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Orientation Control of ZnO Thin Film Prepared by CVD

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Abstract. The orientations of ZnO films parallel and perpendicular to the surface of the substrate were investigated as functions of the deposition temperature and substrate material. The degree of orientation increased with increasing deposition temperature and became perfectly oriented at a characteristic temperature. At a deposition temperature of 620°C, polycrystalline films were obtained on polycrystalline Al_2O_3; substrates. (001) oriented films were obtained on fused silica and (100) rutile substrates. Epitaxially grown (110) and (001) oriented films were obtained on various kinds of single crystal substrates. The difference between the (110) and (001) orientations was explained by the lattice mismatch between the films and the substrates. Epitaxial growth of films exhibiting two directions was observed when the two equivalent directions of lattice mismatch existed. These results show the possible formation of various types of the crystallographic relationships between the grains in the film.

Keywords: zinc oxide, film formation, crystal arrangement

1. Introduction

In sintered ceramics, electrical properties largely determined by the grain boundaries of semiconductive materials are well known. BL(Boundary Layer) capacitors of $SrTiO_3$ and $BaTiO_3$, varistors of ZnO and $SrTiO_3$, and PTCR of $BaTiO_3$ are examples [1]. However, the properties of the grain boundaries are reported to be nonuniform [2]. This originates mainly from inhomogenities in composition, crystal orientation and so on. On the other hand, in films, columnar grains growing normal to the surface of the substrate are often observed. These grains and grain boundaries are well aligned and their composition and crystal structure may be expected to be more uniform.

In a previous study, we showed that nonlinear *I-V* characteristics were observed following in the diffusion of Bi or the partial oxidation of the semiconductive $BaTiO_3$ film [3]. These properties were considered to be generated by the modification of the grain boundaries in the film. This result shows the possibility of generating the same features as in sintered bodies by the modification of grain boundaries in semiconductive films. This $BaTiO_3$ film was epitaxially grown on a (100)MgO substrate. However, the combination of the kinds of films and substrates were limited in the case of epitaxial growth.

ZnO film is known to be easily grown on the *c*-axis-orientation when grown on amorphous substrates [4–15]. However, the orientation behavior on other kinds of substrates has been little reported except for amorphous [4–15] and Al_2O_3 single crystal [16–21] substrates. Therefore, the method to control the orientation of the film has not been established. In the present study, we investigated the orientation of CVD-ZnO films by changing the deposition conditions and the kinds of the substrate. On the basis of the results, we discuss the method of control of the orientation of the ZnO film.

2. Experimental

ZnO films were prepared by MOCVD. Figure 1 shows a schematic diagram of the CVD apparatus similar to already described previously [13]. A Cold-wall

