Reprinted from JOURNAL OF THE ELECTROCHEMICAL SOCIETY
Vol. 122, No. 11, November 1975
Printed in U.S.A.

The Deformation of Anodic Films during the Plasma Anodization of Al-Si Structures

J. J. H. Reche[1] and D. L. Pulfrey

Electrical Engineering Department, The University of British Columbia, Vancouver V6T 1W5, Canada

Although the insulator/semiconductor combination of SiO_2/Si has proved very successful in semiconductor device technology, other combinations are of interest for particular applications. For example, Al_2O_3 on Si would appear to be of interest in devices requiring good radiation resistance (1), low mobility of incorporated impurities, *e.g.*, Na^+ (2), low surface state density (3), and increased oxide dielectric constant (~ 8 *vs.* ~ 4). Memory action in metal Al_2O_3-Si FET's has also been observed (4). The Al_2O_3 film can be deposited in a variety of ways, *e.g.*, pyrohydrolysis of $AlCl_3$ (4), decomposition of Al-alkoxides (5), pyrolytic deposition from AlB_3 (6), rf sputtering (7), and

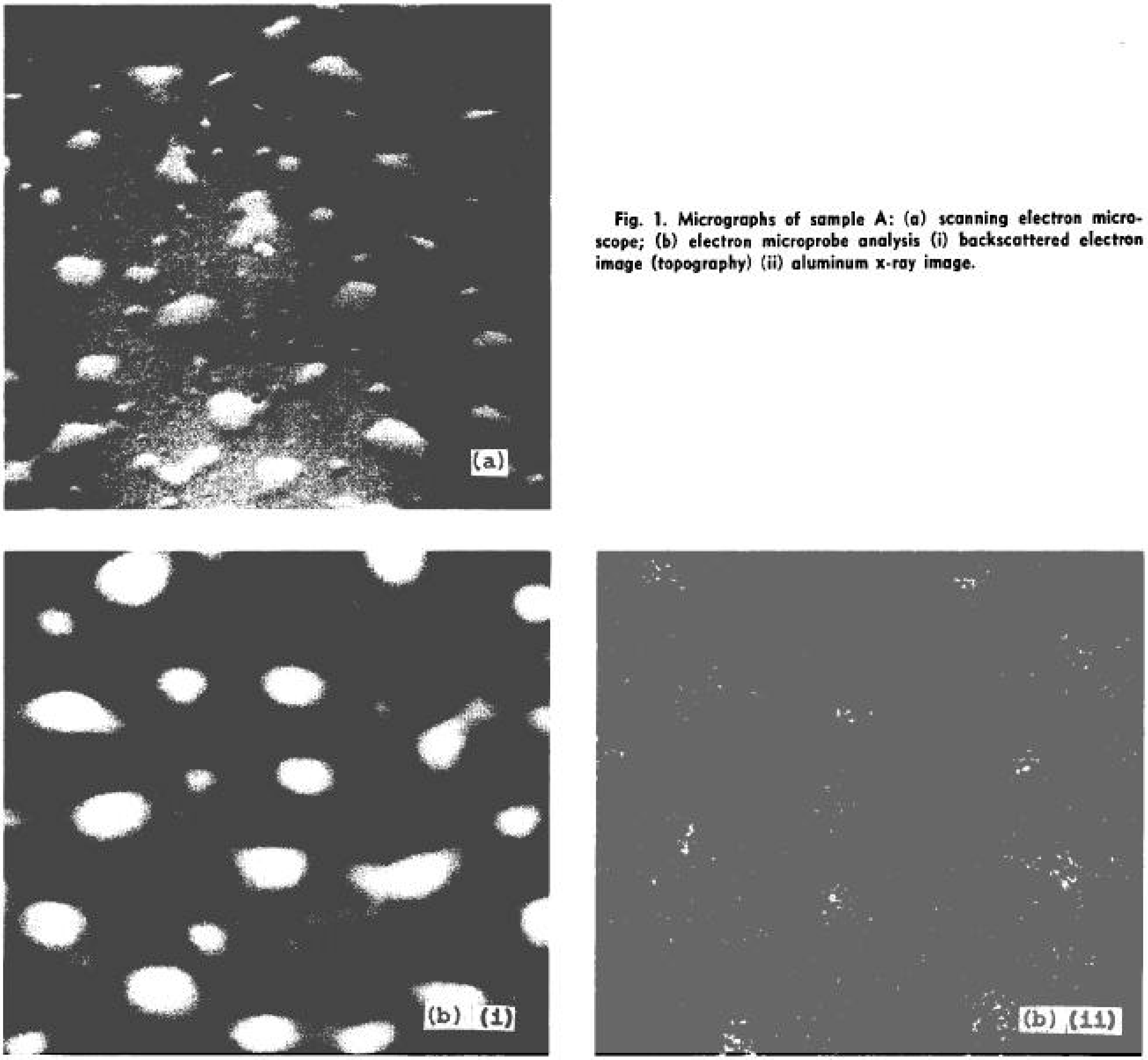

Fig. 1. Micrographs of sample A: (a) scanning electron microscope; (b) electron microprobe analysis (i) backscattered electron image (topography) (ii) aluminum x-ray image.

---

[1] Present address: GTE-Lenkurt Electric (Canada) Ltd., 7018 Lougheed Highway, Burnaby, B.C. V5A 1W3, Canada.

Key words: thin-films, stress, oxidation.

plasma anodization (1, 3). The latter method is considered here and results are presented indicating that severe deformation of the anodic oxide film can occur during anodization.

Anodization in an rf oxygen plasma was carried out utilizing the apparatus described in Ref. 8. The substrates used were (1-1-1) p-type silicon, 3-5 ohm-cm, and were etched in buffered HF and dried in nitrogen immediately prior to insertion in the vacuum chamber. The vacuum system had a liquid nitrogen trap and was operated at a base pressure of about 10^{-5} Torr. 99.999% grade aluminum was thermally evaporated from tungsten coil filaments onto the unheated substrates. The film deposition rate was approximately 100 A $\sec^{-1}$ and the mass deposited was monitored by a quartz crystal oscillator used as a microbalance. Film thicknesses were checked using a Sloan "angstrometer," Model M-100.

