Reconstruction of the La$_{0.9}$Sr$_{0.1}$MnO$_3$–SrTiO$_3$ interface by quantitative high-resolution electron microscopy

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Abstract

Atomic displacements and interface reconstructions near a La$_{0.9}$Sr$_{0.1}$MnO$_3$–SrTiO$_3$ interface are studied by use of the focal reconstruction technique applied in high-resolution electron microscopy. By using a quantitative model, column positions are determined with high precision (better than 0.004 nm) by least-squares minimization. A displacement vector map and interatomic distances are calculated. From these a structure model for the interface is proposed. The interface has a facetted shape, where the interatomic distance is modulated. Possible local oxygen deficiency in SrTiO$_3$ near the interface has been observed.

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The colossal magnetoresistance (CMR) effect in La$_{1-x}$A$_x$MnO$_3$ type materials strongly correlates to various structural features, such as the doping level and corresponding Mn$^{3+}$/Mn$^{4+}$ ratio, the oxygen stoichiometry and the defect structure. In particular, strain and stress relaxation between film and substrate play an important role [1–3]. For thin films and for a small mismatch strain can be accommodated elastically and will influence the CMR properties. In a stressed thin film, the local structure and even the symmetry [4] may be different from the bulk. Strain may also induce local non-stoichiometry, resulting in small lattice distortions and atom displacements. The knowledge of the atomic structure of the interface is important to understand the accommodation and growth mechanism, and the relation between structural and physical properties.

Since the discovery of CMR in epitaxial thin films of doped LaMnO$_3$ [5,6], high-quality thin films of La$_{1-x}$A$_x$MnO$_3$ (A = Ca, Sr) are now successfully grown on various substrates [4,7–10]. Transmission electron microscopy studies have demonstrated the defect structure, outgrowths and second phases, and pointed out the correlation between the local structure and CMR properties [3,11,12]. Only a few contributions dealt with the fine structure of the interface itself [10] and variations of the local lattice parameters. We report here the first atomic scale information on the interface structure and a quantitative stress in the film.

Direct image analysis of high-resolution transmission electron microscopy (HREM) images in terms of column positions is often extremely difficult, particularly in the immediate vicinity of a defect or an interface. This is mainly due to the delocalization introduced by the objective lens of the microscope, which smears out information, and to multiple scattering in the crystal. Extensive image simulations are needed, which are time consuming, certainly if no other information about the structure is known. By exit plane wave (EPW) reconstruction [13–16] the signal-to-noise ratio is increased and the information is localized as delocalization introduced by the electron microscope is eliminated. This allows accurate atom column position determination. Therefore an EPW reconstruction is an ideal starting point for a quantitative atomic scale analysis of interfaces.

Multiple scattering often hampers a straightforward contrast interpretation of the EPW. By simulation of EPWs of a bulk material a contrast model can be obtained, which can be used to determine atomic column positions,
with high precision by a least-squares minimization. In this way the local structure can be determined with a precision better than 0.004 nm.

In this contribution, the atomic configuration for a La$_{0.9}$Sr$_{0.1}$MnO$_3$–SrTiO$_3$ interface with a (110) terminating substrate is determined and stress induced atom column displacements are measured down to the picometer scale by quantitative HREM.

La$_{0.9}$Sr$_{0.1}$MnO$_3$ (LSMO) thin films are grown epitaxially on a (110)-SrTiO$_3$ (STO) substrate by pulsed laser deposition [11]. Resistivity and magnetization measurements show that the film exhibits CMR properties [17]. HREM on cross-section samples was performed using a Philips CM30 FEG ultratwin electron microscope (information limit of 0.1 nm) operated at 300 kV. A series of 20 images, with an equidistant focal decrement, was recorded with a slow-scan CCD camera. The numerical reconstruction of the EPW was carried out using the Philips/Brite-Euram

