First phase selection during interfacial reactions in oxide systems

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Interfacial solid state reactions are important in fundamental investigations and in industrial applications. Because of wide application in microelectronics, thin film solid state reactions between metal (thin film) and silicon (substrate) are well studied. It has been well established that the phases during such reactions appear sequentially and this behaviour is different from bulk reactions where the phases form simultaneously. Correspondingly, various reasons and a number of models have been given in the literature, including kinetic [1], thermodynamic [2] and nucleation-controlled models [3]. However, factors influencing the first phase selection in oxide thin film systems have not been considered so far. In the present work, we have tested the above models for their ability to explain first phase selection in oxide systems. For this purpose, interfacial reactions in model experiments [4,5] in the oxide systems like SrO-TiO_2, CaO-TiO_2 and MgO-TiO_2 were studied.

One-side polished (100) and (110) surfaces of commercial TiO_2 (rutile) single crystals were used as substrate materials. The substrates were subjected to either SrO, CaO or MgO vapour as described in Reference [4]. The phases present in the thin films after growth were investigated by transmission electron microscopy (TEM) as well as by X-ray diffraction (XRD, Philips X'Pert MRD) [4]. TEM investigations were carried out in a Philips CM 20 T whereas a Tecnai F30 STwin was applied for high-resolution TEM (HRTEM).

In the systems SrO-TiO_2 (Figure 1(a)) and CaO-TiO_2 (Figure 1(b)) there are several possible reaction compounds. The two phases $SrTiO_3$ and TiO_2 form a eutectic at 1440°C while $CaTiO_3$ and TiO_2 form a eutectic at 1450°C. According to the thermodynamic model [2], the $SrTiO_3$ and $CaTiO_3$ phase will be the first phase to grow in the systems SrO-TiO_2 and CaO-TiO_2, respectively. Figures 2(a) and 2(b) are HRTEM images of samples prepared by a reaction between SrO (vapour) and (110) TiO_2 and CaO (vapour) and (110) TiO_2, respectively. Figure 2(a) shows the formation of the $SrTiO_3$ phase as the first phase after the reaction while Figure 2(b) shows the formation of the $CaTiO_3$ phase as the first phase after the reaction. These results are in good agreement with the thermodynamic model.

In the system MgO-TiO_2 (Figure 1(c)) there are three possible reaction products: $MgTi_2O_5$, Mg_2TiO_4 and $MgTiO_3$. According to the thermodynamic model [2], the $MgTiO_3$ will be the first phase to grow in this system. However, previous investigations of vapour-solid reactions in the system MgO-TiO_2 using (100) MgO substrates showed topotaxial formation of Mg_2TiO_4 on MgO [6]. Consequently, the thermodynamic model is not suitable for the system MgO-TiO_2. Figure 3(a) is a HRTEM image of a sample prepared by a reaction between MgO (vapour) and (100) TiO_2. The TEM image shows the formation of $MgTiO_3$ as the first phase after the reaction (also Figure 3(b)). The growth of $MgTiO_3$ on TiO_2 is topotaxial (Figure 3(c)). Thus, the choice in the nucleation and growth of the kind of first phase in this system is defined by the crystallography of the substrate serving as reactant.

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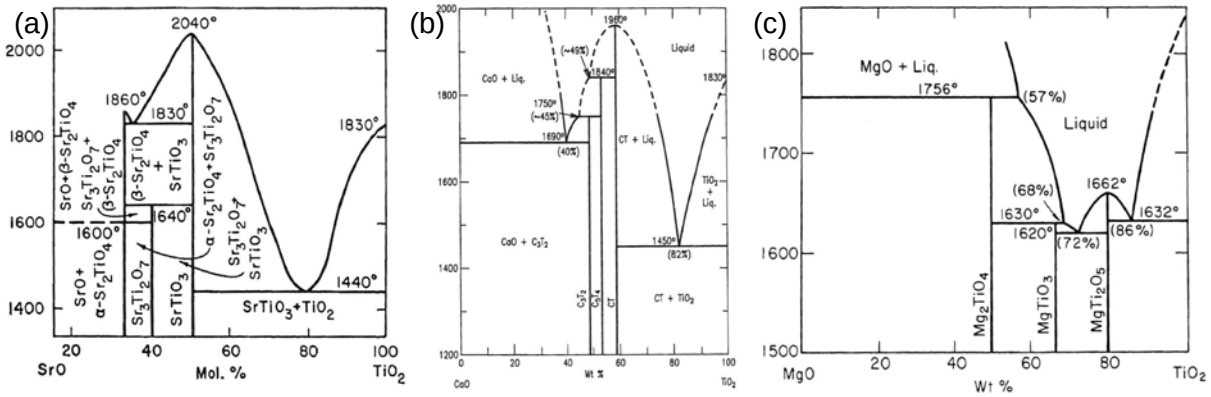

Figure 1. Phase diagrams of the systems: (a) SrO-TiO_2, (b) CaO-TiO_2. C=CaO, T=TiO_2 and (c) MgO-TiO_2. The diagrams were taken from the book Phase diagrams for ceramists, ed. by M.K. Reser, American Ceramic Society, Columbus, OH, 1969.

