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Studies on optical and dielectric properties of Al_2O_3 thin films prepared by electron beam evaporation and spray pyrolysis method

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Abstract

Al_2O_3 thin films find a number of applications in optoelectronics, sensors and tribology. In this paper, we report the preparation and characterization of alumina films prepared by both electron beam evaporation and spray pyrolysis method. The electrical properties of alumina films were determined by measuring (C–V) and (I–V) characteristics in a metal oxide semiconductor (MOS) structure. A relative dielectric constant (ε_r) of 9.6 for spray pyrolysed films and 8.3 for evaporated films was obtained. The breakdown electric field was found to be around 5 and 1 MV/cm, respectively for spray pyrolysed and evaporated films. The refractive index of alumina films by evaporation was found to be 1.71 and 1.61 at 275 and 500 nm, respectively. The optical band gap of spray pyrolysed films deposited at 300 °C was found to be in the range of 5.40–5.55 eV. Structural, elemental analysis and stoichiometry of the films was studied by scanning electron microscope (SEM), energy dispersive X-ray analysis (EDAX), Auger electron spectroscopy (AES) and Rutherford back scattering (RBS) spectra.

Keywords: Al_2O_3 films; Spray pyrolysis; Electron beam evaporation; Optical properties; Electrical properties; Structure; Humidity sensor

1. Introduction

Al_2O_3 coatings have become more popular for their high dielectric strength, exceptional stability, and durability against hostile environments and high transparency down to 250 nm. During the last few years Al_2O_3 coatings have been widely used for their practical applications, such as refractory coatings, antireflection coatings, anticorrosive coatings [1], microelectronic devices [2], capacitance humidity sensors [3] and also in heat sinks in IC's and passivation of metal surfaces [4]. These films have been prepared by various techniques such as CVD [5], MOVCD [6], spray pyrolysis [7], thermal evaporation [8], sputtering [9], etc. Films can be easily prepared by spray pyrolysis since it is very simple, low cost and does not require vacuum or exotic gas [10]. In this work, we report the preparation and characterization of Al_2O_3 films prepared by spray pyrolysis and electron beam evaporation on various substrates such as quartz, steel, glass and silicon wafer at different substrate temperatures ranging from 250 to 350 °C and with varied molar concentrations (0.1 and 0.2 M). Optical constants like refractive index (n), absorption coefficient (α) in the UV region, extinction coefficient (k) and optical band gap (E_g) have been evaluated. Aguilar-Fruits et al. [7] prepared alumina thin films by spray pyrolysis using aluminum acetylacetonate dissolved in a *N*,*N*-dimethylformamide and have studied mainly dielectric properties of the films. They have reported the electric breakdown field of about 5 MV/cm, which is a very good indication of alumina thin films being alternative gate dielectrics which can replace SiO_2 films. Guha et al. [11] prepared the alumina films by ultra high vacuum reactive atomic beam deposition and evaluated the microstructure of the films and concluded that the polycrystallinity does not compromise leakage currents. They also reported that the leakage current densities of Al_2O_3 thin films are five orders of magnitude lower than that observed for SiO_2 insulators of the same thickness. In the present work, we have made an attempt to study the optical and dielectric properties of Al_2O_3 thin films as a function of substrate temperature and annealing temperature.

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2. Experimental details

2.1. Spray pyrolysis

Spray pyrolysis is a simple and low cost method of depositing transparent oxide films over large area. In this method, the film formation takes place by the condensation of atoms or molecules onto a heated substrate. Thus, the substrate temperature, carrier gas flow and solution flow rate play an important role in forming the structure of the films ranging from amorphous to crystalline. Generally, slow reaction at lower temperatures (<250 °C) would yield foggy films due to insufficient time for the spreading of the droplets. At higher temperatures (250–500 °C) the evaporation and precipitate sublimation occurs in succession and the vapors diffuse towards the substrate, where they react chemically in heterogeneous gas–solid form to give the final film. At very high temperatures chemical reaction takes place before the vapor reaches the substrate and gives powdery coating. The spray set up used in this work was presented elsewhere [12]. In this method, a simple glass nozzle was fabricated to spray a very fine and small droplets, when the solution is driven by either air from the compressor or nitrogen from a cylinder. Al_2O_3 films were prepared by spraying the resultant solution of 0.1 and 0.2 M concentration of aluminum acetylacetonate dissolved in dimethyl formamide on heated substrates like glass, quartz and silicon. Films coated on quartz were used for optical studies and those on silicon were used for dielectric studies. The substrate temperature was kept between 250 and 350 °C. While coating the films on silicon substrate precaution has been taken to remove the native SiO_2 layer which affects the dielectric properties of any insulating films such as Al_2O_3. This is done by immersing the silicon wafers in HF solution for 30 min and finally cleaning them with distilled water and storing them in the desicator. The substrate was not kept in the heating chamber for a longer duration before spray deposition, to avoid the oxidation of silicon to SiO_2.

