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PE MOCVD of Thin High Transparent Dielectric Amorphous Films of Aluminium Oxide

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Abstract. Thin transparent amorphous films of aluminum oxide have been obtained using PE MOCVD technique and aluminum β -diketonate as precursor in controlled mixture of gas reagents Ar and O_2 . The films were deposited on glass, quartz and stainless steel substrates at temperature range of 100 -- 250°C. The correlation between electric properties and such deposition parameters as r.f. power W_p , the total gas pressure in chamber P_0 , O_2 partial pressure, the substrate temperature T_s and gas carrier flow rate were determined. Optimal deposition conditions of Al_2O_3 layers with high dielectric characteristics were established.

Auger analysis showed that the composition of films obtained was stoichiometric. Auger depth profiles showed the existence of the transition area enriched with oxygen in the film/substrate heterostructure.

1. INTRODUCTION

Recently aluminum oxide films have become widely applied in different electronic devices [1,2]. The main functional characteristics of these films are higher than those of dielectric usually used [3,4]. Al_2O_3 could be obtained using various techniques; r.f. reactive and electron beam evaporations [5,6,7], MO CVD [8], LA CVD [9], chemical and plasma oxidation of aluminum [10,11], anodization [2], thermal evaporation [12], plasma chemical deposition [13], etc. PE MOCVD is one of the most promising for deposition of functional layers on the structures with developed surface relief that does not allow high temperature effect [2,6].

The quality and physical properties of deposited layers significantly depend on constructive peculiarities of equipment used for deposition and technological parameters of deposition process [14]. Since there are insuperable mathematical difficulties the optimization of synthesis based on data about mechanism of plasmachemical reactions is found to be difficult nowadays. So we have conducted the optimization proceeding from correlation between technological parameters and the main physical properties of the films.

In this paper we report on Al_2O_3 films obtained by PE MOCVD technique using aluminum β -diketonate AlL_3 as precursor. The object of our work was also to determine the technological parameters which affect the chemical composition and physical properties of films obtained.

2. EXPERIMENTAL DETAILS

Aluminum oxide films were deposited in tunnel plasma chemical reactor with capacitor excitation of plasma discharge. Output power of generator and working frequency was $W_p=0.2$ -- 0.7 kW and 13,5 MHz correspondingly. The pumping system was equipped with a liquid nitrogen trap between the throttle and the deposition chamber. Films deposition was carried out in the mixture of argon and oxygen ($Ar:O_2$ was 1:1) under the pressure of $P_0=0.2$ -- 1 Torr. Gas mixture composition was controlled using rotameters.

Argon used as gas carrier passed through cylinder heater which contained precursors put into quartz ampoule with calibrated orifice. The control of precursor vapors flows ingress into deposition zone was carried out using ampoules with outlets of different diameters (from 0.2 to 1.2 μm), adjustment of gas carrier flow (20 - 100 ml/min) and evaporation temperatures.

Coordination compound of $\text{Al}(\text{AA})_3$ was used as precursor. Its evaporation temperature equals to 155 - 160°C and temperature dependence of saturated vapor pressure as determined using derivatography and gas chromatography correspondingly. Silicon, quartz, glass and stainless steel used as substrates were heated within the temperature range of 100 - 250°C. Thermocouple insulated and screened from RF discharge was used to control substrate temperature. Since the working chamber was rather large (300 mm length, 200 mm diameter) it was necessary to convey β -diketonate vapors by quartz tube into the deposition zone to increase reagents concentrations near the substrate surface. The substrate was plasma chemically purified during 5 minutes in argon and oxygen atmospheres subsequently before the deposition started (plasma discharge power was 700 W).

Auger spectrometer "JAMP - 10S" was used to determine chemical composition of the films. Films' structures were examined with the help of diffractometer "DRON - 3" and rotation chamber. Optical transmission was measured using two beam spectrometers "Specord UV-VIS" and "PYE-UNICAM-8800" with spectral range of 200 - 800 nm and 190 - 850 nm correspondingly.

3. RESULTS AND DISCUSSION

In situ grown Al_2O_3 films were light-yellow due to carbon presence as evident from Auger spectrum studies (Fig. 1a). The carbon content in film was shown to be dependent on the tube length L of quartz injector of precursor ($\text{Al}(\text{AA})_3$) and on gas carrier flow rate Q , that is on plasma discharge activation time. It was determined that there are no carbon impurities in the films obtained under different deposition conditions when the tube used was more than 17 cm long (Fig1b,2).

