Orientation Relationships of SrTiO₃ and MgTiO₃ Thin Films Grown by Vapor—Solid Reactions on (100) and (110) TiO₂ (Rutile) Single Crystals

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SrTiO₃ and MgTiO₃ thin films were grown by vapor—solid reactions on TiO₂ (rutile) single crystals with different surface orientations. The crystallographic relations between the product phases and the TiO₂ substrates were studied by X-ray diffractometry (XRD) and transmission electron microscopy. XRD pole figure analysis revealed more than one orientation relationship for SrTiO₃ depending on deposition temperature. All observed orientations have a common [110] SrTiO₃ || [001] TiO₂ tilt axis. Alternatively, a topotaxial formation of MgTiO₃ on the rutile crystals was found. The crystallographic relationships between the reaction products and the TiO₂ substrates and their origins as well as the role of crystallography for first phase selection are discussed.

1. Introduction

Solid-state reactions in ceramic materials have been investigated for many years under both fundamental and technological points of view. Model experiments are well-suited to study various aspects of complex solid-state reactions. In this approach, instead of using polycrystalline materials, one reactant is a bulk single crystal. In such model experiments, the formation and orientation of the reaction products can be well-characterized by several structural techniques such as X-ray diffractometry and transmission electron microscopy (TEM). This approach has been used successfully by several research groups to study interfacial reaction mechanisms and reaction kinetics in oxides. Recently, we investigated the formation of BaTiO₃ in model experiments on (110) and (100) TiO₂ (rutile) single crystals. We found more than one orientation relationship for BaTiO₃ (which is cubic at temperatures higher than 120 °C, a ≈ 0.4 nm, but tetragonal at room temperature) grown on the rutile substrates, depending on the reaction temperature. X-ray texture investigations and high-resolution TEM images showed that all of the observed orientations of BaTiO₃ grains on the TiO₂ substrates have a common [110] TiO₂ || [001] TiO₂ tilt axis. In the present work, these studies are extended to two other oxide systems, viz., SrO—TiO₂ and MgO—TiO₂, which involve product phases containing Sr²⁺ (r_{Sr²⁺} ≈ 1.18 pm) and Mg²⁺ (r_{Mg²⁺} ≈ 75 pm) ions, respectively, the ionic radii of which are lower than that of Ba²⁺ (r_{Ba²⁺} ≈ 138 pm).

In the bulk phase diagram of the SrO—TiO₂ system, only the compound SrTiO₃ exists up to 1200 °C. SrTiO₃ has a cubic perovskite structure (space group Pm³m) with a = 0.39 nm at room temperature and higher. In the MgO—TiO₂ system, several compounds are known, such as Mg₂TiO₄, Mg₂Ti₂O₅, and Mg₂Ti₅O₁₀. Mg₂Ti₂O₅ (karooite) has a pseudobrookite structure (space group R3m) with a = 0.97 nm, b = 1.0 nm, and c = 0.37 nm, whereas Mg₂Ti₅O₁₀ (quandilite) has either a cubic structure (space group Fd3m, spinel) with a = 0.84 nm at 700 °C or a tetragonal structure (space group P4/ñm) with a = 0.59 nm and c = 0.84 nm at 300 °C. Mg₂Ti₅O₁₀ (gekkelite) has a rhombohedral ilmenite structure (space group R3) with a = 0.505 nm and c = 1.389 nm.

In this work, the orientation relationships of the metatitanate phases growing in the SrO—TiO₂ and MgO—TiO₂ systems on TiO₂ substrates with different orientations are studied. The primary aims of this study are the following: (1) To compare the orientation relationships previously found for the pseudo-cubic BaTiO₃ perovskite grown on TiO₂ (rutile) substrates with those for the cubic SrTiO₃ perovskite and for the rhombohedral MgTiO₃; (2) To determine possible topotaxial orientation relationships between the tetragonal TiO₂ (rutile) and rhombohedral MgTiO₃ phase. As has been shown recently on the example of the noncubic, corundum-type phases Mg₄Ta₂O₉ and Mg₄Nb₂O₉ growing topotaxially on cubic MgO single-crystal substrates, surprising topotaxial orientation relationships and corresponding reaction mechanisms can be found in the case of noncubic reactants and/or reaction products. (3) To study the role of crystallography in topotaxial first phase formation in the MgO—TiO₂ system, taking into account previous results of investigations of vapor—solid reactions on MgO substrates in this system. The question of which phase forms first in a thin-film solid-state reaction, if the corresponding phase diagram permits the formation of several phases, is of considerable scientific and technological significance. Correspondingly, a number of models have been put forward, including kinetic, thermodynamic, and nucleation-related models. To our knowledge, the role of crystallography in topotaxial first-phase selection has not been sufficiently considered so far.

