

Photoemission investigation of surface states on strontium titanate*

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Ultraviolet photoemission spectroscopy has been used to search for surface states on SrTiO₃. No evidence was found for such states and an upper limit of about $3 \times 10^{12}/\text{cm}^2$ is placed on surface states in the gap from the valence-band maximum to within 0.2 eV of the conduction-band minimum. (The latter limit is set by the bulk Fermi-level position of the *n*-type crystal studied.) These results are discussed in terms of the large ($\approx 10^{15}/\text{cm}^2$) density of empty surface states predicted by Morin and Wolfram.

Theoretical calculations of the surface energy bands of SrTiO₃ have been reported.^{1,2} Of particular interest are recent calculations by Morin and Wolfram¹ which predict a large density of empty surface states for the (001) face of SrTiO₃ ($\approx 1.2 \times 10^{15}$ states/cm²) derived from the lower conduction bands. Furthermore, these surface states consist of nearly pure *d* orbitals and are highly localized near the center of the 3.24-eV band gap; viz., about 1.2×10^{14} states/cm² are centered in an interval about 0.13 eV wide at the center of the forbidden gap. It has been argued¹ that the presence of such a large density of localized electronic states of *d* symmetry could be a significant factor in determining the catalytic properties of the *d*-band perovskites, of which SrTiO₃ is one example. In particular, by providing orbitals of the proper symmetry, these surface states could allow an important class of otherwise symmetry-forbidden chemical reactions to proceed, e.g., the oxidation of CO and the reduction of NO₂. No experimental evidence has been presented to allow a decision to be made for or against a large, localized density of *d*-band surface states on the *d*-band perovskites. Recently, however, increasing success has been achieved in probing the surface states of solids with uv photoemission spectroscopy.³⁻⁵

In this paper, we report the use of uv photoemission to investigate surface states on SrTiO₃. The two samples studied were large single crystals approximately $10 \times 5 \times 5$ mm³ which were cleaved *in situ* along the (001) face in ultrahigh vacuum of pressures $\lesssim 5 \times 10^{-10}$ Torr. Since the *d*-band surface states in an insulating perovskite such as SrTiO₃ are normally empty,² sample A was doped with ≈ 30 ppm of Mo to place the bulk Fermi level well within the calculated surface-state distribution, which extends from midgap to the conduction-band edge. The crystal was also reduced by heating in H₂ at 1070°K resulting in a blue-green color and a carrier concentration of about $3 \times 10^{17}/\text{cm}^3$. Sample B, which was also cleaved *in situ*, was heavily doped with 0.05% Nb by weight but was not reduced by heating in H₂ as

was sample A. Both the samples studied were *n*-type so that, as will be discussed later, surface states in excess of about $3 \times 10^{12}/\text{cm}^2$ would pin the surface Fermi level.³⁻⁵

In Figs. 1 and 2 we present energy distributions of the photoemitted electrons (EDC's) from the (001) cleavage face of sample A, and in Fig. 3 EDC's from samples A and B are compared. The EDC's are plotted versus the energy of the states from which the electrons are excited. For convenience the zero of energy is taken as the top of the valence band (VBM). The EDC's consist of two contributions: one from states lying in the valence band and the other from states within the band gap. To better visualize the relative strength of valence-band and band-gap emission, the EDC's have been normalized to the quantum yield (presented as Fig. 4). That is, the area under an EDC equals the measured yield at that photon energy. From Fig. 1 the valence-band emission is seen to drop rapidly within an eV of the VBM, with the band-gap emission barely discernible. In Fig. 2, however, where valence-band emission is greatly reduced at the lower photo energies used, band-gap emission shows up clearly and is observed

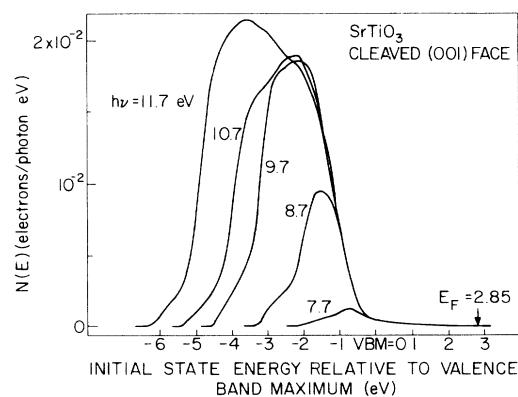


FIG. 1. Normalized energy-distribution curves (EDC's) from a cleaved (001) crystal of SrTiO₃ (sample A) at $h\nu = 7.7$ – 11.7 eV showing the valence-band maximum (VBM) and Fermi level at the surface (E_F).

