Highly textured and conductive undoped ZnO film using hydrogen post-treatment

Seung Jae Baik, Jae Hoon Jang, Chang Hyun Lee, Woo Yeong Cho, and Koeng Su Lim

Citation: Appl. Phys. Lett. **70**, 3516 (1997); doi: 10.1063/1.119218
View online: http://dx.doi.org/10.1063/1.119218
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v70/i26
Published by the American Institute of Physics.

Highly textured and conductive undoped ZnO film using hydrogen post-treatment

Seung Jae Baik, Jae Hoon Jang, Chang Hyun Lee, Woo Yeong Cho, and Koeng Su Lim
Department of Electrical Engineering, Korea Advanced Institute of Science and Technology, 373-1 Kusong-dong, Yusong-gu, Taejon 305-701, Korea

(Received 18 July 1996; accepted for publication 28 April 1997)

We proposed a method to enhance the characteristics of undoped ZnO films by H_2 post-treatment using photochemical vapor deposition. The resistivity of a H_2-treated film decreased from 1×10^{-2} to 2×10^{-3} Ω cm, the haze ratio increased from 37% to 48%, and no degradation of total transmittance was observed. There are two possible explanations for these phenomena. First, hydrogen atoms assist the desorption of oxygen atoms from the film, resulting in decreased resistivity. Second, hydrogen atoms etch small grains growing among large ones on the surface of the film, resulting in a rough surface. © *1997 American Institute of Physics.* [S0003-6951(97)00826-7]

ZnO films are widely used as transparent electrodes for thin-film solar cells. Previous reports of ZnO deposited by metal–organic chemical-vapor deposition (MOCVD) suggest that MOCVD is one of the most promising methods for fabrication of ZnO film because of its low deposition temperature, low resistivity of the films, and good surface texture.[1–4] As a transparent electrode of thin-film solar cells, undoped ZnO film has several advantages, such as high transmittance in the long-wavelength region and simplicity of process. However, obtaining sufficiently low resistivity is very difficult. In this study, we prepared a ZnO film, highly textured with moderate resistivity, from diethylzinc (DEZ) and H_2O using the MOCVD method, and hydrogen treated it to enhance the film characteristics.

ZnO film has a property regarding oxygen desorption and adsorption, which is closely related to the electrical properties of film. When a ZnO film is irradiated by ultraviolet (UV) light, surface-adsorbed oxygen is desorbed and a high-conductivity layer is produced on the surface.[5] In a hydrogen plasma ambient, ZnO films are hydrogenated and film resistivity decreases.[6,7] At this point, it might be easily conjectured that hydrogen treatment may have a beneficial effect on the ZnO film. Moreover, if the equipment for the hydrogen treatment is mercury-sensitized photo-CVD, it could be assumed that some combined effect of UV light irradiation and atomic hydrogen might occur. For these reasons, hydrogen treatment of the ZnO film using photo-CVD was performed.

As previously mentioned, a ZnO film was deposited by a MOCVD apparatus. Figure 1 represents its schematic diagram. The deposition conditions are as follows: the H_2O/DEZ is 2 (mole/mole), the substrate temperature is 170 °C, and the total pressure is 6 Torr. During film growth, UV irradiation was not used. The growth rate at those conditions was 2.2 μm per hour. The characteristics of the sample are summarized as follows: the resistivity is 10^{-2} Ω cm, the haze ratio at 550 nm is 37%, the total transmittance at 550 nm is 86%, and the thickness is 2.2 μm. The H_2 treatment was performed using a mercury-sensitized photo-CVD system. A low-pressure mercury lamp with resonance lines of 1849 and 2537 Å was used as an UV light source. The H_2 treatment conditions were as follows: the H_2 flow rate was 100 sccm, the substrate temperature was 130 °C, the total pressure was 1 Torr, and the temperature of the mercury bath was 20 °C. Sheet resistance, mobility, and carrier concentration were measured by the van der Pauw method utilizing Hall measurements. Transmittance was measured using an UV/visible spectrophotometer in the range of 300–800 nm. The haze ratio, which indicates the measurement of surface roughness, was calculated by the ratio of diffused transmittance (difference of total transmittance and specular transmittance value); surface morphology and cross sections were observed by scanning electron microscopy (SEM) photomicrographs. The change in the crystal orientation was determined by an x-ray diffraction measurement.

