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X-ray photoelectron spectroscopy and auger electron spectroscopy studies of Al-doped ZnO films

M. Chen [a,*], X. Wang [a], Y.H. Yu [a], Z.L. Pei [b], X.D. Bai [b], C. Sun [b], R.F. Huang [b], L.S. Wen [b]

[a] *Ion Beam Laboratory, Shanghai Institute of Metallurgy, Chinese Academy of Sciences, Shanghai 200050, People's Republic of China*
[b] *Institute of Metal Research, the Chinese Academy of Sciences, Shenyang 110015, People's Republic of China*

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Abstract

The chemical state of oxygen, aluminum and zinc in Al-doped ZnO (ZAO) films was investigated by X-ray photoelectron spectroscopy (XPS), as well as the transition zone of the film-to-substrate, by auger electron spectroscopy (AES). The results show that zinc remains mostly in the formal valence states of Zn^{2+}. A distinct asymmetry in Al $2p_{3/2}$ photoelectron peaks has been resolved into two components, one is metallic Al and the other is oxidized Al. The depth profile of the two components revealed that metallic Al mainly exists in the thin surface layer. The close inspection of O1s shows that O1s is composed of three components, centered at 530.15 ± 0.15, 531.25 ± 0.20 and 532.40 ± 0.15 eV, respectively. AES reveals an abrupt transition zone between the ZAO and quartz substrate.

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Keywords: Al-doped ZnO (ZAO); XPS; Al; Oxygen; Transition zone

1. Introduction

Transparent conductive oxide (TCO) films have been extensively used in a variety of electronic and opto-electronic applications because of the high transmission in the visible region, the high infrared reflection and the low DC resistivity. The great mass market of panel flat display is the main momentum of TCO system research. The most important TCO film in practical applications nowadays is the Sn-doped In_2O_3 (ITO) [1]. However, just recently, Al-doped ZnO (ZAO) is emerging as an alternative potential candidate of ITO thin films due to its cheap and abundant raw material and nontoxic feature, which is comparable with the ITO electrical and optical properties, as well as being cost-effective, easy to fabricate and have a good stability (in plasma) [2,3]. Most researches have been focused on the improvement of electrical and optical properties of ZnO:Al films by choosing optimum substrate temperature or post-treatment process (including annealing temperature, annealing time and ambient, etc.) because high temperature helps the bigger growth of crystalline and the out-diffusion of oxygen to increase the number of oxygen vacancies. Consequently, this condition increases the carrier mobility

* Corresponding author. Tel.: +86-21-62511070/8305; fax: +86-021-62513510.
E-mail address: mchen@itsvr.sim.ac.cn (M. Chen).

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and carrier concentration [1–3,5]. However, the low temperature deposition (LTD) is recently attracting interests because it shows the significant advantages in the deposition of TCO films on temperature-sensitive substrates [4]. Regarding the limits of our knowledge, the quantitative micro-compositional analysis of both of the undoped and doped bulk zinc oxide and their stoichiometric deviation have been reported in the literatures, but a detailed study on the aluminum-doped transparent conducting films of zinc oxide is lacking. Only Islam et al. [5] recently reported the X-ray photoelectron spectroscopy (XPS) study of ZAO films, and no information about Al $2p_{3/2}$ peak was given out.

In this paper, we try to give the chemical state of Zn, Al and O in ZAO films by comparing and studying the XPS data of as-deposited and annealed film.

2. Experimental

The ZAO films were prepared by DC magnetron reactive sputtering of an alloy target of Zn/Al (98.5:1.5 wt.%) in an oxygen and argon mixture. Quartz glass substrates were used and rinsed in acetone, ethanol and distilled water, sequentially [6]. The substrates were not intentionally heated during sputtering. The as-deposited films were annealed for 60 min in vacuum (the pressure is prior to 3×10^{-3} Pa) at different temperatures. All films have a hexagonal structure of bulk ZnO and a high-preferred orientation with the *c*-axis ((200) plane) perpendicular to the substrate, which was determined from the X-ray diffraction patterns. Both of the as-deposited and annealed films show an average transmittance of above 90% in the visible region. X-ray photoemission spectroscopy (XPS) and auger electron spectroscopy (AES) were performed using the LAS-3000 surface analysis system (RIBER, France). XPS measurements were carried out using Al-K_α X-rays (1489.6 eV, width 0.85 eV), the energy scale of the spectrometer has been calibrated with pure Cu samples, and the pressure in the XPS analysis chamber was $\sim 1 \times 10^{-7}$ Pa. In order to examine the chemical state of each element in film body and investigate the transition zone of film/substrate, some samples were etched by Ar^+ bombardment ($\sim 5 \times 10^{-5}$ Torr) with an energy of 2.5 kV and a current of 2.0 μA. The etching rate of the sample was 1.5 nm min^{-1}. The position of the C1s peak was taken as a standard (with a binding energy of 285.0 eV). For the comparison of Al with ZAO films, we have also made XPS measurements on a piece of metal aluminum with a purity of 99.999% before and after etching in 20 min by Ar^+ bombardment.

