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Nanostructural Characterization of Interfaces of thin films of $\text{YBa}_2\text{Cu}_3\text{O}_7$ with various kinds of substrates.

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Abstract

The interfaces between thin film of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and various kinds of substrates were studied by high resolution electron microscopy. In the case of SrTiO_3 as substrate, the interface contains no other phases and atomic stacking sequence was found to be: bulk(SrTiO_3)- SrO - TiO_2 - BaO - CuO_2 - Y - CuO_2 - BaO - CuO -bulk(YBCO). Misfit dislocations in the $\text{YBa}_2\text{Cu}_3\text{O}_7$ film were mostly found to extend only up to first few unit cells of $\text{YBa}_2\text{Cu}_3\text{O}_7$. With MgO as substrate the first YBCO layer is the CuO layer, regardless whether the grain boundary is clean or contains a thin amorphous layer. In case of a clean grain boundary some strain occurs near the grain boundary, in particular in the MgO lattice. The interface of a YSZ substrate contains almost always an extra phase, which is probably BaZrO_3 . The first YBCO layer is also in this case a CuO layer. On the substrate NdGaO_3 also a extra phase can occur, which is closely related to $\text{YBa}_2\text{Cu}_3\text{O}_7$. This phase misses two layers of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ structure, resulting in a composition YBaCu_2O_5 . The strain observed in the YBCO layer appears to decrease along the series SrTiO_3 - NdGaO_3 -YSZ- MgO .

1. Introduction

YBCO thin films grown on various substrates such as SrTiO_3 [1,2,3], LaAlO_3 [4], YSZ [5], Al_2O_3 [6], MgO [7] and NdGaO_3 [8] have been studied with transmission electron microscopy (TEM) by a number of groups. Mostly intermediate resolution TEM was applied to check the quality of the thin films by determining the amounts of defects, outgrowths, and second phases [9,10]. One of the interests is the actual sequence at the interface. Establishing this sequence can be relevant to the layer by layer growth and for the preparation of very thin YBCO layers either as a single film or as a component of a multilayer (for instance YBCO/ SrTiO_3 multilayer).

Only a few electron microscopy papers giving information on the interface at an atomic scale have been published [11,12]. Ramesh et al [12] have reported that the interface structure of c-axis

oriented films grown on SrTiO_3 and LaAlO_3 is governed by the minimization of the interfacial energy between the first layer of the film and the surface layer of the substrate. They claimed that the first layer of the c-axis oriented YBCO films grown on SrTiO_3 appears to be either a BaO layer or a CuO_2 plane depending on whether the surface layer of substrate is a TiO_2 layer or a SrO layer. On the other hand, for LaAlO_3 substrate, they reported that the first layer of YBCO is always a CuO chain layer. On the other hand, Basu et al [12] have reported that both BaO layer and CuO layer occur as the first layer of YBCO for this substrate.

In this paper we review the results of several of our studies on the interface of YBCO with the substrates SrTiO_3 [13], YSZ [14], MgO [15] and NdGaO_3 [16], and on (001) grain boundaries in polycrystalline YBCO.

2. Experimental

YBCO thin films were prepared using different techniques e.g. thermal evaporation, sputtering and laser ablation. Cross-section specimens for transmission electron microscopy were first mechanically grinded directly down to a thickness less than 10 μm . A specimen was mounted on a slot-hole (1x2 mm) copper grid. During ion-milling (GatanTM Duo Mill 600), the specimen was ion milled from one side without rotation of the sample. By using this method, the substrate is used as an ion beam blocker to minimize preferential milling of the YBCO film. The ion milling conditions are acceleration voltage 4.5 kV, gun current 0.5 mA, ion milling angle 15° and no liquid nitrogen cooling. When color fringes (thin film reflection) appear on the edge of the specimen an ion polishing procedure is applied to thin the specimen to electron transparency with the condition: acceleration voltage 3 kV, gun current 0.3 mA, ion milling angle 8°. This specimen preparation technique provides large thin areas

which enables checking of the thin film quality by HREM over an area of more than 200 μm . More details of the sample preparation will be reported elsewhere [17].

