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Inductively Coupled-plasma Dry Etching of a ZnO Thin Film by Ar-diluted CF_4 Gas

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In this paper, the behavior of zinc oxide (ZnO) thin films etched by using a diluted CF_4 plasma was investigated. We controlled the substrate bias power of the inductively coupled-plasma (ICP) etching system and the CF_4/Ar gas ratio to improve the etching rate. We accomplished a high etching rate of 144.85 nm/min at a substrate bias power (Sbp) of 200 W under a low ICP power of 200 W. Chemical bonding evaluated by using X-ray photoemission spectroscopy shows the formation of zinc compounds as byproducts during the etching process. Also, we systematically investigated the CF_4-based plasma etching mechanism of ZnO in an ICP reactive etching system.

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I. INTRODUCTION

Zinc oxide (ZnO) is a typical II-VI semiconductor oxide with a direct band gap of 3.36 eV. Besides its wide band gap, ZnO has various interesting properties, such as large exciton binding energy, high chemical stability, good piezoelectric properties [1], non-toxicity and biocompatibility [2,3]. Additionally, ZnO has a larger exciton binding energy, 60 meV, than gallium nitride (28 meV) or zinc selenide (19 meV), which enables exciton radiative recombination at room temperature [4]. ZnO is also studied for use as a transparent conductive electrode in the fabrication of hydrogenated amorphous silicon solar cells [5] due to the low fabrication cost caused by high abundance of raw material and the stability in a hydrogen plasma. Furthermore, ZnO thin films have potential applications for microelectronics such as active layers in thin-film transistors [6], resistive random access memories (ReRAM) for nonvolatile memories [7], and ZnO nanowire gas sensors [8].

For microelectronic and photovoltaic device applications, a fast dry etching process of ZnO thin films with high selectivity over mask materials and a highly anisotropic etch profile is required. Generally, chlorine (Cl_2) or boron trichloride (BCl_3) is used as a reactive etchant to achieve a high etch rate. A recent report has shown that a BCl_3 based etching process is fast because the byproducts during the oxide etch process, such as $(BOCl)_3$, BOCl, and boron dioxide, are highly volatile [9]. However, this process has a problem of Cl contamination caused by B-Cl residues, which requires an additional buffered oxide etch (BOE) treatment. Carbon tetrafluoride (CF_4) is a well-known etchant, which can remove the Cl contamination problem and has been well studied for Si [10]. However, the reactive ion etching (RIE) of ZnO using CF_4 has been considered not of great use due to its very small etching rate. Recently, Lee *et al.* reported that a high etching rate of ZnO using H_2-diluted CF_4 etchant is achievable by increasing the radio-frequency power [11]. However, they used a very high inductively coupled-plasma (ICP) power of 1500 W.

In this study, we tried to achieve a high etch rate at a low ICP power. To do so, we systematically investi-

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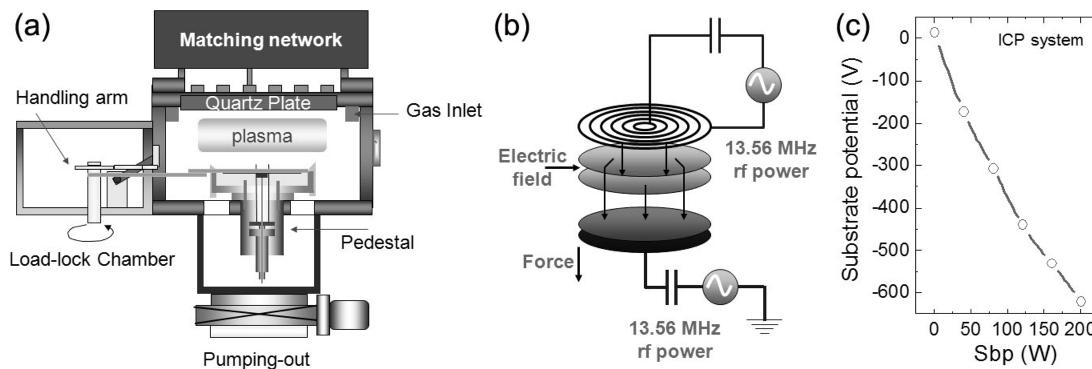

Fig. 1. Schematic diagram of the inductively coupled plasma (ICP) reactive etching system: (a) electric field distribution and ion acceleration direction (b), substrate potential as a function of Sbp, and (c) a schematic of ICP reactive etching system.

