Evidence for a new aluminum oxidation state

G. Faraci, S. La Rosa, and A. R. Pennisi

*Dipartimento di Fisica, Università di Catania, Consorzio Interuniversitario di Fisica della Materia,
Corso Italia 57, 95129 Catania, Italy*

Y. Hwu

Synchrotron Radiation Center, University of Wisconsin—Madison, Madison, Wisconsin 53706

G. Margaritondo

Institut de Physique Appliquée, Ecole Polytechnique Fédérale, PH-Ecublens, CH-1015 Lausanne, Switzerland

We present experimental evidence of a previously unknown aluminum oxidation state due to chemisorbed atomic oxygen. This new oxidation state has been detected at room temperature on the chemically shifted Al $2p$ core level by photoemission spectroscopy. The state was already obtained at submonolayer coverage by a nonconventional deposition of aluminum oxide on cleaved Si. At low metal coverage, only this partially oxidized state is visible, whereas at higher deposition the clean Al $2p$ doublet is accompanied by the standard alumina peak and other two substoichiometric oxide configurations, shifted to larger binding energy. The Al $2p$ spectra indicate the growing of clusters or islands with a large fraction of Al-O bonds. These results have been confirmed by similar experiments performed on other substrates (SiO_2, graphite), showing that this Al intermediate oxidation state is substrate independent but is confined at the interface.

Aluminum and aluminum oxide are of particular interest in semiconductor technology and device applications, and many efforts have been devoted to a complete characterization of their interfaces with metals or semiconductors.[1-13] As the deposition of the stoichiometric Al_2O_3 cannot be obtained by usual crucible evaporation because of its high melting point (2045 °C), other methods have been used such as electron bombardment[3] or laser ablation. In these cases, the layers of Al oxide are amorphous, and the lattice mismatch with the substrate always produces an incoherent interface.[14] Furthermore, when a few monolayers of Al oxide must be obtained on a substrate like Si, it is not convenient to use a preliminary Al deposition followed by oxidation in an O_2 atmosphere, because at low coverage clusters of the metal are formed and this implies the oxidation of the support and not of the metal only.[15,16]

Photoemission measurements, reported in the literature for clean Al(111) surface exposed to O_2 at several temperatures and different exposures,[1-8] show, with the clean Al $2p$ doublet, additional features due to Al oxide. In particular, for 100-L (1 L=10^{-6} Torr s) exposure, at 200 °C the Al^{3+} $2p$ core level is shifted to 2.8 eV higher binding energy from the clean Al $2p_{3/2}$ position, whereas at 400 °C the shift increases up to 3.3 eV,[1] because of a phase transition from amorphous to γ alumina. At room temperature, on the contrary, only a peak at 1.4 eV is visible, attributed to the intermediate oxidation state of the Al atom interacting with the chemisorbed oxygen. This feature disappears at 200 °C or higher temperature. Similar intermediate oxidation states have been reported for Si.[15,16]

In the present paper we report the discovery of a new oxidation state of aluminum clusters. The clusters were deposited on several substrates by thermal evaporation of Al, assisted, at a pressure of 10^{-10} Torr, by sputtering of atomic oxygen. In these conditions the metal has a high probability to bind an oxygen atom and this produces clusters of substoichiometric aluminum oxide on the substrate. This effect was investigated by core-level photoemission spectroscopy; at low coverage, in the Al $2p$ spectrum we found only one peak, not previously observed, shifted towards higher binding energy from the Al $2p_{3/2}$ position. We attribute this feature to entirely oxidized clusters of Al^{2+}-O. This new Al oxidation state was observed on different substrates (Si, SiO_2, graphite). However, in this paper only the data obtained for the Si substrate will be presented, and a complete discussion of all substrates will be reported in a forthcoming paper.