The data presented in this note refer to two samples anodized at a constant current of 16 mAcm^{-2}. Sample A had an aluminum film of initial thickness 450A and was anodized to slightly past the point at which *in situ* reflectance measurements (9) indicated, assuming homogeneous anodization, all the metal had been converted to oxide. Sample B's initial aluminum film thickness was 1650A and this was anodized until the Al_2O_3 was approximately 1000A thick.

Figure 1 shows a scanning electron microscope (SEM) micrograph and electron microprobe results for a section of the anodic film on sample A. Small hillocks are clearly visible on the two topographical photographs and these can be identified in Fig. 1 b(ii) as aluminum-rich regions. The hillocks are not thought to be related to structure in the as-deposited aluminum film as a SEM micrograph of an unanodized sample, deposited at the same time as sample A, revealed only very fine structure with any small visible features being spatially unrelated to the hillocks shown in Fig. 1.

Figure 2 shows SEM micrographs of a variety of hillocks and extrusions resulting from the anodization of sample B. Electron microprobe data from the same portion of sample B are shown in the four photos of Fig. 3. The four extrusions shown are clearly of a high aluminum content, yet possessing little or no oxygen or silicon. The dark vertical trails on the silicon x-ray image recording are the result of shadowing effects due to the low angle of the x-rays emitted by the silicon.

From the data presented it would appear that during anodization migration of aluminum in the metal film occurs and accumulation at sites of the order 10-20 μm apart develops. If anodization is continued for a long enough time (which will only be permitted by a thick enough metal film) these accumulations or hillocks of aluminum actually rupture the overlying anodic film and extrude.

The cause of the mass transport is unlikely to be electromigration (10), a source of failure in some IC's using aluminum interconnects and current densities $>10^6$ A-cm^{-2}, as the mass transport is in the direction of electron current flow (*i.e.*, opposite to that observed here) and, furthermore, the current densities are not high enough. *E.g.*, even if all the anodization current is assumed to flow through the hillocks, the current density would only be of the order of 10 A-cm^{-2}. A more probable cause is the presence of a film with high compressive stresses (the aluminum) under another film with lower diffusion rates (the aluminum oxide).

