Ferroelectric Relaxation of the $SrTiO_3(100)$ Surface

N. Bickel, G. Schmidt, K. Heinz, and K. Müller

Lehrstuhl für Festkörperphysik, Universität Erlangen-Nürnberg, Erwin-Rommel-Strasse 1,
Federal Republic of Germany

(Received 7 February 1989)

The surface structure of $SrTiO_3(100)$ was analyzed at $T=120$ K by means of low-energy-electron diffraction. The best theory-experiment fit results for a surface containing domains of two different layer terminations. Both of them show a first-layer puckering, with oxygen ions being pulled out of the surface by $s(\mathrm{Ti})=0.08$ Å and $s(\mathrm{Sr})=0.16$ Å, combined with a relaxation of the first two layer distances. This proves the surface to be ferroelectric, different from the bulk property in agreement with theoretical predictions.

PACS numbers: 61.14.Hg, 61.50.Em, 77.80.−e

Strontium titanate is known to be of the perovskite structure. A number of materials belonging to this class show ferroelectric phase transitions, the transition temperature being the Curie temperature T_C. The ferroelectric state usually is interpreted by the appearance of a soft phonon which freezes displacements of the ionic sublattices below T_C, leading to a permanent electric polarization.[1] For $SrTiO_3$ no ferroelectric bulk state is found at finite temperatures. Nevertheless, there is a tendency for a ferroelectric transition for $T\rightarrow 0$ but the paraelectric state remains stable.[2,3] However, these findings may only hold for the bulk and the modification of force constants and phonon spectra at the surface may lead to a ferroelectric reconstruction in the surface region for finite temperatures. In fact this is supported by theoretical investigations based on slab calculations.[4] We therefore tried to detect the suggested surface reconstruction by means of low-energy-electron diffraction (LEED). Another motivation came from the fact that $SrTiO_3(100)$ is used as a substrate for epitaxial films of high-T_c superconductors, particularly for YBa_2CuO_7 whose lattice constant is close to that of the perovskite. It is apparent that structural details of the substrate surface can be important for the epitaxial growth of the superconductor.

The crystal was mounted in a conventional UHV chamber equipped with a four-grid LEED optics. The sample was prepared by argon-ion sputtering at 550 K and 0.2 Pa for 1 h with a current of 10 μA. This was followed by annealing at 900 K after which the sputtering-annealing cycle was repeated several times. A final flash to 1400 K with subsequent cycles of annealing in hydrogen and oxygen resulted in a sharp LEED pattern. Though $SrTiO_3$ is known to be an insulator no charging of the surface by the impinging electron beam was observed after the preparation described. This is in agreement with earlier findings[5,6] according to which the preparation procedure is equivalent to an n-type doping. This is accompanied by a darkening of the surface color which was also observed in the present case. As the doping defect density[5] is reported to be rather low (10^{17} cm^{-3}) no distortion of the surface structure and LEED intensities is expected. This is in agreement with the observation of sharp 1×1 diffraction spots and the absence of any superstructure spots. Evaluation of the spot positions gives a lattice constant of 3.82 ± 0.15 Å which agrees with that reported in the literature, i.e., 3.9051 Å.[7] The intensities of the five beams (10, 11, 20, 12, and 22) were recorded at 120 K by use of a video camera which faces the LEED pattern from outside the UHV equipment. The video signal is evaluated under computer control whereby the movement of the spots with energy is automatically followed with a simultaneous correction for thermal diffuse background.[8,9]

Full dynamical calculations were performed to analyze the measured spectra. The combined space method and renormalized forward scattering were used to treat intralayer and interlayer diffraction, respectively.[10,11] Phase shifts were tested for both atoms and ions (O^{2-}, Sr^{2+}, and Ti^{4+}) and only minor differences resulted for spectra above 200 eV. As we have no precise information about the electronic configuration of the surface atoms, we limited the analysis to above 200 eV. The atomic phase shifts used were corrected for thermal diffuse scattering using a Debye temperature of 400 K. For a quantitative theory-experiment comparison the Pendry R factor was used.[12] Computational details of the structure determination will be published elsewhere.[13]

