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Abstract

Titanium and vanadium oxide systems were selected to study the growth of thin epitaxial film in a metal-organic chemical vapor deposition (MOCVD) process. Epitaxial TiO_2 and VO_2 films were obtained on sapphire $(11\bar{2}0)$, (0001), and $(1\bar{1}02)$ but not on Si (111). Eight distinct substrate-film epitaxial relationships have been determined by X-ray diffraction studies using a four-circle diffractometer. It was found that none of the eight epitaxial systems had a good lattice match between substrate and film. But further investigation revealed that substantial similarity existed in the local atomic patterns of the substrate and the film for all these systems. Nevertheless, it should be emphasized that mismatches of the local atomic patterns for these systems are, in general, substantially larger than those observed in the epitaxial systems containing semiconductor materials such as silicon and GaAs.

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Introduction

Oxide materials have a tremendous variety of unique and interesting physical properties that can be, and many of them have been, used for technological applications [1]. Also, many oxide materials have been extensively used in the form of thin film because the applications involve microdevices which require the materials to be fabricated into micron or submicron sizes [1,2]. Many applications employ the films in polycrystalline form. In many other cases, however, single crystal films are either required or preferred [3-6]. Moreover, obtaining high quality, single layer epitaxial film provides the foundation for fabricating novel devices made of multilayers or superlattice configurations which may exhibit new or tailored physical properties. Despite its great potential impact on future technology, very little work has been done on the epitaxial growth of oxide thin films [7]. It is the goal of our research to obtain an understanding of the various fundamental aspects of epitaxial growth of oxide materials. At the present stage, we have selected TiO_2 and VO_2, due to their simple crystal structures [8] and well-characterized physical properties, as the starting materials to investigate the processing parameter-structure-property relationship in an MOCVD process for epitaxial growth. In this work, focus has been on the effects of the substrate surface orientation and growth temperature on the crystal structure of the deposited films and the epitaxial relationship between the film and the substrate.

Experimental

The films were grown in a cold-wall horizontal low-pressure MOCVD system. Detailed description of the apparatus and the sample preparation procedure was given elsewhere [9]. Titanium isopropoxide ($Ti(OC_3H_7)_4$) and vanadium triethoxide oxide ($VO(OC_2H_5)_3$) were used as metal-organic precursors. Pure nitrogen and oxygen were used as carried gas and oxidant, respectively. Except for the substrate and the growth temperature, all the other growth parameters were fixed as follows: total gas flow rate, 1300 sccm (standard c.c. per min); pressure, 10 Torr; oxygen flow rate, 200 sccm; metal-organic source temperature, 50°C; metal-organic source (carrier gas) flow rate, 100 sccm. Films were grown on the (111) plane of silicon substrate and the

$(11\bar{2}0)$, (0001), and $(1\bar{1}02)$ planes of sapphire substrate in the temperature range of 400 to 800°C. Typical film thicknesses ranged from 1000 to 3000 Å.

The structural phase and the crystallinity of the deposited films were characterized using the X-ray diffraction technique. In order to unambiguously examine the epitaxial characteristic of the films and to determine the orientation relationship between the film and the substrate, a four-circle diffractometer designed and built based on the method originally developed by W. R. Busing and H. A. Levy [10] was employed. The diffractometer was equipped with a rotating anode with Cu Kα radiation and a bent graphite monochrometer. The sample was mounted such that its surface normal was perfectly parallel to the rotating axis for the ϕ angle scanning. Also, the central point of the diffractometer would always lie on the sample surface at an unchanged location regardless of how the sample was rotated with respect to the incident X-ray beam.

<u>Results</u>

The films, both TiO_2 and VO_2, grown on Si (111) were always polycrystalline within the temperature range studied as evidenced by their X-ray diffraction data [9]. Since we are mainly interested in single crystal films, we will concentrate on the films grown on sapphire substrates.

