Solid-State Electronics, 1974, Vol. 17, pp. 627–632. Pergamon Press. Printed in Great Britain

PREPARATION AND PROPERTIES OF PLASMA-ANODIZED SILICON DIOXIDE FILMS

D. L. PULFREY and J. J. H. RECHE
Department of Electrical Engineering, University of British Columbia, Vancouver 8, Canada

(*Received* 24 *September* 1973; *in revised form* 8 *November* 1973)

Abstract—The preparation and properties of thin films of silicon dioxide formed at ~200°C by anodization in an RF plasma are described. A suitable procedure for obtaining good quality films is given along with information on the effects of film sputtering and internal stress build-up during anodization. Measurements on MOS capacitors utilising the plasma-grown oxide yielded information on oxide charges, Si/SiO_2 interface state density, oxide permittivity, leakage resistance and film breakdown strength. Additional measurements determined the physical properties of stochiometry, impurity content, refractive index and etching behaviour. The plasma-anodized films can be routinely grown to a quality comparable with the best thermally-grown oxides.

1. INTRODUCTION

The formation of thin film SiO_2 on Si is a very important aspect of modern integrated circuit technology: the thin insulating film can serve as a dopant mask, surface protector and passivator, component isolator and as an insulator in MOS structures. For details on the various methods available for forming SiO_2 on Si and for some discussion on the properties of the variously-formed films see, for example, refs.[1] and [2]. The oxidation of Si by thermal means is the most widely-used technique, but there would appear to be a need for a low temperature oxidation process that is compatible with other steps in the device-processing sequence. The wet solution anodization of Si satisfies the first of these conditions and recent work[3] has indicated that SiO_2 films with electrical properties similar to those of thermally-grown films can be prepared by this method. However, solution anodization has obvious disadvantages in the fabrication of devices, particularly integrated devices. It is preferable that all the steps in device manufacture be compatible with automated production in a multistation vacuum system, the sample being moved from station to station for each stage of development e.g. sputter etching, ion implantation of dopants, insulator formation, metallization, reactive sputtering. A method which would appear suitable for insulator production in such a scheme, and moreover can be accomplished at temperatures which are low compared to thermal oxidation, is plasma anodization[4, 5]. This technique has already been applied to Si[6–10] and the possible usefulness of the method has been demonstrated, although no comprehensive picture as to the precise and predictable properties of the plasma oxides has emerged.

The work described in this paper has sought to provide detailed information on the properties of plasma-anodized SiO_2 films as formed using an induced RF discharge[10]. Particular attention has been paid to setting up an anodization procedure that enables films of good quality to be grown reproducibly.

2. ASPECTS OF FILM GROWTH

2.1 *Apparatus and procedure*

The apparatus used differed only slightly from that described in detail in Ref.[10]. The modifications made pertained to the sample holder and the cathode used to return the anodization current to the plasma. The object of these changes was to enable the anodization of larger area samples and to reduce the possibility of film contamination by sputtered material. The sample holder was enlarged to a diameter of 2·5 cm and the quartz retaining shield (Fig. 1, ref.[10]) was replaced by a similar structure fashioned out of 0·01 cm thick aluminum and lined on the inside with mica. The cathode was changed from a 10 cm long, 1·5 cm dia. Al rod to a 3 cm dia. Al rod in which a series of grooves 12 mm deep, 3 mm wide was cut along its 15 cm length. This design served to increase the surface area exposed to the plasma (and thus improve coupling to

the discharge), but at the same time assisted trapping of much of the sputtered cathode material within the grooves.

After installation of the Si sample (prepared as described below) the discharge cell was evacuated to the limit, about 2 mtorr, of the absorption pump (see ref.[10]) and then back-filled with oxygen (Matheson ultra high purity grade) to about 1 torr. During anodization the pressure was maintained at typically 30 mtorr by manual adjustment of a leak valve in the gas supply line. The system was continually pumped during anodization. The plasma was initiated by an external tesla discharge and the sample to be anodized was situated at one edge of the luminous region of the plasma while the cathode penetrated into the plasma about 5 cm from the other boundary. The cathode-sample distance was about 30 cm and the exciting coil was centred over a region about 10 cm from the sample. The discharge frequency was 1 MHz and a generator output power of around 3 kW was employed. Forced air cooling of the sample was used and, over the range of anodization currents used, the temperature, measured by chromel–alumel thermocouple, at the back face of the Si ranged from 170 to 220°C.

Anodizations were always performed in the constant current mode: a changeover to constant voltage operation at some predetermined voltage, a step often used in solution anodization to improve film quality, was not found desirable (see section 2.4). Current densities in the range 5–30 $mAcm^{-2}$ were used. Anodization was terminated when the reflectance data[11, 12] indicated that the desired film thickness had been reached.

