The Korean Journal of Ceramics, 1 [3] 143-146 (1995)

Transmission Electron Microscopy Observation of (20$\bar{2}$) and (211) Twins in Monoclinic ZrO_2 Thin Film

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(Received August 10, 1995)

Twins along (20$\bar{2}$) and (211) planes are observed in monoclinic ZrO_2 thin film, which is deposited on Si substrate by MOCVD at 350°C and annealed at 1150°C for 10 hours in air. These types of twin have not been reported in monoclinic ZrO_2. The twins seem to be originated from the two dimensional tensile stresses applied to the ZrO_2 thin film due to the different thermal expansions of ZrO_2 thin film and Si substrate.

Key words : Twin, ZrO_2 thin film, Annealing, Stress

I. Introduction

ZrO_2 has three crystal structures of polymorphism: cubic above 2370°C, tetragonal between 2370°C and about 1000°C, monoclinic below about 1000°C. The transition from tetragonal phase to monoclinic phase is known to be a martensitic transition and it has been extensively studied by Rühle and Heuer.[1] The grain growth of monoclinic ZrO_2 polycrystal usually induces a twinning in the grain along (100) plane, whereas the martensitic transformation induces a {110} twin.[2,3] The twinning along the (100) plane of monoclinic ZrO_2 is known to increase the volume free energy of the crystal by a very small amount[1] because the structure of the (100) twin plane is very similar to (100) plane of the normal crystal. Therefore, single crystalline or polycrystalline ZrO_2 is usually twinned along (100) and {110} planes at room temperature. However, Bischoff and R hle[4] reported that (100), (001) and {110}, {011} twins occur in monoclinic ZrO_2 particles which are confined in mullite matrix, and explained that the twin variants are formed by stresses due to the different thermal expansions of monoclinic ZrO_2 particles and mullite matrix. In this study, another twin modes - twinning along the (20$\bar{2}$) and (211) planes - are found in a ZrO_2 thin film which is deposited on a Si substrate, and the possible formation mechanism of those twins is presented.

II. Experimental Procedure

A monoclinic ZrO_2 thin film is deposited on a silicon (100) substrate by a metal-organic chemical vapor deposition (MOCVD) at a substrate temperature of 350°C using zirconium-trifluoroacetylacetonate and O_2 as the source materials. The detailed description of the deposition process are reported elsewhere.[5] The ZrO_2 thin film is annealed in air at 1050°C and 1150°C for 10 hours to grow the as-deposited very fine grains into larger ones. The films are prepared to cross-sectional and plan-view transmission electron microscopy (TEM) specimens by mechanical grinding and dimpling followed by Ar^+ ion milling at 6 kV. Two TEM's are operated to obtain the images and the selected area diffraction patterns (SADP); one at 200 kV (JEOL, JEM-200CX) for the conventional bright field images, and the other at 400 kV (JEOL, JEM-4000FX) for the SADP's and high resolution images.

III. Results

Figures 1(a) and (b) show cross-sectional TEM micrographs of the as-deposited ZrO_2 thin film and the film annealed at 1050°C for 10 hours in air, respectively. The as-deposited film has very fine grains of a few nanometers in diameter. Grain growth and densification occur during the heat-treatment and the average grain size is about 50 nm as shown in Fig. 1(b). However, the grain indicated with a white arrow in the inset dark field image of Fig. 1(b) shows fine fringes which is supposed to take place by the usual growth twinning of monoclinic ZrO_2. However, the grain is too small to obtain a clear SADP and identify the fringes.

ZrO_2 thin film annealed at 1150°C for 10 hours in air shows large enough grains (about 300 nm in diameter) to obtain the SADP's, as shown in Fig. 2 and Fig. 3. Fig. 2 is a cross-sectional TEM micrograph with a low magnification, which also shows that the interfacial silicon dioxide layer is formed by the oxidation of Si substrate during annealing. Fig. 3(a) and (b) are the bright field and dark field images, obtained from a plan-view sample, of a large grain which is nearly same in size with the thickness (~300 nm) of the ZrO_2 film. Fig. 4 is the SADP which has [1$\bar{3}$1] zone axis obtained from the grain shown in Fig. 3.

