Journal of Electronic Materials, Vol. 13, No. 2, 1984

THIN FILMS OF ZrO_2 METAL ORGANIC CHEMICAL VAPOR DEPOSITION

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(Received August 26, 1983)

ZrO_2 layers were deposited for the purpose of obtaining high dielectric constant insulating layers for capacitance applications. Trifluoroacetylacetonate of zirconium was used as the source material in our open MOCVD system. Layer thickness was in the range 300-1500 Å, the substrate being degenerate n-type silicon wafers. Under optimum conditions layers with good adhesion and uniformity were obtained. The layers were polycrystalline with characteristic linear dimensions of 400 Å. Electrical measurements were used for characterization and the relative dielectric constants obtained were 30 ± 1.

Key words: ZrO_2, MOCVD, high dielectric constant materials.

Introduction

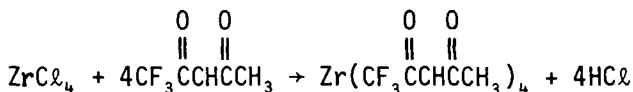
Deposition of thin layers is playing an increasing role in microelectronics technology. Among the various methods, MOCVD has gained popularity in the last decade [1]. Insulating layers of high dielectric constant are becoming essential for such application as high density dynamic memories [2]. One of the promising candidates for this application is ZrO_2 which has a relative dielectric

constant between 20 and 30 [3-5]. The aim of this work was to study in detail the deposition of ZrO_2 by MOCVD and its correlation to the electronic properties in MIS capacitors.

Experimental

Material Preparation

Zirconium trifluoroacetylacetonate [$Zr(tfacac)_4$] was chosen as the source material due to its relative stability and ease of preparation. The organo-metallic material was prepared according to [6]:



$$ZrCl_4 + 4CF_3\overset{O}{\overset{\|}{C}}CH\overset{O}{\overset{\|}{C}}CH_3 \rightarrow Zr(CF_3\overset{O}{\overset{\|}{C}}CH\overset{O}{\overset{\|}{C}}CH_3)_4 + 4HCl$$

Trifluoroacetylacetone (Alfa) freshly distilled and $ZrCl_4$ (Alfa) were reacted in dry petrol ether under a flow of Ar gas. The material precipitates in the form of a white crystalline product, is filtered under vacuum, washed with cold, dry petrol ether and stored until use in a dark box in a refrigerator. The reaction yield was found to be 89% and the observed stoichiometry, gathered from chemical micro-analysis, fitted well with the theoretical values.

CVD System

A standard open MOCVD system with a rotating sample holder was used for growing ZrO_2 films. The source organo-metallic compound was placed in a U-tube immersed in a silicon-oil bath. Dry nitrogen gas was used both as carrier and as diluting gas and was preheated in the same oil bath. Oxygen gas was introduced directly into the bell-jar where it was mixed with the other gases. A schematic drawing of the system is shown in Fig. 1. The system was loaded, the substrate holder heated to the required temperature and the system was continuously flushed with dry nitrogen before the deposition. The ZrO_2 layers were deposited on 7.5 cm diameter degenerated n-type <111> silicon wafers which were precleaned by standard microelectronic techniques: immersing in $H_2SO_4:H_2O_2$ followed by dip in $HF:H_2O$, rinsing and drying. Silicon substrate was chosen for: (a) being a common substrate in microelectronics technology; (b) enabling

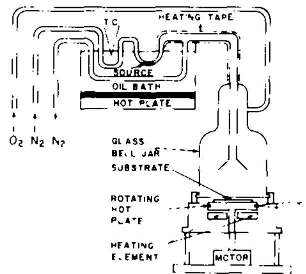


Fig. 1. MOCVD system - schematic presentation.

handy C-V measurements. Typical deposition conditions are listed in Table I.

