

I-8. Photoemission Studies on Strontium Titanate

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Photoemission studies have been carried out on etched (100) surfaces of single crystal SrTiO_3 cleaned by heating in ultra high vacuum. A low energy tail in the yield versus photon energy curve has been identified as emission from defects located in the forbidden gap. Measurements at higher photon energies, together with measurements of the energy distributions of emitted electrons, are explained in terms of the calculated band structure. The results are compared with reflectivity measurements on SrTiO_3 .

§ 1. Introduction

SrTiO_3 has a simple cubic structure and is characterized by a forbidden gap of 3 eV and a dielectric constant of 220 at room temperature. Depending on the degree of reduction and the temperature, it can act as an insulator, a semiconductor or a superconductor. Kahn and Leyendecker,¹⁾ using the L.C.A.O. method, have made an approximate band structure calculation for this material using the 2p oxygen states and the 3d titanium states. The valence bands are largely derived from the former and the conduction bands from the latter. A correction to the calculation has been pointed out by Simanek and Sroubeck.²⁾ Reflectivity measurements by Cardona³⁾ are in fair agreement with the band calculation.

The present study was carried out in order to obtain further information about the band structure and to elucidate the influence of surface conditions on the effective work function. The latter information is of importance in understanding the behaviour of contacts on this material.

Complications arising from the bending of the energy bands will be unimportant in the photoemission spectrum of SrTiO_3 as the high dielectric constant and the low defect density cause the bending to occur over a distance large as compared to the escape depth of the photoelectrons. A similar state of affairs exist in the case of BaTiO_3 .⁴⁾

§ 2. Experimental

SrTiO_3 crystals cannot be cleaved and the surfaces were thus prepared as follows. Boules supplied by the National Lead Company and prepared by the flame fusion technique were

sliced along the (100) plane. These were etched at 130°C in H_3PO_4 in order to remove the region of mechanical damage. After degreasing and washing in deionised water the crystal under study was mounted and was baked, together with the apparatus, for 24 hours at 400°C and at a pressure of the order of 10^{-7} torr. The crystal was then heated to 400°C in a vacuum of 10^{-9} torr. Measurements were taken at room temperature in a time short as compared to that for a monolayer of gas to form on the surface. There is some doubt as to the nature of the final surface but, in view of the results presented below, it is reasonable to assume that an approach to an atomically clean surface was achieved.

The experimental technique used in the determination of the photoelectric yield has been described elsewhere.⁴⁾ Energy spectra of electrons for fixed incident photon energies were obtained using a retarding field method. Photocurrent versus energy was recorded automatically and the energy spectra were obtained by graphical differentiation.

The photocell used was spherical and had a thick evaporated layer of gold acting as the collector.

§ 3. Results

Quantum yield versus photon energy curves for the (100) surface of SrTiO_3 prepared as described are shown in Fig. 1. Correction for reflectivity has been made from the data of Cardona.³⁾

The curve exhibits a low energy tail beginning at a photon energy of about 3.8 eV and extending over a range of almost 1 eV. Above about 4.7 eV the yield rises linearly with photon energy.

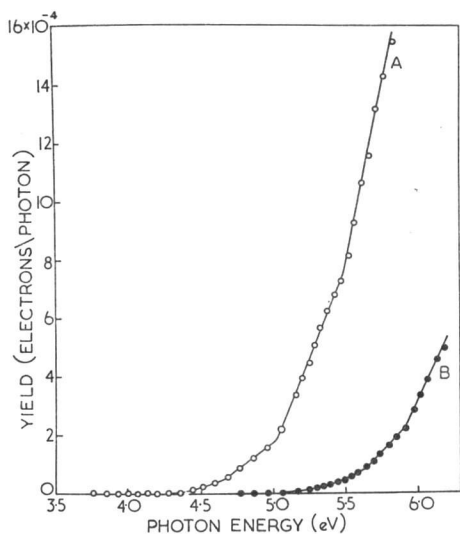


Fig. 1. Photoelectric yield, in electrons per absorbed photon, versus photon energy for SrTiO₃ single crystal. (A) Baked at 400°C in a vacuum of 10^{-9} torr. (B) Exposed to the atmosphere for 5 minutes.

