Electronic structure of strontium titanate

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We have employed the techniques of photoelectron spectroscopy (with tunable synchrotron radiation $30 \le h\nu \le 100$ eV) and inverse photoemission spectroscopy at $h\nu=9.7$ eV to study respectively the occupied and unoccupied electronic states of *n*-type SrTiO₃ doped with 1 at. % Nb. Doped samples have the advantage that charging effects are avoided and hence a rather accurate determination of peak positions is possible. The total (occupied and empty) experimental density of states agrees with the calculated density of states of Pertosa and Michel-Calendini when their band-gap energy is readjusted. We have no evidence for intrinsic surface states either in the band gap or in the conduction band, as was calculated by Wolfram *et al*. The admixture of Ti 3*d* states in the O 2*p* valence states is small, as can be concluded from the Ti 3*p* \rightarrow 3*d* resonance behavior.

I. INTRODUCTION

Photoelectron spectroscopy (PES) and inverse photoemission spectroscopy (IPES) provide means for testing theoretical calculations of the occupied and unoccupied electronic structure of solid materials, respectively. Owing to the surface sensitivity of these techniques, modifications of the bulk electronic states at the surface (e.g., surface states) as well as their possible role in chemical reactions at the surface can be studied. The oxidation or oxide formation is a process which starts at the surface, and is of fundamental interest. Hence, oxides represent a class of prototype materials for which theoretical calculations should provide good agreement with experiments.

The oxides of perovskite structure ABO_3 (A, group I-II element; B, transition metal) are particularly interesting, since they exhibit a broad range of physical phenomena. For instance, the metallic sodium tungsten bronzes (Na_xWO₃) show similarities with mixed-valent systems, while the conduction bands are filled with x in a rigid-band manner.¹ In insulating SrTiO₃ and related compounds, there is the structural phase transition and the critical behavior connected to it, which have stimulated many investigations, as well as the fact that many of these systems are ferroelectrics.² SrTiO₃ is also very interesting from the electronic-structure point of view. State-of-the-art band-structure calculations³⁻⁶ obtain the correct value for the band-gap energy $(E_G = 3.2 \text{ eV})^7$ by adjusting parameters. Existing photoemission data in the $ultraviolet^{8-11}$ and x-ray regime^{12,13} agree on first sight with calculated densities of the occupied states, however, the correct relative intensities of the three major photoemission features (mostly O2p-derived with some admixture of Ti 3d's) agree with experiment only when an unrealistic ratio of 2p to 3d photoemission cross section is assumed.14

Another interesting question is the existence of surface states (SS) in the band gap, and whether they are intrinsic or extrinsic, i.e., created by certain surface preparations. Such surface states have been predicted by Wolfram *et al.*,⁵ but measurements by Powell and Spicer¹⁵ and Henrich *et al.*⁹ gave a much smaller density of intrinsic SS on SrTiO₃. SS could play a decisive role in the surface chemistry and bonding properties of SrTiO₃.

Finally, so far, experimental work involving electron spectroscopies has had to deal with the problem of sample charging owing to the insulating character of intrinsic $SrTiO_3$. This may result in shifted peak positions in photoemission, and absolute determination of binding energies is not possible. In cases where the conductance of $SrTiO_3$ is increased by extensive heating which results in a reduction, band-gap emission occurs owing to oxygen deficiencies.^{9,11} This may mask emission from intrinsic surface states.

Here, we have employed photoelectron spectroscopy with tunable synchrotron radiation $30 \le h\nu \le 100$ eV to study the occupied electronic states. Variations of photoemission intensities with $h\nu$ allow determination of their orbital characters, as well as their possible hybridization with other states.¹⁶ In addition, we have applied the novel technique of inverse photoemission spectroscopy¹⁷ at $h\nu=9.7$ eV to obtain information about the unoccupied electronic states.

