NOTICE

CERTAIN DATA CONTAINED IN THIS DOCUMENT MAY BE DIFFICULT TO READ IN MICROFICHE PRODUCTS.

Conf-901105--68

CONF-901105--68

DE91 006544

Electron Microscopy Study of MOCVD-Grown TiO_2 Thin Films and TiO_2/Al_2O_3 Interfaces

Y. Gao, K. L. Merkle, H. L. M. Chang, T. J. Zhang and D. Lam
Materials Science Division
Argonne National Laboratory
Argonne, IL 60439

NOVEMBER 1990

* This work was supported by the U. S. Department of Energy, Offices of Basic Energy Sciences - Materials Science under contract No. W-31-109-ENG-38.

To be presented at MRS Fall Meeting, Symposium K, Boston, MA, November 26-December 1, 1990.

ELECTRON MICROSCOPY STUDY OF MOCVD-GROWN TiO_2 THIN FILMS AND TiO_2/Al_2O_3 INTERFACES

Y. Gao, K. L. Merkle, H. L. M. Chang, T. J. Zhang, and D. J. Lam
Materials Science Division, Argonne National Laboratory
Argonne, IL 60439

ABSTRACT

TiO_2 thin films grown on $(11\bar{2}0)$ sapphire at 800 °C by the MOCVD technique have been characterized by transmission electron microscopy. The TiO_2 thin films are single crystalline and have the rutile structure. The epitaxial orientation relationship between the TiO_2 thin films (R) and the substrate (S) has been found to be: $(101)[0\bar{1}0]_R \| (11\bar{2}0)[0001]_S$. Growth twins in the films are commonly observed with the twin plane {101} and twinning direction <011>. Detailed atomic structures of the twin boundaries and $TiO_2/\alpha\text{-}Al_2O_3$ interfaces have been investigated by high-resolution electron microscopy (HREM). When the interfaces are viewed in the direction of $[0\bar{1}0]_R/[0001]_S$, the interfaces are found to be structurally coherent in the direction of $[\bar{1}01]_R/[1\bar{1}00]_S$, in which the lattice mismatch at the interfaces is about 0.5%.

INTRODUCTION

The study of epitaxial growth of ceramic oxide thin films on various substrates has recently received considerable attention [1-3] since the unique physical properties of the ceramic thin films may be useful in electronic and optical device applications. The metal organic chemical vapor deposition (MOCVD) technique, which has been applied with great success in the semiconductor industry, can also be a potential technique for the epitaxial growth of oxide thin films. However, the use of the MOCVD technique for the fabrication of epitaxial oxide films is still in its infancy. Therefore, atomic-resolution characterization of the interface configuration is very important for understanding the epitaxial growth and the fabrication processes.

In the present study, titanium oxide (TiO_2) grown on $(11\bar{2}0)$ sapphire ($\alpha\text{-}Al_2O_3$) was chosen as a model system to study the epitaxial growth since the bulk structure and physical properties of TiO_2 are well characterized. In addition, these materials exhibit little interdiffusion and no reaction at the growth temperature used in this study. The present work is part of a larger investigation of the heteroepitaxial growth of ceramic oxide films and the orientation relationship between the oxide films and their substrates [2-3]. The structure of the TiO_2/Al_2O_3 interfaces and defects in the TiO_2 films were characterized using transmission electron microscopy (TEM) and high-resolution electron microscopy (HREM), and the results of this investigation are presented in this paper.

EXPERIMENTAL

TiO_2 thin films were prepared in a cold-wall horizontal low-pressure MOCVD system. Titanium isopropoxide ($Ti(OC_3H_7)_4$) was used as metal-organic precursor. The precursor vapor was introduced into the reactor by high-purity nitrogen as carrier gas. The TiO_2 thin films were grown on $(11\bar{2}0)$ Al_2O_3 at 800 °C. Other growth parameters have been described in detail elsewhere [2].

Cross-sectional specimens for TEM and HREM investigations were prepared using a standard technique. In brief, the epitaxial surfaces of interest are glued face to face. Previously, the cross-sectional specimens have been clamped until epoxy sets to insure good bonding. The specimens are then mechanically polished and dimpled to obtain a thin area of about 15 μm in thickness at the center of a 3 mm diameter. The final specimens for TEM and HREM observations are obtained by ion thinning at liquid-nitrogen temperature. The observations were performed on a Philips 420 for electron diffraction analysis and on a Hitachi 9000 for high-resolution imaging.

