Evidence that LVV Auger transitions in oxygen can result in low-energy electron emission

Alex J. Fairchild¹, Varghese A. Chirayath¹, Randall W. Gladen¹, Ali R. Koymen¹, and Alex H. Weiss¹

¹Department of Physics, University of Texas at Arlington, Arlington, Texas 76019, United States

ABSTRACT

In this paper, we present evidence of low-energy electron emission resulting from the LVV Auger decay of oxygen 2s holes. Low-energy Auger electron emission is difficult to observe principally because of the large, primary beam-induced secondary electron beam. We have overcome this background limitation by using positron-electron annihilation to initiate the Auger process. We present time-of-flight positron annihilation-induced Auger electron spectroscopy measurements of Cu, Si and TiO₂ surfaces using positrons with kinetic energies less than 1.5 eV. These experiments demonstrate that the majority of spectral weight in the annihilation-induced Auger electron spectra in the energy range of 0-15 eV is associated with the presence of oxygen at the surface. Using an empirically derived lineshape model that takes into account final state effects and the oxygen 2s photoemission line width, we argue that the low-energy intensity is consistent with the Auger decay of annihilation-induced 2s holes in oxygen (O LVV). In addition, we have calculated theoretically the electron kinetic energy distribution of O LVV Auger electrons emitted from a TiO₂(110) surface. The calculated lineshape is in excellent agreement with our experimental results. Finally, using the measured Auger intensities and the calculated O LVV lineshape, we estimate that the positron annihilation probability for O 2s electrons on a TiO₂ surface is 5.86%.

1 Introduction

Studies of the interactions between O₂ and clean metal surfaces are important for understanding the catalytic activation that adsorbed oxygen can have on metal surfaces [1, 2, 3]. For studying clean and adsorbate covered surfaces, Auger electron spectroscopy (AES) has found widespread success and has become an almost indispensable technique for determining surface cleanliness, adsorbate coverage, and surface electronic information [4]. For example, AES studies have yielded important insights into the oxygen-driven catalysis of nanoporous gold and provided quantitative information regarding the surface oxidation states of oxides [5, 6]. Historically AES studies have exclusively examined oxygen KVV, in which the initial core hole is in the oxygen 1s levels, and/or core-valence-valence (CVV) Auger processes from the oxygen bonded metal atoms. In this manuscript, we present time-of-flight positron annihilation-induced Auger electron spectra (ToF-PAES) of O₂ adsorbed Cu and Si surfaces and an oxide TiO₂ surface which contain large contributions from oxygen LVV Auger processes, in which the initial core hole is in the oxygen 2s levels. The O LVV Auger process is initiated when a surface trapped positron annihilates with a 2s electron in oxygen which is subsequently filled by a less tightly bound valence electron. The energy associated with this hole filling is then coupled to a third electron in the valence band which can escape as an Auger electron. This process is schematically represented in Fig. 1.

O 2s binding energies are typically on the order of 25 eV so O LVV Auger electrons are expected to be emitted with energies less than 20 eV. This low-energy region of the Auger spectra is particularly difficult to observe in traditional photon or electron stimulated AES due to the large beam-induced secondary electron background. However, this obscuring secondary electron background can be completely eliminated by using matter-antimatter annihilation to initiate the Auger process. In positron annihilation-induced Auger electron spectroscopy (PAES), incident beam energies well below typical electron work functions can be used to initiate the Auger process making possible the measurement of background-free Auger spectra [7, 8, 9, 10]. An added advantage of PAES is that it is a top-most layer selective...
Figure 1: Schematic representation of an O LVV Auger process. A surface trapped positron annihilates with an L-shell electron with binding energy $E_L$. An Auger transition occurs in which a valence band electron, with binding energy $E_1$, comes to occupy the energy level of the core hole. The energy associated with this transition is coupled to another valence electron with binding energy $E_2$, which then escapes to the vacuum.

surface spectroscopy since the positrons localize in an image-potential induced surface state at the vacuum-surface interface prior to annihilation [11, 12]. Finally, the elimination of the secondary electron makes PAES unique in its capability to study Auger transitions resulting in low-energy electron emission (< 20 eV) which is an important energy range for biological important processes such as DNA strand breaks through dissociative electron attachment [13, 14].