2.2 *Substrate preparation*

Both p- and n-doped substrates, of orientation 1-1-1 and resistivity 3–5 Ω cm, were used and were received with one face having a mirror finish, the latter the result of standard mechanical and chemical polishing treatments. The samples were cut with a diamond-tipped scriber to fit the sample holder and the area subsequently exposed to the plasma was about 2·0 cm^2. A number of wafers was subjected to a two-solutions cleaning treatment[13] devised to remove organic and metallic contaminants. Some other substrates were immersed in a standard buffered HF solution to remove any native SiO_2 present. As the cleaning techniques used did not appear to influence the properties of the subsequently-grown anodic films the substrates utilised in the work reported here were used as supplied from the manufacturer.

2.3 *Growth rate*

In this work no attempt was made to carry out the different constant current anodizations under the conditions of rigorous temperature control necessary for analysis of film growth kinetics. Figure 1 merely serves to indicate the magnitude of the attained growth rates and also to demonstrate that the latter depend certainly on anodization current and probably on sample temperature. The linear relationship between oxide thickness and time makes comparison of growth rates with other methods

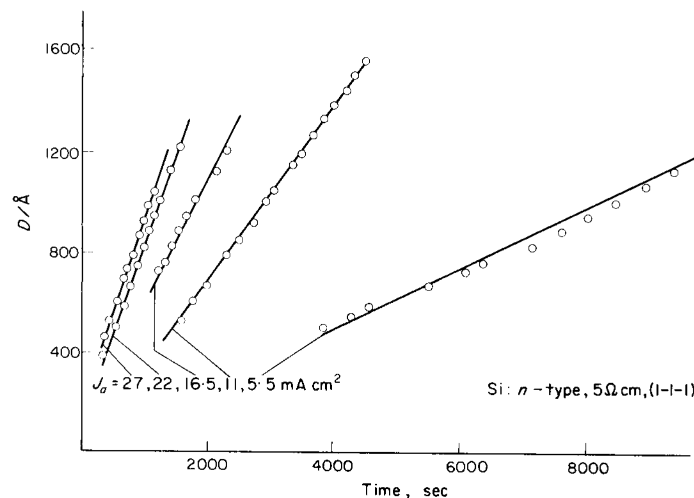

Fig. 1. Growth rate of SiO_2 for different anodizing current densities. (Approx. sample temperatures, left to right, 220, 200, 185, 175, 170°C).

(e.g. thermal oxidation[1] and plasma anodization in microwave frequency discharges[6, 7]) where a parabolic relation holds somewhat arbitrary. However, typical figures are 20 Å/min for oxidation at 1100°C in dry oxygen[1], 100 Å/min for microwave-plasma anodization[6] at about 400°C, 25 Å/min for oxidation[1] in high pressure steam at 650°C, and 52 Å/min for RF plasma anodization at 220°C (see Fig. 1). Comparable growth rates to the above have not been recorded in d.c. plasma anodization[8, 15], but this may be a result of the low temperatures used (less than 100°C) and not necessarily indicative of a relevant fundamental difference between d.c. and high frequency plasmas.

2.4 *Film sputtering during growth*

Some sputtering of the film during anodic growth can be expected owing to the combined presence of ions within the plasma and a potential difference across any sheath that might separate sample and bulk plasma. In this work any sputtering action at the sample due to bombardment by particles removed from the metallic components in contact with the plasma was minimized by the geometrical design of the anodization cell. No aluminum that could have originated at the cathode or sample holder, could be detected in the SiO_2 films using electron microprobe analysis. A possible mild sputtering action of the plasma itself has been previously commented upon[7, 9] and evidence for such action has been noted in this study. e.g. On interruption of the anodizing current slow changes in reflectance took place that could be interpreted as a decreasing of the oxide thickness. Hence it appears that film growth is a dynamic balance between anodization and mild sputtering.

Providing that the film growth rate is large compared to the sputtering rate, the continuous removal of surface material may be beneficial in that it would automatically eliminate positive ions attracted (or repelled) to the film surface. Sodium ions and protons in particular are known to cause instabilities in MOS devices fabricated using thermally-grown oxides. In addition, work[16] on sputtered SiO_2 films indicates that re-emission of SiO_2 during actual film deposition aids in the preparation of high quality films possessing high breakdown strength and low ratio of "pinhole breakup thickness" to total film thickness.

