Enhancement of pH Tolerance in Conductive Al-Doped ZnO Nanofilms via Sequential Annealing

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ABSTRACT: Chemically stable and electrically conductive metal oxide nanofilms are promising as robust electrodes for chemical/biosensors and for photoelectrochemical applications, which require harsh conditions (e.g., acidic or basic environments). Among the various conductive metal oxides, impurity-doped ZnO nanofilms deposited on substrates are chemically nonresistive to acidic and basic environments because of the inevitable etching effects. Herein, we demonstrate a strategy to enhance the pH tolerance of Al-doped ZnO (AZO) nanofilms using a sequential annealing technique for film preparation. This technique involves first annealing in air followed by annealing in Zn vapor atmosphere. Although the as-grown AZO nanofilms rapidly dissolved in acidic and basic solutions, the sequentially annealed AZO nanofilms exhibited excellent pH tolerance toward the chemical etching rate and electrical resistance in buffer solutions, with pH ranging from 3 to 11. This enhancement effect of pH tolerance was considerably weakened when sequential annealing was performed in reverse (Zn vapor/air). The origin of the enhanced pH tolerance of the sequentially annealed AZO nanofilms is discussed in terms of the compensation of the anion/cation vacancies and the surface polarity of the ZnO(0001) surface.

KEYWORDS: Al-doped ZnO nanofilms, chemical stability, sequential annealing, transparent conductive oxides, defects compensation

INTRODUCTION

Electronic devices interacting with chemical species, such as chemical/biosensors and photoelectrochemical devices, have attracted significant attention because of the increasing social demands for collecting chemical and biological data and for addressing energy and environmental issues.1–3 These emerging electronic devices inherently require electronic materials whose electrical characteristics are highly stable even under chemically harsh conditions. For example, a fluorescent sensor to detect toxic Al3+ ions is typically operated under acidic conditions (pH ≈ 4.5).4 Biological applications, such as neural recording and use of antimicrobial devices, are performed in acidic aqueous solutions (pH 4–7).5,6 In contrast, basic environments are required for photoelectrochemical devices, including water splitting and CO2 reduction (pH 6.8–13).7,8,9 Thus, chemical stability under acidic or basic conditions is strongly desired for these sensing electronic materials, in addition to other requirements of physical properties, stability in atmospheric air, and/or stability at high temperatures.10

Among various electric materials, electrically conductive impurity-doped metal oxides are promising for emerging electronics because of their inherent atmospheric stability and temperature resistance.11–15 Al-doped ZnO (AZO) films have been intensively studied as conductive metal oxide electrodes because of their high electrical conductivity and visible-light transmittance as well as abundance of resources.16–21 However, it has been reported that deposited AZO nanofilms are easily dissolved in acidic or basic solutions,22,23 limiting their utilization under harsh conditions. To overcome the chemical instability of AZO, the formation of a chemically stable capping layer (TiO2) on AZO nanofilms has been proposed.24 Although the capping layer can enhance the chemical stability of the fabricated layered structures in acidic or basic solutions, the intrinsic properties of AZO, including optical transmissivity and surface chemical activities, are partially sacrificed.

Recently, we reported that sequential thermal annealing in air and in Zn vapor atmosphere significantly enhanced the thermal stability of AZO nanofilms without a capping layer.25 In the sequential annealing method, AZO nanofilms deposited on Al2O3 or SiO2/Si substrates were first annealed in air and subsequently annealed in Zn vapor atmosphere. The long-term stability and low-resistivity characteristics of the sequentially

