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Preparation of boron-doped ZnO thin films by photo-atomic layer deposition

Y. Yamamoto[a,*], K. Saito[a], K. Takahashi[a], M. Konagai[b]

[a]*Department of Electronics and Information Science, Teikyo University of Science and Technology, 2525 Yatsusawa, Uenohara-machi, Kitatsuru-gun, Yamanashi 409-0193, Japan*

[b]*Department of Electrical and Electronic Engineering, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan*

Abstract

Low-resistivity and high-stability ZnO films were grown by photo-atomic layer deposition (photo-ALD) technique using boron as an n-type dopant. The effect of the UV-irradiation was quantitatively evaluated by controlling the intensity of the incident light. The growth mechanism of ZnO films under UV-irradiation was investigated by varying the UV-irradiation period. In addition to the UV-irradiation, n-type doping using B_2H_6 was carried out. By optimizing the introduction cycle of B_2H_6, the lowest resistivity of $6.9\times10^{-4}\,\Omega$cm was obtained. Furthermore, ZnO films grown by photo-ALD exhibit excellent stability in the electrical properties under air exposure.

Keywords: ZnO; Photo-atomic layer deposition; Transparent conductive oxide

1. Introduction

Recently, ZnO has been attractive as a transparent conductive oxide (TCO) for solar cell applications. These films have been applied to the front and rear contacts of a-Si and Cu(InGa)Se_2 solar cells. In our previous work, we have developed the growth of low-resistivity and highly transparent ZnO films by using photo-atomic layer deposition (photo-ALD) technique [1]. The resistivity of the ZnO films grown with UV-irradiation was about one order of magnitude lower than that of the ZnO films grown without UV-irradiation. Furthermore, boron-doped ZnO films were grown by the atomic layer deposition (ALD) technique [2]. Diborane (B_2H_6) gas has been used

* Corresponding author.

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as an n-type doping gas. The electrical properties of ZnO films were improved by boron doping.

In this study, at first, to evaluate the effect of the UV-irradiation quantitatively, the intensity of the light source was controlled. The growth mechanism of ZnO films under UV-irradiation was investigated by varying the period of UV-irradiation onto the growth substrate. Second, n-type doping using B_2H_6 in addition to the UV-irradiation during the growth was examined. Furthermore, the stability of the ZnO films grown by photo-ALD was investigated.

2. Experimental

ZnO deposition system and growth conditions are similar to those reported before [1]. ZnO films were deposited on Corning 7059 glass substrates. The substrate temperature during deposition was fixed at 136°C. Diethylzinc (DEZ) and H_2O reactant gases were alternately fed into the growth chamber with argon as a carrier gas. The opening and closing sequences of the air valves were controlled by using a personal computer. The typical pulse lengths were 2 s for the reactants and 8 s for the evacuation between the reactants. The flow rates of DEZ and H_2O were controlled by varying the bubbler temperature, and the flow rates were typically 67.0 and 17.5 μmol/min for DEZ and H_2O, respectively. The UV light was irradiated onto the substrate through the top quartz window of the chamber. A low-pressure mercury lamp was employed as a light source, radiating intense 184.9 and 253.7 nm resonance lines. The intensity of the light source was reduced by placing a perforated aluminum plate (mesh) between the light source and the incident quartz window of the reaction chamber. The period of UV-irradiation onto growth substrate was varied by inserting a shutter. In addition to the UV-irradiation during the growth, n-type doping using B_2H_6 was carried out. The stability of the ZnO films grown by photo-ALD was investigated by measuring the electrical properties of the as-deposited films and those after exposure to air ambient at room temperature for a certain period.

3. Results and discussion

3.1. Considerations on the growth mechanism

First, to evaluate the effect of the UV-irradiation quantitatively, the intensity of the light source was controlled by placing a perforated aluminum plate (mesh) between the light source and the incident quartz window of the chamber. Fig. 1 shows the electrical properties of the ZnO films as a function of light intensity ratio I/I_0. I_0 and I denote the light intensity emitted from the light source and the light intensity received by the substrate, respectively. The light intensity was measured at a wavelength of 253.7 nm and $I_0 = 7.5\,\mathrm{mW/cm^2}$. Electrical properties are changed continuously with light intensity. The carrier concentration increases with increasing light intensity. However, the electron mobility decreases with increasing light inten-