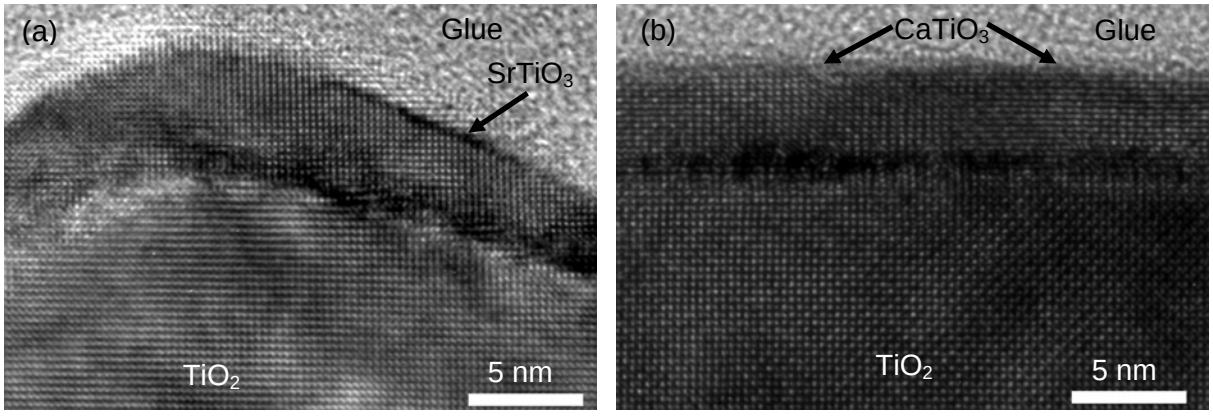

Figure 2. (a) HRTEM image of the $SrTiO_3/TiO_2$ reaction front in $[001]\,SrTiO_3 \| [1\bar{1}0]\,TiO_2$ viewing direction. The sample was reacted at 700°C for ~39 min. (b) HRTEM image of the $CaTiO_3/TiO_2$ reaction front in [110] $CaTiO_3$||[001] TiO_2 viewing direction. The sample was made at 700°C for ~7 min.

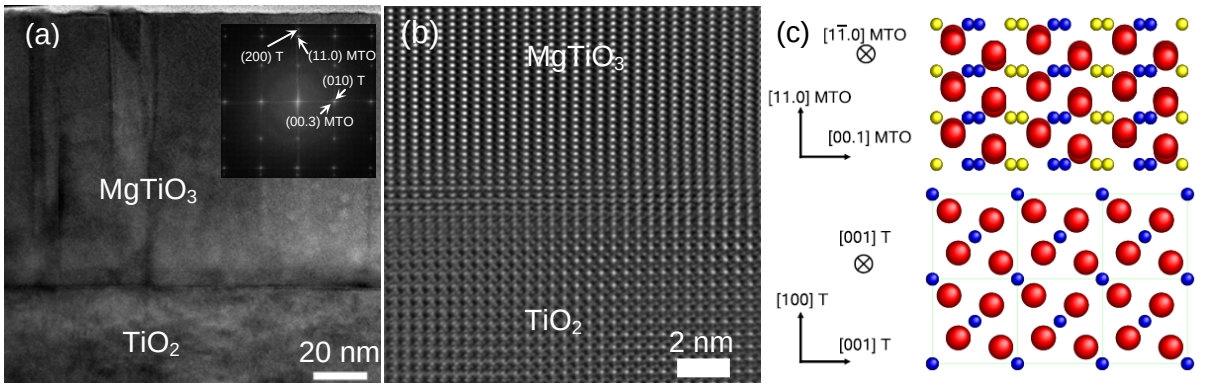

Figure 3. HRTEM image of the $MgTiO_3$ (MTO)/TiO_2 (T) reaction front. The sample was reacted at 600°C for ~35 min. The inset shows a fast Fourier transform image of Figure (a). (b) Computer-processed image of the $MgTiO_3/TiO_2$ interface. Viewing direction is $[1\bar{1}0]\,MgTiO_3 \| [001]\,TiO_2$. (c) Schematic cross-section representation of the interface between the $MgTiO_3$ phase and TiO_2 (rutile) substrate.

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