Received: November 30, 2020
Accepted: January 25, 2021
Published: February 3, 2021
Annealed AZO nanofilms were demonstrated through thermal tolerance tests at 400 °C in ambient air. The improvement of thermal stability was attributed to the sequential compensation of dual-anion/cation defects in as-grown AZO nanofilms through sequential annealing. This method could enhance the chemical stability of AZO nanofilms. However, the effect of the sequential annealing on the chemical stability of AZO nanofilms is unclear because the surface properties of sequentially annealed AZO nanofilms, especially the chemical etching process that occurs on the surface, have not been investigated in the previous study. In this study, we investigated the effects of the sequential annealing method on the chemical stability of AZO nanofilms by evaluating the morphological and electrical variations of AZO nanofilms in acidic and basic solutions. Both chemical etching and electrical degradation were significantly suppressed for the devices based on sequentially annealed AZO nanofilms over a wide pH range of 3–11, indicating the high chemical stability of the sequentially annealed AZO nanofilms. The origin of the chemical stability of AZO nanofilms is discussed in terms of defect compensation effects during sequential annealing and the surface polarity of the ZnO(0001) surface.

Results and Discussion

First, we examined the chemical stability of the as-grown AZO nanofilms. AZO nanofilms were deposited on Al₂O₃(110) substrates through pulsed laser deposition (PLD) with deposition parameters optimized to obtain low electrical resistivity.⁶ The details of film deposition are provided in the Methods section. Figure 1a illustrates the procedure for the chemical stability tests. The fabricated AZO nanofilm devices were immersed in buffer solutions with a controlled pH of 3–11 for a controlled duration. The etched thickness and four-probe electrical resistance of the AZO nanofilms were measured in ambient air at room temperature after each immersion. Detailed fabrication processes and characterization of the AZO nanofilm devices are discussed in the Methods section. Note that both the etched thickness and resistance must be constant for chemically stable samples during stability tests, whereas those values will increase as the test duration increases for chemically unstable samples because of the etching of AZO nanofilms in acidic/basic solutions. Figure 1b,c shows the etched thickness and resistance values of the as-grown AZO nanofilms during chemical stability tests at pH 3. The as-grown AZO nanofilm, whose initial thickness was approximately 140 nm, was rapidly etched and fully dissolved within 35 min, indicating the chemical instability of the as-grown AZO nanofilms in acidic solutions. Although the present as-grown AZO nanofilms show a sufficiently low resistance (resistivity: ~1.9 × 10⁻³ Ω·cm) before the stability tests, the resistance significantly increased as the test duration increased because chemical etching reduced the cross-sectional area of the electrical current flow (Figure 1c). The rapid resistance increase near 2 orders of magnitude can be attributed to the nonuniform chemical etching of AZO surfaces during the stability tests at
pH 3. The nonuniform chemical etching causes a significant resistance increase because partially survived current paths within AZO nano films determine measured resistance. Note that changes in the contact resistance between Pt electrodes and AZO nano films do not affect the measured resistance because the resistance was measured by the four-probe technique. The deposition parameters of the as-grown AZO nano films were optimized to obtain low resistivity, resulting in inevitable crystal defects within AZO.23 Thus, the as-grown AZO nano films, which are deposited to be electrically conductive, are not stable in acidic aqueous solutions.

To overcome the above limitation of the chemical stability of the as-grown AZO nano films, we focus on reducing the crystal defects within the as-grown AZO nano films during film deposition. This is because such crystal defects inherently accelerate chemical etching events.26 The inset in Figure 1b shows the etched thickness of the as-grown AZO nano films deposited at room temperature, which has a much lower crystallinity than optimized samples deposited at 300 °C (Figure S1). The AZO nano films deposited at room temperature rapidly dissolved within 40 s at pH 3, verifying the strong correlation between crystallinity and chemical stability. As reported previously,23 we performed sequential annealing to compensate for crystal defects in the as-grown AZO nano films. Figure 2a illustrates the sequential annealing processes employed for the AZO nano films before the chemical stability tests. The sequential annealing method consists of a set of two thermal annealing steps: annealing in air and in Zn vapor atmosphere. These air and Zn vapor annealing steps were employed to compensate for oxygen and Zn defects in AZO nano films, respectively.23,27,28 Details of air and Zn vapor annealing steps are provided in the Methods section. In this study, the effects of sequence I annealing (annealing in Zn vapor atmosphere followed by that in air) and sequence II annealing (annealing in air followed by that in Zn vapor atmosphere) on the chemical stability of AZO nano films were investigated (Figure 2a). Figure 2b shows the ultraviolet-visible (UV–vis) transmission spectra of the as-grown, sequence-I-annealed, and sequence-II-annealed AZO nano films. Excellent visible-light transparency, which agrees with previous reports,29,30 was observed in all films, including sequentially annealed AZO nano films. Therefore, the present sequentially annealed AZO nano films are compatible with applications based on optical transmissivity of AZO, such as photoelectrochemical devices.22,31,32