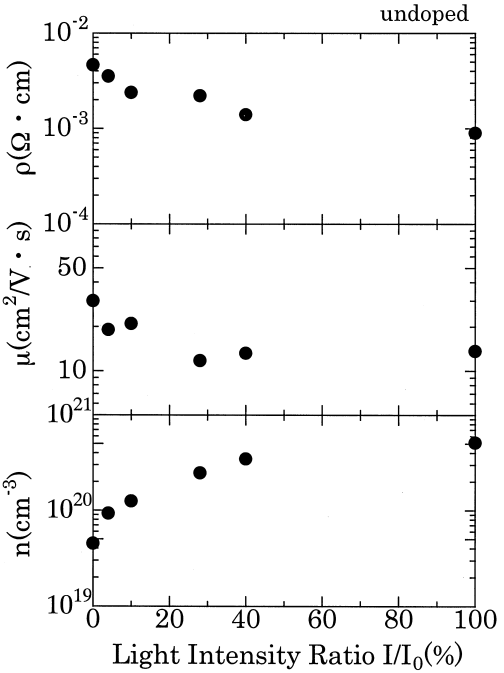

Fig. 1. Electrical properties of ZnO films as a function of the light intensity ratio I/I_0.

sity. As a result, the resistivity decreases with increasing light intensity up to $I/I_0 = 40\%$ and then saturates at higher light intensities. Also, the effect of the UV-irradiation is confirmed even at $I/I_0 = 4\%$.

The above experiments were performed by continuous UV-irradiation during the growth. In order to further investigate the effects of UV-irradiation, the period of UV-irradiation onto growth substrate was varied. The sequence of the light irradiation was controlled by inserting a shutter between the light source and the incident quartz window of the reaction chamber. The effects of the UV-irradiation on the properties of ZnO thin films were studied under the following growth conditions: (A) UV-irradiation at DEZ injection period, (B) UV-irradiation at H_2O injection period, (C) UV-irradiation during the evacuation of DEZ, (D) UV-irradiation during the evacuation of H_2O. Fig. 2 shows these shutter sequences. At first, the intensity of the UV-irradiation was fixed at $I/I_0 = 100\%$. However, the UV-light intensity was so strong that we could not find the difference of the electrical properties. Therefore, in this experiment, the light intensity was fixed at $I/I_0 = 28\%$ (2.1 mW/cm^2).

The electrical properties of the ZnO films deposited at various UV-irradiation sequences are shown in Fig. 3. The electrical properties of ZnO films obtained without UV-irradiation (1) and with continuous UV-irradiation (2) are shown for comparison. It can be seen from Fig. 3 that the carrier concentrations of samples (A)–(D) are lower than that of sample (2). However, the mobilities of samples (A)–(D) are larger than that

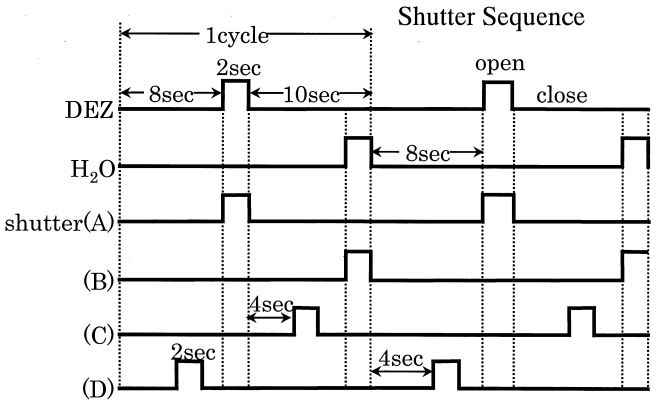

Fig. 2. Various UV-irradiation sequences.

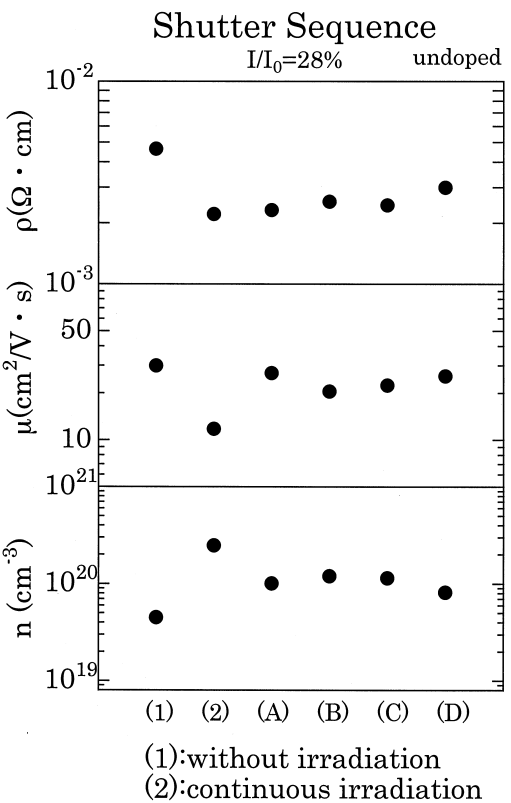

Fig. 3. Electrical properties of ZnO films deposited at various UV-irradiation sequences. (A)–(D): as shown in Fig. 2.

of sample (2). As a result, the resistivities of these samples are comparable. The reason for this is the shorter UV-irradiation period for samples (A)–(D), which causes less excess Zn in the grown films. Moreover, the resistivity of sample (D) is larger than that of samples (A) and (C). This result can be explained by the fact that the UV-light is effective for the decomposition of DEZ, which causes point defects such as Zn interstitials or O vacancies. In this experiment, UV-light was irradiated perpendicular to the substrate. Therefore, we cannot distinguish the vapor phase reaction and the surface reaction. Further investigation of the growth mechanism under UV-irradiation is necessary.