II. EXPERIMENTAL

In both experiments (PES and IPES), we used *n*-type $SrTiO_3$ with 1 at. % Nb as dopant to avoid any charging effects during the electron spectroscopic measurements. All samples were cut from the same batch of single-crystalline material. The starting material was 99.99% pure, and the flame-fusion method was used to produce high-quality single crystals with a shiny black color.¹⁸ X-ray diffraction and microprobe analysis showed that the batch was single phase according to the limits of these methods.

PES spectra were recorded with the IBM twodimensional display spectrometer¹⁹ now installed²⁰ at the Brookhaven National Laboratory. The synchrotron radiation from the 750-MeV storage ring was monochromatized with a 3-m toroidal grating monochromator. In the angle-integrated mode used here, photoelectrons were accepted within an 86° cone of emission angles. The overall resolution (electrons and photons) was 0.3 eV at hv=40eV and was determined from the onset of photoemission at the Fermi level E_F of a metallic reference sample [i.e., UBe_{13} (Ref. 20)] in electric contact with the SrTiO₃. The samples were cleaved (or rather fractured perpendicular to the $\langle 001 \rangle$ axis) in a vacuum of 2×10^{-10} Torr, and immediately transferred to the measurement position which held a vacuum of 5×10^{-11} Torr. The surfaces were usually curved rather than being flat, and were inert to contaminations by residual gases for at least 24 h, during which the PES spectra did not change essentially.

For the inverse photoemission experiment, the samples were bombarded with electrons of energies $5 \le E \le 24$ eV from a custom-made electron gun.²¹ Outcoming photons were filtered at hv=9.7 eV and detected with a Geiger-Müller-type counter.¹⁷ The resolution was determined to be 0.7 eV (Ref. 21) from the onset at E_F of a polycrystalline silver sample in contact with SrTiO₃. As samples, we again used SrTiO₃ with 1 at. % Nb, which were measured after (i) mechanical polishing in air and insertion into vacuum, (ii) sputter cleaning (1 kV Ar⁺, 2 μ A) and annealing, and (iii) fracturing in situ. The cleanliness as well as the relative composition of strontium, titanium, and oxygen could be checked by Auger electron spectroscopy (AES) with 3 kV primary electrons.²¹ The data presented below were obtained from samples which exhibited the following AES signals normalized to the Ti(383 eV) signal: Sr(105 eV) = 0.5 - 0.7, O(510 eV) = 2.8 - 3.3, Nb(178) $eV \approx 0.1$, and C(270 eV)=0.3-0.4. The variance in the AES signal ratios is due to different surface preparations. Our O/Ti ratios agree with the 2.9 value of Chung and Weissbard¹⁰ for the well-ordered SrTiO₃(100) surface, while our Sr/Ti ratios are somewhat larger than their 0.3 value. The clean and ordered SrTiO₃(111) surface prepared with 2 kV, 20 μ A Ar⁺ sputtering by Lo and Somorjai⁸ exhibited AES ratios 3.0 for Sr/Ti and 2.0 for O/Ti.

III. RESULTS AND DISCUSSIONS

In Fig. 1(a), we present an experimental overview of the occupied and unoccupied electronic structure of SrTiO₃ as measured with PES and IPES, respectively. Although the use of two different photon energies implies somewhat different surface sensitivities, we show in Fig. 2 that the occupied parts of the density of states (DOS) do not change as a function of photon energies (and therewith photoelectron escape depth) with respect to peak positions and overall shape. (There are, however, variations in relative peak intensities, which will be discussed below.) Therefore, in general, we believe that the PES spectrum at hv = 50 eV, and the IPES spectrum at an isochromat energy of hv = 9.7 eV, reflect equally well the bulk electronic structure, but are sufficiently surface sensitive to reveal possible emission from intrinsic or extrinsic surface states. Extrinsic surface states, but not intrinsic surface states, were detected for $h\nu \le 7.0$ eV (Ref. 15) and at $h\nu = 21.2$



Sr TiO3 + 1 at. % Nb

FIG. 1. (a) Experimental density of states as obtained by photoelectron spectroscopy at $h\nu = 50$ eV from a cleaved SrTiO₃(100) surface, and inverse photoemission spectroscopy at $h\nu = 9.7$ eV from a sputter-cleaned (500 eV Ar⁺, 2 μ A) and annealed SrTiO₃(100) surface. (b) Calculated density of states of Pertosa and Michel-Calendini (Ref. 4). The occupied part is shifted by -0.8 eV to have the O 2s states coincide with peak E, the unoccupied part is shifted by + 0.7 eV to have the maximum of the Ti 3d states coincide with F.

eV (Refs. 8 and 11).

