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DUAL-DIELECTRIC MEMORY CELL FABRICATION BY ANODIZATION

by

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ABSTRACT

This letter presents a concept for producing the two insulators in a dual-dielectric memory cell by a single anodization step. Some benefits that should result from this process are discussed and preliminary data is presented.

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Dual-dielectric memory cells have recently become available commercially and possess attractive features as regards long information-retention time and electrical alterability[1]. The cell structure is usually metal|Si_3N_4 or Al_2O_3|SiO_2|Si with the silicon dioxide being formed by thermal oxidation followed by, for example, reacting silane with ammonia[2] to form silicon nitride or pyrolytically depositing aluminum oxide[3] from aluminum bromide in a nitric oxide-forming gas mixture. As an alternative to the above two-step dielectric formation processes we propose the fabrication of two dissimilar insulating layers by a single anodization process. The scheme is illustrated in fig. 1. Initially a metal layer is deposited on the silicon and immersed in an electrolyte suitable for converting the metal to an oxide. The choice of metal is thus limited to the group that can be anodized:[4] the electrolyte could be either an aqueous solution[4] or a gaseous plasma[5]. At some time t_1 after commencement of anodization (fig. 1b) the metal layer (e.g. Al) will be partially converted to anodic oxide (e.g. Al_2O_3) until at time t_2 all the metal is consumed (fig. 1c). Anodization past this point could lead to oxidation of the underlying semiconductor substrate (e.g. Si) leading to the formation of, e.g. SiO_2.

In dual-dielectric memory cells it is necessary to have a thin ($\sim$50 Å) bottom imsulating layer to facilitate charge exchange by tunnelling between the semiconductor and traps at the dual-dielectric interface, and a somewhat thicker ($\sim$1000 Å) top layer to help achieve long charge-storage times. With regard to the suggested process the top layer thickness can be predetermined by simply measuring the original thickness of the deposited metal layer and knowing the densities of the metal and resultant anodic oxide. The bottom layer thickness can be estimated by either *in-situ*

optical measurements (see below) or by monitoring the anodization parameters e.g. the voltage rise on constant current anodization. Because film formation by plasma anodization can be a slow process (typically 5Å min^{-1}) and slow rates can also be achieved in dilute solution anodization, good control over the critical thickness of the bottom insulating layer can be attained.

In principle, the detection of the point at which all the deposited metal is converted to oxide is not difficult when using *in-situ* ellipsometry. By way of an example fig. 2 shows the expected ellipsometry curve for the anodization of 670 Å of Al on top of silicon. The point of aluminum-anodization completion appears well-defined and the subsequent growth of silicon dioxide is detectable, and the cases of growth above and below the aluminum oxide layer are distinguishable. Experimental data for the anodization in the negative glow of an oxygen discharge[6] of a 670 Å Al film are also shown in Fig. 2. The experimental points follow the expected curve until about 70 Å of Al remain, at which point anodization does not proceed according to the assumed model of a well-defined planar oxide-metal interface moving uniformly towards the silicon surface (and parallel to the latter) until the metal layer thickness decreases to zero. Instead there appears to be a gradual transition of the 70 Å layer between the Al_2O_3 and the silicon from a metallic nature to a dielectric nature. This effect could result from the Al_2O_3-Al interface having a roughness on the scale of 100 Å, such that the Al film eventually becomes discontinuous with a topography similar to a slice of Swiss cheese. The oxide holes would then grow at the expense of the metal until the film becomes islands of aluminum which eventually disappear completely. The

1 mm. diameter of the ellipsometer light beam would have an averaging effect on these processes, giving the measured gradual transition. The experimental data between points X and Y in Fig. 2 are more consistent with oxygen ion motion producing SiO_2 under the Al_2O_3 layer than with silicon ion motion producing SiO_2 on top of the Al_2O_3 - the broken line shown in the figure is the calculated curve for the latter possibility.

Another possible source of the effect is the thin native oxide present on the silicon surface, which has been ignored in calculating the theoretical curve, Fig. 2. However, this oxide is expected to be largely 'absorbed' by the highly reactive aluminum when it first arrives from the evaporation source, and cause only a minor change in the optical properties of the aluminum next to the silicon. Even if the oxide persists as an intact layer, it would only move the turning point slightly.