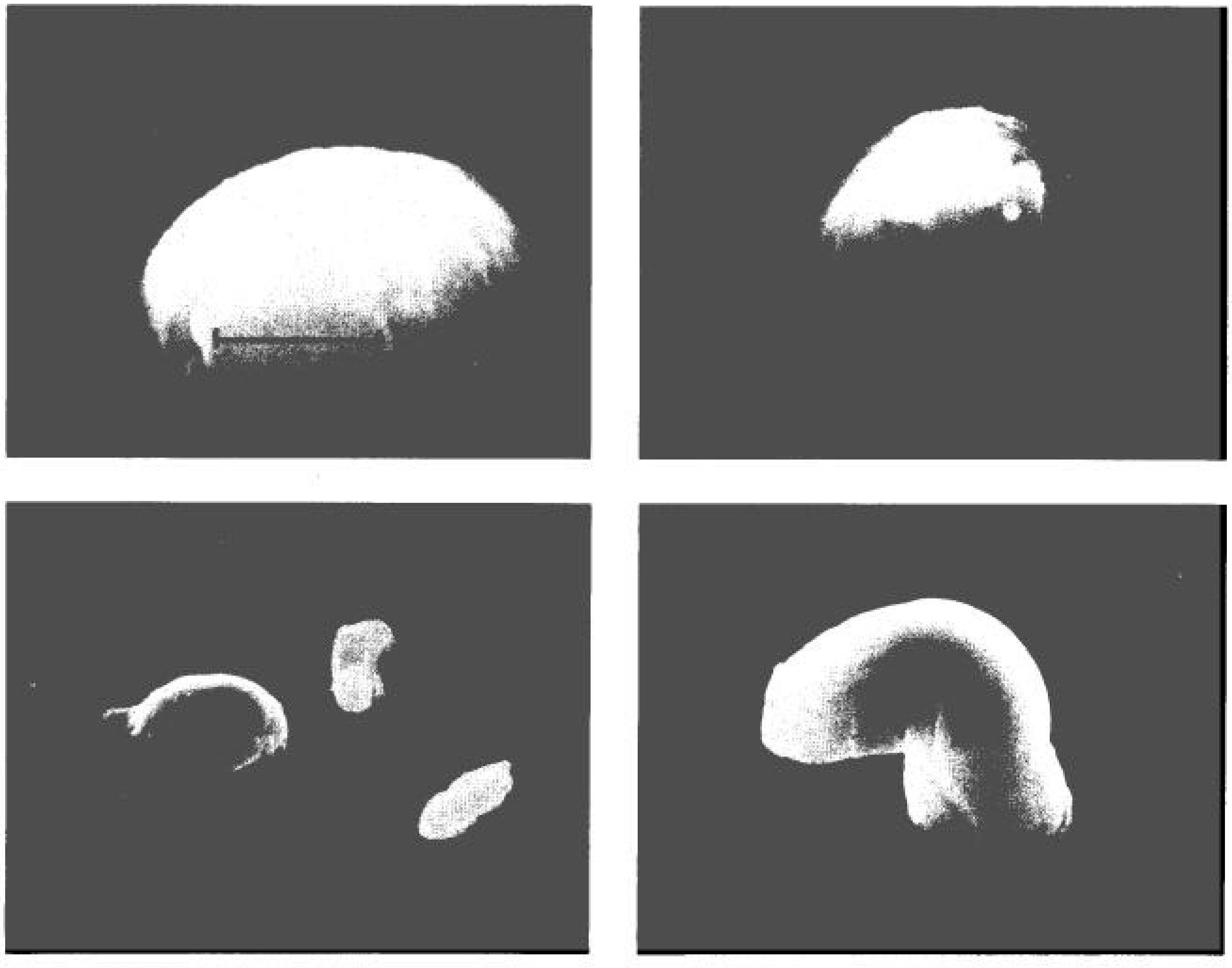

Fig. 2. Scanning electron microscope micrographs showing hillock formation and aluminum extrusions in sample B