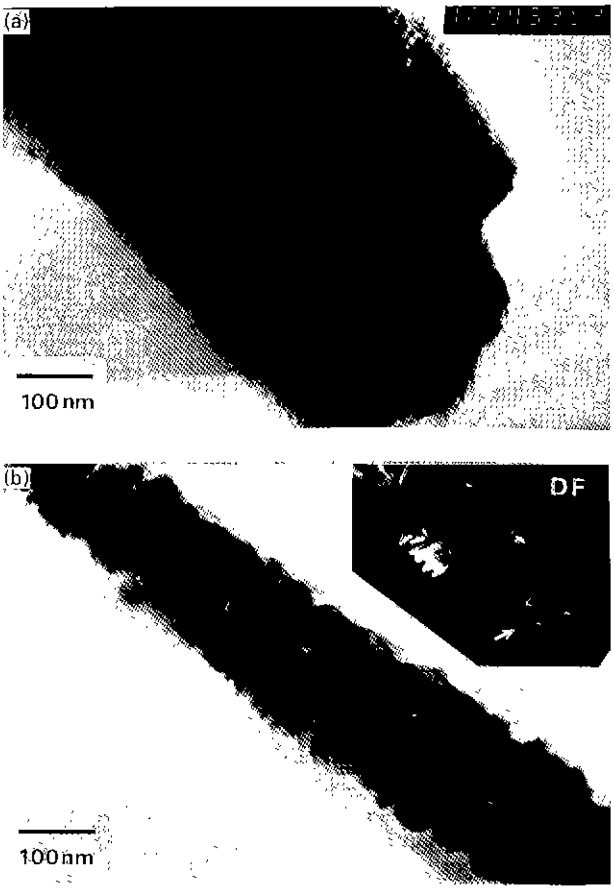

Fig. 1. Cross-sectional TEM micrographs of (a) as-grown ZrO_2 thin film and (b) ZrO_2 film annealed at 1050°C for 10 hours in air with an inset dark field image showing fine fringes.

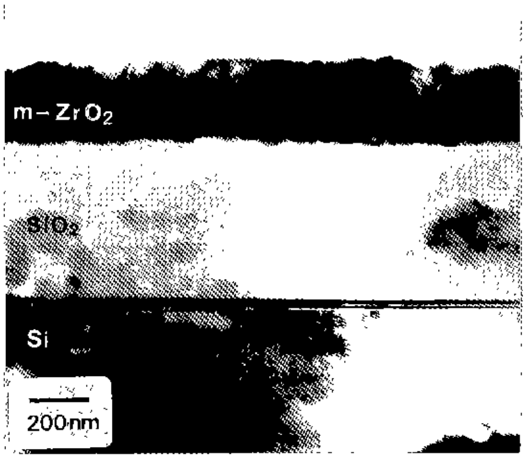

Fig. 2. Cross-sectional TEM micrograph of ZrO_2 thin film annealed at 1150°C for 10 hours in air.

Figure 3(a) shows that the grain is composed of stacked lamellae developed in two directions. Fig. 4 shows that these lamellae are twins, where the twin planes are (20$\bar{2}$) and (211) planes. The strong diffraction spots due to the (20$\bar{2}$) twinning and weak spots due to the (211) twinning imply that volume fraction of the (20$\bar{2}$) twinned crystal is larger than that of the (211) twinned crystal. Fig. 3(b) is a dark field image obtained from the 211_{T1} spot in Fig. 4, which clearly shows that the relatively thick lamellae of Fig. 3(a) is the (20$\bar{2}$) twinned crystal. The (20$\bar{2}$) twin is termed T1 twin. The other very thin twin lamellae of Fig. 3(a) are the twin lamellae along the (211) plane and are termed T2 twin. The iden-