2. Experimental Methods

One-side polished (100) and (110) surfaces of commercial TiO₂ (rutile) single crystals (from CrysTec GmbH, Berlin, Germany) were used as substrate materials. Before the experiments, the substrates were thermally treated in air at 1100 °C for 1 h. TiO₂ (rutile) has a tetragonal structure (space group P4₃/mnm) with a = 0.459 nm and c = 0.295 nm.

The substrates were subjected to either SrO or MgO vapor. The vapors were obtained in a high-vacuum chamber by electron-beam evaporation of either a SrCO₃ or MgO powder.
3. Results

The substrates were heated in a tube furnace directly by thermal irradiation during deposition. The substrates were put into a holder placed in the middle of the furnace and were hanging down with the polished surface pointing toward the electron-beam evaporator. The substrate temperature was varied from 700 to 900 °C for the reaction of SrO vapor with TiO\textsubscript{2} crystal and from 600 to 800 °C for the reaction of MgO vapor with TiO\textsubscript{2} substrates. The distance between the evaporator and the substrates is ~20 cm, which is quite large. This minimizes the heat load on the sample and thus prevents a rise in sample temperature during deposition. The temperature was measured by a Pt/PtRh10 thermocouple, which was installed at a distance of 5 mm behind the substrate. The base pressure of the system was less than 1 × 10\textsuperscript{-3} Pa. Pure oxygen was introduced during deposition to establish a pressure of (1–4) × 10\textsuperscript{-2} Pa. The deposition rate (~0.01 nm/s) and the thickness of the thin film (~100 nm) were monitored in situ by a quartz microbalance. A complete deposition/reaction experiment required about 35 min.

The phases present in the thin films after deposition and their orientation relationships were investigated by X-ray diffraction (XRD, Philips X’Pert MRD) with CuKα radiation. The investigations were performed outside the growth chamber at room temperature. The transfers of the samples were made through air. θ–2θ and 2θ measurements were performed to identify the oriented and polycrystalline products. Pole figure measurements (center, ψ = 0°; rim, ψ = 90°) were performed to find out the crystallographic orientation of the thin films relative to the substrates. Microstructure analysis of the interface between the thin films and the substrates was performed by cross-sectional TEM. The samples for TEM were made by standard methods. They were glued together face to face with epoxy resin, then mechanically polished to a thickness of about 100 µm, dimpled from one side to get a thickness of about 20 µm at the center, and followed by ion milling using a Gatan precision ion polishing system. TEM investigations were carried out in a Philips CM 20 T (200 keV).

3. Results

3.1. Reaction of SrO Vapor with TiO\textsubscript{2} Substrates. The reaction of SrO vapor with the TiO\textsubscript{2} substrates was systematically investigated by XRD as a function of deposition temperature. Only SrTiO\textsubscript{3} was found after vapor–solid reaction at temperatures between 700 and 900 °C.