The experiments were performed in ultrahigh vacuum using the Mark II beamline at the Wisconsin Synchrotron Radiation Center. The substrate [Si(111) cleaved *in situ*] was reached by an evaporated beam of Al in the presence of sputtered oxygen at a low rate. The pressure in the chamber was always maintained at about 10^{-10} Torr during the evaporation and the rate was monitored with a quartz crystal microbalance. The substrate was kept at room temperature and placed at a distance of about 10 cm from the source. Synchrotron radiation was energy filtered by a Grasshopper monochromator in the range 40–400 eV. Photoemission spectra were collected in the energy-distribution-curve mode; the electrons per unit time were detected with a double-pass cylindrical mirror analyzer as a function of the electron kinetic energy at a fixed photon energy. We measured the Al $2p$ and Si $2p$ levels at $h\nu = 130$ eV, the valence band at $h\nu = 60$ eV. The substrate has been checked by Auger electron spectroscopy and by monitoring the Si $2p$ at all deposi-

tions. The exciting photon energy was selected in order to minimize the effective escape depth so as to enhance the surface contributions.

Al $2p$ spectra at different coverages are shown in Fig. 1. At high coverages, we see the Al $2p$ doublet (splitting 0.38 eV) and the higher binding energy features due to intermediate oxidation states and to Al_2O_3.[17] On the contrary, at low coverages the clean Al doublet is totally absent and we see only a peak due to one substoichiometric oxide which is attributed to Al^{2+}-O.

The spectra shown in Fig. 1 have been deconvolved in Gaussian components identifying two additional contributions at high coverages. A typical analysis is shown in Fig. 2 for an intermediate coverage; the shoulder on the right-hand side of the spectrum has been fitted with the Al $2p$ doublet and the feature on the left was found as superposition of two intermediate aluminum oxidation states (Al^{1+}, Al^{2+}), and the standard alumina contribution (Al^{3+}). Their binding energy is shown in Fig. 3, as a function of the coverage, together with the binding energy of the clean Al $2p_{3/2}$, whenever present. This last energy at the maximum coverage was taken as a reference.

Note that, up to 1-Å coverage, only one peak is obtained, whose binding energy changes from 1.35 eV at the lowest coverage up to 2.2 eV at 2 Å, decreasing to about 2 eV at 35 Å. In the highest range of Fig. 3 all the peaks show quite a similar shift. This can be attributed to a final-state interaction between the hole and the electron in the photoemission process, when the coverage is not sufficient to produce a uniform layer of homogeneous
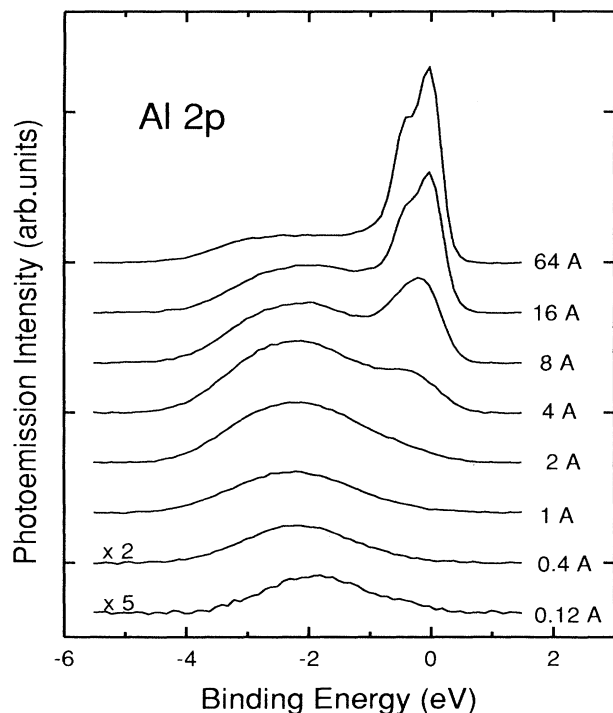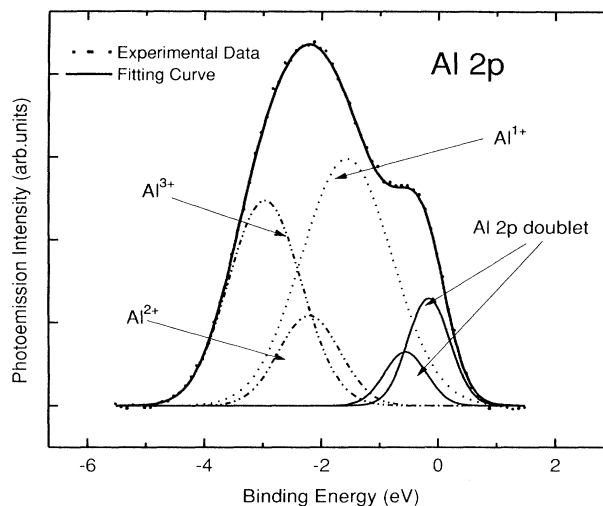

