_2$ and Ar/H$_2$O plasma treatments introduced defects in the ZnO-NR surface-near region. Ar/H$_2$O plasma treatments steadily increased the SO phonon mode throughout the complete plasma treatment, most likely caused by an increased roughness of the surface as seen in HRTEM. Contrary, Ar/O$_2$ led to a rapid increase in oxygen-related defect density (e.g., $V_O$) mainly during the initial phase of the plasma treatment. Thereby, the presented in situ studies demonstrated that oxygen-related reactive species must be present in the plasma effluent in order to introduce defects via interactions with the Zn sublattice. Ex situ measurements showed that the plasma-induced oxygen defects using Ar/O$_2$ were not stable, whereas the SO phonon mode induced by the Ar/H$_2$O plasma treatments was stable over the long-time storage. These results have a strong impact on the understanding of oxidative plasma catalytic processes.

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REFERENCES

[1] L. Černáková, D. Kováčik, A. Zahoránová, M. Černák, M. Mazúr, Plasma Chem. Plasma Process. 2005, 25, 427.
[2] I. Belhaj Khalifa, N. Ladhari, J. Textile Inst. 2019, 1, 1.
[3] Z. Ke, Z. Yu, Q. Huang, Plasma Processes Polym. 2013, 10, 181.
[4] J. Jeon, T. G. Klaempfl, J. L. Zimmermann, G. E. Morfill, T. Shimizu, New J. Phys. 2014, 16, 103007.
[5] P. A. Christensen, Z. T. A. W. Mashhadani, P. A. Martin, Plasma Chem. Plasma Process. 2018, 38, 293.
[6] A. Zhou, D. Chen, C. Ma, F. Yu, B. Dai, Catalysts 2018, 8, 256.
[7] S. Futamura, M. Sugasawa, IEEE Trans. on Ind. Appl. 2008, 44, 40.
[8] A. Rodrigues, J.-M. Tatibouët, E. Fourrè, Plasma Chem. Plasma Process. 2016, 36, 901.
[9] M. Černák, L. Černáková, I. Hudec, D. Kováčik, A. Zahoránová, Euro. Phys. J. - Appl. Phys. 2009, 47, 22806.
[10] B. Eliasson, U. Kogelschatz, IEEE Trans. Plasma Sci. 1991, 19, 1063.
[11] A. Schutze, J. Y. Jeong, S. E. Babayan, J. Park, G. S. Selwyn, R. F. Hicks, IEEE Trans. Plasma Sci. 1998, 26, 1685.
[12] P. Bruggeman, R. Brandenburg, J. Phys. D: Appl. Phys. 2013, 46, 464001.
[13] P. A. Christensen, Z. T. A. W. Mashhadani, M. A. Carroll, P. A. Martin, Plasma Chem. Plasma Process. 2018, 38, 461.
[14] M. Budde, C. Corbella, S. Große-Kreul, T. de los Arcos, G. Grundmeier, A. von Keudell, Plasma Processes Polym. 2018, 15, 1700230.
[15] C. Corbella, A. Pranda, S. Portal, T. de los Arcos, G. Grundmeier, G. S. O. A. Keudell, Plasma Process Polym 2019, 16, 190019.
[16] A. Kolodziejczak-Radzimiska, T. Jesionowski, Materials (Basel, Switzerland) 2014, 7, 2833.
[17] M. M. Arafat, B. Dinan, S. A. Akbar, A. S. M. A. Haseeb, Sensors (Basel, Switzerland) 2012, 12, 7207.
[18] R. S. Kate, S. A. Khalate, R. J. Deokate, J. Alloys and Comp. 2018, 734, 89.
[19] E. C. Neyts, K. K. Ostrikov, M. K. Sunkara, A. Bogaerts, Chem. Rev. 2015, 115, 13408.
