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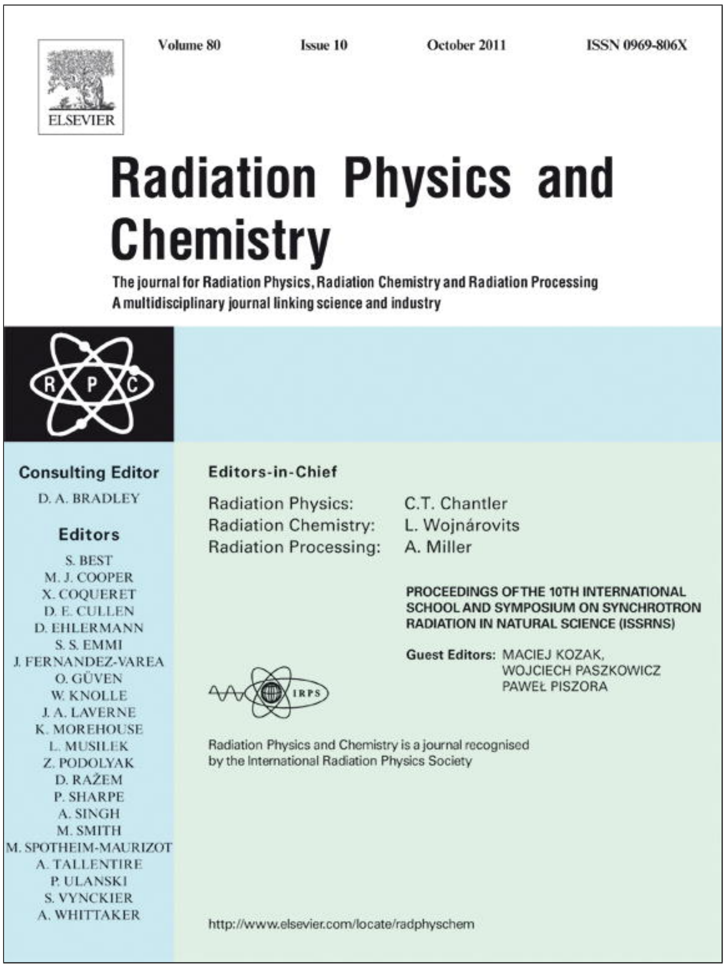

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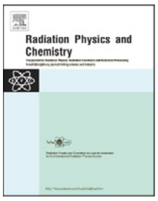

Review

Electronic structure of epitaxial $SrRuO_3$ films studied by resonant photoemission

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ABSTRACT

The electronic structure of epitaxial $SrRuO_3$ thin films annealed at 300 °C in ultra high vacuum is studied by resonant photoemission spectroscopy using synchrotron radiation. The valence band photoemission spectra show a good agreement with theoretical band structure calculations indicating a good quality of the film surface. A method was proposed, which allows extracting the partial density of states in the case of weak and broad resonance. The Ru 4d spectral weights obtained experimentally are in a very good agreement with theoretical predictions, confirming a strong mixing between Ru 4d and O 2p states, as well as the signature of electron correlation near the Fermi level in $SrRuO_3$.

1. Introduction

$SrRuO_3$ has a nearly cubic perovskite structure (Callagham et al., 1966; Jones et al., 1979). The combination of good chemical stability, metallic conductivity and easy epitaxial growth on various perovskite substrates makes it attractive for multilayer device application (Lee et al., 2002; Eom et al., 1992; Mercurio et al., 2000). The integrability of $SrRuO_3$ into the device fabrication process requires surface stability with respect to reduction, contamination, or loss of volatile ruthenium oxides. A minute deviation in the stoichiometry of $SrRuO_3$ surface prior to the second component deposition could result in the formation of weakly conductive dead-layers.

It was shown (Shin et al., 2005) that exposure to the atmosphere, even for a short time, leads to the hydrocarbon contamination of the $SrRuO_3$ surface. Under high vacuum annealing this hydrocarbon layer leads to the surface decomposition at temperatures above ~300 °C, accompanied by the desorption of SrO and metallic Ru with a subsequent formation of nanoparticles of Sr-rich ruthenates and metallic Ru.