FIG. 2. Decomposition of the spectrum shown in Fig. 1 for a coverage 4 Å of aluminum, in Gaussian components to best fit the experimental data. The only constraint in the fit was the splitting and the branching ratio of the Al doublet.

composition; however, we have a mixing of clean aluminum agglomerates together with three-dimensional islands of oxidized metal. The behavior at low coverage for the single oxidized component present in the range 0.04–1 Å, shifting towards lower binding energy, suggests that in the very small cluster regime this component (and its energy) originate from surface bonds involving the substrate and oxygen. We shall explain this point in more detail later.

From the previous paragraphs the following conclusions are evident: our evaporation method allows the deposition at low coverages of small clusters or islands of completely oxidized Al, in a substoichiometric
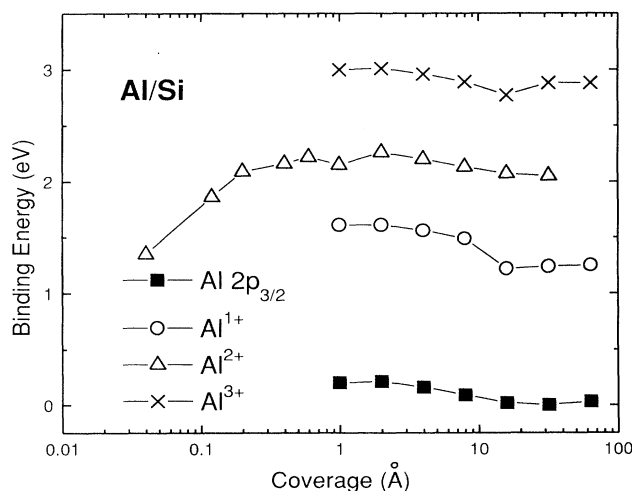

FIG. 1. Photoemission intensity vs energy of the Al $2p$ core level for several Al depositions on a cleaved Si substrate. The reference energy $E = 0$ was taken at the Al $2p_{3/2}$ peak. Note that the clean Al $2p$ doublet is absent at low coverage.

FIG. 3. Binding energy vs Al coverage of the Al $2p_{3/2}$ and of the aluminum oxide components. At the highest coverage the point of the Al^{2+} intermediate oxidation state is missing because its intensity was zero. Typical uncertainty: ±0.15 eV.

configuration with respect to alumina. The cluster regime is supported in fact by the nonexponential decay of the substrate Si $2p$ core level, observed at all depositions; the substoichiometry of the Al-O bonds is suggested by the binding energy of the corresponding Al $2p$. The data reported are in fact chemically shifted: the lowest Al^{1+} intermediate oxidation state at a value 1.25–1.4 eV; the Al^{2+} feature at 1.35–2.2 eV; the Al^{3+} at 2.8–3.0 eV.

We compare our data and those reported in Ref. 1 for aluminum oxide grown on Al(111) surface by exposition to 100 L of O_2 at room temperature (1.4 eV) and at 200 °C (2.8 eV). The comparison shows clear evidence that we have found a feature not reported in the literature.[1,8,13] We note that the absence in our graphs of a clean Al doublet at low coverage demonstrates the complete binding of aluminum with oxygen. Furthermore, we argue that the oxidation occurs before the aluminum reaches the substrate, i.e., Al binds with the sputtered oxygen in flight near the crucible and not on the silicon surface, as confirmed by the Si $2p$ core level that remains absolutely clean without any appearance of silicon oxide[15,16]— whereas the substrate would appear oxidized if the oxidation process had occurred after the Al arrival on the cleaved Si surface.