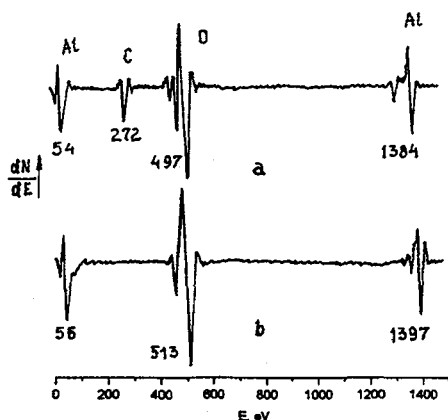


Figure 1: Auger spectra of aluminum oxide films deposited at different length of injector tube: (a) $L=5$ cm; (b) $L=20$ cm. $W_p=400$ W; $Q=500$ ml/min.

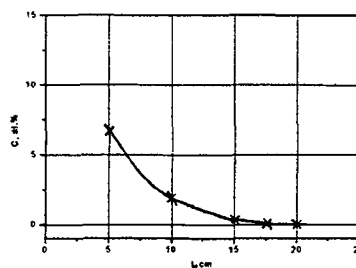


Figure 2: Carbon content in aluminum oxide films as a function of injector tube length (according to Auger spectra data).

Aluminum oxide films deposition process conditions (W_p , T_s , Q , P_0) were optimized for such qualitative characteristics as film resistivity ρ and breakdown field E . Figure 3a shows the positive effect of temperature increase on resistivity and breakdown field values. Taking into account the unaltered chemical compositions of the films deposited under different temperatures we supposed that these temperature relationships depend on increase of structural order (degree) in the films [12]. This process causes ρ and E decrease when gas carrier flow rate increases (Fig.3b). Besides when $Q > 70$ ml/min the film fogging due to carbon impurity's presence could be observed. When plasma discharge power increased resistivity of the

film grew insignificantly. However, there was a pronounced decrease of the breakdown field values starting from the value of 450 W that was probably connected with film's porosity increase due to intensive bombardment of growing layer by high energy plasma discharge components (Fig.3c). This reason also caused E decrease when chamber pressure during deposition process was low.

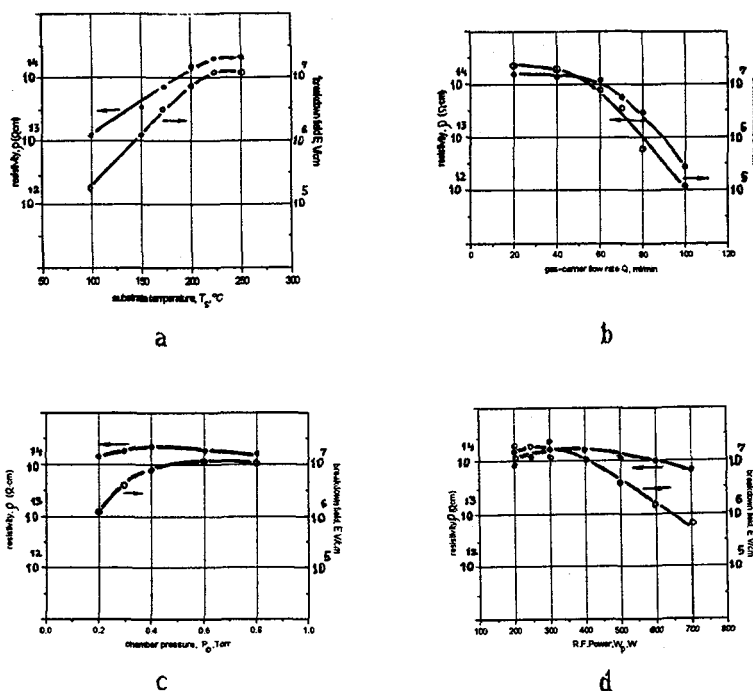


Figure 3: Resistivity and breakdown field dependence versus:

(a) substrate temperature ($W_p=400$ W, $Q=50$ ml/min, $P_0=0.6$ Torr);
 (b) gas carrier flow rate ($W_p=350$ W, $T_s=230^\circ$ C, $P_0=0.6$ Torr); (c) chamber pressure ($W_p=350$ W, $T_s=230^\circ$ C, $Q=50$ ml/min); (d) r.f. power ($T_s=230^\circ$ C, $Q=50$ ml/min, $P_0=0.6$ Torr).