Electron microscopy was performed with a Philips CM30ST electron microscope operating at 300 kV and equipped with side-entry 25°/25° tilt specimen holder. Some of the experiments were carried out with this microscope after it was equipped with a Field Emission Gun.

The HREM images were recorded at a defocus of about -40 nm at which all cations are imaged as dark dots and/or at about -80 nm where the cations are imaged as white dots. A number of experimental HREM images were averaged over a number of unit cells along the interface to improve the ability to measure the spacings and the positions and intensities of the different dark and bright dots. Images were digitized with about 50 pixels per nm. These images were noise reduced by averaging each pixel over itself and its 8 neighbors. Next the images were averaged over a number of unit cells along the interface.

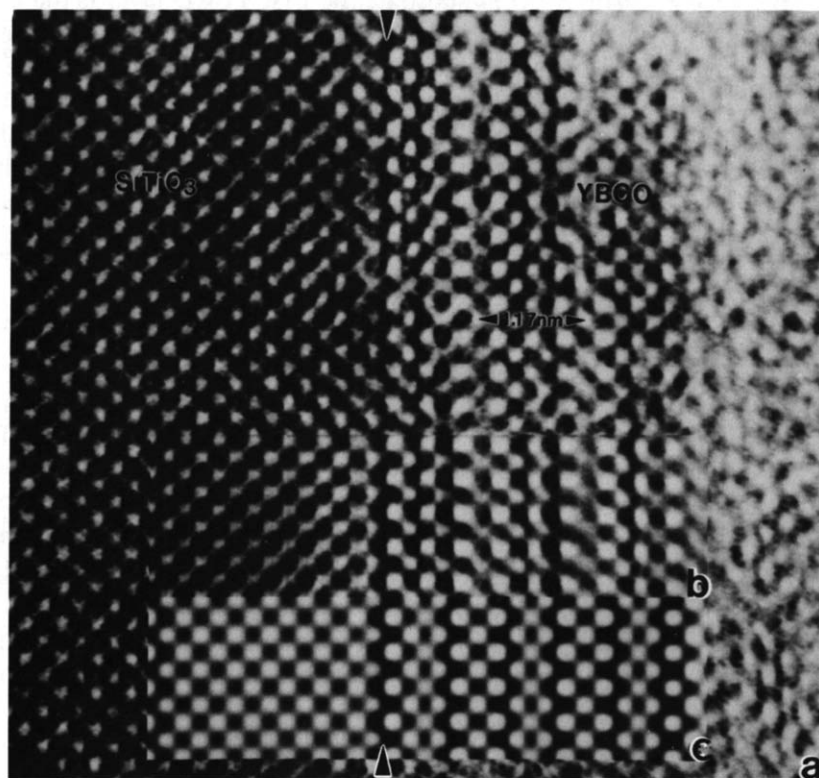


Fig. 1 [010] HREM image of a YBCO/SrTiO₃ interface, showing a stacking sequence as bulk-SrO-TiO₂-BaO-CuO₂-Y-CuO₂-BaO-CuO-bulk. The interface is indicated by two solid black arrow-heads. (a), (b), and (c) give the experimental HREM image, the averaged image obtained by averaging over 8 units along the interface and the calculated image for a thickness of 2nm and a defocus of -80nm.

3. Results

3.1 SrTiO_3 as Substrate

HREM performed on the interfaces between thin film of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and SrTiO_3 (see Fig 1) showed that the interface contains no other phases and atomic stacking sequence was found to be: bulk-SrO-?-BaO-CuO₂-Y-CuO₂-BaO-CuO-bulk. From the HREM image it could not be determined whether the ? mark is a TiO_2 layer or a CuO_x layer. HREM of the surface of a crushed SrTiO_3

single crystal indicated that the surface atomic layer is always the TiO_2 layer [18,19,20]. Therefore the stacking sequence must be: bulk-SrO- TiO_2 -BaO-CuO₂-Y-CuO₂-BaO-CuO-bulk.