RESULTS AND DISCUSSION

Electron diffraction analyses indicate that the TiO_2 thin films have the rutile structure and grow with the (101) lattice plane parallel to the substrate surface. The TiO_2 films are shown to be single crystalline, and the epitaxial relationship between the TiO_2 films (R) and their substrates (S) has been determined to be: $(101)[0\bar{1}0]_R \| (11\bar{2}0)[0001]_S$. These results are consistent with X-ray diffraction and Raman scattering data [2].

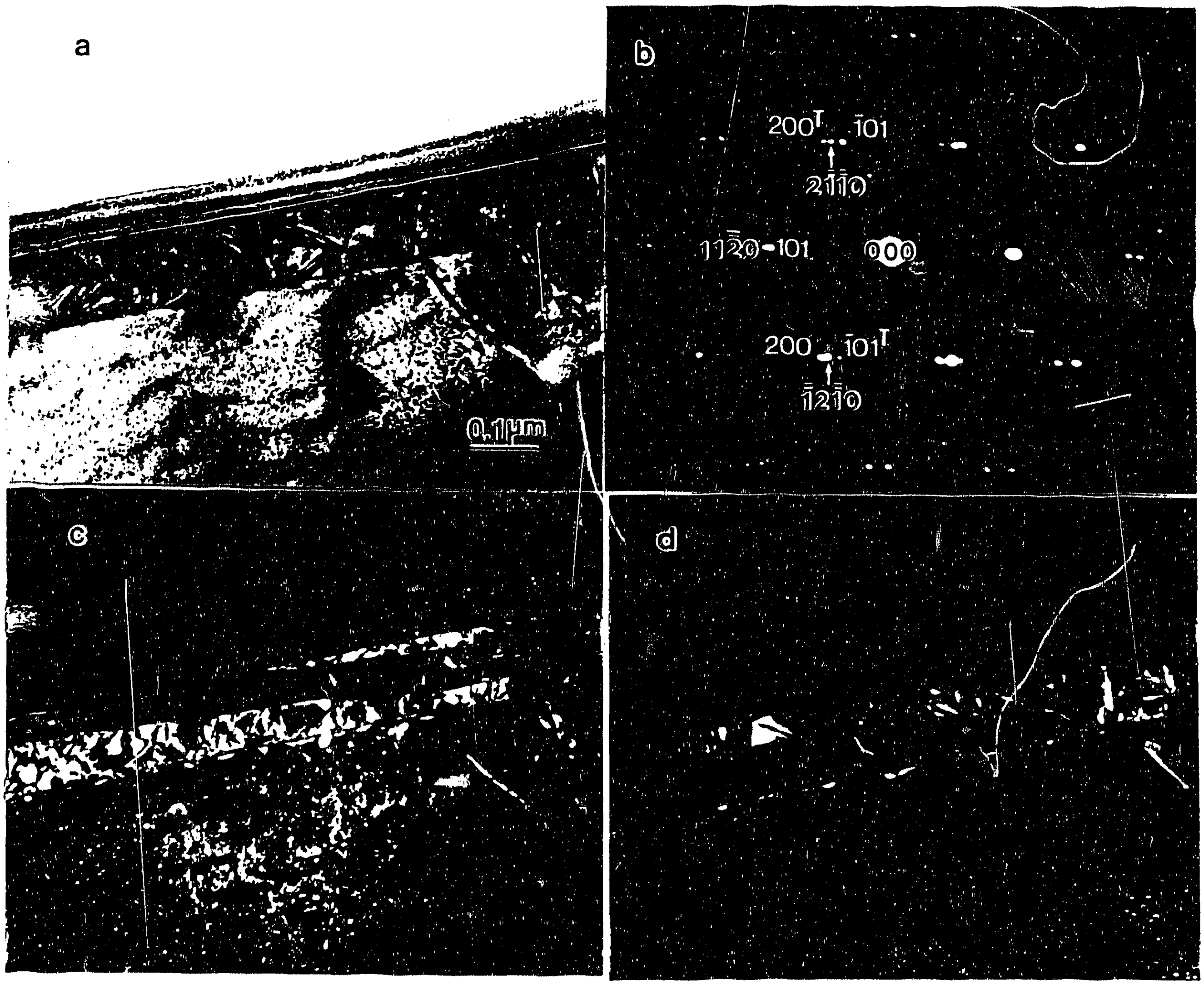

Fig. 1 a) A cross-sectional, bright-field image of a TiO2 film. b) A selected-area diffraction pattern (SADP) which consists of a $[0\bar{1}0]$ SADP of rutile and a [0001] SADP of Al_2O_3. The extra spots due to twinning are indicated by T. The twin boundaries are clearly shown in dark-field images c) and d), obtained using $(\bar{1}01)$ spot of rutile matrix and (200) twin spot, respectively.

Fig. 1(a) shows a cross-sectional, bright-field image of a TiO_2 film. It can clearly be seen that the TiO_2/Al_2O_3 interface is flat without any second phase. The film is single crystalline, and contains a number of planar defects. The defects are either parallel to the interface or inclined by about 60° with the interface. The parallel defects appear to be very sharp while the inclined ones contain a quite broad region of strain contrast. These defects cause extra diffraction spots in the selected-area diffraction pattern (SADP) shown in Fig. 1(b), which contains a $[0\bar{1}0]$ SADP of rutile and a [0001] SADP of Al_2O_3. The SADP has been carefully analyzed, and completely indexed. It has been found that the extra spots are caused by twinning in the film. The twin plane is (101) and the twinning direction is $<01\bar{1}>$. The twin boundaries have been observed using a dark-field technique [4]. The matrix of the film appears bright in Fig. 1(c) imaged using the $(\bar{1}01)$ spot from the matrix, while the twin region becomes bright in Fig. 1(d) obtained using the (200) twin spot. Therefore, it is known that the parallel defects are twin boundaries. However, it is still not clear, from the diffraction analysis, what the inclined defects are. HREM studies show that these defects have a variety of origins. They can be twin-related defects, or surface-step-induced defects. Some of the results are presented later in this paper.