On the other hand, a photoemission spectroscopy (PES) study of $SrRuO_3$ polycrystalline samples and thin films revealed that surface cleaning by annealing at moderate temperatures of ~400–450 °C in an oxygen atmosphere (Park et al., 2004b; Kim et al., 2005) provides a film surface more suitable for studying an intrinsic electronic structure than the polycrystal samples prepared by *in situ* scrapping (Fujioka et al., 1997; Okamoto et al., 1999).

The PES technique is known as a powerful tool for the direct investigation of the valence states of atoms in solids. In principle, resonant photoelectron spectroscopy may be utilized to deduce a partial spectral weight (PSW) of elements in the valence band (VB) by making use of the Ru 4p→4d resonance, which was reported to occur around 52–54 eV (Park et al., 2004a, 2004b; Fujioka et al., 1997). However, the previous attempt (Fujioka et al., 1997) in this direction was not quite successful partly because the resonance is not very strong compared with the cross-section (CS) variation of the O 2p level. Another method based on the Cooper minimum (CM) phenomenon of Ru 4d photoionization CS (Fano and Cooper, 1968) was used to deduce the Ru PSW in $SrRuO_3$ (Park et al., 2004b) and $Bi_{2-x}Y_xRu_2O_7$ (Park et al., 2004a). In spite of the fact that the main features of so obtained PSWs agree with the theoretical band-structure computations, the apparent disagreement between the PSWs and calculations calls for an explanation. This is especially true in regard to Ru 4d spectral weights around the Fermi level.

First of all, both band calculations and experimentally derived PSWs testify that strong hybridization occurs between the Ru 4d and O 2p states of $SrRuO_3$. That is the reason why valence states in solids reveal a much less pronounced CM than respective states in free atoms (Molodtsov et al., 2000). Additionally, CM in solids are shifted in energy and broadened, compared to their positions

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and widths in free atoms. In turn, the Ru 4d orbitals admixture should enhance O 2p photoionization CS dependence on the incident photon energy. Finally, the Ru/O CSs ratio at CM ($h\nu = 100$ eV) may be much greater than that expected from atomic estimations ($\approx 2\%$) (Park et al., 2004b). Thus, the assumption that a VB spectrum measured at CM is essentially O 2p in nature underestimates the contribution of Ru 4d states.

The second aspect, which should be carefully taken into account in extracting the PSWs of Ru 4d and O 2p states separately is the necessity to eliminate the CSs energy dependence. A possible way to do it is to utilize the similarity in the photon energy dependence of the CSs for 2p states in oxygen and (O 2p–C 2s) orbitals in CO (Wilhelmy et al., 1994; Plummer et al., 1977; Yeh and Lindau, 1985). Such normalization to the intensity of adventitious contamination peaks around ~ 10 eV binding energy (BE) from carbon monoxide in principle should provide almost flat O 2p spectral weight in this region (Park et al., 2004a, 2004b). However, the possible enhancement of O 2p CS due to the hybridization with Ru 4d orbitals in ruthenium compounds may destroy this balance, resulting in considerable energy dependence of normalized O 2p PSWs. Then, the difference between PSWs obtained by subtracting the spectrum measured at CM ($h\nu \approx 100$ eV) and that at resonance condition ($h\nu \approx 52$–54 eV) may contain not only Ru 4d but a significant admixture of O 2p PSW.

In this paper, we report synchrotron-radiation PES data on epitaxial films $SrRuO_3$ to study their electronic structure, focus in particular on the role of the Ru 4d electronic states. The procedure utilizing a relatively weak Ru 4p→4d resonance phenomenon accompanied with the strong O 2p CS's variations was proposed to deduce the Ru 4d PSW's.