In the case of a single unit cell step on the surface of the SrTiO_3 substrate, on both sides of the step the stacking sequence is SrO- TiO_2 -BaO-CuO₂-Y-CuO₂-BaO-CuO, resulting in a $c/3$ antiphase boundary at the step.

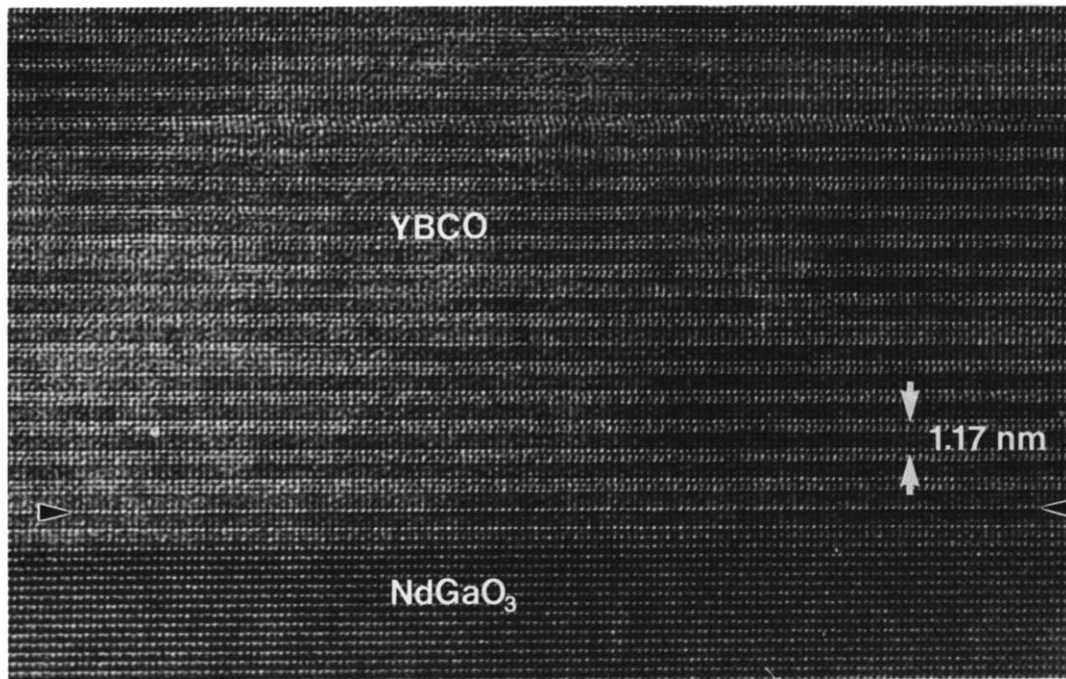


Fig.2 [110] HREM image of a YBCO/ NdGaO_3 interface, showing the presence of a second phase at the interface. The interface phase is probably YBaCu_2O_5 ; it is indicated by black arrows.

3.2 NdGaO_3 as Substrate

HREM on the interfaces between thin film of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and NdGaO_3 showed that the interface contains no amorphous phase. However, in about 50% of the area another crystalline phase could be observed. This other crystalline phase is related to $\text{YBa}_2\text{Cu}_3\text{O}_7$ and differs from the structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$ in the absence of two layers (see Fig 2). Image calculations were carried out to determine the nature of this additional phase at the interface. A good lattice match can be obtained for the model

assuming the interface phase has the composition YBaCu_2O_5 , with the layer sequence: bulk(substrate)- NdO-GaO_2 --(BaO-CuO_2 -Y-CuO₂)_n-BaO-CuO₂-Y-CuO₂-BaO-CuO-BaO-bulk(film). The GaO_2 layer at the interface could be a CuO_x layer as well as a $(\text{Ga,Cu})\text{O}_x$ layer. In [100] or [010] micrographs this layer shows a 0.77 nm repetition period (a doubling of the a or b axis of YBCO), whereas no doubling is observed in the [110] orientation. Since NdGaO_3 shows also this 0.77 nm period it is most likely that the layer is

part of the NdGaO_3 lattice. Presently image calculations are performed to determine the composition of this layer.

