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ABSTRACT

A four-circle diffractometry technique is used to determine the heteroepitaxial relations of VO_2 and TiO_2 thin films grown by an MOCVD technique on sapphire (0001) and $(11\bar{2}0)$ surfaces. The use of a reflective geometry eliminates special sample preparation of the sample for the x-ray diffraction measurements. The distribution of epitaxial domains is found to depend strongly on the symmetry of the underlying substrate.

INTRODUCTION

Among several metal oxide materials that have potentials for device applications,[1] TiO_2 and VO_2 are chosen for our MOCVD study because of dissimilarity in physical properties despite their structural similarity. At high temperatures, both TiO_2 and VO_2 form rutile structure but TiO_2 is an insulator while VO_2 is a conductor. At room temperature, TiO_2 remains in the rutile structure while VO_2 transforms into a monoclinic structure by doubling the unit-cell through the metal-insulator transition. TiO_2 is sometimes found in an anatase form at room temperature. A comparison of the unit cell parameters for TiO_2, VO_2, and sapphire at room temperature is given in Table I. Our main interest is to study the formation of single-crystal quality epitaxial film on a common, readily avilable substrate such as sapphire. In this paper we will focus on the use of four-circle x-ray diffractometry to study the detailed epitaxial relations between these oxides and the substrate.

X-ray diffraction is one of the most common techniques to study heteroexpitaxy. A two circle diffractometry method is commonly used in materials studies, but it only allows one-dimensional scans. However epitaxial information is three-dimensional in nature and is often difficult to obtain with a two circle spectrometer.

Table I

	a	b	c	α	β	γ
Rutile	4.594	4.594	2.959	90	90	90
Anatase	3.785	3.785	9.515	90	90	90
VO_2	5.759	4.531	5.386	90	122.56	90
Sapphire	4.759	4.759	12.99	90	90	120

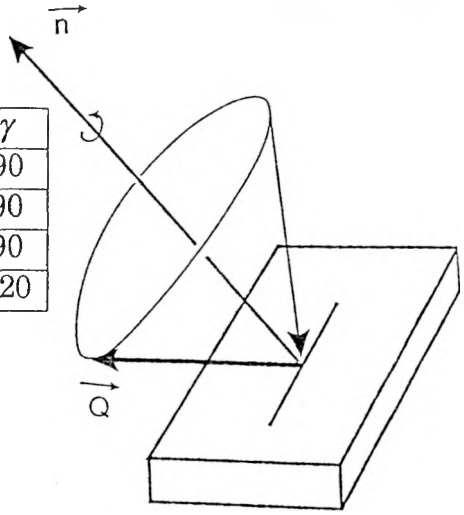

Fig. 1. A schemactic representation of ϕ scan.

Therefore in many cases it is necessary to use a four-circle spectrometer to study epitaxial relations. While most crystallographic operations of a four-circle spectrometer are designed with single crystals in mind, the surface x-ray scattering orientation matrix method[2] allows accesss to half of the momentum space above the sample surface in a reflective geometry and is very useful in epitaxial studies. In this method, the orientation matrix of the sample is calculated such that the sample can always remain in a reflective geometry. This is done by orienting the norm of the sample surface (approximately) parallel to the ϕ axis as shown in Fig. 1. The in-plane reciprocal vectors are of course difficult to reach unless a highly flat surface is prepared for a glancing angle geometry. With the four circle spectrometer, as we will see, all the epitaxial information can be obtained by studying off-specular reflections.

EXPERIMENTAL

The films were grown in a cold-wall horizontal low-pressure MOCVD system and were typically ~ 1000 Å thick. Detailed description of the growth appartus and the sample preparation procedure are given elsewhere.[3] Copper $K_{\alpha 1}$ x-rays generated with a 12 KW rotating anode x-ray source were focused with a bent graphite monochromator at the center of the Huber four-circle spectrometer. A sample was initially mounted on a Huber goniometer head with two arcs and X-Y translation. The sample surface was oriented approximately parallel to the X-Y plane of the goniometer head. Then the goniometer head with the sample was mounted onto the ϕ table and centered by a microscope. For experimental simplicity, the two arcs of the goniometer head are accurately adjusted so that the diffraction intensity of the sapphire $(11\bar{2}0)$ or (0001) is independent of ϕ rotation. This procedure ensures that a ϕ scan rotates the sample about the substrate $(11\bar{2}0)$ or (0001) axis (about the surface normal when there is no miscut). The ϕ scan is schematically shown in Fig. 1 with the reflection of interest is in the horizontal plane (scattering plane). Next a careful specular scan along the sapphire $(11\bar{2}0)$ or (0001) direction was made. This step normally determines the growth plane of the film. Once the growth plane is determined, additional Bragg reflections parallel to the substrate surface (in-plane reflections) should be found. For a thin sample these reflections can be studied in a transmission mode and provide complete expitaxial information. For a thick sample, however, the transmission measurements are not practical because of absorption of x-rays through the substrate. Nonetheless, the same information that we may get from the in-plane reflections in the transmission measurements can be obtained in reflection measurements by studying off-specular reflections which have both specular and in-plane components. Following the procedures described above, we can obtain the in-plane characteristics of a diffracting planes perpendicular to the substrate surface from simple ϕ scans of off-specular reflections.