3. Results and discussions

XPS survey spectra (100–1500 eV) on the initial surface and on the bulk of ZAO films was first produced before the high-resolution scan for Al, Zn and O. The elements Al, Zn, O and C were found in the spectra.

3.1. Zn $2p_{3/2}$ peaks

The core line of Zn $2p_{3/2}$ shows a similar feature in both the as-deposited and annealed ZAO films. Fig. 1 gives the typical XPS data of Zn $2p_{3/2}$ in ZAO film before and after etching of 5 min. On the surface, the core line of zinc shows a little asymmetry, which was attributed to the presence of excess zinc in the films [5]. However, the asymmetry of the zinc line disappears after an etching of 1 min (not shown here). Then, the core line of Zn 2p exhibited high symmetry (the open circle line) in the film

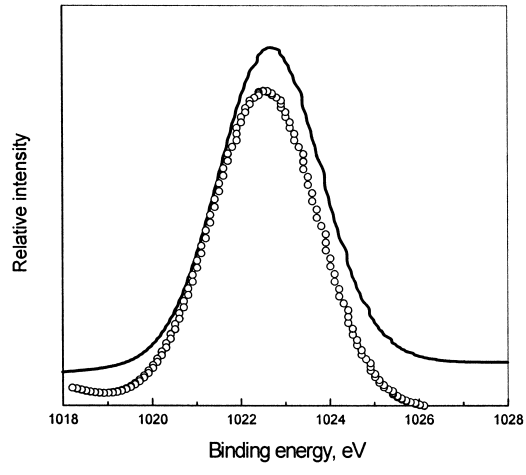

Fig. 1. XPS data of Zn $2p_{3/2}$ in ZAO film before (circle) and after etching for 5 min (line), respectively.

body, indicating that most of the asymmetry feature of zinc resides only on the very thin layer. In all cases, the binding energy of Zn $2p_{3/2}$ remains at 1022.40 ± 0.10 eV, which is larger than the value of Zn in bulk ZnO. It also confirms that the largest and the majority of Zn atoms remain, in all probed films, in the same formal valence state of Zn^{2+} within an oxygen deficient ZnO_{1-x} matrix [3]. No metallic Zn with a binding energy of 1021.50 eV [5] was observed, which confirms again that Zn exists only in the oxidized state. For both of the as-deposited and annealed films, the position of Zn $2p_{3/2}$ shows little variation with the increase in etching time, indicating the stable chemical state of Zn in the film body.

