

Aluminum oxide thin films prepared by chemical vapor deposition from aluminum 2-ethylhexanoate

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Aluminum oxide thin films were prepared by a low-temperature atmospheric-pressure chemical vapor deposition method. The raw material was aluminum 2-ethylhexanoate, which is nontoxic and easy to handle. At a reaction temperature above 480 °C, an amorphous film can be obtained on glass and silicon (100) substrates. The reaction temperature and the deposition rate are comparable to the corresponding values in the low-temperature chemical vapor depositions of Al₂O₃. In addition, the deposition can be carried out in air. Aluminum 2-ethylhexanoate appears to offer a viable alternative to alkylaluminum, aluminum β-diketonate, and alkoxide for low-temperature Al₂O₃ production.

Aluminum oxide thin films are widely used in a variety of applications including gate insulator and passivation layer on Si in semiconductors. High quality Al₂O₃ layers have traditionally been prepared by rf magnetron sputtering, reactive dc sputtering, or reactive vacuum evaporation. An alternative is to deposit Al₂O₃ by chemical vapor deposition (CVD) methods. Various CVD methods have been proposed, for example high-temperature (800–1100 °C) CVD of the AlCl₃-CO₂-H₂ system (CO₂ method),¹ metalorganic chemical vapor deposition of alkylaluminum, such as Al(CH₃)₃-O₂ system (350–500 °C), CVD of alkoxides, such as Al(*i*-OC₃H₇)₃ (aluminum-tri-isopropoxide, 420–600 °C),² and CVD of β-diketonate (420 °C).³ The main difficulty of the CO₂ method is the ready nucleation of Al₂O₃ in the gas phase. The Al₂O₃ crystal tends to form needles or other odd shapes. In addition, the CO₂ method often suffers from corrosion of the substrate and reactor vessels caused by the byproducts of hydrogen chloride in the high reaction temperature. For the low-temperature (350–600 °C) CVD methods, obtaining of the metalorganic source materials can be difficult. They are usually expensive or toxic and are not readily available.

In this letter, aluminum 2-ethylhexanoate [Al(C₇H₁₅COO)₃] is proposed as a precursor for obtaining Al₂O₃ films by the low-temperature atmospheric-pressure CVD method. Aluminum 2-ethylhexanoate is nontoxic. It is not expensive and readily available.

Aluminum 2-ethylhexanoate (Nihon Kagaku Sangyo Co., Ltd.) of reagent grade was used as the source material. It is easy to handle in solid form (powder) at room temperature. It was heated at a temperature of 280–300 °C and the generated gas was entrained by nitrogen carrier gas. The flow rate of the carrier gas was 0.3–0.6 ℓ/min.

Borosilicate glass plates, quartz glass plates, and silicon (100) single-crystal wafers were used as the substrates. The substrate was placed in the reactor heated by an external electric furnace. The reaction temperature ranged from 480 to 700 °C. The depositions were carried out at atmospheric pressure in air atmosphere and in an inert (nitrogen) atmosphere.

The composition of the film was measured by x-ray photoelectron spectroscopy (XPS). The infrared spectra were obtained by means of a Fourier transform infrared

spectrometer (Shimadzu FTIR-4300). The samples were prepared by depositing films about 800 nm thick on silicon single-crystal substrates. The crystallinity of the film was analyzed by the x-ray diffraction method with Cu Kα radiation. The optical transmittance of the film was obtained by means of a multipurpose recording spectrophotometer. A blank glass substrate was inserted into the reference beam path of the spectrophotometer.

The film could be grown in both inert (nitrogen) and air atmosphere. This fact means that oxygen in Al₂O₃ originates not from O₂ gas but from oxygen combined with the metal in the raw material. Deposition in an inert atmosphere is also effective to prevent burning of the source gas which occurs at the reaction temperature above 550 °C in air. Hence the data for the reaction temperature above 600 °C are based on the measurements in an inert (nitrogen) atmosphere.