2. Experimental details

Thin $SrRuO_3$ epitaxial films were deposited using reactive d.c. magnetron sputtering onto monocrystalline (1 0 0)-plane oriented $SrTiO_3$ substrates. Sputtering was performed in Ar and O_2 mixture (1:1) at pressure around 15 Pa. To prevent film bombardment by high energy ions during deposition, $SrTiO_3$ substrates were positioned in “off-axis” configuration at a distance of 1 mm from the symmetry axis of the discharge and 20 mm over the target plane. The substrate temperature was set at 600 °C. The thickness of the film was about ~ 100 nm. The epitaxy of the films has been confirmed by XRD (Sobietanskas et al., 2009) and high energy electron difraction (RHEED) studies. Clearly defined XRD reflexes of (n 0 0), $n = 1, 2, 3, \ldots$ family seen in Θ–2Θ XRD scans of the films demonstrated single phase highly [1 0 0]-axis oriented material while point-like RHEED reflexes indicated for the film showed perfect in-plane orientation of the crystallographic planes with cube-on-cube growth epitaxial relationships.

Because of the surface sensitivity, photoemission spectroscopy data should be taken on a clean surface. For polycrystalline samples prepared *ex situ*, *in situ* scraping of the surface has been widely used in PES measurements (Fujioka et al., 1997; Okamoto et al., 1999). However, it was reported that PES spectral features related to electron correlation depend sensitively on the surface preparation method. Actually, $SrRuO_3$ films photoemission spectra taken on the *in situ* prepared specimens (Kim et al., 2005) or on the films cleaned by moderate heating at moderate temperatures ($T \sim 450$ °C) under an O_2 atmosphere (Park et al., 2004b) show more coherent features than the scraped surface (Fujioka et al., 1997; Okamoto et al., 1999). We tried to clean the films by heating them in vacuum. The upper annealing temperature limit should be chosen to be below the surface degradation temperature of the outside prepared thin film (Shin et al., 2005). Thus, the film surface was prepared for PES measurements by relatively low ($T \approx 300$ °C) heating under ultra high vacuum (UHV) conditions ($P \sim 10^{-10}$ Torr). The sample was annealed using a direct current resistance heating and temperature was measured with optical pyrometer. The completion of the sample degassing process was checked by controlling the UHV system pressure.

Resonant photoemission experiments were performed in a synchrotron radiation laboratory HASYLAB, Hamburg (Germany). Synchrotron radiation obtained from the storage ring DORIS III was monochromatized with the FLIPPER II plane grating vacuum monochromator, designed for the photon energy range 15–200 eV. The spectrometer was equipped with a CMA electron energy analyzer. The total energy resolution was kept at 0.1 eV. The origin of the energy axis was set at the Fermi energy E_F as measured for a reference metallic sample. The PESs were measured at the normal emission angle, allowing a large solid angle acceptance, which corresponds to an angle-integrated density of states. The base pressure during PES measurements was $\sim 10^{-10}$ Torr.

To compare our experimental spectra with theoretical band-structure calculations, the data measured were normalized to the photon flux and inelastic backgrounds were removed using the Shirley method (Shirley, 1972).

3. Results and discussion

A set of energy distribution curves (EDC) of the $SrRuO_3$ film for the photon energy range covering the energy of the Ru 4p→4d transition are shown in Fig. 1. All the spectra are normalized to the maximum peak intensity. First, we notice that the spectra for the $SrRuO_3$ surface are quite similar to the recently published data on a single crystalline film cleaned by annealing under an oxygen atmosphere (Park et al., 2004b) and grown and investigated *in situ* by ultraviolet spectroscopy (Kim et al., 2005). However, our spectra show more structures between 3 and 8 eV BE, as compared to previous data taken on a scraped polycrystal surface (Kim et al., 2005; Fujioka et al., 1997; Okamoto et al., 1999). The second derivative technique was used to reveal the hidden features of the spectrum (Fig. 1). The average of the 2nd