In-situ capacitance measurements, utilising a retractable indium probe, made at point X in Fig. 2 varied only very slightly with dc bias, showing that the Al film was still essentially continuous at this stage, but measurements at point Y gave the characteristics high frequency C(V) curve of an MIS capacitor. On application of a gate pulse of -50V for 10 sec. the flat band voltage was observed to shift by 14V in a negative direction. This could indicate the transfer of electrons from interfacial traps to the silicon, although in this particular case the charge retention time was only about 30 minutes.

The above process, then, seems promising for the fabrication of dual-dielectric memory cells as it affords a means of forming two dissimilar dielectrics in a single step, with good control over critical film thicknesses. For the case of anodization in a gaseous plasma the process

step would be compatible with other techniques used in high-vacuum technology. In order for the process to be actualized the problem of interface roughness needs to be eliminated, and this is probably related to the deposition conditions existing during the initial metal film formation. By using heated substrates from which native oxide had been removed by sputter etching some improvement would be expected. This should lead to improvements in the integrity of the very thin bottom insulating layer and thus longer charge retention times. It is interesting that recent work[1] in dual-dielectric memory cells has advocated the deliberate inclusion of discontinuous metal islands at the dual-dielectric interface: such a situation probably arises naturally from the process described above although presently is associated with a poor semiconductor oxide layer.

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FIGURE CAPTIONS

1. Sequence showing the conversion of a deposited metal layer to an insulator followed by partial conversion of the underlying semiconductor to insulator.

2. Ellipsometry data for the anodization of an evaporated aluminum film on a silicon substrate (sample Al - SiI). The solid and broken curves are computer calculations. The solid curve represents an Al film (initial thickness 670Å) forming 1100 Å of Al_2O_3 on Si, followed by growth of an intermediate film of SiO_2. The broken curve is for the case of SiO_2 growth on top of the Al_2O_3 layer. Refractive indices used were Al, 1.21 - 6.80j; Al_2O_3, 1.45 - 0.02j; Si, 3.87 - 0.017j; SiO_2, 1.47. The circles represent experimental data for the plasma anodization of a 670 Å thick Al film on Si. In all cases, the angle of incidence was 69.29° and the laser wavelength 6328 Å.

