Epitaxial growth of ZnO thin films on *R*-plane sapphire substrate by radio frequency magnetron sputtering

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ZnO thin films were deposited on a *R*-plane sapphire substrate. The effects of the thermal energy and the kinetic energy of the sputtered species on the growth of ZnO thin films were investigated. By varying the substrate temperature, chamber pressure, and radio frequency power, the structure of ZnO thin films was transformed from polycrystalline to epitaxial on *R*-plane sapphire substrates. High quality (110) ZnO epitaxial thin films were grown at the condition of 400 °C, 250 W, and 5 mTorr. According to reflection high energy electron diffraction and reflection electron microscopy observations, there were no double diffraction distortion and any other patterns. Its surface roughness observed by atomic force microscopy was about 27 nm. © *1997 American Vacuum Society.* [S0734-2101(97)04303-0]

I. INTRODUCTION

Zinc oxide is an *n*-type semiconductor with a band gap of 3.1–3.2 eV and possesses high piezoelectricity as well as high optical transparency in the visible range. ZnO thin film is widely used as an acoustic element in surface acoustic wave (SAW) devices and a window material in solar cell. Epitaxial ZnO thin film on a sapphire substrate is also very appropriate for SAW filters for GHz range due to its high wave velocity.[1] Epitaxial ZnO thin films can be produced on *A*-, *M*-, *R*-, and *C*-plane sapphire single crystal substrates by sputtering,[2–8] chemical vapor deposition (CVD),[9–13] and by the laser ablation method.[14] Kasuga[11] reported that growing directions of epitaxial ZnO deposited on the same sapphire substrates are different according to the substrate temperature, vapor pressure, and pretreatments, so they are called ''multimode epitaxy.'' In the case of sputtering, it is reported that the substrate temperature and growth rate are the critical sputtering factors for epigrowing, but the effects of sputtering variables on the structural transition have not been discussed sufficiently.

In this study, we investigated the effects of the kinetic energy of the sputtered species as well as the substrate temperature on the structural changes and the deposition mechanism.

II. EXPERIMENT

ZnO thin films were deposited on *R*-plane sapphire substrates by rf magnetron sputtering (Fig. 1). Sintered ZnO ceramics were used as target materials, and Ar/O_2 mixture gas was introduced into a chamber. Chamber pressure was changed from 5 to 50 mTorr. The substrate temperature and rf power were varied from 25 to 300 °C and 100–500 W, respectively.

We have determined the orientation by measuring the main peaks of ZnO thin films with an x-ray diffractometer (Cu $K\alpha$, $\lambda = 1.5405$ Å) with a rotating angle 2θ from 20° to 70°. The degree of deviation from its growing direction was evaluated by the x-ray rocking curve. The thickness of samples was measured by a stylus profiler.

The epitaxial structure was analyzed by reflection high energy electron diffraction (RHEED), and surface morphology by atomic force microscopy (AFM).

III. RESULTS AND DISCUSSION

Figure 2 shows x-ray diffraction (XRD) patterns of ZnO thin films deposited on *R*-plane sapphire substrates at the different substrate temperature and chamber pressure. It was observed that the growing directions were evidently different according to these sputtering parameters. It is well known that epitaxial (110) ZnO thin film is grown on a *R*-plane sapphire substrate, and crystallographically well matched with the *R*-plane sapphire by stereographic projection.[15] But, in this experiment, *c*-axis oriented polycrystalline films were deposited at the condition of Figs. 2(a) and 2(b). In Fig. 2(c), which chamber pressure was lower than that of Fig. 2(b), the structure was changed from (002) preferred polycrystalline to (110) epitaxial even though the films were deposited at the same substrate temperature. From this result, it can be concluded that the chamber pressure is one of the critical deposition parameters for the deposition of epitaxial (110) ZnO thin films. To explain the effects of the chamber pressure, the kinetic energy of the sputtered species should be considered. The energy for atomic rearrangement on the surface is definitely important to deposit epitaxial thin films, and this en-