Figure 1 gives typical pole figures taken at 2θ = 32.4° for samples prepared on (100) TiO\textsubscript{2} at 700, 800, and 900 °C, respectively. Figure 1a shows that at 700 °C only the peaks at ψ = 35° and 90° are present. This result indicates that the orientation relationship is (111) SrTiO\textsubscript{3} || (100) TiO\textsubscript{2}. In Figure 1b for a sample made at 800 °C, in addition to the peaks at ψ = 35° and 90°, there are peaks at ψ = 8°, 54°, and 67°, which are from the second orientation relationship (551) SrTiO\textsubscript{3} || (100) TiO\textsubscript{2}. Figure 1c shows a pole figure of a sample made at 900 °C. In Figure 1c, the strong peaks at ψ = 35° and 90° are due to the (111) orientation of SrTiO\textsubscript{3}, whereas the weak reflections at ψ = 30°, 55°, and 73° are coming from the third orientation relationship (112) SrTiO\textsubscript{3} || (100) TiO\textsubscript{2} and those at ψ = 30°, 48.5°, and 79.5° are due to the fourth orientation relationship (558) SrTiO\textsubscript{3} || (100) TiO\textsubscript{2}.

The in-plane orientation was determined by pole figures recorded at 2θ = 32.4° and 2θ = 46.5° and a ϕ scan of the TiO\textsubscript{2} {110} reflections taken at ψ = 45°. The ϕ positions corresponding to the (001) and (001) substrate planes are denoted by marks A and B, respectively, in all pole figures presented in this work. Thus, the in-plane orientation is always [110] SrTiO\textsubscript{3} || [001] TiO\textsubscript{2} for all of the orientations observed on the (100) rutile substrates. Notably, the (551) orientation of SrTiO\textsubscript{3} deviates from the (111) one by a tilt of 27.2° around the [110] SrTiO\textsubscript{3} || [001] TiO\textsubscript{2} axis, while the (112) and (558) orientations of SrTiO\textsubscript{3} deviate from the (111) one by a tilt of 19.4° and 13.2°, respectively, around the same axis.

Figure 2 shows typical pole figures taken at 2θ = 32.4° for samples prepared on (110) TiO\textsubscript{2} at 700, 800, and 900 °C, respectively. Figure 2a gives a pole figure for a sample made at a deposition temperature of 700 °C. At this temperature, two orientation relations for SrTiO\textsubscript{3} were found. Although the peaks in Figure 2a at ψ = 0°, 60°, and 90° are from the first orientation relationship (110) SrTiO\textsubscript{3} || (110) TiO\textsubscript{2}, those at ψ = 38.5°, 52°, 79.4°, and 90° are from the second orientation relationship (118) SrTiO\textsubscript{3} || (110) TiO\textsubscript{2}. For the samples made at temperatures between 800 and 900 °C, a third orientation relationship for this phase was found. The weak peaks situated at ψ = 45° in Figure 2b for the sample made at a deposition temperature of 800 °C are due to the third orientation relationship (001) SrTiO\textsubscript{3} || (110) TiO\textsubscript{2}. The peak intensity from this orientation becomes stronger at 900 °C (Figure 2c). Alternatively, the peak intensity is getting much weaker for the first orientation.

From a series of pole figures and a ϕ scan of the TiO\textsubscript{2} {100} reflections taken at ψ = 45°, the in-plane orientation is found to be [110] SrTiO\textsubscript{3} || [001] TiO\textsubscript{2} for all of the orientations observed on the (110) rutile substrates. It should be noted that the (118) orientation of SrTiO\textsubscript{3} deviates from the (110) one by
plane, and films on both (100) and (110) TiO$_2$. The misfits were calculated around the [11h] axis.

Table 1 summarizes the orientation relationships at different deposition temperatures and the misfit values found for SrTiO$_3$ films on both (100) and (110) TiO$_2$. The misfits were calculated by using the equation adopted in the near-coincidence site lattice theory (NCSL): $F = 2(n d_1 - m d_2)/n d_1 - m d_2$, where $d_1$ and $d_2$ are lattice spacings of the two materials in the interface plane, and $n$ and $m$ are integers.\textsuperscript{24,25}

### 3.2. Reaction of MgO Vapor with TiO$_2$ Substrates

Only the phase Mg$_2$TiO$_3$ was observed after reaction of MgO vapor with the TiO$_2$ substrates at temperatures between 600 and 800 °C. X-ray diffractometry and pole figure analysis showed that the Mg$_2$TiO$_3$ films grown on (100) and (110) TiO$_2$ substrates are crystallographically well-oriented.