The typical process parameters used for Al_2O_3 films by spray deposition are given below:

Nozzle–substrate distance (cm)	30
Solution concentration (M)	0.1 and 0.2
Solution flow rate (ml/min)	6.0
Carrier gas	Compressed air
Gas pressure (Pa)	46.1×10^4
Substrate temperature (°C)	250–350

2.2. Electron beam evaporation

Electron beam evaporated Al_2O_3 films were deposited in a conventional evaporation system, pumped by rotary pump and diffusion pump combination. Al_2O_3 material supplied by M/S Balzers was directly evaporated by electron beam gun. The base pressure was 2×10^{-5} mbar and deposition pressure was about 2×10^{-4} mbar. The rate of deposition was kept at 4 A°/s and the substrate temperature was 65 °C. Film thickness and the rate of deposition were monitored by a crystal monitor.

2.3. Measurement of layer properties

Optical transmission measurements of all the films were taken in a double beam spectrophotometer (Hitachi 330 model) in the UV-Vis region. X-ray diffraction spectra (XRD) were obtained from an X-ray diffractometer. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX) were used for chemical analysis of the samples. Auger electron spectroscopy (AES) and Rutherford back scattering (RBS) were taken for typical films deposited by both the techniques on silicon substrates to study the depth profile and stoichiometry of the films.

The capacitance versus voltage (*C*–*V*), current versus voltage (*I*–*V*), and capacitance versus frequency (*C*–*f*) measurements were carried out using a 4274A HP Multi frequency LCR impedance meter which has a frequency range from 100 to 100 kHz. The dc bias was supplied by a Keithley 230 programmable voltage source. Current–voltage data were obtained by a Keithley 485 auto ranging Picoammeter. For this purpose the films were integrated in metal oxide semiconductor (MOS) structure [13].

3. Results and discussions

3.1. Optical properties

The optical transmittance spectra of spray pyrolysed Al_2O_3 films were recorded in the wavelength range 200–850 nm. Fig. 1 shows the spectral transmittance characteristics of Al_20_3 films deposited under different conditions such as substrate temperature and molar concentrations.

As the substrate temperature of spray pyrolysed films increased from 250 to 350 °C, the transmittance also increased from 78 to 86% at 400 nm. It was also observed that the transmittance decreased with the increase of molar concentration. The transmittance was about 78% for 0.2 M and 86% for 0.1 M concentration solution keeping the substrate temperature constant at 250 °C as shown in Fig. 1(a) and (b). The thickness of the films was estimated to be in the range 80–135 nm as measured using multiple beam interferometer. Al_2O_3 films deposited by electron beam evaporation (Fig. 1d) showed higher transmittance (about 90%) at all wavelengths compared to the films formed by spray pyrolysis. Further optimization of deposition conditions is necessary to improve the optical transmittance of the films in case of spray pyrolysis. Fig. 2 shows a plot of $[\alpha h\nu]^2$ versus $h\nu$, where α is the absorption coefficient and $h\nu$ is the energy in eV. The absorption coefficient (α) was calculated in the shorter wavelength region as described in the

