X-Ray Photoelectron Spectroscopy of Pure and V-doped Ti₂O₃*

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The X-ray photoelectron spectrum of Ti_2O_3 is reported for binding energies in the range 0 to 600 eV. The effects of heating the material from 300 to 600 eV and of incrementally doping Ti_2O_3 with up to 10 at. % V_2O_3 were investigated. The measurements provide direct information on the nature of the band states which are in good agreement with indirect deductions based on prior electrical measurements.

Introduction

In this publication we report on X-ray photoelectron spectra of pure and V-doped Ti_2O_3. The research was undertaken to obtain more direct information on the nature of the occupied band states in $(V_xTi_{1-x})_2O_3$ for $0 \leqslant x \leqslant 0.1$. This is intended to complement the indirect information available from recent electrical measurements (1). To assist in the understanding of the data presented below it is important to recall that Ti_2O_3, upon being heated in the temperature range from 380 to 550°K, or on being incrementally doped with V_2O_3 in the range between 0 and 10 at. %, undergoes a slow semiconductor–metal transition (1–4). Both processes are associated with the gradual closing of a band gap between a lower-lying filled d–a_1 and a higher-lying empty d–e band. In addition, the introduction of V into Ti_2O_3 yields a spin glass at low V concentrations (5) and ultimately produces (6) an impurity V-band overlapping with the valence band of the host crystal at high V doping levels.

Experimental Techniques

Single crystals were grown from the melt by a technique detailed elsewhere (7). Flat pieces

were cut, etched in CP-4 solution, and washed in deionized water. A commercial X-ray photoelectron spectrometer was used; the instrument was calibrated by evaporation of a thin gold layer on the sample, thus providing a direct measure of the Fermi level position ε_F for the specimens. All energies in this paper are cited with respect to this reference value. The experimental technique was otherwise the same as that used in the study of the band structure of V_2O_3 (8); the reader is referred to this and a related publication (9) for cautionary comments concerning the use of the XPS technique in the study of band structures of solids. Most troublesome of the various difficulties is the fact that surface electronic states may seriously interfere with observation of the bulk electronic properties. The results reported below should be viewed in light of this problem.

General Results

The results obtained over a six-month interval on four distinct Ti_2O_3 specimens are summarized schematically in Fig. 1. The rectangular cross-hatched areas indicate the extension on the energy scale of each spectrum. The various lines show the location of the principal peaks, subsidiary peaks, or shoulders, by large, intermediate, or small straight line segments. The corresponding atomic levels for Ti and O cited by Bearden
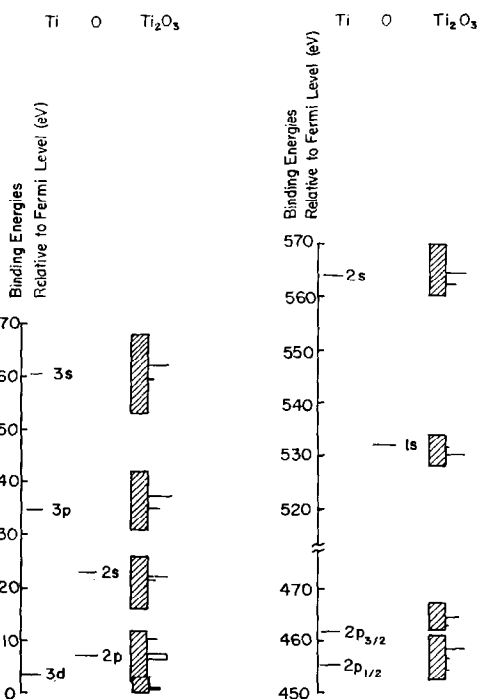
FIG. 1. Schematic representation of the XPS spectrum for pure Ti_2O_3. Atomic energy levels shown under the columns labelled Ti and O (*10*). Cross-hatched areas represent band spectra; line segments of variable length indicate peak positions as well as intensities. Energy levels cited relative to Fermi level of Au.

