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Influence of different carrier gases on the properties of ZnO films grown by MOCVD

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ZnO films were grown on sapphire (001) substrate by atmospheric MOCVD using diethyl zinc and tertiary butanol precursors. The influence of different carrier gases (H_2 and He) on the properties was analyzed by their structural (XRD), microstructural (SEM) and compositional (SIMS) characterization. The intensity of the strongest diffraction peak from ZnO (002) plane was increased by about 2 orders of magnitude when He is used as carrier gas, indicating the significant enhancement in crystallinity. The surface of the samples grown using H_2 and He carrier gases was composed of leaf-like and spherical grains respectively. Hydrogen [H] content in the film grown using H_2 is higher than that using He, indicating that the [H] was influenced by the H_2 carrier gas. Ultraviolet emission dominates the low temperature PL spectra. The emission from ZnO films grown using He show higher optical quality and more emission centers.

Keywords: ZnO thin films; MOCVD; SIMS profile; PL spectra.

Influencia del gas portador en las propiedades de películas de ZnO crecidas mediante MOCVD.

Se depositaron películas de ZnO sobre sustratos de zafiro (001) utilizando dietil zinc y butanol terciario como precursores. La influencia de los diferentes gases portadores (H_2 y He) sobre las propiedades se estudió mediante la caracterización estructural (XRD), microestructural (SEM) y composicional (SIMS). La intensidad del pico de difracción más importante del plano (002) del ZnO aumentó en dos órdenes de magnitud cuando se utiliza He como gas portador indicando un incremento significativo de la cristalinidad. La superficie de las muestras crecidas utilizando H_2 y He está formada por granos en forma de hoja y de forma esférica respectivamente. El contenido en hidrógeno (H) en la película es mayor cuando se utiliza H_2 que cuando se utiliza He, indicando que la cantidad de hidrógeno está influenciada por el H_2 del gas portador. La emisión ultravioleta domina el espectro PL de baja temperatura. La emisión de las películas de ZnO utilizando He muestra mayor calidad óptica y más centros de emisión.

Palabras clave: estructura Capas delgadas de ZnO, MOCVD, perfil de SIMS, espectro PL.

1. INTRODUCTION

Zinc oxide (ZnO) is a promising material with wide band gap (3.37 eV), large exciton binding energy (60 meV), and high optical gain (320 cm^{-1}) at room temperature. Owing to its important applications in short-wavelength (UV/violet/blue) optoelectronic devices, many growth techniques such as molecular beam epitaxy, pulsed laser deposition, metal-organic chemical vapor deposition (MOCVD), sputtering etc. have been employed [1-4]. Among the available techniques, owing to the industrial compatibility, MOCVD has been widely used to grow ZnO [3, 5, 6]. Recently, large breakthrough has been obtained and RT electroluminescence (EL) from ZnO p-n homo-junction grown by MOCVD was observed [1, 5-7]. However, the observed EL was very weak due to the low p- type characteristics and high defects concentration such as hydrogen impurities that are found invariably in the ZnO films deposited by different techniques. It is well known that hydrogen acts as a donor in ZnO. It is very essential to have good control over the hydrogen content in order to decrease the background electron concentration and enhance the p- type characteristics. As most of the MOCVD precursors contain hydrogen, controlling [H] in the films deposited by this technique becomes a serious concern. We have earlier reported high crystalline ZnO films grown by MOCVD using diethyl zinc and tertiary butanol precursors [8], but however with high H content. In order to decrease it, we need to recognize whether the dominating H atoms come from the carrier gas or precursors. Hence, in the present work, ZnO films were grown using different carrier gases namely He and H_2 to find out their influence on the different physical properties. It is believed that the present work may benefit the research to obtain high crystalline ZnO films by MOCVD method.

