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THE DETERMINATION OF THE THICKNESS OF ANODIC Al_2O_3 FILM

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To compare the properties of anodized aluminium oxide layers an easy thickness determination method is wanted. Crevecoeur and De Wit used a method expressing the thickness in terms of peak voltages obtained by forming again after annealing. The aim of the work described here is to relate the value of the peak voltage to the thickness of the layer measured by ellipsometry.

On specimens formed in an aqueous solution of boric acid and ammonium hydroxide the following relation is found between the thickness d (nm) and peak voltage V_p (volt):$d = 1.020\ V_p + (0.00044 \pm 0.00011)\ V_p^2$. On specimens formed in a solution of ammonium pentaborate in ethylene glycol the squared V_p term is of a lower value. however when V_p is less than 150 V the above relation holds for layers formed in both electrolytes, the systematic error then being less than 1%.

1. INTRODUCTION

Thickness determinations are often necessary for investigations into the properties of anodic aluminum oxide film. Oxide films formed under different circumstances exhibit differences in specific densities and dielectric constants[1] and also in optical constants. For the refractive index of the oxide film (n_1) a value of 1.58 was found by Harkness and Young[2] and a value of 1.69 by Moskovits and Ostrowski[3]. Film thickness determinations by density measurements, capacitance measurements and interference measurements are based on the assumption that the material constants are known. As this is not always the case optical measurements such as ellipsometry have to be performed or the constants have to be determined first.

To obtain a simple estimate of the thickness of thin aluminum oxide barrier layers, Hunter and Fowle[4] used a method in which an increasing voltage is applied across the oxide film in an electrolyte solution and the voltage at which the current exceeds a specific value is taken to be indicative of the film thickness. Crevecoeur and De Wit[5] refined this method by using the following phenomenon found by Dignam[6].

Annealed oxide films exhibit a sharp current peak when scanned with a constant voltage rate. The voltage (V_p) at this peak value, which is detectable with an accuracy of 0.1 V, is a linear function of the forming voltage (V_f).

In this article the relationship between film thickness and peak voltage is investigated. The determination of layer thickness is done by ellipsometry. To form the oxide film two solutions are used, viz. 17% w/v ammonium pentaborate in ethylene glycol (short: APB-glycol) and an aqueous solution of boric acid and ammonium hydroxide (short: aqueous borate).

The forming voltages are between 20 V and 200 V.

2. EXPERIMENTAL

2.1. *Material*

The aluminum specimens of 99.99% purity, with Fe, Si, Cu and Mg as the main impurities, are chemically polished for 4 minutes at 90°C in a solution of phosphoric acid (85%), glacial acetic acid (96%) and nitric acid (65%) to a ratio of 16:3:1.

The specimens are rinsed in deionized water until the conductivity of the waste water equals the original value of the water, the specific resistivity of the water used is always greater than 2 MΩ cm.

Just before the film formation the specimens are rinsed in a solution consisting of HF (50%), H_2SO_4 (96%) and H_2O to a ratio of 3:20:180 and thereafter in methanol. The surface used for forming is 10 cm^2. As a roughness factor the value of 4% is used as found by Harkness and Young[2] in similar conditions.

2.2. *Forming*

The APB-glycol solution has a current efficiency of 100%[7]. According to the work of Ikonopisov *et al.*[1,8] an aqueous borate solution is used which consists of 2.5% w/v boric acid adjusted to pH 7 by means of ammonium hydroxide. The film is formed at a temperature of 25°C ± 1°C with a constant voltage rate of 0.167 V/s. The current is removed at once after V_f has been reached.

Though the solutions differ in specific resistance ρ(APB-glycol) = 200 Ω cm and ρ(aqueous borate) = 600 Ω cm the voltage drop over the electrolyte is less than 200 mV. The forming voltages are 16 values between 20 V and 200V.

2.3. *Capacitance Measurement*

The determination of the series capacitance takes place in a solution of 5% w/v ammonium pentaborate in water at frequencies varying from 50–1000 Hz. A platinum plated silver counter electrode is used. The capacitance is a function of frequency, the capacitance at 1000 Hz being 3% lower than at 50 Hz. The 1000 Hz capacitance is used in the calculations.