Two further linear components are observed with thresholds at 5.02 and 5.52 eV. The yield rises linearly up to the short wavelength limit of the monochromator of 6.2 eV. The yield at photon energies above 4.5 eV was reproducible to within a few percent. The reproducibility of this emission and the sharp, linear, increase in yield is typical of emission from valence band states. According to the theory of Kane⁵⁾ such linear dependences can only be described in terms of direct transitions in the bulk crystal followed by the emission of the excited electrons without scattering either in the bulk or at the surface (neglecting surface state emission). In this case the tangential energy of the emitted electron is conserved on passing through the surface barrier. Hence we ascribe the linear portions of the yield spectrum to such emission from the bulk crystal.

The emission in the tail region was not reproducible between different samples. The dependence of the yield on photon energy could be described by a cubic relationship of the type described for BaTiO₃ in ref. 4). Such emission is often described in terms of indirect transitions^{6,7)} or emission from surface states.⁸⁾ In an attempt to establish the origin of the tail emission for SrTiO₃, the sample was heated at 500°C for 2 hours in ultra high vacuum. The effect of such a treatment is shown in Fig. 2

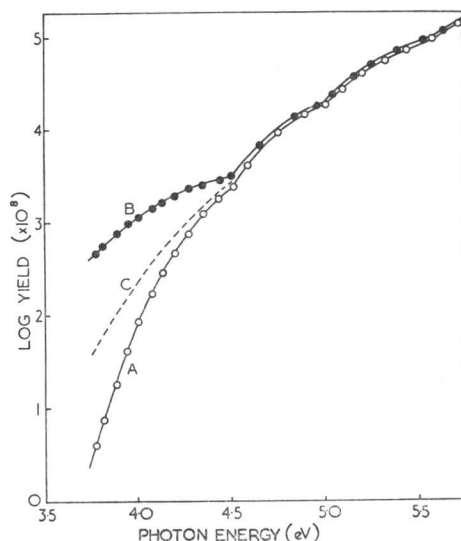


Fig. 2. A plot of log yield versus photon energy for SrTiO₃ single crystal. (A) Baked at 400°C, 10^{-9} torr. (B) Baked at 500°C for 2 hours in vacuum. (C) Baked at 400°C in the atmosphere, followed by baking at 400°C, 10^{-9} torr.

where the yield has been plotted on a log scale to bring out the details. The yield at high photon energies has increased very little, notably the positions of the breaks in the yield curve are unchanged. This substantiates the argument that the emission for $h\nu > 4.5$ eV is due to valence band emission. Such a small change in the form of this emission we take as evidence that the surface is reasonably free of chemisorbed contamination. We cannot, however, be certain that it is the first monolayer that has been removed.

The yield at low photon energies, however, was increased by over two orders of magnitude as seen from curve B of Fig. 2. SrTiO₃ is known to reduce at temperatures in excess of about 400°C. In an attempt to discover whether the increased emission was associated with loss of oxygen from the crystal the following experiment was carried out. A sample baked at 500°C in vacuum was exposed to oxygen at atmospheric pressure and baked at 400°C for 4 hours. The photocell was then re-evacuated and the sample surface cleaned in the usual manner. Curve C of Fig. 2 resulted, the yield in the tail region has decreased towards its original value after oxidation. The effect produced by the same treatment in nitrogen was negligible. Hence the tail emission must be ascribed to defects formed in the forbidden gap due to the loss of oxygen

brought about by the outgassing procedure. Although the yield in this region is dominated by impurity emission, emission from surface states or a component of indirect emission cannot be completely ruled out.

Curve B of Fig. 1 shows results taken after a clean SrTiO_3 surface had been exposed to air or oxygen at atmospheric pressure for 5 minutes. The kinetic of the chemisorption was similar to that discussed for BaTiO_3 in ref. 4), and is explained in terms of a model due to Melnick⁹⁾ and Medved.¹⁰⁾ The yield curve is shifted in a parallel manner by about 1 eV, the tail region being shifted identically, due to the dipole layer formed by the chemisorbed oxygen. The model predicts only a small surface coverage. This is consistent with our results. The effect of chemisorption on SrTiO_3 will be published more fully elsewhere.¹¹⁾

The energy distributions of the photoelectrons are shown in Fig. 3. These were taken on a surface cleaned as described earlier and have been normalized to the same height to bring out the details. The cut off and saturation points in the I-V characteristics were well defined and it was established that the effect of surface charge due to the high resistance of the sample was negligible. The energy zero was established in the customary manner from the saturation points in the I-V characteristics.

