Information on local electronic structure at surfaces and interfaces from analysis and interpretation of electron spectra

L. Kövér

Institute of Nuclear Research of the Hungarian Academy of Sciences, P.O. Box 51, H-4001 Debrecen, Hungary, lkover@atomki.hu

(Received: Mar 3, 2002)

The methods for obtaining information on local electronic structure – around atoms at surfaces and interfaces – from deep core electron spectra, including analyses of Auger parameters, Auger- and photoelectron lineshapes, satellites and excitations, are reviewed. Some applications of these methods, for determining charge transfer, electronic correlation and local density of occupied and unoccupied electron states, are presented. In addition, examples are provided concerning new, electron spectroscopic tools for revealing local electronic structure of nanosized systems.

Introduction

Electron spectra induced from surfaces and interfaces of solids carry relevant information on the chemical state of surface components and on the local electronic structure in the atomic environment around the atom from which the signal electron is originated. Among electron spectroscopies the X-ray excited photoelectron and Auger spectroscopy provide especially rich and unique details on the elecron structure local to the atom with the core hole. In the case of Auger spectra – by the two electron nature of the Auger process – information can be obtained on electron correlation as well for the material studied. Photoinduced electron spectra emitted from surface and interface layers of solids reflect environmentally induced changes in the potential of the atomic cores and in the local density of electron states. The local electronic structure surrounding an atom of a key element in a particular solid can determine the mechanical, electronic, magnetic, optical and chemical character and behaviour of a given material. Especially important is the knowledge concerning the local electronic structures in designing materials with novel properties. In new materials innovation the Localized Quantum Structure, i.e. the electronic states and chemical bonding at special locations in solids (e.g. grain boundary, impurity, atom vacancy) has been proved to be a key concept [1] leading to a considerable and rapid progress of materials science and technology, including nanotechnology. Recent developments of electron spectroscopy and theoretical models in describing materials have resulted in a considerably deeper understanding of the effects of atomic environment on processes and structures reflected in the electron spectra [2,3].

Methods for obtaining information on local electronic structure at surfaces and interfaces from electron spectra

Electron binding energies in an atom of a solid structure are dependent on the atomic environment. For electrons in the atomic core, the change in the binding energy of an electron at a particular core level, due to the difference in the atomic surroundings depends on the change in the response of the system to the creation of the core hole. This response consists of the change in the core potential, in the valence charge and in the charge distribution outside the atom with the core hole [4]. Similar changes are reflected in the dependence of the kinetic energy of the Auger electron (emitted following the decay of the core hole) on the atomic environment [5].

Auger parameter analysis

Information on local charges can be obtained from environmentally induced Auger parameter shifts, performing high resolution energy measurements of core photoelectron and Auger lines and interpreting the derived energy shifts using models based on atomic or electrostatic theory [6].

In the case of binary alloys, the alloy-pure metal Auger parameter shifts $\Delta\xi$ are obtained from the measured Auger kinetic and the corresponding photoelectron binding energy shifts [5,7]:

$$\Delta\xi(j) = \Delta E_k(ijj) - \Delta E_b(i) + 2\Delta E_b(j)$$

where $\Delta E_k(ijj)$ is the shift in the Auger kinetic energy (*ijj* transition) and ΔE_b is the respective binding energy shift. When ΔE_b is similar for all core levels, $\Delta\xi/2$ gives the change in the final state extra-atomic relaxation energy. Adding $2\Delta E_b(i)$ to the expession above, a different Auger parameter shift, $\Delta\beta$, can be defined, $\Delta\beta/2$ reflects the change in the core potential.

Using the model based on atomic structure parameters [7]:

$$\Delta\xi = \Delta[q(dk/dN) + (k - 2dk/dN)(dq/dN) + (dU/dN)]$$

where q is the valence charge, k is the change in the core potential removing a valence electron, N is the core occupancy and U is the contribution from the surrounding atoms. In the case of good conductors, complete screening of the core hole and when the valence electrons belong to a single band:

$$\Delta\xi = \Delta q(dk/dN)$$

i.e. the transferred charge Δq can be derived using dk/dN values obtainable from atomic calculations [8].

This approach for Auger parameter analysis is expected to improve when deep core levels are involved in the Auger transition. Assuming a linear dependence of k on q and N higher accuracy can be achieved [9] in estimating Δq. The described model was applied successfully for interpreting metal-free atom and alloy-pure metal Auger parameter shifts [10].