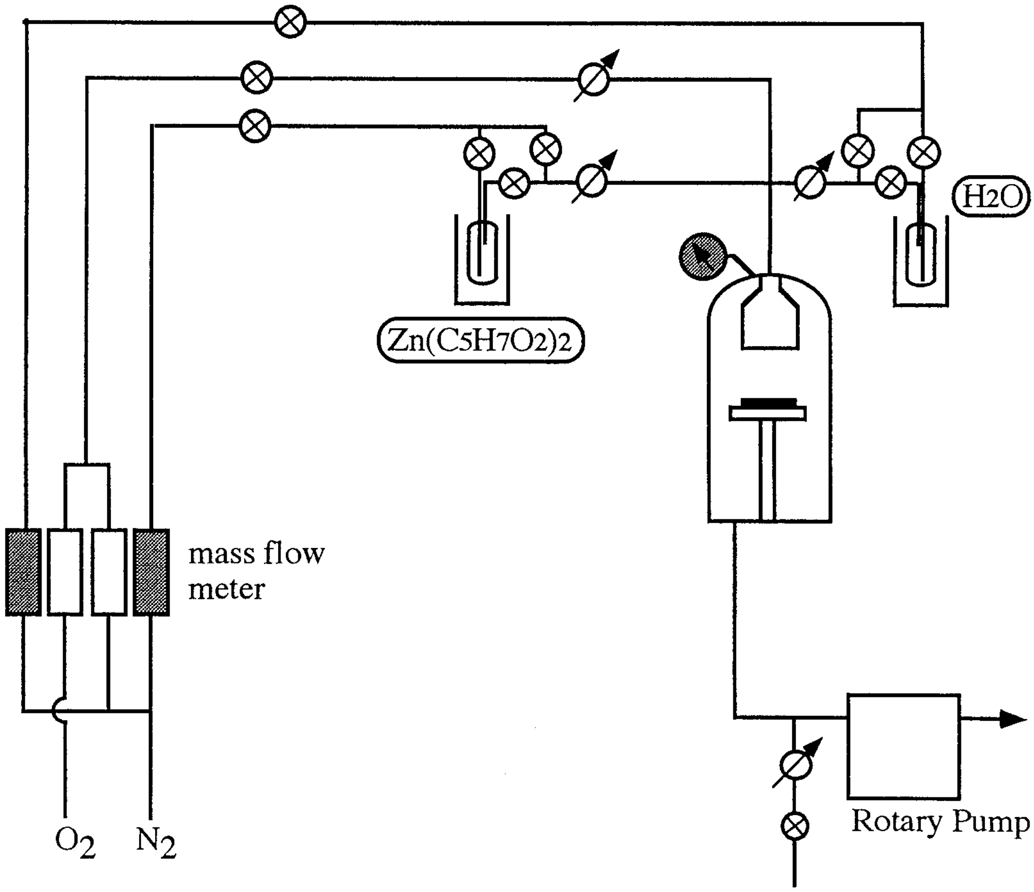

Fig. 1. Schematic diagram of CVD apparatus for the preparation of ZnO films.

vertical reactor was used for the film preparation. $Zn(C_5H_7O_2)_2$, H_2O and O_2 were used as starting materials. The detailed deposition conditions are summarized in Table 1. Single crystals of $SrTiO_3$[(100) and (110) planes], MgO[(100) plane], rutile(TiO_2)[(001)plane] and Al_2O_3[(102)plane and (001)plane] were used as substrates. Polycrystalline Al_2O_3 and amorphous fused silica were also used as substrates. The electrical properties of ZnO films on fused silica, (102)Al_2O_3 and (100)MgO substrates were already reported in a previous paper [13].

XRD was used for the observation of the orientation of the film perpendicular to the surface of the substrate. Rocking curves were measured for

Table 1. Detailed conditions of ZnO film deposition

Source Materials:	$Zn(C_5H_7O_2)_2$, H_2O, O_2	
Reaction Pressure:	1.3 kPa	
Deposition Temperature:	300–650°C	
Reaction Time:	120 min	
Film Thickness:	300–700 nm	
Substrate:	Polycrystal Al_2O_3,	
	Single crystal	Rutile(TiO_2) [(001) Plane],
		$SrTiO_3$ [(100) and (110) Planes]
		MgO [(100) Plane]
		Al_2O_3 [(102) and (001) Planes]
	Amorphous	Fused silica

determination of the degree of orientation of the film. An *X*-ray pole figure apparatus was used for the measurement of the crystal texture parallel to the surface of the substrate and crystal orientation was also observed by TEM.

3. Results and Discussion

3.1. Deposition Conditions for the Preparation of Oriented Films

The degree of orientation of ZnO films deposited on various kinds of substrates was mostly affected by the deposition temperature. Figure 2 shows the degree of (001) orientation of ZnO films deposited on fused silica and (100)MgO substrates, and (110) orientation on (102)Al_2O_3 substrates as a function of deposition temperature. The degrees of (001) and (110) orientations were defined as the summation of the peak intensities of *(00l)* reflections against those of *(hkl)*, $[\Sigma I(00l)]/[\Sigma I(hkl)]$, and the summation of the peak intensities of *(hh0)* reflections against those of *(hkl)*, $[\Sigma I(hh0)]/[\Sigma I(hkl)]$, respectively.

For the films deposited on fused silica and (100)MgO substrates, polycrystalline films formed below 500°C and the degree of (001) orientation of these films was almost the same as that of ZnO powder as shown in Fig. 2. The degree of (001) orientation of ZnO films increased suddenly with increasing deposition temperature at a characteristic temperature. These temperatures were 550° and 620°C for the films deposited on fused silica and (100)MgO substrates, respectively.

