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Deep Level Emission of ZnO and Amorphous SiOC Films by Photoluminescence

Teresa Oh[1] and Chy Hyung Kim[2]

[1]Department of Semiconductor Engineering, 36 Naeduckdong Sangdangku, Cheongju South Korea
[2]Department of Applied Chemistry, 36 Naeduckdong Sangdangku, Cheongju South Korea

teresa@acju.ac.kr

Abstract

Effect of polarity in substrate for ZnO growth was researched. The zinc oxide films were deposited on SiOC/Si wafer by a RF magnetron sputtering system. SiOC film was also deposited by RF magnetron sputtering to obtain a low temperature process. Polarity in SiOC film changed with increasing the oxygen gas flow rates, and the chemical shift in the PL spectra was observed because of lowering the polarity of SiOC film caused by chemical reactions between CH group and OH group as the polar sites by high plasma energy. The chemical shift after ZnO deposition on SiOC film made was attributed to defects owing to the V_o *and* Zn_i *and the valence band in ZnO at interfaces between ZnO and SiOC films. ZnO grown on SiOC film including polar sites changed the roughness owing to the induction of the trap charge resulted from the defects. The roughness of ZnO increased at SiOC with low polarity. SiOC with polar sites enhanced the level of blue emission deeply, and showed the blue shift in PL spectra.*

Keywords: *ZnO, PL spectra, SiOC, Sputter, Polarity*

1. Introduction

The recent advances in ZnO-based oxide semiconductor materials are very important topics for many researchers. Zinc oxide (ZnO) is a wide band gap (3.37 eV) n-type semiconductor with large exciton binding energies. The n-type doping of gallium or aluminum into ZnO is suitable as a transparent conducting material for solar cells and display devices [1-12]. Due to its superior physical and chemical properties, it has been widely used in semiconductor devices. Because of its morphology-dependent properties in practical applications, many efforts have been made on the synthesis of nanostructures ZnO with various morphologies. A number of technology have been used for the deposition of ZnO film, of which the most commonly used technology is radio frequently magnetron sputtering that is considered to be one of the most favorable deposition because of its high reproducibility, low temperature process and the formation of flat surface. However, the growth of ZnO thin films on Si is known to be a difficult task because of the large lattice mismatch between Si and ZnO, and the formation of amorphous SiOx layers. To obtain high quality ZnO films, Si substrate surface was treated by various methods such as passivations. ZnO has been widely investigated on various substrates or porous templates in order to achieve the enhancement of white light emission and high transparent conductivity. Indium-

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gallium-zinc oxide (IGZO) films as transparent conductive oxide (TCO) have accelerated the development of field effect transistors, because of its superior properties of amorphous structure [13-18]. A unique advantage of amorphous materials over crystalline materials is large-area deposition capability of uniform thin films at low temperatures. The multi-level interconnect technology has become attractive to the semiconductor industry, as silicon devices keep shrinking in size while the circuits become more complex. As a silicon device minimizes and their density increases, new materials that can replace the silicon dioxide thin film are required. A low temperature deposition process is needed while maintaining good material quality and electrical characteristics. SiOC film of low dielectric constant (low-k) material formed by high density deposition has been focused on the promising insulator, which can replace the silicon dioxide film. The high density plasma (HDP) reactor such as inductively coupled plasma (ICP) or capacitively coupled plasma (CCP), have been used for SiOC film deposition. HDP dielectric deposition becomes attractive due to its capability of producing good quality material with excellent mechanical properties. SiOC film has a low dielectric constant as an insulator with amorphous structure, which can replace the SiO_2 thin film in semiconductor devices. Especially, low polarity induced by chemical vapor deposition improved the surface properties, and it has been reported that the mobility of organic thin film transistor increased by using the SiOC film as a gate insulator [19-28]. To realize high performance of ZnO-based devices, it is essential not only for the formation of high quality metal electrodes but also for substrate materials such as ZnO. In comparison with undoped ZnO, Al-doped ZnO films have lower resistivity and better stability. Al doped ZnO (AZO) films have attracted much attention because of their comparative high optical transmittance and low electrical resistivity with respect to other TCOs, which are widely used such as Tin-doped Indium Oxide (ITO) films [29-35].