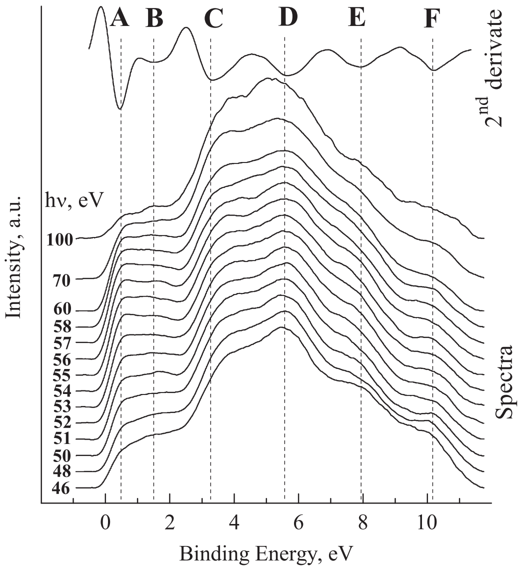

Fig. 1. A set of electron energy distribution curves (EDCs) of the epitaxial $SrRuO_3$ thin film annealed in super-high vacuum at 300 °C at exciting photon energies $h\nu$ between 46 and 100 eV. All the spectra are normalized to the maximum peak intensity. Labeled, dashed lines show the features in valence band spectra and correspond to the second derivative minima.

derivative plots over all exciting photon energies was used to minimize data scattering.

First of all, note that feature F centered ~10.2 eV is known to be due to contaminations, most likely by carbon monoxide, usually present in residual vacuum, while spectra for the $SrRuO_3$ film show five distinct structures (A, B, C, D and E). The fact that these structures are predicted by band-structure calculations (Fujioka et al., 1997; Singh, 1996; Allen et al., 1996; Mazin and Singh, 1997) strongly suggest that the annealed surfaces of an outside prepared films give a VB spectrum suitable for studying intrinsic electron structures of $SrRuO_3$. By comparing our data with the density of states (DOS) from band structure computations, we can assign features centered at ~7.9 eV (E) and ~5.7 eV (D) to primarily O 2p bonding states mixed with Ru 4d states and a single peak around 3.3 eV (C) to non-bonding O 2p orbitals. The Ru 4d antibonding states are located between 2.1 eV and the Fermi level. In particular, a sharp peak (A~0.5 eV) near E_F is assigned to a coherent part, while the broad structure around 1.5 eV (B) is due to the coherent and incoherent parts of the spectral function (Fujioka et al., 1997; Okamoto et al., 1999).

Fig. 2 shows normalized photon flux constant initial-states (CIS) spectra, derived from EDCs at BE corresponding to the observed spectral features in the valence band region (Fig. 1). The evident resonance character of features A and B in the vicinity of the Ru 4p→4d threshold directly confirms that these peaks are mainly Ru 4d in character. The CISs of deeper-lying C, D and E peaks show only a weak structure near the resonance energy and, actually, show the same $h\nu$-dependence as the contamination peak F. This suggests that O 2p states dominate in these peaks. Unfortunately, the resonance intensity is relatively low compared with CS variations. Moreover, the energy dependence of peaks A (which is mostly from the Ru 4d states) and F (CO-contamination peak, essentially O 2p in character) differs not as strongly as it might be expected from the atomic CSs $h\nu$-dependences (Plummer et al., 1977; Yeh and Lindau, 1985). Actually, we observe that upon going from 70 to 100 eV exciting photon energy (i.e. in the off-resonance region) the intensity ratio of peaks A and F decreases less than two times, while the corresponding decrease of the (Ru 4d)/(O 2p) atomic CSs ratio is around 6 (Yeh and Lindau, 1985). As it was discussed in the introduction, this disagreement is not surprising; however, it shows that the assumption about the mainly O 2p character of the VB spectrum at CM (Park et al., 2004a, 2004b; Fujioka et al., 1997) should be treated with caution. From the other hand, the similarity in the energy dependence of the contamination peak F and $SrRuO_3$ VB peaks with dominating O 2p states (C–E) confirms that the first one can be successfully used for the essential flattening of O 2p spectral weight (Park et al., 2004a, 2004b), at least at $h\nu \geq 70$ eV.

