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Growth of Boron-doped ZnO thin films by atomic layer deposition

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Abstract

ZnO films have been grown by atomic layer deposition (ALD) using diethylzinc (DEZn) and H_2O as reactant gases. The diborane (B_2H_6) gas has also been successfully used as an n-type dopant gas to obtain low-resistivity ZnO films. A high electron mobility of about 30 cm^2/V s was obtained for undoped ZnO films of 220 nm thick, and a low resistivity of 6.4×10^{-4} Ω cm was achieved for B-doped ZnO films of only 200 nm thick. It was found that the electrical properties of ZnO films strongly depend on the injected amount of B_2H_6 during the deposition and on the injection timing of B_2H_6 relating to DEZn and H_2O.

Keywords: Transparent conductive oxide; ZnO; Atomic layer deposition

1. Introduction

ZnO film has attracted much attention as a window layer for a-Si and $Cu(InGa)Se_2$ (CIGS) solar cells because of its excellent performance in hydrogen plasma and its low growth temperature. In our previous works, we have reported the growth of textured high conductivity and high transparency ZnO films by the metalorganic chemical vapor deposition (MOCVD) technique. These films have been applied to the front and rear contacts of a-Si solar cells, and a conversion efficiency of 12.5% has been achieved [1].

In order to increase the uniformity of the film thickness and the crystallinity of ZnO films, the atomic layer deposition (ALD) technique was employed, which is capable of

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growing uniform, high quality thin films on large area substrates. By using the ALD technique, it is expected that the electron mobility of the ZnO films can also be increased. Consequently, the transparency of the films should improve.

We have reported the self-limiting growth of undoped ZnO films by ALD method [2]. Self-limiting growth was observed for substrate temperatures ranging from 105°C to 165°C, and also at certain DEZn and H_2O flow rates. The uniformity of film thickness was found greatly improved by ALD technique compared with the conventional MOCVD technique. In this paper, the electrical properties of the undoped ZnO films were studied in detail. The dependence of the electrical properties of undoped ZnO films on the growth temperature and on the flow rate of the reactant gases was demonstrated. Furthermore, the boron doping using B_2H_6 as a dopant was carried out to obtain the low-resistivity ZnO films. The influences of the injected amount of B_2H_6 during the deposition and of the injection timing of B_2H_6 relating to DEZn and H_2O on the electrical properties of ZnO films were also investigated.

2. Experimental

ZnO films were deposited on Corning 7059 glass substrates using a modified CVD system. Diethlyzinc (DEZn) and H_2O were kept in bubblers and were bubbled with purified argon gas. Diborane (B_2H_6) diluted with H_2 was used as a dopant gas. These source gases were alternately fed into the chamber through separate inlet lines and nozzles. The opening and closing sequences of the air valves were automatically controlled by using a computer. The typical pulse lengths were 2 s for the reactants and 8 s for the evacuation between the reactants. The flow rates of DEZn and H_2O were controlled by changing the temperature of the bubbler. The flow rate of DEZn fed into the growth chamber was varied from 41.3 to 84.7 μmol/min, and the flow rate of H_2O was changed from 8.9 to 24.2 μmol/min, respectively. The substrate temperature was from 105°C to 165°C. In these ranges of substrate temperature and flow rates of DEZn, H_2O, the deposition rate of ZnO films remained constant with a value that corresponds to the thickness of a ZnO (100) monolayer [2]. The pressure in the chamber during the deposition was between 0.09–0.10 Torr. The flow rate of B_2H_6 introduced to the chamber was varied from 0.084 to 1.05 μmol/min. The Hall measurement using a van der Pauw configuration was used to evaluate the electrical properties of the obtained ZnO films. The measurements were carried out at room temperature using samples cut into 1×1 cm^2 pieces.

3. Results and discussion

3.1. The electrical properties of the undoped ZnO films

At first, the influences of growth temperature and flow rates of the reactant gases on the electrical properties of the undoped ZnO films were investigated. The deposition