In the case of non-local screening of the core hole the relaxation mechanism is expected to depend strongly on the electronic polarizability of the atomic environment (e.g. ligands) and the charge transfer process involves spatially extended orbitals. The Auger parameter shifts and the extra-atomic polarization energies corresponding to the non-local screening case can be estimated by using the electrostatic model of Moretti [6]. This model interprets the final state polarization calculating the electric field generated by the core hole as well as by the induced dipoles. Using the matrix representation the total electrostatic field $\vec{F}_{Li}$ on ligands i and the electric field $\vec{F}_i$ due to the core hole are related through a matrix containing geometrical parameters and ligand polarizabilities [11]:

$$[F_{Li}]\,[D_{ij}] = [F_j]$$

Solving the corresponding system of linear equations, $\vec{F}_{Li}$ and the total relaxation energy or the final state Auger parameter shift can be determined. Alternatively, from the experimental Auger parameter shifts information can be obtained on the ligands and on their local geometry.

Local charges and the ground state local density of electron states (LDOS) can be independently calculated using cluster molecular orbital models. The discrete variational Xα (DV-Xα) model [12,13,14] uses numerical basis sets and the self-consistent charge scheme. Instead of calculating multicenter integrals, the integrandus is computed in discrete points and the LDOS is obtained by replacing the calculated MO levels with respective energy distribution functions. A stringent test of the model calculations is the comparison of the theoretical XPS valence band spectrum, based on the computed LDOS data, with the high resolution experimental spectra. The transferred charges derived from the Auger parameter analysis can be compared to the

charge distribution obtained using cluster MO calculations.

In the case of alloys containing transition metals, high resolution electron spectra excited by Cu X-rays or synchrotron radiation, provide advantageous possibilities for achieving considerable accuracy in measuring deep core Auger parameter shifts and for determining very small transferred charges [15,16].

Combined with a proper analysis of the shape of the inelastic background in these high energy electron spectra, the method can be applied even for studies of buried interfaces and surface nanostructures as well [17].

Auger parameter shifts are often utilized in studies of electronic parameters of metal particles deposited on oxides. A recent work introduces a new concept, the "chemical state vector" for systematizing the variation of the Auger parameters determined at metal-oxide interfaces and for describing the changes in the electronic parameters of these systems [18].

Excitations and Auger satellites

Initial state and final state excitations accompanying Auger processes in solids can lead to the appearance of strong satellite structures. These satellites can be attributed to "atomic" shake up or shake off excitations when the creation of the initial or final state vacancies results in the excitation of an outer shell electron in the atom into an unoccupied or continuum state. The following Auger decay either can involve (participator transition) or not (spectator transition) the excited electron.

In the case of free atoms the shake excitations are expected to be monopole transitions. Such a way the satellite structure and the lineshape of the satellites carry information on the local density of the unoccupied states. Therefore the experimentally derived satellite-main line energy separations and lineshapes can be compared to the results of theoretical (e.g. cluster-type MO) calculations of unoccupied electronic states and of excitations providing information on the role of electronic correlation and of extra-atomic screening processes as well [19,20]. In addition to the monopole type excitations, e.g. in the F KLL Auger spectra of fluorides, a different mechanism participation type transition leading to a strong satellite, can occur, attributed to the resonance between two electronic states existing during the ionisation and the decay/relaxation processes (between the highest occupied molecular orbital of the ground state and the lowest unoccupied molecular orbital of the ionised state) [21, 22]. The resonance energy of this Resonant Orbital Rearrangement (ROR) process can be interpreted using the DV-Xα cluster MO model [22] and the lineshape of the satellites seems to reflect a strong dependence on the density of the unoccupied electronic states around the atom with the core hole.

Sensitivity of these strong, localized effects in Auger spectra, on the size of the system is a very interesting field to explore.

Lineshape analysis

The lineshapes of core-valence Auger spectra of solids (in the case of negligible configuration mixing – localization and shake) can be related to the LDOS using atomic Auger transition matrix elements and the model proposed by Ramaker [2].

The experimental lineshapes $A(E)$ for the core-core-valence (CCV) and for the core-valence-valence (CVV) Auger processes can be described as:

$$A_{ccv}(E) = C_s \rho'_s(E) + C_p \rho'_p(E) \quad \text{and}$$

$$A_{cvv}(E) \cong C_{ss} R_s^2 \rho_s(E) \otimes \rho_s(E) + C_{sp} R_s R_p \rho_s(E) \otimes \rho_p(E) + C_{pp} R_p^2 \rho_p(E) \otimes \rho_p(E),$$

where ⊗ denotes convolution integral, ρ_l ($\rho_{l'}$) is the local density of electron states, LDOS (screened DOS) of the final state without (with) core hole, C_l,C_{ij} denote atomic Auger intensities (Auger transition matrix elements) normalized per filled shell, and the R_l factors provide the ratio of local charges in the screened initial state to that in the unscreened final state of the CVV process.

