The oriented growth of zirconia thin films on NaCl (0 0 1) surface

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Abstract

Nanosized cubic and tetragonal ZrO\textsubscript{2} were formed as thin nanocrystalline film on NaCl (1 0 0) plane by radio frequency ion beam sputtering. The microstructure and the epitaxy relationship with the NaCl (1 0 0) plane were studied by a high-resolution transmission electron microscope. The epitaxy orientation was found to be [0 0 1]\textsubscript{Z}||[0 0 1]\textsubscript{N}, [1 0 0]\textsubscript{Z}||[1 0 0]\textsubscript{N}, (group A), [0 1 1]\textsubscript{Z}||[0 0 1]\textsubscript{N}, [1 0 0]\textsubscript{Z}||[1 0 0]\textsubscript{N}, (group B\textsubscript{1}) and [0 1 1]\textsubscript{Z}||[0 1 0]\textsubscript{N}, [1 0 0]\textsubscript{Z}||[0 1 0]\textsubscript{N} (group B\textsubscript{2}) between zirconia (Z) and NaCl (N). Groups B\textsubscript{1} and B\textsubscript{2} are the dominant type. The possible causes for the epitaxy relationship are discussed. Crystallites within the same group can merge by rotation and coalesce into a single crystal, whereas crystallites in different groups can form high-angle grain boundaries.

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1. Introduction

Metal or oxide clusters on oxide or halide surface have been the subjects of many researches. Thin metal clusters have many practical applications due to their special catalytic, magnetic and electric properties and attracted a large number of studies. Most widely used substrates are the single-crystal NaCl (0 0 1) and MgO (0 0 1) cleavage surfaces. Many metals such as Au [1,2], Ti [3,4], Rh [5], Pd [6,7], and others [8] have been applied, to list just a few of the reports. Theoretical investigations of the nucleation and growth process have also been performed [9,10]. Interesting epitaxy relations between the metal clusters and the ionic substrate have been established in the above researches.

Epitaxial oxide thin films, such as ZrO\textsubscript{2} [11], ferrite [12], VO [13], NiO [14] have been applied to MgO (0 0 1) cleavage surface by various methods including molecule beam epitaxy, laser ablation, sol–gel, or evaporation for various purposes. However, there are relatively few reports of preparing oxide films or clusters on NaCl surface. ZnO [15] has been applied to NaCl (0 0 1) cleavage surface to control its texture to be c-axis oriented. MnO\textsubscript{2} [16] was applied to various halide single crystal (0 0 1) surfaces to control its desired phases according to the lattice mismatch. ZrO\textsubscript{2} was evaporated onto NaCl (0 0 1) surface and stripped for heat treatment and transmission electron microscopic (TEM) examination by El-Shanshoury et al. [17]. In their deposition condition uniform diffraction ring was observed, indicating no epitaxy relationship between the film and the NaCl substrate.

Zirconia is an important catalyzer, hard coating and thermal barrier coating material. Its high-temperature polymorph of tetragonal (t-) structure can be stabilized to room temperature by crystallite size effect alone, as suggested originally by Garvie [18] who showed that the critical size for t- to monoclinic (m-) ZrO\textsubscript{2} transformation is about 30 nm. In this experiment, radio frequency (RF) ion beam sputtering was used to prepare nano-sized ZrO\textsubscript{2} crystallite on NaCl (0 0 1) surface.
relationship, the crystallite size and the phases were determined in detail. The kinetics of crystallite growth by rotation and coalescence were studied by high resolution transmission electron microscope.

2. Experimental procedure

Zirconia films were prepared using a RF ion beam sputtering system with a base pressure of $1 \times 10^{-3}$ Pa. The target was a 3-inch-diameter Zr disk of 99.9% purity. Zr was deposited onto the rectangular NaCl (1 0 0) crystal slabs under a working pressure of $7 \times 10^{-2}$ Pa. The substrate temperature was 400°C, oxygen flow rate was 1, 5, 15 and 20 sccm and the deposition time was 25 min.