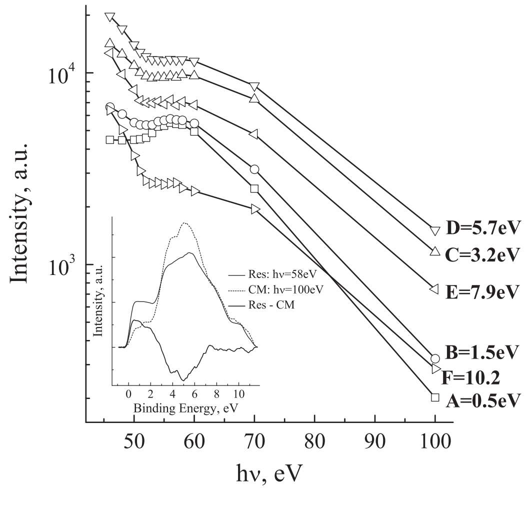

Fig. 2. Constant initial-states spectra (CISs) at select energies obtained from data presented in Fig. 1. Curves denoted A–F correspond to the features in EDCs. All the spectra are normalized to the incident photon flux. In the insertion, the EDCs obtained at ON-resonance condition ($h\nu = 58$ eV) and Ru 4d CM ($h\nu = 100$ eV) and normalized to contamination peak F intensity at these energies together with their difference are shown.

In order to obtain the Fano resonance (Fano, 1961) curve and to determine the resonance energy, CIS spectra (Fig. 2) were normalized to the CO-peak F intensity. In Fig. 3 the Fano resonance curves for peaks A and B originating from the Ru 4d orbitals are presented. Although this resonance effect was found rather broad and subtle, compared with well-known 2p→3d and 4d→4f cases (Sato et al., 1998; Orlowski et al., 2007), the Fano-type profile of A and B spectra clearly shows the enhancement of 4d shell related to VB spectral features. The shape of Fano resonance can be expressed as

$$I(h\nu) = I_0 + H\frac{(\varepsilon+q)^2}{1+\varepsilon^2},$$

where $\varepsilon = (E_{res} - h\nu)/w$, w describes the spectral width of the autoionized discrete state, q is the Fano's asymmetry parameter and H is the intensity of nonresonant photoemission. The parameters describing the shape of Fano-type resonance were determined by curve fitting (Fig. 3). For both spectra, parameters coincide within the experimental error, and our obtained value of the resonance energy $E_{res} = 53 \pm 1$ eV agrees with the published data (Park et al., 2004a, 2004b; Fujioka et al., 1997). The relatively large linewidth ($w \approx 9$–10 eV) of resonance is consistent with the expectation that the 4d orbital is quite extended and bonding with the O 2p orbitals is strong (Park et al., 2004b).

In principle, resonance in photoemission allows one to estimate the contribution of the Ru 4d shell to the VB density of states. In particular, a difference between EDCs taken for photon energies corresponding to the maximum (close to the resonance energy) and relatively far from the resonance in the Fano profile should provide PSW. However, this is only true if the variation in O 2p CSs in this region may be neglected. This condition is easily satisfied in case of sharp and strong resonance, and difference between spectra measured at resonance and antiresonance (at which emission from the open shell is suppressed) conditions is usually used to estimate the partial DOS. However, in case of

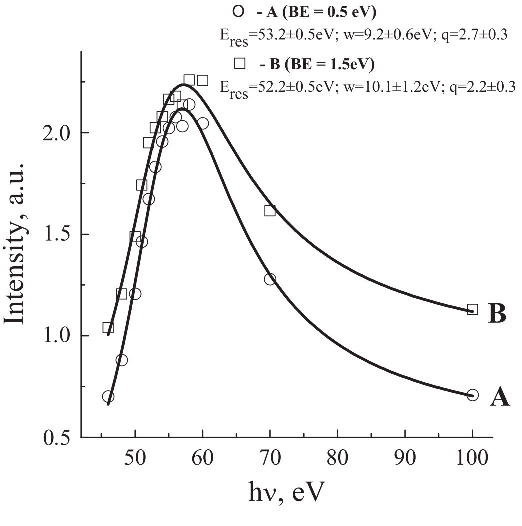

Fig. 3. Fano resonance curves for coherent, A (~0.5 eV), and incoherent, B (~1.5 eV), Ru 4d peaks in a $SrRuO_3$ thin film in the vicinity of the Ru 4p→4d threshold. The spectra are normalized to the CO-contamination peak F (~10.2 eV) intensity (Fig. 2).