Figure 1(a) shows the X-ray θ-2θ scan data of a TiO_2 film grown on sapphire $(11\bar{2}0)$ at 800°C. A single strong diffraction peak with $2\theta = 36.12$ is clearly seen in the spectrum. The 2θ value corresponds well to that of the (101) plane of a rutile single crystal [8]. The rocking curve of the growth plane (θ scan) as shown in Fig. 1(b) shows a full width at half maximum (FWHM) of 0.18° indicating a high degree of orientation. However, this does not necessarily mean the film is a single crystal. In order to determine whether the film was truly a single crystal, a ϕ scan of the $(1\bar{2}1)$ plane was carried out, which was equivalent to the rocking of the $(0\bar{1}0)$ plane, and the result is shown in Fig. 1(c). From the peak position of ϕ, it was determined that the $(0\bar{1}0)$ plane of the film was in parallel with the (0001) plane of the substrate. Also, the 0.46° of the FWHM indicated that the film was well aligned with the substrate laterally. Therefore, this is a single-crystal rutile film with (101) being the growth plane and the $\langle 0\bar{1}0\rangle$ direction being in parallel with the $\langle 0001\rangle$ direction of the substrate. Using the same method and procedure described above, we have also determined the structural phase and the epitaxial relationship of the films grown at 400°C as well as those grown on sapphire (0001) at 400 and 800°C. The structural phases and the epitaxial relationships of the films grown on sapphire (11$\bar{2}$0) and (0001) at 400 and 800°C are summarized and illustrated in Table I. As can be seen, except for brookite, all the other three phases of TiO_2, i.e., rutile, anatase, and TiO_2 II (high pressure form or α-PbO_2 type structure) [8], have been obtained.

Unlike TiO_2, bulk VO_2 has only one stable phase at room temperature, i.e., monoclinic VO_2 [8]. At growth temperatures higher than 700°C, vanadium oxide films with smooth and continuous morphology were not obtainable. At temperatures lower than 500°C, the deposited films were not stoichiometric VO_2 and the composition and structure of the films are not known at the present time. In the temperature range of 500 to 700°C, single crystal VO_2 films with monoclinic phase were obtained on sapphire substrates. The orientation relationship between the film and the substrate depends on, as in the case of TiO_2, both the substrate surface orientation and the growth temperature. The functional dependence has been discussed elsewhere [11]. Four distinct epitaxial relationships have been observed and the results can be summarized as follows:

VO_2 (010)//Sapphire (11$\bar{2}$0), (001)//(0001)

VO_2 (010)//Sapphire (0001), (100)//(2$\bar{1}\bar{1}$0)

VO_2 (100)//Sapphire (11$\bar{2}$0), (010)//(0001)

VO_2 (100)//Sapphire (1$\bar{1}$02), (010)//(11$\bar{2}$0)

A total of eight distinct epitaxial systems have been obtained in this study. We have found that the rutile film on sapphire (11$\bar{2}$0) has the highest degree of crystallinity as compared to other systems based on the FWHM's of both the θ and the ϕ scans. However, for all these systems, the values of the FWHM's (both in θ and ϕ) were generally between 0.5 and 2 degrees.

Discussion

It is interesting to note that none of the eight epitaxial systems obtained in this study have a good lattice match between the substrate and the film. In fact, these systems are heteroepitaxial systems and the film and the substrate have different crystallographic structures. However, in all cases, the local atomic arrangements of the film growth plane and the substrate surface bear substantial resemblance to each other despite the apparent unit cell dissimilarity. To further illustrate this point in detail, let us take one of the epitaxial systems, anatase (112) on sapphire (0001), as an example. Plotted in Fig. 2(a) and (b) are the planar atomic arrangements viewed along the normal directions of the anatase (112) plane and the sapphire (0001) plane, respectively. Let us define the normal direction of the sample surface to be Z-axis with positive direction pointing out of the paper. $Z = 0$ corresponds to the topmost layer of atoms. The metal cations and the oxygen anions are represented in the figure by black dots and open circles, respectively. Atoms with different distances from the topmost layer have different values of Z (all negative) and are represented by different sizes of dots or circles. Larger sizes correspond to smaller $|Z|$'s which means the atoms are closer to the top layer. However, the meaning of the size does not apply to the comparison between dots and circles. In Fig. 2, dots are always closer to the surface ($Z = 0$) than circles irrespective of their sizes. Three layers of atoms are plotted in both Fig. 2(a) and 2(b). In Fig. 2(b), the top two layers are composed of Al atoms with two slightly different values of Z. But the two layers can be actually considered as one layer of atoms with a slightly corrugated arrangement. The bottom layer is composed of nearly ideally close-packed oxygen atoms. In Fig. 2(a), the top layer is composed of Ti atoms and the bottom two layers are composed of oxygen atoms and can be considered as one layer of atoms with a corrugated arrangement. The corrugated oxygen layer also has an atomic pattern similar to that of an idealized close-packed structure although the deviation is larger than that of Fig. 2(b). The unit cells of the substrate and the film are outlined by solid lines in the figure. As can be seen, they belong to two different crystal structures. However, the oxygen anion patterns of the film and the substrate are quite similar to each other. During the initial layer growth in the deposition process, the titanium atoms or titanium oxygen radicals that were transported from the gas phase to the sapphire surface would "see" an oxygen anion pattern similar to that of the anatase (112) plane. Therefore, an anatase single crystal film was easily formed by way of seeding on an appropriate atomic pattern. It should be noted that although the atomic patterns of the film growth plane and the substrate surface are compatible, there is still a considerable amount of local mismatch between the film and the substrate. Comparing the region outlined by the dotted line in Fig. 2(b) to the unit cell in Fig. 2(a), a mismatch of 14.7% was found along the ⟨0001⟩ direction of sapphire.