The Fermi levels as determined from metallic reference samples in contact with the SrTiO₃ samples (see above and Refs. 20 and 21) were used to match the two independently obtained spectra of Fig. 1(a) on a common energy scale with $E_F \equiv 0$. The relative intensities of the two spec-



FIG. 2. The valence-band emission A, B, and C of Fig. 1(a) as a function of photon energy $30 \le hv \le 100$ eV.

tra were arbitrarily normalized so that the ratio of the emission features A and F becomes 1.6, which is the average value in the density-of-states calculation of Mattheiss,³ Pertosa and Michel-Calendini⁴ [see also Fig. 1(b)], and Selme and Pecheur.⁶ The energy E_V of the top of the valence band is determined from the intercept of a linear fit to the right shoulder of feature A with the zero line. In the IPES spectrum, the experimentally determined Fermi level coincides with the bottom of the conduction band, as expected for a heavily doped n-type semiconductor. Hence, the band gap is given by $E_G = E_F - E_V = 3.2(2)$ eV [see Fig. 1(a)], a value which agrees quite well with optical data for heavily Nb-doped bulk SrTiO₃.²² In view of our enhanced surface sensitivity (as compared with optical techniques) this agreement implies that there does not seem to be any band bending occurring near the surface nor a pinning of the Fermi level due to intrinsic or extrinsic surface states.9,15

For the valence-band emission, in Fig. 1(a) we use the notation A, B, and C for the mainly O2p-derived emission features as in earlier ultraviolet¹¹ and x-ray⁴ photoemission work. The peak positions of A, B, and C are essentially independent of photon energy for $30 \le h\nu \le 100$ eV as demonstrated in Fig. 2. We find A at -4.75 eV, B at -6.75 eV, and C at -7.9 eV. These numbers deviate from the findings of Courths¹¹ (A, -4.6 eV; B, -6.9 eV; and C, -8.3 eV) for an Ar⁺-sputtered and annealed $SrTiO_3(100)$ surface. In Fig. 1(b), we compare the experimentally obtained DOS with the calculated DOS of Pertosa and Michel-Calendini.⁴ In order to obtain best agreement between the photoemission peaks and the theoretical features, we had to shift the theoretical DOS by 0.8 eV towards lower energies (away from E_F). The oxygen 2s states around -20 eV then coincide with feature E, so does the O 2p DOS at the top of the valence band with feature A. Battye et al.¹² noted in their x-ray photoemission work that the O 2s and Sr 4p emissions overlap. In Fig. 1(a), the Sr 4p level gives rise to the broad shoulder at the right side of feature E.

Owing to the calculation of Pertosa and Michel-Calendini,⁴ feature A arises from almost pure-oxygen states, while B and C are mostly O 2p derived with some admixture of Ti 3d's. The relative intensities of A, B, and C in the x-ray photoemission work could only be calculated, if unrealistic photoemission cross sections σ_{3d} and σ_{2p} were assumed. To check up on some 3d admixture in the mainly O 2p valence band, we performed a resonant photoemission study¹⁶ employing the Ti 3p core level around -38 eV, i.e., we measured PES spectra between hv = 28 and 50 eV in 2-eV steps. No noticable enhancement of any of the valence-band features could be observed, although the effect should be quite pronounced. Recently, Bertel et al.²³ have reported on the $2p \rightarrow 3d$ resonance behavior in Ti and TiO2 and found the onresonance energy¹⁶ around hv = 47 eV. From these findings (see, e.g., the 40- and 50-eV spectra in Fig. 2), we have to conclude that the admixture of Ti 3d in the valence-band states is rather small. On the other hand, when we follow the spectral behavior of A, B, and C with hv in Fig. 2 we note a relative increase of A, which could indicate a higher *l* character of A than of B and C. Some

admixture of s character in the lower valence band could account for such effects, although final-state or joint DOS effects could also be the reason for the intensity variations observed in Fig. 2.