In this work to understand the characteristic of substrate effect in TCO, ZnO was prepared on SiOC/p-Si by RF magnetron sputter. SiOC film was prepared by inductively coupled plasma chemical vapor deposition with various gas flow rate ratios [36]. To achieve high mobility performance of AZO, the influence of properties of SiOC film was studied.

2. Experiment Method

SiOC films were formed by inductively coupled plasma chemical-vapor deposition (ICP-CVD) using the oxygen and dimethyldimethoxysilane (DMDMOS) mixed gases. The DMDMOS was vaporized and carried by argon gas at 35 ℃ with a thermostatic bubbler with 3 to 8 sccm. SiOC films were prepared with various $Ar:O_2$ gas flow rates, and Ar was changed from 3~8 sccm but total 10 sccm was maintained. The base pressure of the mixture was kept at 3 Torr and the rf power was 800 W in each experiment. The ZnO targets (99.99% purity) were supplied by LTS Research Laboratories, Inc., U.S.A. ZnO thin film was deposited on SiOC/p-type Si wafers by RF magnetron sputter at a pressure of 0.01 Torr in argon atmosphere. The target to substrate distance was kept at 100 mm and the base pressure was 4.5×10^{-5} Pa and the working pressure of the chamber with argon gas was $1.2 \sim 1.4 \times 10^{-3}$ Torr. The flow rate of the argon (99.9999%) was controlled by mass flow controller (MFC) with 30 sccm for 5 min, and the sputtering RF power was 80W. The chemical-optical analyses of the film were performed using Photo Luminescence. PL spectra were researched by the UV-visible spectrometer with xenon lamp as a light source at High Technology Components & Materials Research Center, Busan, South Korea. The roughness was

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observed by the atomic force microscopy (AFM, S.I.S., GmbH at Cheongju University). ZnO film on SiOC/Si was prepared at room temperature.

3. Results and Discussion

The characteristics of SiOC film have been defined by the decreasing of polarization between OH and CH different polar group. The SiOC film with the lowest polarity has the lowest dielectric constant and shows the decrease of thickness due to weak bonding length by the weak boundary condition. These results affect the high quality amorphous structure of SiOC.

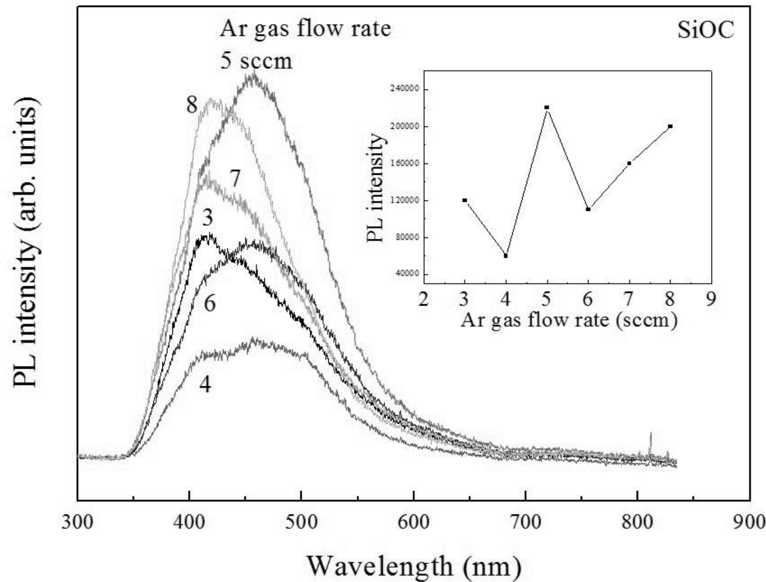

Figure 1. Photoluminescence of SiOC film at various Ar gas flow rates and intensity of inset

Figure 1 is the photoluminescence of SiOC film at Ar gas flow rate from 3 sccm to 8 sccm on Si substrate. Concerning the possible influence of SiOC film with polarity to the characteristic of substrate for the growth of ZnO film, amorphous SiOC film due to the low polarity will lead to an increase of the crystallinity of ZnO film that will affect the electrical properties of the film. Inset of Figure 1 shows the PL intensity of SiOC at various Ar gas flow rates, and the highest PL intensity was observed at SiOC with Ar:O_2 = 5 sccm : 5sccm. Change of the intensity abruptly happened at the sample with the low polarity. Fig. 2 is the photoluminescence vs. wavelength of SiOC films with the polarity. The highest peak at the wavelength 410 nm was observed due to CH or OH polarity in SiOC films, but SiOC with the Ar:O_2= 5 sccm : 5sccm showed the highest peak at 430 nm. This was due to the difference in polarity or non-polarity. The polarity increased the crystallinity of SiOC but the non-polarity weakened bonding strength between atoms and lowered surface energy, which showed the red shift in PL spectra as shown in sample with Ar:O_2= 5 sccm : 5sccm. The red shift was abruptly occurred and involved the increment of intensity because of weak boundary condition due to the weak bonding strength.

