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Aluminum oxide thin films prepared by chemical vapor deposition from aluminum acetylacetonate

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Amorphous aluminum oxide thin films were prepared on glass and silicon (100) substrates by a low-temperature atmospheric-pressure chemical vapor deposition method. The raw material was aluminum acetylacetonate, which is nontoxic and easy to handle. The substrate temperature could be lowered to 250 °C by the thermal decomposition of aluminum acetylacetonate in air.

Among various chemical vapor deposition (CVD) methods for preparing aluminum oxide (Al_2O_3) thin film, metalorganic chemical vapor deposition (MOCVD) of alkylaluminum, such as the Al $(CH_3)_3 - O_2$ system, gives the lowest deposition temperature (350–500 °C). However, obtaining the metalorganic source materials can be difficult. They are usually expensive or toxic and are not readily available. Alternatives to the metalorganic source materials are $Al(i-OC_3H_7)_3$ (aluminum-tri-isopropoxide, 420–600 °C),[1] aluminum acetylacetonate (420–450 °C),[2–4] and aluminum 2-ethylhexanoate (500–600 °C).[5]

Korzo *et al.*[2] prepared amorphous Al_2O_3 film by vacuum pyrolysis of aluminum acetylacetonate on silicon substrate which was heated at a temperature above 450 °C. They reported that the temperature at which the film begins to form increased with increasing resistivity of the silicon. Ajaya *et al.*[3,4] prepared amorphous Al_2O_3 film by atmospheric-pressure pyrolysis of aluminum acetylacetonate on glass substrate which was heated at 420 °C. Aluminum acetylacetonate powder as the source material was carried by argon carrier gas into a working chamber.

This letter will show that the substrate temperature in the CVD of Al_2O_3 film can be lowered to 250 °C by the thermal decomposition of aluminum acetylacetonate in air.

Aluminum acetylacetonate [$(Al(C_5H_7O_2)_3$ Nihon Kagaku Sangyo Co., Ltd.] of reagent grade was used as the source material. It is nontoxic and easy to handle in solid form (powder) at room temperature. It was heated at a temperature of 150 °C and the generated gas was entrained by nitrogen carrier gas. The flow rate of the carrier gas was 0.3–1.0 ℓ/min.

Borosilicate glass plates, quartz glass plates, and silicon (100) single-crystal wafers were used as the substrates. The substrate was placed on a temperature-controlled electric heater. The substrate temperature ranged from 250 to 600 °C. The depositions were carried out at atmospheric pressure in air atmosphere.

The composition of the film was measured by x-ray photoelectron spectroscopy. The infrared spectra were obtained by means of a Fourier transform infrared spectrometer (Shimadzu FTIR-4300). The samples were prepared by depositing films on silicon single-crystal substrates. The crystallinity of the film was analyzed by x-ray diffraction with Cu $K\alpha$ radiation. The optical transmittance of the film was obtained by means of a multipurpose recording spectrophotometer with a blank glass substrate inserted into the reference beam path of the spectrophotometer.

The films were transparent and showed no apparent peeling. The lower limit of the reaction temperature was 250 °C, which is very low compared to those reported by Korzo *et al.*[2] (450 °C) and Ajaya *et al.*[3,4] (420 °C). They prepared films in inert atmosphere, whereas in this study the film was grown in air atmosphere. The x-ray photoelectron spectroscopy showed that the oxides were near-stoichiometric Al_2O_3. For the film obtained in an inert atmosphere, however, a carbon contamination and a little excess of oxygen (O/Al = 1.75–1.85) were observed in preliminary experiments. The carbon contamination and an excess of oxygen were reported also by Ajaya *et al.*[3,4] for deposition in an inert atmosphere.