Table I. ZrO_2 Deposition Parameters

Parameter	Value
Source temperature	190°C
Substrate temperature	450°C
N_2 carrier flow rate	300 cm^3/min
N_2 diluting flow rate	1750 cm^3/min
O_2 flow rate	650 cm^3/min
Substrate rotation rate	20 rpm
Deposition rate	350 Å/min

Characterization Methods

Alfa step and ellipsometer were used to determine the thickness and refractive indices of the layers. The accuracy in the measurement of the thickness taking into account layer non-uniformity was ±70 Å. The electrical properties were obtained from I-V and C-V measurements on MIS structures fabricated by evaporation of 1 μm aluminum layers and defining capacitors of 1.35×10^{-4} cm^2 by photolitography.

Results and Discussion

Layer Thickness and Uniformity

The range of layer thickness studied was between 300-1500 Å. The typical uniformity on the 7.5 cm wafer was

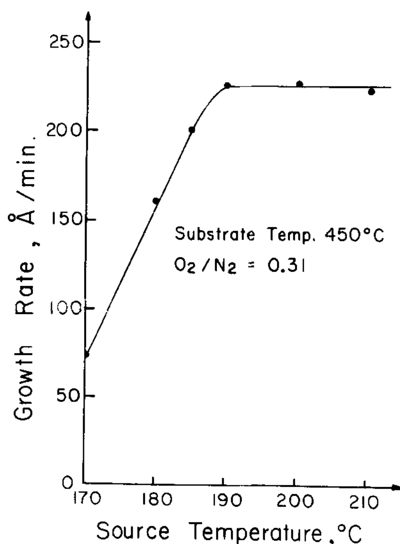


Fig. 2. Dependence of growth rate on source temperature.

±100 Å. The growth rate dependence on source temperature is shown in Fig. 2. Linear dependence was observed up to 190°C above which saturation of the growth rate is obtained. In fact, partial decomposition of zirconium trifluoroacetylacetonate occurred already at ca. 200°C limiting the maximum layer thickness obtained in a single deposition run. Based on these facts, the optimum source temperature chosen was 190-195°C. The dependence of growth rate on substrate temperature is given in Fig. 3. For maximum deposition rate substrate temperature of 450°C was used. The nitrogen flow rates were adjusted to obtain uniform deposited layers. The addition of oxygen to the reaction chamber was needed to reduce the defect density and to improve the electrical properties. Good adhesion of the layers was verified by the "scotch tape test". The refractive index $n = 2.00 \pm 0.07$ is in the acceptable range for the material [3]. SEM micrographs revealed that the layer is polycrystalline with typical grain dimension of 400 Å. In layers thicker than 2000 Å coallescence and growth of the crystallites is observed in the bottom layer. This was the reason for limiting the growth thickness below 2000 Å.

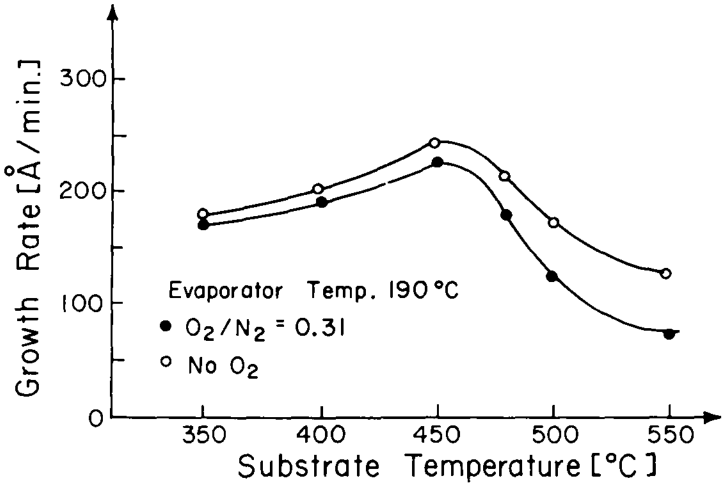


Fig. 3. Dependence of growth rate on substrate temperature in the presence and absence of oxygen flow.