After deposition the specimens were immersed in distilled water to dissolve the NaCl substrate so that the prepared ZrO$_2$ films floated on the water surface. The film was caught from under by copper grid covered with carbon-coated collodion film, which is commercially available. The orientation relationship between ZrO$_2$ and NaCl was determined by specimens caught before the NaCl was completely dissolved.

The specimens were examined by transmission electron microscopic (TEM, JEOL 3010, under 200 and 300 kV). Aperture of 50 μm in diameter was used to take selected area electron diffraction (SAED) patterns. TEM images were taken under bright field image (BFI) and dark field image (DFI) modes using a focal-plane aperture of 10 μm in diameter. SAED patterns of cubic (c-) and t-phases of zirconia were indexed according to the distorted c-fluorite cell [19].

3. Results

3.1. SAED pattern

The diffraction pattern in Fig. 1 shows that the thin ZrO$_2$ film carries strong preferred orientation. The pattern, indexed as ring pattern with strong arcs, can be shown to be that of cubic (c-) and/or t-ZrO$_2$, indexed as high-temperature fluorite structure. The preferred orientation

![SAED patterns](image)

Fig. 1. SAED patterns of the films formed on NaCl (1 0 0) plane by ion beam sputtering of Zr target and reacting with oxygen at 400°C for 25 min. The phases identified and the oxygen flow rates are: (a) (c + t)-zirconia, 1 sccm, (b) (c + t)-zirconia, 5 sccm, (c) (c + t)-zirconia, 15 sccm, and (d) (c + t)-zirconia, 20 sccm.
develops more strongly at increased oxygen flow rate as shown in Figs. 1c and d of 15 and 20 sccm oxygen flow rates, respectively. The c- and/or t-ZrO₂ crystallites condensed at 1–20 sccm coalesced into a thin film with negligible pores and a uniform grain size of 10–20 nm (Figs. 2a–d).

Detailed analysis of the diffraction pattern in Fig. 1 is shown in Fig. 3. Fig. 3a is the diffraction pattern of (c+t)-zirconia grains in Z = [001], which is defined as group A, while Fig. 3b is that in Z = [011], defined as group B₁. Group B₂ shown in Fig. 3c is the same as Fig. 3b, except that it has been rotated by 90°. Fig. 3d is the composite diffraction pattern formed by summing up Figs. 3a–c. Fig. 3e is the same diffraction pattern from Fig. 1, and it is clear that Fig. 3d is consistent with the SAED patterns in Fig. 1. In Fig. 3e the diffraction spots from groups A, B₁, and B₂ are labeled.

The SAED pattern of both ZrO₂ thin film and NaCl (1 0 0) taken simultaneously is shown in Fig. 4a, from which the crystallographic relationship between each of the zirconia group and NaCl can be determined. Fig. 4b is the index of the diffraction pattern of NaCl crystal. The epitaxial orientation relationships, as illustrated in Fig. 5, can be specified as [001]Z//[001]N, [100]Z//[1 1 0]N for group A, [0 1 1]Z//[0 0 1]N, [1 0 0]Z//[1 0 0]N for group B₁, and [0 1 1]Z//[0 0 1]N, [1 0 0]Z//[0 1 0]N for group B₂, where Z and N denote zirconia and NaCl of rock salt structure, respectively. Groups B₁ and B₂ are two variants of the same epitaxy orientation relationship with a 90° rotation.

By selecting the specific diffraction spot, the zirconia particles in each group can be separately imaged. Fig. 6a is the DFI of crystallites in zone axis [0 0 1] (group A), which shows the loosely distributed crystallites with grain size 10–15 nm. Fig. 6b is the DFI of crystallites in zone axis [0 1 1] (group B₁ and B₂ together). The crystallites, of grain size 15–20 nm, are much more numerous. This can be expected since the diffract spots of group B₁ and B₂ are much stronger in intensity than those of group A in Fig. 3e.
3.2. High-resolution image

Fig. 7a shows the lattice image of two c- and/or t-ZrO$_2$ nanoparticles with zone axis of [0 0 1] (group A), and [0 1 1] (indexed as group B$_1$), respectively. Fig. 7b is the Fourier transformation of the square region in Fig. 7a, in which the diffraction patterns of both grains are shown. Fig. 7c is the reconstructed image from the diffraction spots in Fig. 7b, in which the angle difference of the two {2 0 0} planes is about 45°, consistent with Fig. 3. Fig. 7c shows that the angle difference between the two {2 0 0} planes is about 90°, and that between the two {1 1 1} planes is 18.5°. All the results above are consistent with Fig. 3. The boundaries between the particles in Figs. 7 and 8 are apparently high-angle grain boundaries.

