Substrate Surface Structure Effects on Microstructure of Epitaxial Films*

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SUBSTRATE SURFACE STRUCTURE EFFECTS ON MICROSTRUCTURE OF EPITAXIAL FILMS

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ABSTRACT

The microstructure of epitaxial thin films grown on sapphire substrates using the metal organic chemical vapor deposition (MOCVD) technique were found to depend on the substrates surface structure. The epitaxial TiO_2 films grown on the sapphire (0001) substrates were highly-oriented polycrystal and the films on the $(11\bar{2}0)$ substrates were single crystal. First-principles total energy calculations were carried out to gain atomistic understandings of sapphire surface structures and their effects on microstructure of epitaxial films. The surface terminating atom planes were found to be Al atoms for the (0001) surface and O atoms for the $(11\bar{2}0)$. The minimum step heights were found to be one sixth of the lattice constant c for the (0001) and one half of the lattice constant a for the $(11\bar{2}0)$. The steps of the minimum height or its odd multiples on sapphire (0001) surface were shown to double the number of variants in the deposited films. The symmetry and step of the substrate surface and the symmetry of the epitaxial growth plane were found to control the microstructure of the epitaxial films.

INTRODUCTION

Over the past several years there have been increasing efforts in growing epitaxial oxide films because of their potential for novel device application.[1] Sapphire is a commonly used substrate for epitaxial oxide film deposition. For heteroepitaxial growth of oxide thin films on single crystal oxide substrates, in generally, the sub-

strate crystallographic plane were found experimentally to play a major role in determining the epitaxial relationship of the overlayer to the substrate.[2] For example, in the MOCVD growth of TiO_2 thin films on single crystal sapphire substrates, Anatase TiO_2 (112) films were grown on the (0001) sapphire surfaces with its $[\bar{1}10]$ parallel to sapphire $[1\bar{1}00]$. Rutile TiO_2 (100) films were grown on $(11\bar{2}0)$ surfaces with its $[010]$ parallel to substrate $[0001]$. The epitaxial TiO_2 films grown on the sapphire (0001) substrates were highly-oriented polycrystal and the films on the $(11\bar{2}0)$ substrates were single crystal. In this brief report, we relate the microstructure of epitaxial films to the substrate surface structures.

EXPERIMENTAL RESULTS ON THE FILM MICROSTRUCTURE

Details in the MOCVD growth of the epitaxial anatase TiO_2 films of tetragonal structure can be found in the previous work.[2] The polycrystal nature of the anatase TiO_2 film on the sapphire (0001) substrate were determined by the plane view transmission electron microscopy (TEM) image shown in Fig. 1. The size of the grains are of the order of $0.1 \mu\text{m}$. Their off-plane orientations were determined by the x-ray θ - 2θ scan shown in Fig. 2. Only one film peak corresponding to the anatase (112) growth plane shows up beside the strong substrate (0006) peaks. The in-plane orientation were determined by the x-ray ϕ scan of the anatase (004) reflection as shown in Fig. 3. Since the (004) plane normal is a nondegenerate direction of the (112) films, the appearance of the six peaks indicate that the grains in the epitaxial films have six orientations of 60° apart.

On the other hand, the rutile (100) films grown on the $(11\bar{2}0)$ sapphire substrates were found to be single crystals by the combination of the x-ray diffractions shown in Fig. 4 and TEM images and electron diffraction patterns.[3]

0.1 μm

Figure 1: A plane view TEM image of an anatase (112) film on a sapphire (0001) substrate.

Figure 3: X-ray ϕ scan around (112) plane normal at the anatase (004) reflection plane for the same sample.

Figure 2: X-ray θ - 2θ scan of the same sample.

Figure 4: X-ray θ - 2θ scan of a rutile (100) film on a sapphire ($11\bar{2}0$) substrate.

Figure 5: A perspective view of the hexagonal unit cell of sapphire. The filled circles label Al atoms, and open circles O atoms. The dark thick lines label the short Al-O bonds (1.86 Å), the light thin lines the long Al-O bonds (1.97 Å).

THEORETICAL RESULTS ON THE SUBSTRATE SURFACE STRUCTURE

In order to understand why the microstructures of the epitaxial films grown on the two sapphire substrate surfaces differ so much, we need the microscopic understanding of the sapphire substrate surface structures. However, it is very difficult to determine the atomic arrangement of the terminating plane of the substrate surface experimentally. We relied on the theoretical calculations to provide us information about surface atomic structures. Recently we have developed the first-principles self-consistent discrete variational embedded cluster method for calculating surface electronic structure and energetics of complex oxide surfaces.[5]

Sapphire, $\alpha\text{-Al}_2\text{O}_3$, has a trigonal crystal structure of the $R\bar{3}c$ space group.[4] Its hexagonal unit cell is shown in Fig. 5 with $a = 4.76\text{Å}$ and $c = 13.00\text{Å}$. [4] The (0001) surface is the basal plane of the unit cell

Figure 6: Cross section and plane views of the (0001) and (11 $\bar{2}$ 0) sapphire surface with the minimum height step. Same convention as Fig. 5. The smaller the radius, the farther the atom away from the surface layer.

shown in Fig. 5. The (11 $\bar{2}$ 0) surface is the plane perpendicular to the basal plane and contains the two vertical solid lines on the two sides in Fig. 5. From Fig. 5, we see that the (0001) surface can have three possible terminations. One is terminated by one O layer, and another by two Al layers as indicated by the upper horizontal solid line. The lower horizontal solid line produces two equivalent surfaces terminated by one Al layer. Based on the first-principles total energy calculations on these three possible terminating atomic planes, we found that the lowest energy surface plane is terminated by one Al layer. Furthermore, the minimum step height on (0001) is found to be one sixth of the lattice constant c to guarantee the terraces connected by the step has the lowest energy Al terminating layer as shown in Fig. 6. Similarly, the lowest energy surface plane was found to be terminated by one O layer and the minimum step height to be one half of the lattice constant a for sapphire (11 $\bar{2}$ 0) surfaces as shown in Fig. 6. From the plane views shown in the bottom portion of Fig. 6, we see that the

($11\bar{2}0$) and the (0001) have 2-fold and 3-fold rotational symmetry, respectively. The two terraces joined by the step are the same for ($11\bar{2}0$) surfaces. However, the two terraces are related by the reflection about the ($11\bar{2}0$) plane for the (0001) surfaces. This is also true for portions of a (0001) surface joined by steps of height of any odd multiples of the minimum height. Therefore, any nucleation growth of thin films on ($11\bar{2}0$) surface can have two symmetry equivalent in-plane orientations 180° apart. On a perfect (0001) surface, thin films can have three symmetry equivalent in-plane orientations 120° apart. The special steps will double the number of the orientations, resulting six variants in the film with in-plane orientations 60° apart. From the symmetry consideration, variants in epitaxial film can not coalesce into a single crystal when the point symmetry group of the substrate surface is not the subgroup of the film growth plane. Since anatase (112) surface has no symmetry, the six variants will occur on the stepped (0001) surfaces. This is consistent with the experimental results discussed earlier. On ($11\bar{2}0$) substrate, epitaxial thin films whose growth planes have 2-fold or 4-fold rotational symmetry can coalesce into a single crystal as observed.

CONCLUSIONS

The surface terminating atomic plane is different for different crystallographic plane of sapphire substrates. The surface step on certain crystallographic plane of sapphire substrates will double the number of variants in the epitaxial films. The substrate surface structure such as its symmetry and steps and the symmetry of the film growth plane control the microstructure of the epitaxial film.

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