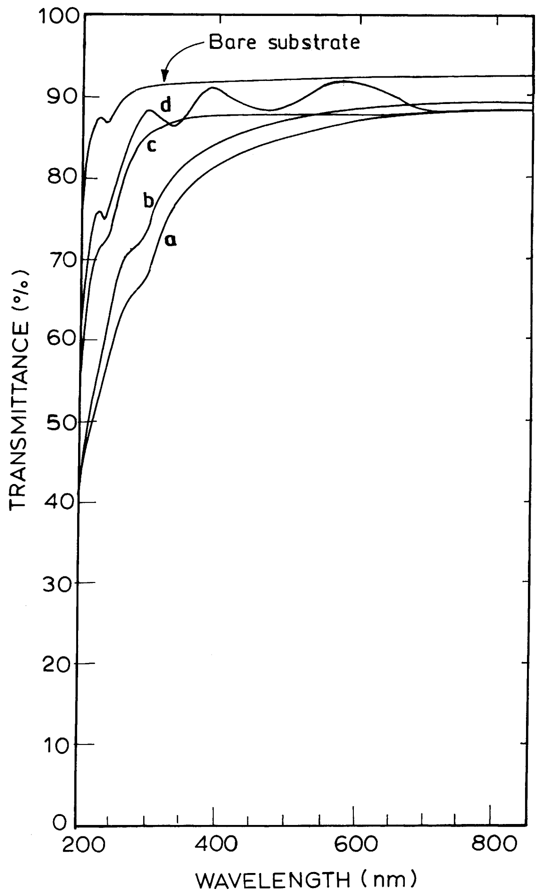

Fig. 1. Transmission spectra for Al_2O_3 films deposited by spray pyrolysis (a, b, and c) and electron beam evaporation method (d). (a) Film deposited at substrate temperature of 250 °C quartz (0.2 M); (b) film prepared at substrate temperature of 300 °C on quartz (0.2 M); (c) film prepared at 250 °C on quartz (0.1 M); (d) film prepared by electron beam evaporation method at ambient substrate temperature.

reference [14]. The absorption coefficient of various films prepared by spray pyrolysis method was found to be in the range (2.4–3.4) $\times$ 10^4 cm^{-1} at a wavelength of 300 nm. The corresponding extinction coefficient (k) was found to be in the range 0.0568 to 0.0807. Absorption coefficient and extinction coefficients of the evaporated films prepared at ambient temperature (65 °C) were found to be 1.16×10^3 cm^{-1} and 0.003, respectively. It was observed that the absorption coefficient of evaporated film was one order of magnitude lower than that of spray deposited films. The linear portion of the curve is extrapolated to meet energy axis at $\alpha = 0$ and the corresponding value of energy is taken as the optical band gap. This was found to be in the range 5.40–5.55 eV for spray deposited films and 5.75 eV for evaporated films. The value of refractive index estimated from the transmission spectra for spray deposited and evaporated films was found to be around 1.58 and 1.61 at 500 nm, respectively. These values are in good agreement with the values reported in literature [8,15]. Fig. 3 shows the variation of refractive index as a function of wavelength for an evaporated film. It was found that the refractive index decreases with increase

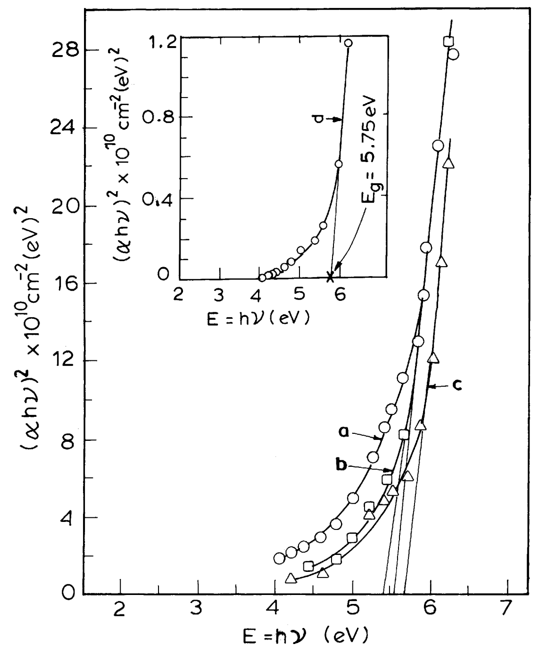

Fig. 2. $(\alpha h\nu)^2$ vs. $E = h\nu$ for Al_2O_3 films prepared by spray pyrolysis and evaporation. (a) Film thickness 115 nm (0.2 M); (b) film thickness 131.7 nm (0.2 M); (c) film thickness 82.4 nm (0.1 M); (d) for electron beam evaporated film.

in wavelength and becomes almost constant at higher wavelengths beyond 400 nm.