The above argument can be applied equally well to all the other seven epitaxial systems listed in this paper. Similar to that depicted in Fig. 2, Fig. 3 shows the atomic arrangements of the other three epitaxial systems containing TiO_2 films. Plotted in Fig. 4 are the atomic arrangements of the four epitaxial systems involving VO_2 films. As is seen from these atomic patterns, all the substrate surfaces and the film growth planes have, to different degrees, distorted (corrugated) close-packed arrangements of oxygen anions. The cations occupy the interstices of the close-packed anion network in different ways for different crystal structures. So the occurrence of epitaxial growth may be viewed as a continuous extension of the anion network from the substrate to the film with the two different types of cations arranging differently, in the anion interstices, for the film and the substrate.

Conclusion

TiO_2 and VO_2 thin films have been prepared in a cold-wall, low-pressure MOCVD system. Epitaxial films were easily obtained on sapphire substrates of various surface orientations whereas films grown on Si (111) were always polycrystalline. This fact clearly indicates that the substrate material plays the most important role in epitaxial growth. Further, once an appropriate substrate material (sapphire in our case) is selected, the structural phase and the growth plane of the deposited film depend on both the substrate surface orientation and the growth temperature.
It seemed surprising at first glance that single crystal films could be obtained despite the large differences in the lattice constants of the film and the substrate. Further investigation into the local atomic arrangement, however, revealed that substantial similarity in the atomic pattern existed in all of the epitaxial systems studied. It should be emphasized, nevertheless, that mismatches of the local atomic patterns for these systems are, in general, substantially larger than those typically observed in the epitaxial systems containing semiconductor materials such as silicon and GaAs. This discrepancy may be related to the difference in the nature of chemical bondings.

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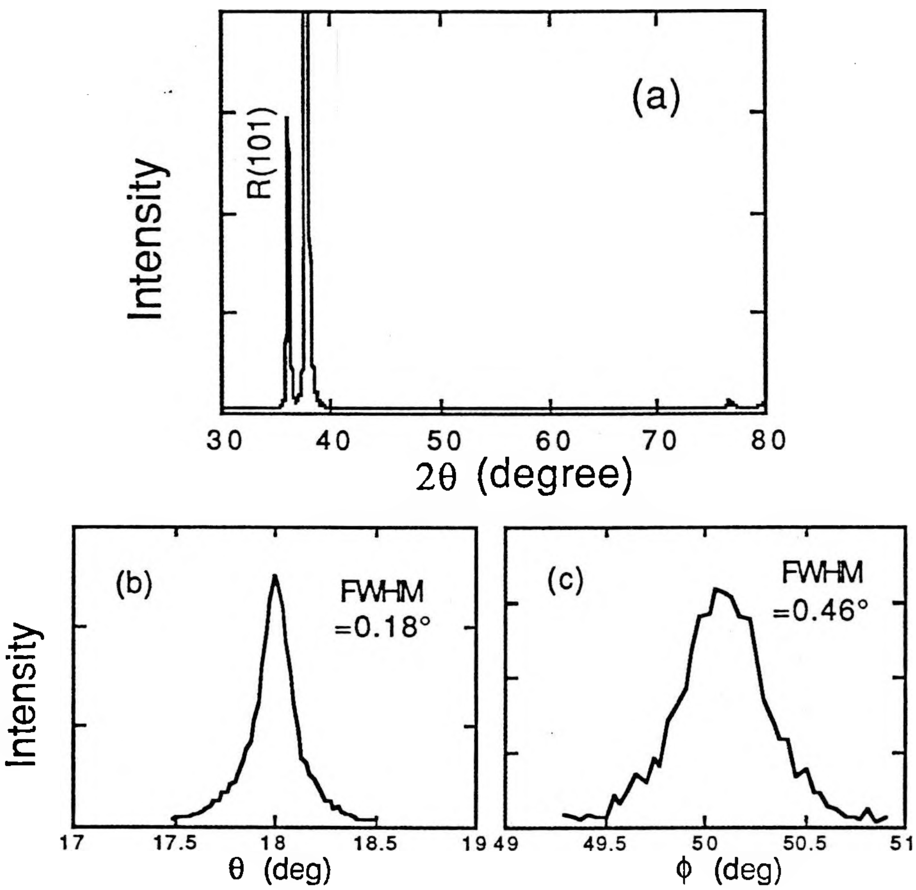
Figure Captions