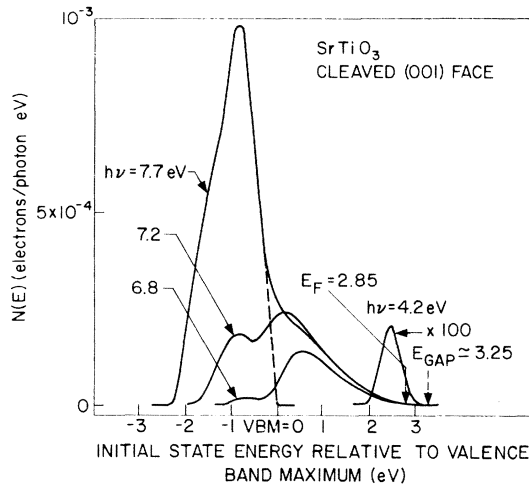


FIG. 2. Normalized EDC's at various $h\nu \leq 7.7$ eV for a cleaved (001) crystal of SrTiO_3 (sample A) showing valence-band and band-gap emission.

to extend from the VBM to the Fermi level at 2.85 eV. We will discuss later the origin of this band-gap emission and the possibility that it represents emission from filled surface states. The surface position of the Fermi level was experimentally determined by using the measured value of the collector work function.⁶ For photon energies $h\nu \geq 8.5$ eV valence-band emission dominates the EDC's, while for $h\nu \lesssim 7.0$ eV band-gap emission is dominant for sample A, but not B. This is brought out also in the quantum yield (Fig. 4), which has been separated into two contributions based on the relative areas of valence-band/band-gap emission found in the EDC's. These results are in good agreement with previous unpublished uv photoemission studies of SrTiO_3 .⁷

Information regarding surface states on SrTiO_3 can be obtained from the measured position of E_F . We consider surface states which are charged when filled and neutral when empty in accordance with the calculations of Morin and Wolfram.^{1,2} There is no suggestion in those calculations that surface states on SrTiO_3 will be neutral when filled as was found, e.g., for intrinsic surface states on Si.⁵ From the EDC's (Figs. 1-3), the Fermi level is seen to lie about 0.3 eV below the conduction-band edge for sample A. This is within experimental error the location expected for the Mo dopant levels and suggests that the position of E_F at the surface is set by the bulk doping in the sample rather than by the surface-state energy. From Fig. 3, it is seen that the surface Fermi level lies slightly higher in sample B than A. It is clear from the EDC's that the surface Fermi level is not pinned near midgap as would be expected for the high empty-surface-state density predicted there ($\approx 10^{15}/\text{cm}^2$).¹ In photo-

emission studies of Si, e.g., where a comparable surface-state density was predicted for the (111) face, the surface states were found to pin the surface position of the Fermi level for bulk doping as high as $10^{20}/\text{cm}^3$ in n^+ Si.⁵ In our case the bulk donor concentration was only about $10^{18}/\text{cm}^3$. With this doping level, a filled-surface-state density of only $\approx 3 \times 10^{12}/\text{cm}^2$ would have been sufficient to pin the surface Fermi level (assuming that surface charge produces band bending over a reasonable distance of ≈ 10 - 100 Å). These results suggest that from the VBM to within about 0.2 eV of the conduction band, the surface-state density is 2 to 3 orders of magnitude less than predicted.^{1,2} Since one expects on the order of $10^{15}/\text{cm}^2$ intrinsic surface states, we concluded that there is no band of intrinsic surface states from the VBM to within 0.2 eV of the conduction-band minimum.

We now consider the photoemission observed from the band-gap region. Assuming the matrix elements for transitions from states in the band gap are about the same as for valence-band states, a rough estimate based on the yield and EDC's places the total density of occupied electronic states in the band gap for sample A at about $5 \times 10^{19}/\text{cm}^3$, corresponding to a surface density of $\approx 10^{13}/\text{cm}^2$. For surface states that are charged when filled, $\approx 3 \times 10^{12}$ filled-surface-states/ cm^2 would have been sufficient to pin E_F well within this distribution. The band-gap emission cannot, therefore, be attributed to such states. Another possibility is that the band-gap emission is due to surface states which are neutral when filled, so that E_F need not be pinned within the distribution. However, this possibility is ruled out by data from sample B (Figs. 3 and 4). Although E_F for sample B lies somewhat higher in the gap than for sample A, no band-gap emission could

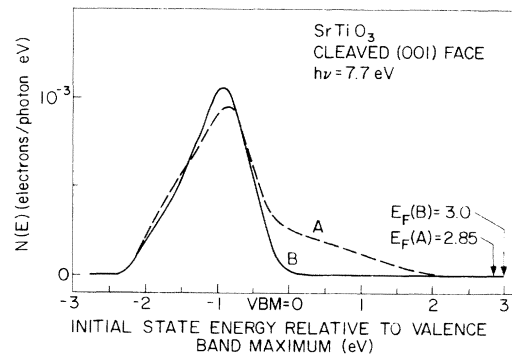


FIG. 3. Comparison of EDC's at $h\nu = 7.7$ eV for samples A and B. Sample B was heavily doped with 0.05% Nb by weight whereas sample A was doped with about 30 ppm of Mo. Sample A was reduced by annealing in H_2 while sample B was not.