We have constructed an empirical lineshape model which takes into account the width of the oxygen 2s photoemission lines for CuO, SiO$_2$, and TiO$_2$ as well as final state effects such as the hole-hole correlation strength. Finally, the O LVV Auger electron energy distribution from a TiO$_2$ surface has been calculated using a first principles based model which incorporates the occupied O 2s and valence states of TiO$_2$. The agreement between the theoretical calculation and our measurements indicate that, like the O KVV Auger line, the O LVV Auger line is a probe of the surface electronic structure which is expected to be important for future studies and applications. Few reports of O LVV Auger electron emission exist in the literature [15, 16, 17] and no mention is found in the Auger handbook [18]. We believe this manuscript to represent the first quantitative analysis of O LVV Auger electron emission and the first observations of O LVV Auger emission from the surfaces of oxygen adsorbed Cu, oxygen adsorbed Si and the oxide TiO$_2$ surface.

2 Experimental

The experiments presented in this manuscript were carried out using the University of Texas at Arlington’s positron beam system. The system is comprised of three parts: a positron beam with magnetic transport, a ToF energy spectrometer, and a sample preparation chamber. A more complete description of the system and its capabilities is provided in reference [19] and so only a brief summary will be presented here. Positrons from a $^{22}$Na source are moderated using a thin tungsten foil in transmission geometry before being magnetically guided to the sample. A permanent samarium–cobalt magnet is mounted a few mm behind the sample which parallelizes the positron-induced electron momentum. The ToF of the electrons is measured as the time difference between the detection of the 511 keV annihilation gamma rays by a fast scintillator, BaF$_2$ or NaI(Tl), and the detection of the electrons by a microchannel plate (MCP). The sample chamber is kept at a base pressure less than $10^{-8}$ Pa. The incident positron beam energy was measured to be less than 1.5 eV using a retarding field analyzer. The polycrystalline Cu and Si(100) samples were sputter cleaned every 24 hours before exposure to $1.8 \times 10^3$ and $2.7 \times 10^5$ Langmuir of O$_2$ respectively. A rutile TiO$_2$(110) sample, purchased from Sigma-Aldrich, was sputter cleaned then annealed at 875 Kelvin in an O$_2$ environment of $1 \times 10^{-3}$ Pa for 30 minutes prior to measurements. Each spectrum has been divided by a number proportional to the number of positrons annihilating at the sample as determined using a NaI(Tl) detector mounted near the sample.

3 Results and Discussion

3.1 ToF-PAES measurements of Cu, Si and TiO$_2$.

Figs. 2-4 are the ToF-PAES measurements for the clean Cu and Si surfaces, before and after exposure to O$_2$, and the TiO$_2$ surface. In Fig. 2 the sputter cleaned Cu ToF-PAES spectrum exhibits peaks due to the Auger decay of
annihilation-induced 3p holes (Cu M$_{2,3}$VV) at 58 eV and annihilation-induced 3s holes (Cu M$_1$VV) at 103 eV. After exposure to O$_2$ gas, the Cu M$_{2,3}$VV integrated intensity decreased by 42%, the low-energy integrated intensity (0-15 eV) increased by 68%, and the O KVV Auger peak (515 eV) appeared. The O KVV Auger peak is due to the Auger decay of 1s holes in oxygen and indicates clearly that oxygen is present on the surface.

Figure 2: ToF-PAES measurements of clean Cu before and after exposure to O$_2$ gas. Peaks associated with O KVV (a), Cu M$_{2,3}$VV (b), and Cu M$_1$VV (c) Auger processes are present. The data were normalized as described in the experimental section.

Figure 3: ToF-PAES measurements of clean Si before and after exposure to O$_2$ gas. Peaks associated with O KVV (a) and Si L$_{2,3}$VV (b) Auger processes are present. The data were normalized as described in the experimental section.