Fig. 1. Reconstructed EPW of a LSMO–STO interface. On the amplitude of the EPW (a) a modulation of the interatomic distance is visible near the interface. The inset shows an enlargement. From the phase of the EPW (b) it is clear that the interface can be localized and is not flat but has a faceted shape. The inset shows a simulation for a specimen thickness of 8 nm. The zigzag line marks the SrO terminating layer of the substrate.
Fig. 2. The amplitude of the EPW of a thin region (a) shows a similar contrast in film and substrate. The white rectangle marks a region where the contrast cannot be explained by a contrast difference between Sr and TiO columns but by a possible oxygen deficiency. The displacement vector map evaluated from (a) is shown in (b). The vectors are multiplied by two. Displacement vectors smaller than 0.02 nm are represented by circles. The SrO terminating layer of the substrate is denoted by a zigzag line. The reference region was chosen far from the interface in the substrate. Only the last three rows at the bottom of (b) belong to the reference region, the rest is not shown for reason of compactness.
focal-series reconstruction package [16]. After reconstruction and correction of the aberrations the complex EPW was retrieved and split into amplitude and phase. For measuring the actual interatomic distances and for determination of displacement vector maps the dali program [18] was used. EPWs for various specimen thickness values were simulated using the mac tempas program.

Fig. 1 shows the amplitude and phase of a reconstructed EPW of a STO–LSMO interface with superimposed EPW simulations. The position of the interface is well defined. The amplitude of the EPW highlights a modulation of the interatomic distance at the interface; the phase of the EPW clearly shows that the interface is not flat but has a faceted shape. Fig. 2a shows the amplitude of the EPW of the thinner region. The film and the substrate now have a similar contrast pattern, different from the EPW of the thicker region of Fig. 1. On the one hand this hampers the exact localization of the interface, but on the other hand allows quantitative measurements with high precision using a relatively simple contrast model, as will be shown later. According to EPW simulations of STO and LSMO black dots in the amplitude of the EPW are heavy atom columns. La/Sr columns can be distinguished from the MnO columns in the film; they show a darker contrast. Sr and TiO columns in the substrate are hard to distinguish for a thin area. Calculations show that Sr and TiO have a rather similar mean column potential. This results in a similar contrast variation in function of thickness of the amplitude and phase of the EPW, which can be shown by multislice simulations [19]. Therefore, the observed contrast difference in the amplitude of the EPW in the substrate near the interface (Fig. 2a) cannot be explained as a contrast difference between the Sr and TiO columns. From EPW simulations it can be shown that such a contrast difference can be caused by a local oxygen deficiency in SrTiO$_3$ near the interface. This is also observed by energy filtered transmission electron microscopy [20].

To describe black dots as columns a set of parabolas is used as contrast model. To determine the column positions with high precision the dali program is performed in three steps. In the first step the positions $M(1)$ of pixels corresponding to the local brightness minima are found. In the second step parabolas are fitted to the intensity profiles along the perpendicular directions across $M(1)$ by means of least-squares yielding a more accurate position $M(2)$. In the last step parabolas are fitted to the intensity profiles along four lines rotated over $\pi/8$ radians across $M(2)$, resulting in a final position $M(3)$ by averaging. To facilitate the peak position determination the noise is reduced by weak Wiener filtering, where the noise level is estimated locally in the Fourier-transformed image [21]. By taking into account the mean block intensity instead of the maximum block intensity in the noise reduction procedure, half of the noise is left after filtering. Therefore, the weak filter will not alter information in the image. The mean standard deviation of the position determination is $\sigma_x = 0.0026$ nm and $\sigma_y = 0.0035$ nm.

From the column positions the displacements can be calculated with respect to a reference region chosen in the undeformed substrate. By fitting straight grid lines through all positions in the reference region the directions of the base

![Graph](image-url)
lattice vectors are deduced from the average gradient of the gridlines. The lengths of the base vectors are calculated from the average distances between neighboring points, which are projected on the base vector directions. The precision of the displacement determination is dependent on the precision of the atom column position determination and the deviation of the reference region from the perfect structure.

Fig. 2b shows the displacement vector map of the atom columns in the vicinity of the interface. Close to the reference region most vectors are smaller than 0.02 nm and randomly oriented, which indicates perfection of the substrate. Near the interface region the displacement vectors are increasing due to strain induced at the interface. A clear modulation of the interatomic distance is visible along the interface whereas in the film region the displacement is homogeneous.