XRD $\theta-2\theta$ scans of the films produced on the (100) TiO$_2$ substrates show the appearance of characteristic reflections of (11.0) Mg$_2$TiO$_3$ at $2\theta = 35.5^\circ$ and (22.0) Mg$_2$TiO$_3$ at $2\theta = 75.1^\circ$ beside the (200) and (400) substrate reflections. This means that the (11.0) plane of Mg$_2$TiO$_3$ is parallel to the (100) surface of TiO$_2$. Figure 3a shows a cross-sectional transmission electron micrograph of a Mg$_2$TiO$_3$ thin film grown by vapor–solid reaction on (100) TiO$_2$ at a deposition temperature of 700 °C. The interface between the thin film and the substrate is flat. This is in contrast to the interface after reaction of BaO vapor.
with (100) TiO$_2$ facets, the SrTiO$_3$ grains grew oriented with the observed various orientations with respect to deposition temperature and substrate orientation. The growth of the SrTiO$_3$ grains with the observed various orientations of SrTiO$_3$. By comparing the orientation relationships found for MgTiO$_3$ films on both (100) and (110) TiO$_2$ substrates.

4. Discussion

4.1. Orientations of SrTiO$_3$. The SrTiO$_3$ grains grew oriented with respect to the (100) and (110) TiO$_2$ substrates. Three or four different orientation were found for SrTiO$_3$ depending on deposition temperature and substrate orientation. The growth of the SrTiO$_3$ grains with the observed various orientations with respect to the (100) and (110) substrates is characterized by a common relation, [110] SrTiO$_3$ || [001] TiO$_2$, which makes the [001] TiO$_2$ axis a unique tilt axis for BaTiO$_3$ and SrTiO$_3$ grains grown on (100) and (110) TiO$_2$ substrates.

Table 2 summarizes the orientation relationships at different deposition temperatures and the misfit values observed for MgTiO$_3$ films on both (100) and (110) TiO$_2$ substrates.

### Table 2: Orientation Relationships and NCSL Misfit Values ($F_1$ and $F_2$) for MgTiO$_3$ (MTO) Thin Films Grown on (100) and (110) Rutile Substrates (T)

<table>
<thead>
<tr>
<th>$T$, °C</th>
<th>parallel planes</th>
<th>parallel direction</th>
<th>$F_1$, % (in-plane)</th>
<th>$F_2$, % (in-plane rotated by 90°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600–800</td>
<td>(11.0) MTO</td>
<td></td>
<td>(100) T</td>
<td>[11.0] MTO</td>
</tr>
<tr>
<td>600–800</td>
<td>(22.11) MTO</td>
<td></td>
<td>(110) T</td>
<td>[11.0] MTO</td>
</tr>
</tbody>
</table>

### Table 3: Angles between Crystal Planes Observed for SrTiO$_3$ (STO) and BaTiO$_3$ (BTO) Thin Films Grown on (100) and (110) TiO$_2$ Substrates

| (hkl)$_{\text{STO}}$ || (100) TiO$_2$ | (hkl)$_{\text{STO}}$ || (110) TiO$_2$ | $\angle(S_1); (S_2)$, (deg) | (hkl)$_{\text{STO}}$ || (100) TiO$_2$ | (hkl)$_{\text{STO}}$ || (110) TiO$_2$ | $\angle(B_1); (B_2)$, (deg) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| (111)           | (118)           | 44.7            | (111)           | (119)           | 45.8            |
| (558)           | (001)           | 41.5            | (223)           | (001)           | 43.3            |
| (558)           | (110)           | 48.5            | (223)           | (110)           | 46.7            |
|                 |                 |                 | (112)           | (331)           | 41.4            |
|                 |                 |                 | (225)           | (331)           | 47.2            |

The Major orientations are marked by bold font, and minors are marked by italic font.
grown on (100) and (110) TiO₂ substrates will also be close to 45°. The results of such a consideration are presented in Table 3. From Table 3, it can be seen that there are only small deviations from the value of 45° (ca. 3.6°). The orientation relationships summarized in Table 3 are shown schematically in Figure 5. Thus, the growth of some SrTiO₃ and BaTiO₃ grains occurs with a three-dimensional orientation relationship with respect to the TiO₂ substrates, irrespective of the orientation of the substrate surface.