Single unit cell steps on the surface of NdGaO_3 result in $c/3$ antiphase boundaries, similar to the effect of steps on a SrTiO_3 substrate.

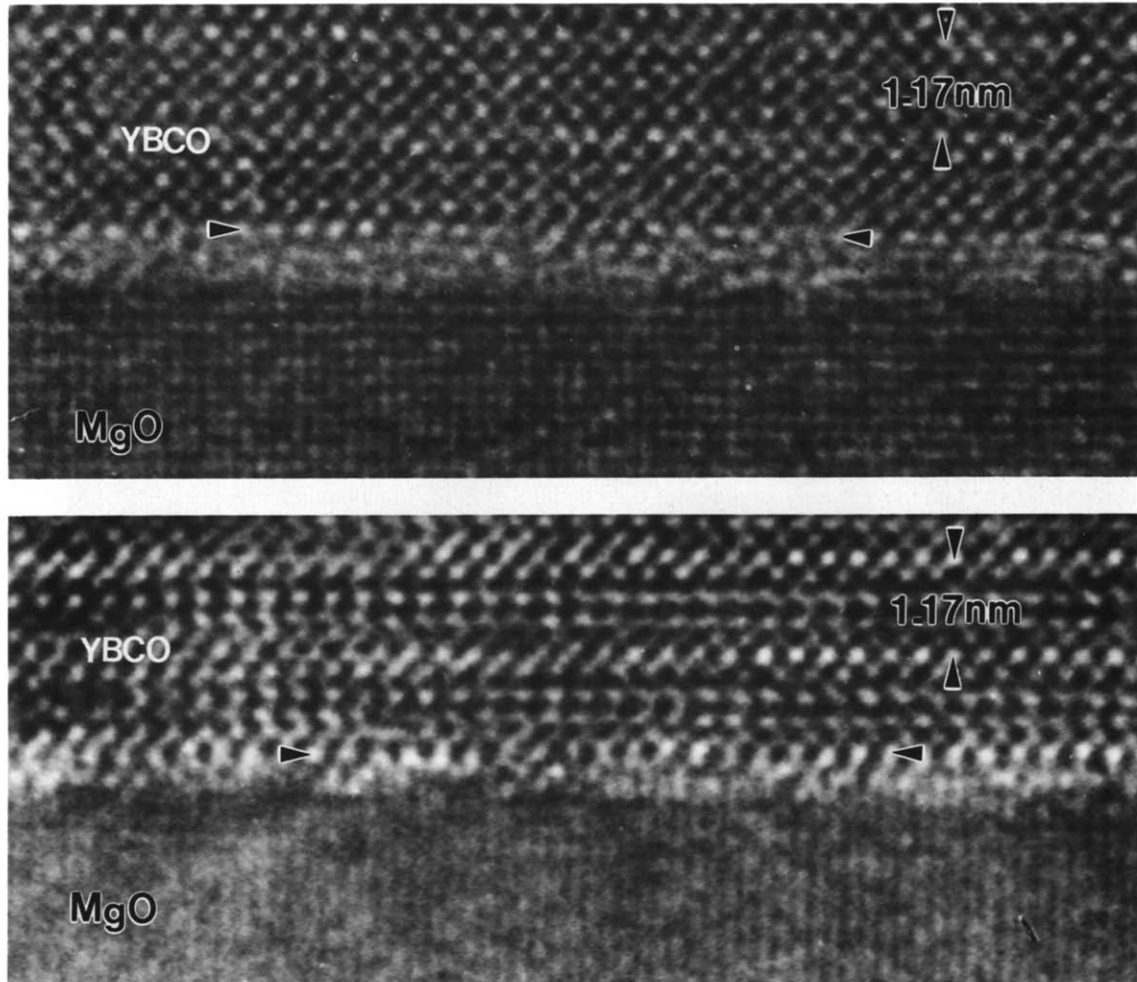


Fig. 3 The [010] or [100] HREM images of a YBCO/MgO interface, showing (a) the presence of an amorphous layer at the interface and (b) a clean interface. In both cases the terminating YBCO layer is the CuO layer (indicated by arrows). In (b) variation in the contrast can be seen in the MgO lattice along the interface, indicating the presence of strain due to the misfit between the lattices of YBCO and MgO .