The perovskite structure of $SrTiO_3$ is shown in Fig. 1 and it is apparent that two terminations of the surface are possible: one with two atoms in the unit cell (O-Sr, "Sr termination") and one with three atoms per cell (O-Ti-O, "Ti termination"). Trial calculations with either one of the two terminations yield R factors above 0.63. The assumption of the presence of a 1:1 mixture of both terminations gives a minimum R factor of $R=0.529$ with both surface domains puckered. In order to find this best-fit model the interlayer distances d_{12} and d_{23} were varied (in steps of 2% of the bulk value $d_0=1.95$

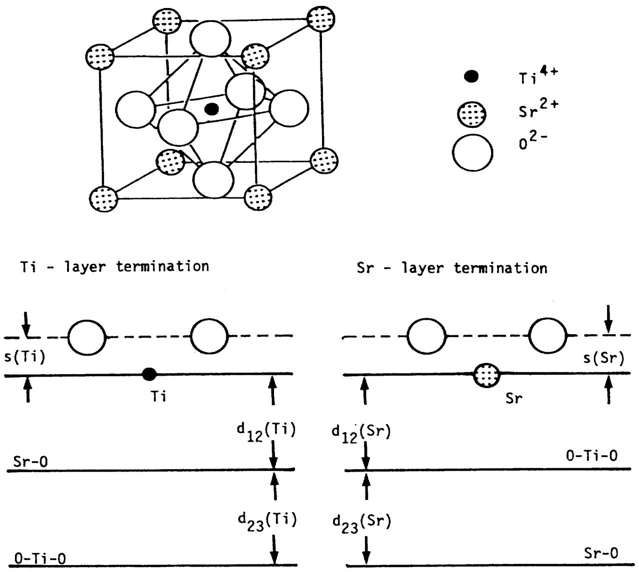

FIG. 1. Unit cell of $SrTiO_3$ and structural parameters for the two terminations.

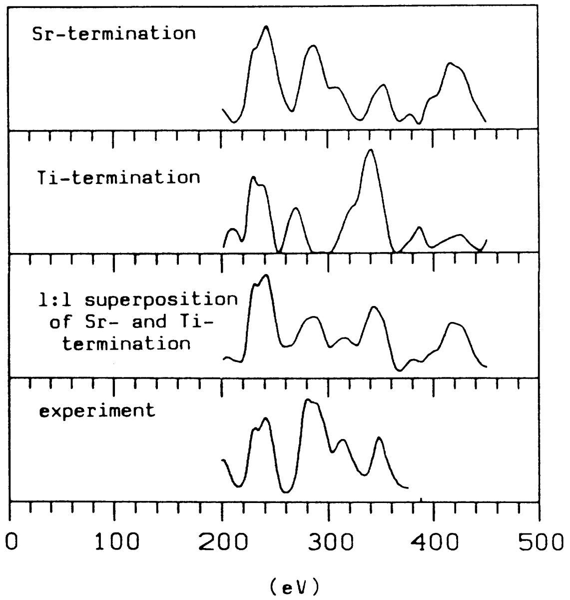

FIG. 2. Comparison of experimental and theoretical (upper three curves) spectra of the 10 beam calculated for two single terminations and a 1:1 mixture.