The photoemission peak D at -10.7 eV in Fig. 1(a), not accounted for in the theoretical DOS of Fig. 1(b), is attributed to carbon 2s emission.⁴ Carbon is present as a bulk impurity and could also be detected by AES [typically C(270)/Ti(383)=0.3-0.4]. Heating SrTiO₃ in 10⁻⁵-Torr oxygen atmosphere reduced the carbon signal D due to CO formation, but did not change the true SrTiO₃ emission features. Therefore, we show PES spectra in Figs. 1 and 2, obtained from SrTiO₃ samples without heat treatment in oxygen. Although not specifically mentioned, C 2s emission is also present in the PES spectra of Refs. 11-13.

The IPES spectrum [right panel of Fig. 1(a)] reveals a rather structureless unoccupied DOS. The onset of emission at the bottom of the conduction band is rather shallow, as expected for a semiconductor. The rise from 10% to 90% of the F intensity occurs within a $\Delta E_{90-10} = 1.6$ eV in Fig. 1(a), while we get $\Delta E_{90-10} = 0.7$ eV (i.e., the energy resolution) for the intensity rise at E_F of a metal.²¹ We associate the empty Ti 3d states with the broad Femission feature in Fig. 1(a). To obtain better agreement, we shifted the calculated empty DOS by 0.7 eV towards higher energies in Fig. 1(b), so that the maximum of the Ti 3d states coincides with the F tickmark. The broad experimental structure G then overlaps with the calculated Sr 5s states. As pointed out by Cardona,⁷ Ti 4s states around 10 eV should also be present in the conduction band DOS, but have not been included in the calculations of Pertosa and Michel-Calendini.⁴ These 4s states are responsible for the structureless increase of the unoccupied DOS with energy. Therefore, in order to achieve best agreement between the experimental and theoretical DOS's in Fig. 1, we have increased the gap of the calculated DOS from $E_G = 3.0$ to 4.5 eV in Fig. 1. We feel that this is quite justified, since E_G was an input parameter of the calculation rather than a result of the selfconsistently computed charge neutrality.⁴ If the latter is included in a new calculation, significantly better agreement between theory and experiment is to be expected.

The IPES spectrum of Fig. 1(a) was measured on a sputter-cleaned and annealed $SrTiO_3(100)$ surface. We also measured a mechanically polished sample, which had been inserted into vacuum immediately after having been rinsed in acetone. The IPES spectrum was essentially identical to the one in Fig. 1(a) for a sputter-annealed surface. We did not notice any changes of relative intensities, when different Ar-ion energies were used for sputtering. Exposure of a clean surface to several langmuirs of oxygen (1 $L=1\times10^{-6}$ Torr sec) did not produce any change in the experimental conduction-band DOS. Such changes would have been indicative of intrinsic surface states, as was calculated by Wolfram and co-workers.⁵

Powell and Spicer¹⁵ and Henrich *et al.*⁹ have given an upper experimental limit of $\sim 10^{13}$ SS/cm² as compared to $\sim 10^{15}$ SS/cm² in the first calculations of Wolfram *et al.* New calculations⁵ including the Coulomb repulsion among the *d* electrons found the SS always above E_F , so

that in Nb-doped or heavily reduced samples with E_F at the conduction-band edge, the SS remain unoccupied and fall within the bulk conduction band. They should be detectable with inverse photoemission similar to SS as found on GaAs(110).²⁴ According to our findings [cf. Fig. 1(a)], there is no evidence for unoccupied surface states on SrTiO₃(100).

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