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Blocking Oxidation of Al Surfaces with Organic Thiol Monolayers Cured by Electron Beam

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In order to expand the processing utility of metallic aluminum as a material for nanometer-scale fabrication, we attempted to block oxidation of Al(111) surface in O_2 gas up to 1000 Torr, by predeposited organic monolayers. A full monolayer of biphenyl-4-thiol (BPT), appropriately treated by electron-beam irradiation, exhibited a significantly enhanced robustness against oxidation, compared to clean Al(111).

Aluminum has various useful physical properties, such as low electric resistance ($2.7 \times 10^{-8}\,\Omega\,m$), high thermal conductivity ($2.4 \times 10^{2}\,W\,K^{-1}\,m^{-1}$), and low density ($2.7\,g\,cm^{-3}$).[1] Thanks to these attractive properties, Al was widely applied in fabricating leading-edge semiconductor devices until the late 90's. However, as the design rules of devices reached <100 nm, the roughness of Al surfaces become uncontrollable partly because of unwanted surface oxidation during the fabrication process. An industrial solution for this was the development of damascene copper electroplating at IBM,[2] which is now in practical use and under further improvement for today's high-density devices.

Metallic Al surfaces are easily oxidized in the atmosphere, and it is a challenging attempt to find an ultimately thin coating layer to block oxidation. Adsorption of organic molecules on clean Al surfaces was studied for aldehydes,[3] formic acid,[4] and a series of halogenated hydrocarbons.[5] Al surface passivation against low exposures of H_2O or O_2 was attempted with C_{60} (ref. 6) or perfluoropropionic acid.[7] Surface passivation of bare Al nanoparticles has been demonstrated using perfluoroalkyl carboxylic acids.[7,8] Al nanoparticles are expected to be useful for explosives and rocket propellants because of the high specific surface area.

In regard to practical protection of Al substrate against oxidation, we formulate our goal as to prepare a passivating organic monolayer on the surface that can block substrate oxidation by O_2 gas at atmospheric pressure or higher. The ultimate thinness of passivating monolayer, below a few nanometers, is beneficial in application of Al in nanometer-scale technology. The oxide layer thickness on Al metal in air can range between 1.7 and 6.0 nm.[9] For example, if an Al nanowire with a diameter of 50 nm is covered by 6 nm oxide layer, the oxide represents nearly half of the total mass. However, if we can limit the oxide layer to 0.25 nm, which corresponds to Al_2O_3 monolayer thickness, the oxide layer occupies only a few % of the mass. We fixed our testing conditions up to 1000 Torr of O_2 at room temperature, to meet practical conditions of fabrication.

For this purpose, we examined various organic adsorbates for the passivation. Due to the highly reactive nature of Al surfaces, it is difficult to apply methods of monolayer deposition on Si, such as the Grignard reaction.[10] In this survey we found that evaporation of various kinds of hydrocarbon thiols form monolayers on Al(111). Such monolayers can retard substrate oxidation but not at high ambient O_2 pressures. Among such thiols, biphenyl-4-thiol (BPT) was previously studied on Au substrate and reported to exhibit a notable robustness, when crosslinking between the adsorbates was introduced.[11,12] In this work, we demonstrate that BPT forms a monolayer on Al(111), and that the BPT monolayer bombarded with electron beam gains an excellent robustness against O_2 at atmospheric pressure or higher. The process of monolayer formation and O_2 exposure was monitored by X-ray photoelectron spectroscopy (XPS).

The Al(111) substrate (diameter: 10 mm, thickness: 2 mm) and the BPT reagent were purchased from Matek, Germany and Platte Valley Scientific, USA, respectively. The Al substrate was cleaned by Ar ion bombardment for 1 h and annealing at approximately 400 °C for 3 min. For BPT deposition, BPT powder was fused at approximately 50 °C and charged into a Ta crucible (diameter: 3 mm, depth: 5 mm) with resistive heater wires. This crucible was housed usually in a differentially pumped chamber. After thermal degassing, the crucible was driven near the Al(111) sample and heated up to 60 °C for a few minutes for evaporation to deposit a full monolayer coverage. Electrons were irradiated to the BPT-modified Al(111) by a flood gun composed of a Th–W coil filament connected to ground, placed at a distance of 60 mm from the sample surface. The filament was heated by a few A of DC current, and the sample was positively biased from ground, with a voltage from 0 to 500 V. Typically $40\,mC\,cm^{-2}$ of current density at the sample surface was obtained at 100 V. When the electron kinetic energy exceeded 100 eV, the C 1s signal of BPT apparently decreased, due to electron-stimulated desorption. As for oxidation, the surface was subjected to O_2 exposures for 100 s at given pressures, and the O uptake was measured by XPS.