A feature of the plasma-anodized films prepared in this study that may be related to sputtering effects is that the quality of the oxide appeared to depend on the anodizing current density. Films grown at low current densities, 0·25–2·5 $mAcm^{-2}$, often exhibited damaged regions[10] where the oxide film was completely missing. A photograph of such a region is shown in Fig. 2; the most damaged area was usually situated at the edge of the sample which is shown here. Irregular sputtering seems to have taken place leaving an extremely rough surface (this damage is obviously different from that caused by internal stresses, see section 2.5 and Fig. 3). The area where reflectance monitoring was carried out displayed only few irregularities, but even a small number of pinholes in the film thus exposing the substrate, would be necessary to explain the measured small imaginary component of the refractive index of these samples, see section 3.6. On the other hand, films displaying good electrical characteristics, i.e. those grown at current densities in the range 5–30 $mAcm^{-2}$, were completely featureless at magnifications as high as 10,000-times. It would thus appear that the sputtering rate varies very little with anodizing current when compared to the dependence exhibited by the growth rate (see Fig. 1), and that at low anodizing currents (low film growth rates) the sputtering action can dominate in some regions of the oxide, thus creating serious flaws.

2.5 *Film stresses*

A well-known aspect of anodization[17] is that anodic films will breakdown during formation if growth is attempted beyond a certain thickness, or range of thicknesses. This "critical thickness" depends upon the material and the conditions of film growth.

Our experimental evidence points to breakdown due to large stresses in the silicon dioxide films leading to stress relief by visible deformation, followed by eventual lift-off of the film from the substrate. A current density–thickness product seems to bear some relation to the film growth limit, e.g. at about 2 $mAcm^{-2}$ films can be grown beyond 3000 Å before breakdown, while at 30 $mAcm^{-2}$ breakdown occurs around 1200 Å. Much thicker films (~ 8000 Å) have been obtained in microwave plasmas[6, 7], but the important factor here is probably sample temperature i.e. in the latter works temperatures around 400°C were used, probably enabling considerable thermal relief of stresses. Figure 3 shows a SEM micrograph of a film in the process of breaking down. Stereoscopic views were taken in order to ensure that the film was effectively buckling up, indicating compressive stresses. Similar damage has been reported[18] for Al_2O_3 films grown in a d.c. discharge. Some of the "blisters" shown in Fig. 3 have collapsed, indicating that the compressive stresses decrease somewhat after the

[Facing p. 628]

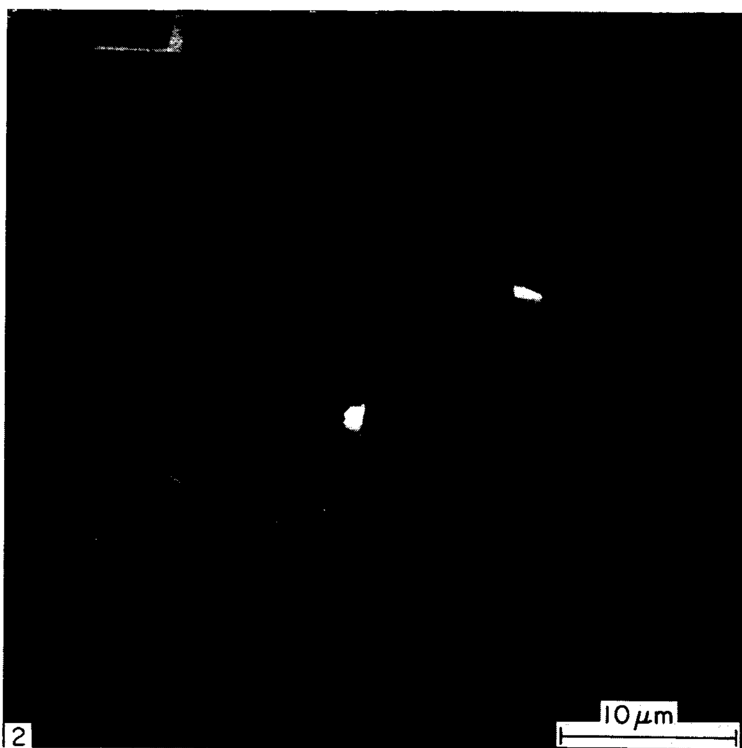

Fig. 2. SEM micrograph of outer region of SiO_2 film grown at 1·5 $mAcm^{-2}$. The white specks are dust particles.

