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다층 구조를 이용한 Phosphorus 도핑된 ZnO 박막 제작

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Fabrication of phosphorus doped ZnO thin film using multi-layer structure

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Abstract - ZnO and phosphorus doped ZnO thin films (ZnO:P) are deposited by pulsed laser deposition grown on (001) Al_2O_3. ZnO/ZnO:P/ZnO/Al_2O_3 (multi-layer) structure was used for phosphorus doped ZnO fabrication. This multi-layer structure thin film was annealed at 400℃ for 40 min. The electron concentration of that was changed from 10^{19} to 10^{16}/㎤ after annealing. ZnO thin films with encapsulated structure showed the enhanced structural and optical properties than phosphorus doped ZnO without encapsulated layer. In this study, encapsulated ZnO structure was suggested to enhance electrical, structural and optical properties of phosphorus doped ZnO thin film and it was identified that encapsulated structure could be used to fabricate high quality phosphorus doped ZnO thin film.

1. Introduction

ZnO is wide and direct band gap materials of 3.37 eV at room temperature and a Ⅱ-Ⅵ compound semiconductor having potential applications such as transparent electrode, thin and bulk gas sensor, varistors, surface electro-acoustic wave devices, photo detector, ultraviolet (UV) hetero- and homo-junction diode [1-7]. Interest of application for optoelectronic devices such as light emitting diode (LED) and laser diode (LD) using ZnO is increasing because of a large exciton binding energy of 60 meV and fabrication of commercial ZnO substrate. ZnO shows *n*-type semiconducting properties with many defects, such as the lack of O and the excess of Zn [5,8,9]. This leads difficulty of systematical control of electron concentration in ZnO despite of importance of electron concentration control for optoelectronic device application such as LED and LD.

In this study, various ZnO structure such as pure ZnO, phosphorus doped ZnO (ZnO:P), and ZnO/ZnO:P/ZnO multi-structure were grownon (001) Al_2O_3 depending on deposition temperature and oxygen pressure by pulsed laser deposition (PLD). Electron concentration was systematically controlled depending on deposition conditions and annealing conditions.

2. Experimental

Various ZnO thin films such as pure ZnO thin films, phosphorus doped ZnO thin films and ZnO/ZnO:P/ZnO multi-structure were grown on (001) sapphire substrate by pulsed laser deposition, using a Q-switched Nd:Yttrium aluminium garnet laser operating at a wavelength of 355 nm and a repetition rate of 5 Hz. ZnO ceramic target and ZnO:P ceramic target (Pure ZnO target + 0.1 mol% phosphorus) were used as a source of target materialsfor fabrication of ZnO thin films. The substrate temperatures and oxygen pressures during deposition were systematically varied from 200 ℃ to 600 ℃ and from 50 mTorr to 500 mTorr.The ZnO multi structure thin films have been annealed to diffuse phosphorus atoms into ZnO films at 400℃ in atmospheric oxygen partial pressure after deposition. The structural properties of the sample have been investigated by XRD with Ni-filtered Cu-K (=1.541810-10m) source. Electrical properties were measured by using Van der Pauw Hall measurement method.

3. Results and disscussion

In previous results, ZnO thin films deposited at the deposition temperature of 400℃ in oxygen partial pressure of 350 mTorr showed only c-axis orientation growth and high ratio of UV/visible emission [5, 10-13]. The XRD spectra of pure ZnO film deposited on (001) Al_2O_3 at the deposition temperature of 400℃ in oxygen partial pressure of 350 mTorr shows only (002) ZnO peak as shown in Fig. 1(a). However, ZnO:P thin film fabricated on (001) Al_2O_3 at the same deposition conditions shows two orientation growth such as (002) and (101) orientation as shown in Fig. 1 (b), it means that phosphorus diffused into ZnO leads to disturb only *c*-axis orientation growth of ZnO.

Figure 2 shows the variation of electron concentration of pure ZnO and ZnO:P depending on deposition temperature from 200? to 600? in oxygen pressure of 350 mTorr. Pure ZnO deposited at 200℃ and at 400℃ shows the electron concentration of 2.286×10^{18} cm^{-3} and 4.259×10^{19} cm^{-3}. Electron concentration of ZnO:P was increased from 2.203×10^{16} cm^{-3} to 4.321×10^{18} cm^{-3} depending on increasing of deposition temperature from 200℃ to 600℃. Pure ZnO and ZnO:P exhibit the lowest electron concentration at the deposition temperature of 200℃, the electron concentration of ZnO:P was lower than that of pure ZnO and it could be suggested that phosphorus was diffused into ZnO thin film. The effect of phosphorus diffusion into ZnO was not observed above the deposition temperature of 400℃ due to the low boiling point of phosphorus of 280.5℃.