Fig. 3 shows the ToF-PAES measurements for the sputter cleaned Si(100) before and after exposure to O$_2$ gas. Prior to oxygen exposure the Si L$_{2,3}$VV (89 eV) Auger peak is present. After exposure to oxygen the O KVV Auger peak (505 eV) appears in addition to a 61% decrease in the L$_{2,3}$VV integrated PAES intensity and a 177% increase in the low-energy integrated intensity (0-15 eV). The ToF-PAES measurements from TiO$_2$ are presented in Fig. 4. Both the O KVV (512 eV) Auger peak and the Ti M$_{2,3}$VV (16 eV) Auger peak are visible alongside a broad low-energy peak which we argue is largely due to O LVV Auger electron emission. Figs. 2 and 3 are consistent with previous PAES studies of a sub-monolayer of adsorbed oxygen on Cu and Si surfaces which showed similar reductions in the Cu M$_{2,3}$VV and Si L$_{2,3}$VV integrated intensities [20, 21, 22]. Fig. 4 is the first low-energy PAES spectra of the oxide TiO$_2$ surface and conclusively demonstrates that a positron surface state exists. The relatively small Ti M$_{2,3}$VV Auger signal relative to the two oxygen-derived Auger signals is consistent with the experimental and theoretical results of references [23, 24] in which the authors argue that the wave function of the positron in the surface state primarily overlaps with the oxygen atoms and not the titanium atoms.

Figs. 2-4 demonstrate that the large spectral weight below 15 eV is associated with the presence of oxygen at the surface. Figs. 2 and 3 also demonstrate that this increased low-energy spectral weight cannot be due exclusively to increased inelastic scattering of the main Auger peaks (Cu M$_{2,3}$VV and Si L$_{2,3}$VV). The increased low-energy intensity
is 4 times the decrease in the Cu M$_{2,3}$VV in Fig. 2 and 18 times the decrease in the Si L$_{2,3}$VV in Fig. 3. A ratio of 1 between the increase in the low-energy intensity and the decrease in the main Auger peak intensity is expected if inelastically scattered high energy Auger electrons are responsible for the spectral changes. We argue that the decrease in the main Auger peak intensities is due to the displacement of the positron surface state away from the Cu and Si atoms resulting in a reduced wave function overlap and annihilation rate with the 3p orbitals of Cu and 2p orbitals of Si. This is consistent with previous theoretical and experimental PAES studies of adsorbed oxygen on Cu and Si [20, 21, 22]. It is appropriate to emphasize again that the incident positron beam energy has a maximum kinetic energy cutoff of 1.5 eV. Auger emission processes are the only energetically possible electron emission mechanisms as secondary electron emission process are energetically forbidden at these incident positron beam energies. Accordingly, we argue that the only possible explanation of the large increase in spectral weight below 15 eV is oxygen LVV Auger electron emission.

3.2 Empirical O KVV lineshape model.

In order to test this hypothesis, we have constructed an empirical lineshape model which exploits the fact that the O LVV Auger process has the same final state as the O KVV Auger process. The principal difference between the two Auger processes is the initial energy that the system must dissipate i.e. the difference in the oxygen 1s and 2s core binding energies. Therefore, as a first approximation of the O LVV Auger lineshape, we have taken measured O KVV Auger lineshapes, subtracted the O 1s binding energies and then convoluted them with the O 2s photoemission lines as measured by x-ray photoemission spectroscopy (XPS). The CuO, SiO$_2$, and TiO$_2$ O KVV Auger lineshapes were taken from references [25], [26], and [27] respectively. The XPS data for CuO, SiO$_2$, and TiO$_2$ were taken from references [28], [29], and [30] respectively. The XPS O 1s binding energies are very sharp, typical FWHMs are on the order of 1 eV, and so each O KVV Auger lineshape was shifted to lower kinetic energies by the peak of the O 1s binding energies. Finally, an empirical function which models the probability that an electron has sufficient momentum parallel to the surface to escape was applied. The parameters for this empirical function were taken from reference [12].