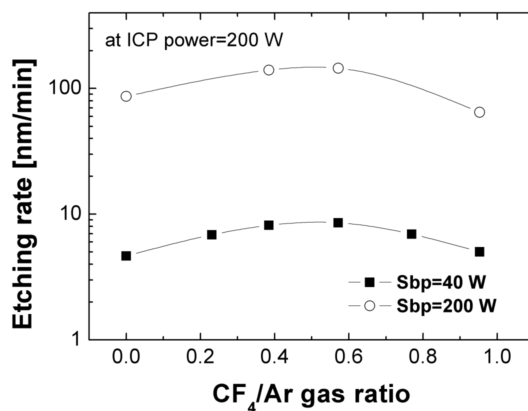

Fig. 2. ZnO etching rate as a function of CF_4/Ar gas ratio for Sbp = 40 W and Sbp = 200 W.

gated the effects of the CF_4/Ar gas ratio and the substrate bias power on the etch rate at a low ICP power of 200 W. Also, we studied the CF_4-based plasma etching mechanism of ZnO in an ICP reactive etching system.

II. EXPERIMENTAL DETAILS

ZnO films were grown on (100) silicon substrates by using a low pressure chemical vapor deposition (LP-CVD) system at 200 °C with diethylzinc (DEZ) and oxygen gas. The prepared ZnO samples were etched in an ICP system (made by SNTEK Co.). A schematic diagram of the ICP etching system is shown in Fig. 1(a). The plasma is generated by a circular coil antenna at a 13.65 MHz rf power (Fig. 1(b)). Separate rf power was applied to the substrate to induce a dc self-bias voltage [12]. Eventually, that power causes a substrate potential. We defined the rf power applied to substrate as the surface-biased power (Sbp). The substrate potential as a function of Sbp was measured and is shown in Fig. 1(c). The substrate potential decreased with increasing Sbp. At a Sbp of 200 W, the substrate potential was minus 620 V, which means that our ICP system could generate high substrate potential even at a low Sbp. The CF_4/Ar mixing ratio was varied from 0 to 0.95, and the Sbp was varied from 0 to 200 W to examine the maximized etching rate. All other experimental parameters were fixed as room temperature, a total pressure of the CF_4/Ar mixture of 5 mTorr, and an ICP power of 200 W. The change caused in the film's thickness by etching was measured by using spectroscopy ellipsometry (Elli-SE, Ellipso tech. Co.). X-ray photon spectroscopy (XPS, VG instrument Korea, ESCALAB 2201) was performed to investigate the surface chemical bonding of ZnO before and after etching.

III. RESULTS AND DISCUSSION

In Fig. 2, closed squares shows the etch rate of ZnO as a function of the CF_4/Ar gas mixture under a Sbp of 40 W. It is noted that etch rate slightly increased from 4.65 to 8.53 nm/min as the CF_4/Ar gas ratio was increased from 0 to 0.57. However, the etch rate decreased from 8.53 to 5.01 nm/min as the CF_4/Ar gas ratio was increased above 0.57. In Fig. 2, open circles shows the etch rate of ZnO as a function of the CF_4/Ar gas ratio at a Sbp of 200 W at room temperature. As the Sbp was increased from 40 W to 200 W, the etch rate increased greatly by 17 times. As the CF_4/Ar gas ratio was increased, the etch rate increased from 86 to 144.85 nm/min, but it decreased from 144.85 to 64.62 nm/min for CF_4/Ar gas ratios >0.57, which is the same tendency in case of the 40 W Sbp. It indicates that the etch rate of ZnO is depend considerably on the Sbp. However, the CF_4/Ar gas ratio does not strongly influence the etch rate in comparison with the Sbp because the variation in the Ar content in the CF_4/Ar plasma is insensitive to the electron temperature, electron density and electron impact coefficients [13]. The highest etch rate was obtained at a Sbp of 200 W and a CF_4/Ar gas ratio of 0.57 under a low ICP power of 200 W. This result shows that