RESULTS ON SAPPHIRE $(11\bar{2}0)$ SUBSTRATE

Figure 2 (a) and (b) shows typical mosaic and radial scans for TiO_2 (101) parallel to sapphire $(11\bar{2}0)$ substrate. The mosaic width of the sapphire peak is resolution limited while that of film peak is 0.5 degree in FWHM indicating that the film is oriented parellel to the substrate surface within a few tenths of degree. The radial scan shows that the film peak is somewhat broader than the instrumental resolution. We calculate the substrate orientation matrix from the specular and off-specular reflections of substrate. Similarly we calculate the film orientation

matrix from the specular and off-specular reflections of the film. Then comparision of these two orientation matrices determines the three-dimensional epitaxial relation between the substrate and film. In general, however, the epitaxial films have several microdomains depending on the substrate symmetry and lattice mismatches. Fig. 2(c) shows ϕ scans, which measure the degree of epitaxial alignment and single crystallinity of the film, of the TiO_2 (121) reflection for a few samples grown in different conditions. The substrate temperature and the oxygen partial pressure were 825, 775, and 775 K and 1000, 0, and 1000 torr, respectively. The ϕ = 0 direction is the direction of sapphire (0001) planes whose lattice constant closely matches with that of TiO_2 (020) planes. In the early growth stage (as early as in the monolayer regime), the absorbed layer preferentially rotates slightly away from the major crystallographic axis of the substrate to minimize the strain energy due to the small lattice mismatch.[4] The angle of rotation depends on substrate temperature and growth condition. The rotational epitaxy remains over the entire thickness of the film because the initial layers determine the orientation of microdomains. In the bottom scan at 775 K of growth temperature the rotational epitaxy disappears and the film becomes well aligned along the sapphire (0001). At lower substrate temperatures (below ~ 600 K) the anatase form or a distorted rutile form are often found. Although the reflection intensities of the distorted rutile structure are essentially those of rutile structure, the refined unit cell paramters of the distorted rutile structure are 4.564, 4.609, 2.950, 90, 90, and 90.