3.2. Structural properties

X-ray diffraction patterns (not shown here) were recorded for various films. It was found from the XRD data that the films deposited by both the methods were amorphous in nature as there were no significant peaks found except one broad peak, which is the characteristic peak of the glass substrate. Spray deposited films were annealed in air in the temperature range from 400 to 600 ° for 4 h. The films do not show any improvement in the crystallinity. However, transmission electron microscopy (TEM) showed improvement in the crystal nature for the evaporated films annealed in air at 800 °C for 12 h [8]. It was observed from the literature [16] that polycrystalline Al_2O_3 thin films have been grown

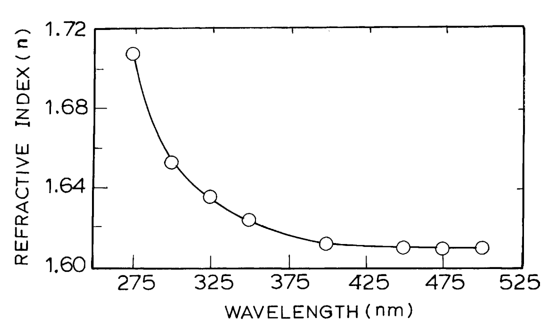

Fig. 3. Refractive index (n) vs. wavelength for electron beam evaporated film deposited at 65 °C.

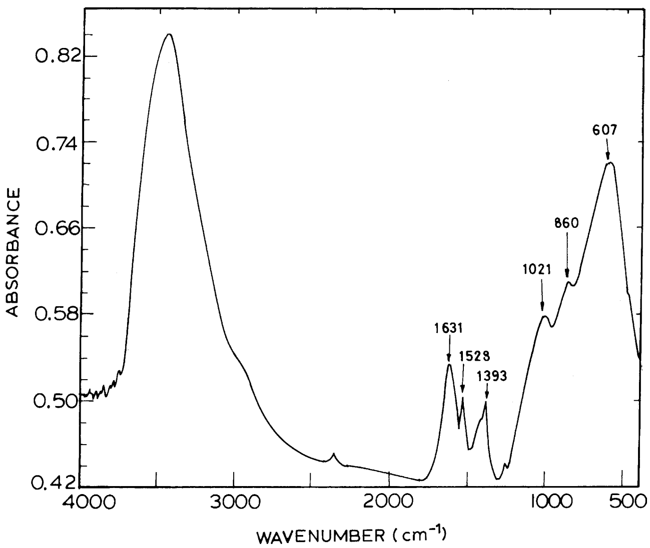

Fig. 4. FTIR spectrum of the spray deposited film on glass substrate at 250 °C.

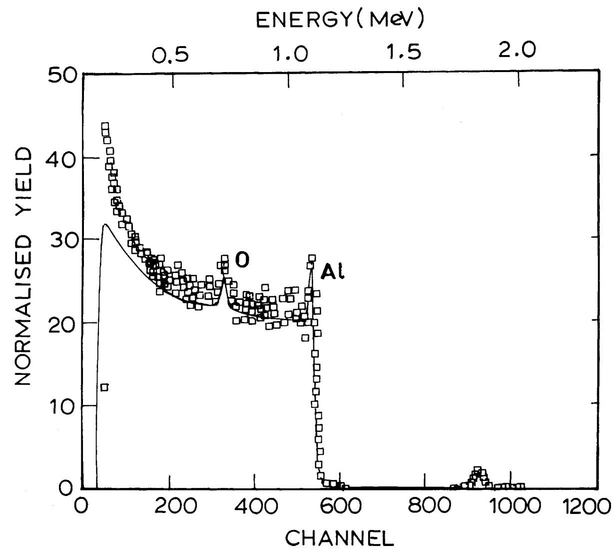

Fig. 6. Rutherford back scattering spectrum of an evaporated film prepared at 65 °C on silicon.

on silicon substrates by ionized beam deposition using an aluminum solid source in O_2 at 700 °C.