broad resonance having rather flat maxima, CS variations may be compared or even exceed the resonance intensity, and additional spectra normalization is required to compensate this variation. In part, this can be achieved by appropriate normalization of data (Park et al., 2004a, 2004b). Unfortunately, although the use of the CO-peak as a reference allows reducing CS energy dependence, this compensation is insufficient for the direct extraction of the Ru 4d PSW. It is noteworthy that for our $SrRuO_3$ film spectra at ON-resonance condition and at CM normalized to the contamination peak intensity (see insertion in Fig. 2) contradict to those reported by Park et al. (2004b). At $BE < 2$ eV the difference spectrum in Fig. 2 is quite similar to that obtained by Park et al. The main discrepancy is that in spite of an intense decrease in peak intensity at $BE < 2$ eV (i.e. for the Ru 4d states), at higher BE (corresponding to the O 2p states) the spectrum measured at CM becomes more intensive than that at ON-resonance. The source of this disagreement is evident: the contamination peak is not purely CO in nature; thus, its CS $h\nu$-dependence may be strongly affected by surface preparation. This evidently shows that spectra calibration by means of the contamination peak is insufficient to eliminate O 2p CS energy dependence.

Fig. 4 presents the EDCs of a $SrRuO_3$ film measured at the maximum of Fano profile (ON-resonance: $h\nu = 58$ eV) and two equidistant from the resonance exciting photon energies ($OFF^{(-)}$- and $OFF^{(+)}$-resonance: $h\nu = 46$ and 70 eV, respectively). Strong resonant behavior occurs at $BE < 2$ eV, which is in agreement with the Ru 4d character of DOS at these energies. At the same time, an appreciable discrepancy between the ($ON-OFF^{(-)}$) and ($ON-OFF^{(+)}$) difference spectra at $BE > 2$ (i.e. in the region where O 2p states dominate in VB) clearly shows that they cannot be used directly for Ru PSW estimation. The origin of this disagreement is clear: the incomplete compensation of O 2p CS variation is by means of calibration to the CO-peak intensity. The stronger peak F energy dependence than that for C–E peaks at $h\nu < 70$ eV (Fig. 2) leads to the overestimation of the O 2p PWSs at $OFF^{(-)}$ and underestimation at $OFF^{(+)}$ points, relatively to the ON-resonance condition (Fig. 3).

On the other hand, such normalization substantially attenuates CS $h\nu$-dependence in the VB O 2p region ($BE > 2$ eV). This allows one to hope that the averaging of the equidistant OFF-resonance spectra should provide a spectrum with O 2p PSW close to that in the ON-resonance spectrum. We utilize this feature of equidistant spectra to extract PSW of Ru 4d states and compare it with the band structure calculations. For this purpose, the average OFF-resonance spectrum $(OFF^{(-)}+OFF^{(+)})/2$ was subtracted from one measured at ON-resonance conditions. The main advantage of this technique is that the autocompensation of the CSs variation can be achieved (in case of monotonic CSs energy dependence) within the range of interest, and one needs no detailed knowledge of the SCs $h\nu$-dependence. Moreover, the OFF-resonance energy selection is unattached to some preferred energy, such as Fano-antiresonanse or CM and no additional assumptions about partial DOSs at these points are required.