Å) as well as an additional displacement s of the oxygen ion according to Fig. 1. This is equivalent to a surface puckering with amplitude s. For each termination 588 trial structures were calculated. However, each structure of one termination has to be combined with each of the other, and so a total of about 3.5×10^5 R-factor calculations had to be performed. Figure 2 demonstrates the improvement of the 10-beam spectrum by averaging intensities from differently terminated domains using the final best-fit parameters. Unfortunately the scattering strength of Ti and Sr is much larger than that of oxygen. This entails that the intensity spectra are dominated by the strong scatterer positions while the positions of oxygen can cause only more or less slight modifications. In fact this is displayed by the different sensitivity of R factors as shown in Fig. 3. The dependence of R on d_{12} which describes the position of the strong scatterers is much more pronounced than that on the relative displacements s between strong and weak scatterers. Therefore, for the determination of s a larger error bar has to be conceded than for the determination of d_{12} and d_{23}. However, it is hard to make a definite decision about the size of the error. The change of the structural parameters predicted by the evaluation of single beams rather than their average is not larger than the step width with which the different parameters were varied. Hence, the step widths of 0.08 Å for s and 0.04 Å for d_{12} and d_{23} which equals 2% of d_0 seem to be conservative estimates. So, the best-fit structure was obtained for a mixture of both terminations with oxygen atoms being pulled out of the surface under a simultaneous multilayer relaxation. For the Sr termination the values are $s(\mathrm{Sr})=+0.16\pm0.08$ Å, $d_{12}(\mathrm{Sr})/d_0=(-10\pm2)\%$, and $d_{23}(\mathrm{Sr})/d_0=(+4\pm2)\%$, while for the Ti termination $s(\mathrm{Ti})=+0.08\pm0.08$ Å, $d_{12}(\mathrm{Ti})/d_0=(+2\pm2)\%$, and $d_{23}(\mathrm{Ti})/d_0=(-2\pm2)\%$ result.

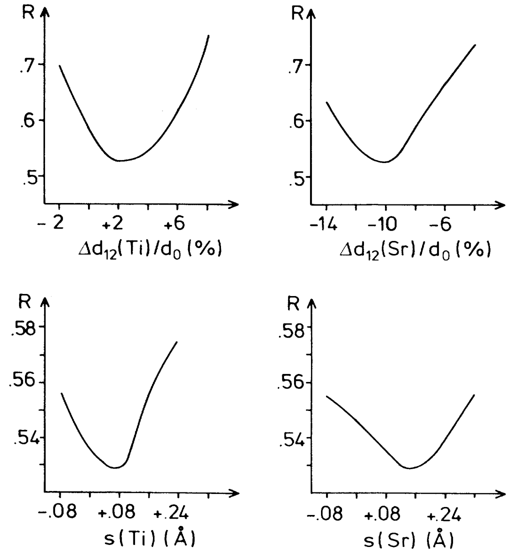

FIG. 3. Dependence of the Pendry R factor on the first-interlayer distance and the oxygen displacement according to the definitions in Fig. 1. The fixed parameters correspond to the best-fit structure.

The minimum R factor of about $R=0.529$ is acceptable in view of the complexity of the structure and the atomic approximation used for the scattering potential. The reliability of the structure determination is further supported by the fact that the evaluation of single beams leads to nearly the same inner potential, i.e., -10 ± 2 eV with respect to the crystal's Fermi level. Nevertheless, the level of the minimum R factor indicates that the structure found can be refined by additional structural variations which we could not consider because of limited computer time. So, the reconstruction may extend also to deeper layers and possibly the assumed 1:1 mixture of the terminations is only an approximation.

The level of the minimum R factor is rather high compared to that found for single-component systems. It is well known, however, that the quality of theory-experiment comparison becomes worse with increasing complexity of the surface. In the present case the complexity comes from three features, which are the existence of three different atoms, the existence of two terminations, and the appearance of surface puckering. It is hard to find an equivalent system in the literature for comparison. Perhaps the most similar system is that of aluminum adsorption on GaAs(110) for which a minimum Zanazzi-Jona R factor $R_{ZJ}=0.29$ was reported.[14] This corresponds to about the same quality of agreement as in the present paper because R_{ZJ} is frequently found to have about half the numerical value of the Pendry R factor applied here.

