Angle resolved photoemission of single crystal SnO2 using synchrotron radiation
by Peter Leland Gobby

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR oF philosophy in Physics
Montana State University

Abstract:
Polarization dependent angle-resolved ultraviolet photoemission (PARUPS) measurements have been performed on single crystal SnO2(001) using synchrotron radiation. Using photon energies up to 40 eV angle-integrated data revealed a total valence band width of approximately 9 eV, with a large density of states centered about 1.5 eV below the valence band maximum due to oxygen 2p states. A core level and its associated excitons were also investigated and have been interpreted as due to tin 4d levels.

Angle-resolved measurements allowed certain lower valence band structures to be emphasized which also showed strong polarization dependences. These structures have also been interpreted as due to tin 4d states. A covalent model was proposed which' allowed this tin 4d character in both the ohserved core and the lower valence bands, though the two were separated by about 15 eV. Another initial state feature just above the valence band maximum was studied and has been interpreted as due to a large concentration of oxygen vacancies near the surface. It was felt that these vacancies were induced by annealing the crystal in vacuum.

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ABSTRACT

Polarization dependent angle-resolved ultraviolet photoemission (PARUPS) measurements have been performed on single crystal SnO_2(001) using synchrotron radiation. Using photon energies up to 40 eV angle-integrated data revealed a total valence band width of approximately 9 eV, with a large density of states centered about 1.5 eV below the valence band maximum due to oxygen 2p states. A core level and its associated excitons were also investigated and have been interpreted as due to tin 4d levels.

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I. INTRODUCTION

Since the pioneering work of Berglund and Spicer[1] less than 15 years ago, ultraviolet photoemission spectroscopy (UPS) has grown to be one of the leading tools of the solid-state physicist. Its appeal is two-fold. First the photon energy range of 1 - 50 eV used is in the range necessary to excite valence electrons and shallow core electrons into normally unoccupied states. It is these valence and shallow core electrons which contribute to molecular and crystal binding and are consequently of primary interest to the solid-state physicist. The second appeal lies in the fact that UPS is a double spectroscopy. That is, electron emission is determined as a function of the final energy of the electron as well as the photon energy. In contrast, a reflectance experiment, for example, is a single spectroscopy, since the reflectance is determined as a function of only the photon energy.

More recently, the availability of synchrotron radiation[2] with its intense continuum has made it practical to restrict the emission angle of the detected electron over a wide range of final energies. In effect, this allows one to measure the momentum as well as kinetic energy of the emitted electron. The polarized nature of the synchrotron radiation has also been utilyzed to help bring about polarization dependent angle-resolved photoemission. These studies have allowed

the determination of high densities of states in the electronic energy band structure of gallium arsenide[3] and tungsten[4] and, in the case of some two dimensional crystals[5] and surface states[6,7], direct measurement of the total electronic energy bands.

Tin oxide provides an interesting challenge for this powerful tool. It is known to be a wide band gap (E_g ~ 3.5 eV) semiconductor crystallizing in the rutile structure. Naturally occuring crystals are known as cassiterite. It is chemically inert, with a high melting point, perhaps as high as 2000°C.[8] Its most notable current use is as a transparent conducting film on airplane windows for purposes of defrosting.

Relatively little is known about the electronic structure of SnO_2 compared to, say, silicon, gallium arsenide, tungsten or even the alkali halides. Most experimental work has centered on electrical conductivity measurements[9,10,11] and optical studies[12-18] at or near the band gap. Conductivity experiments have particularly been hampered by a lack of good quality single crystals. Prior to this work, no photoemission work had been reported. Theoretical studies are few; this is due in part to the complicated rutile structure. There have been two band calculations reported in the literature, with values for the valence band widths of approximately 5 eV[19] and more than 10 eV[20], respectively.

Furthering the understanding of SnO_2 - particularly its

electronic structure - can benefit two scientific groups: theoretical physicists and semiconductor device physicists. The benefits to the latter group are straightforward and uncomplicated. The search for rugged high temperature semiconductor devices remains in progress. Tin oxide, with its chemical inertness and wide band gap, definitely has potential in this regard. In a related vein, some work has been done on indium-tin oxide and antimony doped tin oxide films regarding selective surfaces for solar collectors.[21] Pertinent data on the electronic structure of tin oxide will be necessary to maximize the probability of success in these two areas.