[20] Y. Wang, H. Arandiyian, J. Scott, A. Bagheri, H. Dai, R. Amal, J. Mater. Chem. A 2017, 5, 8825.
[21] Z. L. Wang, J. Phys.: Condens. Matter 2004, 16, R829.
[22] D. Meinderink, K. J. Nolkemper, J. Bürger, A. G. Orive, J. K. Lindner, G. Grundmeier, Surf. Coat. Technol. 2019, 375, 112.
[23] M. Skompska, K. Zarębska, Electrochim. Acta 2014, 127, 467.
[24] L. Xu, Y. Guo, Q. Liao, J. Zhang, D. Xu, J. Phys. Chem. B 2005, 109, 13519.
[25] M. Ščepanovič, M. Grujić-Brojičin, K. Vojisavljević, S. Bernik, T. Srečkovič, J. Raman Spectrosc. 2010, 41, 914.
[26] V. Russo, M. Ghidelli, P. Gondoni, C. S. Casari, A. L. Bassi, J. Appl. Phys. 2014, 115, 73508.
[27] S. Lee, S. Bang, J. Park, S. Park, W. Jeong, H. Jeon, Phys. Stat. Sol. (A) 2010, 207, 1845.
[28] X. Q. Meng, D. X. Zhao, J. Y. Zhang, D. Z. Shen, Y. M. Lu, L. Dong, Z. Y. Xiao, Y. C. Liu, X. W. Fan, Chem. Phys. Letters 2005, 413, 450.
[29] O. Ozcan, K. Pohl, P. Keil, G. Grundmeier, Electrochem. Commun. 2011, 13, 837.
[30] J. S. Meena, M.-C. Chu, Y.-C. Chang, H.-C. You, R. Singh, P.-T. Liu, H.-P. D. Shieh, F.-C. Chang, F.-H. Ko, J. Mater. Chem. C 2013, 1, 6613.
[31] S. Knust, A. Kuhlmann, T. de los Arcos, G. Grundmeier, RSC Adv. 2019, 9, 35077.
[32] S. Knust, A. Kuhlmann, A. G. Orive, T. Arcos, G. Grundmeier, Surf. Interface Anal. 2020, 52, 1077.
[33] D. Meinderink, A. G. Orive, S. Ewertowski, I. Giner, G. Grundmeier, ACS Appl. Nano. Mater. 2019, 2, 831.
[34] H. Zeng, X. Ning, X. Li, Phys. Chem. Chem. Phys. 2015, 17, 19637.
[35] H. Fukushima, H. Uchida, H. Funakuba, T. Katoda, K. Nishida, J. Ceram, Soc. Japan 2017, 125, 445.
[36] S. S. Gaikwad, A. C. Gandhi, S. D. Pandit, J. Pant, T.-S. Chan, C.-L. Cheng, Y.-R. Ma, S. Y. Wu, J. Mater. Chem. C 2014, 2, 7264.
[37] S. Khachadorian, R. Gillen, S. Choi, C. Ton-That, A. Kliem, J. Maultzsch, M. R. Phillips, A. Hoffmann, Phys. Status Solidi B 2015, 252, 2620.
[38] S. Pal, N. Gogurla, A. Das, S. S. Singha, P. Kumar, D. Kanjilal, A. Singha, S. Chattopadhyay, D. Jana, A. Sarkar, J. Phys. D: Appl. Phys. 2018, 51, 105107.
[39] Y. Y. Tay, T. T. Tan, M. H. Liang, F. Boey, S. Li, Appl. Phys. Lett. 2008, 93, 111903.
[40] E. Alarcón-Lladó, R. Cuscó, L. Artús, J. Jiménez, B. Wang, M. Callahan, J. Phys.: Condens. Matter 2008, 20, 445211.
[41] A. Mondal, S. Pal, A. Sarkar, T. S. Bhattacharya, S. Pal, A. Singha, S. K. Ray, P. Kumar, D. Kanjilal, D. Jana, J. Raman Spectrosc. 2019, 50, 1926.
[42] H. Zeng, W. Cai, B. Cao, J. Hu, Y. Li, P. Liu, Appl. Phys. Lett. 2006, 88, 181905.
[43] A. Janotti, C. G. van de Walle, J. Crystal Growth 2006, 287, 58.
[44] G.-D. Wei, C.-S. Ren, M.-Y. Qian, Q.-Y. Nie, IEEE Trans. Plasma Sci. 2011, 39, 1842.
[45] Y. Du, G. Nayak, G. Oinuma, Z. Peng, P. J. Bruggeman, J. Phys. D: Appl. Phys. 2017, 50, 145201.

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