Correlation effects on CVV Auger lineshapes $A_{cvv}(E)$ can be approximated using the Cini-Sawatzky theory assuming on site hole-hole interaction and completely filled bands [23]

$$A_{cvv}(E) \sim \frac{\rho \otimes \rho'(E)}{\left[1-\Delta U I(E)\right]^2 + \left[\Delta U \pi \rho \otimes \rho'(E)\right]^2}$$

where $I(E)=\int(\rho\otimes\rho(E)/(E-\varepsilon))d\varepsilon$, and ΔU is the effective hole-hole correlation parameter.

For calculating the respective LDOS distributions in the case of Al and Al-Ni alloys, the DV-Xα model was used [24,25]. Profiles of deep inner-shell Auger spectra, obtained at subthreshold photoexcitation not only exhibit a Raman-type energy dispersion, but show additional structures which correspond to the partial density of the unoccupied LDOS [26].

The asymmetric XPS lineshape of the deep core photolines as observed in the case of metals, also carries information on the density of the unoccupied states in the conduction band in the neighbourhood of the given atom emitting the photoelectron [27].

Case studies

Charge transfer in CuPd

Table 1 illustrates the achieved accuracy of determining charge transfer in CuPd alloy from deep core Auger parameter shifts [15]. The very small charge transferred from the Pd to the Cu site is confirmed by the DV-Xα cluster MO theory.

Table 1.
CuPd Auger parameter shifts (eV) and transferred charges Δq [15]

		Δq(Cu)	Δq(Pd)
Δξ(Cu)	0.03	-0.01	
Δβ(Cu)	-1.30	-0.05 (0.08*; -0.23[+])	
Δβ(Pd)	0.70		0.05
DV-Xα cluster MO theory (g.s.)		-0.03[++]	0.03[++]
dk^{Cu}/dN=-3.30* est. err. <|0.10| eV			k^{Pd}(average)=11*

* R.J. Cole and P. Weightman, in Metallic Alloys: Experimental and Theoretical Perspectives, eds. J.S. Faulkner and R.G. Jordan (Kluwer, 1994)

[+] R.J. Cole, N.J. Brooks, P. Weightman, S.M. Francis and M. Bowker, Surf. Rev. Lett. **3**, 1763 (1996).

[++] I. Cserny, private communication

Difference in screening of the core hole between Cu and Ni metals

In Table 2 the experimentally derived shake up satellite – $^1D_2$ main line energy separations are compared to the calculated values obtained by using the DV-Xα cluster MO model (clusters of 43 atoms) in the case of KLL Auger spectra photoexcited from Cu and Ni metals [20]. As it seems, the difference in energy separations, which can be attributed to different screening, is correctly interpreted by the calculations [20].

Table 2
Energy separation between the shake up satellite and the main Cu and Ni KLL Auger line (eV) [20]

			DV-Xα MO cluster model
Sample	Exp.	Transition	
Cu	11.9	$22e_g \rightarrow 42e_g$	10.9
Ni	6.4	$22e_g \rightarrow 42e_g$	5.9

New methods

Information on LDOS can be obtained with sub-nanometer spatial resolution from Energy Loss Near Edge Structure (ELNES) spectra using a high spatial resolution transmission electron microscope and an energy analyzer for measuring the core energy loss structure in the electron spectra and performing cluster MO calculations for interpreting the spectral shape [28].

Scanning tunneling microscopes (STM) can be combined with an electron energy analyzer for measuring electron energy loss and Auger electron spectra with high spatial resolution. After STM imaging, the tip serves as a field emission electron source ensuring the primary beam for electron spectroscopies. The applicability of such a system for studying low coverage Ge layers on Si(111) has been discussed recently [29]. The plasmon loss features of Ge nanostructures were found to be different from those of the bulk [30]. The STM itself can also be used for revealing the local electronic structure. Differential tunneling conductance spectra (dI/dV versus V, where I is the tunneling current and V is the sample bias) map the LDOS as a function of energy. Applying this technique, the two separate electronic phases of the electrons in a high-temperature superconductor have been observed at the atomic scale [31].

Conclusion

Electron spectroscopic methods provide a wide range of possibilities for obtaining information on the local electronic structure at surfaces and interfaces, even in the case of nanosized systems. A rapid progress in experimental technique and interpretation of observations is expected in the near future, yielding a fast extension of important practical applications.