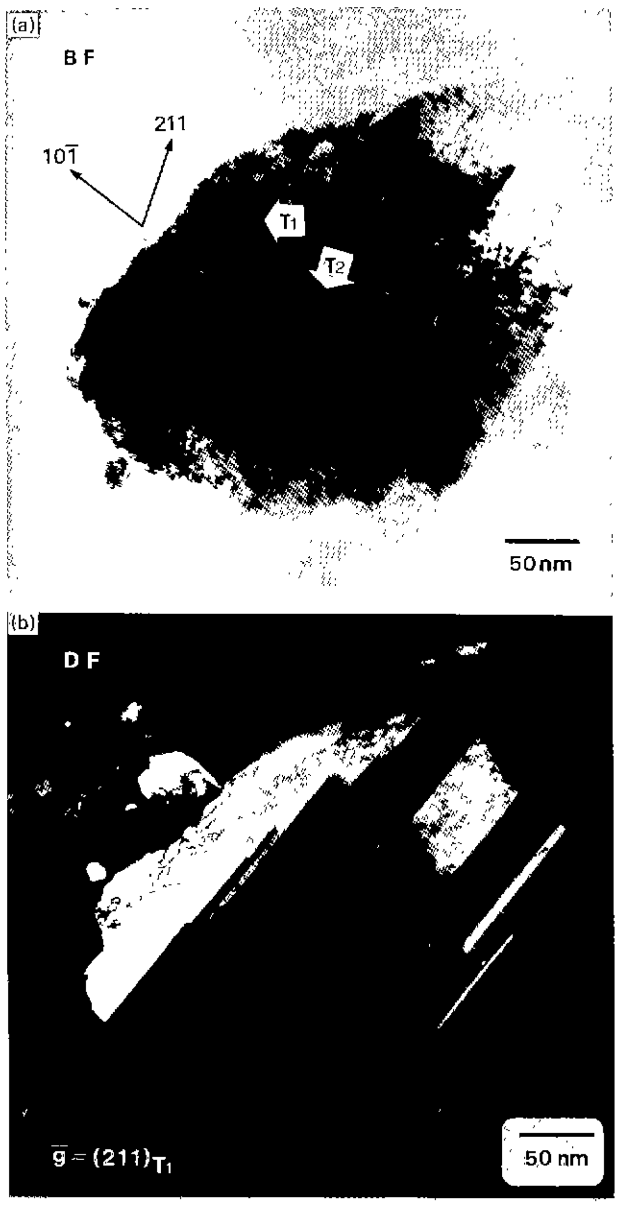

Fig. 3.(a) Bright field image of a ZrO_2 grain which contains (20$\bar{2}$) and (211) twin lamellae and (b) dark field image obtained from the 211_{T1} diffraction spot.

tification of the two twins are further confirmed by the rotation calibration of the electron microscope.

Figure 5 is a high resolution TEM image obtained from the T2 region of Fig. 3(a). It confirms that T2 is a very thin twin lamellae with thickness about 5 nm along the (211) plane, and also shows that twin dislocations exist at the twin boundary.

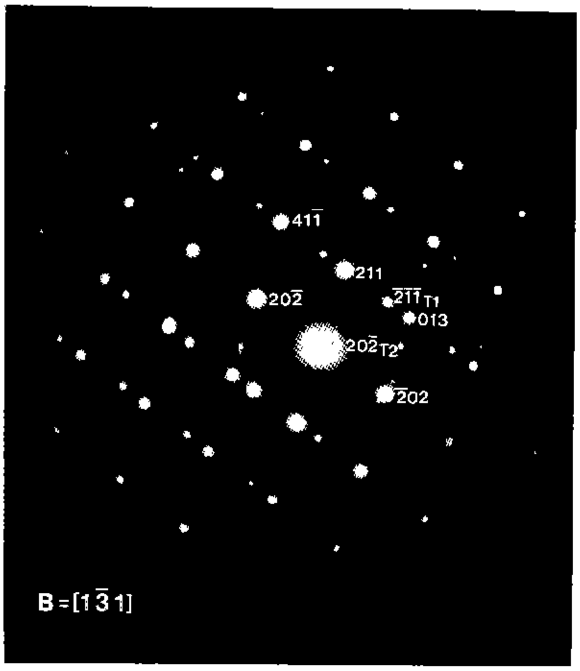

Fig. 4. Selected area diffraction pattern of the grain in Fig. 3.

