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Citation: Applied Physics Letters **90**, 042108 (2007); doi: 10.1063/1.2430929
View online: http://dx.doi.org/10.1063/1.2430929
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/90/4?ver=pdfcov
Published by the AIP Publishing

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(Received 6 August 2006; accepted 8 December 2006; published online 25 January 2007)

Electronic structures of the nanorods of RuO_2 and IrO_2 metallic oxides were investigated by x-ray absorption near-edge structure (XANES) and scanning photoelectron microscopy (SPEM). O *K*-, Ru, and Ir L_3-edge XANES results reveal that hybridization between O $2p$ and metal t_{2g} orbitals is weaker in IrO_2 than in RuO_2. The enhancement of the tip-region SPEM intensities relative to those in the sidewall regions for both RuO_2 and IrO_2 nanorods is found to extend over a large energy range in contrast to those of carbon nanotubes and ZnO nanorods, which are confined to deep below and near the Fermi level, respectively. © *2007 American Institute of Physics*.
[DOI: 10.1063/1.2430929]

One-dimensional (1D) nanomaterials, including nanorods, nanowires, and nanotubes, have attracted extensive attention because of their technological applications in nanodevices and fundamental scientific interest.[1–3] 1D nanomaterials with sharp tips of a high tip-height to base-diameter ratio are promising candidates for field emission applications.[4] Among various 1D nanostructures, carbon nanotubes (CNTs), which have been widely studied, exhibit excellent field emission properties with a low turn-on field. However, CNTs lack long-term stability, which is an important property for device applications.[4] Nanorods of metallic oxides such as IrO_2 and RuO_2 have recently been successfully synthesized. These oxides demonstrated to be potential candidates for use in field emission applications.[5,6] For instance, vertically aligned IrO_2 nanorods have been shown to exhibit excellent field emission characteristics that are comparable with those of CNTs and have a low turn-on field and more importantly the long-term stability.[5] The knowledge of their electronic structures is crucial in understanding field emission properties of these nanorods. The tips of nanotubes/nanorods of aligned CNTs (Ref. 7) and ZnO (Ref. 8) have recently been found to have enhanced electronic densities of states (DOSs). It is interesting to know whether RuO_2 and IrO_2 have similar enhancement of DOS's at the tips. Thus, the electronic structures of the nanorods of RuO_2 and IrO_2 metallic oxides have been investigated in this study by x-ray absorption near-edge structure (XANES) and scanning photoelectron microscopy (SPEM) measurements.

O *K*-, Ru, and Ir L_3-edge XANES and SPEM measurements were carried out at the National Synchrotron Radiation Research Center, Hsinchu, Taiwan. RuO_2 and IrO_2 nanorods were grown on a Si(100) substrate by chemical vapor deposition. Details of the preparation can be found elsewhere.[5,6] X-ray diffraction data presented in Fig. 1 show that RuO_2 and IrO_2 nanorods have a rutile structure and lattice constants agree with those reported in the literature. Scanning electron microscopy (SEM) images in insets (a) and (b) of Fig. 1 show nanorods with lengths (diameters) of ~700 nm (50–100 nm) and ~350 nm (50–70 nm) for IrO_2

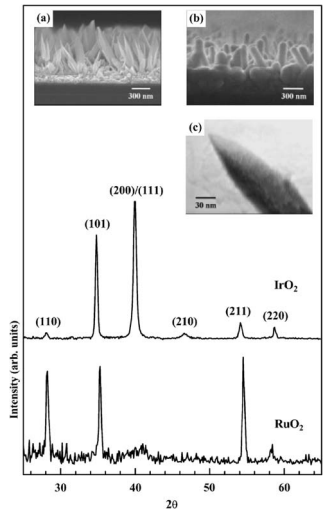

FIG. 1. X-ray diffraction patterns of RuO_2 and IrO_2 nanorods. Insets present SEM images of nanorods; (a) IrO_2, (b) RuO_2, and (c) TEM picture of the IrO_2 nanorod tip.