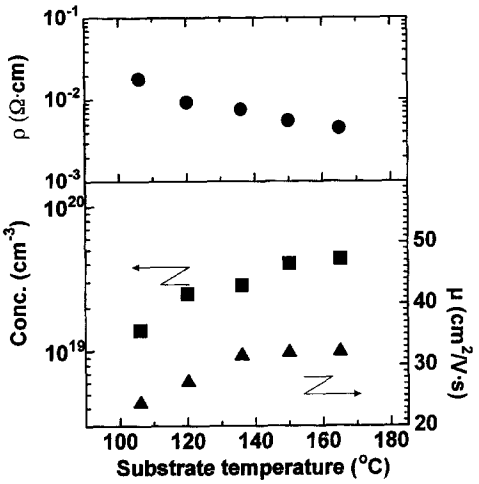

Fig. 1. The electrical properties of undoped ZnO films as a function of the growth temperature. The flow rates of DEZn and H_2O were 52.8 and 24.2 μmol/min, respectively.

rate of the ZnO films remained constant as described above, and the film thickness for all of the samples was about 220 nm. Fig. 1 shows the mobility (μ), carrier concentration (Conc.) and resistivity (ρ) as a function of substrate temperature. As the substrate temperature increases from 105°C to 165°C, the electron mobility increases from 23 to 33 cm^2/V s, the carrier concentration increases from 1.4×10^{19} to 4.3×10^{19} cm^{-3}, whereas the resistivity decreases from 1.8×10^{-2} to 4.5×10^{-3} Ω cm. It is noticeable that a higher electron mobility of 30 cm^2/V s was obtained for ZnO films of only 220 nm thick, while the electron mobility and the carrier concentration of 2400 nm thick ZnO films, grown by MOCVD, were 14.5 cm^2/V s and 2.6×10^{19} cm^{-3} [3], respectively. This indicates that the mobility of ZnO film can be increased by using the ALD technique rather than the MOCVD technique. For the application to a-Si solar cells as a transparent conductive oxide, the ZnO films should exhibit high conductivity and high transparency. In order to achieve these properties, it is required to grow films of high electron mobility.

Fig. 2 show the dependence of the electrical properties of undoped ZnO films on DEZn and H_2O flow rates. The electron mobility of the films remains almost constant, while the carrier concentration increases and the resistivity decreases with the increasing of DEZn flow rates. On the contrary, the carrier concentration decreases and the resistivity increases with the increasing of H_2O flow rates. As we know, the excess zinc, incorporated either as oxygen vacancies or zinc interstitials, acts as a donor, which gives rise to n-type electrical conductivity in undoped ZnO. Therefore, the change of the carrier concentration and resistivity of undoped ZnO films with DEZn and H_2O flow rates is originated from the variation of the density of point defects like oxygen vacancies or zinc interstitials.

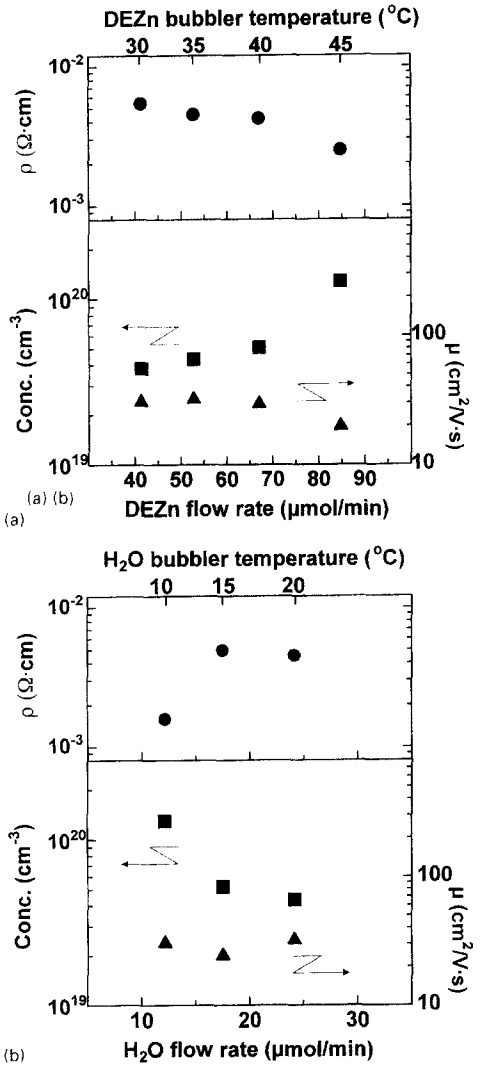

Fig. 2. (a) The dependence of the electrical properties of undoped ZnO films on DEZn flow rate. The growth temperature was 165°C, and the flow rate of H_2O was 24.2 μmol/min. (b) H_2O flow rate dependence of the electrical properties of undoped ZnO films. The growth temperature was 165°C, and the flow rate of DEZn was 52.8 μmol/min.