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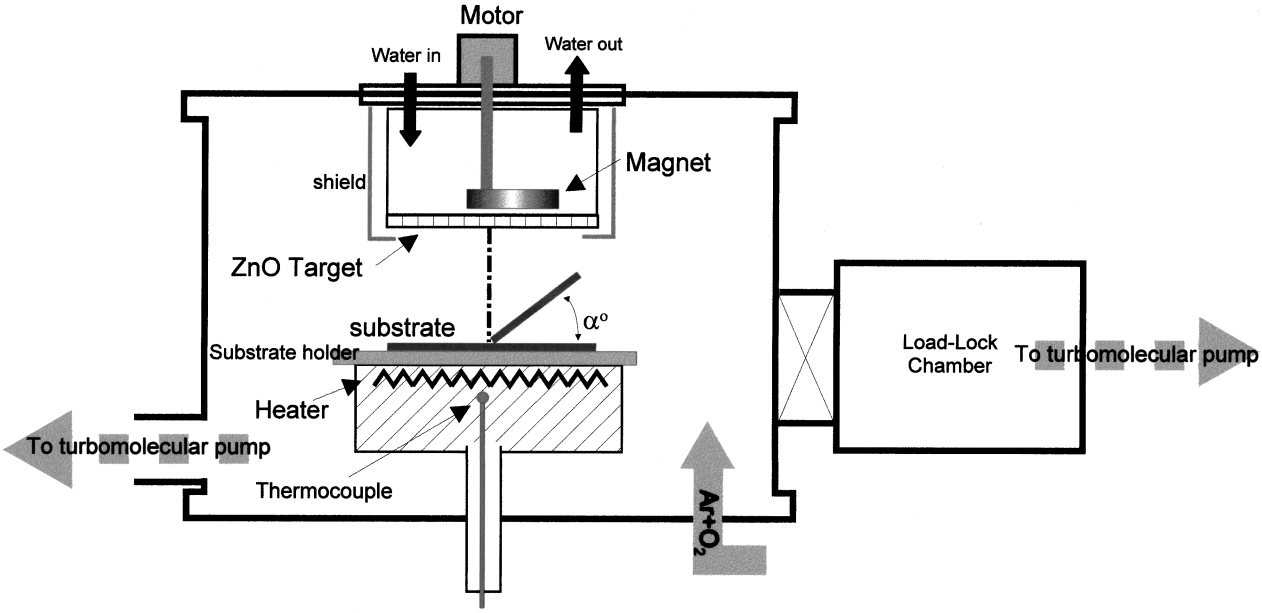

FIG. 1. Schematic diagram of rf magnetron sputter.

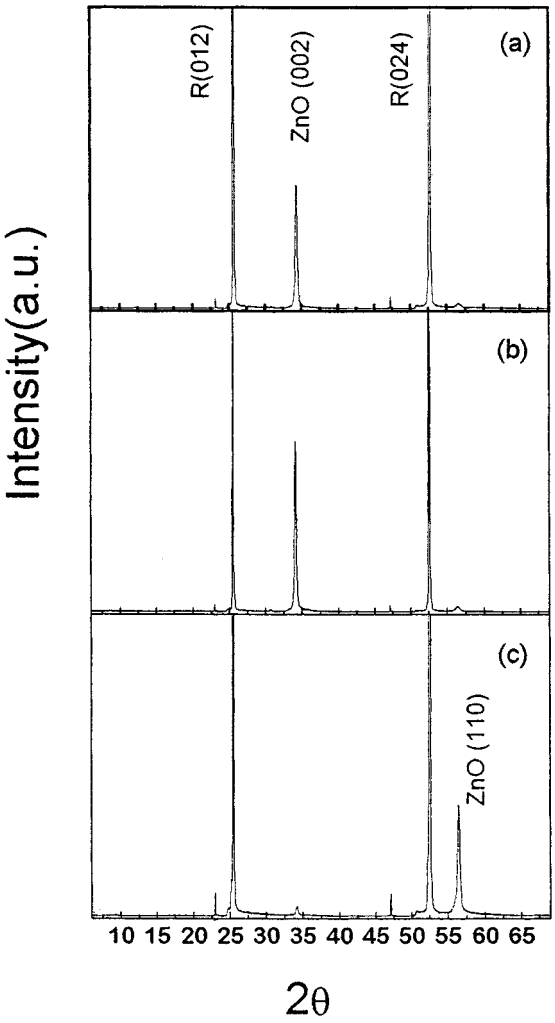

FIG. 2. Variation of XRD patterns of ZnO thin films deposited under a condition: (a) 10 mTorr, 200 °C, (b) 10 mTorr, 300 °C, and (c) 5 mTorr, 300 °C.