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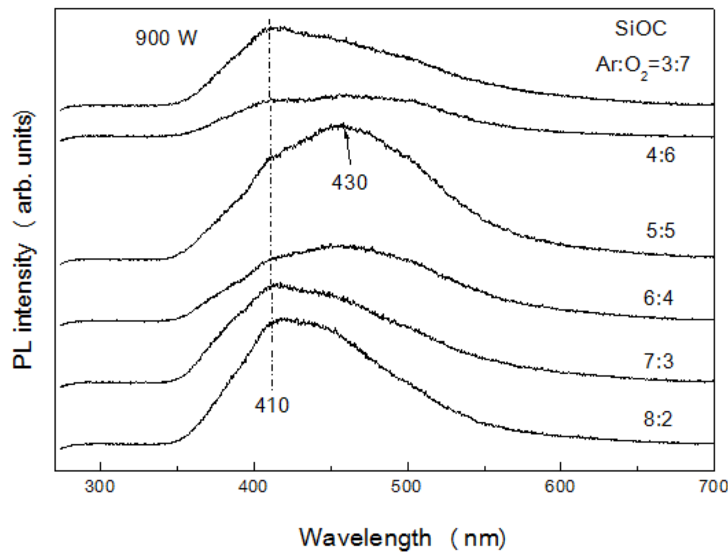

Figure 2. Photoluminescence of SiOC film with the polarities of OH and CH

Figure 3(a) is the PL spectra of ZnO grown on SiOC film. Intensity was also the highest at ZnO/SiOC with Ar gas rate of 5 sccm. PL spectra of ZnO/SiOC film showed the broad band in the range of 350~800 nm, in spite of 350~650 nm at SiOC films. Polarity of SiOC film induced deep level emissions at ZnO/SiOC and then made the broad band PL spectra in the range of 350~800 nm. The chemical shift of PL spectra originated from the existence of trap charges and interface traps due to the oxygen vacancy in ZnO film. Therefore the intensity of PL spectra in ZnO on SiOC film decreased in comparison with that of SiOC film. The chemical shift could be attributed to electron transitions between point defects, such as V_o and Zn_i and the valence band in ZnO. The intensity of PL spectra increased at ZnO growth on SiOC film at Ar = 5 sccm, with the increase of crystallinity and thickness. Figure 3(b) is the roughness of ZnO grown on SiOC film. High roughness was obtained due to the SiOC film with non-polarity and the increament of ZnO crystallinity.

Figure 3(c) and (d) are the optical characteristics of ZnO/SiOC film using Ar gas with 3, 4, 5, 6, 7 and 8 sccm. There was a difference in the formations of DL (deep level) between 3~5 sccm and 6~8 sccm. Group of 3-5 sccm was performed at a relatively high oxygen amount condition and induced high DL_G (green emission). However, a group of 6~8 sccm was performed at stable high Ar gas circumstance and induced strong DL_B (blue emission). The oxygen vacancy was formed by the low Ar gas flow rates in ZnO. It has been known that the oxygen vacancy at the interface between SiOC and ZnO improved the electrical mechanism in semiconductor devices. The tunneling of minority carrier such as oxygen vacancy enhanced the current mechanism in TCO.