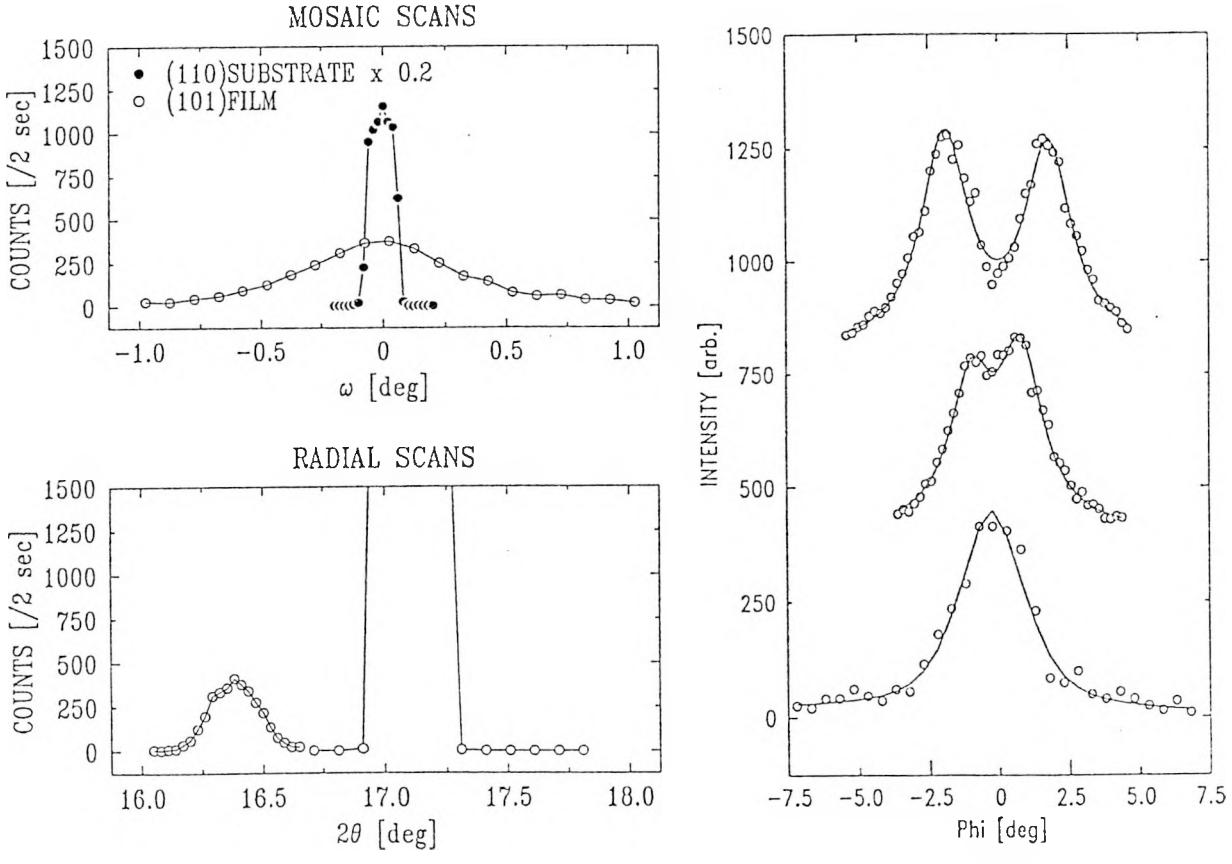

Fig. 2. (a) Radial and (b) mosaic scans of TiO_2 on sapphire ($11\bar{2}0$). (c) The ϕ scans of rutile (121) reflection from three different samples grown in different conditions. The scans are offset for display.

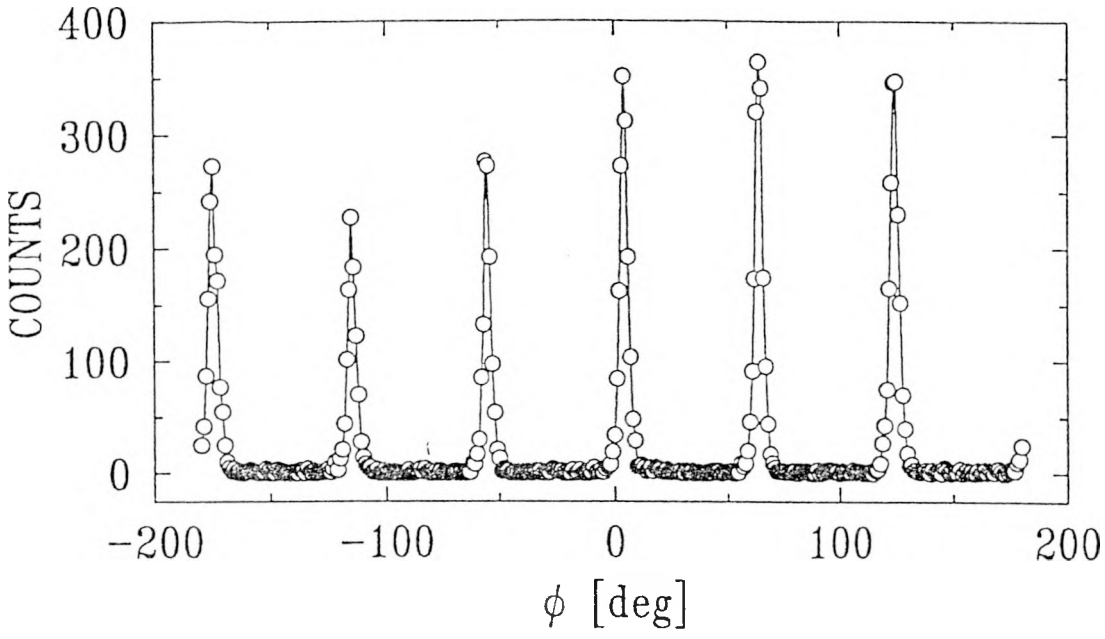

Fig. 3. The ϕ scan at VO_2 (004) reflection on sapphire (0001).