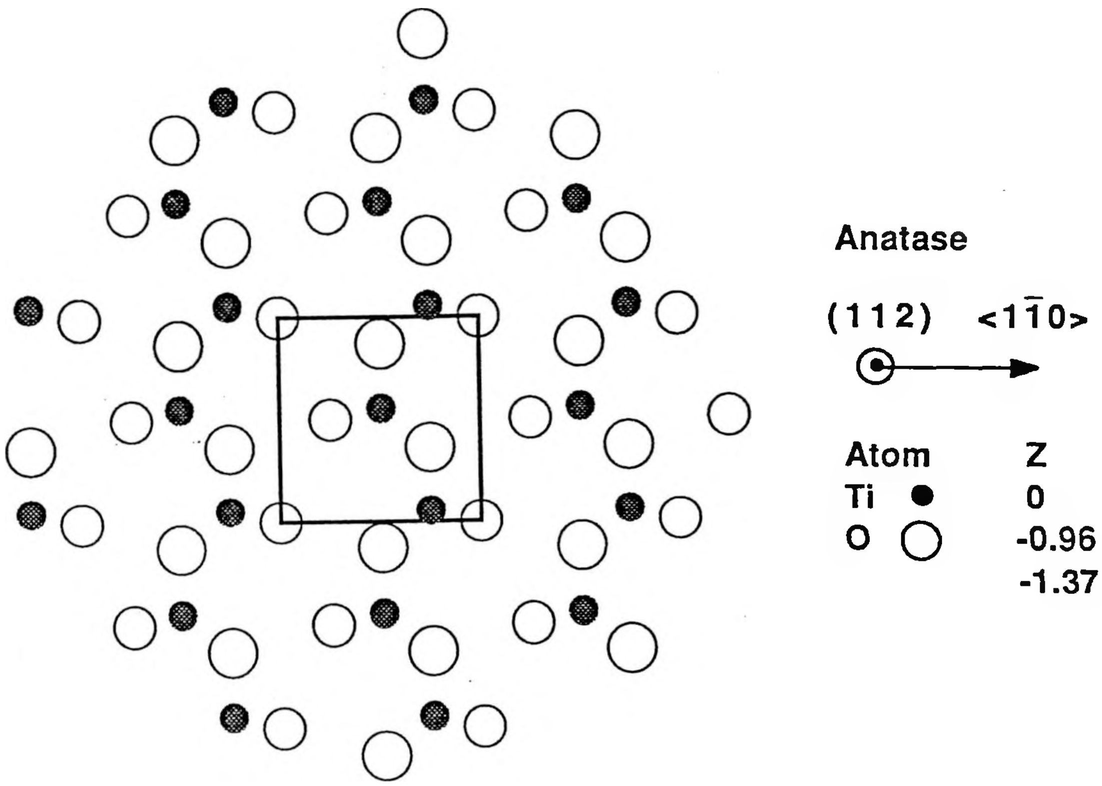
Fig. 1. X-ray diffraction data of a TiO_2 (rutile) film grown on sapphire $(11\bar{2}0)$ at 800°C: (a) θ-2θ scan; (b) rocking curve of the (101) growth plane; (c) ϕ scan of the $(1\bar{2}1)$ plane.

Fig. 2. The atomic arrangements of (a) the anatase (112) plane and (b) the sapphire (0001) plane. The $\langle 1\bar{1}0 \rangle$ direction of anatase is parallel to the $\langle \bar{1}100 \rangle$ direction of sapphire.