3.3 MgO as Substrate

HREM performed on the interfaces between thin film of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and MgO showed (see Fig 3) that the interface can be either clean or contain a thin amorphous layer, being several atomic layers thick. If an amorphous phase is present the interface contains no strain, which is also to be expected because the effect of lattice mismatch is annihilated by the amorphous layer.

The amorphous phase was probably present on the surface of the MgO substrate when the YBCO film growth started, since it cannot be the result of a reaction of the YBCO lattice and the MgO after formation of the film because in that case the first YBCO layer (the CuO layer) should be absent. Still the amorphous layer does not result in the absence of epitaxial growth. This could be due to the tendency of the YBCO film to grow epitaxial,

even on an amorphous region or the epitaxial growth occurs due to this type of growth in nearby areas containing a clean YBCO/MgO interface.

Steps in the surface of MgO do not result in antiphase boundaries, which is contrary to the

effect of steps in SrTiO_3 or NdGaO_3 . This indicates that the interaction between YBCO and SrTiO_3 is much stronger than that between YBCO and MgO.

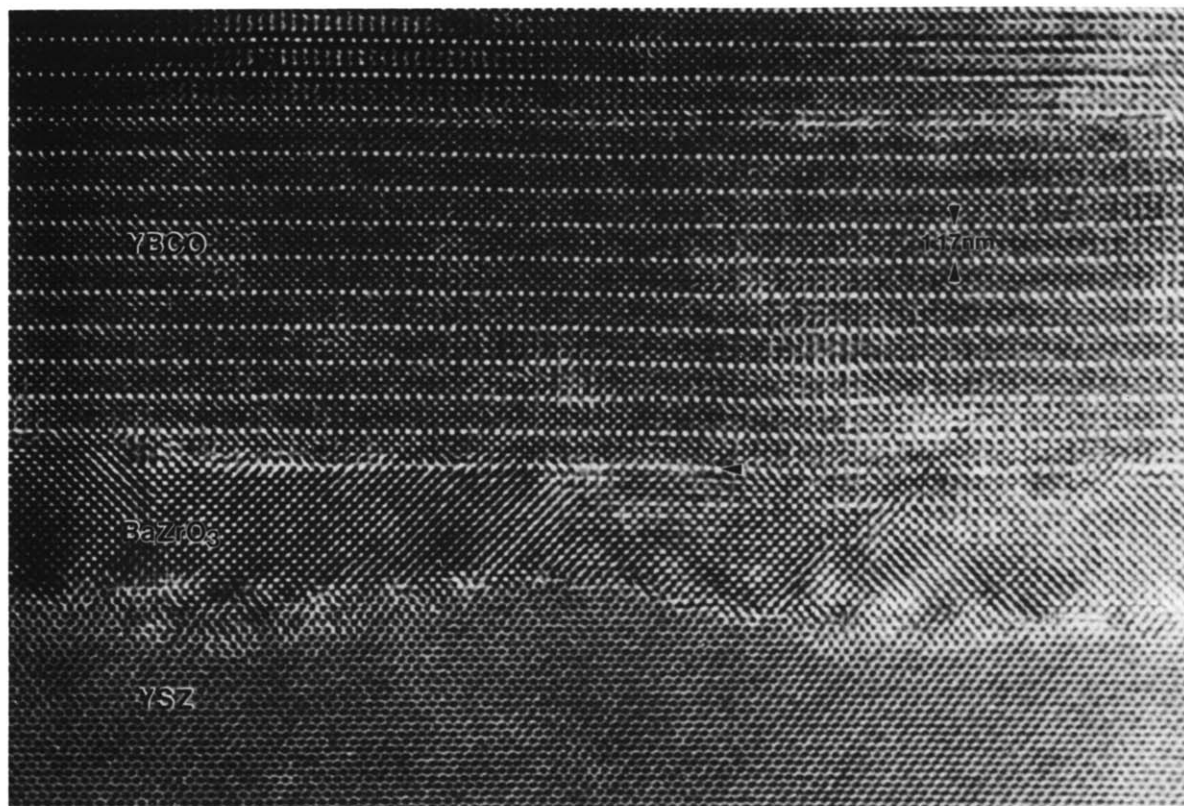


Fig. 4. HREM image of a YBCO/YSZ interface with the YBCO lattice in [100] or [010] orientation, showing a presence of another crystalline phase at the interface (BaZrO_3). Most of the lattice mismatch between the YBCO lattice and the YSZ lattice is compensated by dislocations in the BaZrO_3 phase at the interface.