In order to remove contributions to the integrated intensity below 15 eV associated with Cu M$_{2,3}$VV Auger transitions, we have normalized the Cu M$_{2,3}$VV integrated intensities before and after exposure to O$_2$ and subtracted the clean spectrum from the spectrum exposed to oxygen. The same procedure was applied to the Si data using the Si L$_{2,3}$VV Auger peak. These corrected spectra, after being converted from ToF to kinetic energy, are shown in Figs. 5 and 6 alongside the empirical OKVV lineshape models. Fig. 7 shows the energy converted spectrum for TiO$_2$ along with its modeled lineshape. To obtain a best fit with experiment, an additional rigid shift of -2.0 eV was applied to the CuO, -2.2 eV was applied to the TiO$_2$ models and a shift of -7.5 eV was applied to the SiO$_2$ model before application of the escape function. An overall scale factor was chosen to bring the peak intensities into agreement. From the comparisons in figs. 5 and 6, we conclude definitively that O LVV Auger electron emission is energetically possible for all measured samples. This taken together with the fact that the low-energy spectral weight is associated with the presence of oxygen at the surface provides compelling evidence that the large, low-energy spectral weight is due to O LVV Auger electron emission.
Figure 5: Comparison between the energy converted ToF-PAES measurements of Cu exposed to O₂, corrected for intensity contributions from the Cu M₂,3VV Auger peak, and the empirical O KVV model lineshape.

Figure 6: Comparison between the energy converted ToF-PAES measurements of Si exposed to O₂, corrected for intensity contributions from the Si L₂,3VV Auger peak, and the empirical O KVV model lineshape.

3.3 Theoretical calculation of the positron annihilation-induced O LVV Auger spectrum from TiO₂.

Fig. 8 is the energy converted ToF-PAES spectrum for TiO₂ alongside an instrumentally-broadened theoretical calculation of the O LVV Auger electron energy distribution, A(ε_{esc}), using:

$$A(ε_{esc}) = \int dε_h \lambda(ε_h) P(ε_{esc}) T[ε_h, ε_{vac} + ε_{esc}]$$  \hspace{1cm} (1)

where ε_{esc} is the kinetic energy of the Auger electron after it has exited the surface, λ(ε_h) is the annihilation rate with electron states of energy ε_h, P(ε_{esc}) is the electron escape probability described above, and T[ε_h, ε_{vac} + ε_{esc}] is the Auger transform. The Auger transform is taken to be the typical self-convolution of the occupied density of valence states used to describe band-like CVV Auger transitions. The calculated density of states for TiO₂(110) was taken from reference [31]. The positron annihilation rate with O 2s electrons is taken to be the calculated density of oxygen 2s states which corresponds to a relatively constant partial annihilation rate. The calculated spectrum was shifted to lower kinetic energies by 8.3 eV to account for the combined effects of the electron work function and final state hole-hole correlation effects. The calculated O LVV Auger spectrum was used as an input to a SIMION® 8.1 simulation of our ToF-PAES spectrometer to account for the effects of instrumental broadening on the outgoing electron energy distribution. Additional details of the simulated ToF-PAES spectrometer can be found in references [32] and [12]. Finally, an overall scale factor was applied to bring the experimental and calculated peaks into agreement. The excellent agreement between the experimental and theoretical results provides strong evidence that the broad, low-energy peak observed experimentally is the O LVV Auger peak from TiO₂.
3.4 Estimation of the annihilation probability with O 2s electrons.

Using the O KVV and model O LVV lineshapes together with the measured Auger intensities we have estimated the annihilation probabilities for the O 2s levels according to:

\[
\frac{\lambda_{O2s}}{\lambda_{O1s}} = \frac{I_{OLVV} A_{O_{KVV}}}{I_{OKVV} A_{OLVV}} \int dE \int dE' f_{O_{KVV}}(E') \Omega(E') T(E') \eta(E') \int dE f_{O_{LVV}}(E) \Omega(E) T(E) \eta(E)
\]  

