

## DIRECT CURRENT REACTIVE SPUTTERING OF ALUMINIUM

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The influence of the oxygen content in the gas flow on the discharge current and on the chemical composition of sputtered  $AlO_x$  was investigated. Unlike  $SiO_2$ ,  $Al_2O_3$  films are formed on the substrate only for oxygen contents sufficient for full oxidation of the target surface. The minimum oxygen content can be determined by the sharp change in discharge current at constant working voltage and total gas pressure. Infrared spectra confirming this statement are given. The kinetics of the processes of forming and sputtering off of an oxide layer on the aluminium target surface were also investigated. Some speculations about the interrelation between oxide formation on the substrate and on the target for direct current reactive sputtering are given.

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### 1. INTRODUCTION

For some important applications in microelectronics aluminium oxide has definite advantages over the most widely used dielectric  $SiO_2$ . This has stimulated investigations of  $Al_2O_3$  film preparation by different methods compatible with planar technology. One method is the d.c. reactive sputtering of aluminium in an oxidizing ambient. This technique has been successfully used to prepare experimental semiconductor devices<sup>1, 2</sup> but the mechanism of oxide formation and the effect of deposition conditions on the film properties and composition are not completely understood.

In the study of reactive sputtering three possible mechanisms of formation of the chemical compound are considered:

(1) the direct sputtering of molecules of the compound formed on the target surface as a result of chemisorption of reactive gas;

(2) compound formation in the gas phase as a result of collisions of sputtered metal atoms on their way to the substrate with reactive gas molecules (this mechanism is considered to be unlikely because of problems in conservation of momentum and in the dissipation of the heat of reaction);

(3) compound formation at the substrate through chemisorption of reactive gas by the sputter deposit.

For the sputtering of aluminium in an argon-oxygen mixture Stirling and Westwood<sup>3</sup> have determined that an  $Al_2O_3$  layer is formed on the substrate only for oxygen contents  $Q$  greater than a critical value above which the target surface is

covered with an oxide layer and the deposition rate is very small compared with the deposition rate from an unoxidized target. According to them, under such conditions the chemical compound is formed mainly by mechanism (1). To determine when the oxide has been removed from the target surface they suggest the use of atomic absorption spectroscopy.

In contrast, our investigations on the reactive sputtering of silicon have demonstrated that it is possible to form an  $\text{SiO}_2$  film on the substrate not only through mechanism (1) but also through mechanism (3), *i.e.* by the sputtering of silicon atoms from an unoxidized target and their combination with oxygen on the substrate. Mechanism (3) occurs only for a definite optimum value  $Q^\circ$  of the oxygen content which is dependent on the sputtering conditions. We found that  $Q^\circ$  can be determined using the relation between the discharge current and the oxygen content at constant working voltage and constant total gas pressure (Fig. 1)<sup>4</sup>.  $Q^\circ$  is the value of  $Q$  at which a simultaneous sharp decrease of the deposition rate and sharp increase of the discharge current begin ( $Q^\circ = 1\%$  in this particular case). Both these effects are due to the formation of an oxide layer on the target surface for  $Q > Q^\circ$ . The former effect has been described by many authors for various target materials. The latter effect was investigated in detail in ref. 5 where it was explained by a change of the secondary ion-electron coefficient  $\gamma$  of the target surface due to its oxidation.

The fact that in the case of the reactive sputtering of silicon it is possible to obtain  $\text{SiO}_2$  on the substrate through mechanism (3) is of great practical importance because the film properties are considerably better and the deposition rate is 3–4 times higher than the deposition rate achieved by mechanism (1). These advantages of mechanism (3) in the case of  $\text{SiO}_2$  deposition encouraged us to study the possibility of its application in the deposition of  $\text{Al}_2\text{O}_3$  films.