2. EXPERIMENTAL DETAILS

Epitaxial growth of ZnO was performed in a vertical, radio-frequency heated, water cooled (20 °C) quartz MOVCD reactor operated at atmospheric pressure. ZnO thin films were grown on sapphire (001) substrates using diethyl zinc and tertiary butanol precursors. The substrate temperature was controlled at ~425 ºC during the growth time of 120 min. H_2 and He was employed as carrier gases, respectively. The corresponding gas flows passed through diethyl zinc and tertiary butanol were 10.7 and 13.2 sccm. The total flow in the reactor was 2 L/mn. The films grown with H_2 and He carrier gases are denoted as S1 and S2, respectively. The crystal structure was confirmed by a high-resolution X-ray diffraction (HRXRD) with Cuk$_\alpha$ line. The surface microstructure was analyzed by scanning electron microscopy (SEM). The photoluminescence spectra were recorded at low temperature (1.5 K) using the Ar ion laser (λ = 351 nm) as excitation source. The composition of the samples was investigated by SIMS technique using Cs ion beam.

3. RESULTS AND DISCUSSION

The HRXRD spectra are shown in Figure 1 as a function of the scan angle, 2θ (degrees). The obtained diffraction peaks are matched with the standard data (ICDD card no. 36-1451) and confirmed that the films are hexagonal ZnO (space group #186). It is perceptible that the films grow along the (002) plane and show a strong orientation. The intensity of the (002) peak of the films is increased by 2 orders of magnitude when deposited with He (S2), as compared to sample S1. The increase in diffraction intensity suggests that the crystalline quality is improved when He is used as a carrier gas. Further, a secondary diffraction peak (004) was observed at ~72.9° of 2θ. A diffract peak from the sapphire (006) substrate is also observed at ~42°.

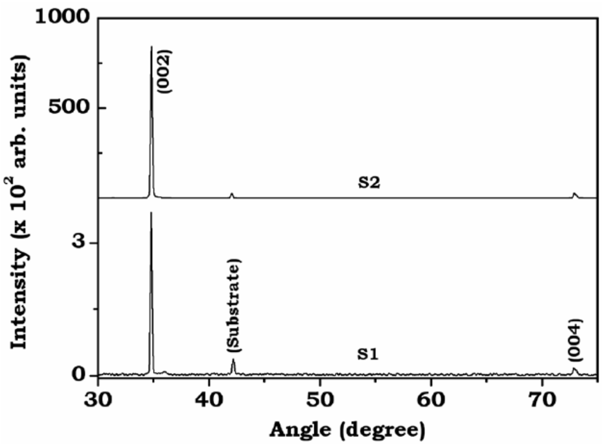

Fig. 1- XRD spectra of the ZnO films.

The surface microstructures obtained from SEM analyses on the samples S1 and S2 are shown in Fig. 2. It can be noticed straightforwardly that the carrier gas has influenced the surface significantly. The surface of the S1 is composed of leaf-like shaped grains measuring ~7 and 3 μm in length and width respectively. A random arrangement of these grains contributes to the highly rough surface. Whereas, the S2 is comprised of uniform spherical shaped grains size of which is measuring ~250 nm. It is perceptible that the surface of S2 is smoother and the grains are packed tightly. The difference in morphology may have resulted from the different growth model influenced by the respective carrier gases. The growth model of a thin film on the substrate may be categorized as island growth, layer growth and mixed growth. The relatively rough surface of both samples suggests that the grown films do not belong to the layer growth model. The surface of S1 suggests a possible growth through mixed growth model and that of S2 through island growth model.