and Burr (*10*) are also indicated. Inspection shows: (a) that all observed bands can be correlated with their corresponding atomic levels. (b) Each principal peak of the various Ti and O bands is inevitably accompanied by a subsidiary peak or shoulder or by marked line asymmetry. For Ti and for O the subsidiary maximum occurs at lower and higher binding energies respectively. We attribute this primarily to deviations from stoichiometry, balanced by the conversion of corresponding numbers of cations to a different valence state. As has recently been pointed out (*11*), such deviations can produce localized energy states that occur in the gap separating the a_1 and e bands; these have been detected in electrical measurements (*11*). (c) On the other hand, these shoulders may be associated with surface states since they are largely eliminated by Ar^+ ion bombardment; they reappear again on subsequent exposure of the samples in the vacuum chamber maintained at ca 10^{-8} Torr. By contrast, bulk Ti_2O_3 may be stored for long periods of time at room temperature under atmospheric conditions without noticeable deterioration. (d) Smoothed traces of the bands in the 0 to 15 eV binding energy range taken over a 26 hr period are shown in Fig. 2, curves (a) and (b), along with a possible deconvolution, curves (c) and (d). These results point up the difficulty in the study of
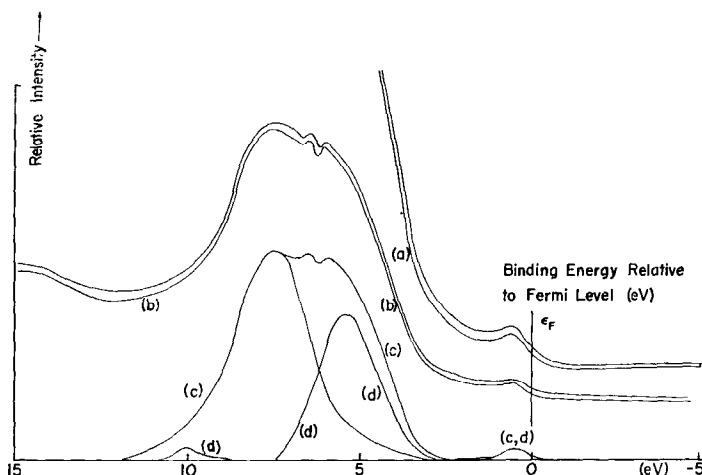

FIG. 2. XPS Spectrum for Ti_2O_3. Curve (b): Ti 3-d and O-2p bands in the range of -5 to $+15$ eV, relative to the Fermi level of Au. Curve (a): same, at greater magnification. Curve (c): obtained on correction of Curve (b) for sloping baseline. Curve (d): a possible deconvolution of spectrum (c). (Double line is envelope of noise.)

the valence band in Ti_2O_3, which is a factor of 20 weaker in intensity than the proximate O $2p$ band.

Effects of Heating and of Doping with V_2O_3

A special effort was made to compare the valence band spectrum of Ti_2O_3 obtained at room temperature with the corresponding band observed at 580°K. At $T = 300°K$ the solid is an insulator with a bandgap of $\varepsilon_g \simeq 0.1$ eV; above 550°K the material is metallic (12, 13). The highest occupied Ti $3d$ bands obtained at high sensitivity levels are compared in Figs. 3(a) and 3(b). Careful examination shows: (a) that the spectrum at

