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FIRST PRINCIPLES ENERGETIC CALCULATIONS OF SAPPHIRE (0001) AND ($1\bar{1}02$) SURFACES*

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DISCLAIMER

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Introduction

Various crystallographic faces of sapphire, the undoped single crystal α-Al_2O_3, have been widely used as substrates for depositing thin films of metals, semiconductors, and insulators for basic scientific studies and for microelectronic applications [1]. Epitaxial TiO_2 and VO_2 thin films were successfully grown on (0001), ($1\bar{1}02$) and ($11\bar{2}0$) surfaces of sapphire substrates by the Metal Organic Chemical Vapor Deposition (MOCVD) technique in our experimental program [2-3]. It was found that the substrate surfaces play a major role in determining the structures and orientations of the deposited films [2-3]. However, there exist very few experimental or theoretical studies concerning the atomic structures and terminations of sapphire (0001) and ($1\bar{1}02$) surfaces.

The present paper is one of our theoretical efforts in parallel with the experimental program to gain microscopic understandings of the effects of substrate structure on the epitaxial relationship and the overlayer lattice structure of thin film deposition. The first principles energetic calculations on the complicated surfaces like sapphire can now be carried out because of the recent development in our computer programs and availability of high speed super computers. The phase *first principles* means that the calculations are based only on the known physical laws and approximations, and are free of any adjustable parameters. A complete discussion of the theoretical formalism has been presented in our previous works [4-5].

Results and Discussions

For the (0001) surfaces, we found that cleaving at plane A shown in Fig. 1, which produced two symmetry equivalent surfaces terminated with an Al layer, has a cleavage energy of 9 eV per unit mesh area (19.64 A^2) or 7.4 J/m^2. The cleavage energy is 17 eV per unit mesh area for cleaving at plane B, which produced two surfaces with different terminations. Therefore, based on the energetic consideration the (0001) surface cleaved from the sapphire single crystal will be terminated with an Al top layer.

For the $(1\bar{1}02)$ surfaces, we found that cleaving at the plane A, which produced two symmetry equivalent surfaces terminated with an O layer shown in Fig. 2 has a cleavage energy of 9 eV per unit mesh area ($24.42A^2$) or 5.9 J/m^2. The cleavage energies are 22 and 17 eV for cleaving at the other two planes B and C shown in Fig. 2, respectively. Therefore, the $(1\bar{1}02)$ surface is terminated with an O layer.

The cleavage energies given above were calculated while the nuclei are fixed at their bulk positions. We did not allow for local relaxation and reconstruction of the surface. This form of rearrangement can affect the calculated cleavage energies. However, recent energetic calculations on the relaxation of the (0001) surface shown that the relaxation energy is less than 1 eV per unit mesh area. In view of the ~8 eV advantage in the cleavage energy per unit mesh area, it is unlikely that the surface relaxation can reverse the trends given above.

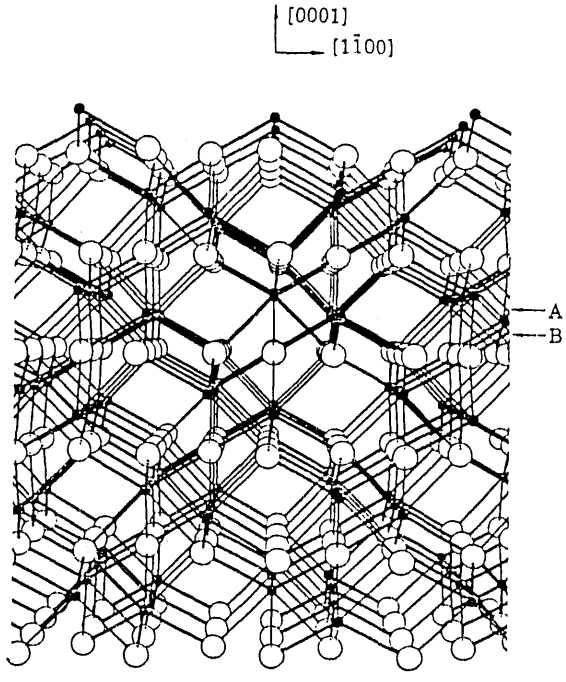

Fig. 1. Side view of sapphire (0001) surface along the $[11\bar{2}0]$ direction. The two arrows labeled A and B indicate the two different (0001) cleaving planes. The open and filled circles label O and Al atoms, respectively.

