

# Threshold Al KLL Auger Spectroscopy of Oxidized Aluminum

A.N. Buckley,<sup>1</sup> R.N. Lamb,<sup>1</sup> A.P.J. Stampfl,<sup>2</sup> J.W. Freeland,<sup>3</sup> I. Coulthard<sup>4</sup>

<sup>1</sup>School of Chemical Sciences, University of New South Wales, Sydney, New South Wales, Australia

<sup>2</sup>Bragg Institute, Australian Nuclear Science and Technology Organisation (ANSTO),  
Lucas Heights, New South Wales, Australia

<sup>3</sup>Experimental Facilities Division, Argonne National Laboratory, Argonne, IL, U.S.A.

<sup>4</sup>Canadian Light Source Inc., University of Saskatchewan, Saskatoon, Saskatchewan, Canada

## Introduction

The modification of the surface of aluminum for its use in electronic devices and other manufactured products continues to be of interest. The modified surfaces are typically characterized by means of x-ray photoelectron spectroscopy (XPS) and x-ray absorption near-edge structure (XANES) spectroscopy. Nevertheless, new approaches are needed for a more detailed characterization, particularly approaches that can detect a buried interface and hence contribute to the assembly of a nondestructive chemical depth profile.

A report by Coulthard et al. [1] of resonant Auger studies of some metallic systems revealed the possibility that threshold Al KLL Auger spectra may be able to provide additional information on the oxidation products at the surface of aluminum. In that work, three different chemical states were identified in the threshold KLL Auger spectra from the surface of air-exposed pure Al foil. The three principal  $KL_{2,3}L_{2,3}$  peaks observed near 1382, 1385, and 1388 eV were assigned, respectively, to an ~2.5-nm  $Al_2O_3$ -like oxide layer, to an ~0.2-nm suboxide layer in which the aluminum formal oxidation state would have been between three and zero, and to the metallic Al substrate (about 0.4 nm of which would have been included in the depth analyzed). Spectator Auger peaks associated with the oxide layer were not evident, unlike the situation for oxidized silicon [2, 3].

In the work reported on here, threshold Al KLL Auger spectroscopy was used to examine Al foil of technical purity (99.5%) before and after electrochemical treatment that altered the thickness and degree of hydroxylation of the oxidized layer. The emphasis was on whether the spectra were consistent with the model developed previously [1], and, in particular, on whether the intermediate Auger component could have been a spectator peak.

## Methods and Materials

The threshold Auger spectroscopy was carried out at beamline station 4-ID-C at the APS [4]. Using the 600 L/mm grating and 20- $\mu$ m slits, the spherical grating monochromator provided an energy resolution of 0.7 eV at 1500 eV. The beam size on the sample was  $\sim 2 \times 0.5$  mm. A Physical Electronics 10-366HR

hemispherical analyzer with 16-channeltron detection was used at a pass energy of 5.8 eV. Auger spectra were fitted by using XPSPEAK Version 4.1 [5]. Total electron yield (TEY) and fluorescence yield (FY) Al and O K-edge absorption spectra were obtained by using 50- $\mu$ m slits. FY detection was effected by means of a liquid-nitrogen-cooled, ultralow-energy germanium diode detector.

Specimen A was the untreated technically pure Al foil. Specimens B and C were prepared by polarizing similar foil in an organic electrolyte containing 1 mol  $dm^{-3}$  tetrafluoroborate and ~0.2% water for 16 hours at -0.4 V (versus SHE) for specimen B and at +1.6 V for specimen C. Specimen D was obtained by chemically etching the foil in 0.5% hydrofluoric acid to reduce the oxide layer thickness. The dull side of each foil was analyzed at ambient temperature. Surface chemical characterization was carried out by means of monochromatized Al  $K_{\alpha}$ -excited photoelectron spectroscopy on a VG 220-iXL spectrometer.

## Results and Discussion

Al 2p and O 1s photoelectron spectra indicated that compared with the native oxide on specimen A, the oxidized layer was thicker and more hydroxylated for specimen B, and even more so for specimen C. For specimens A, B, and D, the first absorption peak in the TEY Al K-edge spectrum was at a photon energy near 1565.5 eV, 6.5 eV higher than the substrate absorption edge. For Al in different oxygen environments, an absorption peak near 1566 eV is indicative of tetrahedral coordination (and hence an amorphous structure), whereas for octahedral coordination, the lowest energy absorption peak is near 1568 eV [6-8]. Thus, the predominant Al environment in the oxidized layer for specimens A, B, and D was tetrahedral rather than octahedral. For specimen C, the absorption maximum occurred at ~1568 eV, indicating that in this case, Al in an octahedral oxygen environment was the predominant species.

