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LETTER TO THE EDITOR

Structural characteristics of Al_2O_3 thin films prepared by spray pyrolysis

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Abstract

The crystalline and structural characteristics of aluminium oxide (Al_2O_3) thin films deposited by ultrasonic spray pyrolysis have been analysed using conventional and high resolution transmission electron microscopy. The aluminium oxide films were deposited on silicon (100) wafers, using a solution of aluminium acetylacetonate in dimethylformamide. The films were deposited with and without the addition of water mist generated in parallel to the spraying solution. The substrate temperatures during deposition of the films were in the range of 500–650 °C. The results indicate that the thin films deposited without water mist have an amorphous structure, while those films deposited with the addition of water mist show a two-face nature, formed by small crystallites embedded in an amorphous matrix. The crystalline phase has been determined, through the indexing of the electron diffraction patterns. It is found that it corresponds to $5Al_2O_3 \cdot H_2O$ in a Tohdite hexagonal structure with unit cell lattice constants $a = 5.575$ Å and $c = 8.76$ Å.

Aluminium oxide thin films have generated increasing interest due to their excellent properties as an insulator with a high dielectric constant. Aluminium oxide also has a high refractive index, excellent chemical stability and high radiation resistance, among other properties [1–3]. The potential for applications of these films range from microelectronics and optoelectronic devices, as well as protective coatings on different substrates. Most of the work reported on alumina films with crystalline or polycrystalline characteristics involve deposition temperatures higher than 700 °C [4–6]. It is uncommon to get any degree of crystallinity in alumina thin films deposited or annealed at temperatures below 700 °C. Recently, the optical and electrical characteristics of alumina thin films deposited at temperatures between 450 and 650 °C by spray pyrolysis were reported [7, 8]. In these papers the films were deposited using aluminium

acetylacetonate ($Al(acac)_3$) dissolved in *N*, *N*-dimethylformamide (*N*, *N*-DMF). However, no formal work was carried out concerning the crystallinity of these films as a function of the deposition parameters. In this letter we report studies on the crystalline and structural characteristics of these types of alumina films, deposited on silicon substrates, as a function of substrate temperature, and the addition of water mist during deposition. The characterization was made by conventional and high resolution transmission electron microscopy.

The spray pyrolysis technique has been described in detail previously [9]. This technique has been used to deposit materials in thin film and fine powders. It consists of an ultrasonic generator operated at 0.8 MHz for mist generation from a solution of a proper organic or inorganic salt in an appropriate solvent. The mist is transported by a carrier gas to the substrate surface, which is heated to achieve a pyrolytic chemical reaction after producing evaporation of the solvent and leaving a solid film on the substrate. The substrate temperature during deposition was in the range from 500 to 650 °C. The carrier gas used was air at a flow rate of 8 l min^{-1}. A solution of 0.36 mol of $Al(acac)_3$ in *N*, *N*-DMF was used. The substrate used was an n-type silicon (100) wafer cut into 1 cm × 1 cm pieces, the thickness of the films measured by ellipsometry was in the range of 900–1100 Å and the deposition rate was of the order 510 Å min^{-1}. The silicon substrate was cleaned by a standard RCA procedure before the deposition process [10]. Transmission electron microscopy (TEM) characterization was carried out with a JEOL 1200 EM and a JEOL 4000 EX transmission electron microscopes operated at 100 and 400 kV, respectively. The preparation of the samples for TEM studies did not include an ion milling step in order to rule out any crystallite formation produced by this process that could confuse the results observed by TEM. This preparation procedure was similar to that reported in the literature [11, 12] and is described as follows. The samples were first cut into 2 mm × 2 mm squares. These pieces were glued with molten wax onto a glass support. The silicon substrate was ground until it reached 300 μm thick using a 600 grid sandpaper. A further thinning to 100 μm was achieved with the use of a tripod device (South Bay Technology model 590) and 9, 5 and 3 μm coarse silicon carbide sandpaper. Subsequently, a dimple grinder (Gatan model 658) was used to form a semi-spherical cavity, leaving approximately 40 μm in thickness of sample material (from the substrate to the alumina film). The remaining substrate layer was removed by chemical etching with an acid solution (5 parts of nitric acid, 5 parts of acetic acid and 3 parts of hydrofluoric acid) [13]. The etching process was continuously monitored with an optical microscope in reflection mode and, in the last stage, in transmission mode. By this process, wide zones were obtained suitable for TEM analysis.