Fig. 3. The planar atomic arrangements are plotted for the following three epitaxial systems that contain TiO_2 films: (a) rutile (101) // sapphire $(11\bar{2}0)$, $(0\bar{1}0)$ // (0001); (b) TiO_2 II (100) // sapphire $(11\bar{2}0)$, (001) // $(\bar{1}102)$; (c) TiO_2 II (100) // sapphire (0001), (001) // $(\bar{1}2\bar{1}0)$. The patterns are plotted in a way similar to that used for Fig. 2.

Fig. 4. The planar atomic arrangements are plotted for the four epitaxial systems that contain VO_2 films: (a) VO_2 (010) // sapphire $(11\bar{2}0)$, (001) // (0001); (b) VO_2 (010) // sapphire (0001), (100) // $(2\bar{1}\bar{1}0)$; (c) VO_2 (100) // sapphire $(11\bar{2}0)$, (010) // (0001); (d) VO_2 (100) // sapphire $(1\bar{1}02)$, (010) // $(11\bar{2}0)$. The patterns are plotted in a way similar to that used for Fig. 2.


(a)
R(101)
Intensity
30
40
50
60
70
80
2θ (degree)
(b)
FWHM
=0.18°
Intensity
17
17.5
18
18.5
19
θ (deg)
(c)
FWHM
=0.46°
49
49.5
50
50.5
51
ϕ (deg)


Anatase
(112) <1$\bar{1}$0>
Atom Z
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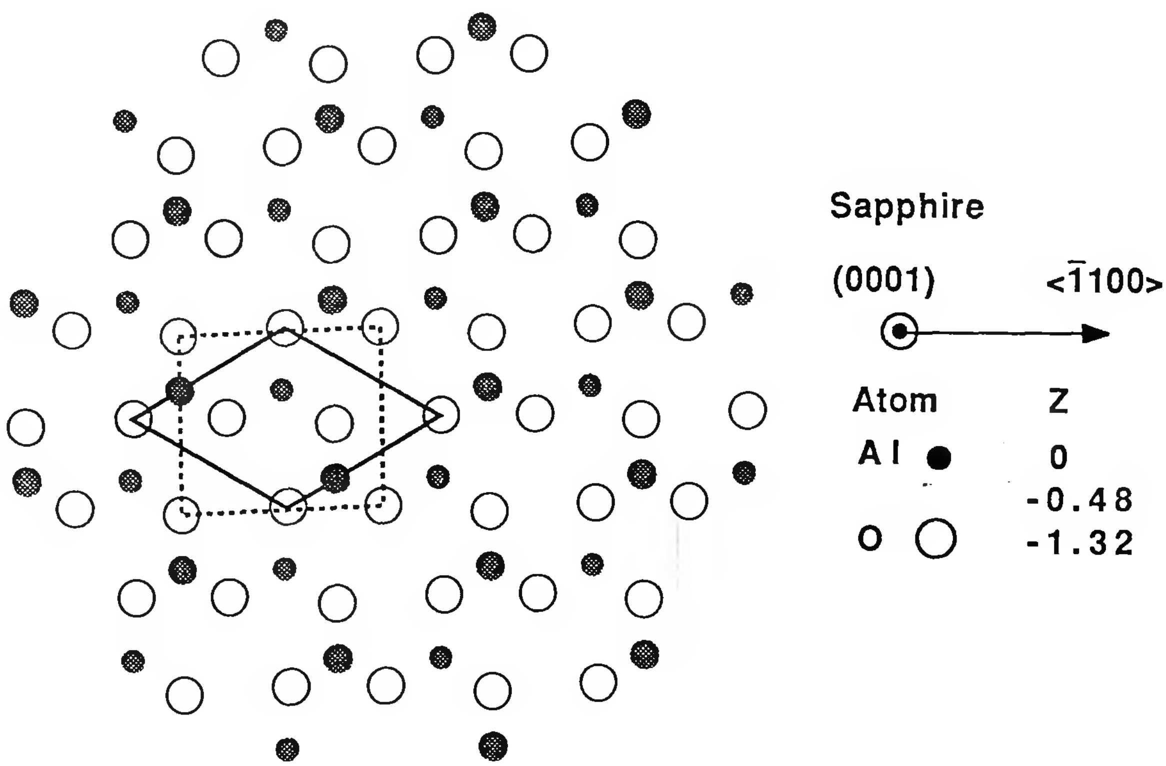
O -0.96
-1.37