Figure 3 shows the etched thickness of the as-grown, sequence-I-annealed, and sequence-II-annealed AZO nano films during the chemical stability tests over a wide pH range of 3–11. First, the as-grown AZO nano films started to dissolve in both acidic and basic solutions within 1 h. Furthermore, the as-grown AZO nano films were etched gradually even in a neutral solution (Figure 3d, pH 7). This chemically unstable property of the as-grown AZO nano films is consistent with the previously reported chemical etching effects of doped or undoped ZnO nanostructures, which is attributed to the amphoteric character of ZnO.26,33 Second, in the sequence-I-annealed (Zn vapor/air) AZO nano films, chemical etching was significantly decreased slightly compared with that of the as-grown samples. However, the rapid dissolution of the AZO nano films in acidic solution (pH 3) still existed even for the sequence-I-annealed samples (Figure 3a). Third, in the sequence-II-annealed (air/Zn vapor) AZO nano films, chemical etching was significantly
suppressed over the entire pH range, indicating superior chemical stability under both acidic and basic conditions. Note that the surface topology of the sequence-II-annealed AZO nanofilms also did not change during the chemical stability tests at pH 3 (Figure S2). Interestingly, the chemical stability of the sequence-II-annealed samples is consistent with our previously reported thermal stability tests of a series of sequentially annealed AZO nanofilms. Similar to Figure 3, only the sequence-II-annealed AZO nanofilms showed thermal stability and sufficiently low resistivity during thermal tolerance tests up to 500 °C in ambient air. Figure 4 shows the electrical resistance of the as-grown, sequence-I-annealed, and sequence-II-annealed AZO nanofilm devices during the chemical stability tests. Note that the high initial resistance of the sequence-I-annealed AZO nanofilms originates from the remaining Zn defects in the AZO nanofilms, which trap mobile charges. Each sample and data point in Figure 4 corresponds to that of the chemical etching evaluation shown in Figure 3. A clear correlation between chemical etching and resistance increase was observed in all samples and tested pH values because chemical etching causes reduction of the cross-sectional area of the current flow. Note that the enhancement of chemical stability induced by sequence II annealing can be observed in the AZO nanofilms deposited on SiO2/Si substrate (Figure S3), indicating the general applicability of this strategy. Thus, these series of data on the chemical stability of AZO nanofilms highlight that sequence II annealing (air/Zn vapor) only enhances the chemical stability of AZO nanofilms.

Figure 5 summarizes the pH dependence on the chemical etching rates and the increase in the electrical resistances of the as-grown, sequence-I-annealed, and sequence-II-annealed AZO nanofilms during the chemical stability tests. An enhancement of the pH tolerance toward chemical etching and electrical resistance of the conductive AZO nanofilms can be achieved only through sequence II annealing (air/Zn vapor). The etching rate at pH 3 of the sequence-II-annealed AZO nanofilms was calculated to be 0.2 nm/min. We compared the etching rates of the sequence-II-annealed AZO nanofilms to previously reported etching rates as shown in Table 1. For example, Olvera et al. investigated the chemical stability of doped ZnO microcrystalline films deposited using the spray pyrolysis technique in hydrochloric acid solution (pH ≈ 3), reporting that Cr-doped ZnO exhibits the lowest etching rate of 2.5 nm/min and Al-doped ZnO (AZO) shows the highest chemical etching rate of 6.5 nm/min. Heinonen et al. reported an etching rate of 9.167 nm/min in solution at pH 3 for hydrothermally grown polycrystalline ZnO films. The etching rates of 15 nm/min in NH4Cl (pH ≈ 4) solution has been reported for PLD-deposited ZnO. Thus, these comparisons of etching rates of previous and present studies highlight
that sequence-II-annealed AZO nanofilms prepared in this study exhibit superior pH tolerance compared to previous AZO nanofilms to the best of our knowledge.