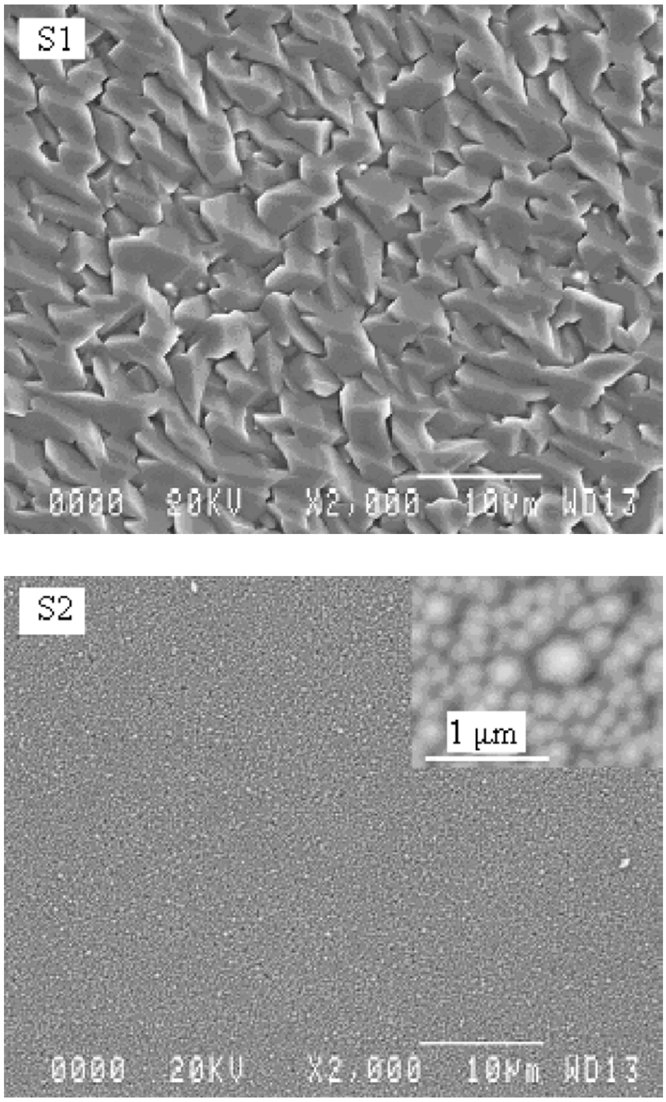

Fig. 2- SEM microstructure of the ZnO films.

The influence of the carrier gas on the composition of ZnO films was studied by SIMS analyses and the corresponding spectra recorded for H atoms in the film are shown in Fig. 3. It is evidence that the level of [H] at the surface is very stronger than that inside the films, which probably results from the surface absorption. It can be deduced that the H concentration in the films decreases with increasing etching time from the surface to the interface between the film and substrate. The average intensity of the H concentration of the S1 is an order of magnitude higher than that of S2. The foregoing discussion indicates that during growth, H atoms in the H_2 carrier gas were incorporated into the film. Additionally, the thickness of S1 and S2 was about 1 and 3 μm, respectively, which indicates that the H_2 carrier gas decreases the sample growth rate. It is presumably resulted from the reduced reaction rate between the oxygen source and H_2 carrier gas at high temperature.

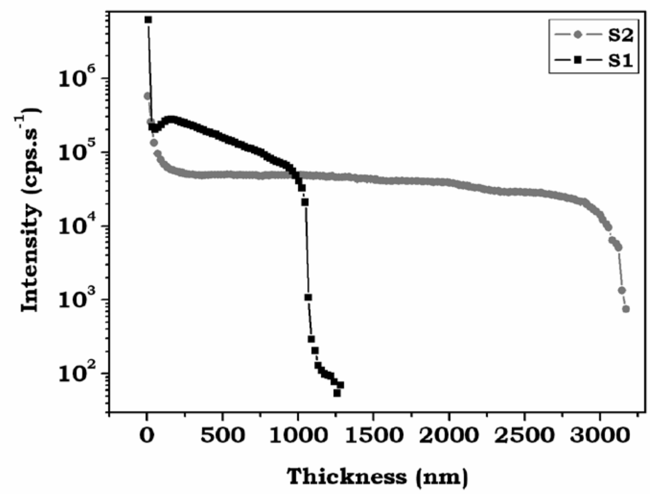

Fig. 3- SIMS profiles of H in ZnO films.

The influence of H_2 and He carrier gases on the optical properties was investigated through PL spectra, which is shown in Fig. 4 as a function of photon energy ranging from 3.20 to 3.40 eV. At liquid He temperature, UV emission dominated the PL spectra and the defects-induced green emission was not observed during measurements. It is evident that in the PL spectra of S2, the peak at about 3.356eV sharply decreases, and the peak at 3.361eV obviously increases and becomes stronger. Corroborating with the SIMS analyses, the peak at 3.356 may probably be related to H donor defects in the films. When He is used as carrier gas, the H defects concentration decreases which in turn results in the decrease of the related emission intensity. Furthermore, the improvement in the film crystallinity makes the other binding exciton peaks stronger and provides more emission centers appear.