Below, we describe factors influencing the nucleation of SrTiO₃ on TiO₂. We first consider the structural similarities between TiO₂ (rutile) and SrTiO₃ (perovskite). The fundamental structural building elements of both the TiO₂ and SrTiO₃ structures are the TiO₆ octahedra. Figure 6 shows a schematic projection of the SrTiO₃ /TiO₂ interfaces constructed from TiO₆ octahedra for different orientations of SrTiO₃ on TiO₂ substrates looking along the [110] SrTiO₃ || [001] TiO₂ direction. The octahedra in the TiO₂ rutile structure are both corner- and edge-
shared and lie along the [001] TiO$_2$ direction while the octahedra in the perovskite structure are only corner-shared and lie along the [110] SrTiO$_3$ direction. The different types of linkage of TiO$_6$ octahedra in the substrate and overgrowth are clearly seen in Figure 6, making structural consideration easy. Some similarities in the alignment of the TiO$_6$ octahedra can be seen in Figure 6a for the (111) SrTiO$_3$/TiO$_2$ interface. Ignoring small misorientations of the octahedra, the (111)-oriented SrTiO$_3$ can be nucleated in such a way that the TiO$_6$ octahedra of rutile in the surface layer can be taken over by the growing SrTiO$_3$ (the octahedra required for the nucleation are highlighted). The presence of (118)-oriented SrTiO$_3$ grains on (110) TiO$_2$ substrates can be explained by the fact that the surface of (110) TiO$_2$ substrates has terraces that are separated by monatomic step edges running predominantly along [001] TiO$_2$ and [110] TiO$_2$ directions. These reconstructed surfaces are nonstoichiometric and oxygen-deficient. Our experiments were performed using an oxygen pressure of $10^{-2}$ Pa. Thus, we expect that the temperatures of oxygen losses of the surface are shifted to higher temperatures compared to heating in vacuum. The interaction of different metals and metal oxides with the single-crystalline TiO$_2$ surfaces has also been investigated. When a Ca overlayer precipitated from the bulk of (110) TiO$_2$ crystals is annealed at

![Figure 7](image-url)

**Figure 7.** Schematic cross-section representations of the interface between the MgTiO$_3$ phase (MTO) and TiO$_2$ (rutile) substrates (T). Orientation relationships are (a and b) (11.0) MgTiO$_3$ || (100) TiO$_2$ and (c and d) (22.11) MgTiO$_3$ || (110) TiO$_2$. Viewing directions are (a and c) [11.0] MgTiO$_3$ || [001] TiO$_2$, (b) [00.1] MgTiO$_3$ || [010] TiO$_2$, and (d) [11 1.4] MgTiO$_3$ || [110] TiO$_2$. The dashed line in part c indicates (11.0) MgTiO$_3$ || (100) TiO$_2$. Different colors for oxygen atoms used in b and d show different height levels of the atoms in the projections.
...800 °C for several hours, a p(1 × 3) surface reconstruction extending over large surface areas is formed as was shown by a combination of experimental and theoretical methods. No experimental data on the influence of Sr or Ba on the reconstruction of rutile surfaces have been reported until now. Because they are alkaline-earth metals, like Ca, the formation of various surface structures after adsorption of Sr on hot rutile substrates is expected. The nucleation kinetics and conditions on these changed TiO₂ surfaces may be different. As a consequence, a nucleation of differently oriented SrTiO₃ grains may occur with some of them being favored during the initial stage of the nucleation.

4.2. Orientations of MgTiO₃. Previous investigations in the MgO—TiO₂ reaction couples using (100) MgO substrates showed that the kind of observed product depends on the reaction geometry used. In planar reaction couples of solid TiO₂ (anatase) thin films with (100) MgO crystals, Mg₃TiO₄ was found as the first phase. However, in the vapor—solid approach the formation of MgTiO₃ was always suppressed and Mg₂TiO₄ formed instead. In our case, the vapor—solid reaction between MgO vapor and TiO₂ rutile substrates results in the nucleation and growth of MgTiO₃. This feature can be explained on the basis of crystallographic similarity of the two lattices.