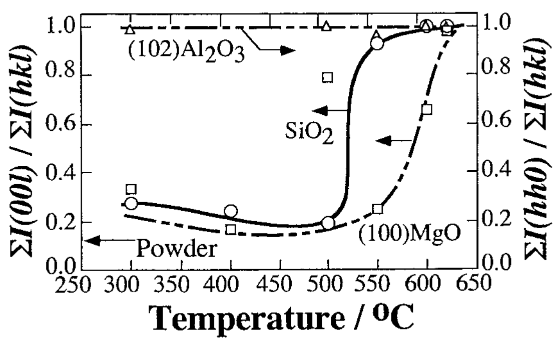

Fig. 2. Degree of (001) orientation of ZnO films deposited on fused silica and (100)MgO substrates and (110) orientation on (102)Al_2O_3 substrate as a function of deposition temperature. The degrees of (001) and (110) orientations were defined as the summation of the peak intensities of *(00l)* reflections against that of *(hkl)* ones, $[\Sigma I(00l)]/[\Sigma I(hkl)]$, and the summation of the peak intensities of *(hh0)* reflections against that of *(hkl)* ones, $[\Sigma I(hh0)]/[\Sigma I(hkl)]$, respectively.

The deposition of (001) oriented film on amorphous substrates has been reported by many authors [4–15]. For the CVD-ZnO films prepared from the $Zn(C_5H_7O_2)_2$-H_2O-O_2 system, perfectly *c*-axis oriented films were reported to be obtained above 550°C [5–11]. This temperature was almost the same as the present study. On the other hand, when the film was prepared from $Zn(CH_3)_2$-O_2 or $Zn(C_2H_5)_2$-O_2, *c*-axis oriented films were deposited even at 300°C [12]. The higher temperature of the deposition of *c*-axis oriented films from $Zn(C_5H_7O_2)_2$-O_2 is related to the high decomposition temperature of $Zn(C_5H_7O_2)_2$ compared with those of $Zn(CH_3)_2$ and $Zn(C_2H_5)_2$.

ZnO films deposited on (102)Al_2O_3 substrates showed only (hh0) reflections besides those from the substrate, and other reflections of the ZnO phase were not detected on XRD patterns for the film deposited at 300°C. This result was the same regardless of the deposition temperature from 300° to 620°C. Figure 3 shows the (100) pole figures of ZnO films deposited on (102)Al_2O_3 substrates at 300° and 650°C. The two are nearly alike. Only two high concentration poles were observed at a radius corresponding to $\Psi = 30°$ and 180° along Φ. This shows that both ZnO films deposited at 300° and 650°C grew epitaxially on (102)Al_2O_3 substrates. Sricant et al. [17] reported the deposition temperature dependency of the orientation of epitaxially grown ZnO films on (102)Al_2O_3 substrates prepared by pulse laser deposition; (001) orientation below 550°C changed to (102) above 650°C when the deposition temperature was increased. This result was different from the present study.

Figure 4 shows the full width of half maximum intensity of the rocking curve of (110) reflection of ZnO films deposited on a (102)Al_2O_3 substrate as a function of the deposition temperature. It decreased continuously with increasing deposition temperature. This result shows that the degree of (110) orientation increase with increasing deposition temperature even though all films grew epitaxially on (102)Al_2O_3 at all deposition temperature. A higher degree of (110) orientation was obtained at higher deposition temperatures within the limits of the present study.

Given that the highly oriented ZnO films were deposited at 620°C, it was of interest to investigate the