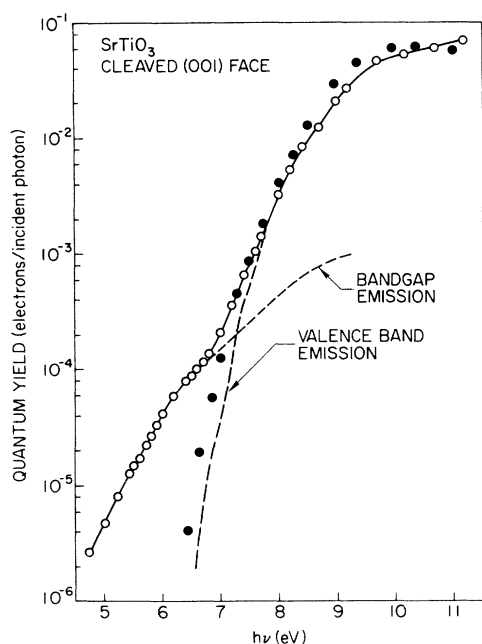


FIG. 4. Absolute quantum yield of cleaved (001) SrTiO_3 . The open circles are for sample A while the filled circles are for sample B.

be detected in the EDC's for B (Fig. 3). In the quantum yield as well (Fig. 4) the band-gap emission seen for A is notably absent for B. Since the magnitude of this emission depends so strongly on bulk doping conditions, it is unlikely that it is associated with intrinsic surface states in the gap. Rather, it appears to be due to extrinsic states lying in the band gap. While the detailed nature of these extrinsic states is not known, they may be related to (i) the large number of oxygen vacancies introduced when the crystal A was reduced in H_2 and/or (ii) Fe impurities which were present in it at about 3 ppm, although in the latter case the impurity density ($\approx 6 \times 10^{17}/\text{cm}^3$) seems too small to account for the magnitude of the emission observed.

On the basis of the uv photoemission data presented, there is no evidence for a large ($\approx 10^{15}/\text{cm}^2$) density of surface states localized at midgap. The data do not rule out the possibility that intrinsic surface states exist on the (001) face of SrTiO_3 ; however, it strongly suggests that for the sample studied their density is considerably smaller (2 to 3 orders of magnitude) than predicted by theory¹ throughout most of the forbidden gap. If they exist in larger numbers, their location must be within a few tenths of an eV of the

conduction-band minimum, about a volt higher in the gap than predicted. In this case, it is not possible to set an upper bound on the density of states. It has been pointed out by Morin and Wolfram⁸ that the surface states might be raised in energy if occupied by an electron owing to their highly localized *d*-state nature. Another possibility concerns the condition of the (001) surface studied in the present work. In the calculation of Morin and Wolfram,¹ the location of the surface-state band at midgap holds for an idealized (001) surface, i. e., one free of irregularities, impurities, vacancies, etc. The exact position of the surface band within the gap will depend on the condition of the surface. On the other hand, the large density of states predicted, on the order of one state per transition-metal ion, should be valid even for surfaces far from the ideal. For a highly imperfect surface then, a high density of surface states lying within a few tenths of an eV of the conduction band could be consistent with theory. If this is in fact the case for a single crystal of SrTiO_3 cleaved in ultrahigh vacuum, it will probably be the case for practical SrTiO_3 catalysts as well, since their surfaces are expected to be more imperfect than the one reported here. Finally, it should be recognized that two different types of (001) surface can occur for SrTiO_3 .² In one case (type I) the surface layer contains oxygen and Ti ions, while in the second case (type II) Sr and oxygen ions are on the surface. Calculations for an ideal type-II surface of SrTiO_3 predict a large density of oxygen surface states (on the order of one state per oxygen ion) near the center of the band gap.² In the event that the samples studied here give predominantly type-II surfaces after cleavage, surface states associated with oxygen, not Ti, are expected to dominate. In this case the discussion and the conclusions we have drawn previously from the UPS data regarding the density and location of surface states on (001) SrTiO_3 will be taken to apply to oxygen derived surface states rather than states associated with Ti. That is, the density of oxygen surface states is considerably smaller than predicted by theory^{1,2} throughout most of the forbidden gap. Of course, the oxygen derived surface states do not have strong *d*-like character and the arguments made in Ref. 1 regarding the catalytic behavior of such states does not apply.

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