(2)

where \(\lambda_{O2s}\) and \(\lambda_{O1s}\) are the 2s and 1s annihilation probabilities respectively. \(\lambda_{O1s}\) is taken to be 0.1 \[33\]. \(I_{OLVV}\) and \(I_{OKVV}\) are the measured PAES integrated intensities. \(A_{O_{KVV}}\) and \(A_{OLVV}\) are the probabilities that an oxygen 1s core hole and an oxygen 2s core hole decay via a core-valence-valence Auger (CVV) process respectively. Both probabilities are assumed to be unity. The functions \(f(E)\) are the probabilities that an Auger electron is generated through either an O LVV or an O KVV Auger process and is emitted with energy \(E\). These functions are taken to be the O LVV model lineshapes and O KVV lineshapes normalized to unity. \(\Omega(E)\) is an empirical function which models the probability that the escaping electrons have sufficient momentum parallel to the surface to escape with kinetic energy \(E\). The parameters used in this empirical escape function taken from \[12\]. \(T(E)\) is the transmission factor which is an empirical model that takes into account the inelastic mean free path of electrons generated from an escape depth \(z\) below the surface. It models the probability that an electron generated within the material escapes with energy \(E\) without scattering \[34, 35\].

Due to the top-most atomic layer selectivity of PAES, the Auger electrons are assumed to be generated from at most one atomic layer below the surface giving values of \(z = 1.95\ \text{Å}\) for TiO\(_2\) \[36\]. Finally, \(\eta(E)\) is the simulated transport
efficiency of our ToF-PAES spectrometer and gives the probability that an electron travelling with kinetic energy $E$ will reach the MCP detector $[22]$. The estimates of the O 2s annihilation probabilities along with the relevant quantities used to calculate them are listed in Table 1.

| Sample | $I_{O\,LVV}$ | $I_{O\,KVV}$ | $I_{O\,LVV}/I_{O\,KVV}$ | $\lambda_{2s}/\lambda_{1s}$ | $\lambda_{O\,1s}$ | $\lambda_{O\,2s}$ |
|--------|--------------|--------------|--------------------------|---------------------------|-------------------|-----------------|
| TiO$_2$ | $7.82 \times 10^{-3}$ | $1.62 \times 10^{-4}$ | 48.1 | 58.6 | 0.1 | 5.86 |

Table 1: Table of quantities used in equation $\lambda_{O\,2s}$ to estimate $\lambda_{O\,2s}$.

4 Conclusions

In this manuscript, we have presented measurements of the low-energy Auger electron spectra from oxygen adsorbed Cu and Si surfaces and a TiO$_2$ surface. These spectra contain large contributions from Auger processes consistent with LVV Auger transitions in oxygen. Low-energy Auger transitions are particularly difficult to observe in traditional electron or photon stimulated AES due to the obscuring, beam-induced secondary electron background. We have overcome this background limitation by using mater-antimatter annihilations to initiate the Auger process. We believe these results to be the first quantitative investigations of these low-energy O LVV Auger transitions. The evidence that the large spectral weight below 15 eV in each of our ToF-PAES measurements is due to O LVV Auger electron emission is as follows:

1. The incident positron beam energy is less than 1.5 eV, which is below the energy threshold required for generating secondary electrons. The only energetically allowable electron emission processes at these incident positron beam energies are Auger electron emission processes.
2. The large spectral weight below 15 eV is seen alongside the emergence of the O KVV Auger peak in each spectra. This is direct evidence that the low-energy intensity is associated with the presence of oxygen at the surface.
3. In the oxygen exposed Cu and Si data, the decrease in the Cu M$_{2,3}$VV and Si L$_{2,3}$VV Auger intensities does not match with the increase in the spectral weight below 15 eV. The redistribution of these higher energy Auger electrons to lower kinetic energies due to inelastic scattering through an oxygen overlayer cannot account for the increases in low-energy intensity observed.
4. We were successfully able to model each spectra using a shifted O KVV Auger lineshape convoluted with the O 2s photoemission line. This shows that the O LVV process is energetically possible and that the measured O LVV Auger lineshape samples the same 2 hole final states as O KVV Auger transitions.
5. We found excellent agreement between the measured O LVV Auger spectrum from the TiO$_2$ surface and a first principals based calculation of the O LVV Auger electron energy distribution. The calculation amounts to the convolution of the calculated O 2s density of states with the self-fold of the calculated valence density of states for TiO$_2$(110). This demonstrates that the O LVV Auger line is sensitive to the surface electronic structure and local chemical environment of the oxygen atoms.

Further studies and more detailed calculations could reveal important catalytically relevant information such as active adsorption cites, surface oxidation states, and metal-ligand orbital hybridization.

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