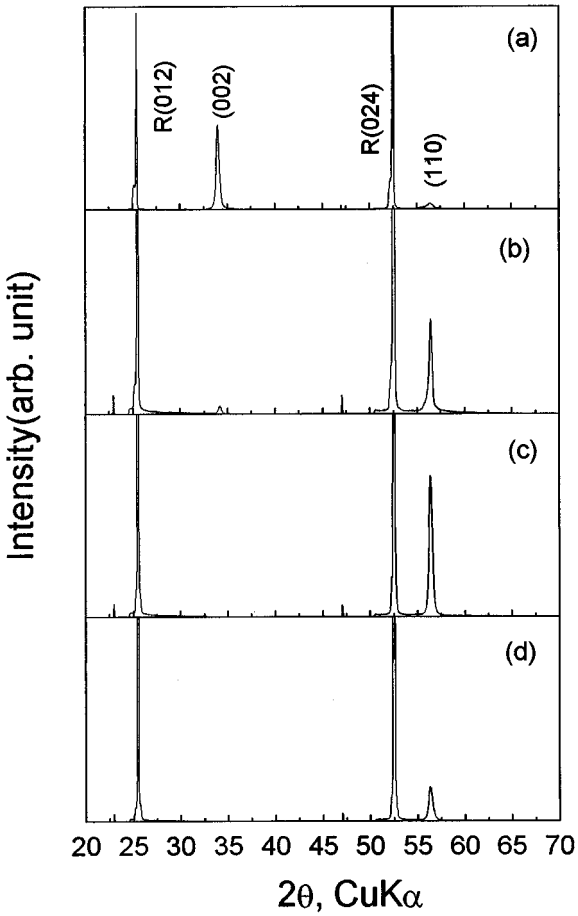

FIG. 3. Variation of XRD patterns of ZnO thin films with a substrate temperature: (a) 200, (b) 300, (c) 400, and (d) 450 °C (rf power=300 W, Ar/O_2=50/50).

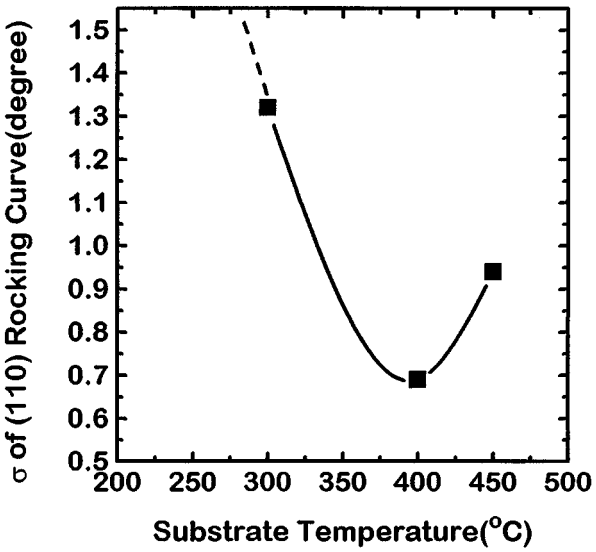

FIG. 4. Variation of standard deviation of (110) rocking curve with a substrate temperature.

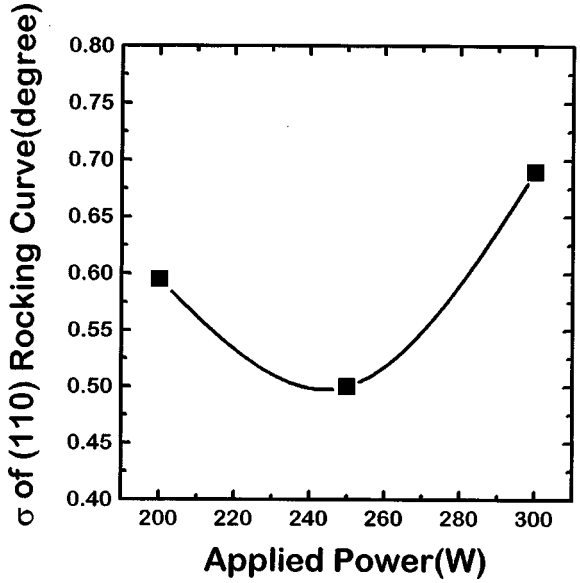

FIG. 6. Variation of standard deviation of (110) rocking curve with an applied rf power.

ergy is supplied mostly by heating the substrate. However, in the case of the sputtering method, the kinetic energy of the sputtered species as well as the thermal energy is a very important energy source, and is related to the chamber pressure. The sputtered species can arrive at the surface of the substrate with higher kinetic energy at low chamber pressure than at high pressure, because the gases at high chamber pressure scatter the sputtered species so much that they lose their kinetic energy before arriving onto the substrate. This scattering effect also could be observed indirectly by measuring the growth rate. On increasing the chamber pressure, the growth rate was decreased due to the scattering.