Fig. 4 shows the FTIR spectra of alumina thin film on silicon wafer in the range 500–4000 cm^{-1}. The general pattern of the spectra consists of bending vibrations of O–H and stretching vibrations of the Al–O. The absorption peak at 3500 cm^{-1} is assigned to the O–H stretching vibration. The bending vibration of O–H appears at 1532 cm^{-1} where as stretching vibration of terminal Al=O and Al–O were the common features that appear below 900 cm^{-1}, with two distinct maxima around 835 and 865 cm^{-1} are attributed to the film surface which will be passive at lower substrate temperatures (<400 °C). These results were in good agreement with the earlier literature [17].

Fig. 5 shows the Auger electron spectroscopy depth profile signals of a 110 nm thick spray deposited alumina film on Si substrate. It was found that the film consisted of oxygen and aluminum atoms. The atomic percentage, ratio of oxygen to aluminum (O_2/Al) is 1.5, which confirms the stoichiometric phase of Al_2O_3. The depth profile of the film shows that the diffusion of aluminum is slightly less than that of oxygen (almost 110 nm) which shows that oxygen is well diffused into the film.

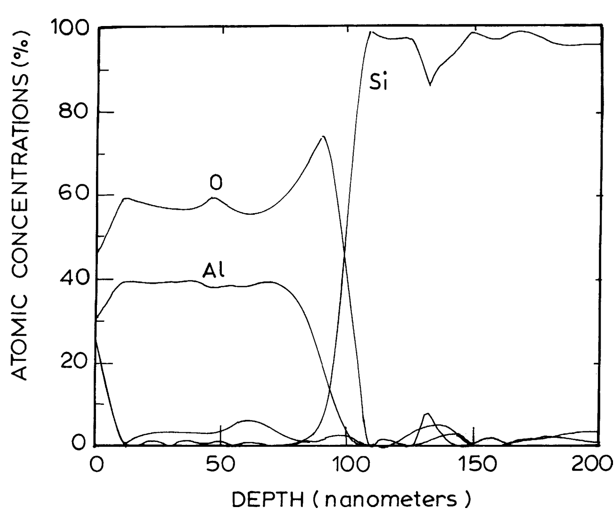

Fig. 5. Auger electron spectroscopy of the spray deposited film on silicon substrate at 350 °C.

Fig. 6 gives the RBS for an evaporated film of thickness 230 nm on a silicon substrate. It gives the normalized yield of oxygen and aluminum versus energy of the impinging electrons. A characteristic peak, which was found at 1.1 MeV for Al and 0.7 MeV for $O_{2,}$ confirms the near stoichiometric phase of Al_2O_3.

Scanning electron micrographs of Al_2O_3 thin films prepared by spray pyrolysis method were studied and it was found that the film deposited on glass at 250 °C shows the island like structure and it is not continuous. However, the film deposited at 350 °C on glass is uniform and continuous.

3.3. Electrical properties

To study the electrical properties of the alumina films, MOS structures were fabricated by thermally evaporating aluminum contacts with an area of (2.8–8.5) × 10^{-3} cm^2 on top of the insulating oxide film which is deposited on p-type silicon wafers (0.1 Ω cm resistivity and 0.25 mm thickness). These dot electrodes are called gates. A second metallic layer usually aluminum is evaporated thermally on the bottom of the silicon, called the back contact which provides the ohmic contact to the silicon substrate. Very thin gold wire and silver paste were used for making contacts. After metallization, the devices were kept for annealing at 200 °C to remove any water content and hence to reduce interface trap density [18].

Fig. 7 shows a plot of *C–V* characteristics taken in the frequency range of 10 Hz to 100 kHz and the inset gives

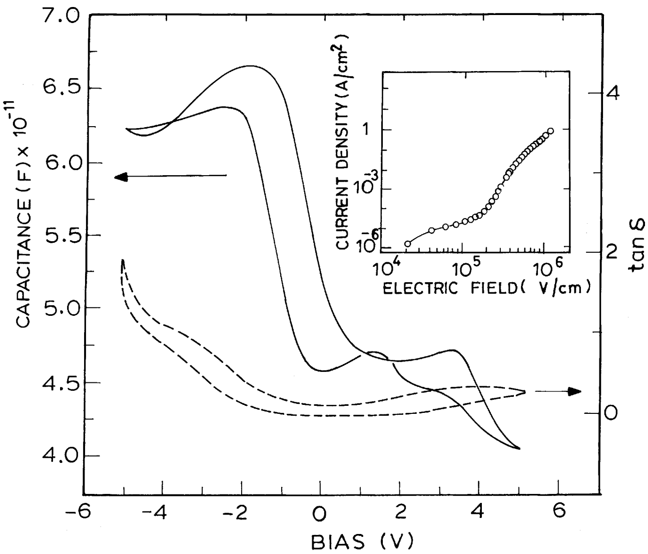

Fig. 7. Plot of *C–V* and current density vs. electric field for spray pyrolysed film of thickness 130 nm.

