Optical and electrical properties of aluminum oxide films deposited by spray pyrolysis

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Optical and electrical properties of aluminum oxide films deposited by spray pyrolysis

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The optical and electrical characteristics of spray pyrolysis deposited aluminum oxide films are reported. The films were deposited from a spraying solution of aluminum acetylacetonate in *N*,*N*-dimethylformamide using an ultrasonic mist generator on (100) Si substrates. The addition of water mist during the spraying deposition process resulted in an overall improvement of the films characteristics. The substrate temperature during deposition was in the 450–650 °C range. Deposition rates up to 90 Å/s were obtained depending on the spraying solution concentration and substrate temperature with an activation energy of the order of 31 kJ/mol. The optical energy band gap for these films was 5.63 eV and the refractive index at 630 nm up to 1.66 was measured by ellipsometry. The electrical characteristics of the films were determined from the capacitance and current versus voltage measurements of metal–oxide–semiconductor (MOS) structures incorporating them. A dielectric constant of 7.9, interface states density of the order of $10^{11} \times 1/\mathrm{eV\,cm}^2$ as well as breakdown fields higher than 5 MV/cm were determined in this way. © *1998 American Institute of Physics.* [S0003-6951(98)03514-1]

Aluminum oxide films deposited by a wide range of deposition techniques have been evaluated for their application as dielectric layers on different types of microelectronic devices.[1,2] In particular the high chemical stability, high radiation resistance, high thermal conductivity and low permeability to alkali impurities that these films present make them good candidates for application on metal–oxide–semiconductor (MOS) structures as gate oxides among several other applications such as passivation layers, and dielectric films in chemical sensors.[3,4] All these applications required films with good homogeneity and low surface roughness and good control of thickness for films of the order of 1000 Å thick or less. Also good dielectric characteristics and density of the films are required for such applications. Spray pyrolysis is a deposition technique which is frequently used for film deposition on applications that require large area, low cost processes. However it is not regarded as a technique with a large degree of control when thin films below 1000 Å are required. In the present work we report the deposition of thin aluminum oxide films using the spray pyrolysis technique in which excellent control of thickness homogeneity and surface roughness has been achieved for films of the order of 1000 Å or less. The optical characteristics of these films indicate a dense material with a refractive index of 1.66. An activation energy (E_a) of the order of 31 kJ/mol was determined from the deposition rates at different substrate temperatures. These films have good dielectric characteristics with a dielectric constant of the order of 7.9 and they are able to stand electric fields up to 5 MV/cm without destructive breakdown.

The spray pyrolysis deposition system has been described in detail previously.[5,6] It consists of an ultrasonic generator used for mist generation from a spray solution. The mist is transported through a glass tube to the substrate surface which is being heated to achieve the pyrolysis reaction. For this work, aluminum acetylacetonate dissolved in *N*,*N*-dimethylformamide has been used as a spraying solution. The concentration of this solution was varied from 1 to 12 gm of aluminum acetylacetonate in 100 ml of dimethylformamide. Some of these samples were deposited by adding a stream of water mist in parallel to the spraying solution. The films were deposited on *n*-type silicon wafers of 0.1 Ω-cm and on quartz slides for the optical absorption measurements to a thickness in the range of 900–1300 Å. For the electrical measurements MOS structures were fabricated by thermally evaporating aluminum contacts with an area of 1.1×10^{-2} cm^2 on top of the aluminum oxide film deposited on the silicon substrates. The silicon substrates were given the standard RCA cleaning procedure before the deposition process. Substrate temperatures in the range of 450–650 °C were used during film deposition. Thickness and refractive index were measured with a manual ellipsometer at 630 nm. The optical absorption measurements were performed with a commercial ultraviolet-visible (UV-Vis) spectrophotometer in the 190–900 nm range. Commercial automated equipment was used for the capacitance and current versus voltage measurements.

The aluminum oxide films were deposited at different spraying solution concentrations and at different temperatures. The activation energy for the deposition process (E_a) was determined by plotting the deposition rate (R_d) as a function of the reciprocal substrate temperature ($1/T_s$) in a

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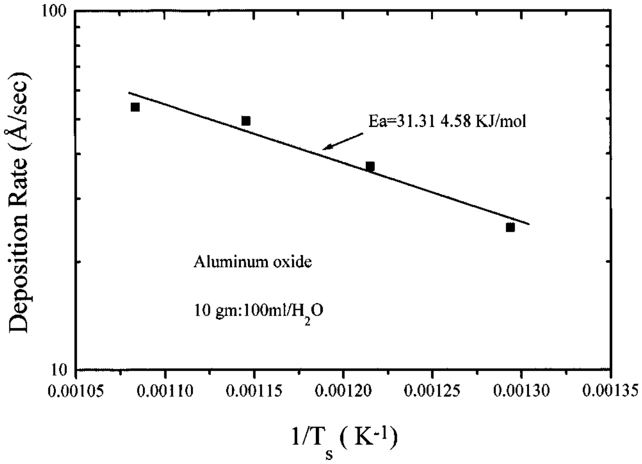

FIG. 1. Arrhenius plot of the deposition rate.