Electrical Measurements

Typical I-V curve is shown in Fig. 4. Three distinct ranges are observed: an exponential growth for voltages below

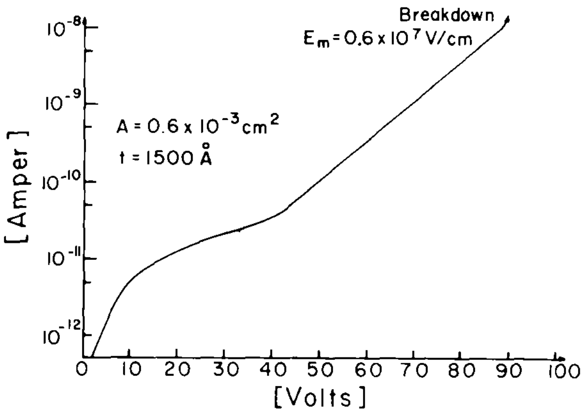


Fig. 4. Typical I-V curve for ZrO_2 MIS structure showing 3 distinct ranges of behavior.

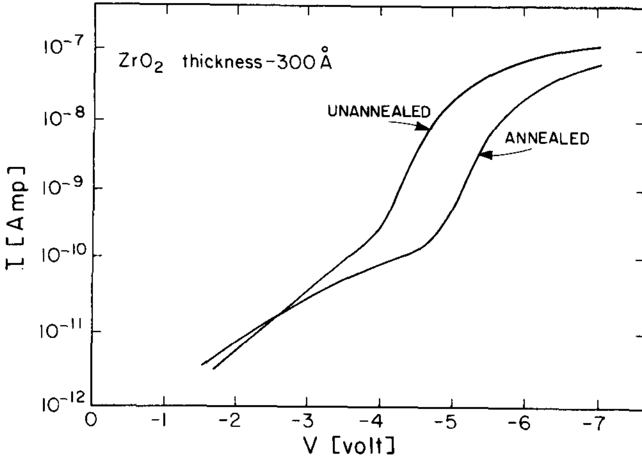


Fig. 5. Effect of nitrogen anneal for 1 hr at 750°C on I-V curve.

10 V (~10^6V/cm) followed by ohmic behavior till about 40 V (~3×10^6V/cm) and ending with an exponential dependence up to the breakdown voltage of 90 V (6×10^6V/cm). Experiments were performed to investigate the effect of nitrogen anneal at

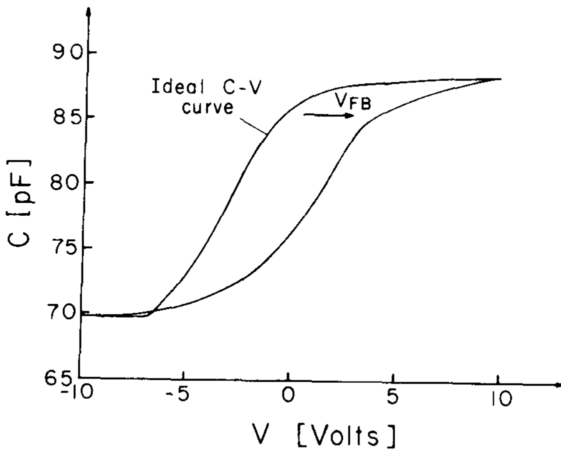


Fig. 6. Typical C-V curve for ZrO_2 MIS structure. For comparison ideal C-V curve for the same structure is shown. The direction of the V_{FB} shift is indicated.

high temperatures on the leakage current. Samples were cleaved prior to metal electrode evaporation and one half of each wafer was treated at 750°C in a nitrogen atmosphere for one hour. Reduction in the leakage current was observed as shown in Fig. 5. This is in qualitative agreement with previous results [7]. The value of the leakage current is by about one order of magnitude higher than that of silicon dioxide.

From C-V measurements both the dielectric constant was calculated and an insight was obtained on the oxide charge and interface properties. Typical C-V curve is given in Fig. 6. The value of the dielectric constant, as obtained from the saturation value of the capacitance in the accumulation region, varied with the oxygen concentration in the gas mixture; the latter also affected the oxide resistivity as shown in Fig. 7. Based on these two dependences, the ratio of 0.32 was chosen for the O_2/N_2. Under these conditions, a value of 30 ± 1 was obtained for the relative dielectric constant as calculated from the slope of the straight line of Fig. 8. The existence of a 13 Å thick silicon dioxide native layer was also obtained from the intercept of the straight line with the ordinate. The ideal C-V curve, based on substrate and layer parameters, is shown in Fig. 6.