The chemical structures of surfaces were investigated with an X-ray photoelectron spectrometer equipped with a Mg Kα source and a rapid sample transfer/introductory system. Oxide layer thickness was calculated from the peak intensity ratio of O 1s to Al 2s. A sapphire (Al_2O_3) single crystal surface was measured to determine the relative sensitivity for O 1s to Al 2s. The signals of the test samples were normalized by this sensitivity, and converted into the effective Al_2O_3 layer thickness, using the values of photoelectron mean free paths for Al and Al_2O_3, established by Battye et al.[13,14]

Figure 1 shows XPS for (a) clean Al(111), (b) Al(111) after O_2 exposure at 1000 Torr for 100 s ($=10^{11}$ Langmuir, 1 Langmuir $\equiv$ 1 L $= 10^{-6}$ Torr s) at room temperature, and (c) BPT-modified Al(111) (with a BPT-saturated monolayer irradiated with $40\,mC\,cm^{-2}$ of 100-eV electron beam) after O_2 exposure at 1000 Torr for 100 s. The left frame shows the

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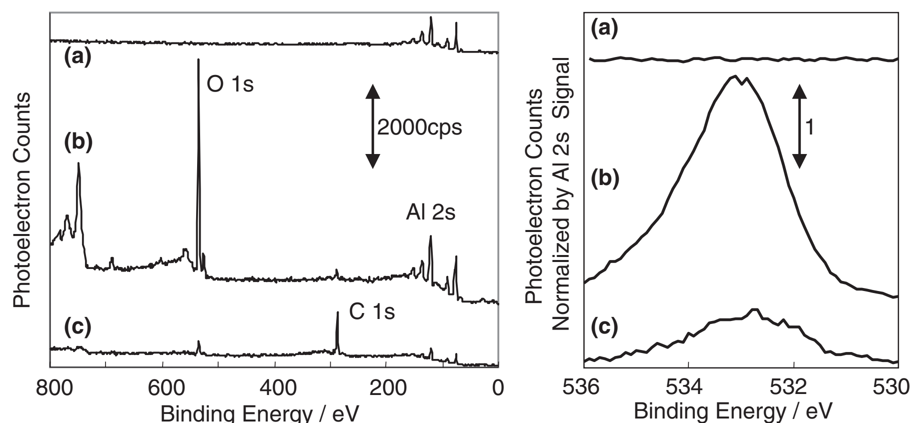
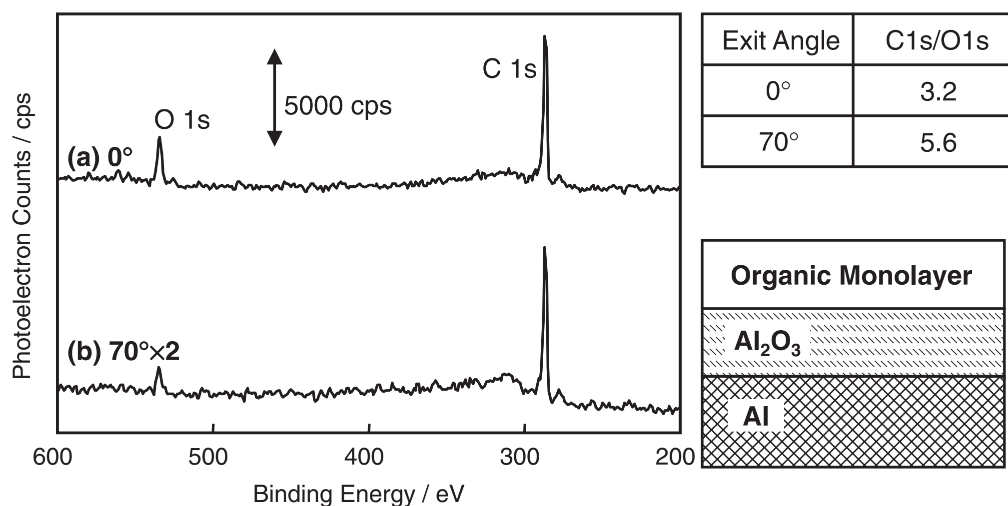