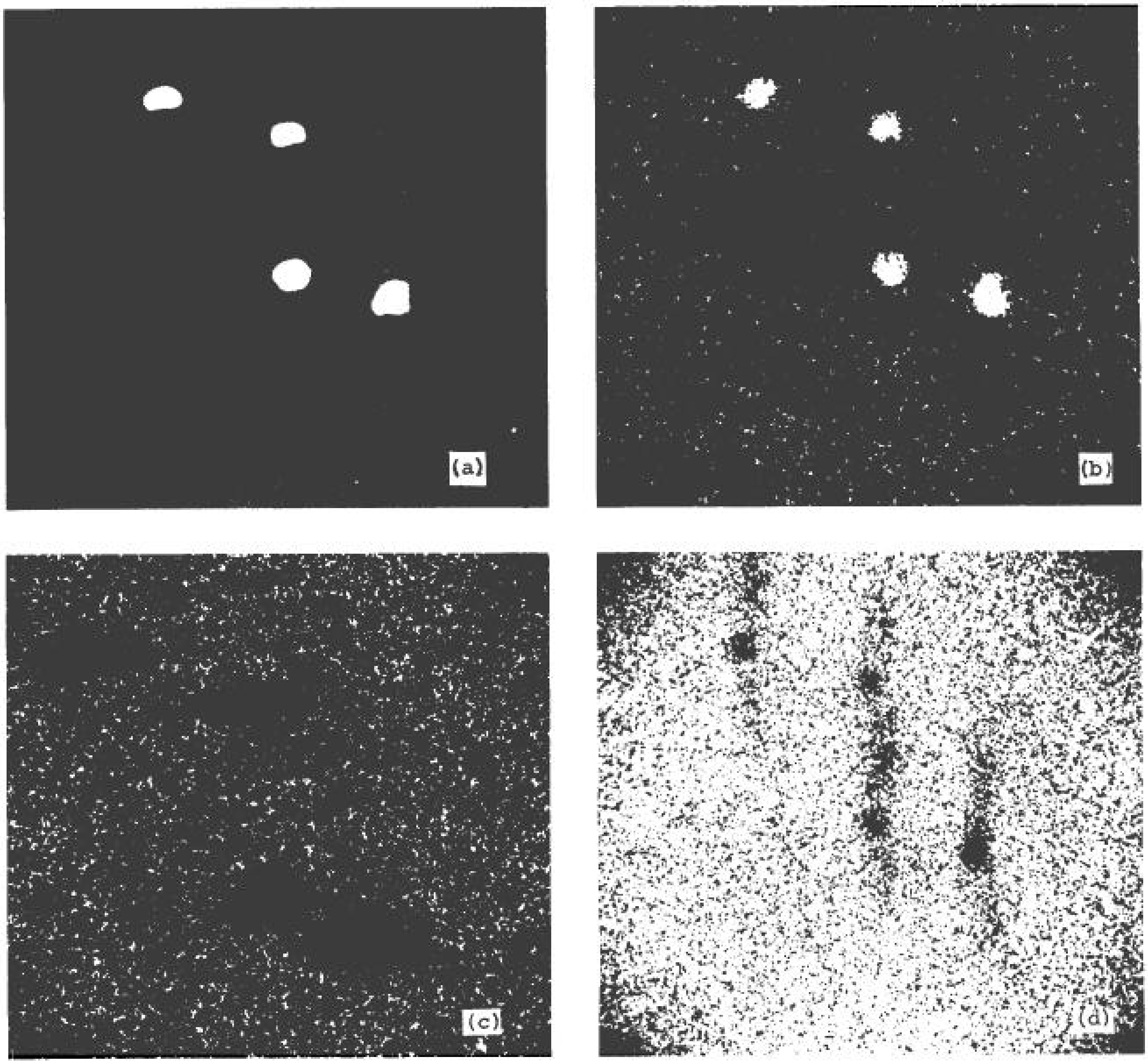

Fig. 3. Electron microprobe analysis of region of sample B: (a) backscattered electron image (topography); (b) aluminum x-ray image; (c) oxygen x-ray image; (d) silicon x-ray image.

The mechanism of stress relief is shown schematically in Fig. 4 and is similar to that treated theoretically by Chaudhari (11). In the case of compressive biaxial stress in the aluminum, the film will seek relief through the path of least resistance, *i.e.*, push the covering anodic film upwards. Although the oxide will accommodate some deformation by manifesting itself in hillocks, a crack will eventually occur, thus opening a path for stress relief by extrusion of the aluminum toward the free surface.