3.2. Al $2p_{3/2}$ peaks

An attempt to detect Al in ZAO film using XPS, and thereby, predicting its chemical state is not successful because of (i) the low concentration of Al in the ZnO matrix, and (ii) the low values of the ionization cross-section of Al. Additional difficulties are caused by the presence of X-ray satellites on the low binding energy side of the Zn-3p photoelectron peak [5]. However, the content of Al in ZAO films is usually varied from 1.5 to 7.0 at.% [7–10]. The optimum content of Al used in the alloy target of Zn/Al is 1.5 wt.%, which always causes an atomic content of Al in ZAO films above 4.0 at.% [7,8,10]. It is possible to detect the Al in ZAO films in order to determine its chemical state. Fig. 2 shows the typical XPS data of Al $2p_{3/2}$ in both of the as-deposited and the annealed ZAO films. In this work, the Al $2p_{3/2}$ peak shows a much smaller peak intensity compared to that of the Zn $2p_{3/2}$ peak. The Al $2p_{3/2}$ exhibits an asymmetry feature with a broader FWHM of above 2.5 eV, indicating the possibility of existence of a multi-component Al. The Gaussian-resolved result shows that there are two components in both of the as-deposited and annealed ZAO films. The strong intensity component, with a binding energy of 74.20 ± 0.10 eV, is slightly shifted towards a lower binding energy, compared to the 74.60 eV peak position in stoichiometric Al_2O_3, an indication of an oxygen-deficient ZnO matrix [3,11]. The component centered at 72.20 ± 0.05 eV is characteristic of metallic Al. The variation of the relative intensity ratio of metallic Al component to oxidized Al component on etching time in both of the as-deposited and annealed ZAO films is shown in Fig. 3, respectively. The relative intensity of the metallic Al decreases with increasing etching time. As the etching time increases to 10 min, this component cannot be effectively detected in the present testing resolution; thus, the core line of Al 2p exhibits a high symmetry, indicating the possibility that the asymmetry of Al $2p_{3/2}$ mostly exists in a thin surface layer. In order to estimate the influence of Ar^+ bombardment on the variation of metallic Al component with etching time, a piece of

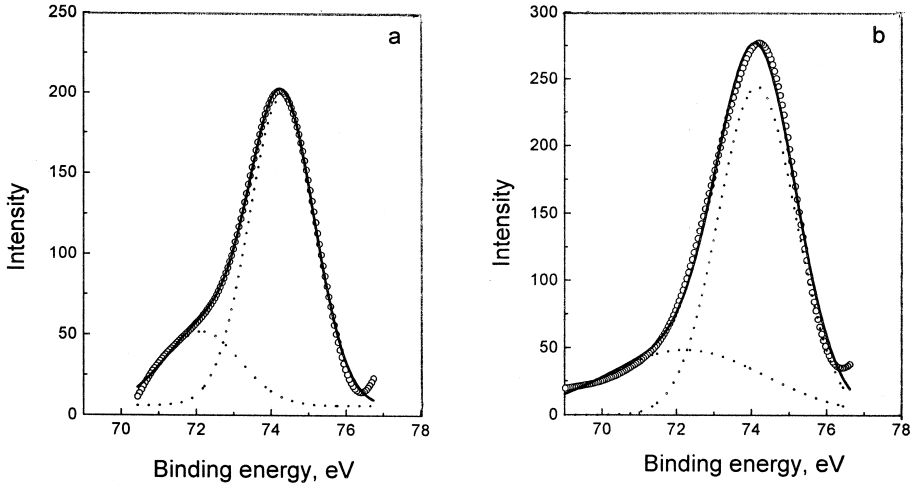

Fig. 2. Typical XPS data of Al $2p_{3/2}$ and its Gaussian-resolved component for (a) as-deposited and (b) annealed ZAO film, respectively.

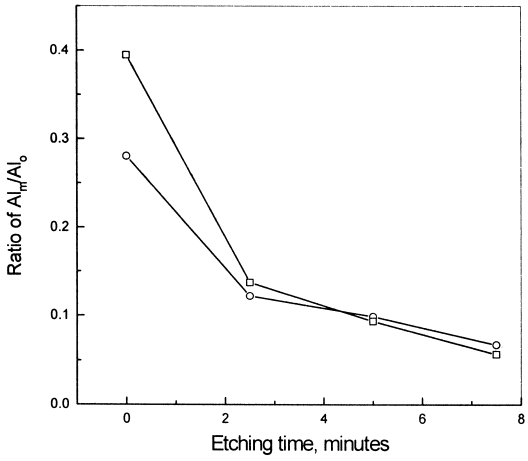

Fig. 3. Dependence of relative intensity ratio of metallic Al (Al_m) to oxidized Al (Al_o) on etching time for (a) as-deposited (circle) (b) annealed ZAO film (square), respectively.