Conclusively, at high chamber pressure, (002) oriented ZnO thin films were deposited on *R*-plane sapphire substrate regardless of the surface effect of the single crystal substrate because of the insufficient kinetic energy for epitaxial growing even though the substrate temperature was increased. This (002) preferred ZnO thin film can be deposited even on the glass substrate whose amorphous surface has no relation to the growing plane of ZnO, because this direction is a close-packed one.

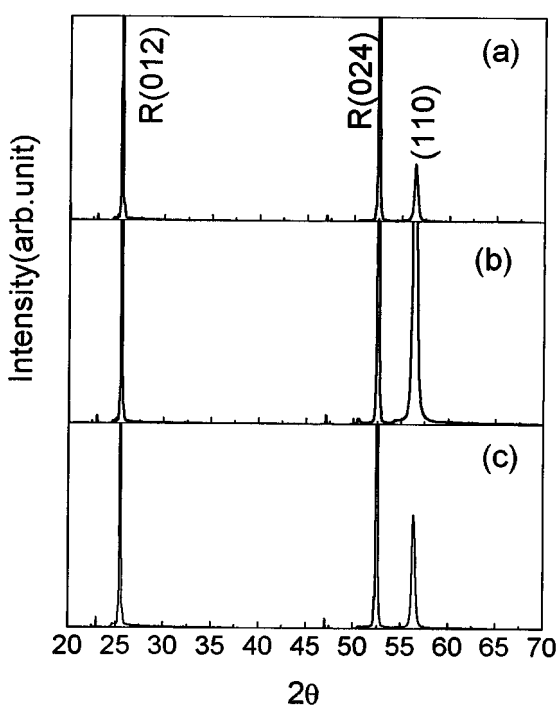

FIG. 5. Variation of XRD patterns of ZnO thin films deposited under a condition of substrate temperature 400 °C, Ar/O_2=50/50 with applied rf power: (a) 200, (b) 250, and (c) 300 W.

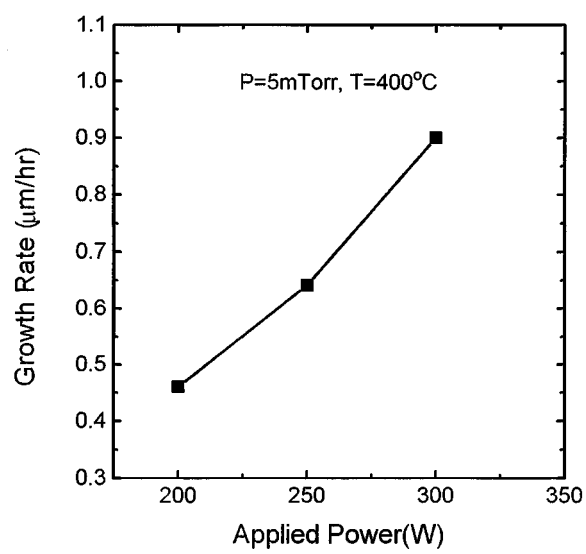

FIG. 7. Variation of growth rate of ZnO thin films with an applied rf power.

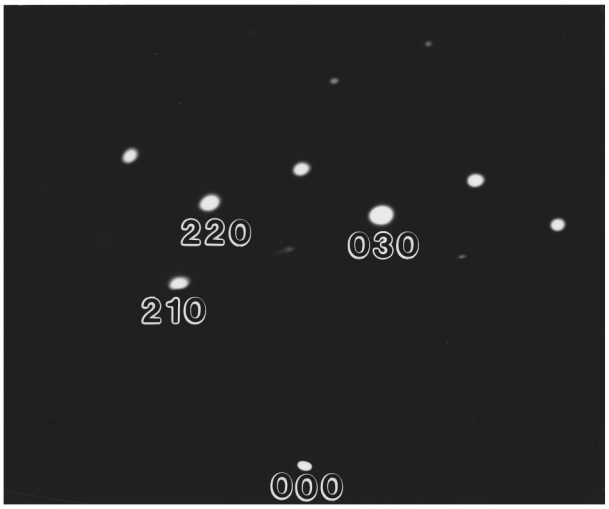

FIG. 8. RHEED pattern of ZnO thin films deposited under a chamber pressure of 5 mTorr, an Ar/O_2 ratio of 50/50, and a substrate temperature of 400 °C.