Figure 1 shows the Arrhenius plot of deposition rates, which were obtained at a source temperature of 150 °C and a N_2 flow rate of 0.3 ℓ/min. The straight lines in this figure show that the activation energy is ca. 28.0 kJ/mol (0.29 eV/molecule) which is comparable to that of CVD of Al_2O_3 from 2-ethylhexanoate.[5]

Figure 2 shows infrared absorption spectra of films deposited at four different reaction temperatures. The spectra are very characteristic of Al_2O_3 films; i.e., broad absorption bands at about 1100–500 cm^{-1} represent the vi-

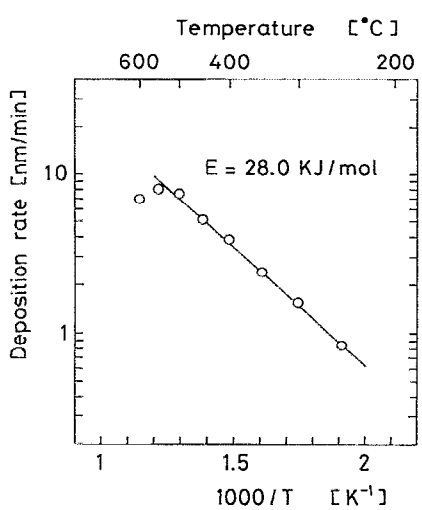

FIG. 1. Arrhenius plot of deposition rate.

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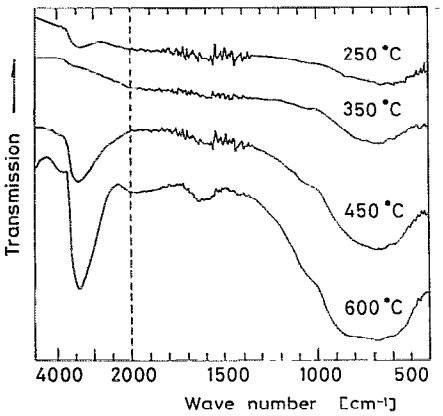

FIG. 2. IR transmission spectra of 220, 180, 350, and 970-nm thick films deposited at substrate temperatures of 250, 350, 450, and 600 °C. (The wave number scale is linear with a scale change at 2000 cm^{-1}.)

brations of Al_2O_3. Absorption peaks at about 2000–1250 and 700–400 cm^{-1} represent vibrations of water in gas phase. Absorption peaks at about 3400–3200 cm^{-1} represent O—H bond vibration. The O—H bond is inferred to belong to the water adsorbed to the film surface, because the surface of Al_2O_3 becomes active at higher substrate temperatures (>450 °C). Absorption peaks at about 1100–1050 cm^{-1} represent Si—O bond vibration. The Si—O bond is attributable to a thermal oxidation of the surface of the Si substrate. The x-ray diffraction pattern of the film showed that the films were amorphous.

Figure 3 shows the optical transmittance for the 970-nm thick film deposited on the quartz glass substrate at 600 °C. The optical transmittance was more than 95% in the wavelength range of 400–2600 nm. The refractive index obtained from the curve measured with brank reference was 1.56.

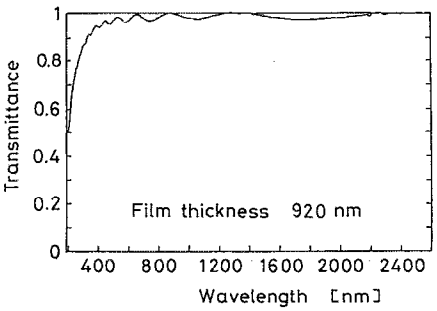

FIG. 3. Optical transmittance of a 970-nm thick film deposited on quartz glass substrate at 600 °C.

In conclusion, an amorphous aluminum oxide thin film was prepared on glass and silicon (100) substrates by a low-temperature atmospheric-pressure chemical vapor deposition method. The raw material was aluminum acetylacetonate, which is nontoxic and easy to handle. The substrate temperature could be lowered to 250 °C by the thermal decomposition of aluminum acetylacetonate in air.

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