§ 4. Discussion of Results

We have seen that the yield versus $h\nu$ curve for SrTiO_3 is made up of a low energy tail which is predominantly due to emission from impurities located in the forbidden gap, followed by a linear rise in yield which is characteristic of emission from valence band states. The latter emission is direct, according to Kane,⁵⁾ and involves no scattering of excited electrons before escape. The tangential momentum of the emitted electron is conserved and, according to the theory, if the surface is a symmetry plane, the emission near threshold should occur on this symmetry axis, so that no tangential momentum is required on emission.

As the SrTiO_3 surfaces consist predominantly of the (100) plane, emission near threshold should occur on this axis in k space. We hence proceed to analyze our results in terms of the calculated band structure¹⁾ moving from the centre to the edge of the Brillouin zone in the [100] direction. The calculated band structure in this direction is shown in Fig. 4.

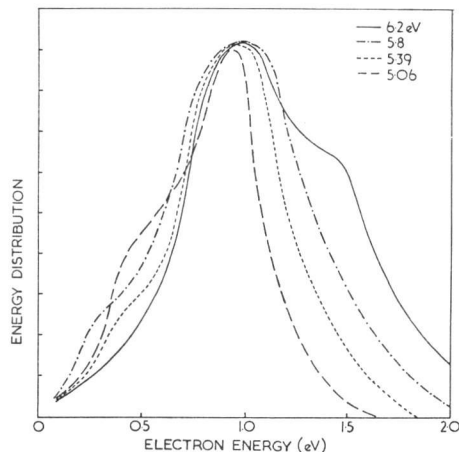
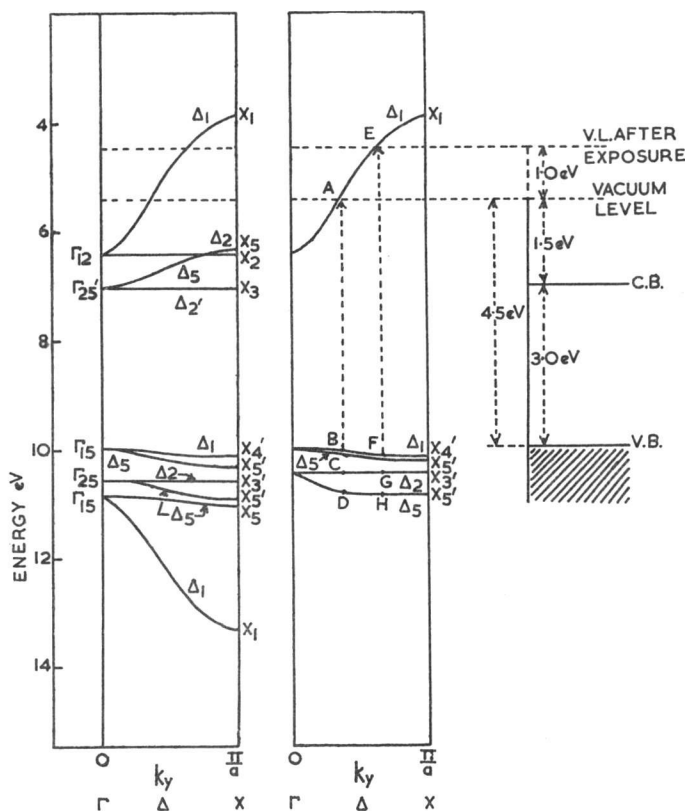


Fig. 3. Energy distributions of emitted electrons for SrTiO_3 single crystal, normalized to the same height.

According to the calculation of the upper valence band Δ_1 is almost flat as k increases from the centre of the zone at Γ to the edge at X . In the yield spectrum of SrTiO_3 the threshold for the first direct emission occurs at the extrapolation to zero yield of the first linear portion. This occurs at $h\nu = 4.55$ eV. The position of the vacuum level is obtained by drawing a vertical line 4.55 eV long from the upper valence band. The only conduction band intersected by the vacuum level in the [100] direction is Δ_1 . Hence all transitions must occur to this Δ_1 conduction band. The electron affinity of the surface is then about 1.5 eV.

Parity and group theoretical selection rules allow transitions between the upper Δ_1 valence band and the Δ_1 conduction band. The only other transitions allowed to Δ_1 are from the upper and second Δ_5 valence bands which we label $\Delta_5^{(1)}$ and $\Delta_5^{(2)}$ respectively and the Δ_2 band. Hence we attribute the first linear component to direct transitions from Δ_1 or $\Delta_5^{(1)}$ to Δ_1 with a threshold at 4.55 eV. The second component is attributed to Δ_2 to Δ_1 , and the third to $\Delta_5^{(2)}$ to Δ_1 , transition with thresholds at 5.02 and 5.52 eV respectively. The separation of the valence bands is given by the difference in these threshold energies.