By HREM it is found, in general, that when the $(101)TiO_2/(11\bar{2}0)Al_2O_3$ interfaces are viewed in the direction of $[0\bar{1}0]_R/[0001]_S$, the interfaces typically are structurally coherent in the direction of $[\bar{1}01]_R/[1\bar{1}00]_S$. This is due to the small lattice mismatch (~0.5%) at the interfaces in this direction. However, misfit dislocations are occasionally observed at the interfaces when defects, e.g. surface steps, exist at the interface. A representative HREM image of the interfaces is shown in Fig. 2(a). A large step (S) and two inclined defects (D) can be observed in the image. In addition, other defects directly located at the interface are also visible, as indicated by letters O. An enlarged image of area A in Fig. 2(b) shows that the segment of the interface consists of a structurally coherent region (C) and a region where the perfect coherence is interrupted. The interface at the coherent region can be easily recognized by viewing the image under a shallow angle, leading to a slight lattice bending across the interface. A misfit dislocation is observed at the defective region, as indicated by an arrow. A Burgers circuit has been performed around the dislocation core, indicating a Burgers vector $\mathbf{b} = [a/2,a/2,c/2]$. However, the dislocation appears to be associated with the defects at and near the interface. By close inspection of the defects, one finds that the defects are stacking faults in the film positioned one or two layers away from the interface. By a careful examination of the image, one can also recognize a monolayer step at the substrate surface, where the dislocation core is located. However, the interpretation of this defect structure and possible compositional variations should be verified by carrying out detailed image simulation, which is under active investigation. Nevertheless, it appears that the formation of the misfit dislocations is largely a consequence of accommodation of the defects rather than the misfit at the interface, since the spacing between the steps is considerably smaller than the dislocation spacing required for accommodating the misfit. Another reason is that the observed dislocations are always associated with the steps.

A small rigid-body translation at the inclined defect in area A, as shown by D in Fig. 2(b), can be recognized, when the image is viewed under a shallow angle, parallel to the interface. This defect is terminated at a lattice dislocation. It is clear that the rigid-body translation is associated with the end of the stacking fault, since the stacking fault can cause a slight lattice distortion in the rutile (tetragonal) structure. Similar rigid-body translations are also observed at the inclined defects associated with surface steps.