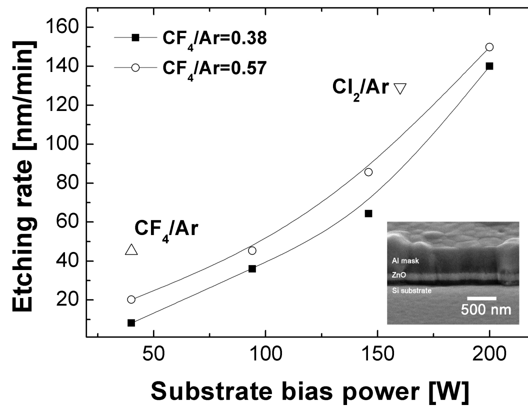

Fig. 3. ZnO etching rate as a function of Sbp for CF_4/Ar = 0.38 and CF_4/Ar = 0.57. The etching rate of the CF_4/Ar, Cl_2/Ar plasma in Ref. 11 is independent of our substrate bias power.

a high etching rate comparable to that obtainable using a Cl_2/Ar plasmas is achievable using a CF_4 plasma [9].

Figure 3 shows the etch rates of ZnO as functions of Sbp for CF_4/Ar gas ratios of 0.38 and 0.57. As the Sbp is increased, the ZnO etch rate increased as a quadric function and reached a maximum at 200 W. In the insert of Fig. 3, we observe a vertical feature in ZnO etched at a Sbp of 200 W and a CF_4/Ar gas ratio of 0.57 with an Al metal mask. It shows that the cross section of ZnO is roughly smooth. The Si substrate is a little over-etched due to a mistake of etching time. However, that could be fixed through precise machine control. These results show that the Sbp plays a key role in achieving a high etching rate. The Sbp plays an important role in etching ZnO by accelerating particle such as F atoms, CF_x radicals, or Ar ions. However, Woo *et al.* [14] reported that the low etch rate of ZnO when using a diluted CF_4 gas plasma was connected two effects. The first is effective removal of O from the surface of ZnO, resulting in ion sputtering. However, this effect leads to a decrease in the efficiency of ion-stimulated desorption of reaction products such as ZnF_2. An etch rate due to the high melting point (872 °C) required for removal of by-products [14]. However, our result was different from that of Woo *et al.* We achieved a faster etch rate around 145 nm/min compared to the 45.2 nm/min of Ref. 14, which should mean that our chemical etching behavior is different from that in the previous report.

For further detailed investigation on the chemical bonding between ZnO and F or CF_x radicals before and after plasma etching, an XPS analysis was performed. Figures 4(a) and (b) show XPS narrow scan results for Zn 2p and O 1s peaks before and after etching in a CF_4/Ar plasma. As shown in Fig. 4(a) for the as-grown ZnO film, the Zn 2p peak can be separated into two peaks at binding energies of 1044.8 eV (Zn 2p1/2) and 1021.8 eV (Zn 2p3/2), respectively [15]. After etching in a CF_4/Ar plasma, the Zn 2p peaks is shifted by 1 eV toward higher binding energy. This binding energy shift is due to changes in the chemical binding states after surface reaction of CF_4 radicals with Zn atoms. The