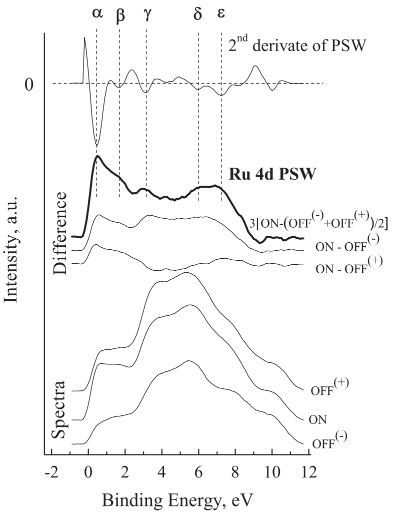

Fig. 4. A method to obtain a Ru 4d partial spectral weight of $SrRuO_3$. The exciting photon energy $h\nu = 46$, 58 and 70 eV for $OFF^{(-)}$, ON and $OFF^{(+)}$ resonance conditions, respectively. The spectra are normalized to the contamination peak F (~10.2 eV) intensity (Fig. 2).

We could notice a few things in the resulting Ru 4d PSW shown in Fig. 4. First, Ru 4d states spread over a wide energy range, confirming very strong hybridization between Ru 4d and O 2p orbitals in this compound. This is consistent with the published data on the experimentally derived Ru 4d partial DOS (Park et al., 2004b; Fujioka et al., 1997) and VB computations (Fujioka et al., 1997; Singh, 1996; Allen et al., 1996; Mazin and Singh, 1997) and due to that 4d orbital is quite extended and makes strong binding. We can also see that the intense and narrow Ru 4d coherent part of spectra near the Fermi level expected from the band calculations is clearly identified in our obtained Ru 4d PSW, while this peak is suppressed in the earlier published PSWs (Park et al., 2004b; Fujioka et al., 1997). This apparent disagreement may be related to both the surface preparation (the film and the scraped polycrystal surface) (Kim et al., 2005) and the PSWs extraction method. We believe, however, that in the case of *in situ* grown film (Park et al., 2004b) this dissimilarity could be attributed to the incomplete compensation of the O 2p CS energetical dependence together with a large difference between resonance and CM energies (~50 eV), resulting in a significant admixture of O 2p states to the final difference spectrum, especially as this feature is clearly seen on the ON-resonance spectrum (Park et al., 2004b).

To reveal the hidden features in the Ru 4d PSW, the 2nd derivative technique was used (Fig. 4). Five distinct structures (α–ε) can be easily seen in the Ru 4d density of states image. Note that all these features were predicted by the band structure calculations (Fujioka et al., 1997; Singh, 1996; Allen et al., 1996; Mazin and Singh, 1997) and their energetic positions and their relative strengths are found to be in a very good agreement with theoretical predictions.

Now they may be identified by comparison of their binding energy values (Fig. 4) with those from the band structure calculations as follows: the sharp peak ($\alpha \sim 0.5$ eV) near the Fermi level may be attributed to a coherent part; a relatively weak feature ($\beta \sim 1.7$ eV) – to the extended incoherent parts of the spectral function; a single peak ($\gamma \sim 3.1$ eV) – to hybridizated non-bonding 2p–4d states; while structures ($\delta \sim 5.9$ eV) and ($\varepsilon \sim 7.2$ eV) – to bonding 2p-4d orbitals.

4. Summary and conclusions

The electronic structure of epitaxial $SrRuO_3$ thin films was investigated by resonant PES using synchrotron radiation facilities. The experimentally deduced Ru partial spectral weight is in good agreement with theoretical DOS computations. The broad Fano-type Ru $4p \rightarrow 4d$ resonance observed at $E_{res} \approx 53$ eV for VB peaks at 0.5 and 1.5 eV, confirming that between the Fermi level and 2 eV DOS is mainly Ru 4d in character.

It was shown that EDCs calibration by means of the contamination peak is insufficient to eliminate O 2p CS $h\nu$-dependence. A method was proposed to extract Ru 4d PSW without any additional assumptions about the Ru 4d and O 2p CSs ratio at

CM and their energy dependences. The experimentally obtained PSW is in a very good agreement with theoretical calculations.

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