This particular mode of obtaining the oxidation is very likely to be responsible for the Al $2p$ component. Usually, the oxidation process is performed by exposure of a clean Al layer to molecular oxygen[1] and not, as in our case, to atomic oxygen. This can produce an Al-O atom-by-atom binding and therefore substoichiometry with respect to alumina, contrary to a metal layer where molecular oxygen is chemisorbed.

The binding energy of this Al^{2+} oxidation state is coverage dependent, as is clearly visible in Fig. 3, most notably at very small coverages, i.e., in the cluster regime. For these small agglomerates a strong influence of the substrate can be hypothesized since covalent bonds can be established between the semiconductor and the metal at the Si/Al interface. In this hypothesis, Al could share one electron in a covalent bond with Si and the other two with oxygen. This possibility would enhance the role of the surface establishing Si-Al-O bonding on the surface of the cluster with a charge transfer causing the binding-energy shift at low coverage. However, these Al intermediate oxidation states are not formed only on this particular substrate. In fact, we have found the same aluminum oxidation states on different substrates (SiO$_2$ and graphite) with very different characteristics from those of cleaved Si. Even though a complete analysis of these results will be done elsewhere, we can say that the Al^{2+} intermediate oxidation state found at low coverage does not depend on the substrate surface, but its binding energy does. This suggests that at submonolayer coverage the agglomeration of aluminum with oxygen proceeds via a saturation of the couple of oxygen electrons because of the high electronegativity of the oxygen (3.5) with respect to aluminum (1.5), whereas the spare electron of the metal can be shared with a dangling bond of the semiconductor. This effect of course ceases when the Si substrate is entirely covered by an amount of Al oxide of the order of a monolayer as actually confirmed by Fig. 3. This is con-

sistent with scanning tunneling microscopy measurements[5] of Al overlayers on Si(111): at submonolayer Al coverage, saturation of the Si dangling bonds may be accomplished by Al clusters in different geometric structures growing on twofold or threefold sites of the surface.

In Fig. 4, the photoemission intensity of the various components is shown as a function of the coverage. We see that the novel component increases in intensity from low coverage up to 1 Å when it reaches its maximum value. Afterwards, with the appearance of the other contributions it decreases exponentially confirming that this component is confined at the Al/Si interface where it remains buried. The other components, on the contrary, are distributed in a relatively thick layer at coverages larger than 4 Å as indicated by their intensity.

This may explain why this Al^{2+} oxidation state has not been detected previously: it can be observed only at coverage of the order of a monolayer, since the other oxide contributions growing at higher coverages mask the interface oxide because of the short electron escape depth [~5 Å (Ref. 1)]. The previous conclusions on the core-level photoemission spectra have been confirmed observing the valence-band features where the progressive oxidation of the aluminum was indicated by the increase of the oxygen broad peak. However, no quantitative analysis on the valence band was performed because of the overlap of the aluminum, silicon, and oxygen features in the same energy range. A comparison of the present results with those obtained for the Al/Al$_2$O$_3$ interface[1] strongly supports the attribution of the additional feature found in this work to the Al^{2+} oxide state. A different Al-O bonding occurring during the formation of aluminum oxide clusters can be attributed to a different site symmetry around the absorbing atom and the
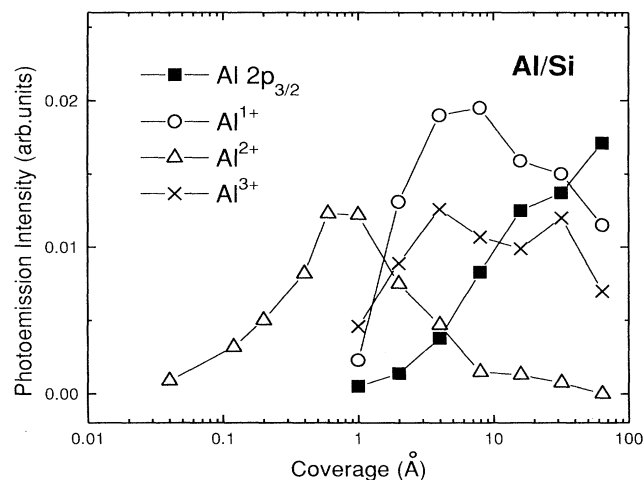