From the actual column positions the interatomic distance between neighboring columns in the planes parallel to the interface is calculated in pixels. The pixel size was calibrated in the reference region of the STO (0.3905 nm) substrate. To achieve statistics of the actual interatomic distance between neighboring columns, the mean and the standard deviation are calculated. Take the upper left corner of the grid as origin ($i = 1$ and $j = 1$) with $i$ as the vertical counter and $j$ as the horizontal counter from left to right. Two sets of mean interatomic distances $\Delta^{(1)}_{yij}$ and $\Delta^{(2)}_{yij}$ are determined:

$$\Delta_{yij} = y(i + 1,j) - y(i,j),$$  

$$\Delta_{yij} = \frac{1}{N} \sum_{j=2n} \Delta_{yij}$$  \hspace{1cm} (2)

where $n \in (1, \ldots, N)$ with $N$ the largest even $i$ index divided by two

$$\Delta_{yij} = \frac{1}{N} \sum_{j=2n-1} \Delta_{yij}$$  \hspace{1cm} (3)

where $n \in (1, \ldots, N)$ with $N$ the largest odd $i$ index plus one divided by two

$$\Delta^{(1)}_{ij} = (\Delta^{(1)}_{y11}, \Delta^{(1)}_{y22}, \Delta^{(1)}_{y33}, \ldots),$$  

$$\Delta^{(2)}_{ij} = (\Delta^{(2)}_{y11}, \Delta^{(2)}_{y22}, \Delta^{(2)}_{y33}, \ldots).$$  \hspace{1cm} (4)

Fig. 3 shows $\Delta^{(1)}_{ij}$ and $\Delta^{(2)}_{ij}$. In the reference region they have a similar path. Near the interface $\Delta^{(1)}_{ij}$ increases and reaches a maximum whereas $\Delta^{(2)}_{ij}$ decreases and reaches a minimum, which is due to a strained interface region.

In the film region $\Delta^{(1)}_{ij}$ and $\Delta^{(2)}_{ij}$ have again a similar path. Note that the mean of $\Delta^{(1)}_{ij}$ and $\Delta^{(2)}_{ij}$ in the film and substrate are different, which shows that the interplanar distance in the substrate is smaller than in the film.

These results allow proposing a model for the interface. From the phase of the EPW in Fig. 1 it is clear that the interface has a facet structure along the cubic directions. The ideal bulk structure of the (110)-SrTiO$_3$ surface consists either of a positively charged SrTiO or a negative charged O$_2$ terminating layer. In the earliest nucleation stage it is
likely that Ti is substituted by Mn. Mn$^{4+}$ has the same valence as Ti$^{4+}$, a similar ionic radius and is also situated in the center of the oxygen octahedral. This model preserves the continuity of the perovskite blocks and the charge balance. The reason for the one out of two modulation of the interatomic distance at the interface, which is clear from Fig. 2 and $\Delta(1/y)$ and $\Delta(2/y)$ in Fig. 3, can be twofold. On the one hand, in case of La in the vicinity of Mn, caused by a repulsion of Mn$^{4+}$ by La$^{3+}$ due to a different symmetry of Sr$^{2+}$ and La$^{2+}$ atoms. On the other hand, in case of a Sr atom in the vicinity of Mn, caused by the local structure SrMnO$_{3-\delta}$ which has a perovskite mesh $a_p = 0.38$ nm, which is smaller than $a_p = 0.39$ nm in the substrate or film. The resulting model for the interface is presented in Fig. 4.

Subtle atom displacements (quantified in Fig. 3) make that at the interface the interatomic distance will be modulated as visualized in Fig. 1. The column positions near the interface were calculated with a precision better than 0.004 nm and interatomic distances could be quantified.

A number of questions may be asked, either about the validity of the approach or about the relevance of the results obtained in very thin foils. The validity of the focus variation method has been demonstrated before [23] and all possible deviations such as stigmatism or distortions of the camera have been taken into account. The question of the relevance of thin foil results is not straightforward. The thickness of the samples studied is less than 10 nm and extrapolation to bulk is not evident. It is known that in thin foils artifacts may occur and that, e.g. phase transformations may be induced because of the stress relief in one dimension. Here the stress is certainly relieved along the direction parallel to the electron beam. This however does not influence our results since displacements and interatomic spacings are only measured perpendicular to the electron beam. The fine structure of the interface is of extreme importance to understand the physical properties of CMR, superconducting, ferroelectric, etc. thin films and to correlate them to structural properties.

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