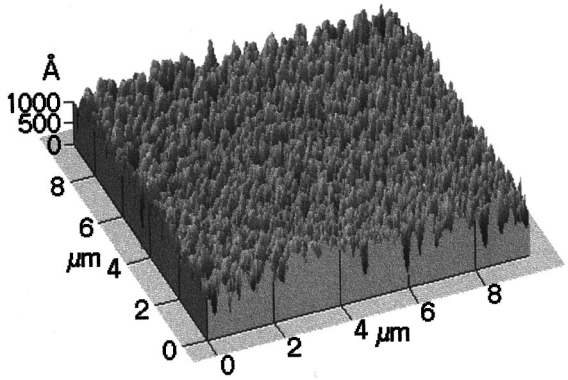

FIG. 9. Surface morphology of ZnO films, deposited under a chamber pressure of 5 mTorr, an Ar/O_2 ratio of 50/50, and a substrate temperature of 400 °C, observed by AFM.

XRD patterns of Fig. 3 show the effects of the substrate temperature on the structural changes. At a low temperature, as discussed before, (002) ZnO thin films were deposited regardless of the surface effect of *R*-plane sapphire because of the insufficient thermal energy. Increasing the temperature, (002) peak became weak, and (110) peak apparently appeared, finally only the (110) peak was observed at the substrate temperature of 400 °C. However, at 450 °C, the crystallinity was deteriorated again, which result is consistent with that of x-ray rocking curve of Fig. 4. It can be assumed that a substrate temperature that is too high contributes to breaking the bonding of Zn–O and to re-evaporating the deposited films rather than enabling the atoms to move to their stable sites.

Figure 5 shows rf power effects on the crystallinity of ZnO thin films. By increasing the rf power from 200 to 250 W, high quality thin films could be achieved, but the crystallinity was deteriorated at an rf power of 300 W. This result can also be observed from the standard deviation (σ) of x-ray rocking curve in Fig. 6, in which σ increased at the rf power of 300 W. It is known that[7] there are three possible factors which contribute to the decrease in structural order of the films as the rf power level is increased. First, the deposition rate increases linearly with rf power as shown in Fig. 7, giving newly arrived species less time to move to their stable sites for epitaxial growing. Second, the relative number of Zn to ZnO ions arriving at the substrates increases with increasing power.[7] Aita[6] reported that the additional step of forming an oxide at the substrate results in films which are more crystallographically disordered than if the arriving species were already in oxide form. Third, the energy of secondary electrons emitted from the target during the sputtering process increases as the target voltage, hence the rf power, is increased. Impact with the growing film causes the bombarding electron to lose energy which results in film heating.[16,17] This additional heating creates a stress gradient across the film thickness,[15] thereby promoting nonuniform film growth. Furthermore, electron bombardment of a solid surface upon which there is an absorbed oxygen layer can promote desorption of it.[18–20] This effect would decrease the probability of forming a stoichiometric oxide at the growth interface before the next layer of film is deposited.

Figure 8 is a RHEED pattern obtained from ZnO surface with electrons accelerated by 100 keV and with incoming angle of 27 mrad. Azimuthal angle is 0° off the ⟨001⟩ direction. Because there were no double diffraction, distortion, and any other pattern throughout the RHEED observation, it was concluded that high quality ZnO crystals with orientation of {110} were grown on the sapphire *R*-plane. There were also no particular defects or features on the ZnO surface with the reflection electron microscopy (REM) observation using the spot 220 in Fig. 8.

The root mean square surface roughness measured from the surface morphology of AFM (Fig. 9) was 27 nm.

IV. CONCLUSIONS

ZnO thin films were deposited on *R*-plane sapphire substrate by rf magnetron sputtering. The structural change from polycrystalline to (110) epitaxial was observed by varying the substrate temperature, chamber pressure, and rf power. From the RHEED and AFM, smooth and high quality ZnO thin films could be achieved.

ACKNOWLEDGMENTS

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