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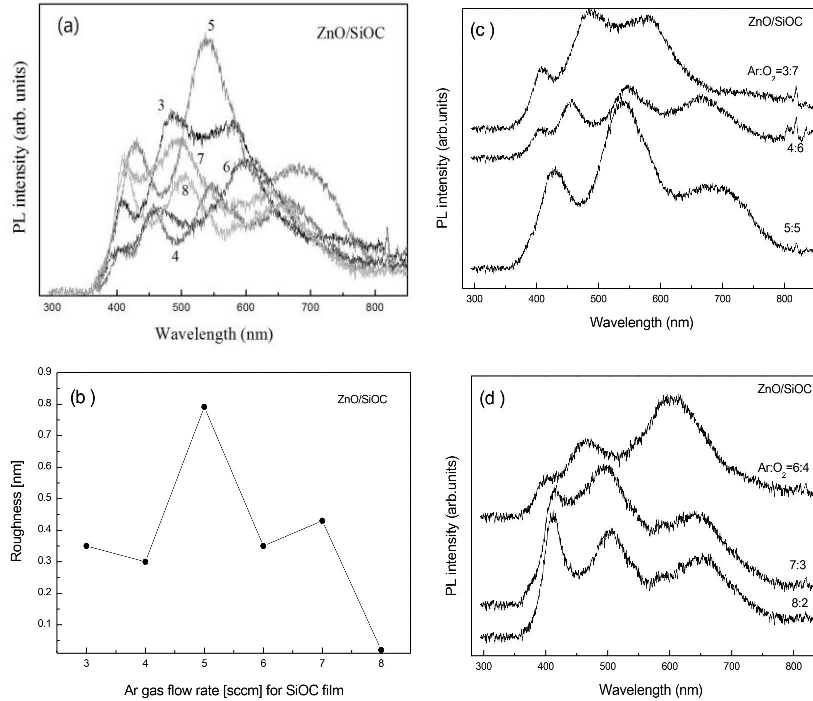

Figure 3. Photoluminescence of ZnO grown on SiOC film, (a) PL ntensity, (b) roughness, (c) 3-5 samples, (d) 6-8 samples

Figure 4 is the PL spectra of ZnO/SiOC film and SiOC with Ar:O_2= 5 sccm : 5 sccm. The deep level emission was occurred at 420 nm (DL_B), 540 nm (DL_G) and 680 nm (DL_R). The blue emission (DL_B) was caused by the recombination of free excitons, and the green emission (DL_G) was due to the structural defects of zinc interstitial (Zn_i). The oxygen vacancy (V_o) and the orange-red emission (DL_R) was resulted from the oxygen interstitial defects. Oxygen vacancy (V_o) induces excess carriers in TFTs (thin film transistor).

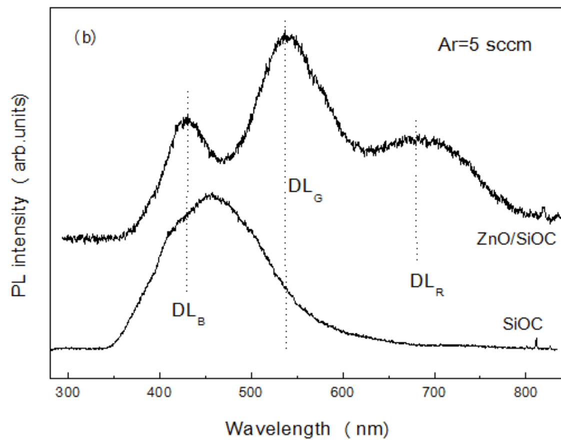

Figure 4. Comparison of PL spectra between ZnO/SiOC and SiOC with Ar:O2= 5 sccm : 5 sccm

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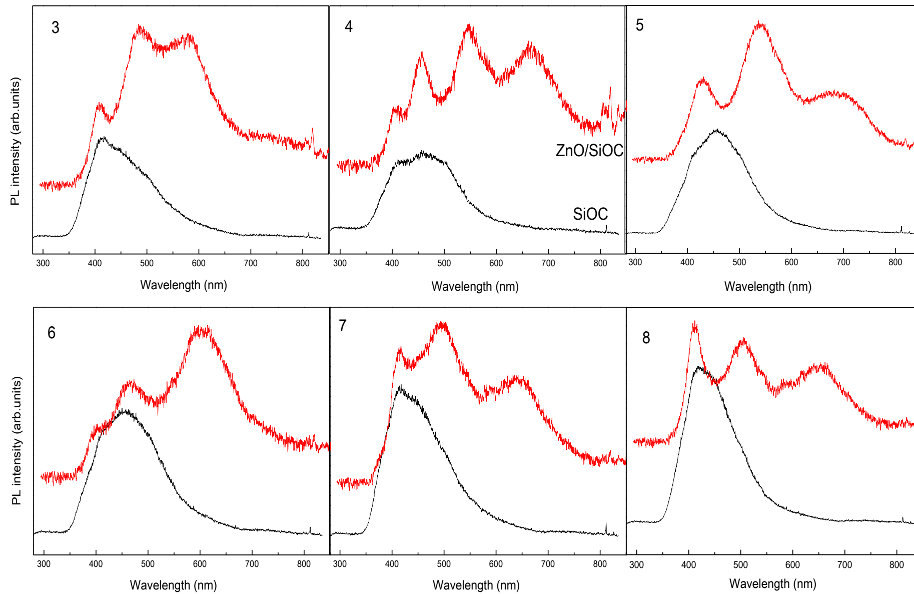