Finally, we discuss the origin of the enhanced pH tolerance of AZO nanofilms prepared via the sequential annealing method, which should correlate with the chemical etching process of ZnO crystals because of the low Al content of AZO nanofilms (1% in sintered tablets used for PLD). In general, the deposited ZnO films form wurtzite (0001)-oriented crystal structures on substrates, and the presence of this ZnO(0001) structure has been confirmed in our AZO nanofilms (Figure S1). The chemical etching process of single-crystalline ZnO can be explained by a model based on a dangling bond on polar Zn-terminated and O-terminated surfaces of the wurtzite structure.26,37 The dangling bonds on Zn-terminated and O-terminated surfaces are charged as $\delta^+$ and $\delta^-$, respectively. These charged dangling bonds are easily attacked by etchant ions such as $\text{H}_3\text{O}^+$ and $\text{OH}^-$, resulting in the chemical etching of ZnO(0001) surfaces. In an ideal single-crystalline ZnO wurtzite crystal structure, only ions having the charge opposite to that of polar surfaces can attack these dangling bonds, i.e., $\text{H}_3\text{O}^+$ (acidic) etching on the O-terminated surface and OH$^-$ (basic) etching on the Zn-terminated surface. To investigate the effects of polar surface etching on the stability of the sequentially annealed AZO nanofilms, the chemical stability of single-crystalline ZnO(0001) substrates was evaluated. Figure 6 shows the etched thickness characteristics of a single-crystalline ZnO(0001) substrate, where surface polarity is predefined by the supplier, during the chemical stability tests at pH 3. The O-terminated surface is etched much faster than the Zn-terminated surface, supporting the chemical etching model based on the charged dangling bonds. Note that the chemical etching of the as-grown and sequentially annealed AZO nanofilms was slower than that of the O-terminated surface, whereas it was faster than that of the Zn-terminated surface (Figure 6), indicating the Zn-terminated-rich surface of these AZO nanofilms. This speculation is consistent with previous studies that reported the faster formation of Zn-terminated surfaces than that of O-terminated surfaces during conventional ZnO film deposition.26,38−40 However, the significant increase in the chemical stability of the AZO nanofilms prepared by sequential annealing in this study cannot be explained by only the model based on dangling bonds on polar surfaces. This is because the difference between sequence I (Zn vapor/air) and II (air/Zn vapor) annealings is only the sequence of the postdeposition annealing atmosphere. We have proposed a model of sequential defect compensation effects during the sequential annealing in a previous study.23 Dual defects of cation (Zn$^{2+}$) and anion (O$^{2-}$) in as-grown AZO nanofilms can be compensated successfully only in the annealing sequence of first in air and subsequently in Zn vapor atmosphere because of a sequential energy benefit during annealing.23 The high electrical conductivity of the as-grown n-type AZO nanofilms (resistivity: $\sim 1.9 \times 10^{-3}$ $\Omega \cdot \text{cm}$) suggests excess cation (Zn ion) and insufficient anion (oxygen ion) in the as-grown AZO nanofilms because oxygen defects generate mobile electrons. Therefore, cation defect compensation via Zn vapor annealing must be limited because the initial state, namely, as-grown AZO nanofilms, is already cation excess. In contrast, air annealing of the as-grown AZO nanofilms can effectively compensate anion defects because cation and anion contents are balanced via air annealing. Zn vapor annealing can sufficiently compensate Zn defects in these ion-balanced AZO nanofilms after air annealing, resulting in defectless AZO nanofilms via sequence II annealing. Therefore, the as-grown and sequence-I-annealed AZO nanofilms contain many crystal defects, and these crystal defects are compensated in the sequence-II-annealed AZO nanofilms. More importantly, these defects degrade chemical stability because the surface defects on ZnO films act as starting points for the chemical etching process, even for Zn-terminated surfaces in acidic solutions.41−43 Defect-triggered chemical etching occurs in the as-grown and sequence-I-annealed AZO nanofilms, resulting in faster etching compared to that of the single-crystalline Zn-terminated surface and sequence-II-annealed AZO nanofilms (Figure 6). Density functional theory (DFT) calculations reported that Fermi-level shift near conduction band edge decreases the formation energy of Zn defects in wurtzite ZnO crystal.44 Therefore, n-type (Al) doping generally increases the amount of Zn defects in as-grown AZO films, supporting the proposed model for the enhancement of chemical stability caused by defects compensation via sequential annealing. Note that annealing in only Zn vapor atmosphere could not suppress the chemical etching of the AZO nanofilms (Figure S4), thus supporting our model (which requires two-step sequential annealing). Therefore, the significant improvement of the chemical stability of the sequence-II-annealed AZO nanofilms is attributed to the suppression of defect-triggered chemical etching on the Zn-terminated wurtzite (0001) surface through sequential compensation of dual-anion/cation defects. Because
sequence II annealing also significantly enhances the thermal stability of highly conductive AZO nanofilms up to 500 °C.23, the sequential annealing method facilitates the utilization of abundant AZO nanofilms in emerging applications under a wide variety of harsh conditions.