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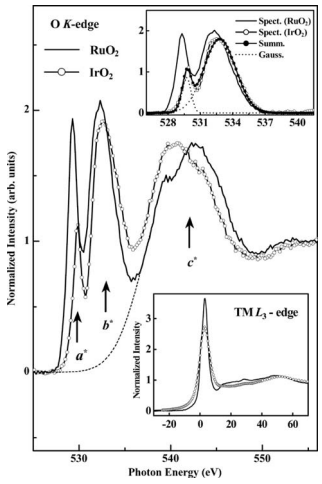

FIG. 2. O *K*-edge XANES spectra of RuO_2 and IrO_2 nanorods. Upper inset presents background corrected $\boldsymbol{a}^*$ and $\boldsymbol{b}^*$ features and the lower inset displays Ru and Ir L_3-edge XANES spectra.

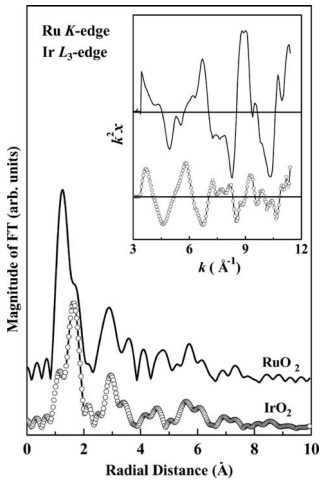

FIG. 3. Fourier transform spectra of EXAFS $k^2\chi$ data from $k=3.5$ 11.5 $Å^{-1}$ at Ru *K*- and Ir L_3-edge of RuO_2 and IrO_2 nanorods. Inset shows EXAFS $k^2\chi$ oscillations.

and RuO_2, respectively. Nanorods are more or less standing vertically though the alignment is not perfect. Transmission electron microscopy (TEM) reveals that IrO_2 nanorod tips displayed in the inset (c) of Fig. 1 are very sharp.

Figure 2 presents the normalized O *K*-edge XANES spectra of RuO_2 and IrO_2 nanorods. The O *K*-edge spectra of both RuO_2 and IrO_2 nanorods resemble closely with those of corresponding films, which were also collected as reference but not shown in the figure. The two sharp features denoted by $\boldsymbol{a}^*$ and $\boldsymbol{b}^*$ are attributable to the excitation of the O $1s$ core electrons into hybridized states between O $2p$ and Ru $4d$/Ir $5dt_{2g}$ and e_g states, respectively, due to splitting by the crystal field. The broad feature at higher energies denoted by $\boldsymbol{c}^*$ is due to excitation of core electrons into O $2p$ and Ru 5/Ir $6sp$ hybridized states. The intensity of the t_{2g} ($\boldsymbol{a}^*$) feature is much lower for IrO_2 than for RuO_2. The upper inset magnifies t_{2g} and e_g ($\boldsymbol{a}^*$ and $\boldsymbol{b}^*$) features after background subtraction. The background is shown by a dashed line in the spectrum of RuO_2 as an example. The t_{2g} and e_g features in the spectra were deconvoluted by fitting two Gaussian profiles (represented by dotted lines shown in the upper inset for IrO_2 as an example). The area under each Gaussian curve gives the integrated intensity of the corresponding feature. The ranges of energies used to calculate integrated intensities of t_{2g} and e_g features are 527.5–530.9 and 527.5–537.5 eV for RuO_2, and 528.5–531.1 and 528.3–537.7 eV for IrO_2, respectively. The t_{2g}/e_g intensity ratio decreases from ~0.29 for RuO_2 to ~0.12 for IrO_2 by a factor of ~2.4. The decrease is much greater than would be expected based on the electron count only. Assuming that RuO_2 and IrO_2 are 100% ionic, the tetravalent metal ions in RuO_2 and IrO_2 have four and five electrons left to fill $4d$ and $5d$ orbitals,[9] respectively. The t_{2g}/e_g intensity ratio determined purely from the numbers of electrons needed to fill all $4d$ and $5d$ orbitals would decrease from 0.5 to 0.25 if one assumes that e_g orbitals are completely empty. Note that under these assumptions the empty t_{2g}- and e_g-orbital number ratios are 2:4 (0.5) and 1:4 (0.25) for RuO_2 to IrO_2, respectively. This result indicates that IrO_2 has a lower degree of hybridization between O $2p$ and t_{2g} orbitals than RuO_2 since other factors such as crystal structure and symmetry around O ions are similar. If the hybridization argument was right, the present O *K*-edge XANES result suggests that RuO_2 be more covalent than IrO_2, though Ru and Ir have electronegativity of 2.2.[10]