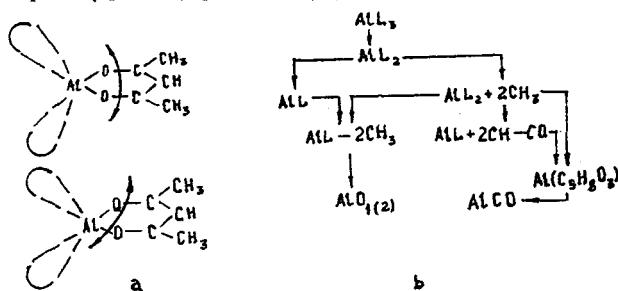


Figure 4: Possible fragmentation ways of aluminum β -diketonate by mass spectroscopic data (L is β -diketone).

Resistivity and breakdown field values of films deposited under different oxygen partial pressures in working chamber remained almost unchanged. This fact could be explained by high probability of $Al(AA)_3$ dissociation proceeding by fragment channel where Al-O fragment is formed [16] (Fig.4). As a consequence there was an unsuccessful attempt of aluminum nitride thin film deposition using ammonia as nitrogen precursor. Only aluminum oxynitride films with nitrogen content of 10-15 at.% and dielectric characteristics slightly different from those ones of Al_2O_3 films have been deposited.

Since the optimization of deposition process based on main technological parameters effecting the qualitative characteristics of aluminum oxide films was carried out only the films deposited under optimal conditions have been examined. These high quality colorless dense Al_2O_3 films have smooth surface morphology and good adhesion to the substrate as it was shown by the results of scratch method [17].

Along with the values of resistivity $\rho \approx 10^{14}$ Ohm·cm and breakdown field $E \approx 10^7$ V/cm some other parameters have been determined for capacitor MIM structures. Leakage current density was $3 - 10$ mA/cm² under applied voltage of 50 V (film thickness was $0,2 - 0,3$ μm). The value of $\tan \delta$ for different samples varied in the range of 0.001 - 0.005 when the frequency was 1 kHz and the voltage was 15 V; dielectric constant ϵ has the value of 7.8 - 8.3.

Auger spectra showed the stoichiometric composition of the films obtained. Auger spectroscopy also has been used to study Al_2O_3 film chemical composition as a function of film's thickness (Fig.5). Film's composition was determined from the relative intensities of Auger peaks when the film was etched layer by layer in the chamber of Auger spectrometer using argon ions. Heterostructure profiles indicated the oxygen content to increase in the film area close to the substrate that is in agreement with [10].

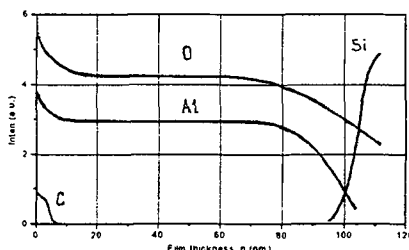


Figure 5: Auger depth profiles of component distribution in heterostructure of $\text{Al}_2\text{O}_3/\text{Si}$ film (h is film thickness).

X-ray studies revealed the amorphous structure of the as-deposited films. However the analysis of dependence of the film electric characteristics on the parameters of the deposition process shows the possibility of deposition of aluminum oxide layers with the resistivity and breakdown field magnitudes close to those in crystalline films.

The transmission spectra of aluminum oxide films deposited on transparent substrates (quartz, glass) have been studied. The transmission factor in the visible spectrum range was 85-95 % when the film thickness was $0.2 - 0.3$ μm .

4. CONCLUSIONS

Examination of how such deposition parameters as the substrate temperature, gas carrier flow rate, chamber pressure and r.f. power effect on dielectric characteristics of the films obtained allowed to optimize PE MOCVD process.

Amorphous high transparent aluminum oxide films of stoichiometric composition with suitable dielectric properties ($\rho \sim 10^{14}$ Ohm·cm, $E \sim 10^7$ V/cm) and good adhesion have been deposited at the temperature range of $200 - 250^\circ\text{C}$.

Auger profiles of chemical components through film thickness revealed the presence of oxygen enriched transition area in film -- substrate heterostructure.

We suppose that plasma enhanced chemical vapor deposition of aluminum oxide thin films using aluminum β -diketonate as precursor shows promise for dielectric layers deposition on the structures with developed relief that does not allow high temperature effect.

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