YSZ as Substrate

HREM performed on many thin films of YBCO on Yttrium Stabilized Zirconia (YSZ) show every time the presence of an additional crystalline phase at the interface. The thickness of this additional phase varies from sample to sample and varies also within a given specimen. In Fig. 4 an example is given of a rather thick additional layer. The lattice parameters of this phase suggest it to be BaZrO_3 . This is in accordance with local element analysis using a spot size of about 1.5 nm.

Compared to the YBCO/ SrTiO_3 system the

YBCO films on YSZ contain much less defects, indicating a smaller strain in the YBCO film. On the other hand, the intermediate BaZrO_3 lattice contains many defects; it is in fact rather difficult to find an area as "perfect" as the one shown in Fig. 4. This indicates that most of the strain due to the misfit between the YSZ and YBCO lattices is compensated by misfit dislocations in the intermediate BaZrO_3 slab.

Single unit cell steps on the YSZ surface do, in general, not lead to antiphase boundaries as for SrTiO_3 and NdGaO_3 , but are smoothed by the formation of the intermediate BaZrO_3 slab. Large steps in the YSZ surface lead mostly to a locally

different orientation of the film. The presence of an amorphous phase on the surface was found to lead to a film, which its c axis perpendicular to the substrate surface. Thus if the amorphous surface is inclined with respect to the (110) plane of YSZ the

c axis of the film does not coincide with the [110] direction of the YSZ lattice, e.g. the absence of epitaxial growth.