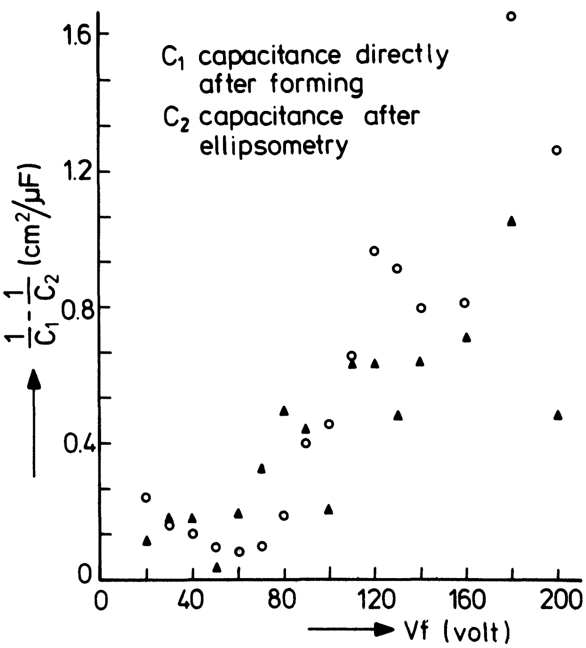

FIGURE 1 Differences in reciprocal capacitances found after forming and those found after ellipsometry measurements which took place 3 to 4 days after forming.
▲—▲ films formed in a solution of ammonium pentaborate in ethylene glycol at 25°C
○—○ films formed in an aqueous solution of borate at 25°C.

To obtain information on the effect of ageing during the period between forming and ellipsometry, which is 3 to 4 days, the capacitance is measured directly after forming and after ellipsometry. In Figure 1 the differences of the reciprocal capacitances are plotted versus the forming voltage. Further analyses show that at room temperature capacitance values seem to decrease to a stable level within 15 hours. After annealing at 400°C for 15 minutes the same stable level is reached, 24 hours after forming the annealing has no effect on the capacitance.

Peak voltages determined just after forming or two or three days later are the same. So it is concluded that the value of the dielectric constant changes during the period directly after forming.

This may be due to loss of water in the layer.

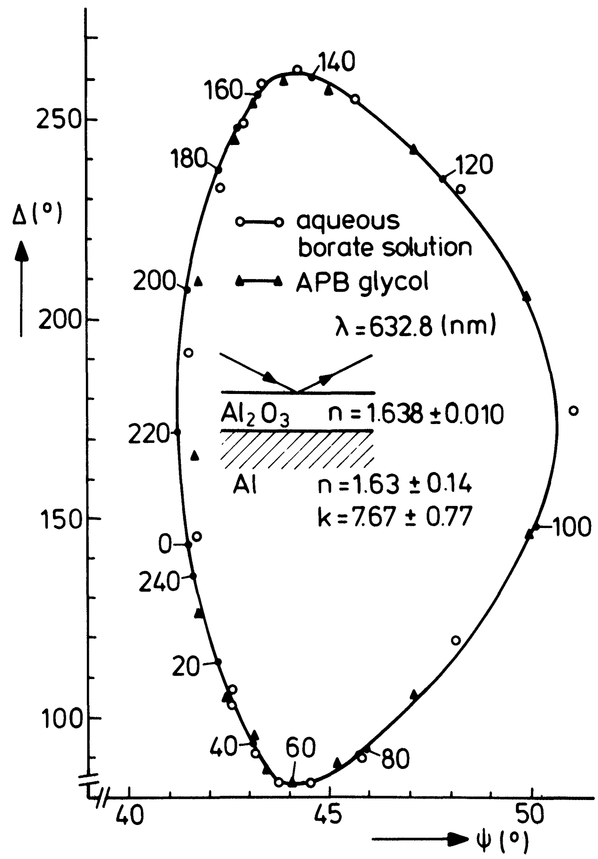

FIGURE 2 Ellipsometry curve obtained by the least squares method and the observations.
▲—▲ films formed in a solution of ammonium pentaborate in ethylene glycol at 25°C
○—○ films formed in an aqueous solution of borate at 25°C

2.4. *Ellipsometry*

The light source of the apparatus is a He–Ne laser (λ = 632.8 nm). The angle of incidence is chosen at 70°. To determine both the optical constants of the aluminum and the aluminum oxide at least square computer programme is used. The absorption coefficient k of the oxide layer is neglected.