■ CONCLUSIONS

We demonstrate chemically stable and highly conductive Al-doped ZnO (AZO) nanofilms in both acidic and basic aqueous environments; the films are prepared via a sequential annealing method. When AZO nanofilms are thermally annealed first in air and subsequently in Zn vapor atmosphere (sequence II), the chemical etching of AZO nanofilms in pH buffer solutions was significantly suppressed over a wide pH range of 3–11. The highly conductive characteristics of the AZO nanofilms are also maintained in the sequence-II-annealed AZO nanofilms during the chemical stability tests. Conversely, in the as-grown and sequence-I-annealed (first annealed in Zn vapor atmosphere and subsequently in air) samples, the AZO nanofilms start to dissolve in both acidic and basic solutions within 1 h, resulting in a significant increase in resistance. Chemical etching analysis of single-crystalline ZnO(0001) substrates reveals that the AZO nanofilms have a Zn-terminated-rich surface with a wurtzite crystal structure, where chemical etching is enhanced by surface defects serving as attacking sites of etchant ions. Because sequential compensation effects successfully compensate for dual defects of cation (Zn2+) and anion (O2−) in the AZO nanofilms, the sequence-II-annealed samples contain much fewer defects than the as-grown and sequence-I-annealed samples. Therefore, defect-triggered chemical etching on the Zn-terminated surface is considerably suppressed in the sequence-II-annealed AZO nanofilms, resulting in their superior chemical stability. The sequential annealing method also enhances the thermal stability of conductive AZO nanofilms and does not require the addition of a capping layer, which possibly sacrifices other properties such as surface reaction and transparency. Thus, the proposed sequential annealing method can facilitate emerging applications using abundant AZO in harsh environments such as biosensors operated in acidic or basic environments.