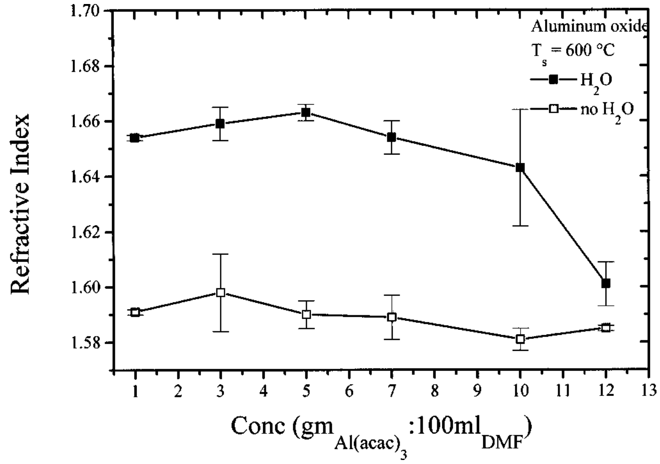

FIG. 3. Refractive index as a function of the spraying solution concentration for samples deposited with and without an additional stream of water mist.

semilogarithmic scale and fitting a line to the data. Figure 1 shows this type of plot for films deposited with a spraying solution of 10 gm of aluminum acetylacetonate in 100 ml of dimethylformamide. The activation energy in all cases was in the range of 27–35 kJ/mol. These values are in agreement with previously reported activation energies for aluminum oxide films deposited by the chemical vapor deposition technique.[7,8] Figure 2 shows the square of the optical absorption times the photon energy as a function of photon energy. From this plot it is possible to determine the optical energy band gap for these films. In this case the band gap is equal to 5.63 eV. It is observed that these films are transparent in the whole visible range, and comparable to the best quality films obtained by other techniques.[9] The films were found to be amorphous by x-ray diffraction measurements in all cases. The refractive index as determined by ellipsometry is shown as a function of the concentration of the spray solution in Fig. 3 for samples deposited with and without water. It is observed that the higher refractive indexes are obtained for the films in which water was added during the deposition process. These results might indicate that films deposited with water have better density. This is confirmed by the electrical measurements of the films, since the MOS structures fabricated with films containing water in the spray solution presented the best dielectric characteristics. It is assumed that the role that water plays during the deposition process is to collect the residual carbon from the acetylacetonate decomposition process, reducing in this way the total amount of carbon and water impurities that remain in the oxide film after deposition. The optical absorption measurements performed in the UV-Vis range studied were not able to determine whether this is the case or not. Further measurements in the infrared (IR) region are under way to assess this point. Figure 4 shows the 1 MHz and quasistatic capacitance versus voltage characteristics and the density of the states determined for these measurements, respectively. The inset shows the density of interface states obtained from these data. It is observed that the density of the states at midgap is of the order of $10^{11} \times 1/\text{eV cm}^2$. These density values are comparable to a good quality dielectric layer usually required for many microelectronic applications.[10] The insulating characteristics of these films are illustrated by the electrical current density versus voltage characteristic curves shown in Fig. 5 for a MOS structure fabricated with an aluminum oxide film deposited at 550 °C. The current density observed at electric fields below 2 MV/cm is of the order of 10^{-9} A/cm^2 and it is

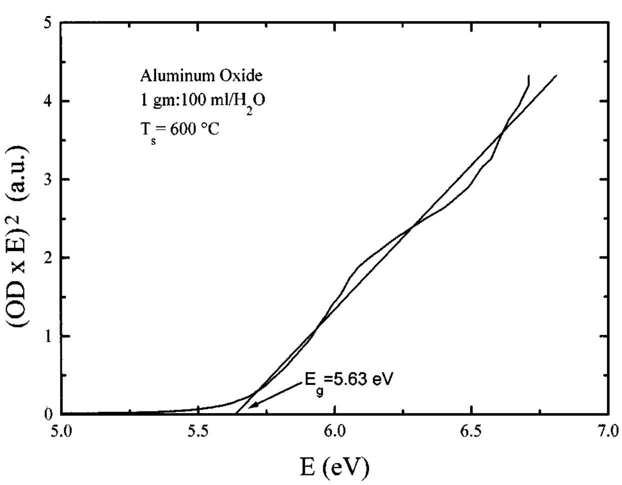

FIG. 2. Squared of the optical absorption times the photon as a function of photon energy for a film deposited on quartz. The line represents the best linear fit to determine the energy gap.