The aluminium oxide films were transparent in the visible range, with a refractive index of 1.66 measured by ellipsometry at 630 nm (1.59 was obtained when no water mist was added) and surface root-mean-square (rms) roughness less than 20 Å. The chemical composition, as determined by wavelength dispersive spectroscopy for the films deposited with water mist, was close to the Al_2O_3 stoichiometry. This was not the case for films deposited without water, in which the ratio of oxygen to aluminium was higher. Figure 1 shows a micrograph and the corresponding diffraction pattern for an alumina film deposited at a substrate temperature of 650 °C without water mist added. The microstructure and the diffused diffraction pattern in a cloud form are characteristic of an amorphous material. This behaviour was observed in all films prepared without water mist added.

A micrograph and corresponding diffraction pattern for alumina films deposited at a substrate temperature of 550 °C with water mist added is shown in figure 2. In this particular transmission image it is possible to observe tiny crystalline zones of ∼20 nm, immersed in an amorphous matrix. These types of crystalline zones appear in all films deposited with water mist. However, the crystallite average size was strongly dependent on the deposition temperature and it was in the range of 10–400 nm. The largest crystallites were obtained when

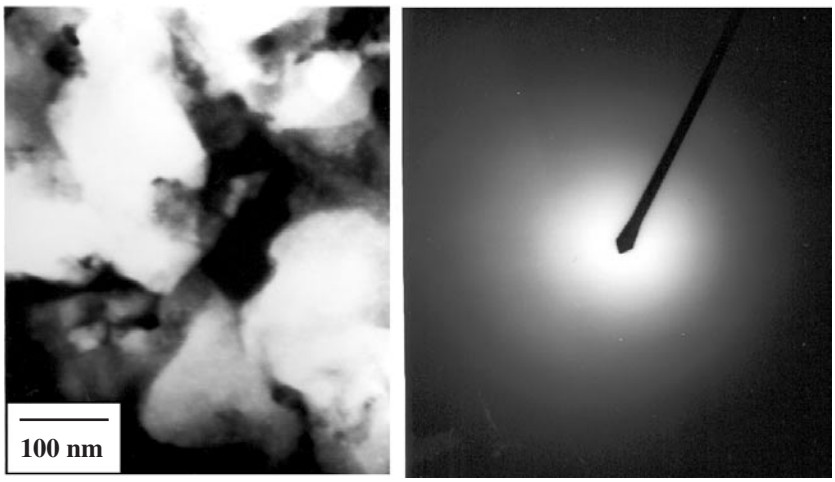

Figure 1. Transmission electron micrograph and diffraction pattern for alumina film deposited at a substrate temperature of 650 °C without water mist added.

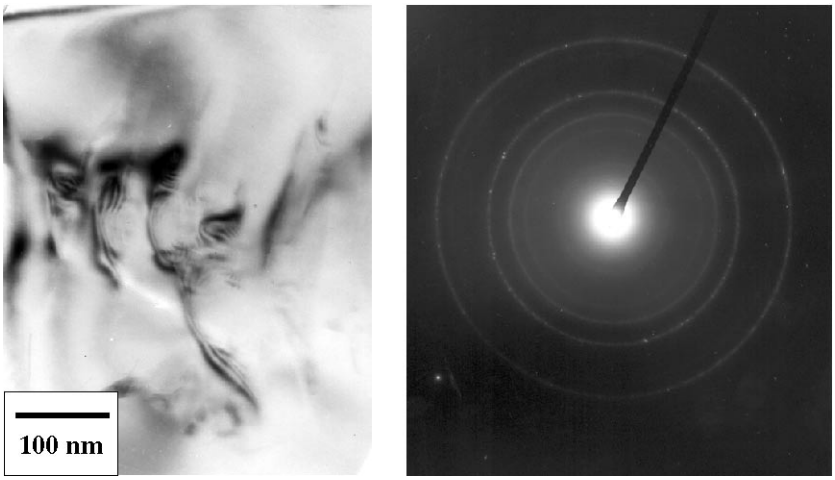

Figure 2. TEM image and diffraction pattern for alumina film deposited at a substrate temperature of 550 °C with water mist added.

the films were deposited with the highest deposition temperature. In particular, the diffraction pattern for a thin film deposited at 650 °C (not shown in the figure) presented rings formed by discrete points, giving an idea of the relatively large size of the crystalline zones. The interplanar distances (d_{hkl}) of the crystalline phase were calculated by means of the following expression:

$$d_{hkl} = \lambda L/R$$

where λ is the electron wavelength at 100 kV, L is the camera length of the TEM and R is the radius of the rings from the electron diffraction pattern. Table 1 shows the calculated interplanar distances and the values given in the ASTM diffraction card[5] no. 22-1119 for the

[5] ASTM Diffraction Card No 22-1119, ASTM Philadelphia, PA.