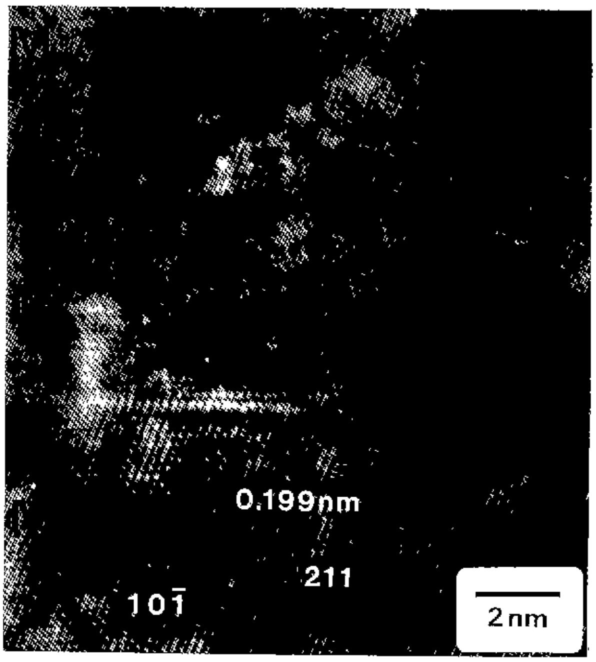

Fig. 5. High-resolution TEM micrograph of a 5 nm thick (211) twin.

IV. Discussions

As discussed in the introduction, well known twins of monoclinic ZrO_2 are the twin along (100) plane, which is the growth twin, and along {110}, which are the transformation twins. However, these two types of twins are not observed in this experiment. The deposition and heat-treatment process of the ZrO_2 thin film could have produced the growth twin, but the very fine grain size of the as-deposited film - about a few nanometers in diameter - probably surpresses formation of the growth twin.

Bischoff and Rühle[4] showed that (001) and {011} twins are developed in a monoclinic ZrO_2 particle confined in mullite matrix in addition to the ordinary (100) and {110} twins because of the thermal stress which is induced by the different thermal expansions of ZrO_2 and mullite. The T1 and T2 twins, observed in this experiment, might also be produced by thermal stress, which is introduced by the two dimensional confinement of ZrO_2 film to the substrate. The thermal expansion coefficients of tetragonal ZrO_2, monoclinic ZrO_2, fused silica, and Si are listed in Table 1. According to the data, the ZrO_2 film should be under two dimensional tensile stress parallel to the substrate surface at room temperature. The tensile stress mainly originates from the difference between thermal expansions of ZrO_2 and Si. The SiO_2 layer formed at the interface between ZrO_2 film and Si substrate, shown in Fig. 2, does not seem to reduce the thermal stress because of its small thickness compared to that of the Si substrate. It is generally known that the formation of a twin parallel to the stressed direction reduces the elastic energy of the stressed crystal.[6] The grains in the ZrO_2 film have random orientational relationship with the substrate. If some of the randomly oriented ZrO_2 grains have the (100), (001), {110} or {011} plane coinciding with the two-dimensionally stressed direction, they would have the usual (100), (001), {110} or {011} twin. With the same opportunity, some grains with $(20\bar{2})$ or (211) plane parallel to the two dimensional thermal stress direction may have T1 and T2 twins since (100), (001), {110} or {011} plane of these grains does not coincide with the stressed direction. Unfortunately, we

Table 1. Thermal Expansion Coefficients of ZrO_2, SiO_2 and Si.

speies	$\alpha(10^{-6}K^{-1})$
mono ZrO_2 (100)	10.31[a]
mono ZrO_2 (010)	1.35[a]
mono ZrO_2 (001)	14.68[a]
tetra ZrO_2 (100)	11.60[a]
tetra ZrO_2 (001)	16.80[a]
fused silica	0.5[b]
Si	2.3~3.5[c]

[a]; data obtained from Bischoff and Rühle,[4] [b]; datum obtained from Kingery et al.,[7], [c]; datum obtained from Brown.[8]