Sapphire
(0001) <$\bar{1}$100>
Atom Z
Al 0
-0.48
O -1.32

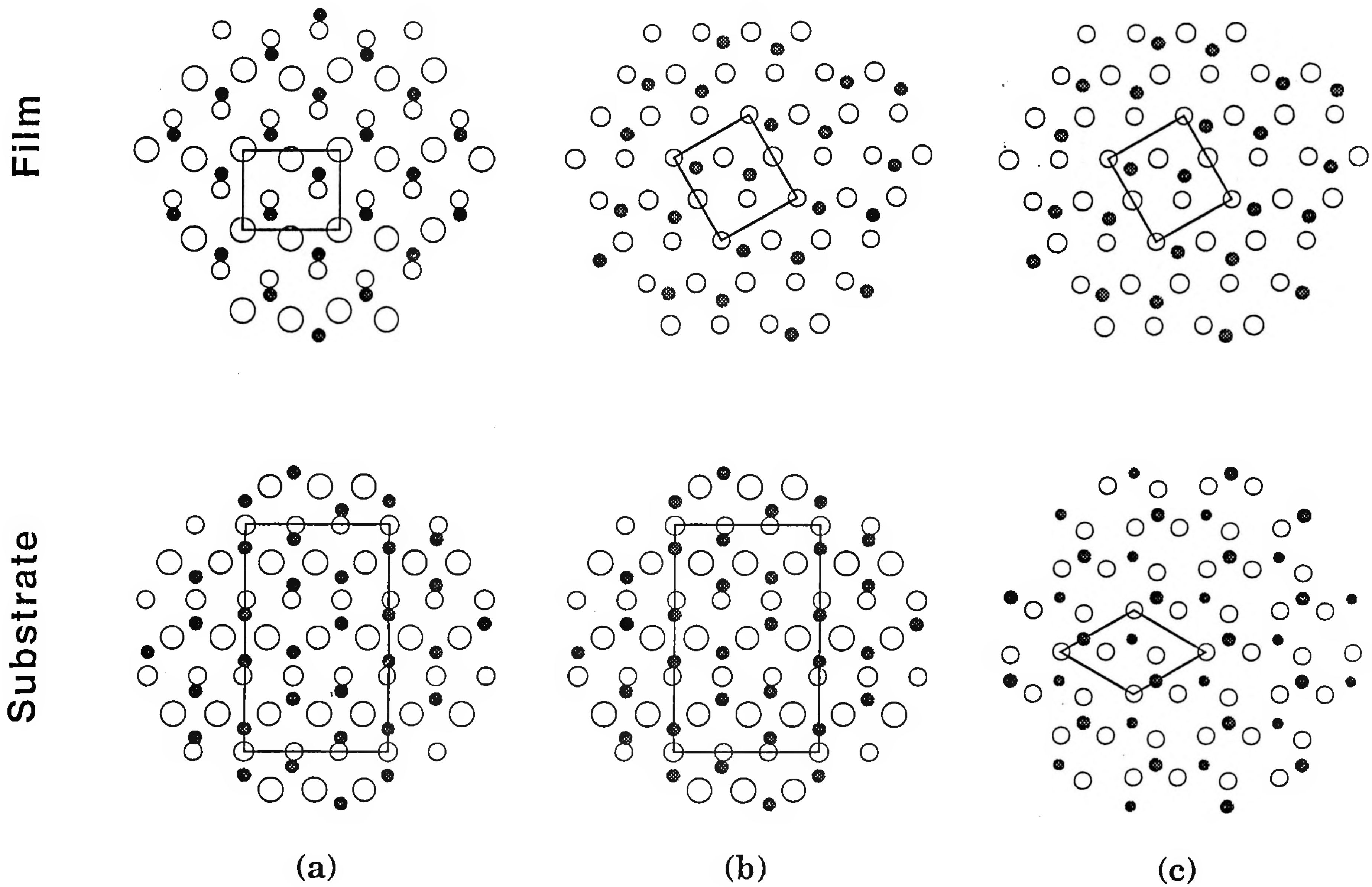


Fig 3

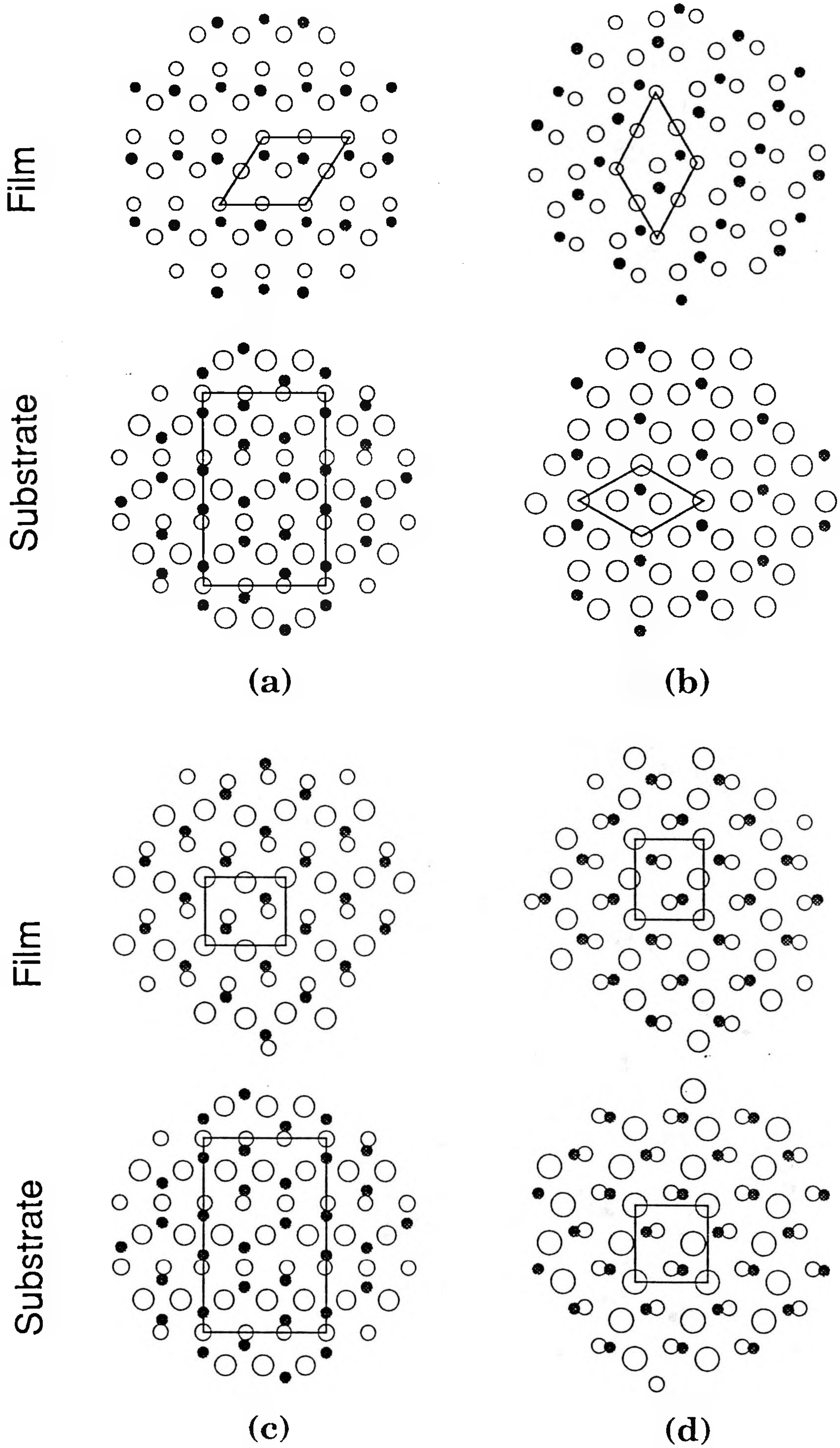

Film
Substrate
(a)
(b)
Film
Substrate
(c)
(d)

TABLE I. Structual Phases and epitaxial relationships of TiO_2 films grown on sapphire substrates.

	Sapphire (0001)		**Sapphire (11$\bar{2}$0)**	
	TiO_2 II	Sapphire	Rutile	Sapphire
800 °C	(100) (001)	(0001) ($\bar{1}$2$\bar{1}$0)	(101) (0$\bar{1}$0)	(11$\bar{2}$0) (0001)
	Anatase	Sapphire	TiO_2 II	Sapphire
400 °C	(112) (1$\bar{1}$0)	(0001) ($\bar{1}$100)	(100) (001)	(11$\bar{2}$0) ($\bar{1}$102)