3.2. *The boron doping processes and the electrical properties of the B-doped ZnO films*

N-type doping using B_2H_6 has been attempted to obtain low-resistivity ZnO films. Firstly, the dependence of the electrical properties of ZnO films on the injected amount of B_2H_6 during the deposition was observed. The change in injected amount

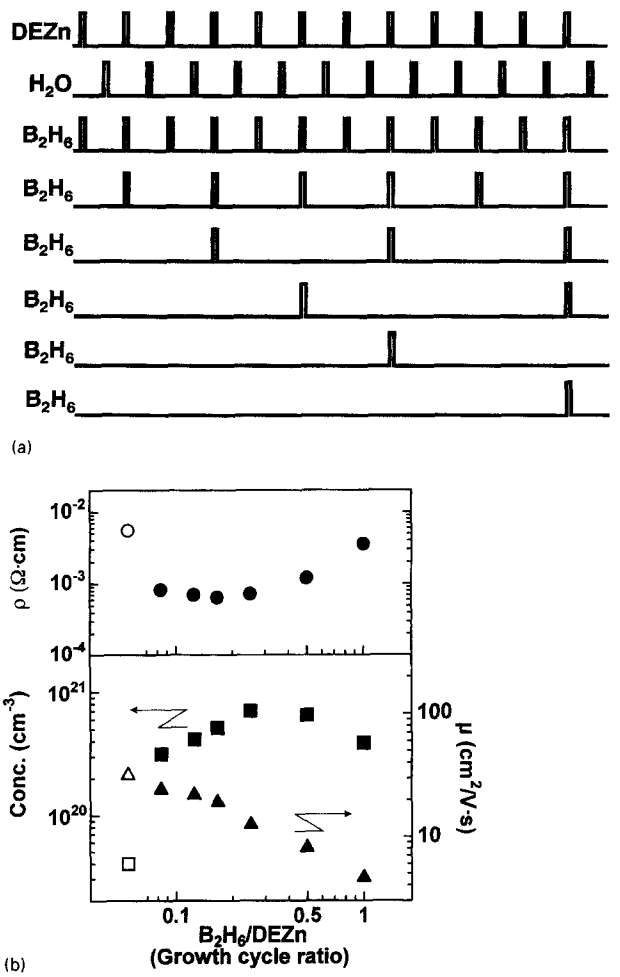

Fig. 3. (a) Various B_2H_6 injection sequences. (b) Dependence of the electrical properties of ZnO films on the injected amount of B_2H_6. The unfilled marks denote the electrical properties of undoped ZnO films. The thickness of the B-doped films was about 200 nm. The flow rates of DEZn, H_2O and B_2H_6 were 52.8, 24.2, and 0.42 μmol/min, respectively.

of B_2H_6 was carried out by changing the growth cycle of B_2H_6, while the flow rates of B_2H_6 was fixed. B_2H_6 was introduced into the chamber once in every several cycles of DEZn injection as shown in Fig. 3a. 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 DEZn (B_2H_6/DEZn). Fig. 3b shows the resistivity (ρ), carrier concentration (Conc.) and electron mobility (μ) of the boron (B)-doped ZnO films as a function of growth cycle ratio of B_2H_6 to DEZn (B_2H_6/DEZn). The substrate temperature was set to 150°C