Figure 5. Comparison of deep level emissions between ZnO/SiOC and SiOC, (a) Ar:O_2= 3 sccm : 7 sccm, (b) Ar:O_2= 4 sccm : 4 sccm, (c) Ar:O2= 5 sccm : 5 sccm, (d) Ar:O_2= 6 sccm : 4 sccm, (e) Ar:O_2= 7 sccm : 3 sccm, (f) Ar:O_2= 8 sccm : 2 sccm

Figure 5 shows the comparison of deep level emissions between ZnO/SiOC and SiOC. The substrate characteristic affected the crystallinity of ZnO from the results obtained by the PL intensity. The PL spectra of SiOC showed a blue shift with increasing polarity for samples 3 and 8, which had the peak at 400 nm and blue emission (DL_B) due to the recombination of free excitons. But PL spectra of ZnO on SiOC with low polarity such as in sample 5 displayed three deep levels, DL_B, DL_G and DL_R. So we could confirm that the high band gap for transparent conducting oxide was made from SiOC containing polarity, and the green emission for oxygen vacancy was related to the SiOC with non-polarity. Lowering the poalrization in SiOC made the flat surface by the weak boundary condition between atoms. Therefore, to improve the electrical properties in TCO-TFTs, the trap band gap for the formation of oxygen vacancy was prepared in ZnO [37-41].

4. Conclusion

SiOC and ZnO film was prepared by an RF magnetron sputtering system to make a low temperature process. SiOC films showed various types of polar or non-polar depending on Ar:O_2 gas flow rates. Their physical-chemical properties were easily observed from the results of polarity measured by PL spectra or roughness. SiOC film lowering polarity showed a chemical shift in the PL spectra, because of lowering of the polarity due to chemical reactions between CH group and OH group as polar sites by high plasma energy. The chemical shift after ZnO deposition on SiOC film was attributed to the defects related to the V_o, Zn_i, and the valence band at interfaces between ZnO and SiOC films. ZnO film leads to high existence of defects at the interface between the ZnO and SiOC film. There was the existence of trap charges due

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to many defects in ZnO grown on SiOC film with polarity. High roughness was observed at ZnO grown on low polarity SiOC film. Moreover, the ZnO grown on low polarity SiOC film showed the induction of DL_G.

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Authors

Teresa Oh received an M.S degree in electronic engineering and a Ph. D. degree in telecommunication engineering from the Cheju National University, Cheju, Korea, in 1996 and 2000 respectively. She was with Nano Thin Film Materials Research Laboratory, Cheju, Korea, from 2001 to 2002. She was a Special Researcher in the Research Institute of Advanced Technology, Cheju National University, Cheju, Korea from 2003 to 2004. In 2005, She was a Research Professor in the School of Nano and Advanced Materials Engineering, Changwon National University, Changwon, Korea. Since 2006, She has been a Professor at School of Electronic and Information Engineering, Cheongju University, Korea. Her research interests include silicon interconnection technology associated with solar cell, display, oxide semiconductor and flexible-substrate technology for electric paper application.

Chy Hyung Kim obtained M.S. and Ph. D. majoring in inorganic chemistry at Polytechnic Institute of New York University, U.S.A. in 1983 and in 1985 respectively. She has been a professor in Department of Applied Chemistry at Cheongju University since 1985. She worked as a visiting professor in Department of Chemistry at Michigan State University from 2002 to 2004, in Materials Research Laboratory from 1995 to 1996 and in Department of Chemistry at the Pennsylvania State University from 1996 to 1999. Her research areas include superionic conductors, dielectric materials, and mesoporous carbon materials.

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