3.3. Lattice image of the condensates in coalescence

Lattice image in Fig. 9a shows the c- and/or t-ZrO$_2$ nanoparticles in group B of $Z = [0 1 1]$ in the process of coalescence. The (1 1 1) plane of the small particle 1 has a small orientation difference with the large central particle. The particle can be expected to achieve perfect match with a small rotation, so can the particle 3. The particle 2 has already reached perfect match in (1 1 1) plane. The 2-D Fourier transform of Fig. 9b indicated these particles were coalesced toward the same orientation in [0 1 1] zone axis. The reconstructed image of Fig. 9c shows that although
the (1 1 1) plane has reached perfect match in the large particle, the (2 0 0) and (1 1 1) planes have not as can be observed clearly in the figure by viewing the corresponding lattice fringes. Therefore a small misorientation persists along the indicated trace, which is the approximate boundary of the two merged particles. Therefore the indicated trace is the vestige of the two particles coalesced with a small misorientation in (2 0 0) and (1 1 1) plane. Dislocations were left at the indicated interface due to the imperfect attachment. The c- and/or t-ZrO$_2$ nanoparticles in group A of Z = [0 0 1] orientation are shown in Fig. 10. The particle 1 is still in the process of coalescence, and the misaligned (1 0 0) plane and misfit dislocations are clearly visible.

4. Discussion

4.1. Orientation relationship

In this experiment two orientation relationship of [0 0 1]$_Z$ ||[0 0 1]$_N$, [1 0 0]$_Z$ ||[1 1 0]$_N$ (group A) and [0 1 1]$_Z$ ||[0 0 1]$_N$, [1 0 0]$_Z$ ||[1 0 1]$_N$ (group B) were observed. The group B is the dominant group as the intensity of the diffraction spots is much stronger than those of group A. The results show that increasing oxygen flow rate from 1 to 15 sccm facilitates the development of the preferred orientation between zirconia and NaCl (Figs. 1a–c). The microstructure stabilizes with further increase in the oxygen flow rate to 20 sccm as the diffraction pattern shows no observable difference (Figs. 1c and d), and there is no observable change in the ratio of A/B groups distribution as indicated by the intensities of the diffraction spots. No observable difference in the grain size is observed by the different oxygen flow rate, as shown in Fig. 2.
In general, interfacial energy and misfit strain energy are the most important factors in achieving epitaxy growth in specific direction. Since both crystals are essentially ionic, added complexity due to strong Coulomb interaction is expected. Fig. 11 shows the surfaces of c+t ZrO$_2$ (0 0 1) and NaCl (0 0 1), which are in contact in group A. Since c+t ZrO$_2$ (0 0 1) is an unmixed plane, it can be zirconium layer (Fig. 11a) or oxygen layer (Fig. 11b) in contact with NaCl (0 0 1) plane (Fig. 11c). Fig. 11d is a tentative composite figure of the oxygen layer of Figs. 11b and c, also obeying the group A orientation relationship. Similarly, Fig. 11b is rotated 45° and the position marked by x is placed on top of Na$^+$ ion of Fig. 11c. This is the best fit we can manage. In the figure, the anions and cations are more equally spaced while at the four corners of the indicated square O$^2-$ anion and Na$^+$ cation overlap. This interface appears to be of lower energy in terms of Coulomb energy of group A. Certainly some shift in position may happen if Coulomb interaction and strain energy are taken into account, as discussed later in this section.