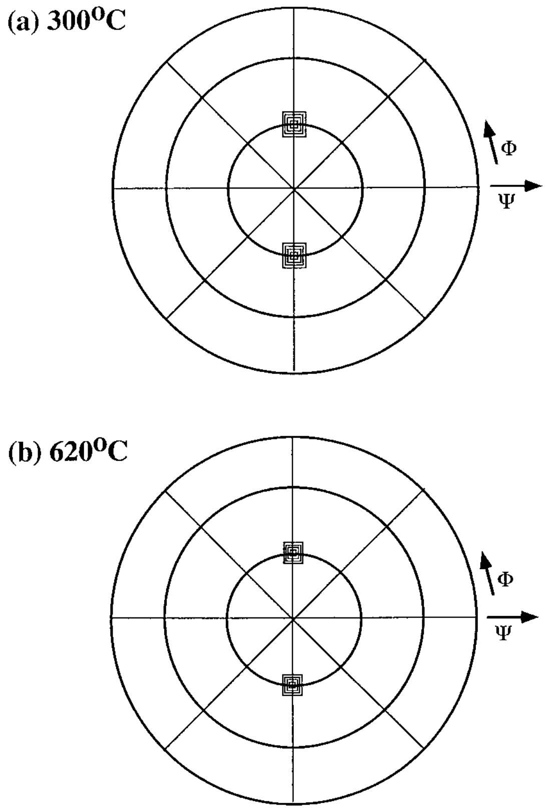

Fig. 3. (100) pole figures of ZnO films on (102)Al_2O_3 substrates at (a) 300°C and (b) 620°C.

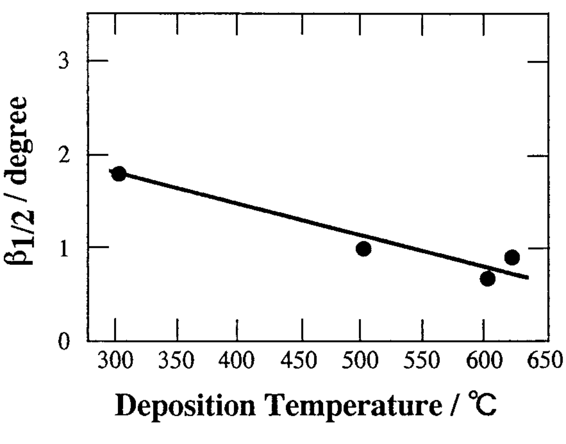

Fig. 4. Full width of half maximum intensity of the rocking curve of (110) reflection of ZnO film on (102)Al_2O_3 substrate as a function of the deposition temperature.

crystal texture of the films deposited at this temperature.

3.2. Orientation of ZnO Films on Various Types of Substrates

ZnO films were deposited on various types of substrates at 620°C. Table 2 summarizes the result of the analysis of the orientation of ZnO films by XRD and X-ray pole figures. We can divide the orientation of ZnO films into three categories. First is the polycrystalline film deposited on a polycrystalline Al_2O_3 substrate. Second is the one-axis oriented films. These films had (001) orientation perpendicular to the surface of the substrate, but not oriented along the surface of the substrate. Third is the three-axis oriented, epitaxially grown, film.

3.2.1. Nonoriented film. On polycrystalline Al_2O_3 substrates, nonoriented films were deposited. As shown in the section 3.2.3, epitaxially grown films were deposited on Al_2O_3 single crystal substrates. Moreover, M. Kasuga et al. [16] reported the epitaxial growth of ZnO films on various kinds of Al_2O_3 single crystal planes. Therefore, polycrystalline films deposited on polycrystalline Al_2O_3 were considered to be the aggregates of the three-dimensionally oriented ZnO film on each single crystal grain of the polycrystal substrate.

3.2.2. c-axis oriented films. On fused silica and (110) rutile TiO_2 substrates, (001) orientation was observed on XRD patterns. From (102) pole figure measurements, the strong ring was observed at a radius corresponding to $\Psi = 30°$. This result shows that there was no special orientation parallel to the surface of the substrate. *c*-axis oriented films were reported to be deposited on amorphous substrates and the present result was in good agreement with the previous reports [4–15].

The result of the TEM observation of ZnO films deposited on fused silica substrates is shown in Fig. 5. The randomly oriented film was ascertained to be deposited from the selected area diffraction(SAD) of the plane view shown in Fig. 5(a). This result corresponds to that of the *X*-ray pole figure. Moreover, the film was observed to consist of grains of about 100 nm in diameter from the bright and dark field images shown in Fig. 5(b). On the other hand, from the cross section of the same film, the grains

Table 2. Result of the analysis of the orientation of ZnO films by XRD and X-ray pole figure

No Orientation

Polycrystalline Al_2O_3

c-axis Orientation (Perpendicular)

SiO_2 , (001)Rutile(TiO_2)

Three Directional Orientation (Epitaxial)