FIG. 4. Photoemission intensity of the various Gaussian components located under the spectra Al $2p$ as a function of the Al coverage. The uncertainty introduced by the fitting procedure for the vertical scale is of the order of 5%. Note the exponential decrease of the intensity of the Al^{2+} component at a coverage larger than 1 Å showing that this intermediate oxidation state is confined to the silicon–aluminum oxide interface.

modification of the electronegative potential barrier due to the oxygen ion can produce the shifts observed in Fig. 3. The lower symmetry present in a cluster also implies a geometric distortion of the Al-O bonding, taking into account that even in crystalline alumina the distance between the metal and the oxygen can be 1.86 or 1.97 Å.[18] A charge transfer related to the geometric distance could be hypothesized then from the metal towards the oxygen and towards the Si substrate. However, we can rule out this last hypothesis because the energy of the Si $2p$ core level was found constant at all metal deposition excluding a participation of the support to the charge transfer that occurs only in the oxide.

[1]A. Bianconi, R. Z. Bachrach, S. B. M. Hagstrom, and S. A. Flodström, Phys. Rev. B **19**, 2837 (1979).

[2]G. V. Hansson, R. Z. Bachrach, R. S. Bauer, and P. Chiaradia, Phys. Rev. Lett. **46**, 1033 (1981).

[3]C. A. Schug, B. Konrad, B. Heisenhut, E. Bertel, and W. Steinmann, Surf. Sci. **225**, 58 (1990).

[4]K. Horn, Appl. Phys. A **51**, 289 (1990).

[5]R. J. Hamers, Phys. Rev. B **40**, 1657 (1989).

[6]M. K. Kelly, G. Margaritondo, L. Papagno, and G. J. Lapeyre, Phys. Rev. B **34**, 6011 (1986).

[7]M. K. Kelly, E. Colavita, G. Margaritondo, J. Anderson, L. Papagno, D. J. Frankel, and G. J. Lapeyre, Phys. Rev. B **32**, 2693 (1985).

[8]S. A. Flodström, R. Z. Bachrach, R. S. Bauer, and S. B. M. Hagström, Phys. Rev. Lett. **37**, 1282 (1976).

[9]W. Eberhardt and F. J. Himpsel, Phys. Rev. Lett. **42**, 1375 (1979).

[10]W. Eberhardt and C. Kunz, Surf. Sci. **75**, 709 (1978).

[11]C. W. B. Martinson, S. A. Flodström, J. Rundgren, and P. Westrin, Surf. Sci. **89**, 102 (1979).

[12]P. Hofmann, C. V. Muschwitz, K. Horn, K. Jacobi, A. M. Bradshaw, K. Kambe, and M. Scheffler, Surf. Sci. **89**, 327 (1979).

[13]K. Wandelt, Surf. Sci. Rep. **2**, 1 (1982).

[14]F. A. Ponce, Appl. Phys. Lett. **41**, 371 (1982).

[15]G. Hollinger and F. J. Himpsel, Phys. Rev. B **28**, 3651 (1983).

[16]G. Faraci, S. La Rosa, A. R. Pennisi, Y. Hwu, L. Lozzi, and G. Margaritondo, J. Appl. Phys. (to be published).

[17]A. Balzarotti, A. Bianconi, E. Burattini, G. Grandolfo, R. Habel, and M. Piacentini, Phys. Status Solidi B **63**, 77 (1974).

[18]Ralph W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Wiley, New York, 1964), Vol. 2.