The O K-edge spectra for specimens A, B, and D were broadly similar to those for thin film and bulk alumina reported on previously, including a weak feature that was 2-3 eV below the main edge [9-11]. The O K-edge spectra from specimen C reproducibly

displayed a sharp and relatively intense pre-edge feature at 530 eV. As indicated above, such a sharp feature is not usually observed for Al oxide, but it can arise in O K-edge absorption spectra from oxygen bonded to transition metals or from oxygen multiply bonded to carbon [12, 13]. However, no transition metal impurities in any of the specimens were detected by XPS, and the C 1s spectra for specimens B, C, and D were not discernibly different, so the pre-edge feature was unlikely to have arisen from oxygen bonded to a transition metal or to carbon. Experiments on Al foils treated in hot water indicated that neither water nor hydroxyl groups throughout the oxidized layer on specimen C were the source of the feature. A possible source is oxygen present in an interfacial region of surface area significantly enhanced by the particular treatment used for specimen C. In any case, it is clear that the oxidized surface layer on specimen C was fundamentally different from that on the other three specimens.

The threshold Al  $KL_{2,3}L_{2,3}$  spectra from the air-exposed-only surface (A), shown at representative photon energies in Fig. 1, are in broad agreement with those obtained previously if the photon energies are assumed to be  $\sim 14$  eV higher and the Auger electron kinetic energies are assumed to be  $\sim 5$  eV higher than those indicated in the Coulthard et al. report [1]. The intensities of the minor peaks near 1377 and 1380

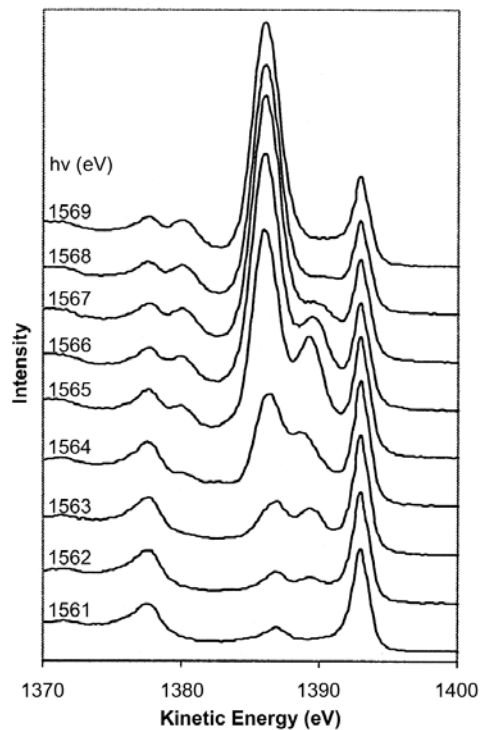


FIG. 1. Al  $KL_{2,3}L_{2,3}$  spectra for specimen A at the near-threshold photon energies indicated. Reproduced by permission of John Wiley & Sons Limited.

correlate with those of the principal metal and oxide peaks, respectively. The 1381-1395 eV region of the KLL spectra could be fitted adequately with three predominantly Gaussian-shaped ( $<20\%$  Lorentzian) components, one near 1393 eV from the metallic Al, one near 1386 eV from the oxide, and an intermediate one near 1390 eV. For each specimen, the position of the principal peak assigned to the metal remained constant at 1393 eV. The position of the peak assigned to the oxidized layer remained near 1386 eV for photon energies above 1555 eV, but the kinetic energy increased to approximately 1387 eV for photon energies below 1554 eV. The intermediate peak had a kinetic energy that was approximately constant at 1389.5 eV.

The threshold Al  $KL_{2,3}L_{2,3}$  spectra from the electrochemically treated foils B and C were also qualitatively similar to the spectra from the air-exposed-only foil reported on previously [1]. Furthermore, the relative intensities of the three principal peaks for specimens A and B were consistent with the layer model proposed by Coulthard et al. [1]. When it is assumed that the interfacial species cannot be a bulk phase, the thickness of the interfacial layer should not increase with increasing thickness of the surface oxide layer, but the interfacial area could be increased by roughening. The native oxide layer on specimen A was thinner than that on the pure Al foil studied previously [1]; therefore, for the former foil, the maximum intensity of the interfacial species peak should be greater relative to the maximum intensity of the surface oxide peak. That is indeed what was observed, with the intensity ratios being  $\sim 1:2$  and  $\sim 1:3$ , respectively. For specimen B, the corresponding intensity ratio was  $\sim 1:4$ , and the metallic substrate peak was less intense than that for specimen A — observations consistent with the significantly thicker oxidized surface layer.

At first sight, the data for the specimen bearing the thickest oxidized layer (C) did not appear to be consistent with the interfacial layer model, in that the intermediate energy Auger component was too intense relative to the oxide component. As revealed by the O K-edge spectra, however, this oxide overlayer appeared to be fundamentally different from the others. Thus it is possible that a significantly greater interfacial surface area had been generated by the particular treatment used for specimen C.

The intermediate Auger peak did not behave like a photoelectron line fortuitously passing through the kinetic energy range of interest, nor did it behave like a typical spectator Auger line, since its position did not vary linearly with photon energy. The peak remained at an essentially fixed kinetic energy between the metal and oxide peaks, while its intensity increased and then decreased as the photon with incremental changes in energy. It is pertinent to note that spectator peaks are

typically observed at kinetic energies a few electron-volts higher than those for the corresponding normal lines. Accordingly, any spectator peak associated with the oxide would be expected between the peaks from the oxide and the metal (i.e., in the vicinity of the Auger peak from an interfacial species). While an almost linear relationship of 1:1 between the shift of a spectator line and the increase in photon energy is common, shifts significantly lower than 1:1, and even anomalous negative shifts have been observed [2, 3, 14-17]. Therefore, it would appear that an essentially zero shift is possible, and it follows that the previously identified intermediate component could be a spectator peak.