■ METHODS

AZO Nanofilm Fabrication. AZO nanofilms were deposited on Al2O3(110) or 100 nm SiO2/Si substrates using the PLD method.23,45 A sintered tablet (1 atom % of Al2O3 in ZnO, 99.99% purity, Kojundo Chemical Laboratory) was utilized as a target for ablation by an ArF excimer laser (λ = 193 nm, Coherent, COMPex Pro). The chamber for deposition was initially evacuated below 5 × 10−6 Pa, following which oxygen gas (99.9999% purity) was introduced. The oxygen pressure, growth temperature, and deposition rate were set to 10−3 Pa, 300 °C, and 100 nm/h, respectively. A part of the deposited nanofilm was then sequentially annealed under two types of conditions: (i) ambient air, 500 °C, and 1 h or (ii) Zn vapor, 600 °C, and 1 h. For Zn vapor annealing, samples were placed in a small crucible with a Zn tablet (99.99% purity, Kojundo Chemical Laboratory) and maintained at 0.1 Pa at 600 °C for 1 h.25 The distance between the samples and the Zn tablet was 3 cm, and the AZO-deposited side of the sample substrates faced downward to prevent direct Zn deposition on the AZO surface. The crucible was then sealed in a quartz tube and evacuated to 0.1 Pa, followed by a temperature increase to 600 °C at a heating rate of 20 °C/min. In sequence I annealing, the samples were annealed first in Zn vapor atmosphere and then in air (Zn vapor/air). In sequence II annealing, the samples were annealed first in air and then in Zn vapor atmosphere (air/Zn vapor). The AZO nanofilms were deposited on a glass substrate for UV–vis spectroscopy.

Sample Fabrication for Chemical Stability Tests. The deposited AZO nanofilms were first patterned by photolithography and chemical etching using a 0.5% HCl solution. Pt (100 nm) was then deposited and patterned by radio frequency (RF) sputtering and a lift-off process with photolithography as four-terminal electrodes on the AZO nanofilm channel. The channel length and width of the AZO nanofilms were 500 and 200 μm, respectively. For the chemical stability tests of the single-crystalline ZnO surface, 100 nm of SiO2 was deposited and patterned on a single-crystalline ZnO(0001) substrate (K&K Creation Co., Ltd.) by RF sputtering and a lift-off process with photolithography to protect a part of the ZnO surface from chemical etching during stability tests. The window on the SiO2-deposited ZnO substrate, which was chemically etched during stability tests, was designed to be the same size as the AZO channels (500 × 200 μm2).

Characterizations. UV–vis transmission spectroscopy was performed using a spectrometer (Jasco V-770). The electrical resistance of the AZO nanofilms was measured by the four-probe technique using a semiconductor parameter analyzer (Keithley 4200SCS) with a probe station in ambient air at room temperature. The etched thickness was calculated from the measured step values using a surface profiler (Alpha-Step IQ, KLA). In the etched thickness measurements and resistance measurements, the averaged values of the etched thickness and resistance were evaluated using at least three samples. Error bars are also calculated using standard deviation for all of the etched thickness and resistance data. The averaged values of the resistance and etched thickness with error bars of standard deviation were calculated using at least three samples. In the chemical stability tests, the samples were immersed in pH buffer solutions (HANNA Instruments, pH: 3.00, 4.01, 5.00, 7.01, 9.18, 10.00, and 11.00) for a controlled period at room temperature.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaelm.0c01052.

X-ray diffraction (XRD) data of AZO nanofilms; scanning electron microscopy (SEM) images of sequence-II-annealed AZO nanofilms; chemical stability tests of AZO nanofilms deposited on SiO2/Si substrate; and chemical stability tests of AZO nanofilms after Zn vapor annealing (PDF)

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https://dx.doi.org/10.1021/acsaelm.0c01052

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by KAKENHI (grant nos.: JP20H02208, JP18H01831, JP18H05243, and JP18KK0112). T.T. was supported by JST PREST grant no. JPMJPR19M6, Japan. T.T., G.Z., K.N., and T.Y. were supported by JST CREST, grant no. JPMJCR1912, Japan. T.Y. and K.N. were supported by CAS-JSPS Joint Research Projects (grant no. JPJSBP120187207) and Mirai R&D of JST. R.Y. was supported by the program of China Scholarships Council (no. 201706090261). This work was performed under the Cooperative Research Program of the “Network Joint Research Center for Materials and Devices” and the MEXT Project of “Integrated Research Consortium on Chemical Sciences”.

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