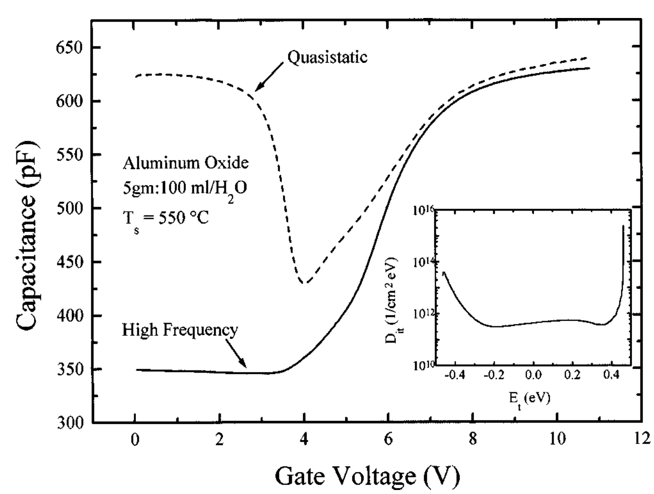

FIG. 4. High frequency (1 MHz) and quasistatic capacitance vs gate voltage for a MOS structure incorporating an aluminum oxide film. The inset corresponds to the density interface states (D_{it}) calculated from capacitance–voltage (C–V) curves (the energy E_1 is measured from midgap).

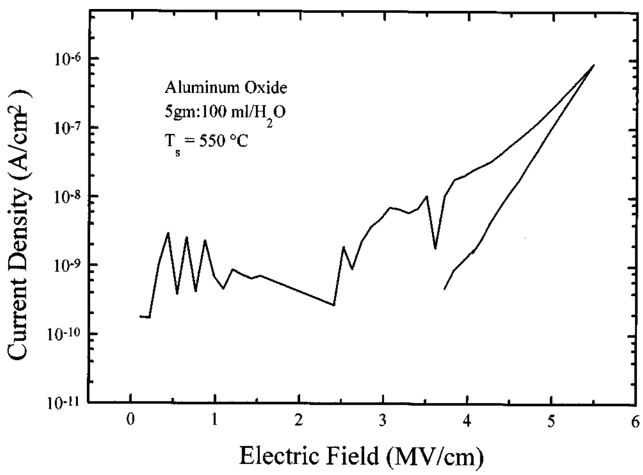

FIG. 5. Electrical current density as a function of applied electric field for a MOS structure similar to the one used for the previous figure.

due to a displacement current associated with the voltage ramp applied to the MOS structure in order to obtain the current versus voltage characteristics. At electric fields higher than 2 MV/cm a real current injection across the aluminum oxide is observed to increase up to 10^{-6} A/cm^2 at approximately 5 MV/cm. It should be pointed out that no destructive breakdown of the film is observed even at these high electric fields and currents.

In conclusion, good quality aluminum oxide films have been deposited by the spray pyrolysis technique using aluminum acetylacetonate dissolved in *N*,*N*-dimethylformamide. It is observed that the addition of a water mist stream into the spraying solution mist during the deposition process has a dramatic effect on the refractive index and on the overall dielectric characteristics of the deposited aluminum oxide films. The density of the states for the MOS structures fabricated with the deposited films is of the order of 10^{11} $\times 1$/eV cm^2, and the destructive breakdown electric field is larger than 5 MV/cm.

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[1] M. Ishida, I. Katakabe, T. Nakamura, and N. Ohtake, Appl. Phys. Lett. **52**, 1326 (1988).
[2] K. Sawada, M. Ishida, T. Nakamura, and N. Ohtake, Appl. Phys. Lett. **52**, 1673 (1988).
[3] J. Saraie and S. Ngan, Jpn. J. Appl. Phys., Part 1 **29**, 1877 (1990).
[4] K. M. Gustin and R. G. Gordon, J. Electron. Mater. **17**, (1988).
[5] G. Blandenet, M. Court, and Y. Lagarde, Thin Solid Films **77**, 81 (1981).
[6] M. Langlet and J. C. Joubert, in *Chemistry of Advanced Materials*, edited by C.N.R. Rao (Blackwell Science, Oxford, England, 1993), p. 55.
[7] T. Murayama and T. Nakai, Appl. Phys. Lett. **58**, 2079 (1991).
[8] T. Murayama and S. Arai, Appl. Phys. Lett. **60**, 322 (1992).
[9] P. Patil, D. Bendale, R. Puri, and V. Puri, Thin Solid Films **288**, 120 (1996).
[10] C. Falcony and F. H. Salas, J. Appl. Phys. **59**, 3787 (1986).

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