Perpendicular	Parallel	
	One Kind	Two Kind
(001)	(001)Al_2O_3 (110)$SrTiO_3$	(100)MgO
(110)	(102)Al_2O_3	(100)$SrTiO_3$

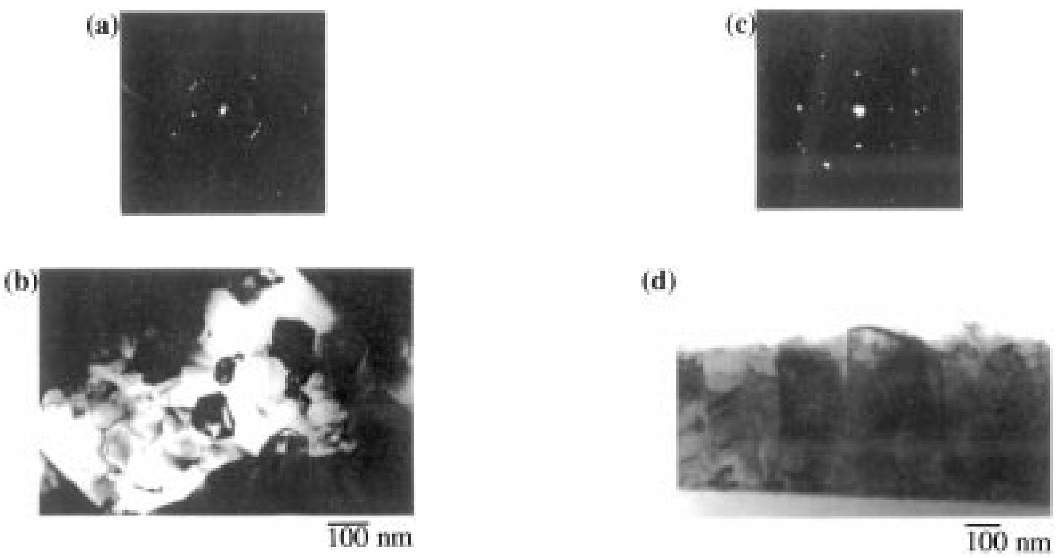

Fig. 5. Results of TEM observation of ZnO films deposited on fused silica substrate. (a) Selected area diffraction (SAD) of the plane view of the film. (b) Bright field image of the plane view of the film. (c) Selected area diffraction (SAD) of the cross section of the film. (d) Bright field image of the cross section of the film.

grown normal to the surface of the substrate were observed as shown in Fig. 5(d) and their (001) orientation was ascertained from the SAD shown in Fig. 5(c). Moreover, the angle of the neighboring grains was found to be within 10% from the surface of the substrate.

c-axis oriented films were also deposited on (110)rutile TiO_2 substrate and no special texture was observed parallel to the surface of the substrate. Based on the degree of lattice mismatch between the film and the substrate, this film was expected to grow epitaxially. However, epitaxially grown films were not obtained as shown in Table 2.

3.2.3. Three dimensionally oriented films. Two types of orientations perpendicular to the plane of each substrate were observed for epitaxially grown films as shown in Table 2. (001) oriented films were deposited on (001)Al_2O_3, (110)$SrTiO_3$ and (100) MgO substrates. On the other hand, (110) oriented films were deposited on (102)Al_2O_3 and (100)$SrTiO_3$ substrates. The difference in the orientation perpendicular to the surface of the substrate was explained by the lattice mismatch between the film and the substrate. Figure 6 shows the lattice mismatch between a (110) plane of ZnO film and the surface of the single crystal substrate versus that between a (001) plane of ZnO and that of the corresponding single crystal substrates when (110) or (001) oriented ZnO films are epitaxially grown on each substrate. Solid line shows that the lattice mismatches of these two planes are the same. When ZnO films were deposited on (100)$SrTiO_3$ and (102)Al_2O_3 substrates, the lattice mismatch with the (110) plane of ZnO was smaller than that with the (001) one. Therefore, the kinetic energy of growth of the (110) oriented film was considered to be lower than that of the (001) orientated one.