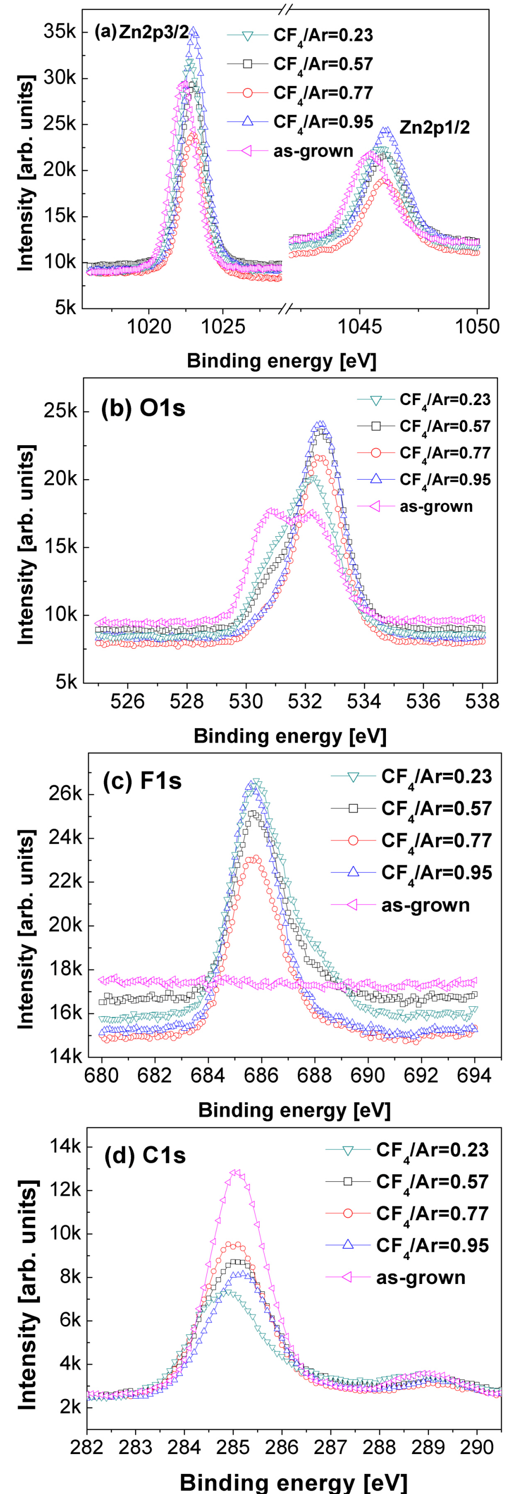

Fig. 4. (Color online) (a) zinc 2p, (b) oxygen 1s, (c) fluorine 1s, and (d) carbon 1s binding energies as functions of the CF_4/Ar gas ratio, as measured by using XPS narrow scans.

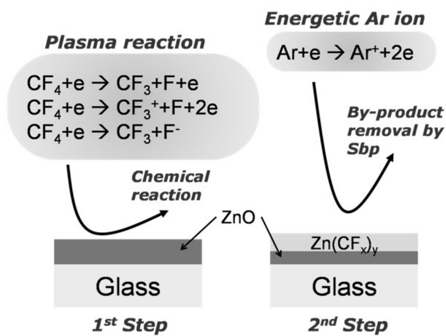

Fig. 5. Illustrated diagrams of the chemical etching mechanism of a ZnO thin film with a diluted CF_4 gas under a low ICP power of 200 W.

O 1s peak also consisted of two maxima 530.7 eV and 532.2 eV, which are the binding energies in related with Zn-O and O-O, respectively. For the O 1s peak after the introduction of a CF_4/Ar plasma, the intensity at 530.1 eV drastically decreased with increasing CF_4/Ar gas ratio, which the binding of Zn-O is effectively broken by a CF_4/Ar plasma. After etching in a CF_4/Ar plasma, the intensity at 532.2 eV increased with increasing CF_4/Ar gas ratio, and the binding energy was shifted by plus 0.6 eV. From these observations, the Zn-O bonds are effectively broken by CF_x radicals based on the decreasing peak at 530.7 eV with increasing CF_4/Ar gas ratio.

In Fig. 4(c), we observe the F 1s peak around 685.8 eV after etching. The F 1s peak exhibits only one maximum value of 685.8 eV, which is not related to any variation in the CF_4/Ar gas ratio. From the Ref. 16, the peak of ZnF_2 is 685.1 ± 0.1 eV. However, our binding energy of ZnF_2 was a different by about 0.7 eV. This might be due to carbon bonding with ZnO, as shown in Fig. 4(d), which shows the intensities of the C 1s spectra for different CF_4/Ar gas ratios and the sample before the etching. The peaks related to hydrogenated carbon (C-H) and carbon contamination (C=C) were observed at around 285 eV and 289 eV, respectively [17]. The bonding intensity of C=C was slightly lower than that of C=C on the ZnO before etching. Furthermore, hydrogen-carbon bonding was decreased with initiation of the CF_4 plasma etching. This result implies the removal of carbon atoms from the surface by the formation of by-products like a volatile Zn compound, $Zn(CF_x)_y$, rather than a non-volatile ZnF_2 fluoride crystal. If ZnF_2 were formed, the etching rate would be very low because it would have a very high melting point of 872 °C. Finally, the volatile Zn compound, $Zn(CF_x)_y$ is removed by Ar^+-ion bombardment the Sbp forces ion acceleration toward the substrate without the formation of a ZnF_2 phase.