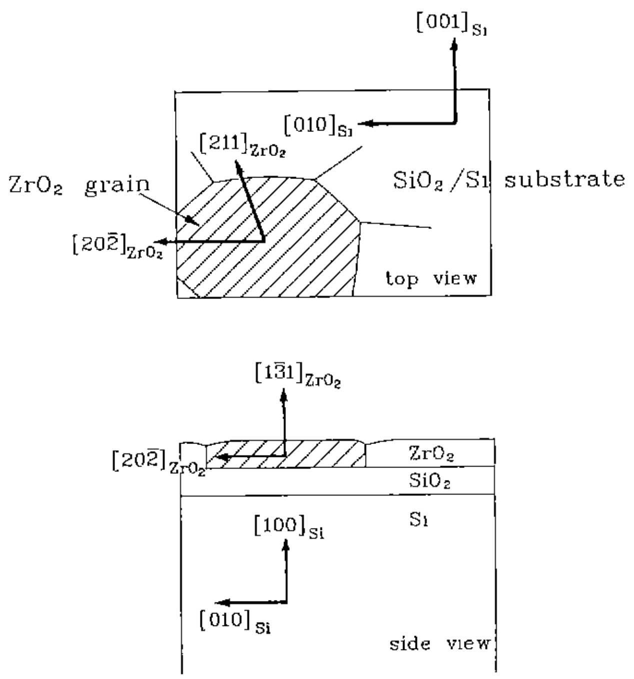

Fig. 6. Schematic diagram of the ZrO_2 film on Si substrate, which shows the orientational relationship between the twinned ZrO_2 grain and Si substrate.

cannot exactly identify the orientational relationship between the twinned grain of ZrO_2 thin film in Fig. 3 and substrate because the substrate is removed by the specimen preparation. However, the [1$\bar{3}$1] direction of the T1 and T2 twinned ZrO_2 grain seemed to be almost normal to the substrate surface because the SADP in Fig. 4 was obtained by a very small tilt of the specimen from the horizontal position. Therefore, the geometrical relationship between the twinned ZrO_2 grain and substrate can be drawn as Fig. 6. [20$\bar{2}$] of the ZrO_2 grain is assumed to be parallel to $[010]_{Si}$, one of the principal direction of the thermal stresses, since T1 twin has larger volume fraction than that of the T2 twin. However, $[211]_{ZrO_2}$ is rotated by 19°, because of the crystal structure of monoclinic ZrO_2, from $[001]_{Si}$, another principal stress direction, so that the thinner T2 twin is resulted. The twin interface energy is dependant on the interplanar spacing of the twin plane as well as other parameters such as composition of the plane and bonding angle. It is interesting that the interplanar spacings of (20$\bar{2}$) plane and (211) plane are equal (0.199 nm), and we believe that this is one of the reasons why the (20$\bar{2}$) twin and (211) twin are coexist in the ZrO_2 grain of Fig. 3. The twin interface energy of T1 and T2 must be larger than that of the usual (100), (001), {110} or {011} twins since the interplanar spacings of (20$\bar{2}$) and (211) planes are smaller than those of the (100), (001), {110} or {011} planes. Therefore, the T1 and T2 twins seem to be formed only in a particular situation where the two dimensional stresses are applied to the along (20$\bar{2}$) or (211) planes.

V. Conclusion

(20$\bar{2}$) and (211) twins in monoclinic ZrO_2, which have not been reported in the literature yet, are observed by TEM in a grain of ZrO_2 thin film which is deposited on Si substrate. The (20$\bar{2}$) and (211) twin lamellae seem to be formed when [1$\bar{3}$1] direction of the ZrO_2 grain is normal to the substrate surface to reduce the two dimensional thermal stress which is a consequence of the difference between the thermal expansion coefficients of ZrO_2 film and Si substrate. The usually known (100), (001), {110} and {011} twins are not observed in this twinned ZrO_2 grain.

Acknowledgement

The authors acknowledge the financial support of this work by the Korea Science and Engineering Foundation and Electronics and Telecommucations Research Institute.

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