As for the strain energy effect, for Fig. 11e to make a perfect match at the four corners of the indicated square, the ZrO$_2$ cell needs to be stretched by about 4.3% with respect to the NaCl lattice, calculated by room temperature lattice constant of 5.09 and 5.54 Å for pure NaCl and c-ZrO$_2$, respectively. Since the grain size of c+t ZrO$_2$ is small (10–15 nm), and at the early stage of growth the contact area may be even smaller, the strain energy may be reduced. Due to the proximity of anions and cations in the interface, the Coulomb interaction may be strong enough to overcome the strain energy. Detailed analysis by computer is necessary to obtain the condition of minimum total energy of the strain energy and Coulomb energy.

In the computer calculation, it may be necessary to take into account the amount of charges; +4, −2, +1, −1, for Zr, O, Na and Cl ions, respectively. The coincidence lattices may be different from those in Fig. 11d and e as some horizontal translation and relaxation may be necessary. Also the Coulomb interaction energy among the second neighbors and the second layers, or more, of atoms above and below the interfacial atoms may be necessary. The calculation is beyond the scope of this paper. However, it is clear that for large contact area the strain energy must be too large for the orientation relationship to hold.

Fig. 12 shows the surfaces of c+t ZrO$_2$ (0 1 1) (Fig. 12a) and NaCl (0 0 1) (Fig. 12b), which are in contact in group B relationship. Fig. 12c is a tentative composite figure of Figs. 12a and b obeying group B orientation relationship. The position marked by x in Fig. 12a is placed on top of Cl$^-$ ion of Fig. 12b. Since c+t ZrO$_2$ (0 1 1) is a mixed surface, proper placement of interface anions and cations may considerably reduce the Coulomb interaction energy and Fig. 12c is the best fit as we see it. In Fig. 12c the misfit in [1 0 0]$_Z$ direction is −10.8% but in [0 1 1]$_Z$ direction is +21.7% with respect to the corresponding NaCl lattice. These are very large strain. However, these misfits are mixed, i.e. tensile in [1 0 0]$_Z$ direction but compression in [0 1 1]$_Z$ direction, which helps to reduce the total strain.
energy. However, even if it can be reached, the positions of cations and anions may not all be favorable for minimum Coulomb interaction energy, as some Zr\(^{4+}\) will nearly sit on top of Na\(^+\). Though it is clear that the Coulomb interaction is strong, and the contact area can be very small, the minimum-energy relaxation needs to be clarified by a computer simulation with proper assumptions as discussed above.

According to theoretical calculation by first principles [20], the surface energy of (1 1 1) surface is the lowest for both c- and t-ZrO\(_2\) surfaces. Surface relaxation is expected for the nano-particles and the surface of c-ZrO\(_2\) will distort to t-ZrO\(_2\) on relaxation. The relaxed surface energy of (1 1 1) is still the lowest (1239 mJ/m\(^2\)) while those of both (1 1 0) and (1 0 0) planes are similar (1500–1700 mJ/m\(^2\)) [20]. However, experimental result shows that no particles of \(Z = [1 1 1]\) are present on NaCl (0 0 1) surface (Fig. 3). The (1 1 1) plane is unmixed and consists of hexagonal arrangements of O\(^{2-}\) ions or Zr\(^{4+}\) ions. Coincidence sites are difficult to arrange for a plane of hexagonal symmetry and a plane of cubic symmetry. The unmixed ions of the plane also make the Coulomb
repulsion worse with respect to the NaCl (100) plane. These may be the reasons why particles of \( Z = [111] \) are not favored.

4.2. Rotation and coalescence

According to SAED pattern in Fig. 3, the intensity of \( B_1 \) and \( B_2 \) are the same but both are much stronger than A. This indicates that group B is dominant and is the lower energy state of the two. The previous discussion is not conclusive, but the mixed (011) ZrO\(_2\) plane appears to be capable of achieving lower interfacial energy. Further there are 12 \{110\} planes and 6 \{100\} planes. In view of probability, if the original ion clusters fall uniformly on the substrate and then rotate to the nearest [110] or [100] direction, one can expect the number of crystallites in group B will be twice as much as those in group A. However, from Fig. 6a, b, the number of crystallites in group B is more than twice of that in A. Therefore, the total energy of c+t ZrO\(_2\) \{001\} and NaCl \{001\} interface (group A) should be local minimum, while that of ZrO\(_2\) \{011\} and NaCl \{001\} (group B) should be global minimum and attracting more particles.