For both types of layers, formed in APB-glycol and in the aqueous borate solution, the refractive index n_s and the absorption coefficient of the aluminum substrate k_s and the refractive index of the layers n_l are identical within the experimental error. The results are presented in Figure 2.

The numerical values of the optical constants are: n_s = 1.63 ± 0.14, k_s = 7.67 ± 0.77 and n_l = 1.638 ± 0.010. The optical constants of the substrate agree with the values found by Fane and Neal[9].

As they used a light source with λ = 549.0 nm, the results are translated to that wavelength by means of the relations of the free electron model. The values of the refractive index of the oxide film agree with those of Dell'Oca[10] and Vašiček cited by Fane and Neal[9] (1.62 ± 0.02 and 1.635).

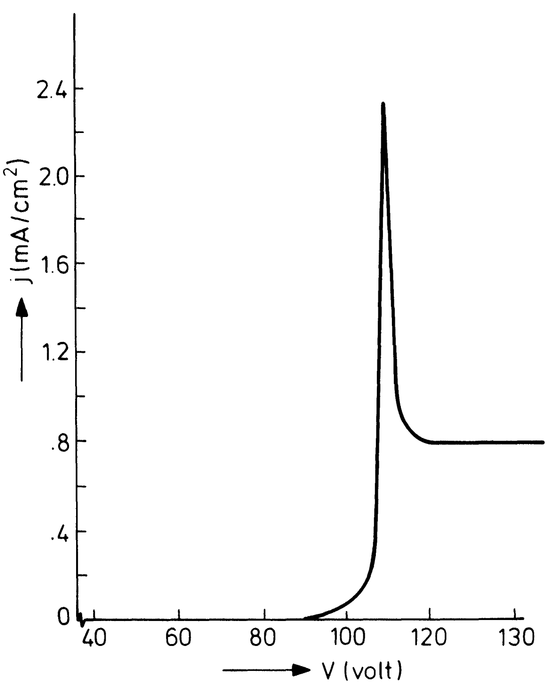

FIGURE 3 Current density versus voltage at a constant voltage rate of 0.367 V/s. Specimens are formed to 100 V and annealed at 400°C for 15 minutes.

2.5. *Determination of the Peak Voltages*

The specimens are annealed in a normal atmosphere at 400°C for 15 minutes. Then a voltage increasing linearly with time at a rate of 0.367 V/s is applied across the oxide film immersed in the APB-glycol electrolyte. The current is recorded and after the peak has been reached the voltage is switched off. An example is given in Figure 3.

To see whether there is a great dependency on the voltage rate, some films are formed in APB-glycol at voltages up to 100 V. Then the peak voltages are determined with voltage rates varying from dV/dt = 0.17 V/s to dV/dt = 0.56 V/s. The results are plotted in Figure 4. With the above layers a change of 10% in dV/dt results in a change in V_p of 0.5 V.

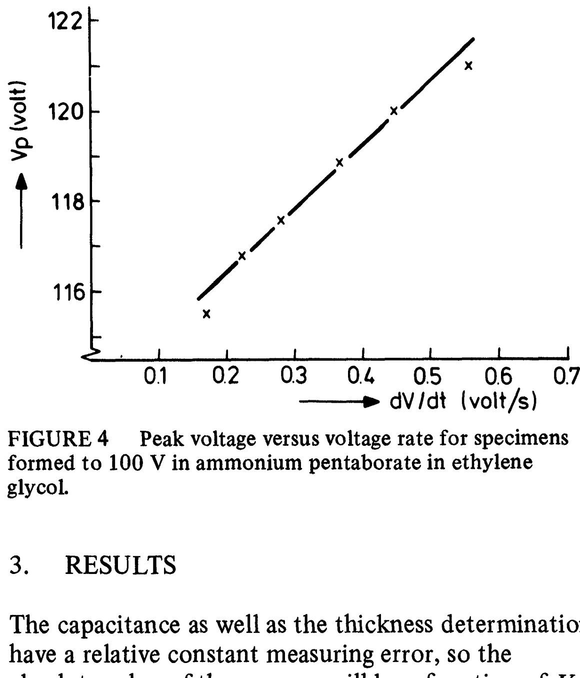

FIGURE 4 Peak voltage versus voltage rate for specimens formed to 100 V in ammonium pentaborate in ethylene glycol.

