Crystalline alumina films prepared by nebulized spray pyrolysis

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MS received 20 January 1998

Abstract. Crystalline alumina films have been successfully deposited on Si(100) and amorphous silica substrates by the nebulized spray pyrolysis technique. The surface morphology of the films has been studied by various microscopic techniques. The films exhibit satisfactory microhardness and frequency independent capacitance.

Keywords. Crystalline alumina; nebulized spray pyrolysis; SEM; AFM; microhardness.

1. Introduction

Alumina films are of considerable interest because of their potential applications for wear resistant coatings and optical coatings. Amorphous alumina thin films have been prepared on glass as well as Si(100) by chemical vapour deposition from aluminum acetylacetonate (Maruyama and Arai 1992). Metal organic chemical vapour deposition by using precursors such as aluminium tris-dipivaloylmethanate (Kim *et al* 1993; Ciliberto *et al* 1995), also yields amorphous films on silicon and glass substrates. Single crystalline gamma alumina films have been grown on silicon substrates by metalorganic molecular beam epitaxy using aluminum alkoxide (Iizuka *et al* 1992), while heteroepitaxial gamma alumina films are obtained with trimethyl aluminum (Ishida *et al* 1988). CVD of alumina on silicon substrates by using aluminum trichloride gives films of κ -Al₂O₃ which transforms to α -Al₂O₃ on being heated to higher temperatures of 1200–1350 K (Fredriksson and Carlsson 1993). By ion-beam-induced chemical vapour deposition, trimethyl aluminum gives crystalline α -Al₂O₃ films at 1273 K (Caballero *et al* 1996). We were interested in exploring whether crystalline alumina films could be obtained by employing the simple technique of nebulized spray pyrolysis.

2. Experimental

The technique of nebulized spray pyrolysis for depositing thin films by employing a home built apparatus has been described elsewhere (Raju *et al* 1995; Aiyer *et al* 1997). The apparatus consists of two zones: (i) the atomization chamber and (ii) the pyrolysis reactor. The source liquid is kept in the atomization chamber which is attached

with a PZT transducer at the bottom which oscillates at a frequency of 1.72 MHz. Aluminium acetylacetonate in a methanol solvent (0.05 M) was employed for all the depositions. When a high-frequency ultrasonic beam is directed at the liquid/gas interface, a geyser forms at the surface of the liquid and the height of the geyser is proportional to the acoustic intensity and the physical properties of the liquid (vapour pressure, viscosity and surface tension). When the amplitude of the acoustic vibrations exceeds a certain threshold value, atomization of the liquid occurs. Above this threshold, a continuous and regular mist is generated. The mist is carried by the carrier gas (dry air in the present case) to the pyrolysis reactor zone onto a pre-heated substrate leading to the mist decomposition and the film formation on the substrate. We have used single crystal Si(100) as well as polished amorphous silica as the substrates in the present study.

Alumina films were characterized by X-ray diffraction, scanning electron microscopy (SEM), electron diffraction, atomic force microscopy (AFM), capacitance measurements and dynamic hardness measurements. A Seifert 3000 X-ray powder diffractometer with Cu-K α radiation (grazing incident geometry) was employed for X-ray diffraction studies. A Leica S440i SEM was used for microstructure studies. Nanoscope II fitted with AFM was used to study the surfaces of the films at high-resolution. Capacitance and $\tan \delta$ were measured between 100 Hz and 10 MHz with HP4296 automatic impedance analyser. Shimadzu dynamic ultra microhardness instrument (DUH 200) was employed to study microhardness of the films. The method of measuring hardness using nano indentation involves making small indentation using Berkovich indenter, while continuously recording the indentation load, $P(gf)$ and displacement, $h(\mu m)$ during one complete cycle of loading and unloading. The $DH = \alpha P/h^2$, where α is a constant

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in accordance with the shape of the indenter (indentation factor).