## 2. EXPERIMENTAL RESULTS AND DISCUSSION

The sputtering equipment and the gas atmosphere control system have been described previously<sup>6</sup>. A glow discharge in an argon flow at a pressure  $p \approx 10$  Pa and with a working voltage of 4 kV was used to preclean the target, which had an active area of  $16 \text{ cm}^2$ . The duration of the precleaning process was from 12 to 90 min depending on the period of target exposure to air and precleaning was accompanied by an intense sparking. The moment when the target became clean was registered by stabilization of the discharge and by a marked decrease of the discharge current from 50–70 mA to 15–18 mA. A record of the current change at the end of the precleaning process is shown in Fig. 2. (This method of controlling the conditions on the target surface is much simpler than the use of atomic absorption spectroscopy.) After the air-formed oxide had been removed from the target surface, oxygen was introduced into the system. Unlike Stirling and Westwood<sup>3</sup>, we kept the pressure  $p$  and the working voltage  $U_a$  constant and recorded the values of the discharge current  $I$  on varying  $Q$ . The relationship  $I(Q)$  obtained for  $U_a = 3.6$  kV and  $p = 10$  Pa is shown in Fig. 3(a). This curve exhibits a step-like increase of the discharge current due to target oxidation, similar to that for the silicon target (Fig. 1). Unlike silicon, however, in the case of the aluminium target a physicochemical investigation of the films showed that the highest oxide is

formed for  $Q \geq Q^f$ , where  $Q^f$  is the value of  $Q$  for which the step-like increase in current occurs ( $Q^f \approx 0.7\%$  in Fig. 3(a)). This is well illustrated by Fig. 3(b) which shows the IR spectra of  $AlO_x$  films deposited on silicon at the indicated values of  $Q$ .

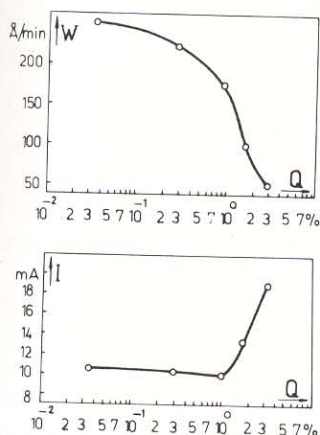


Fig. 1. The dependence of the sputtering rate  $W$  and the discharge current  $I$  on oxygen content  $Q$  at constant working voltage  $U_a = 3.4$  kV and constant total gas pressure  $p = 10$  Pa for a silicon single-crystal target.

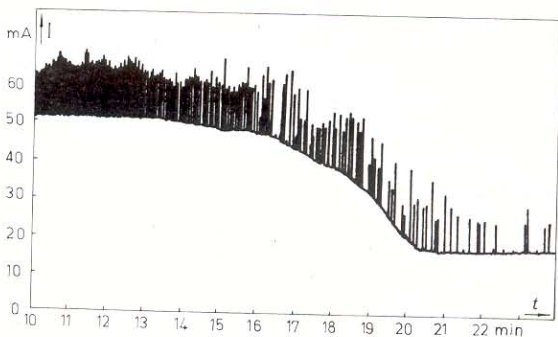


Fig. 2. The discharge current *vs.* time at the end of the precleaning process for an aluminium target.

In more detail, investigation of the films gave the following results.

(i) For  $Q = 0\%$  and  $Q = 0.13\%$  the deposited films are almost metallic, are non-transparent to IR radiation and have a fast etch rate in HF, a low scratch resistance and a grey-brown colour whatever the deposition time, *i.e.* for all film thicknesses.

(ii) For  $Q = 0.36\%$  (the onset of target oxidation) the IR transmittance increases and the spectrum possesses an absorption peak below  $1000\text{ cm}^{-1}$ . The film is harder and has a dark cloudy colouring which varies with thickness.

(iii) For  $Q = 0.45\%$  the absorption peak decreases; the film colour is very bright and depends on the thickness and the film is hard to scratch with a steel edge and possesses definite dielectric properties.