3.2. *Photo-ALD growth of boron-doped ZnO*

In addition to the UV-irradiation, we examined n-type doping by using B_2H_6. At a light intensity of $I/I_0 = 100\%$, by increasing the amount of B_2H_6, the electrical properties of the ZnO films were found to deteriorate. This is because the UV-light intensity was too strong for B doping. Therefore, in this experiment, the light intensity ratio was set to $I/I_0 = 10\%$ ($750\,\mu W/cm^2$). B_2H_6 was introduced into the chamber once in every 1, 2, 4, 6, 8, 12 cycles of DEZ injection as shown in Fig. 4. Therefore, the change of injected amount of B_2H_6 can be represented by the change of the growth cycle ratio of B_2H_6 to DEZ (B_2H_6/DEZ).

Fig. 5 shows electrical properties of the boron-doped ZnO films as a function of the growth cycle ratio of B_2H_6 to DEZ (B_2H_6/DEZ). The carrier concentration increases with the B_2H_6/DEZ ratio up to 1/2. The electron mobility decreases gradually as B_2H_6/DEZ increases, which is mainly originated from the impurity scattering. As a result, at B_2H_6/DEZ = 1/4 a low resistivity of $6.9 \times 10^{-4}\,\Omega$cm was achieved for B-doped ZnO.

Fig. 6 shows X-ray diffraction spectra of ZnO films deposited at various injected amounts of B_2H_6. The crystal orientation of these films was influenced by the boron

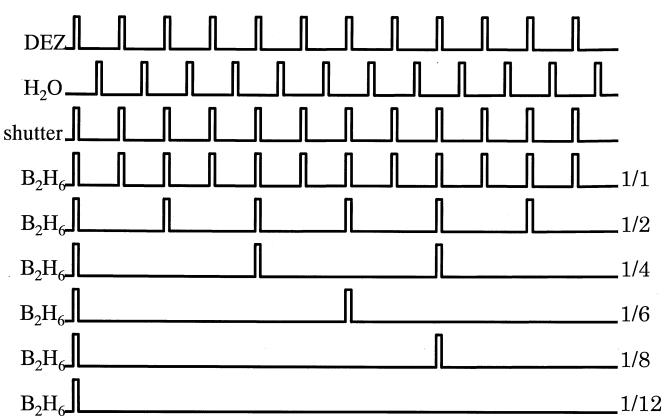

Fig. 4. Various B_2H_6 injection sequences.

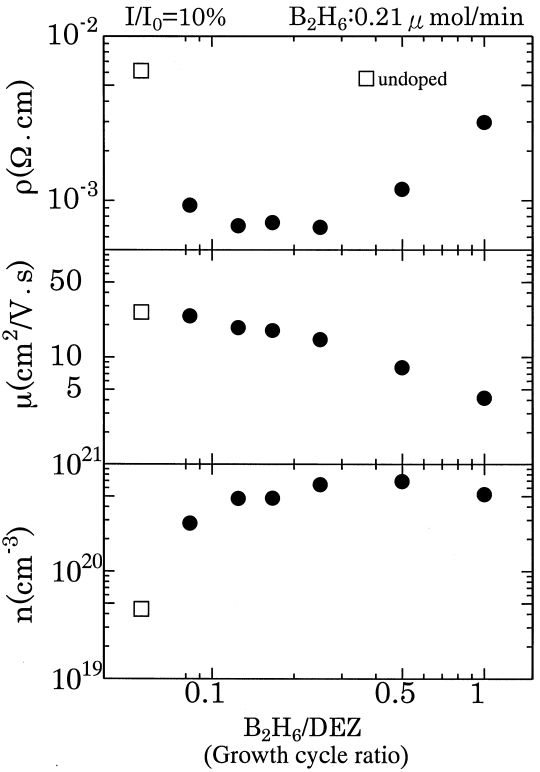

Fig. 5. Electrical properties of ZnO films deposited at various injected amounts of B_2H_6. The open squares denote the electrical properties of undoped ZnO film.

doping when the B_2H_6/DEZ ratio was varied. For the undoped ZnO film, (1 0 0) and (1 0 1) reflection peaks are observed predominantly. The (1 0 1) reflection peak becomes stronger and the other reflection peaks become weaker with increasing B_2H_6/DEZ. The reason why boron doping influences the crystal orientations of ZnO films is still not fully understood.