The electrical properties are shown in Fig. 2. The film resistivity decreases as the treatment time increases, saturating after 30 min. The mobility and carrier concentration increases as the treatment time increases and saturates after 30 min. The decrease in resistivity may be caused by the oxygen desorption effect, which must be supported by UV light and

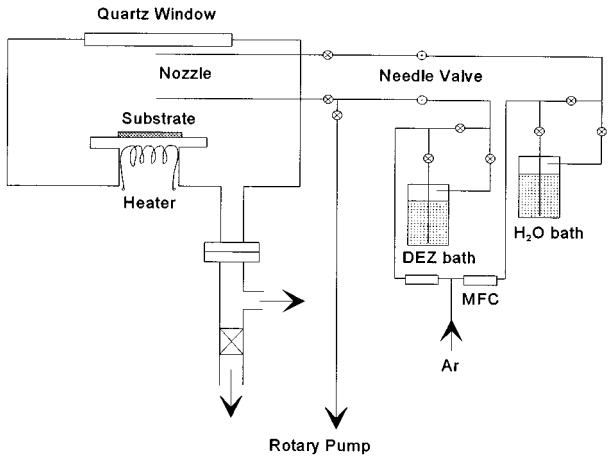

FIG. 1. Schematic diagram of MOCVD apparatus. The flow rate of source materials is controlled by the temperature of the temperature-controlled bath.

 0003-6951/97/70(26)/3516/3/$10.00

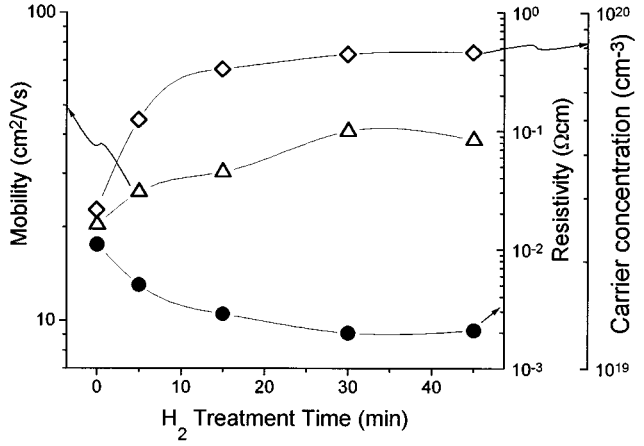

FIG. 2. Resistivity, mobility, and carrier concentration variations for different treatment times. The resistivity value decreases as the treatment time increases, and saturates after 30 min. Also, the carrier concentration value saturates earlier than does the mobility. The increase of the mobility and carrier concentration values means that desorption of oxygen occurs during the hydrogen treatment time. Such processes reach equilibrium after 30 min, thus, the resistivity value saturates.

mercury-sensitized hydrogen. The effect of the oxygen desorption can be summarized in two ways. First, desorption of oxygen at the grain boundary causes lowering of the barrier potential, thus, increasing mobility. Second, the desorption of oxygen on the surface causes removal of the highly resistive surface depletion region.[5]

As the H_2 treatment time increases, the specular transmittance decreases, while the change in the total transmittance is almost negligible, as Fig. 3(a) shows. The haze ratio was calculated from Fig. 3(a), and plotted in Fig. 3(b). For a 45 min H_2-treatment time, the haze ratio is calculated as 48% at 550 nm. Figures 4(a) and 4(b) show SEM photomicrographs of as-deposited and 30 min H_2-treated films. From this, we can observe that the grain size seems to increase with an increase in the H_2 treatment time. From Figs. 4(c) and 4(d), the cross-sectional SEM image of the films, we can conclude that part of the surface is etched by the H_2 treatment; that is, the small grains growing in the valleys among the large grains were removed, deepening the valleys. The grain size, thus, appears to be larger, resulting in a higher haze ratio.

It is thought that small grains are etched due to the removal of oxygen by hydrogen radicals, leaving free Zn atoms behind. It can be presumed that the free Zn atoms vaporize by obtaining energy from the activated hydrogen radicals and the UV light, even though the metallic Zn is hard to vaporize at a temperature of 130 °C with a vapor pressure of 10^{-6} Torr.[8]

We proposed an attractive method for obtaining highly textured and conductive undoped ZnO films by H_2 post-treatment using the photo-CVD method. Utilizing undoped ZnO film as a transparent electrode for thin-film solar cells is attractive, not only for its simplicity, but also for its high mobility and high transmittance in the long-wavelength region compared to doped ZnO films. We showed that the resistivity of undoped ZnO films fabricated by the MOCVD method could be lowered to an applicable region without