The parallel shift in the yield curve on exposure to air indicates that the valence bands are almost parallel. The shift is consistent with the model of transitions from flat valence bands to a rising conduction band at least over a limited range of k . As the electron affinity



changes the vacuum level is moved up the Δ_1 curve by about 1 eV.

The energy distribution measurements are also in partial agreement with this model, although it demonstrates that the model is not complete. We emphasize that our resolution was not good enough to distinguish between direct and indirect transitions in the energy distributions.

The distributions consist of shoulders which move to higher energies with increasing $h\nu$, and an apparently stationary peak situated at an energy of 0.9 to 1.0 eV. The low energy shoulder appearing at an energy of about 0.5 eV for $h\nu=5.06$ eV has moved to a higher energy at $h\nu=6.2$ eV by an amount approximately equal to the difference in photon energy. A second shoulder appears at an energy of about 0.45 eV for $h\nu=5.39$ eV followed by a third at an energy of about 0.4 eV for $h\nu=5.8$ eV. Both these shoulders move to higher energies with increasing $h\nu$ and cannot be resolved from the stationary peak for $h\nu=6.2$ eV. These shoulders are attributed to emission from the flat valence bands A_1 or $A_5^{(1)}$, A_2 , and $A_5^{(2)}$ to the A_1 conduction

band. From the positions of the low energy shoulders the separation of the valence bands are found to be 0.4 ± 0.1 eV for Δ_1 or $\Delta_5^{(1)}$ from Δ_2 , and 0.6 ± 0.1 eV for Δ_2 from $\Delta_5^{(2)}$. These are in good agreement with the values determined from the yield curve.

It is probable that the apparently stationary peak at high photon energies is due predominantly to the direct emission mechanism. At a photon energy of 6.2 eV the shoulders due to transitions from $A_5^{(1)}$ and $A_5^{(2)}$ to the A_1 conduction band have energies in the vicinity of 1 eV. It is probable that these shoulders overlap appreciably and their combined effect could account for the main peak. In addition it is likely that emission centred at an energy of about 1 eV and associated with (110) planes serves to blur out the resolution of the peaks due to direct transitions. Our surfaces are far from perfect and a reasonable area of planes other than the (100) are exposed as consequence of etching. Such an emission could result from transitions from impurities or valence band states to states in the vicinity of M_1 in the band cal-

ulation (not shown in Fig. 4). Such an inflexion point represents a high conduction band density of states and, according to the calculation, it is situated about 1 eV above our vacuum level. This emission is probably small and its effect is not observed in the yield curve. However it is sufficient to blur the resolution of the shoulders due to the direct transitions.

Table I.

	Δ_1 or $\Delta_5^{(1)} - \Delta_2$	$\Delta_2 - \Delta_5^{(2)}$	Δ_1 or $\Delta_5^{(1)} - \Delta_5^{(2)}$	$X_4' - X_5'$
Theory ¹⁾	0.5 eV	0.3 eV	0.8 eV	0.9 eV
Reflectivity ³⁾				0.88
Yield curves	0.47 ± 0.05	0.5 ± 0.05	0.97 ± 0.05	
Energy distributions	0.4 ± 0.1	0.6 ± 0.1	1.0 ± 0.1	

Finally, in Table I, we give our results for the band structure of SrTiO₃ together with the

separation of X_4' and X_5' determined from reflectivity measurements by Cardona.³⁾

References

- 1) A. H. Kahn and A. J. Leyendecker: Phys. Rev. **135** (1964) A1321.
- 2) E. Simanek and Z. Sroubeck: Phys. Status solidi **8** (1965) K47.
- 3) M. Cardona: Phys. Rev. **140** (1965) A651.
- 4) O. H. Hughes, R. H. Tredgold and R. H. Williams: J. Phys. Chem. Solids **27** (1966) 79.
- 5) E. O. Kane: Phys. Rev. **127** (1962) 131.
- 6) G. W. Gobeli and F. G. Allen: Phys. Rev. **137** (1965) 245.
- 7) T. E. Fischer: Phys. Rev. **142** (1966) 519.
- 8) J. J. Scheer and J. Van Laar: Phys. Letters **3** (1963) 246.
- 9) D. A. Melnick: J. chem. Phys. **26** (1956) 1136.
- 10) D. B. Medved: J. Phys. Chem. Solids **20** (1961) 255.
- 11) R. H. Tredgold and R. H. Williams: to be published.