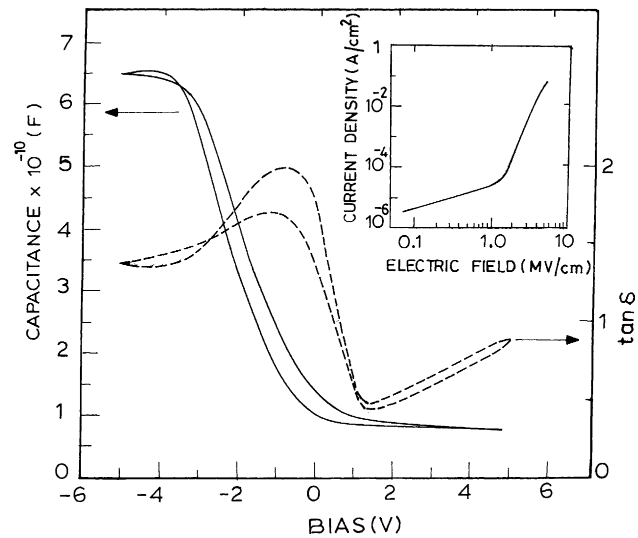

Fig. 8. Plot of *C–V* and the inset gives current density vs. electric field for evaporated film of thickness 250 nm.

(current density versus electric field) plot for a spray deposited film of thickness 130 nm on a silicon substrate at $T_s = 350\,°C$. The dielectric constant is calculated in the accumulation region and it was found to be around 9.6. The gate voltage is varied in steps of 0.5 V/s and the corresponding leakage current was noted using picoammeter. The process is continued for a period of several minutes until a sharp increase in current from microamp to the milliamp range was observed [19]. The resultant average breakdown field was found to be around 5 MV/cm, which are almost in good agreement with the values reported [13,14]. The corresponding current density was around 10^{-5} A/cm^2 at a bias voltage of 5 V and the resistivity of this film was found to be around $3 \times 10^{10}\,\Omega$ cm, which was calculated using the formula $\rho = (V/I)(A/t)$, where I is the current at a gate voltage of V volts, A is the area of the gate electrode in cm^2 and t is the thickness of the films in cm. This was for a typical film of thickness 130 nm deposited at a substrate temperature of 350 °C. Even though the breakdown electric field is comparable with the reported values [15,20], the leakage current in this film was found to be slightly more which may be due to the presence of voids and porosity in the film so that the film may have permanent charge trapping which reduces the dielectric property of the film. Augilar-Fruits et al. [15] have reported that the spray deposited films at $T_s = 450–650\,°C$ showed a break down field of 5 MV/cm and a current density of 10^{-9} A/cm^2 at electric fields below 2 MV/cm, where as in our case the current density was around 10^{-5} A/cm^2 at electrical fields below 2 MV/cm. Resistivity of the same film was around $10^{10}\,\Omega$ cm which is low for any perfect insulating film, and it leads to more leakage current. It was also observed that the hysteresis present in our films confirms the permanent charge trapping at the silicon-oxide interface due to the porosity of the film, which makes the film less denser. One more remarkable point was that higher substrate temperature favours the dielectric strength of the films as observed by Ishida et al. [20] where they have prepared the epitaxial alumina films on Si by low pressure at a substrate temperature of 1000 °C and reported a very low leakage current of 0.7×10^{-11} A/cm^2 at a gate voltage of 3 V without any hysteresis. However, Solanki et al. [21] have deposited alumina films by laser induced photo-deposition technique at a substrate temperature ranging from 150 to 450 °C and reported a resistivity of 3×10^{10} to $5 \times 10^{11}\,\Omega$ cm, at 1 MV/cm which is almost same as our reported value of $3.7 \times 10^{10}\,\Omega$ cm for a film deposited at 350 °C. Ishida et al. [20] reported a less current density of 9.7×10^{-11} A/cm^2 at $V_g = 3.0$ V after annealing the films in N_2 atmosphere.