metal Al with a purity of 99.999%, was etched for 20 min under the same conditions. The XPS results indicate that only a high symmetric signal of metal Al 2p, with a binding energy of 72.20 eV, was observed before and after etching, which obviously excludes the effect of Ar^+ bombardment on the variation of metallic Al component in ZAO films. In fact, the asymmetry character of Al can still be significantly detected even in the ZAO films annealed in oxygen atmosphere, such as air, which is actually the common feature of Al in ZAO films. On the other hand, this behavior of the existence of metallic Al in ZAO films obtained by sputtering an alloy target [5,6,9,12] has never been observed by X-ray diffraction pattern analysis even if the concentration of Al in target exceeds to 3.0 wt.%. That means there are no characteristic peaks of metallic Al that appeared in X-ray diffraction patterns. This may be due to the limited content of metallic Al observed in ZAO films, which is beyond the sensitivity of X-ray diffraction analysis. This metallic Al may be mainly segregated around grain boundaries and may be electrically inactive [1,13] as interstitial atoms, similar to the observation of Sn in Sn-doped In_2O_3 film [13]. It can be noticed from Fig. 3 that the relative content of metallic Al in the annealed film decreases faster with depth than in the as-deposited film. On the other hand, the fact that the relative content of metallic Al in the surface layer of annealed ZAO film is higher than that of the as-deposited film may imply that the annealing procedure helps metallic Al migrate to the film surface. Metallic Al excess in the surface layer suggests that a large oxygen deficiency exists in the surface layer of ZAO films. This was confirmed by the results in Section 3.3 concerning the O1s peak.

3.3. O1s peaks

The typical O1s peak in the surface can be consistently fitted by three nearly Gaussian, centered at 530.15 ± 0.15, 531.25 ± 0.20 and 532.40 ± 0.15 eV, respectively, in both the as-deposited and annealed films (Fig. 4). The fitted results indicate that each resolved component has a FWHM lower than 2.0 eV, while an initial O1s peak commonly has a FWHM above 2.90 eV. The high binding energy component located at 532.40 ± 0.15 eV is usually attributed to the presence of loosely bound oxygen on the surface of ZAO film, belonging to a specific species, e.g., $-CO_3$, adsorbed H_2O or adsorbed O_2 [3,5]. It was also observed that this component disappeared after an etching of 15 min for the as-deposited ZAO film; while for the annealed films, the necessary etching time is about 10 min [6]. It must be mentioned that this component cannot be completely removed, even by annealing the film in vacuum at a temperature of as high as 400°C (see Fig. 6).

The component on the low binding energy side of the O1s spectrum at 530.15 ± 0.15 eV is attributed to O^{2-} ions on wurtzite structure of hexagonal Zn^{2+} ion array, surrounded by Zn (or the substitution of Al) atoms with their full complement of nearest-neighbor O^{2-} ions [9,11,14]. In other words, the intensity of this component is the measure of the amount of oxygen atoms in a fully oxidized stoichiometric surrounding. The medium binding energy component, centered at 531.25 ± 0.20 eV, is associated with O^{2-} ions in the oxygen deficient regions within the matrix of ZnO [15]. Therefore, changes in the intensity of this component may be connected in part to the variations in the concentration of oxygen vacancies. It was also mentioned that the intensity of this component always appears higher than that of the low binding energy component in the surface layer, indicating the large oxygen-deficient state of