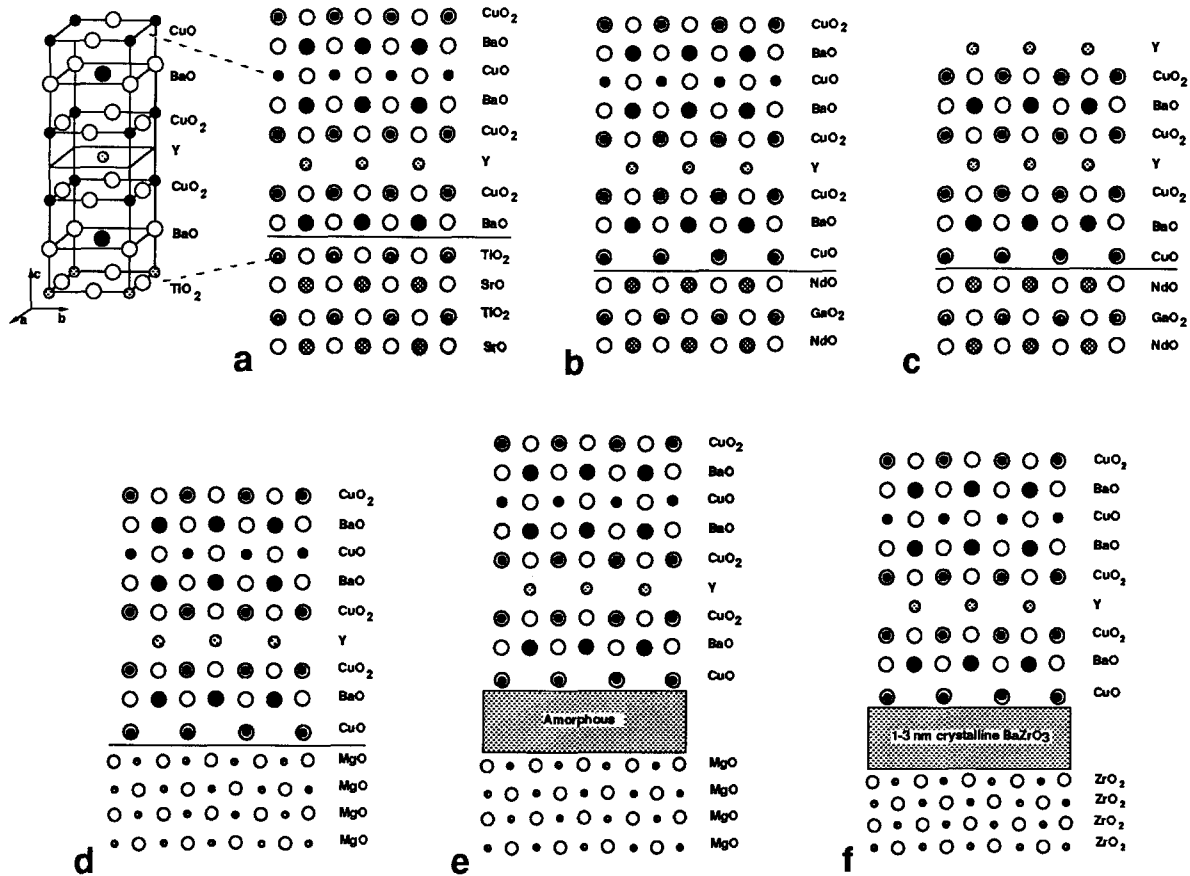


Fig. 5. Schematic representation of the interfaces between YBCO and the substrates (a) SrTiO₃, (b) and (c) NdGaO₃, (d) and (e) MgO and (f) YSZ. (b) and (c) differ in the presence of an intermediate phase YBaCu₂O₅, being four atomic layers thick. (d) and (e) represent the observed two types of YBCO/MgO interfaces.

4. Discussion

The terminating layer of the YBCO lattice was found to depend on the substrate. With SrTiO₃ as interface the YBCO lattice terminates as CuO₂-BaO-interface. HREM shows that a TiO₂ layer is present at the (001) surface layer of (crushed) SrTiO₃ [18]. With TiO₂ as the layer on which the YBCO lattice starts to grow the most logical first YBCO layer is a BaO layer [19]. This is consistent with the HREM observations. In the case of NdGaO₃ as substrate the interface differs

from that of SrTiO₃. The terminating layer of NdGaO₃ has not yet been determined with HREM. In the case the terminating layer is the NdO layer, the most logical first YBCO layer is the CuO layer. Most HREM images are consistent with this assumption, but also deviations from this stacking seem to occur. This will be subject to further research. It should be noted that the scattering potential of Nd is not significantly different from that of Ba, which does not allow a good discrimination between GaO₂-BaO-CuO-BaO-film and GaO₂-NdO-CuO-BaO-

film. In the case of MgO and YSZ as substrates the terminating YBCO layer is the CuO layer. In both cases there is no clear stacking of layers across the interface, making it not useful to determine the stacking sequence at some part of the interface. The interruption film-BaO-CuO is also found at (001) grain boundaries in polycrystalline YBCO [21,22], and at the YBCO/amorphous interface [23].

These results indicate that when YBCO has relatively little interaction with the opposite material on the interface the terminating layer will be the CuO layer. Such kind of termination does not occur for the YBCO/SrTiO₃ interface. This must be due to a rather strong interaction between YBCO and SrTiO₃. Also for NdGaO₃ a strong film/support interaction is expected, but due to the different layer at the surface (with respect to the situation with SrTiO₃) the first YBCO layer is probably still a CuO layer.