300°K terminates just short of the Fermi level ε_F, as indicated by a low spectral intensity at $\varepsilon = 0$, compared to the peak which occurs at 0.6 eV. By contrast, the Fermi level intersects with the Ti $3d$ band at 580°K, witness the dropoff of the band intensity at energies well above the Fermi level. These observations are consistent with deductions based on prior electrical measurements (1). (b) The d-band half-width as determined from Figs. 2 and 3 and from other spectra not reproduced here is in the range 1 to 1.5 eV; this directly substantiates the bandwidth value of 1 eV which was assumed earlier to obtain good fits with electrical (13), thermal (14), and elastic constant (15) measurements. (c) At the higher
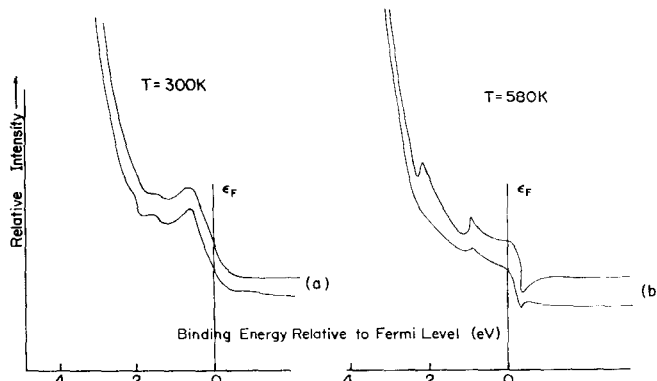

FIG. 3. Effect of raising the temperature of Ti_2O_3 on the Ti 3-d band. (a) Ti-$3d$ band at 300°K. (b) Ti-$3d$ band at 580°K. (Double line is envelope of noise.)
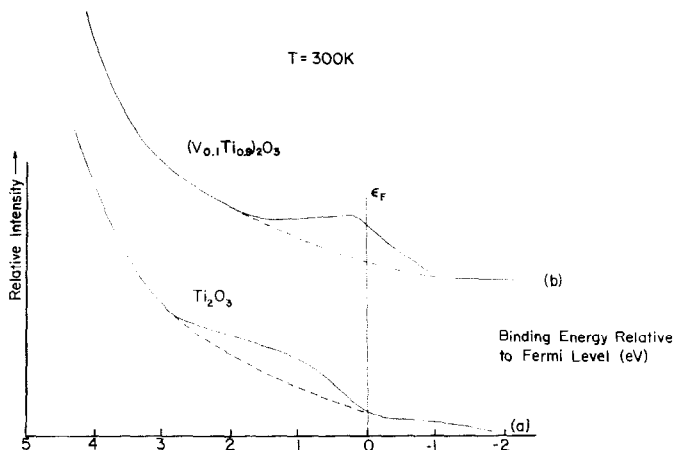

FIG. 4. Effect of Doping of Ti_2O_3 with V_2O_3 on the Ti-$3d$ band. (a) Undoped Ti_2O_3 at 300°K. (b) $(V_{0.1}Ti_{0.9})_2O_3$ at 300°K.

temperature the Ti $3d$ band merges to a greater extent with the O $2p$ band than it does at lower temperature; these findings nicely corroborate similar observations carried out on NbO_2 (*16*), La_2NiO_4 (*16*), and VO_2 (*17*), all of which undergo metal–semiconductor transitions.

The effect of incorporating 10 at. % V_2O_3 in Ti_2O_3 is shown in Fig. 4, where the smoothed d-band spectra of Ti_2O_3 and $(V_{0.1}Ti_{0.9})_2O_3$ taken at 300°K are compared. This figure shows up clearly that for the doped compound the Fermi level intersects the d-band at room temperature, in contrast to undoped Ti_2O_3. These results agree with the observation (*2*) that at room temperature the 10 at. % alloy is metallic. Here, as before, the band shapes are distorted because they are superposed on a strongly sloping baseline whose gradient is rapidly changing. Spectra obtained on Ti_2O_3 doped with 2 at. % V_2O_3 are virtually identical with those of pure Ti_2O_3. The intensity of the peak in Fig. 4(b) is relatively much greater than that encountered in Fig. 3(a), corresponding to the fact that the narrow impurity V band is characterized by a high density of states, $g(\varepsilon)$, as compared to the $g(\varepsilon)$ associated with the Ti-d band. However, because of the rather poor instrumental resolution the very sharp V impurity band is broadened and its relative intensity considerably reduced over what should actually be the case.

Acknowledgments

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