3. RESULTS

The capacitance as well as the thickness determinations have a relative constant measuring error, so the absolute value of these errors will be a function of V_f. Thickness or linear functions of thickness versus V_f or V_p will have a regression line that depends strongly on the values at the high voltages, because of this large absolute error. To get out of this difficulty the thickness is eliminated from the relations. From:

$$C = \epsilon_0 \epsilon_r r A/d \tag{1}$$

$$V = Fd \tag{2}$$

one gets:

$$CV = \epsilon_0 \epsilon_r r A F \tag{3}$$

$$Cd = \epsilon_0 \epsilon_r r A \tag{4}$$

from (4) follows:

$$\epsilon_r = Cd/(\epsilon_0 rA) \qquad (5)$$

from (2) follows:

$$F = V/d \qquad (6)$$

where:

$\epsilon_0 = 8.86.10^{-12}$ (F/m)

ϵ_r = relative dielectric constant of Al_2O_3

r = 1.04, roughness factor

$A = 10^{-3}$, area (m^2)

d = thickness of the layer (m)

F = field strength (V/m)

Presented in the following figures are the constants related to the measurements.

3.1. CV_f versus V_f

The quantity CV is very important in the production of electrolytic capacitors. Then V is an indication of the voltage the oxide film can withstand without exceeding a specific current value. For a first comparison the CV_f product is considered.

Figure 5 gives the quantity versus V_f. Values of CV_f are systematically higher when formed in APB-glycol than when formed in aqueous borate. CV_f seems to exhibit a slight dependency on V_f. This cannot be explained from sequence effects because in the experimental set-up forming voltages are not selected in sequential order. An estimate of the 100 V value of CV_f by averaging the data at voltages from 70 to 140 V is $CV_f = 6.52$ ($\mu C/cm^2$) for films formed in APB-glycol and $CV_f = 6.37$ ($\mu C/cm^2$) for films formed in the aqueous borate solution.

3.2. Thickness versus Capacitance

According to formula 5 the dielectric constants are calculated from the thickness and from the capacitance found after ellipsometry. In Figure 6 ϵ_r is plotted versus V_f for both the solutions. As the relative inaccuracy of the thickness values over 60 nm is less than 1% but that of thickness values under 60 nm is more than 2%, the latter are not included in further calculations. The mean ϵ_r value of layers formed in APB-glycol is $\epsilon_r = 8.65 \pm 0.10$ and in the aqueous borate solution $\epsilon_r = 8.88 \pm 0.14$. The values of ϵ_r are not in constrast with those found by Bernard and Cook[7] for films formed in APB-glycol and are in agreement with the values of Ikonopisov *et al.*[1]

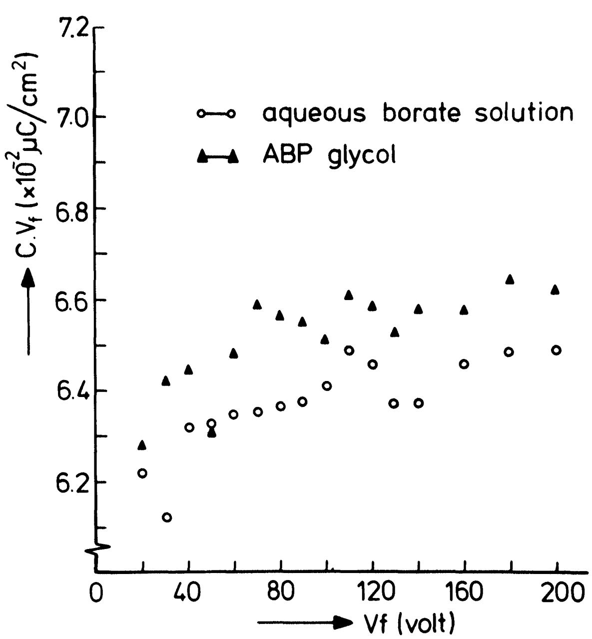

FIGURE 5 CV_f versus forming voltage.
▲—▲ films formed in a solution of ammonium pentaborate in ethylene glycol at 25°C.
○—○ films formed in an aqueous solution of borate at 25°C