(iv) For  $Q = 0.8\%$ ,  $Q = 2.2\%$  and  $Q = 6.3\%$  the absorption peak becomes very low; the deposition rate and the film properties remain nearly the same and the colour depends on the film thickness. The deposited films do not etch in HF and  $H_3PO_4$ , which indicates their polycrystalline structure<sup>7</sup>, but they can be selectively etched in a solution<sup>2</sup> of three parts  $H_3PO_4$  and two parts  $NH_4F$  at  $65^\circ\text{C}$ .

From these results two main conclusions can be drawn. (1) The basic conclusion of Stirling and Westwood<sup>3</sup> that  $Al_2O_3$  is formed on the substrate only for oxygen contents sufficient to oxidize the target surface is valid in the conditions of our experiment also. Therefore the advantages of mechanism (3) cannot be used for the reactive sputtering of aluminium in a conventional diode system. (2) The minimum oxygen content  $Q^f$  for the formation of  $Al_2O_3$  on the substrate can be determined from the relation  $I(Q)$ .

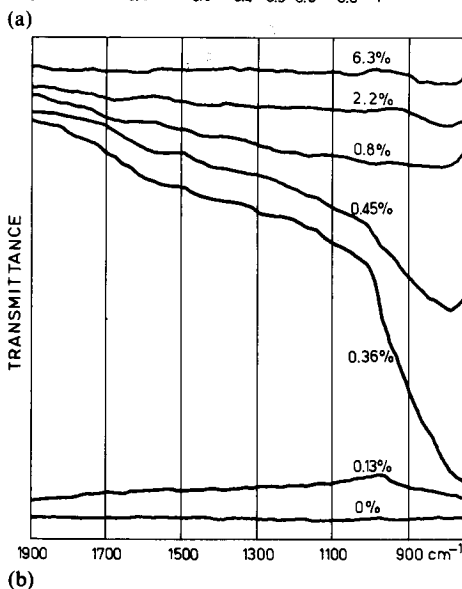
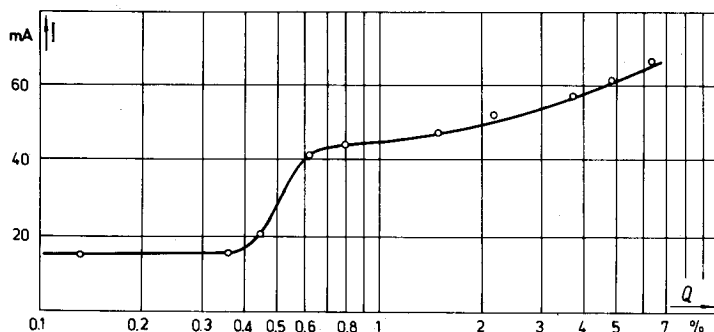


Fig. 3. (a) The dependence  $I(Q)$  for an aluminium target at  $U_a = 3.6$  kV. (b) The IR spectra of films deposited at the indicated values of  $Q$ .

The analysis of the relation  $I(Q)$  together with the IR spectra (Fig. 3) shows that only at the very onset of target oxidation does the deposited film have a stoichiometry of a lower oxide  $AlO_x$  and for  $Q = 0.45\%$  its properties resemble more closely those of a dielectric than those of a metal. This means that the formation of  $AlO_x$  on the target surface is not a necessary condition for the deposition of  $Al_2O_3$  but only a parallel process which takes place before the formation of the highest oxide on the substrate. Thus if in some way the concentration of oxygen in the vicinity of the cathode could be made small enough compared with that near the substrate, mechanism (3) would occur, resulting in a higher deposition rate.

As we have shown<sup>5</sup>, the value of  $Q$  at which the target surface oxidizes depends strongly on the discharge parameters and the target area. Figure 4 shows<sup>5</sup> in log-log scale the  $V-A$  characteristics of the discharge with  $Q$  as parameter, at a constant total gas pressure  $p = 10$  Pa. The N-shaped curves 2, 3, 4 and 5 illustrate the target oxidation process for decreasing voltage, *i.e.* decreasing sputtering rate.