3.3. Stability of the ZnO films

We have already reported the stability of the ZnO films grown by MOCVD, photo-MOCVD, and ALD [3]. In addition, the stability of the ZnO films grown by photo-ALD was investigated, which was carried out by measuring the electrical properties of as-deposited and after exposure to air ambient at room temperature for 18–23 months. Fig. 7 shows the electron mobility and carrier concentration of various ZnO films grown by MOCVD, photo-MOCVD, ALD, and photo-ALD methods. The clear symbols indicate the as-deposited properties of the films, and the filled symbols indicate the properties of the films after exposure to air ambient. The squares

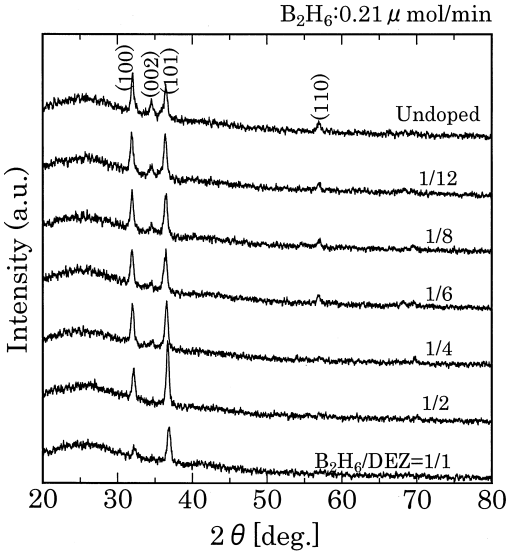

Fig. 6. X-ray diffraction spectra of ZnO films deposited at various injected amounts of B_2H_6.

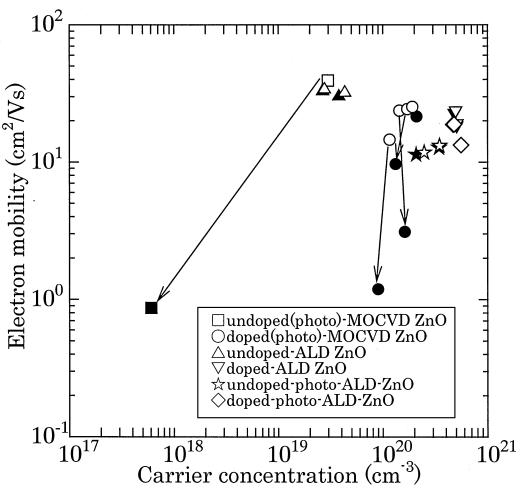

Fig. 7. The electron mobility and carrier concentration of ZnO films. The open marks denote the as-grown properties and the closed marks denote the after-exposure properties.

and dots represent the properties of undoped and boron-doped films deposited by (photo)-MOCVD, respectively. The upright triangles and inverse triangles represent the properties of undoped and doped films deposited by ALD, respectively. The stars and diamonds represent the properties of undoped and doped films deposited by photo-ALD, respectively.

As shown in this figure, almost no degradation of electrical properties is noted for ALD- and photo-ALD-grown ZnO films. It can also be seen that the degradation in the electrical properties of ZnO films grown by (photo)-MOCVD is mainly caused by the decrease in electron mobility, which is consistent with the aforementioned explanation. This decrease in electron mobility of ZnO films following air exposure is attributable to chemisorption of oxygen at the grain boundaries, which in turn leads to the formation of extrinsic trap states localized at the grain boundaries. These states trap free carriers from the bulk of the grains and create potential barriers by causing depletion in regions adjacent to the grain boundaries. These potential barriers decrease the mobility of the carriers. It can be supposed that the migration growth occurring with the ALD and photo-ALD techniques decreases chemical disorder by decreasing the number of dangling bonds and unstable bonds at the grain boundaries of the ZnO films, making oxygen chemisorption at the grain boundaries difficult and thereby preventing deterioration in the electrical properties of the films.

4. Conclusions

In order to evaluate the effect of the UV-irradiation quantitatively, the intensity of the light source was controlled. The resistivity decreases with increasing light intensity up to $I/I_0 = 40\%$ and then saturates at higher light intensities. Also, the effect of the UV-irradiation was confirmed even at $I/I_0 = 4\%$. The n-type doping using B_2H_6 was examined in addition to the UV-irradiation during the growth. By optimizing the introduction cycle of B_2H_6, the minimum resistivity of $6.9 \times 10^{-4}\,\Omega$cm was achieved for B-doped ZnO. These results indicate that in order to reduce the resistivity of the ZnO films, it is necessary to control the UV-light intensity and to optimize the amount of B.

Furthermore, ZnO films grown by photo-ALD exhibit excellent stability in the electrical properties under air exposure at room temperature, indicating high reliability if the films are applied to solar cells.

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