Figure 1. XPS of (a) clean Al(111), (b) Al(111) after O_2 exposure (1000 Torr, 100 s), (c) BPT-evaporated (1.7×10^{-7} Torr, 300 s) and electron-irradiated (100 eV, 40 mC cm^{-2}) Al(111) after O_2 exposure (1000 Torr, 100 s). Left: the wide-region spectra, right: the O 1s region narrow scans (intensity normalized by Al 2s peak intensity).



Exit Angle	C1s/O1s
0°	3.2
70°	5.6

Figure 2. Left: XPS of BPT/Al(111) after O_2 exposure (1000 Torr, 100 s). The photoelectron emission angle was adjusted to (a) 0 and (b) 70°, from the surface normal. The sample preparation was the same as that of Figure 1c. Right-top: C 1s/O 1s peak ratio. Right-bottom: A schematic view of BPT on Al(111) after O_2 exposure.

wide-range spectra, and the right frame shows the corresponding O 1s peaks (intensity normalized by the corresponding Al 2s signal), respectively.

It is seen from the strong O 1s signal that the bare Al(111) is easily oxidized to form a thick layer of oxide (calculated to be 1.8 nm) after exposure to O_2 gas at 1000 Torr for 100 s. The same treatment to BPT-pretreated (with electron bombardment) Al(111) resulted in a limited O 1s signal coexisting with a C 1s signal of organic monolayer. The thickness of organic monolayer, assuming the upright position of BPT molecule, that is, the maximum thickness, is estimated to be 1.2 nm.[15] When the surface is covered with the oxide layer and/or the BPT monolayer, these overlayers attenuate the photoelectrons from the substrate Al and other underlying elements.

The right frame of Figure 1 apparently demonstrates that the clean Al(111) was substantially oxidized, whereas the BPT-covered surface was protected against oxidation. We did not observe a well-ordered surface lattice by low energy electron diffraction (LEED) for the BPT monolayer before and after electron irradiation or O_2 exposure. Since the Al(111) surface unit cell is smaller than that of Au(111), and because of bulkiness of BPT, Al(111) cannot accommodate the admolecules in a commensurate fashion.

Figure 2 shows XP spectra of BPT-precovered Al(111) after O_2 exposure, recorded at 0 (a) and 70° (b) of the photoelectron exit angle with respect to the surface normal, recorded just by rotating the sample. With an inclined exit angle, electrons are emitted toward an inclined direction from the surface. These electrons pass through the sublayer for a longer distance than vertically emitted electrons. Then electrons from the deeper layers are reduced more than from the upper layer. For this reason, XPS scan with inclined incidence angle becomes more surface sensitive. Comparing (a) and (b), C 1s/O 1s peak ratio was larger at 70° (b), than the surface normal direction (a). This means that the BPT monolayer exists as the outermost layer, and the oxide layer exists between BPT and Al. A schematic diagram is shown in Figure 2. We can estimate the thickness of the Al_2O_3 by the O 1s signal normalized by the corresponding Al 2s signal