The lower inset in Fig. 2 displays the normalized Ru and Ir L_3-edge XANES spectra of RuO_2 and IrO_2 nanorods, respectively. The energy scale of the spectra in this figure was adjusted to match the peak positions and the zero energy corresponds to the absolute energies of 2842.4 and 11 217.4 eV in the Ru and Ir L_3-edge spectra, respectively. The sharp single peak corresponds to the electrons transition from the $2p_{3/2}$ level to unoccupied d ($4d$ for RuO_2 and $5d$ for IrO_2) states.[11,12] The t_{2g} and e_g features are not resolved in these spectra. The smaller intensity of the L_3 white-line feature for IrO_2 reveals that the number of unoccupied metal $5d$ states in IrO_2 is smaller than that in RuO_2. Extended x-ray absorption fine structure (EXAFS) analyses at Ru *K* and Ir L_3 edges were performed to check for any difference in the local atomic structures in the two compounds. Figure 3 displays the Fourier transform (FT) of EXAFS $k^2\chi$ oscillations (shown in the inset). In general, the FT spectra of RuO_2 and IrO_2 nanorods are quite similar with those reported earlier,[13] indicating that the local atomic structures in RuO_2 and IrO_2 nanorods are similar to those of other materials with the rutile structure (such as TiO_2, RuO_2, and IrO_2 films/bulks). This implies that the local geometry around the absorbing atom is quite similar in RuO_2 and IrO_2 nanorods, so that differences in the XANES spectra of RuO_2 and IrO_2 nanorods are not due to different local atomic structures.

Figure 4 presents spatially resolved valence-band photoemission spectra (VB-PES) of the tip and sidewall regions of RuO_2 and IrO_2 nanorods. The upper insets show Ru $4d$ and Ir $5d$ SPEM cross-sectional images. The bright regions in the SPEM images correspond to the nanorods with maximum Ru $4d$ and Ir $5d$ intensities. Figure 4 displays the spectra, which show the photoelectron yields from the selected positions indicated in the images presented in the upper insets. These yields are the sum of (s1)–(s3) and (t1)–(t3) contributions from the sidewall and tip regions of RuO_2 and IrO_2 nanorods, respectively. The zero binding energy is set at the Fermi level, E_F, which is the threshold of the emission spectrum. The overall features of these PES are similar to the x-ray photoelectron spectra of bulk RuO_2 and IrO_2 reported previously.[14,15] The sharp features near/below E_F denoted by A in the RuO_2 spectra and A_1 and A_2 in the IrO_2 spectra are basically associated with the d bands of metals. The splitting

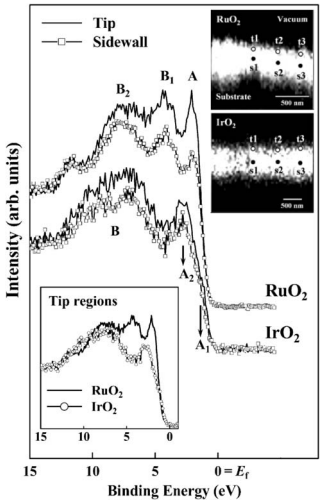

FIG. 4. Valence-band PES of RuO_2 and IrO_2 nanorods from selected regions of tips (t1)–(t3) and sidewalls (s1)–(s3), as displayed in SPEM images (upper insets). The lower inset compares PES data from the tip regions of RuO_2 and IrO_2 nanorods.