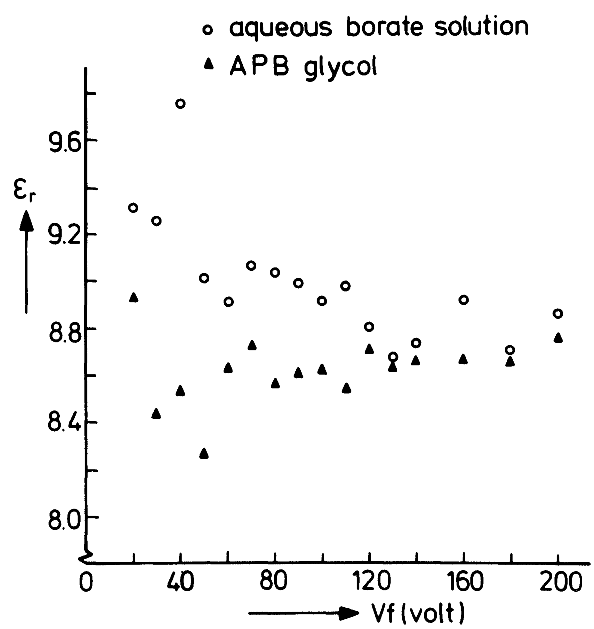

FIGURE 6 Relative dielectric constants versus forming voltage.
▲—▲ films formed in a solution of ammonium pentaborate in ethylene glycol at 25°C
○—○ films formed in an aqueous solution of borate at 25°C

for films formed in the aqueous borate solution. Directly after forming the CV_f products (at 100 Hz) of the films formed in APB-glycol are the same as those found by Bernard and Cook[7].

3.3 *Thickness versus V_f*

According to formula 6 the parameter of this relation is the field strength. This quantity is plotted versus V_f in Figure 7. The field strength during forming in the APB-glycol solution is $F = (8.01 \pm 0.07) \cdot 10^8$ V/m with a current density of $j = 0.34\ mA/cm^2$. In the aqueous borate solution the field strength is $F = (7.60 \pm 0.05) \cdot 10^8$ V/m and the current density $j = 0.35\ mA/cm^2$.

Bernard and Cook[7] found from the optical thickness determinations a value of $F = 8.46\ 10^8$ V/m with $j = 0.34\ mA/cm^2$ and for forming in the aqueous borate solution Andreeva and Ikonopisov[8] found for $j = 0.35\ mA/cm^2$ a value of $F = 7.74\ 10^8$ V/m at 25°C.

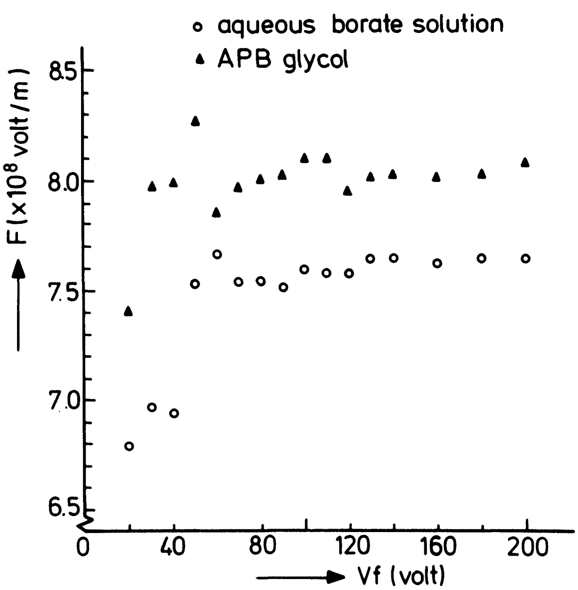

FIGURE 7 Field strength calculated from the ellipsometry thickness measurements and the foming voltage.
▲—▲ films formed in a solution of ammonium pentaborate in ethylene glycol at 25°C
o—o films formed in an aqueous solution of borate at 25°C

3.4. *Thickness versus V_p*

Plotted in Figure 8 is the relation between the thickness and the peak voltage V_p. Linear regression