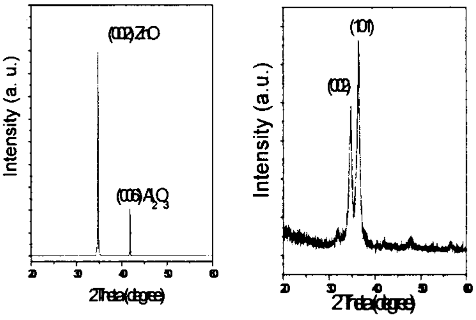
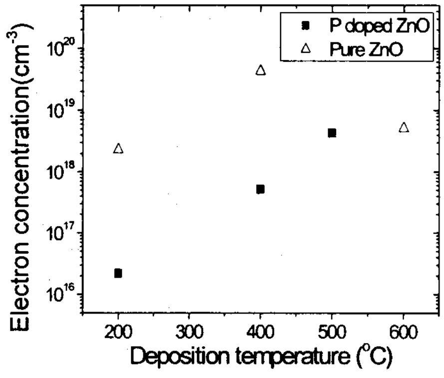


Fig. 1. XRD patterns of (a) Pure ZnO and (b) P doped ZnO deposited on Al_2O_3.

Figure 3 exhibits the electron concentration variation of pure ZnO and ZnO:P depending on oxygen pressure from 50 mTorr to 500 mTorr at the deposition temperature of 200℃ which was showed the lowest electron concentration. Electron concentration of pure ZnO and ZnO:P was decreased from 3.51×10^{19} cm^{-3} to 2.286×10^{18} cm^{-3} and from 7.13×10^{19} cm^{-3} to 2.203×10^{16} cm^{-3} as oxygen partial pressure increased from 50 mTorr to 350 mTorr because content of oxygen in pure ZnO and ZnO:P was increased depending on increasing of oxygen partial pressure, therefore, oxygen deficiency of ZnO was compensated. However, electron concentration of pure ZnO and ZnO:P was increased above oxygen partial pressure of 350 mTorr as shown in Fig. 3. It means that excess of oxygenleads to increase of native defects. Electron concentrationof ZnO:P is smaller than that of pure ZnO due to the effect of phosphorus diffusion into ZnO.



Fiig. 2. Variation of electron concentration of pure ZnO and P doped ZnO thin films depending on deposition temperatures.

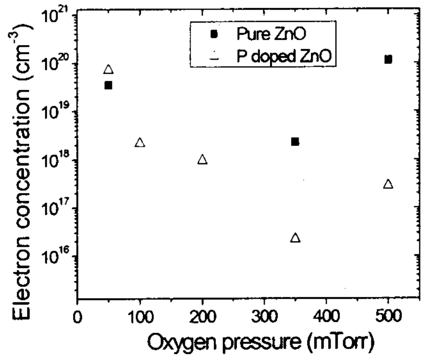


Fig. 3. Variation of electron concentration of pure ZnO and P doped ZnO thin films depending on oxygen partial pressuer.

ZnO/ZnO:P/ZnO/Al_2O_3 multi-structure was fabricated at deposition temperature of 200℃ in oxygen pressure of 350 mTorr which is deposition condition related to the lowest electron concentration and then was annealed at 400℃ in atmospheric oxygen partial pressure depending on annealing time. XRD pattern of multi-structure annealed at 40℃ for 40 min, dominant *c*-axis orientation growth is observed compared to ZnO:P (is not shown). It could be thought that structural property was improved compared to ZnO:P. Electron concentration of encapsulated structure was $3.07\times10^{19}cm^{-3}$ before annealing treatment. Electron concentration of that structure was varied from $1.56\times10^{16}cm^{-3}$ to 2.28×10^{17} cm^{-3} after thermal annealing for 40 min and 60 min as shown in Fig. 4. This means that the effect of phosphorus diffusion into ZnO was observed at that thermal annealing condition compared to electron concentration variation of pure ZnO which was nearly not varied after thermal annealing at 400℃ [5,13]. Encapsulated structure shows lower electron concentration and improved structural property compared to ZnO:P.