At the deposition temperature of 400 °C, the nanocrystallites or initial clusters of ZrO\(_2\) may possess enough thermal energy to achieve rotation for orientation adjustment by Brownian motion on NaCl (100) surface.
Rotation and coalescence can also be expected to occur analogous to the case of metal crystallites on KCl (100) surface [21–25]. When the crystallites in the same group of A, B₁, or B₂ meet, the crystallites may rotate to overcome the small orientation difference and coalesce to form a single crystallite as shown in Figs. 9 and 10. On the other hand, if crystallites in different groups meet, they may not be able to rotate by the restriction imposed by the substrate NaCl (001) surface to maintain the orientation relationship. They may then coalesce to form high-angle grain boundaries, as in Figs. 7 and 8.

4.3. Stabilization of c- and t-ZrO₂

Cations with size larger than Zr⁴⁺ can be added to ZrO₂ to increase the cations/anions size ratio. Cations with lower valences than Zr⁴⁺ are able to introduce charge-compensating oxygen vacancies, which can also increase the

Fig. 9. (a) Lattice image, (b) Fourier transformation from the square region in (a), and (c) inverse Fourier transform from (b). The coalesced c- and/or t-ZrO₂ nanocrystals in [0 1 1] zone axis were deposited on NaCl (100) at 400 °C under 20 sccm oxygen.
Cations with these properties are commonly added to ZrO$_2$ to form the so-called fully stabilized zirconia with c-fluorite type structure, or partially stabilized zirconia with fine precipitates of t-phase in the c-ZrO$_2$ matrix [26].

Garvie [18] originally suggested that pure t-zirconia can be stabilized to room temperature by the very small size of crystallite, based on the observations of particles precipitated from hydrothermal solution. The critical size of t–m transformation of isolated t-ZrO$_2$ particles.

Fig. 10. (a) Lattice image, (b) Fourier transform from the square region in (a) showing the c- and/or t-nanocrystals in [001] zone axis, (c) inverse Fourier transform from (b). ZrO$_2$ deposited on NaCl (100) at 400°C under 20 sccm oxygen.
was estimated to be about 30 nm. The critical size is even larger, around 1 μm, for zirconia particles embedded in ceramic matrices [27] due to the effect of matrix constraint.

The 2-D constraint by the surrounding grains in thin nano crystalline film may also help in the stabilization effect. In this aspect, the critical size of t–m transformation was reported to be 80 nm for thin evaporated zirconia film prepared in vacuum and annealed in vacuum or in air [17].

In this experiment, since pure Zr target was used with adequate O₂ supply, it is suggested that the c- and t-ZrO₂ crystallites are stabilized mainly by their small size of less than 20 nm, smaller than the 30 nm critical size observed by Garvie [18]. For thin film instead of individual particles, the 2-D constraint by surrounding grains may contribute extra stabilization effect for the ZrO₂ crystallite.

5. Conclusions

1. At a substrate temperature of 400 °C and 1–20 sccm oxygen, nanosized c- and t-ZrO₂ were formed as monolayer nanocrystalline film on NaCl (1 0 0) surface.
2. The preferred orientation relationships between zirconia and NaCl (0 0 1) plane can be categorized to different types. The first type of epitaxy is [0 0 1]Z || [0 0 1]N, [1 0 0]Z || [1 0 0]N (group A), and second epitaxy relationship is [0 1 1]Z || [0 0 1]N, [1 0 0]Z || [1 0 0]N (group B). Group B is the dominant type and there are two variants in group B.
3. Particles within the same group (A, B₁, or B₂) can merge by rotation and coalescence into a single crystal particle. Particles in different groups can form high-angle grain boundaries.
4. The c- and/or t-ZrO₂ grains were stabilized by the small grain size of less than 20 nm and the 2-D constraint by the surrounding grains.
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