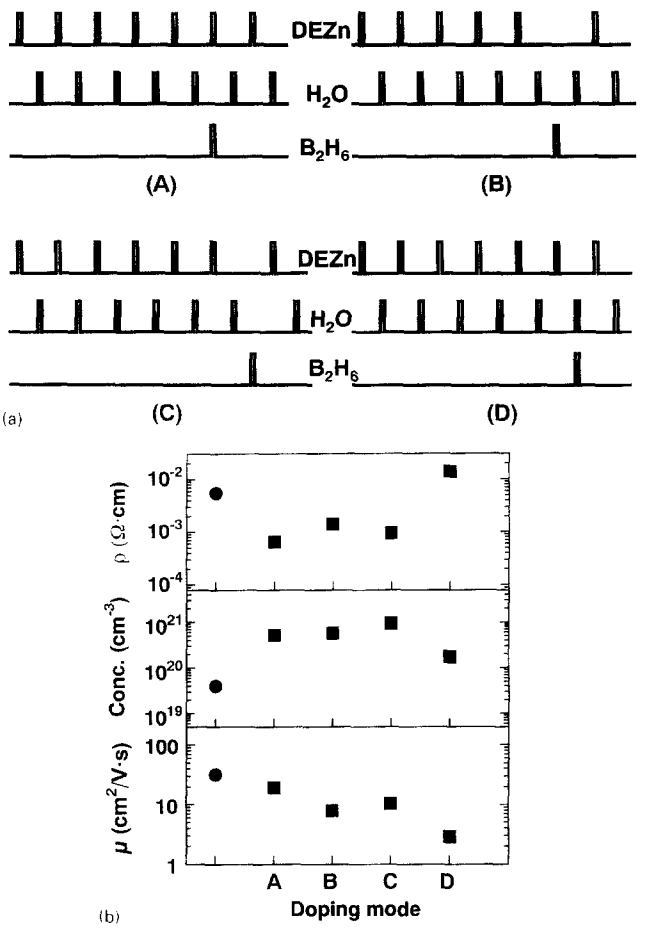

Fig. 4. (a) Doping modes. The dopant gas B_2H_6 was supplied: (A) at DEZn injection period, (B) as a substitute of DEZn, (C) after the evacuation of H_2O injection but before the supply of DEZn, (D) at H_2O injection period, respectively. (b) Electrical properties of ZnO films deposited at various doping modes. The dots denote the electrical properties of undoped ZnO films. The film thickness of the B-doped films was between 170 and 200 nm. The flow rates of DEZn, H_2O and B_2H_6 were 52.8, 24.2, and 0.42 μmol/min, respectively.

and the growth cycle of DEZn and H_2O was kept constant for all samples. As we can see, the electron mobility decreases gradually as the B_2H_6/DEZn increases, which is mainly originated from the impurity scattering. The carrier concentration increases as B_2H_6/DEZn ratio increases up to $\frac{1}{4}$, then decreases at higher B_2H_6/DEZn ratios. As a result, a low resistivity of 6.4×10^{-4} Ω cm, which is about one order of magnitude lower than that of undoped ZnO films, is obtained when the B_2H_6/DEZn is $\frac{1}{6}$. Previously, we have reported the electrical properties of ZnO films grown by MOCVD under the optimum deposition conditions [4]. The resistivity of B-doped films

of about 700 nm thick was 7.0×10^{-3} Ω cm. In this study, a lower resistivity of 6.4×10^{-4} Ω cm B-doped ZnO films of only about 200 nm thick is obtained, which implies that the electrical properties of ZnO are improved greatly by ALD technique compared to the conventional MOCVD technique.

The effects of doping sequence on electrical properties of the ZnO films were studied by the following growth experiments where the dopant gas B_2H_6 was supplied: (A) at DEZn injection period, (B) as a substitute of DEZn, (C) after the evacuation of H_2O injection but before the supply of DEZn, (D) at H_2O injection period, respectively. Fig. 4a shows these doping modes. The growth temperature was 150°C, and the growth cycle ratio of B_2H_6 to DEZn (B_2H_6/DEZn) was kept at $\frac{1}{6}$ for all these cases. The electrical properties of these films are shown in Fig. 4b. For mode (A), (B) and (C), B_2H_6 was introduced into the chamber after supplying of H_2O. The resistivity of the B-doped ZnO films was found decreased compared to the undoped ZnO films. On the other hand, for mode (D), B_2H_6 was fed into the chamber after the supply of DEZn. The resistivity of B-doped ZnO films did not decrease although the carrier concentration increased slightly compared with the undoped ZnO film. Therefore, it can be concluded that the electrical properties of B-doped ZnO films can be improved when the dopant gas B_2H_6 is supplied to the growth chamber after the supply of H_2O instead of DEZn.

4. Conclusions

Boron-doped ZnO films were successfully grown by ALD technique using DEZn and H_2O as reactant gases, and B_2H_6 as a dopant gas. The electrical properties of the undoped ZnO films were studied in details. A high electron mobility of about 30 cm^2/V s was obtained for undoped ZnO films 220 nm thick. The electrical properties of ZnO films were improved by boron doping and a low resistivity of 6.4×10^{-4} Ω cm was obtained for B-doped ZnO films of only 200 nm thick. It can be expected that further improvement in depositing low-resistivity ZnO films can be achieved by optimizing the deposition conditions. It was also found that the electrical properties of B-doped ZnO films were improved when the dopant gas B_2H_6 was introduced to the growth chamber after the supply of H_2O instead of DEZn.

Acknowledgements

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