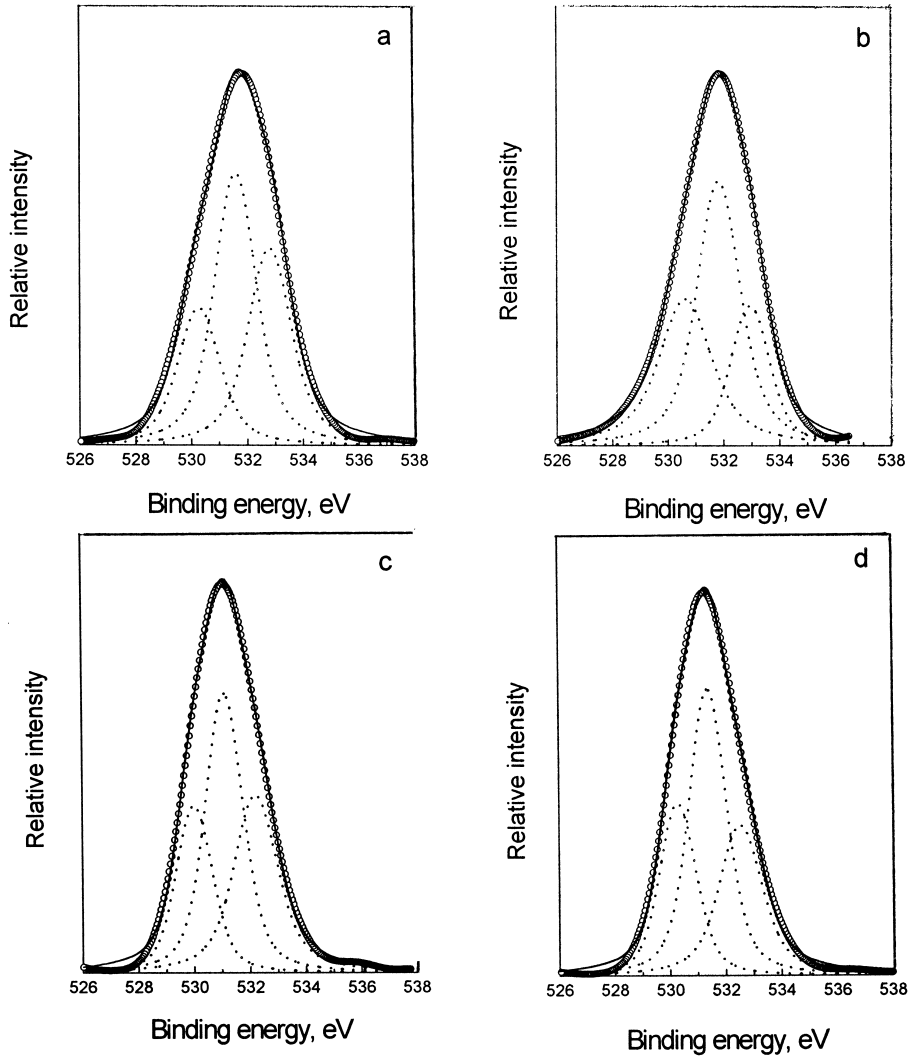

Fig. 4. XPS data (circle: experimental; dot line: components) of as-deposited (a,c) and annealed (b,d) ZAO film before (a,b) and after an etching of 5 min (c,d), respectively.

the surface layer. The large oxygen deficiency in the surface, or in other words, the Zn (or Al) enrichment, was found to be helpful for the stability of ZAO films to plasma condition [3,16]. The variation of the relative intensity ratio of medium component to total O1s is depicted in Fig. 5. It can be seen that the relative intensity of medium component O1s decreases continuously as etching time increases in both of the as-deposited and annealed film. The annealed film exhibits faster decrease than the as-deposited film with etching time, indicating that more oxygen vacancies remain in the surface layer of annealed film than in the as-deposited film.

In addition, the study of the films annealed at different annealing temperature gives the relative intensity variation of each component on the initial (without etching) film surface with temperature (Fig. 6). It can be seen that the relative intensity of high binding energy component decreases continuously with increase annealing temperature, in contrary with the significant increase of relative intensity of the low and medium binding energy components, indi-

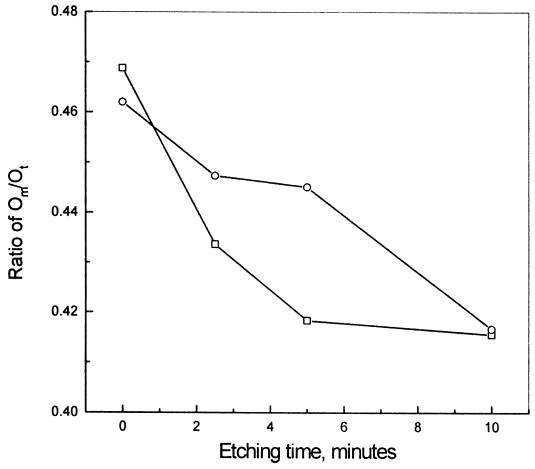

Fig. 5. Dependence of the intensity ratio of medium component (O_m) centered at 531.25 ± 0.20 eV to total intensity (O_t) on etching time for (a) as-deposited (circle) and (b) annealed ZAO films (square), respectively.

cating the clear changes in the oxygen chemical state as a result of the annealing temperature. The increase in the two components seems to come not only from the decrease of high binding energy component, but also to the surface chemical state of oxygen because (i) the total O1s content shows little change with annealing temperature (similar to the observation of Szörényi et al. [11] that the total O1s content did not change with the excimer laser processing fluence in ITO films), and (ii) the relative intensity of medium and low binding energy also changes in the same time. The faster increase of relative intensity of medium component with annealing temperature compared to the low component indicates that the surface gets reduced via oxygen removal in annealed film. Furthermore, it is well known that more oxygen-deficient film commonly exhibits a lower resistivity. It has been reported that the measured resistivity shows strong dependence on annealing temperature. As the annealing temperature increases, the resistivity decreases obviously [7].