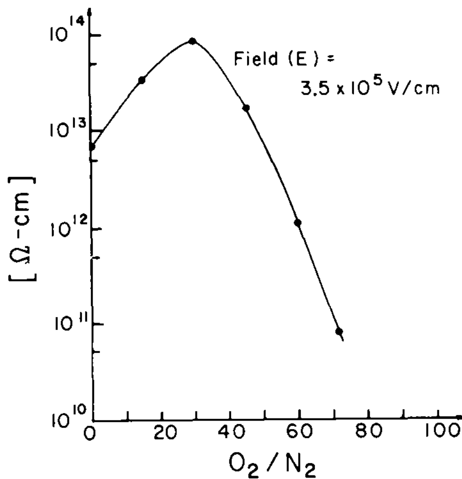


Fig. 7. Dependence of oxide resistivity on oxygen/nitrogen ratio in the reaction chamber.

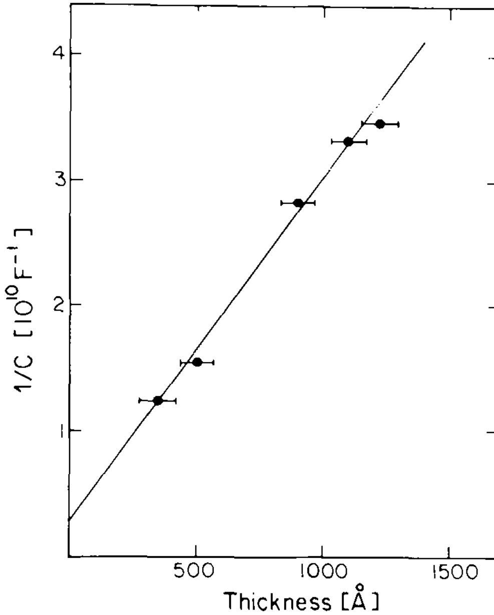


Fig. 8. Dependence of inverse capacitance of the MIS in accumulation on layer thickness.

The two curves observed and calculated, are almost identical in shape indicating surface state density of the order 10^{12} cm The fixed charge in the oxide as obtained from the shift in V_{FB} is 44×10^{12} cm^{-2}. Applying negative voltages on the MIS capacitors, corresponding to electric fields $E \geq 2\times10^{6}$V/cm, caused negative shifts in the flat-band voltage with logarithmic dependence on time as shown in Fig. 9. No shifts were observed for lower fields. This behavior is similar to other MIS systems [8]; however, in this case trapping of positive charge is observed.

Conclusion

ZrO_2 layers obtained by MOCVD have physical and electronic properties making them suitable for various applications such as discrete capacitors as well as miniature capacitors in VLSI.

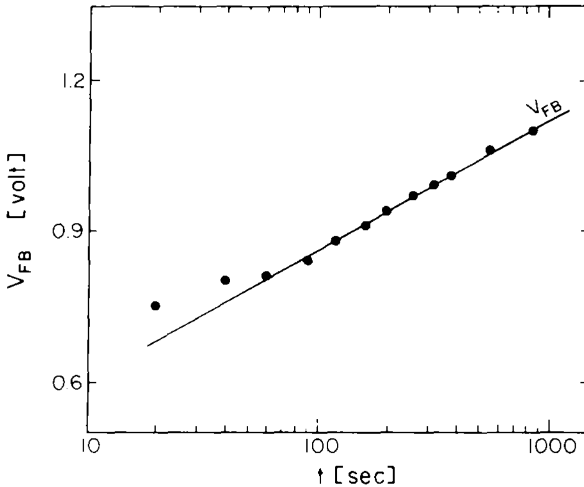


Fig. 9. Dependence of V_{FB} on time of applied negative dc field at 2×10^6 V/cm.

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