In Fig. 5, we summarize the ZnO etching mechanism based on our results. The chemical reaction of CF_4 gas inside the plasma generates excited neutral CF_3 or positive CF_3^+ ions. During the etching process, volatile Zn compounds, $Zn(CF_x)_y$, are synthesized by a reaction with the ZnO film in the first step. Then Zn compounds are removed by Ar^+-ion bombardment under a high negative substrate potential in the second step. Na *et al.* revealed the formation of ZnO_xCl_y by-products in a chlorine-containing ICP system [18]. In turn, these are removed by the Ar^+ ion bombardment. A previous report on chlorine-based dry etching strongly supports our ICP etching mechanism using a diluted CF_4 gas under a low ICP power of 200 W.

IV. CONCLUSION

In this study, we carried out experimental investigations of the etching behavior of ZnO etched by using diluted CF_4 gas in a plasma under a low ICP power of 200 W. We found that an increase in the CF_4/Ar gas ratio led to a slight increase in the etch rate. However, the Sbp mainly dominanted the etch rate, which reached a maximum value of 144.85 nm/min at a Sbp of 200 W. From the results of the XPS analysis, the non-volatile by-product $Zn(CF_x)_y$ was observed. It results from a reaction between ZnO and CF_4 gas. In viewpoint of the etching mechanism, during etching process, ZnO film contains a Zn compound, which can be removed by energetic Ar^+ bombardment under a high negative Sbp.

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REFERENCES

[1] J. Zhou, Y. Gu, P. Fei, W. Mai, Y. Gao, R. Yang, G. Bao and Z. L. Wang, Nano Lett. **8**, 3035 (2008).
[2] Y. L. Wu, C. S. Lim, S. Fu, A. I. Y. Tok, H. M. Lau, F. Y. C. Boey and X. T. Zeng, Nanotechnology **18**, 215604 (2007).
[3] U. Ozgur, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, V. Avrutin, S. J. Cho and H. Morkoc, J. Appl. Phys. **98**, 041301 (2005).
[4] M. Kurimoto, A. B. M. A. Ashrafi, M. Ebihara, K. Uesugi, H. Kumano and I. Suemune, Phys. Status Solidi B **241**, 635 (2004).
[5] W. Beyer, J. Hukes and H. Stiebig, Thin Solid Films **516**, 147 (2007).

[6] E. M. C. Fortunato, P. M. C. Barquinha, A. C. M. B. G. Pimentel, A. M. F. Goncalves, A. J. S. Marques, R. F. P. Martins and L. M. N. Pereira, Appl. Phys. Lett. **85**, 2541 (2004).
[7] S. Lee, H. Kim, D. J. Yun, S. W. Rhee and K. Yong, Appl. Phys. Lett. **95**, 3 (2009).
[8] D. Y. Kim and J. Y. Son, Electrochem. Solid-State Lett. **12**, J109 (2009).
[9] H. K. Kim, J. W. Bae, K. K. Kim, S. J. Park, T. Y. Seong and I. Adesida, Thin Solid Films **447**, 90 (2004).
[10] F. Gaboriau, G. Cartry, M. C. Peignon and C. Cardinaud, J. Phys. D: Appl. Phys. **39**, 1830 (2006).
[11] J. M. Lee, K. M. Chang, K. K. Kim, W. K. Choi and S. J. Park, J. Electrochem. Soc. **148**, G1 (2001).
[12] Y. S. Chang, D. P. Kim, C. I. Kim, K. B. Sim and E. G. Chang, J. Korean Phys. Soc. **42**, S791 (2003).
[13] A. M. Efremov, D. P. Kim and C. I. Kim, Vacuum **75**, 133 (2004).
[14] J. C. Woo, G. H. Kim, J. G. Kim and C. I. Kim, Surf. Coat. Technol. **202**, 5705 (2008).
[15] S. W. Na, M. H. Shin, Y. M. Chung, J. G. Han and N. E. Lee, J. Vac. Sci. Technol., A **23**, 898 (2005).
[16] Y. Kawamoto, K. Ogura, M. Shojiya, M. Takahashi and K. Kadono, J. Fluorine Chem. **96**, 135 (1999).
[17] M. H. Shin, M. S. Park, S. H. Jung, J. H. Boo and N. E. Lee, Thin Solid Films **515**, 4950 (2007).
[18] S. W. Na, M. H. Shin, Y. M. Chung, J. G. Han, S. H. Jeung, J. H. Boo and N. E. Lee, Microelectron. Eng. **83**, 328 (2006).