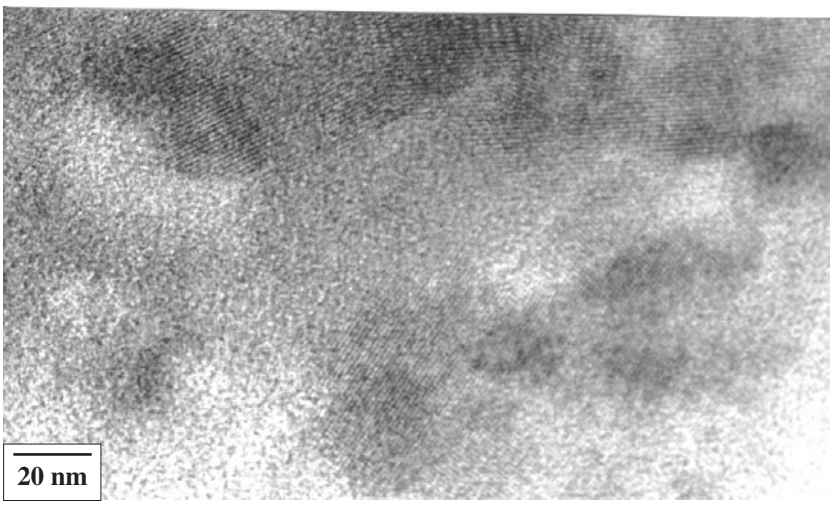

Figure 3. HRTEM image of alumina film deposited at a substrate temperature of 500 °C with water mist added.

Table 1. Measured interplanar distances and the values reported in the ASTM diffraction card for the crystalline structure of aluminium oxide hydrate.

hkl	Intensity	d_{hkl} reported	d_{hkl} measured
100	10	4.85	4.85
102	60	3.25	3.20
103	55	2.500	2.573
202	100	2.115	2.123
204	25	1.623	1.628
302	20	1.511	1.503
312	6	1.281	1.283
313	20	1.217	1.223
403	10	1.114	1.112
008	4	1.096	1.056

crystalline structure of aluminium oxide hydrate with a chemical composition of $5Al_2O_3 \cdot H_2O$ (Tohdite), having a hexagonal unit cell, with lattice constants $a = 5.575$ Å, $c = 8.76$ Å and spatial group $P6_3mc$. This structure shows atomic layers of oxygen and aluminium alternately in sheets perpendicular to the c axis formed by the close stacking of four oxygen layers, with four oxygen atoms each. Aluminium atoms are distributed over four aluminium layers, two containing two aluminium atoms each, while the other two layers contain three aluminium atoms each [14].

Figure 3 shows a typical HRTEM image of the alumina films deposited with water mist added. In this case the film was deposited at a substrate temperature of 500 °C. Even at this low deposition temperature, a set of crystalline zones can be observed, where the atomic positions show a periodic order, immersed in an amorphous matrix. The size of the crystalline zones is of the order of a few nanometres.

The structural characteristics of alumina films deposited with and without water mist have been determined. All alumina films without water mist are amorphous and of a porous nature, as indicated by the low values of the refractive index and the high ratio of oxygen

to aluminium observed. The addition of water mist during the deposition process results in a denser material with crystalline inclusions embedded in an amorphous matrix, even though the temperatures involved in the film preparation process were relatively low (as low as 500 °C). The crystalline phase was identified as aluminium oxide hydrate, composition ($5Al_2O_3 \cdot H_2O$), having a Tohdite crystalline structure with a hexagonal unit cell. The lattice parameters of this cell are $a = 5.575$ Å and $c = 8.76$ Å. The sample preparation method used for the TEM studies was carefully chosen to obtain large zones of the aluminium oxide thin films deposited on the silicon substrates without perturbing the original crystallographic characteristics. The determination of the crystalline structure present in these films throws a new light on their structural characteristics and offers the possibility of finding meaningful correlations with the dielectric and optical characteristics previously determined for this material.

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