The lower limit of the reaction temperature was 480 °C. X-ray photoelectron spectroscopy showed that the film was stoichiometric Al₂O₃. The films were transparent and showed no apparent peeling. The optical transmittance of the 110-nm-thick film was more than 98% in the wavelength range of 330–1000 nm.

Table I shows the atomic ratio of oxygen to aluminum at various substrate temperatures. The ratio is 1.67–1.85 for the inert atmosphere, and is about 1.66 for the air atmosphere. Thus, the oxides are near-stoichiometric Al₂O₃. A little excess of oxygen is attributable to a contamination from the gas phase in the measurements of XPS under the pressure of $\sim 3 \times 10^{-5}$ Pa.

Figure 1 shows infrared absorption spectra of films deposited at three different reaction temperatures. Absorption peaks at about 1100–500 cm⁻¹ represent the vibrations of Al₂O₃. Absorption peaks at about 3400–3200 cm⁻¹ and 1100–1050 cm⁻¹ represent O—H bond vibration and C—O bond vibration. Absorption peaks at about 2000–1250 and 700–400 cm⁻¹ represent vibrations of water. The x-ray diffraction pattern of the film showed that the films were amorphous.

Figure 2 shows the Arrhenius plot of deposition rates, which were obtained at a source temperature of 280 °C and a N₂ flow rate of 0.3 ℓ/min. The deposition rates are of the same order of magnitude as those reported previously us-

TABLE I. Atomic ratio of oxygen to aluminum at various reaction temperatures.

Deposition atmosphere	Reaction temperature	O/Al
Nitrogen	500	1.75
	525	1.67
	550	1.68
	600	1.85
	650	1.74
Air	500	1.66
	525	1.65
	550	1.67

ing the low-temperature CVD methods. The straight lines in this figure show that the activation energy is ~ 28.1 kJ/mol (0.291 eV/molecule).

In conclusion, aluminum oxide thin films were prepared by a low-temperature atmospheric pressure chemical vapor deposition method. The raw material was aluminum 2-ethylhexanoate, which is nontoxic and easy to handle. At

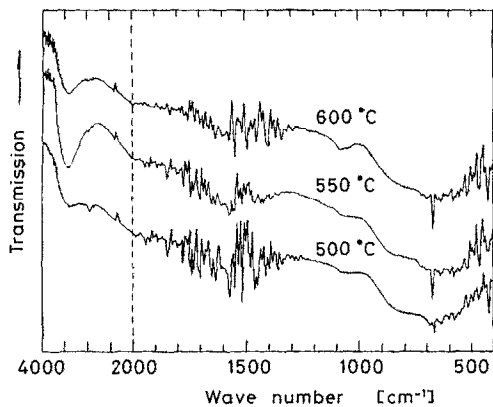


FIG. 1. IR transmission spectra of films deposited at various temperatures. (The wave number scale is linear with a scale change at 2000 cm^{-1} .)

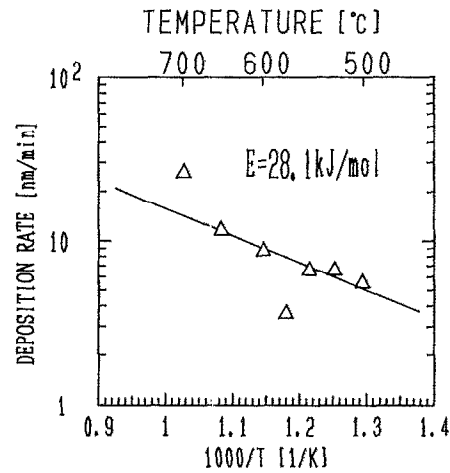


FIG. 2. Arrhenius plot of deposition rate.

a reaction temperature above 480 $^{\circ}\text{C}$, an amorphous film can be obtained on glass and silicon (100) substrates. The reaction temperature and the deposition rate are comparable to the corresponding values in the low-temperature chemical vapor depositions of Al_2O_3 . In addition, the deposition can be carried out in air. Aluminum 2-ethylhexanoate appears to offer a viable alternative to alkylaluminum, aluminum β -diketonate, and alkoxide for low-temperature Al_2O_3 production.

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