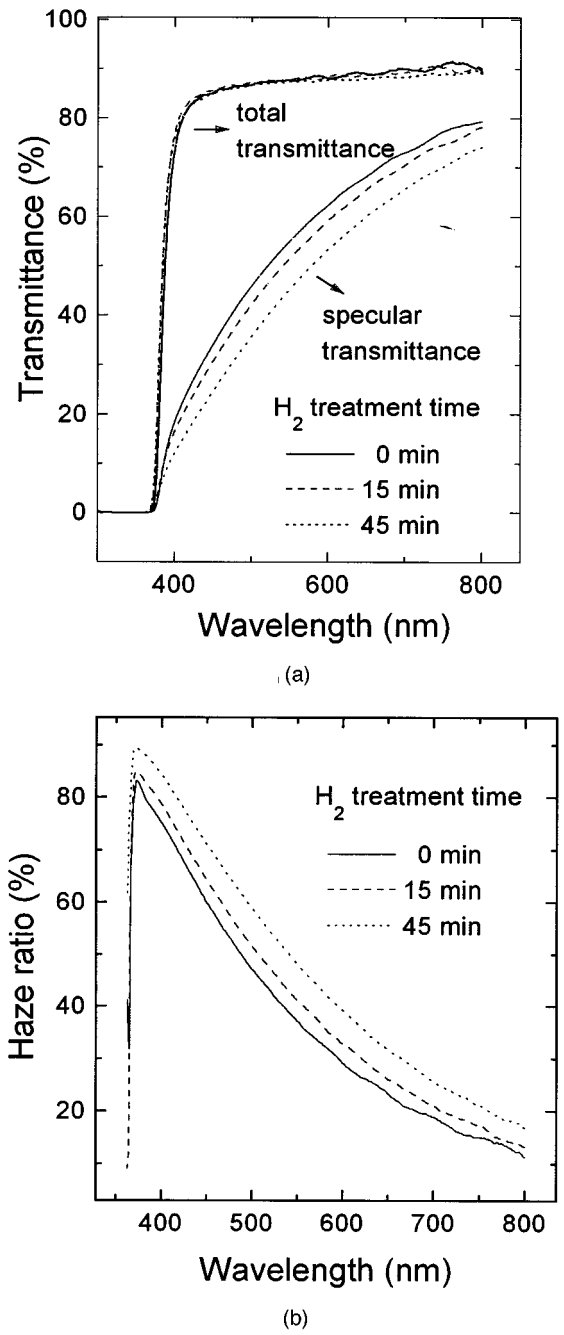

FIG. 3. (a) Total and specular transmittance variations for different treatment times. The solid line represents no treatment, the dashed line represents the 15 min treatment, and the dotted line is for the 45 min treatment. Total transmittance is independent of the hydrogen treatment time. (b) Haze ratio variation. The haze ratio increases as the treatment time increases; the haze ratio at 550 nm of the untreated sample is 37%, and that of the 45 min treated sample is 48%.

decreasing transmittance, and that the surface roughness of the films could be controlled by changing the hydrogen treatment time using the photo-CVD method. The very high haze ratio is useful in enhancing the conversion efficiency of *a*-Si solar cells. Thus, the undoped ZnO films treated with this new method can be applied to transparent electrodes for thin-film solar cells.