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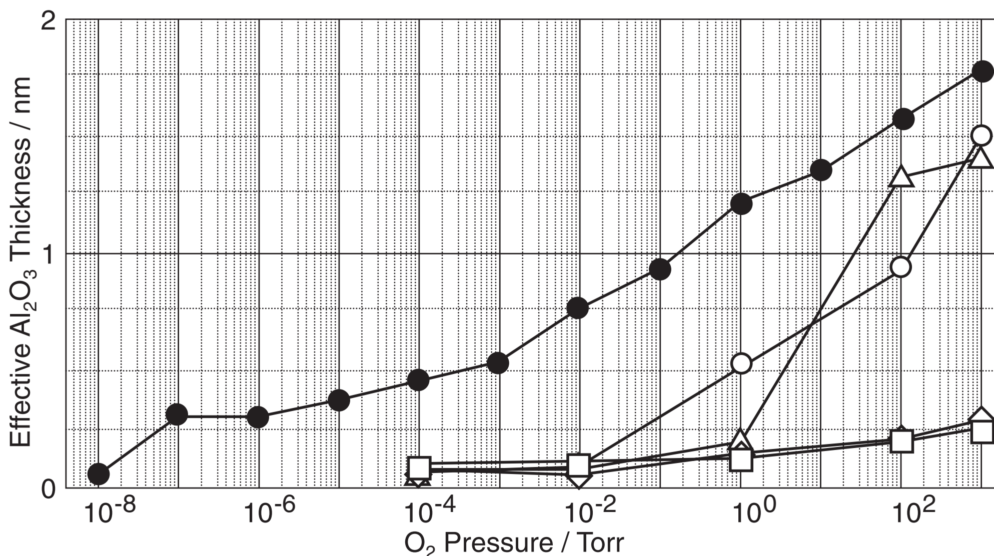

Figure 3. Effective Al_2O_3 thickness at each O_2 exposure. Filled circle: clean Al(111), open circle: BPT monolayer on Al(111) without electron bombardment, open triangle: BPT monolayer after electron bombardment at 100 eV, 5.5 mC cm^{-2}, open rhombus: BPT/Al(111) and 15 mC cm^{-2} electron irradiation, and open square: BPT/Al(111) and 40 mC cm^{-2} electron irradiation. BPT was dosed to clean Al substrate by thermal deposition for 5 min (BPT source temperature: 60 °C, dose pressure: $\approx 10^{-7}$ Torr. The exposure time for O_2 was fixed at 100 s for each of the O_2 pressures.

of the surface-normal photoemission, with or without the organic monolayer.

Figure 3 shows the effective Al_2O_3 layer thickness at each O_2 pressure for clean Al(111), intact BPT monolayer on Al(111), and BPT monolayer on Al(111) after electron beam bombardment. The O_2 exposure time was fixed at 100 s. At each O_2 pressure, the oxide layer thickness was practically constant for longer exposures on clean Al(111), and we consider the equilibrium at room temperature was reached for each O_2 pressure. The resistance of electron-bombarded BPT/Al(111) against oxidation was examined with several electron doses. The BPT monolayer without electron bombardment exhibited a certain resistance for oxidation below 10 Torr, but the oxide layer at 1000 Torr was as thick as on clean Al(111).

Electron beam irradiation at 100 eV of the incident energy dramatically improved the resistivity of BPT/Al(111) against O_2. Electron irradiation at 5.5 mC cm^{-2} had a marginal effect for protection at 1000 Torr. The Al_2O_3 layer thickness drastically decreased with electron irradiation at 15 and 40 mC cm^{-2}. This suggests that the electron irradiation induced formation of bridging bonds between individual BPT admolecules. According to Geyer et al.'s experiments on Au(111),[11] 10 mC cm^{-2} was enough to form a crosslinked BPT monolayer. Electron irradiation of 15 or 40 mC cm^{-2} on Al(111) seems to promote crosslinking within the monolayer to reduce the permeability of gas molecules through itself, forming a robust organic antioxidation monolayer. The effective oxide layer thickness after O_2 exposure at 1000 Torr for 100 s was 0.25 nm, which corresponds to one Al_2O_3 monolayer thickness. This meets our initial aim.

In conclusion, a significant retardation of oxidation of clean Al(111) was achieved in O_2 gas at atmospheric pressure at room temperature with a BPT monolayer crosslinked by electron beam irradiation. Formation of bridging bonds among individual admolecules is a promising idea in fabricating ultrathin layers with functions favorable in the development of nanotechnology. For Al surface passivation, we can further search for suitable molecules to evaporate on Al, out of a diversity of organic molecules, to create thinner, more robust organic monolayers.

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