3. Results and discussion

We have examined morphology of the Al_2O_3 films deposited at 673 K on Si(100) substrates by both SEM and AFM. We show the SEM image in figure 1a and a surface plot from AFM in figure 2a. The surface of the film is quite smooth, consisting of very small well-connected grains of less than 100 nm size, as seen from the AFM surface plot. The surface roughness measured from the AFM surface plot is around 5.75 nm. The thickness of Al_2O_3 film on the Si(100) substrate as obtained from the cross sectional SEM image shown in figure 1b is around 375 nm.

The SEM image of an alumina film deposited on amorphous silica at 673 K is shown in figure 3a. The high-resolution AFM surface plot, given in figure 2b shows the presence of smaller grains (<50 nm). These grains are significantly smaller than those in case of Al_2O_3 films deposited on Si(100) substrates. The surface roughness measured from the AFM surface plot is around 7.13 nm. The thickness of alumina film on amorphous

Figure 1. a. Scanning electron micrograph of an Al_2O_3 film deposited on Si(100), b. cross sectional SEM micrograph of the Al_2O_3 film deposited on Si(100) (film thickness is 350 nm) and c. electron diffraction pattern from the peeled portion of the Al_2O_3 film deposited at 673 K on Si(100) and annealed at 973 K for 12 h.

Figure 2. AFM surface plot of an Al_2O_3 film deposited on a. Si(100) and b. amorphous silica.

silica substrate is around 753 nm as delineated from the cross sectional SEM image in figure 3b.

The as-grown alumina films on both Si(100) and amorphous silica substrates were amorphous. After heating the film deposited on silica at 973 K for 12 h, we obtained the X-ray diffraction pattern shown in figure 4. The pattern corresponding to the κ -phase. We did not see any reflections in the X-ray diffraction pattern of the alumina films deposited on Si(100) substrates at 673 K since the films were very thin. The electron diffraction pattern (figure 1c) of a peeled portion of the annealed alumina film however revealed alumina was in the κ -phase.

In figure 5 we show the variation of dielectric properties with frequency (100 Hz–5 MHz) of Al_2O_3 films on Si(100) as well as SiO_2 substrates. There is only little variation in the capacitance with frequency, whereas the $\tan \delta$ increase at higher frequency in the case of the film on Si and decreases with frequency in the film on SiO_2 .

Figure 3. a. Scanning electron micrograph of an Al_2O_3 film deposited on amorphous silica and b. cross-sectional SEM micrograph of the Al_2O_3 film deposited on amorphous silica (film thickness is 650 nm).

We have measured the dynamic microhardness of the alumina films deposited on Si(100) and amorphous silica substrate with a 50 mg load applied over 10 sec. We obtained a hardness value as high as 2010 in dynamic hardness unit (DHU) and an average of 1330 DHU from 10 measurements on different areas of the alumina film deposited on Si(100) substrate. However, the maximum hardness value of the film deposited on amorphous silica substrate was 2610 DHU with an average value of 1655 DHU from 10 measurements.

4. Conclusions

We have deposited alumina films on Si(100) as well as

Figure 4. X-ray diffraction pattern (θ - θ scan) of an Al_2O_3 film deposited at 673 K on amorphous silica substrate and annealed at 973 K for 12 h.

Figure 5. Capacitance and loss factor ($\tan \delta$) vs frequency of Al_2O_3 film deposited on Si(100) as well as SiO_2 substrates.

SiO₂ substrates by nebulized spray pyrolysis using aluminium acetylacetonate as the precursor. The as-deposited films are amorphous and crystallize to κ -alumina after annealing the films at 973 K for 12 h. Dielectric measurements show variation of the capacitance with frequency in the films to be small, suggesting that they may be useful for high frequency capacitor applications. The average dynamic microhardness of the films deposited on Si(100) and SiO₂ is substantial.

Acknowledgement

The authors thank Prof. C N R Rao for suggesting the problem, useful discussions and advice.

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