On the contrary, the lattice mismatch of the (110) plane was smaller than that of the (001) one when ZnO films deposited on (100)MgO and (001)Al_2O_3 substrates. Therefore, the surface energy of the growth of the (001) oriented film was lower than that of the (110) oriented film. As a result, the orientation perpendicular to the surface of the substrate was mainly determined by the lattice mismatch along the parallel planes of ZnO and the substrate. This result shows that the kinetic energy difference between (110) and (100) planes of ZnO is not large.

In the case of the film deposited on (110)$SrTiO_3$ substrates, the lattice mismatches of the (110) and (001) planes were almost the same and the (001) oriented films were deposited as shown in Fig. 6. This result is considered to be related to the fact that ZnO film tends to be oriented in the (001) direction even on amorphous substrates. As a result, the plane having the lowest surface energy, the closed-packing plane, was tended to be oriented when the lattice mismatches of (100) and (110) planes of ZnO and the substrate were the same.

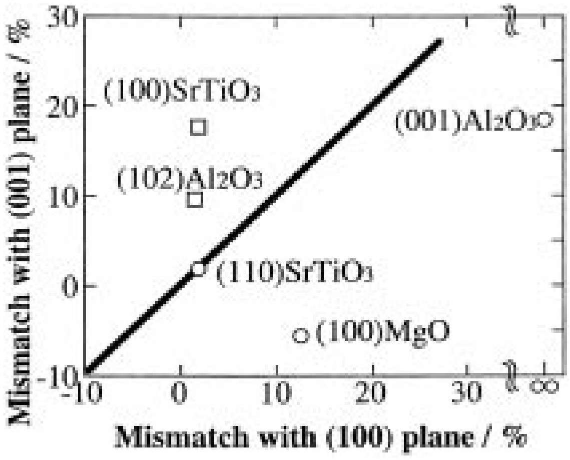

Fig. 6. Lattice mismatch between (110) plane of ZnO and the surface of the single crystal substrate versus that between (001) plane of ZnO and the surface of the single crystal. Solid line shows that the lattice mismatch of these two planes are the same.

As shown in Table 2, two kinds of epitaxial relations were observed on (100)MgO and (110) $SrTiO_3$ substrates. Figure 7 shows the atomic arrangements of (001) oriented epitaxially grown ZnO film on (100)MgO substrates and (110) oriented epitaxially grown ZnO films on (100)$SrTiO_3$ substrates. In the case of the (100)MgO substrate, two equivalent directions with 30 degree tilt to each other were observed as shown in Fig. 7(a). On the other hand, in the case of the (100)$SrTiO_3$ substrate, two equivalent directions with 90 degree tilt to each other were observed as shown in Fig. 7(b). As a result, when two equivalent directions of the lattice mismatch existed as shown in Fig. 7, the epitaxial growth arrangements with two directions were observed. Figure 8 shows the atomic arrangements of ZnO films and the substrates in the case of the films deposited on (001)Al_2O_3, (110)$SrTiO_3$ and (102)Al_2O_3 substrates. In these cases, only one equivalent direction was

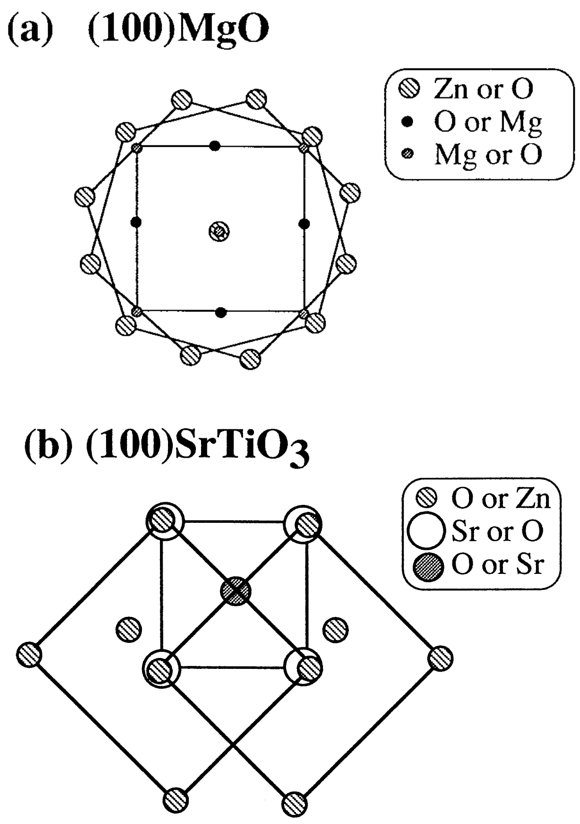

Fig. 7. Atomic arrangements of (a) (001) oriented epitaxially grown ZnO film on (100)MgO substrate and (b) (110) oriented epitaxially grown ZnO film on (100)$SrTiO_3$ substrate.

observed as shown in Fig. 8. Therefore, only one epitaxial growth arrangement was observed.