RESULTS ON SAPPHIRE (0001) SUBSTRATE

A more complicated situation can occur when the substrate has a hexagonal symmetry. Sapphire (0001) has a three-fold symmetry about the c-axis in the hexagonal unit cell, but the adsorption sites in the basal plane have a psudo six fold symmetry. At a deposition temperature fo 400°C, TiO_2 forms anatase structure on sapphire (0001) surface. The growth direction parallel to the substrate is anatase (112) direction and the anatase $(1\bar{1}0)$ direction is parallel to sapphire $(11\bar{2}0)$ direction. Since sapphire (0001) direction has a psudo six fold symmetry, ϕ scan at a off-specular reflection, e.g. anatase (004), shows a near six fold symmetry as shown Fig. 3. The intensities of (004) at different angles represent the sizes of

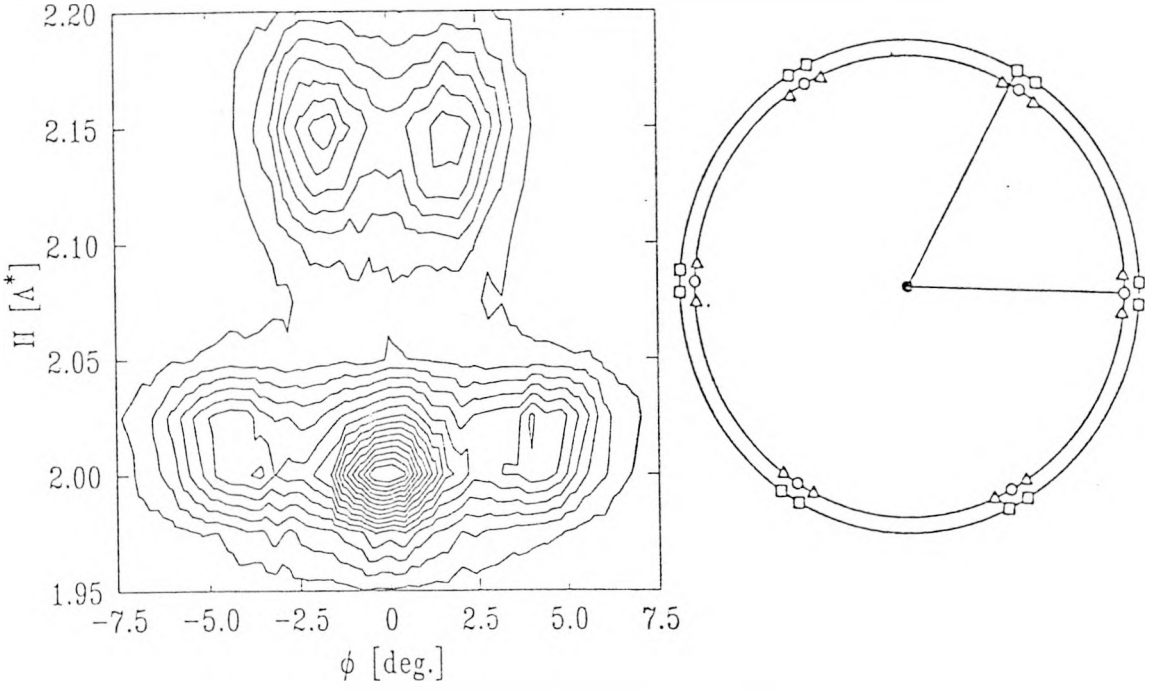

Fig. 4. (a) The mesh scan near VO_2 (220) reflection in (h2l) zone on sapphire (0001). (b) A schematic diagram generated by superposition of VO_2 (220) and (022) reflection.

domain distribution along those directions. At a higher growth temperature, TiO_2 sometimes forms the distorted rutile structure similar to one observed for the low temperature grown structure on sapphire $(11\bar{2}0)$.

Fig.4(a) shows a mesh scan near (220) in the (h2l) zone. In this mesh scan 5 peaks are clearly resolved. Since VO_2 has a monoclinic structure, we can understand these peaks by a superposition of 6 domains with a hexagonal symmetry of (220) and (022) reflections. The schematic representation of the superposition of the peaks are shown in Fig.4(b). Two solid lines represent the unit vectors of the monoclinic unit cell from a single domain. By a successive rotation of this mesh by 60 degrees and by the inversion about the sapphire (0001) direction the observed pattern is reproduced. In this case the (200) plane spacing nearly matches with the sapphire $(11\bar{2}0)$ plane spacing and they are precisely aligned. The monoclinic unit cell can be easily adapted by shearing the (200) planes. The crystallinity is very high because there is virtually no stress in the film.

CONCLUSION

In conclusion, we studied heteroepitaxial relations of TiO_2 and VO_2 on sapphire $(11\bar{2}0)$ and sapphire (0001) at different substrate temperatures. The results are summarized in previous publications.[3] We find that the alignment of the film with respect to the substrate is determined by the best lattice matching condition of the substrate-film interface and the distribution of their microdomains follows the symmetry of the underlying substrate.

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