Twins are commonly observed in the TiO_2 thin films. Fig. 3(a) shows a HREM image of a twin boundary. It can be clearly seen that the (101) growth plane is the twin plane and the twinning direction is $[\bar{1}01]$. A schematic diagram of the twin boundary is given in Fig. 3(b) for a clear picture of twinning. The twins were also observed in the TiO_2 (rutile) precipitates, which grew from star sapphire [5]. Thus, the twins in the thin films are believed to be growth twins.

Since the twin boundaries can not terminate inside the lattice, they have to be connected with a free surface, an interface, grain boundaries, or other defects. In the TiO_2 thin films, we have observed a special defect, which is connected with the twin boundaries. The defects are structurally coherent, except for a small rigid-body translation when viewed along the [001] direction. A HREM image of such defects is shown in Fig. 4. The detailed chemical and structural configuration of the defects is still under investigation by image simulation, and the results will be reported separately.

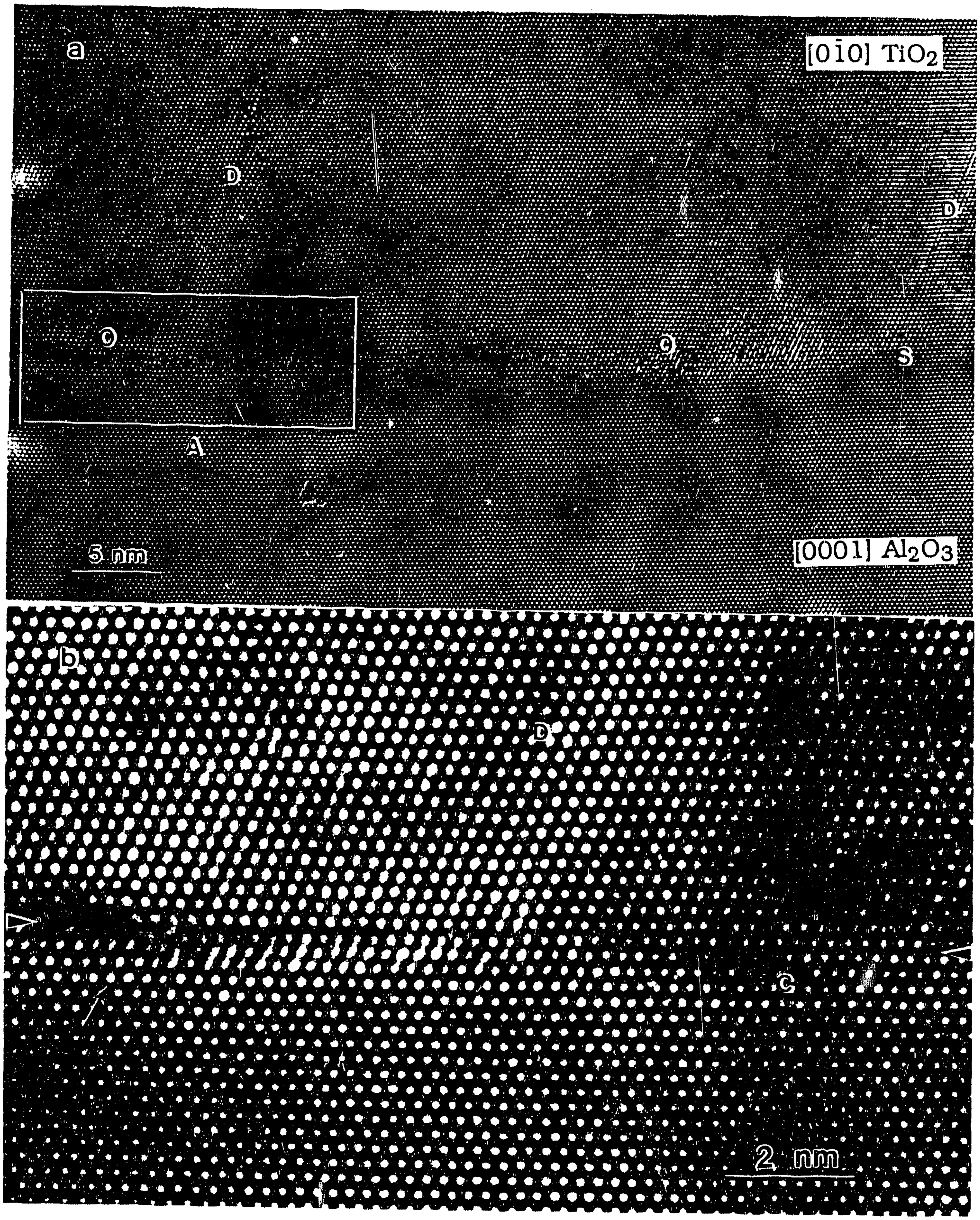

Fig. 2 a) A HREM image of a TiO_2/Al_2O_3 interface. A number of defects are visible, such as surface step (S), inclined defects (D) and other defects (O). b) Enlarged image of area A in a) shows coherent (C) and defective regions of the interface. A dislocation at the defective region is indicated by an arrow.

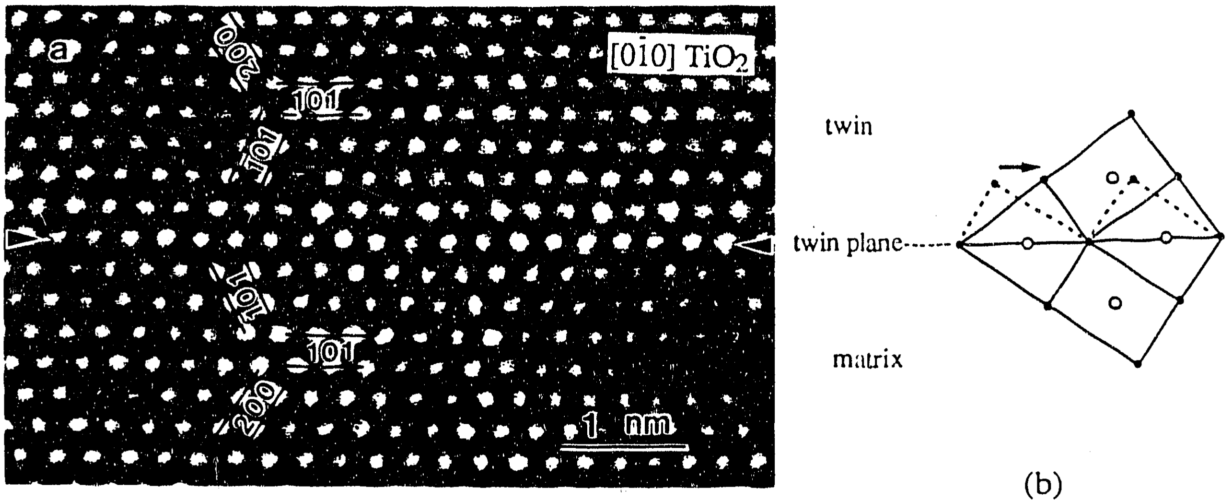

Fig. 3 a) A HREM image of a twin boundary; the twin plane is (101) and the twinning direction is $[\bar{1}01]$. A schematic diagram of the twinning is shown in b).

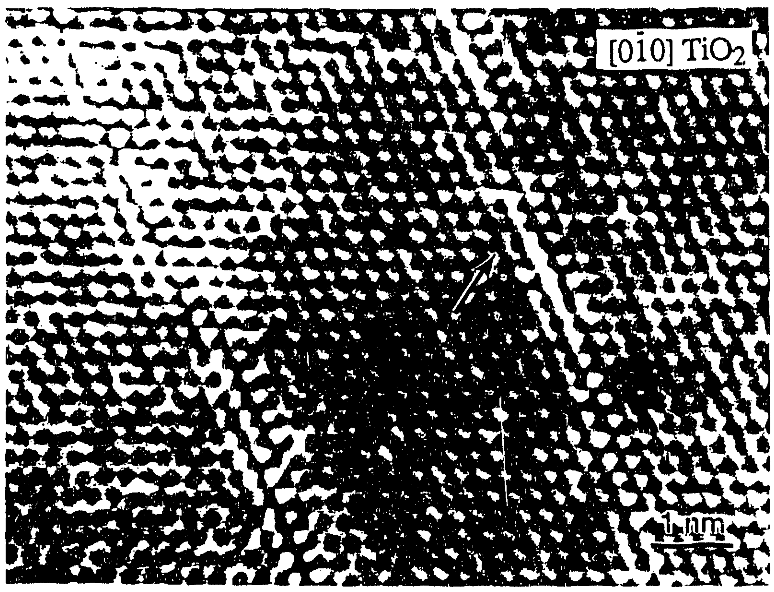

Fig. 4 A HREM image of the twin-related defects. A small rigid-body translation can be observed when viewing the defects along the [001] direction.