YBCO and SrTiO₃ have a reasonably (<2%) good lattice match, but the lattice match between YBCO and NdGaO₃ is better. As a result of the reasonable but not perfect lattice match between YBCO and SrTiO₃, the strong interaction between the lattices, the different thermal expansions and the tetragonal/orthorhombic phase transformation of YBCO, the YBCO film on SrTiO₃ contains a lot of defects and residual strain. These defects and strains are considerably less present in the YBCO film grown on NdGaO₃, probably due to the better lattice match. Defects and strains are even less present in MgO and YSZ. In the latter case most of the misfit is compensated by the formation of defects in the intermediate BaZrO₃ layer present at the interface. In the case of MgO there is relatively little interaction between the MgO and YBCO lattices, even when there is no amorphous phase at the interface, thus resulting in very little strain in the YBCO lattice.

HREM images indicate that the perovskite-like lattice continues across the YBCO/SrTiO₃ and YBCO/NdGaO₃ interfaces, resulting in a continuation of the (Ti or Ga,Cu), (Sr or Nd,Ba/Y) and O sublattices. This implies that the Cu atoms in YBCO occupy the Ti,Ga sublattice of the corresponding SrTiO₃ or NdGaO₃ lattices and the Ba and Y atoms the Sr,Nd sublattice. This is the obvious reason for the strong YBCO/substrate interactions for the YBCO/SrTiO₃ and YBCO/NdGaO₃ systems. Since HREM has shown that the (001) surface

atomic layer of SrTiO₃ is TiO₂, it is obvious that the YBCO film starts with either a BaO layer or a Y layer. In SrTiO₃, both the SrO layer and TiO₂ layer are charge balanced. BaO, Y, and CuO₂ layers have residual charge 0, +3, and about -1.5 respectively. The interface with BaO as the terminating layer is expected to be more stable than that with Y, since Y(+3) has a residual charge +1.5. This is in agreement with the absence of any observation of Y as the termination layer at grain boundaries in bulk materials or at interfaces of YBCO with any substrate. Therefore, the most likely first layer of YBCO on SrTiO₃ is BaO. A similar argument can be given for the YBCO/NdGaO₃ interface. Depending on whether the surface layer of NdGaO₃ is a NdO or a GaO₂ layer the most likely first layers are CuO_x layers or BaO layers respectively. Because the GaO₂ layer is +1 charged it cannot be excluded that the Y layer is adjacent to the GaO₂ layer. However, this last geometry has not yet been observed.

Steps of several atomic layers on the substrate result in a c/3 antiphase boundary for the YBCO/SrTiO₃ and YBCO/NdGaO₃ systems, where mostly single unit cell steps of two atomic layers do occur. This is obviously the result of a rather strict stacking sequence at the interface. At both sides of the step YBCO grows, starting with the BaO layer. This leads to a misfit of the two lattices adjacent to the step. Since the step in the substrate surface is 2 atomic layers high, the misfit is also two atomic layers, which is called a c/3 antiphase boundary.

Misfit dislocations in the YBCO film are only observed near a step in the YBCO/SrTiO₃ system. If the SrTiO₃ substrate is completely flat the dislocations end a few unit cells away from the interface. For the YBCO/NdGaO₃ system the defect density in the YBCO film appears to be higher close to the interface.

5. Conclusions

At the YBCO/SrTiO₃ and YBCO/NdGaO₃ interfaces a continuation of the lattice occurs, based on the continuation of the (Ti or Ga,Cu), (Sr or Nd,Ba/Y) and O sublattices. In the case of SrTiO₃ the stacking sequence is bulk-SrO-TiO₂-BaO-CuO₂-Y-CuO₂-BaO-CuO-bulk; in the case of NdGaO₃ the stacking sequence is probably

bulk-NdO-CuO-BaO-CuO₂-Y-CuO₂-BaO-CuO-bulk. Be-cause of the presence of intermediate phases for the systems YBCO/MgO and YBCO/YSZ no stacking sequence can be defined.

The YBCO film contains the most defects and strain in the YBCO/SrTiO₃ system with a gradual decrease in defect density and strain is observed for the systems YBCO/NdGaO₃, YBCO/YSZ and YBCO/MgO. This indicates that films containing the least amounts of defects can be best obtained on an MgO substrate. However, the defects present in for instance SrTiO₃ can be effective pinning centres which will lead to better superconducting properties.

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