Tin oxide should be interesting to theoretical physicists because of its lack of simplicity. The more standard semiconductors - silicon, germanium and gallium arsenide - have two simplifying things in common: cubic symmetry and predominantly covalent bonding using atomic s and p orbitals. The electronic structures of these materials consequently have a number of similarities. The calculated energy band structures have been checked against much experimental data and have fared well.[3,4] The band structure theorists have thus been able to check and adjust their calculation techniques for these materials and now can extend these techniques to similar materials with a high degree of confidence. But extension to tin oxide is not so straightforward. Evidence of this lies in the difference of the calculated band widths previously mentioned. The unit cell of tin oxide is

tetragonal instead of cubic, and the bonding is probably not well described as either covalent or ionic, but a strong mixture of the two. There is even evidence in this study of significant d as well as s and p atomic orbitals involved in the covalent aspect of the binding. Experimental data on more complicated systems such as tin oxide will allow the theoretical techniques to be advanced still further.

Pertinent data on the electronic structure of tin oxide have been acquired in this thesis project. Using photon energies up to 40 eV, the valence bands (VBs), lower conduction bands (CBs) and an atomic-like core level were studied. A structure lying just above the valence band maximum (VBM) was observed and has been interpreted as due to defects induced by sample preparation. Exclusion of this defect structure from the bulk VBs resulted in a total experimental VB width of ~9 eV. Angle-resolved measurements allowed some VB structures to be further emphasized, so that interpretation of their respective atomic origins was somewhat simplified. These data seem to indicate that bonding in SnO_2 has strong covalent as well as ionic character.

II. SnO_2 BACKGROUND DATA

A. Structure of Tin Oxide

Tin oxide crystallizes in the rutile structure with space group D_{4h}^{14}.[22] The unit cell shown in Fig. 1 is simple tetragonal and contains two tin atoms and four oxygen atoms. $a = b = 4.74$ Å, while $c = 3.19$ Å, and the nearest neighbor oxygen-oxygen distance is 2.54 Å.[23] With these x-ray diffraction data, it is then straightforward to calculate the remaining pertinent parameters.

Each tin atom is surrounded by an irregular octahedron of oxygens. The Sn-O distance is 2.08 Å for those lying in an (001) plane and 2.04 Å for the remaining four. The O-Sn-O "dumbell" in the (001) plane is perpendicular to the plane containing the tin atom and the other four oxygen atoms. The acute angle between two adjacent oxygens with the tin atom at the vertex is 77°.

Another perspective of the tin oxide structure can be attained with the help of Fig. 2, a view of the (001) face of the crystal looking down the $\vec{c}$ axis. The sizes of the tin and oxygen spheres correspond to their ionic radii - Sn^{4+} and O^{2-}, respectively.[24]

For completeness the Brillouin zone (BZ) for stannic oxide is shown in Fig. 3. The irreducible 1/16 zone is labeled with symmetry points and lines following the notation of Koster.[25]

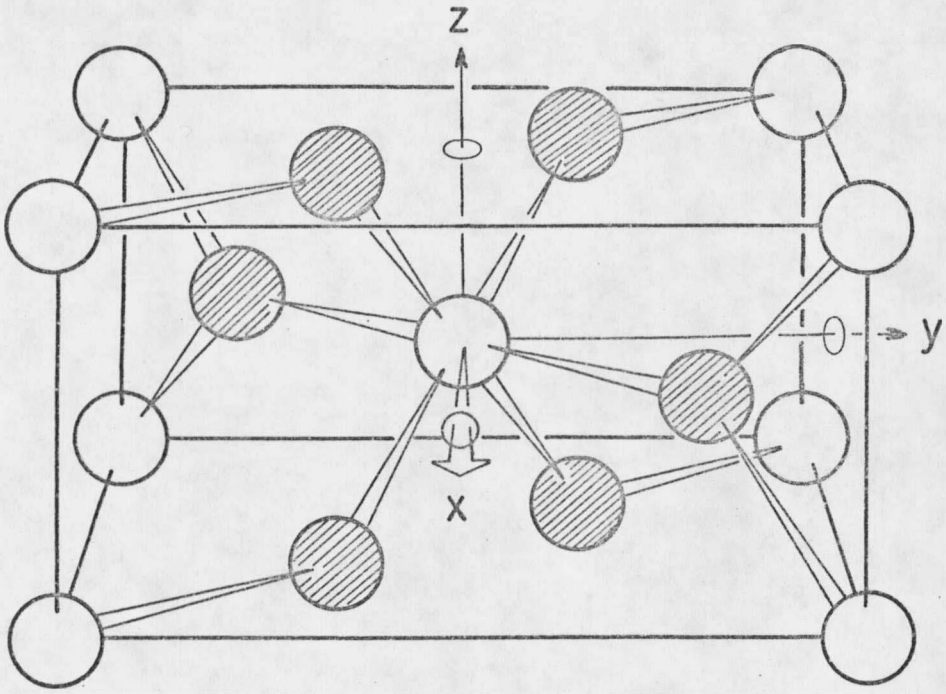

FIG. 1. SnO_2 unit cell. Shaded spheres represent the oxygen atoms.