Crystallographic shears (CS) due to oxygen deficiency in TiO_2 [6-8] have not been observed in the present films. Blanchin *et al.* [6] carried out a extensive examination of the defect structure in slightly reduced rutile to study under what condition, the CS planes are formed in the $TiO_{2-\delta}$, while the point defects exist in the form of solid solution under other conditions. Based on their study, they provided a temperature-composition diagram for these defects in the $TiO_{2-\delta}$. According to this phase diagram, the point defect solid solution rather than the CS planes will exist at our growth temperature (800 °C) if the oxygen deficiency (δ) is less than 0.003. Therefore, it may be concluded that the oxygen deficiency in the present TiO_2 films is less than 0.003, since no CS planes have been observed in the present films by our extensive HREM study.

CONCLUSIONS

TEM and HREM studies indicate that TiO_2 thin films grown on $(11\bar{2}0)$ Al_2O_3 at 800 °C by the MOCVD technique are single crystalline rutile. The epitaxial orientation relationship between the TiO_2 thin films (R) and the substrate (S) has been found to be: $(101)[010]_R \| (11\bar{2}0)[0001]_S$. Growth twins in the films are commonly observed with the twin plane {101} and twinning direction <011>. When the interfaces are viewed in the direction of $[010]_R/[0001]_S$, most parts of the interfaces are found to be structurally coherent in the direction of $[10\bar{1}]_R/[1\bar{1}00]_S$, in which the lattice mismatch at the interfaces is about 0.5%. The misfit dislocations observed occasionally at the interface appear to be associated with the substrate surface steps, rather than the small lattice mismatch at the interfaces.

ACKNOWLEDGMENTS

This work was supported by the U. S. Department of Energy, Basic Energy Sciences - Materials Science under contract No. W-31-109-ENG-38. The use of the H-9000 in the Dept. of Mater. Sci. & Enger., Northwestern University is gratefully acknowledged.

REFERENCES

1. E. G. Bauer, B. W. Dodson, D. J. Ehrlich, L. C. Feldman, C. P. Flynn, M. W. Geis, J. P. Harbison, R. J. Matyi, P. S. Peercy, P. M. Petroff, J. M. Phillips, G. B. Stringfellow, A. Zangwill, J. Mater. Res. 5, 852 (1990).
2. H. L. M. Chang, J. C. Parker, H. You, J. J. Xu, D. J. Lam, in Chemical Vapor Deposition of Refractory Metals and Ceramics, edited by T. M. Besmann and B. M. Gallois (Mat. Res. Soc. Symp. Proc. 168, Pittsburgh, PA, 1990) pp. 343.
3. H. L. M. Chang, H. You, J. C. Parker, J. Guo, Y. Gao, and D. J. Lam, presented at the 7th CIMTEC world ceramics congress, Montecatini Terme, Italy, June 24-30, 1990 (to be published in the Proceedings).
4. P. B. Hirsch, A. Howie, R. B. Nicholson, D. W. Pashley, M. J. Whelan, Electron microscopy of thin crystals, (Butter-worths, London, 1967).
5. D. S. Phillips, A. H. Heuer, T. E. Mitchell, Phil. Mag. A 42, 385 (1980).
6. M. G. Blanchin, P. Faisant, C. Picard, M. Ezzo, G. Fontaine, Phys. Status Solidi (a) 60, 357 (1980).
7. L. A. Bursill, G. Blanchin, D. J. Smith, Proc. R. Soc. London Ser. A 384, 135 (1982).
8. L. A. Bursill and B. G. Hyde, Prog. Solid State Chem., 7 (edited by H. Reiss and J. O. McCaldin), 177 (1972).

END

DATE FILMED

01 / 31 / 91