The presence of biaxial stress in the aluminum film could be due to growth defects, differential thermal expansion, temperature gradients, tensile stresses in the aluminum oxide film, and electrical stresses. In aluminum films internal stresses originating during vapor deposition have been shown (12) to cause hillocks, but this type of deformation does not seem relevant in the present case as SEM micrographs of unanodized aluminum films revealed no hillocks and, furthermore, annealing of the aluminum film prior to anodization did not prevent aluminum oxide film deformation on subsequent anodization. Stress analysis of d-c plasma-grown aluminum oxide (13) indicates the presence of stresses which are most probably tensile as the film apparently contracts in the presence of an anodizing field. In the present case evidence of tensile stresses in the anodic film was provided by the almost complete removal of the film if the anodization field was suddenly removed when either the current was high or the oxide was thick. This can be contrasted to silicon oxide films which appear (8) to relieve stress by forming "bubbles." In the present work no film deformation was ever observed to develop after anodization.

In conclusion it would apear that the hillock and film rupture phenomena are well explained by Chaudhari's (11) model, and that the biaxial compressive forces in the aluminum film result from a combination of some of the factors discussed above, with the presence of an anodizing field being a necessary ingredient.

Acknowledgment

The authors wish to thank Mr. A. Lacis for obtaining the SEM and microprobe data and the National Research Council of Canada for financial support.

Manuscript submitted Feb. 10, 1975; revised manuscript received May 27, 1975.

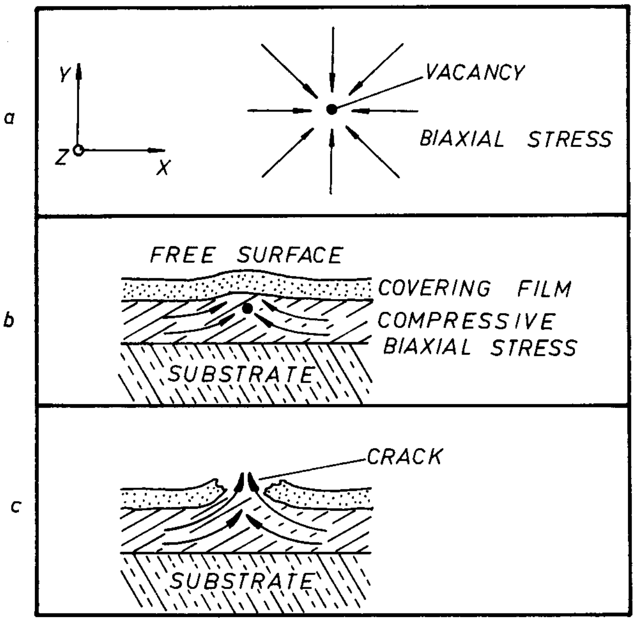

Fig. 4. Film on a substrate covered by another film with lower diffusion rate: (a) biaxial stress forces creating a vertical drift force component at a vacancy site; (b) mass flow under compressive biaxial stress; (c) mass flow toward free surface after rupture of the upper film.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1976 JOURNAL. All discussions for the June 1976 Discussion Section should be submitted by Feb. 1, 1976.

Publication costs of this article were partially assisted by the National Research Council of Canada.

REFERENCES

1. K. H. Zaininger and A. S. Waxman, *IEEE Trans. Electron. Devices,* **ED-16**, 333 (1969).
2. S. K. Tung and R. E. Caffrey, *This Journal*, **115,** 239C (1968).
3. F. B. Micheletti, P. E. Norris, and K. H. Zaininger, *R C A Rev.*, **31,** 330 (1970).
4. S. Nakanuma, T. Tsujide, R. Tgarashi, K. Onoda, T. Wada, and M. Nakagiri, *IEEE J. Solid-State Circuits,* **SSC5,** 203 (1970).
5. J. A. Aboaf, *This Journal*, **114**, 948 (1967).
6. P. Balk and F. Stephany, *ibid.*, **118, 1634** (1971).
7. C. A. T. Salama, *ibid.*, **118,** 1993 (1971).
8. D. L. Pulfrey and J. J. H. Reche, *Solid-State Electron.*, **17,** 627 (1974).
9. D. L. Pulfrey and J. J. H. Reche, *Appl. Opt.*, **12,** 1577 (1973).
10. I. A. Blech and E. S. Meiran, *Appl. Phys. Letters*, **11,** 263 (1967).
11. P. Chaudhari, *IBM J. Res. Develop.*, **13,** 197 (1969).
12. F. d'Heurle, L. Berenbaum, and R. Rosenberg, *Trans. AIME*, **242,** 502 (1968).
13. F. B. Micheletti and S. H. McFarlane, Abstract 22, Electrochemical Society, Extended Abstracts, Spring Meeting, Washington, D.C., May 9-13, 1971.