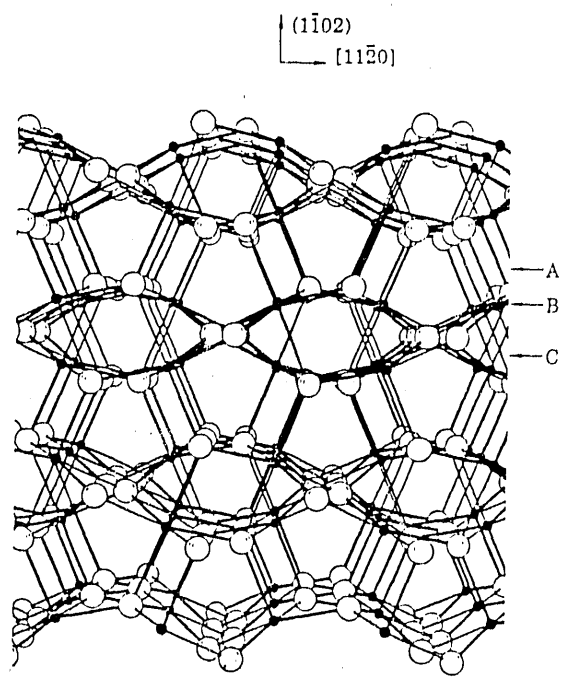

Fig. 2. Side view of sapphire $(1\bar{1}02)$ surface along the $[\bar{1}101]$ direction. The three arrows labeled A, B, and C indicate the three different $(1\bar{1}02)$ cleaving planes. Same conventions as Fig. 1.

Fracture surface energies, which are half of the cleavage energies, of several crystallographic planes of sapphire have been measured by several investigators using different experimental techniques. The reported energy values depend on the crystallographic plane of fracture, the test temperature, sample conditions and experimental techniques. Congleton *et al.* reported a fracture surface energy of 24 J/m^2 for the $(1\bar{1}02)$ plane fractured at -196°C using center-notched plate tension specimen [6]. Wiederhorn reported a fracture surface energy of 6.0 J/m^2 for the same surface at 25°C obtained by a double-cantilever-cleavage measurement [7]. Wiederhorn's reported value was derived from averaging all the measured values of twenty samples. Kingery obtained a fracture surface energy of ~1 J/m^2 using equilibrium interfacial angle measurements at 1850°C [8]. The fracture surface energy thus obtained only represents an average value for all the crystallographic planes of sapphire. Wiederhorn was not able to obtain a fracture surface energy for the (0001) plane because the crack propagated on several lower energy fracture surfaces instead of the (0001) plane in the fracture experiment. He gave an estimated value of ~40 J/m^2 for the fracture surface energy of (0001).

The calculated fracture surface energy of 3.0 J/m^2 for the $(1\bar{1}02)$ plane is lower than the experimental values reported by Wiederhorn and Congleton *et al.* The average fracture surface energy of 6.0 J/m^2 for the $(1\bar{1}02)$ plane obtained by Wiederhorn seems to be more reliable because this average value and the standard deviation of 0.6 J/m^2 were derived from 21 determinations of annealed and as-received single crystal specimens. Our calculated value is about half of the experimental value of Wiederhorn. The calculated fracture surface energy of 3.7 J/m^2 for the (0001) plane is much lower than the estimated value of Wiederhorn. The fact that the calculated fracture surface energy for the (0001) plane is higher than that of the $(1\bar{1}02)$ seems to follow the experimental trend.

In conclusion, the energetic calculations indicate that the low energy (0001) surface is terminated with an Al layer while $(1\bar{1}02)$ is terminated with an O layer.

Acknowledgments

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References

[1] E. Dorre, *Alumina: Processing Properties and Applications,* Springer-Verlag, New York (1984).

[2] H.L.M. Chang, H. You, J. Guo, and D.J. Lam, "Epitaxial TiO_2 and VO_2 films prepared by MOCVD," *Appl. Surf. Sci.* **48/49** (1991) p. 12.

[3] H.L.M. Chang, Y. Gao, J. Guo, C.M. Foster, H. You, T.J. Zhang, and D.J. Lam, "Heteroepitaxial growth of TiO_2, VO_2, and TiO_2/VO_2 multilayers by MOCVD," *Journal de Physique,* **1** (1991) C2-953.

[4] J. Guo, D.E. Ellis, and D.J. Lam, "First-principles calculations of electronic structure of sapphire: Bulk states," *Phys. Rev.* **B45** (1992).
[5] J. Guo, D.E. Ellis, and D.J. Lam, "Electronic structure and energetics of sapphire (0001) and (1$\bar{1}$02) surfaces," to be published.
[6] J. Congleton, H. Hardie, R.N. Perkins, and N.J. Petch, in *Studies of the Brittle Behavior of Ceramic Materials*, ed. N.M. Parikh, Tech. Rept. ASD-TR-61-628, Part III; Contract AF 33(657)-10697 (1964), pp. 133-174.
[7] S.M. Wiederhorn, "Fracture of Sapphire," *J. Am. Ceram. Soc.* **52** (1969), p. 485.
[8] W.D. Kingery, "Metal-Ceramic Interactions: IV," *J. Am. Ceram. Soc.* **37** (1954) p. 42.

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