3.4. Depth profile

AES was performed to determine the depth profile of each element in the ZAO film on quartz substrate. The sample was first annealed at 250°C in vacuum for 60 min (Fig. 7). Though we have not intentionally cared about the effect of the differences in roughness of substrates, three samples cut from the same initial annealed sample have been carried out by AES testing. No significant differences have been observed. The typical results are depicted in Fig. 6, without applying the sensitivity factor correction. It appeared that the ZAO/quartz interface is

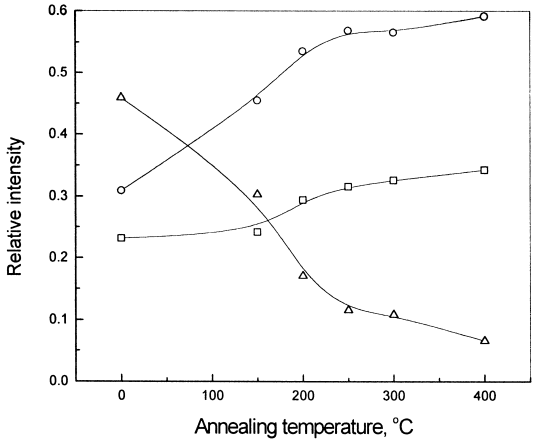

Fig. 6. Dependence of relative intensity of the three fitted components centered at (a) 531.25 ± 0.20 eV (circle), (b) 530.15 ± 0.15 eV (square) and (c) 532.40 ± 0.15 eV (triangle), on annealing temperature, respectively.

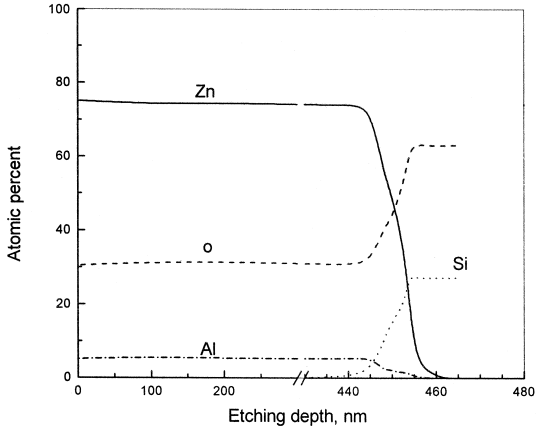

Fig. 7. Atomic depth profile of Zn, Al, and O in ZAO film deposited on quartz substrate after being annealed at 250°C in vacuum.

extremely abrupt: the transition zone between the ZAO and quartz substrate regions is about 20 nm. In the other study of transition zone of ITO/quartz, the value was observed to be about 60 nm [17]. In practical applications, SiO_2 buffer is used to form a sandwich structure of ITO/SiO_2/substrate in order to effectively prevent the inter-diffusion of the film and the substrate [18,19]. The narrower transition zone of the ZAO/quartz than that of the ITO/quartz is an important information for the substitution of ZAO for ITO films.

4. Conclusions

The following conclusions were obtained in this work.

(A) There is an asymmetry on the very thin surface layer and there is a high symmetry in the bulk for the Zn $2p_{3//2}$ XPS peak in both of the as-deposited and annealed ZAO films

(B) Al enrichment in the surface layer of ZAO films has been observed. A clear asymmetry of Al $2p_{3//2}$ XPS peak in the surface layer in both of the as-deposited or annealed ZAO films was resolved into two components: the one centering at 72.20 ± 0.05 eV, which is attributed to metallic Al, and the other has a binding energy of 74.20 ± 0.10 eV due to oxidized Al.

(C) Three distinct components of O1s fitted by Gaussian devolution, which centered at 530.15 ± 0.15, 531.25 ± 0.20, and 532.40 ± 0.15 eV, respectively, are noticed.

(D) A narrow transition zone of ZAO/quartz was observed.

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