The ilmenite MgTiO₃ structure is based on a hexagonal close packing of oxygen ions with cations occupying two-thirds of the available octahedral sites. This structure results from equal amounts of di-(Mg) and tetravalent (Ti) cations, which are ordered at the octahedral sites and alternate along the c axis of the unit cell. A pair of MgO₆ and TiO₆ octahedra share a (001) face. Each octahedron in the ilmenite structure shares an edge with the same type of octahedron and three edges with the other octahedra. Alternatively, the rutile TiO₂ structure is based on a hexagonal close packing of oxygen atoms with Ti cations in octahedral interstitials. Each Ti cation has six octahedral neighbors, and each octahedron is connected to two neighboring octahedra via an edge and eight octahedra via a corner.

A projection of the MgO—TiO₂ interface based on the observed orientations of MgTiO₃ on (100) and (110) rutile substrates is shown in Figure 7. Similarities can be found in the arrangements of oxygen sublattices of the MgTiO₃ and TiO₂ (rutile) structures. However, small deviations of the oxygen positions in TiO₂ from those in MgTiO₃ are seen (Figure 7a and c). This is due to different types of linkage of TiO₂ octahedra in the two structures. In addition, the (11.0) and (22.11) planes of MgTiO₃ are joined by a tilt of 45° around the [11.0] MgTiO₃ axis, whereas the (100) and (110) planes of TiO₂ are aligned by a tilt also of 45° around the [001] TiO₂ axis. Thus, from these considerations, it can be concluded that the growth of MgTiO₃ on TiO₂ rutile substrates is topotaxial. The formation of MgTiO₃ from MgO vapor and TiO₂ crystals seems to have occurred via an in-diffusion of Mg cations into the TiO₂ lattice so that the oxygen sublattice of TiO₂ rutile oxide can be taken over by the growing MgTiO₃ geikielite phase. Thus, the choice in the nucleation and growth of the kind of first phase in the MgO—TiO₂ system is obviously given by the similarity of the crystallographic structures of TiO₂ (rutile) and Mg³TiO₄ (geikielite).

When MgO₂ in involving an oxygen sublattice of face-centered cubic (fcc) type, is used as a single-crystal substrate and simultaneously as a reactant for a topotaxial reaction with TiO₂ vapor, the topotaxially forming first phase is the cubic Mg³TiO₄ spinel, which also involves an fcc-type oxygen sublattice. This shows that in the MgO—TiO₂ system, in case of a topotaxial solid-state reaction, the phase forming first depends on the crystallography of the substrate serving as reactant: For MgO, it is Mg³TiO₄, whereas for TiO₂ (rutile), it is MgTiO₃. Thus, crystallography obviously plays an important, if not dominant, role in the determination of the first growing phase in topotaxial solid-state reactions. To some extent, this effect is similar to the effect of epitaxial stabilization of a certain, for example, metastable, phase in a thin film by the underlying substrate.

5. Conclusions

The crystallographic orientation relationships of SrTiO₃ and MgTiO₃ thin films grown by vapor—solid reactions on (100) and (110) TiO₂ (rutile) single crystals have been studied. Three or four different orientation relationships have been found for SrTiO₃ on the TiO₂ substrates depending on the reaction temperature and substrate orientation, all of which imply, however, a common [001] TiO₂ tilt axis. These differences are explained in terms of the different nucleation kinetics and conditions, which seem to be dependent on the surface structure and morphology of the TiO₂ substrates. An identical tilt axis was observed for BaTiO₃ grown on (100) and (110) TiO₂ in our earlier work. The crystallographic reason for the tilt axis is MgTiO₃, geikielite phase oriented along the [001] direction of TiO₂. Apparently, the oxygen sublattices of MgTiO₃ and TiO₂ rutile structures are chains of TiO₆ octahedra oriented along the [001] direction of TiO₂. Alternatively, the nucleation of MgTiO₃ occurs via in-diffusion of Mg cations into the TiO₂ lattice. Crystallography may play an important, if not dominant, role in the determination of the first growing phase in topotaxial solid-state reactions.

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