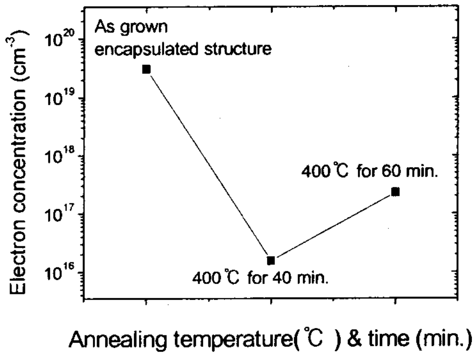


Fig. 4. Electron concentration variation of ZnO/ZnO:P/ZnO multi-structure deposited on Al_2O_3 depending on annealing treatment.

4. Conclusions

Pure ZnO, phosphorus doped ZnO (ZnO:P) and ZnO/ZnO:P/ZnO multi-structure were deposited by pulsed laser deposition grown on (001) Al_2O_3. The effect of phosphorus diffusion into ZnO using phosphorus doped ZnO target was observed through electron concentration variation. Pure ZnO thin films showed the electron concentration from 2.286×10^{18} cm^{-3} to 4.259×10^{19} cm^{-3} and electron concentration of phosphorus doped ZnO was increased from 2.203×10^{16} cm^{-3} to 4.32×10^{18} cm^{-3} depending on deposition temperature in the range of 200℃ to 600℃. Electron concentration of pure ZnO and phosphorus doped ZnO were varied from 2.286×10^{18} cm^{-3} to 1.12×10^{20} cm^{-3} and 2.203×10^{16} cm^{-3} to 7.13×10^{19} cm^{-3} depending on oxygen partial pressure from 50 mTorr to 500 mTorr. The lowest electron concentration of pure ZnO and phosphorus doped ZnO thin films was shown at the deposition temperature of 200℃ and oxygen pressure of 350 mTorr. This multi-structure thin film fabricated at the deposition temperature of 200℃ in oxygen partial pressure of 350 mTorr showed the electron concentration variation from 3.068×10^{19} cm^{-3} to 1.56×10^{16} cm^{-3} after annealing at 400℃ in atmospheric oxygen pressure for 40 min. ZnO thin films with encapsulated structure showed the enhanced structural property and the lowest electron concentration of $1.56\times10^{16} cm^{-3}$ compared to phosphorus doped ZnO without multi layer. In this study, encapsulated ZnO structure was suggested to control electrical and structural properties of phosphorus doped ZnO thin film and it was identified that encapsulated structure could be used to fabricate high quality phosphorus doped ZnO thin film.

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[References]

[1] D. C. Look, Mater. Sci. Eng., B 80(2001)383.

[2] D. C. Look, G. M. Renlund, R. H. Burgener II, J. R. Sizelove, Appl. Phys. Lett. **85** (2004) 5269.

[3] H. Ohta, K. Kawamura, M. Orita, M. Hirano, N. Sarukura, and H. Hosono, Appl. Phys. Lett. **77** (2000) 475.

[4] S.A. Studeninkin, N. Golego, and M. Cocivera , J. Appl. Phys. **84**, (1998) 2287.

[5] Hong Seong Kang, Jeong Seok Kang, Jae Won Kim and Sang Yeol Lee, J. Appl. Phys. **95** (2004) 1246.

[6] Sang Yeol Lee, Y. Li, Jang-Sik Lee, J. K. Lee, M. Nastasi, S. A. Crooker, Q. X. Jia, Hong Seong Kang, Jeong Seok Kang, Appl. Phys. Lett. **85** (2004) 218.

[7] Sang Yeol Lee, Eun Sub Shim, Hong Seong Kang, Seong Sik Pang, Jeong Seok Kang, Thin Solid Films **473** (2005) 31-34.

[8] Leonid V. Azaroff, Introduction to solids, McGRAW HILL BOOK COMPANY, INC (1960) pp 371-372.

[9] F. A. Krger, The chemistry of imperfect crystals, NORTH-HOLLAND PUBLISHING COMPANY, pp 743 - 752 (1974).

[10] Sang Hyuck Bae, Sang Yeol lee, Beom Jun Jin, Seongil Im, Applied Surface Science 169-170 (2001) 525.

[11] S. H. Bae, S. Y. Lee, H. Y. Kim, S. Im, Optical Materials **17**(2001) 327.

[12] E. S. Shim, H. S. Kang, J. S. Kang, J. H. Kim, S. Y. Lee, Applied Surface Science **186**(2002) 474.

[13] H. S. Kang, J. S. Kang, S. S. Pang, E. S. Shim, S. Y. Lee. Materials Science and Engineering B102 (2003) 313.