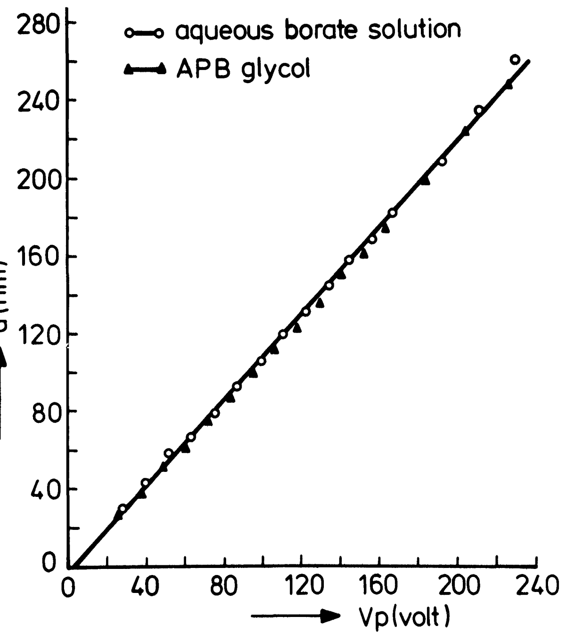

FIGURE 8 Thickness versus peak voltage.
▲—▲ films formed in a solution of ammonium pentaborate in ethylene glycol at 25°C
o—o films formed in an aqueous solution of borate at 25°C

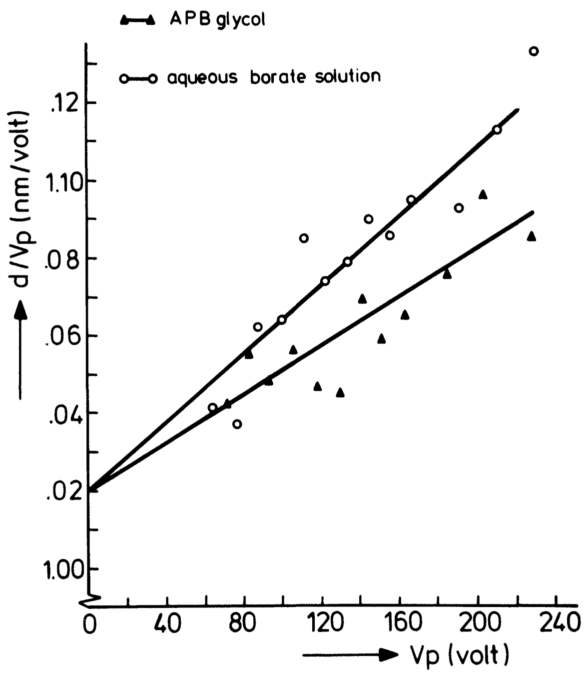

FIGURE 9 Thickness to peak voltage ratio versus peak voltage.
▲—▲ films formed in a solution of ammonium pentaborate in ethylene glycol at 25°C
o—o films formed in an aqueous solution of borate at 25°C

analysis gives the following relation between d and V_p.

$$d = (1.135 \pm 0.012)V_p - 7.8\ (\mathrm{nm}) \qquad \alpha = 5\%$$

α is the level of significance.

When the quantity d/V_p is plotted versus V_p, d/V_p seems to increase with V_p (see Figure 9). Now the curves do not have a good overlap. The regression lines using a linear relation with V_p give the following results:

layers formed in APB-glycol:

$$d/V_p = 1.020 + (0.00031 \pm 0.00012)V_p$$

layers formed in aqueous borate:

$$d/V_p = 1.020 + (0.00044 \pm 0.00011)V_p$$

with $\alpha = 5\%$.

The systematic error in the thickness determination by this method is a function of the film thickness. For voltages up to 150 V the difference in the relation between d and V_p for films formed in the different electrolytes is less than ±1%.

4. CONCLUSION

Crevecoeur and De Wit developed a method in which the barrier aluminum oxide film thickness is expressed in terms of peak voltages

In this work the relation is laid between the peak voltage and the thickness of the films.

The specimens are annealed at 400°C for 15 minutes and then subjected to a constant voltage rate of 0.367 V/s across the layer in a solution of ammonium pentaborate in ethylene glycol. The voltage (V_p) at which a current peak occurs has a well defined relation with the thickness of the oxide film.

The thickness of the layers are determined by ellipsometry. The relation of d and V_p for layers formed in an aqueous borate solution can be described by $d = 1.020 V_p + (0.00044 \pm 0.00011)V_p^2$ (nm). Layers formed in the ammonium pentaborate in ethylene glycol solution give a systematic lower value of d with V_p. For values of V_p lower than 150 V this error is less than 1%. So over a great range of forming voltages this method is a very accurate and easy one for estimating the thicknesses of barrier aluminum oxide layers. With layers formed at 100 V a variation of 10% in the voltage rate results in a 0.5 V change of the peak voltage.

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