References

[1] H. Adachi, in press
[2] D.E. Ramaker, Crit. Rev. in Solid State Mater, Sci. **17,** 211 (1991).
[3] P. Weightman, J. Electron Spectrosc. Rel. Phenom. **68,** 127 (1994).
[4] C.S. Fadley, in C.R. Brundle and A.D. Baker (Eds): Electron Spectroscopy, Theory, Technique and Applications, Vol. 2, Acad. Press, New York, 1978, p. 84.
[5] T.D. Thomas, J. Electron Spectrosc. Rel. Phenom. **20,** 117 (1980).
[6] G. Moretti, J. Electron Spectrosc. Relat. Phenom. **47,** 283 (1998).
[7] P. Weightman, J. Electron Spectrosc. Rel. Phenom. **68,** 127 (1994).
[8] D.A.C. Gregory, A.D. Laine, P.S. Fowles, A. Takahashi and P. Weightman, J. Phys. **C5,** 3843 (1993).
[9] R.J. Cole and P. Weightman, J. Phys. Condens. Matter **6,** 5783 (1994).
[10] R.J. Cole, D.A.C. Gregory and P. Weightman, Phys. Rev. **B49,** 5657 (1994).

[11] Zs. Kovács, L. Kövér, F. Filippone, G. Moretti and J. Pálinkás, Proc. of the 7th European Conference on Applications of Surface and Interface Analysis, Göteborg, June 16-20, 1997 (ECASIA-97), Eds.: I. Olefjord, L. Nyborg and D. Briggs, John Wiley and Sons, 1997, p. 848.
[12] H. Adachi, M. Tsukada and Ch. Satoko, J. Phys. Soc. Jpn. **45,** 875 (1978).
[13] A. Rosén and D.E. Ellis, J. Chem. Phys. **62,** 3039 (1975).
[14] K. Ogasawara, T. Ishii, I. Tanaka and H. Adachi, Phys. Rev. B **61,** 143 (2000).
[15] L. Kövér, Zs. Kovács, P. Weightman, R. Sanjinés, D. Varga, G. Margaritondo, J. Pálinkás and M. Abon, Proc. of the 7th European Conf. on Application of Surface and Interface Analysis (ECASIA-97, June 16-20, 1997, Göteborg), Eds.: I. Olefjord, L. Nyborg and D. Briggs, J. Wiley & Sons, 1997, p. 185.
[16] S. Diplas, G. Shao, P. Tsakiropoulos, J.F. Watts and J.A.D. Matthew, Surf. Interface Anal. **29,** 65 (2000).
[17] L. Kövér, S. Tougaard, J. Tóth, L. Daróczi, I. Szabó, G. Langer and M. Menyhárd, Surf. Interface Anal. **31,** 271 (2001).
[18] A. Barranco, F. Yubero, J.P. Espinós and A.R. González-Elipe, Surf. Interface Anal. **31,** 761 (2001).
[19] L. Kövér, Zs. Kovács, J. Tóth,I,. Cserny, D. Varga, P. Weightman and S. Thurgate, Surface Sci. **433-435,** 833 (1999).
[20] I. Cserny, L. Kövér, H. Nakamatsu and T. Mukoyama, Surf. Interface Anal. **30,** 199 (2000).
[21] M. Uda, T. Yamamoto and T. Takenaga, Adv. in Quantum Chemistry **29,** 389 (1997).
[22] L. Kövér, M. Uda, I. Cserny, J. Tóth, J. Végh, D. Varga, K. Ogasawara and H. Adachi, J. Vac. Sci. Technol. **A18,** 1143 (2001).
[23] M. Cini, Solid State Commun. **20,** 655 (1976); G.A. Sawatzky, Phys. Rev. Lett. **39,** 504 (1997).
[24] Zs. Kovács, L. Kövér, D. Varga, P. Weightman, J. Pálinkás and H. Adachi, J. Electron Spectrosc. Relat. Phenom. **72,** 157 (1995).
[25] Zs. Kovács, L. Kövér, P. Weightman, D. Varga, R. Sanjinés, J. Pálinkás, G. Margaritondo and H. Adachi, Phys. Rev. B **54,** 8501 (1996).
[26] W. Drube, R. Treusch and G. Materlik, Phys. Rev. Lett. **74,** 42 (1995).
[27] S. Hüfner: Photoelectron Spectroscopy, Springer Series in Solid-State Sciences, Vol. 82, Serial Eds: M. Cardona, P. Fulde, K. von Klitzing and H.-J. Queisser, Springer Verlag, Berlin, 1995, p. 114.
[28] I. Tanaka, J. Kawai and H. Adachi, Solid State Commun. **93,** 533 (1995); H. Kanda, M. Yoshiya, F. Oba, K. Ogasawara, H. Adachi and I. Tanaka, Phys. Rev. **B 58,** 9693 (1998).
[29] M. Tomitori, M. Hirade, Y. Suganuma and T. Arai, Surface Science, **493,** 49 (2001).
[30] S. Sato, S. Nozaki and H. Morisaki, Thin Solid Films **343-344,** 481 (1999).
[31] K.M. Lang, V. Madhavan, J.E. Hoffman, E.W. Hudson, H. Eisaki, S. Uchida and J.C. Davis, Nature, **415,** 412 (2002).