From the above results, films with various kinds of orientation not only perpendicular but parallel to the surface of the substrate were observed by selection of the types of substrate. This means that various kinds of grains with uniform composition and crystal orientation can be obtained by changing the types of substrates.

4. Conclusion

The orientations of ZnO films parallel and perpendicular to the surface of the substrate were investigated as functions of the deposition temperature and kinds of substrate materials. The degree of the orientation increased with increasing deposition temperature and reached to perfectly oriented films at elevated temperatures. Polycrystalline films were obtained on polycrystalline Al_2O_3 substrates and *c*-axis oriented films were obtained on fused silica and (100) rutile substrates. Epitaxially grown (110) and (001) oriented films were obtained on various kinds of single crystal substrates. The explain the differences between the

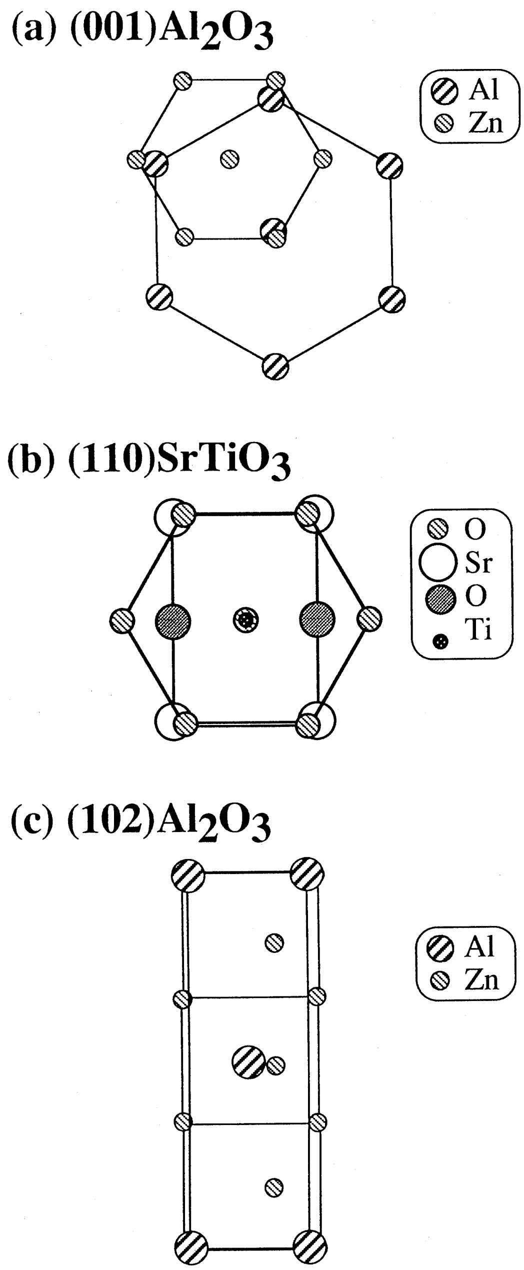

Fig. 8. Atomic arrangements of (a) (001) oriented epitaxially grown ZnO film on (001)Al_2O_3 substrate and (b) (001) oriented epitaxially grown film on (110)$SrTiO_3$ substrate, and (c) (110) oriented epitaxially grown film on (102)Al_2O_3 substrate.

(110) and (001) orientations perpendicular to the surface of the substrate, lattice mismatch between the film and the substrate was identified as a controlling feature. Epitaxial growth arrangements with two directions were observed when the two equivalent directions of the lattice mismatch existed. These results show the possibility of formation of the various kinds of crystal relations between the grains in the film.

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