The surface puckering is equivalent to the existence of a static dipole moment in the surface layer; i.e., unlike the bulk, a thin surface slab is in a ferroelectric state at the temperature of measurement, $T=120$ K. This is consistent with results of recent theoretical investigations where, however, only the Sr termination was considered.[4] The values calculated for the corresponding ion core positions were $s(\mathrm{Sr})=0.35$ Å, $d_{12}/d_0=-15\%$, and $d_{23}/d_0=+9\%$; they are higher than the experimental figures. However, the deviations are moderate and in view of the intrinsic error bars which have to be conceded for a complex LEED structure analysis and for the model parameters entering a slab calculation there is consistency between theory and experiment. Surface puckering and relaxation have also been found in recent atomistic simulations of surfaces of oxides.[15]

Last but not least we want to point out that the polarization of the surface slab, $P=qs/a^2d_0$, gives the same value for the two surface domains (a = lattice constant = 3.9 Å). This is because the size of the charge displaced, $q(\mathrm{Ti})=4e=2q(\mathrm{Sr})$, and the amplitude of the displacement, $s(\mathrm{Sr})=2s(\mathrm{Ti})$, gives the same product for both cases. The numerical value is $P=0.17$ C/m^2 which is near the bulk value of 0.25 C/m^2 found for $\mathrm{BaTiO_3}$ at room temperature. Theory also predicts a phase transition at 105 K which produces octahedral structural elements[4] of atoms which rotate by only 1.4° when going below the transition temperature. Experimentally this reconstruction was confirmed by x-ray[16] and neutron scattering experiments.[17,18] As no superstructure spots show up in the present LEED experiments we cannot add to this confirmation. This is likely to be due to the fact that our temperature of measurement (120 K) is above the transition temperature, though the latter seems not to be well defined.[16,17] However, it is also possible that the slight reconstruction is not resolved by the LEED optics.

The authors are indebted to Deutsche Forschungsgemeinschaft (DFG) for financial support. They also thank the Erlangen research center of Siemens AG for providing the crystal.

---

[1] W. Cochran, Adv. Phys. **9**, 387 (1960).

[2] A. D. Bruce and R. A. Cowley, J. Phys. C **6**, 2422 (1973).

[3] R. Migoni, H. Bilz, and D. Bäuerle, Phys. Rev. Lett. **17**, 37 (1976).

[4] R. Reiger, thesis, Regensburg, 1986 (unpublished).

[5] I. W. Owen, N. B. Brookes, C. H. Richardson, D. R. Warburton, F. M. Quinn, D. Norman, and G. Thornton, Surf. Sci. **178**, 897 (1986).

[6] N. B. Brookes and G. Thornton, Solid State Commun. **64**, 383 (1987).

[7] R. W. G. Wyckoff, *Crystal Structures* (Wiley, New York, 1963).

[8] K. Heinz and K. Müller, in *Structural Studies of Surfaces,* edited by G. Höhler, Springer Tracts in Modern Physics Vol. 91 (Springer-Verlag, Berlin, 1982), p. 1.

[9] K. Müller, K. Heinz, and D. v. Gemünden (to be published).

[10] J. B. Pendry, *Low Energy Electron Diffraction* (Academic, London, 1974).

[11] M. A. Van Hove, W. H. Weinberg, and C.-M. Chang, *Low Energy Electron Diffraction* (Springer-Verlag, Berlin, 1986).

[12] J. B. Pendry, J. Phys. C **13**, 937 (1980).

[13] N. Bickel, G. Schmidt, K. Heinz, and K. Müller (to be published).

[14] A. Kahn, J. Carelli, D. Kanani, C. B. Duke, A. Paton, and L. Brillson, J. Vac. Sci. Technol. **19**, 331 (1981).

[15] W. C. Mackrodt (to be published).

[16] C. N. W. Darlington and D. A. O'Connor, J. Phys. C **9**, 3561 (1976).

[17] R. A. Cowley and G. Shirane, J. Phys. C **11**, L939 (1978).

[18] G. Shirane and Y. Yamada, Phys. Rev. **177**, 858 (1969).