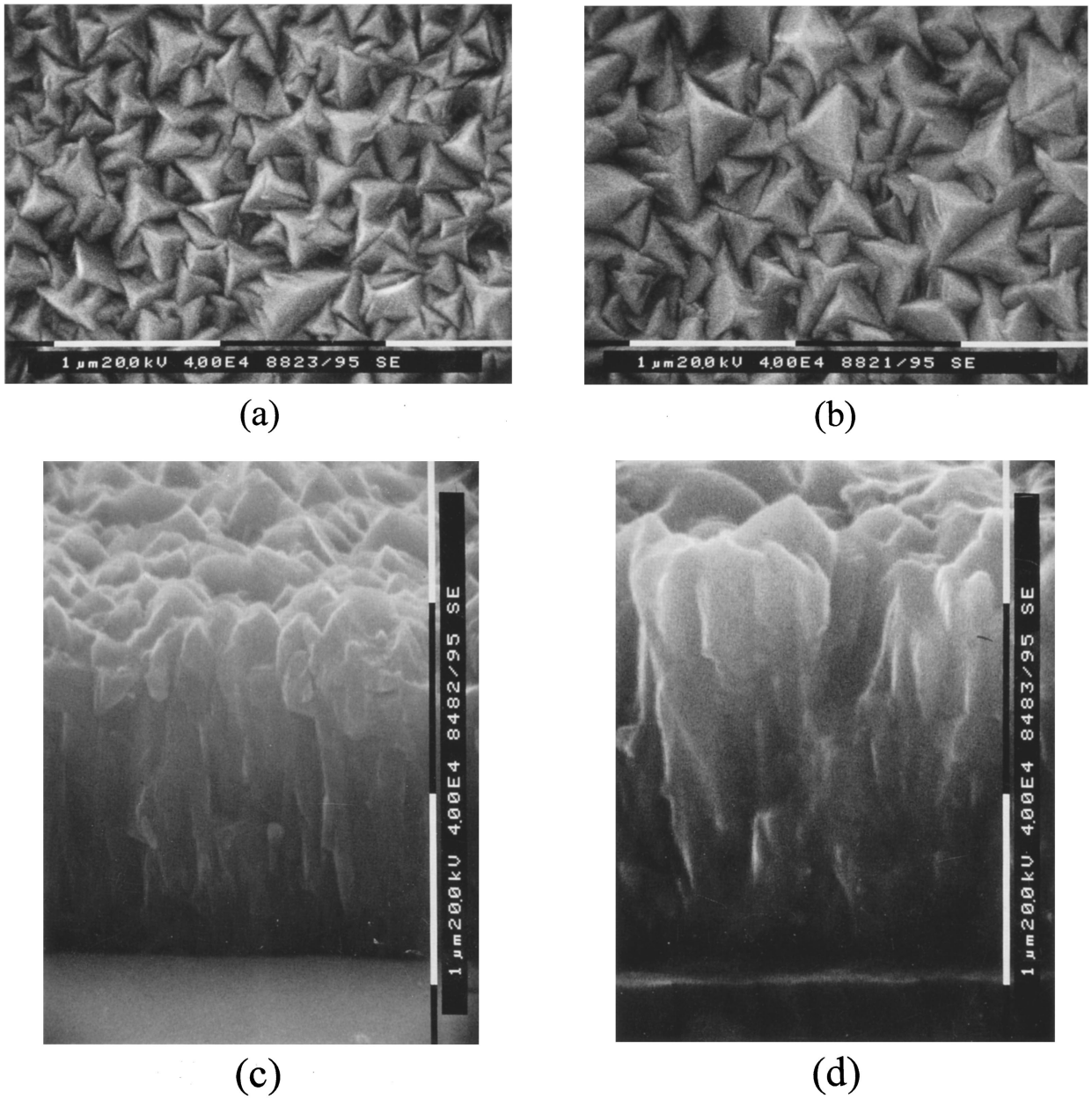

FIG. 4. (a), (b) Surface, (c), (d) cross-sectional views of the as-deposited and 30 min treated samples. From the cross-sectional view, we conclude that the surface of the ZnO film was etched by the hydrogen treatment process, and that the grain size appears to be larger after the hydrogen treatment, as shown in the surface view.

This study was supported by the Korea Electric Power Research Institute (KEPRI).

[1] J. Hu and Gordon, J. Electrochem. Soc. **139**, 2014 (1992).
[2] Sorab K. Ghandhi and Robert J. Field, Appl. Phys. Lett. **37**, 449 (1980).
[3] A. P. Roth and D. F. Williams, J. Appl. Phys. **52**, 6685 (1981).
[4] A. Yamada, W. W. Wenas, M. Yoshino, M. Konagai, and K. Takahashi, 22nd Proceedings of the IEEE *Photovoltaic Specialist Conference*, Las Vegas, Nevada, 1236 (1991).
[5] Y. Takahashi, M. Kanamori, A. Kondoh, H. Minoura, and Y. Ohya, Jpn. J. Appl. Phys. 1 **33**, 6611 (1994).
[6] I. An, Y. Lu, C. R. Wronski, and R. W. Collins, Appl. Phys. Lett. **64**, 3317 (1994).
[7] K. Sato, Y. Matui, K. Adachi, Y. Gotoh, Y. Hayashi, and H. Nishimura, 23rd Proceedings of the IEEE *Photovoltaic Specialist Conference*, Louisville, Kentucky, 855 (1993).
[8] J. C. Bailar Jr., H. J. Emeleus, Sir Ronald Nyholm, and A. F. Trotman-Dickenson, *Comprehensive Inorganic Chemistry*, 1st ed. (Pergamon, 1973), Vol. 3, p. 196.