Fig. 8 shows the plot of (*C–V*) for an electron beam evaporated Al_2O_3 film and the inset shows a plot of current density versus electric field. The dielectric constant calculated in the accumulation region was found to be around 8.32. It was found from the current density versus electric field plot that the breakdown electric field was around 1 MeV/cm which is less than that of spray pyrolysed film. Leakage current and resistivity values were found to be 10^{-5} A/cm^2 and $1.1 \times 10^9\,\Omega$ cm, respectively for an evaporated film of thickness 230 nm deposited at 65 °C at $V_g = 5$ V. The reason for more leakage current could be once again due to porous nature of the film deposited at low substrate temperature, which affects the dielectric properties of the films. Work is in progress to study the characteristics of Al_2O_3 films as humidity sensors.

Al_2O_3 films are extensively used in optics, microelectronics, sensors and tribology. Thin films for optical applications should have high transmittance, reproducible refractive index and low extinction coefficient. Evaporated films deposited at 65 °C showed excellent optical properties. However, the films prepared using ion-assisted deposition technique exhibited higher refractive index [8]. Spray deposited

Al_2O_3 films showed higher transmittance only when they were deposited at higher substrate temperature (350 °C).

Al_2O_3 films for VLSI applications should have high dielectric constant and low leakage current. Electron beam evaporated Al_2O_3 films deposited at 65 °C showed comparatively lesser dielectric constant, high leakage current and low breakdown electric field. This may be due to the fact that the films were deposited at low substrate temperature which may have resulted in porous films. But spray deposited Al_2O_3 films deposited between 300 and 350 °C have enhanced electrical characteristics which could replace SiO_2 films for gate dielectric applications. Since Al_2O_3 films exhibit high thermal conductivity, these are also used as heat sinks in microelectronics.

Al_2O_3 thin film based capacitor is a good humidity sensor having applications in environmental control engineering. Al_2O_3 thin films having high porosity have been found to exhibit high sensitivity in humidity measurements. Al_2O_3 thin films deposited by electron beam evaporation at low temperatures are porous and hence can be used as humidity sensors. Spray deposited Al_2O_3 film deposited at 300 °C has been tested for its humidity sensing property in the form of MOS device and preliminary investigations indicated its suitability as a good humidity sensor.

Al_2O_3 thin films have been reported to prevent corrosion in harsh environment [1]. Films prepared at high substrate temperature by spray pyrolysis could exhibit good anticorrosive properties. Investigations are under progress to test the anticorrosive properties of Al_2O_3 films deposited on steel substrates.

Electron beam evaporated films deposited at 65 °C have exhibited good optical properties but showed poor dielectric characteristics. However, the films deposited by spray pyrolysis technique showed excellent electrical characteristics suitable for use as gate dielectrics in micro electronics and sensor applications.

4. Conclusions

Al_2O_3 films were deposited on glass, quartz, and silicon substrates by spray pyrolysis and by electron beam evaporation. The refractive index of evaporated Al_2O_3 film is 1.71 and 1.60 at 300 and 500 nm, respectively and that of sprayed film is 1.58 at 500 nm. The optical band gap of spray deposited film was found to be in the range of 5.4–5.55 eV and that of evaporated film is 5.75 eV. The films were adherent to all the substrates. Electrical parameters like dielectric constant, resistivity and breakdown electric field were estimated by fabricating MOS structures of Al_2O_3 thin films. These parameters confirmed that the higher substrate temperature greater than 350 °C favours the better dielectric properties of MOS devices by reducing the leakage currents observed at lower substrate temperatures. These Al_2O_3 thin films can replace SiO_2 gate dielectrics successfully. A typical film prepared at 350 °C by spray pyrolysis showed breakdown field of 5 MV/cm, which is comparable with the earlier reports. Al_2O_3 films prepared by spray pyrolysis exhibited good electrical characteristics compared to electron beam evaporated films except optical transparency. Since the techniques is cheap and it could be used to deposit films with desired characteristics for engineering applications.

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