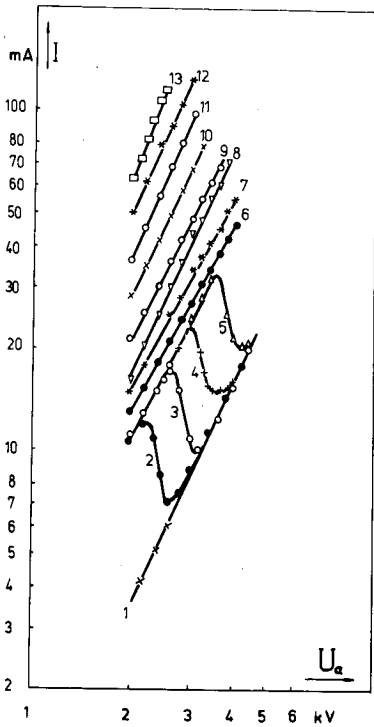


Fig. 4. The dependence  $I(U_a)$  with  $Q$  as parameter for an aluminium target: curve 1,  $Q = 0\%$ ; curve 2,  $Q = 0.10\%$ ; curve 3,  $Q = 0.22\%$ ; curve 4,  $Q = 0.36\%$ ; curve 5,  $Q = 0.6\%$ ; curve 6,  $Q = 1.6\%$ ; curve 7,  $Q = 3.2\%$ ; curve 8,  $Q = 6.7\%$ ; curve 9,  $Q = 10\%$ ; curve 10,  $Q = 20\%$ ; curve 11,  $Q = 40\%$ ; curve 12,  $Q = 70\%$ ; curve 13,  $Q = 100\%$ .

They are useful in the determination of the relation between  $Q^f$ ,  $U_a$  and  $I$ . The dependence of  $Q^f$  on target area can be demonstrated with two aluminium targets connected to the high voltage supply in parallel. A record of the variation of the total current at  $p = 10$  Pa and  $U_a = 3.6$  kV on switching one of the targets off and on is shown in Fig. 5. Both targets were first sputtered clean with  $Q = 0$ . At  $t_1$  we adjusted  $Q$  to  $0.63\%$ —insufficient to oxidize the two working targets. After the target with the greater area had been switched off at  $t_2$  the total number of sputtered aluminium atoms dropped; this caused a decrease of the gettering action on the deposited material. The excess oxygen partially oxidized the small target, as indicated by an increase in the discharge current. The excess oxygen also oxidized the surface of the switched-off target and on switching it on at  $t_3$  a considerable current was recorded. This current fell rapidly to its initial value because  $Q = 0.63\%$  was not enough to replenish the oxide on both targets. At  $t_4$  the oxygen content was raised to  $Q = 0.8\%$  which led to partial oxidation of the targets, indicated by the limited increase in current. At  $t_5$  the target with the greater area was switched off and further oxidation of the small one was recorded. At  $t_6$  the former target was switched on again. In this case, however, we did not observe any cleaning of oxide from the targets and a falling of the current to its initial value. This hysteresis effect can be explained by the much greater sputtering rate from a



metal surface than from an oxidized surface. The entrapment of oxygen is strongly reduced in the latter case, and so the effective partial pressure of oxygen near the cathode at  $Q = 0.8\%$  is sufficient to support the oxide covering. In order to remove the oxide we had to reduce or stop the oxygen flow at  $t_7$ .

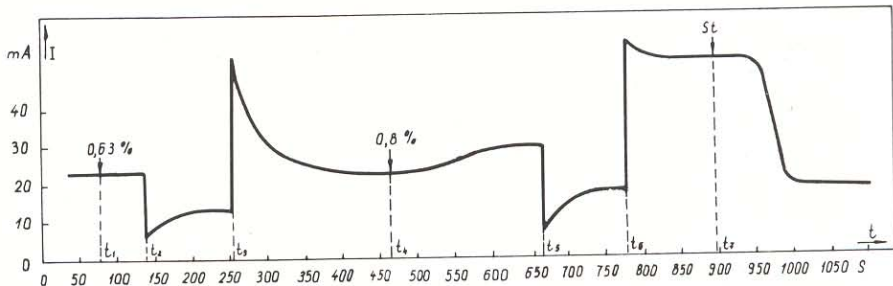


Fig. 5. The discharge current vs. time for two aluminium targets connected in parallel. At  $t_2$  and  $t_5$  the larger target is switched off; at  $t_3$  and  $t_6$  it is switched on again.