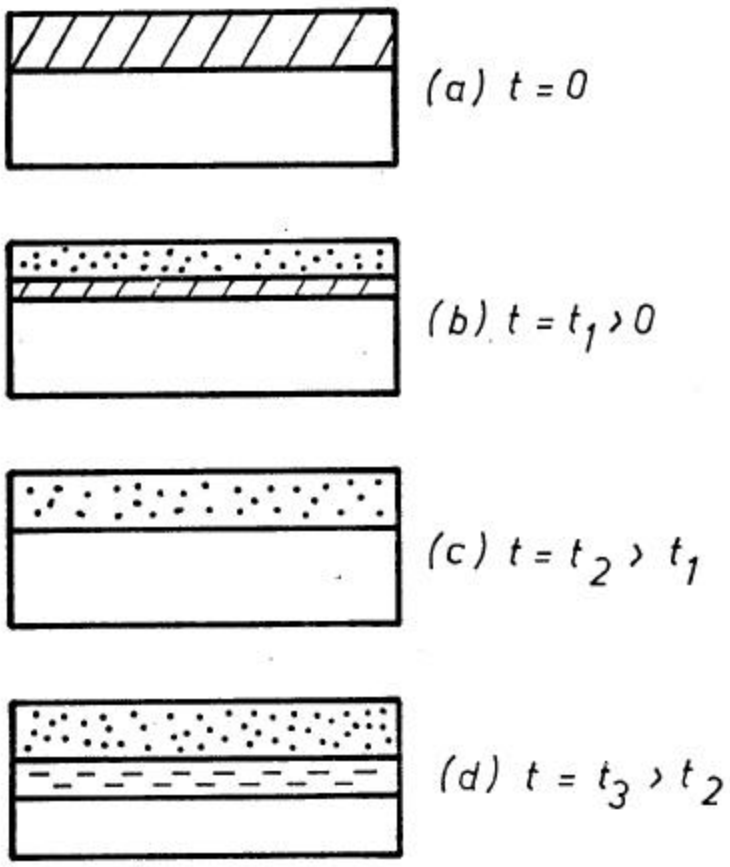

Fig 1 Clive et al

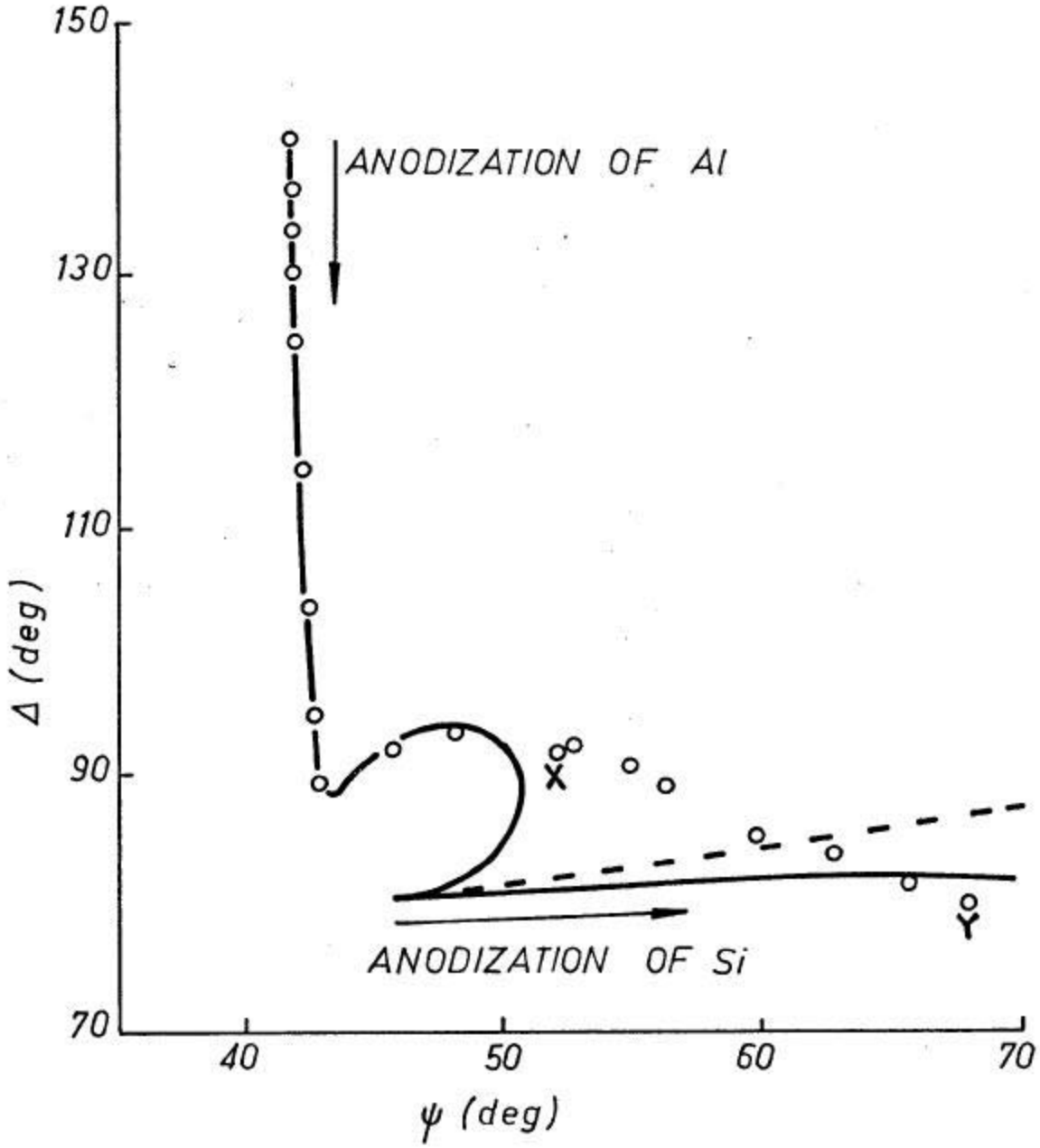

Fig 2 Olivé et al.

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