Nevertheless, for two of the oxidized Al foils investigated in this work, the relative intensity of the intermediate Auger peak near threshold was consistent with the interfacial layer model and inconsistent with the expected behavior of a spectator peak associated with the oxide layer. Thus, on the balance of available evidence, it is concluded that the resonantly enhanced intermediate Auger peak did arise from an interfacial layer and was not a spectator peak. That raises the question as to why spectator peaks were not observed. Spectator lines are a feature of threshold Auger spectra, especially in materials where discrete levels are expected. It is possible that because Al(III)/O species tend to have a high density of unfilled states that have p-character [18] instead of 1s excitation to one particular unfilled p-like state, as the photon energy is increased, excitation to states of slightly higher energy occurs rather than the excess energy resulting in an Auger electron of higher kinetic energy. In that case, no one transition giving rise to a narrow peak would predominate.

### Acknowledgments

This work was supported by the Australian Synchrotron Research Program, which is funded by the Commonwealth of Australia under the Major National Research Facilities Program. Use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. Details on this report can be found in *Surface and Interface Analysis* [19].

### References

- [1] I. Coulthard, W.J. Antel Jr, S.P. Frigo, J.W. Freeland, J. More, W.S. Calaway, M.J. Pellin, M. Mendelsohn, T.K. Sham, S.J. Naftel, and A.P.J. Stampfl, *J. Vac. Sci. Technol. A* **18**, 1955 (2000).
- [2] Y. Baba, T.A. Sasaki, and H. Yamamoto, *Phys. Rev. B* **49**, 709 (1994).
- [3] N. Okude, H. Noro, M. Nagoshi, H. Yamamoto, Y. Baba, and T.A. Sasaki, *J. Electron Spectrosc. Relat. Phenom.* **88-91**, 467 (1998).
- [4] K. J. Randall, E. Gluskin, and Z. Xu, *Rev. Sci. Instrum.* **66**, 4081 (1995).
- [5] R.W.M. Kwok, XPSPEAK Version 4.1, freeware.
- [6] J. Wong, G.N. George, I.J. Pickering, Z.U. Rek, M. Rowen, T. Tanaka, G.H. Via, B. DeVries, D.E.W. Vaughan, and G.E. Brown, Jr., *Solid State Commun.* **92**, 559 (1994).
- [7] D. Li, G.M. Bancroft, M.E. Fleet, X.H. Feng, and Y. Pan, *Am. Mineral.* **80**, 432 (1995).
- [8] D. Cabaret, P. Saintavit, P. Ildefonse, and A-M. Flank, *J. Phys.: Condens. Matter* **8**, 3691 (1996).
- [9] M. Gautier, G. Renaud, L.P. Van, B. Villette, M. Pollak, N. Thromat, F. Jollet, and J-P. Duraud, *J. Am. Ceram. Soc.* **77**, 323 (1994).
- [10] I. Popova, V. Zhukov, J.T. Yates, Jr., and J.G. Chen, *J. Appl. Phys.* **86**, 7156 (1999).
- [11] M. Uda, D. Yamashita, D. Terashi, T. Yamamoto, H. Osawa, K. Kanai, H. Nakamatsu, and R. Pereira, *J. Electron Spectrosc. Relat. Phenom.* **114-116**, 819 (2001).
- [12] J.G. Chen, B. Frühberger, and M.L. Colaiani, *J. Vac. Sci. Technol. A* **14**, 1668 (1996).
- [13] J. Stöhr, *NEXAFS Spectroscopy* (Springer-Verlag, Berlin, 1992).
- [14] M. Finazzi, G. Ghiringhelli, O. Tjernberg, P. Ohresser, and N.B. Brookes, *Phys. Rev. B* **61**, 4629 (2000).
- [15] M. Elango, A. Ausmees, A. Kikas, E. Nommiste, R. Ruus, A. Saar, J.F. van Acker, J.N. Andersen, R. Nyholm, and I. Martinson, *Phys. Rev. B* **47**, 11736 (1993).
- [16] P. Lagarde, M. Pompa, R. Delaunay, and A.M. Flank, *J. Electron Spectrosc. Relat. Phenom.* **94**, 229 (1998).
- [17] F. Yubero, A. Barranco, J.P. Espinos, and A.R. Gonzalez-Elipe, *Surf. Sci.* **436**, 202 (1999).
- [18] S. Ciraci and I.P. Batra, *Phys. Rev. B* **28**, 982 (1983).
- [19] A.N. Buckley, A.J. Hartmann, R.N. Lamb, A.P.J. Stampfl, J.W. Freeland, and I. Coulthard, *Surf. Interface Anal.* **35** (11), 922-931 (Nov. 2003).