The kinetics of the process of formation and removal of the oxide from the surface of the larger target were investigated separately. Some of the results are shown in Fig. 6. The curves are records at  $p = 10$  Pa and  $U_a = 4$  kV of the discharge current variation on introduction of the indicated oxygen contents into the sputtering chamber, after precleaning in argon. It can be seen that the oxide formation time varies from 20 s to 100 s, decreasing with increase in  $Q$ , while the oxide removal time is almost the same. This means that  $Q$  influences the oxidation rate but not the steady state target oxide thickness. The latter can be estimated from the removal time. Assuming that the sputtering rate is close to the deposition rate (about  $80 \text{ \AA min}^{-1}$  under such conditions), we obtain a value of 50–60  $\text{\AA}$  for the target oxide thickness.

### 3. CONCLUSIONS

The reported results represent an addition to our model of d.c. reactive sputtering<sup>5</sup>. They confirm that also for an aluminium target it is possible to use the method proposed in ref. 4 for determining the minimum oxygen content by a change in the discharge current. Using this method it was established, in accordance with ref. 3, that the minimum oxygen content for the deposition of  $\text{Al}_2\text{O}_3$  films corresponds to an oxidized target.

The comparison of the results for silicon and aluminium targets shows that the processes of oxide formation on the target and on the substrate are related only through the redistribution of the amount of oxygen introduced. This redistribution has a complex dependence on the specific properties of the sputtered material and on the discharge parameters, as a result of which target oxidation can take place before or after formation of the highest oxide on the substrate. Therefore the development of a means of controlling the oxygen distribution, aimed at a reduction in target oxidation rate, is still an untried means of achieving a considerable increase in the deposition rate of some oxide films by d.c. reactive sputtering.

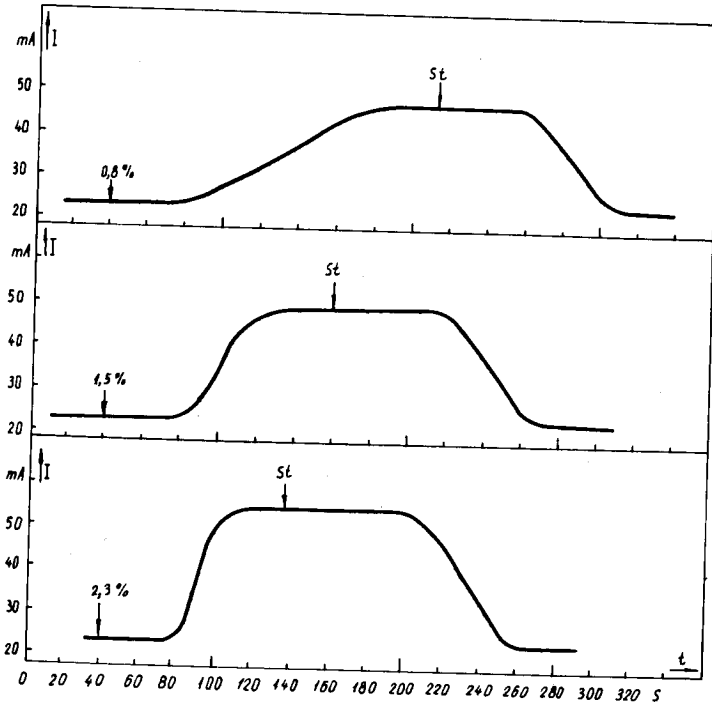


Fig. 6. The kinetics of target oxide formation and sputtering off, indicated by the discharge current at different values of  $Q$ .

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