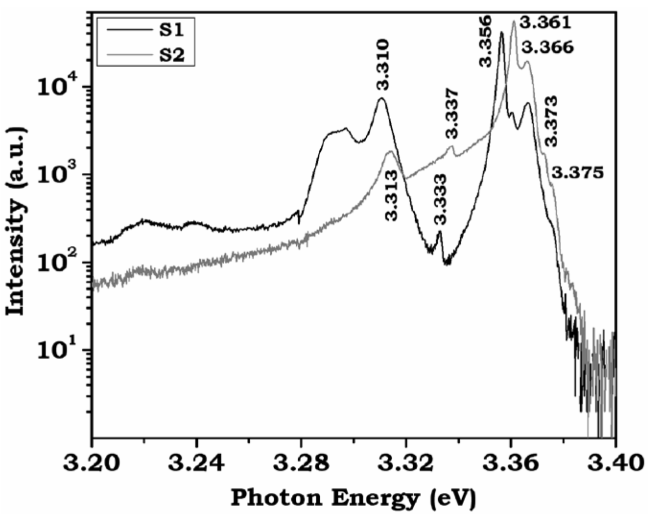

Fig. 4- PL spectra of the ZnO films.

4. CONCLUSIONS

ZnO films were grown on sapphire substrate using H_2 and He as carrier gases. The influence of carrier gases on the properties has been investigated. It is demonstrated that the films grown with He carrier gas leads to improved crystallinity, smooth surface microstructure, and reduced H defects concentration. The film growth rate is decreased if H_2 is used as carrier gas, which is attributed to the reduced reaction rate. PL spectra indicate that the optical quality is increased when the films are grown using He as carrier gas.

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REFERENCES

1. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S. F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma and M. Kawasaki, Repeated temperature modulation epitaxy for p-type doping and light-emitting diode based on ZnO, Nature Mat. 4 (2005) 42-46.
2. X. L. Guo, H. Tabata and T. Kawai, Pulsed laser reactive deposition of p-type ZnO film enhanced by an electron cyclotron resonance source, J. Cryst. Growth 223 (2001) 135-139.
3. J. Wang, V. Sallet, G. Amiri, J. F. Rommelluere, A. Lusson, J. E. Lewis, P. Galtier, E. Fortunato, R. Martins and O. Gorochov, Influence of the self-buffer layer on ZnO film grown by atmospheric metal organic chemical vapor deposition, Thin Solid Films 515 (2006) 1527-1531.
4. J. Wang, V. Sallet, F. Jomard, A. M. B. Rego, E. Elangovan, R. Martins and E. Fortunato, Thin Solid Films (2007) doi: 10.1016/j.tsf.2007.03.062.
5. W. Z. Xu, Z. Z. Ye, Y. J. Zeng, L. P. Zhu, B. H. Zhao, L. Jiang, J. G. Lu, H. P. He and S. B. Zhang, ZnO light-emitting diode grown by plasma-assisted metal organic chemical vapor deposition, Appl. Phys. Lett. 88 (2006) 173506_1-173506_3.
6. J. C. Sun, J. Z. Zhao, H. W. Liang, J. M. Bian, L. Z. Hu, H. Q. Zhang, X. P. Liang, W. F. Liu and G.T. Du, Realization of ultraviolet electroluminescence from ZnO homojunction with n-ZnO/p-ZnO:As/GaAs structure, Appl. Phys. Lett. 90 (2007) 121128_1-121128_3.
7. J. H. Lim, J. H. Yang, D. K. Hwang, E. J. Yang and S. J. Park, The effect of thickness of p-type ZnO film on ZnO homojunction LED, II-VI compounds conference, Warsaw, 2005.
8. J. Wang, M. Peres, J. Soares, O. Gorochov, N. P. Barradas, E. Alves, J. E. Lewis, E. Fortunato, A. Neves and T. Monteiro, Annealing properties of ZnO films grown using diethyl zinc and tertiary butanol, J. Phys.: Condens. Matter 17 (2005) 1719-1724

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