into features A_1 and A_2 was attributed to the spin-orbit effect.[9,14] The features denoted by B in the IrO_2 spectra and B_1 and B_2 in the RuO_2 spectra correspond to the σ- and π-type molecular orbitals resulted from hybridization between O $2p$ and metal d orbitals.[9,14] The lower inset compares tip-region PES data of both RuO_2 and IrO_2 nanorods. The PES data show that the Ir d band is split into two subbands at ~1.1 eV (A_1) and ~2.5 eV (A_2) by the spin-orbit effect, whereas the Ru d band has a single feature at ~2.1 eV (A). The VB-PES results at the first instance appear to contradict the XANES results since Ir has more $5d$ electrons than Ru in $4d$ and hence a larger PES intensity is expected for IrO_2 than RuO_2. This apparent contradiction is removed in the discussion below. In the vicinity of E_F, RuO_2 nanorods appear to have larger valence-band DOSs. Figure 4 clearly reveals that the valence-band DOSs in the tip regions is higher than those in the sidewall regions in both RuO_2 and IrO_2 nanorods. RuO_2 exhibits substantial enhancement of the near/below E_F d-band PES intensity in the tip regions, whereas in the deeper O-$2p$/metal-d region the PES intensity shows a relatively smaller increase in the tip regions. For IrO_2, however, the enhancement is relatively smaller for the entire valence band (features A_1, A_2, and B). The enhancement of valence-band DOSs at the tips is probably due to the increase of the number of dangling bonds and defects at the tips. These effects are also important in the sidewall regions as well but to a lower extent. The tips have much larger surface to volume ratio and the curvatures give rise further surface modification. This together with arguments presented below explains the larger PES intensity for RuO_2 than IrO_2.

A similar enhancement of the SPEM intensity has been observed previously at the tips of CNTs (Ref. 7) and ZnO nanorods.[8] In the case of CNTs, the enhancement of the intensity was observed at the energies more than 10 eV below E_F, which was argued to be caused by the alteration of the local electronic structure due to the curvature at the tip. As for ZnO nanorods, the enhancement of the intensity was observed only near/below E_F, which was argued to be associated with near-E_F O $2p$ dangling-bond states.[8] The present results of the nanorods of metallic rutile oxides differ from those of CNTs and ZnO nanorods by that the enhancement of the valence-band DOSs extends from near E_F down to approximately 10 eV below E_F, including both O $2p$ and metal d states. The present results suggest that dangling bonds be not solely responsible for the enhancement because dangling-bond states lie near/below E_F and are not expected to extend over such a large range of energies. RuO_2 and IrO_2 have a rutile structure, in which the metal atom is surrounded by an oxygen octahedron with six O ions. The coordination number of the metal atoms in RuO_2 and IrO_2 is larger than those in ZnO and the carbon atoms in CNTs. Thus, the termination at the tip is expected to yield more dangling bonds. Ru and Ir have the same electronegativity of 2.2,[10] which is much larger than that of Zn of 1.65. Thus, RuO_2 and IrO_2 are expected to contain a larger covalent character than ZnO, so that O $2p$ and Ru $4d/5sp$ and Ir $5d/6sp$ hybridization is expected to extend much deeper into the valence band than that of O $2p$ and Zn $3d/4sp$. Thus, the alteration of the coordination numbers and bonding arrangements of tip atoms affect even O $2p$ states deep in the valence band. The more significant enhancement of the tip-region PES intensity for RuO_2 nanorods than for IrO_2 nanorods can be attributable to their different tip shapes. The SEM pictures in the insets of Fig. 1 show that RuO_2 nanorods have round tips, while IrO_2 nanorods have pointlike tips, so that RuO_2 nanorods have a larger effective tip area and consequently a larger enhancement. The dangling bonds, defects, and other causes discussed above are also important in the nanorod sidewall region as well as the nanosized rods will have larger surface to volume ratio. However, their effect at tips is much more larger due to much larger surface to volume ratio and also due to curvature at the tips which give rise further surface modification. This together with arguments presented in previous paragraphs explains the larger PES intensity for RuO_2 than IrO_2.

This work was supported by the NSC of the ROC under Contract No. NSC 95-2112-M032-014.

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