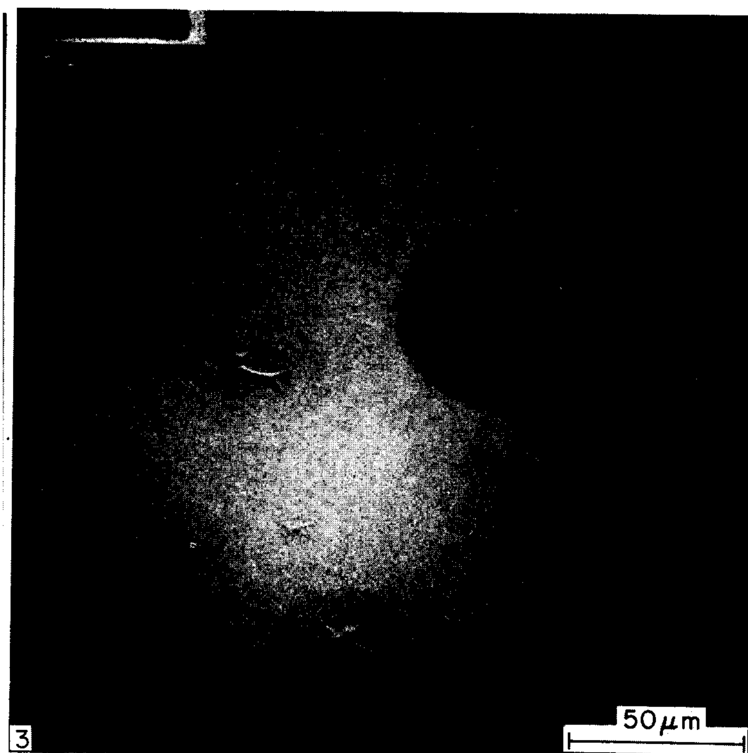

Fig. 3. SEM micrograph of SiO_2 film grown to a thickness close to the "critical value".

removal of the film-forming bias current. Further evidence that the stresses are strongly related to electrical conditions in the film is demonstrated by the fact that, if the film is thick enough, the film can break down if the anodizing current is suddenly switched off, i.e. the film can only accommodate the sudden reduction in stresses by drastic restructuring.

3. FILM PROPERTIES

Silicon dioxide films used in the following measurements were uniform in appearance and did not exhibit any of the damaged features reported in sections 2.4 and 2.5, i.e. films were grown at anodizing currents in the range 5–30 $mAcm^{-2}$ and to a thickness less than the "critical" value.

3.1 *MOS capacitance and related properties*

Electrical test patterns, consisting of an array of evaporated aluminum dots 0·12 mm radius with centres spaced 0·58 mm yielding about 400 capacitors per sample, were used. Capacitance measurements were carried out in a light-proof, electrically-shielded chamber using a Boonton 71A capacitance meter for the high frequency tests and a quasi-static method[19] for obtaining low frequency data. A ramp rate of 80 mV sec^{-1} was found suitable to maintain thermal equilibrium[20] during the low frequency measurements.

Samples tested with no annealing treatment displayed flat band voltages up to -25 V, indicating the presence of a large positive charge[10]. However this charge could be greatly reduced by low temperature annealing and its initial presence did not seem to influence subsequent oxide quality. It is likely that the space charge is generated by ionizing radiation from the plasma, e.g. electrons, X-rays or ultra-violet photons, although the trapping of Si ions, participating in the film growth process, is another possibility. With further regard to plasma-induced charge recent work[21] has shown that fixed charge and interface state density increases can be caused in SiO_2 by bombardment with ions even of the low energies expected to be present in the discharge arrangement used here.

Samples, with counterelectrodes, annealed at 450°C in dry N_2 for 15 min typically displayed a flat band voltage of $-1{\cdot}7$ V and the variation in flat-band voltage between capacitors on the same wafer never exceeded $\pm 0{\cdot}2$ V. No room temperature instabilities or hysteresis effects were observed. Surface state densities were computed using the procedure outlined by Kuhn[23] and a typical distribution across the silicon band gap is shown in Fig. 4, which indicates a mid-gap density of 5×10^{11} states $cm^{-2}eV^{-1}$. For comparison purposes a silicon sample from the same batch as that used in obtaining the data of Fig. 4 was used to prepare a 1100 Å-thick oxide by oxidation in dry O_2 at 1150°C using the Bell–Northern Laboratories pilot line facility in Ottawa. After annealing under the same conditions as above the thermally-grown sample exhibited a mid-gap surface state density about nine times less than the plasma-grown film. This probably indicates that the annealing treatment used, while known[24] to be good for thermally-grown SiO_2 is not optimum for the plasma-grown films. For example, while the annealing-out[22] of charges and instabilities caused by electrons, X-ray or ultra-violet light requires temperatures of about only 300°C, the effects of ion bombardment[14, 21] need temperatures in the 600–800°C range. It appears, therefore, that there is some ionic trapping in the plasma-grown films. Trapped charges in d.c. reactively-sputtered SiO_2 have been attributed[14] to O_2^+ being continually adsorbed at the film-plasma interface;* a similar situation may exist here. Further evidence of the need for a high temperature anneal of plasma-grown films is given by Ligenza and Kuhn[9] who reported surface state densities of $1\text{–}3 \times 10^{11}$ states $cm^{-2}eV^{-1}$ for d.c. arc-grown SiO_2 annealed in H_2 at 350°C. This figure could be reduced to less than 10^{10} states $cm^{-2}eV^{-1}$ by a 30-min treatment in H_2 at

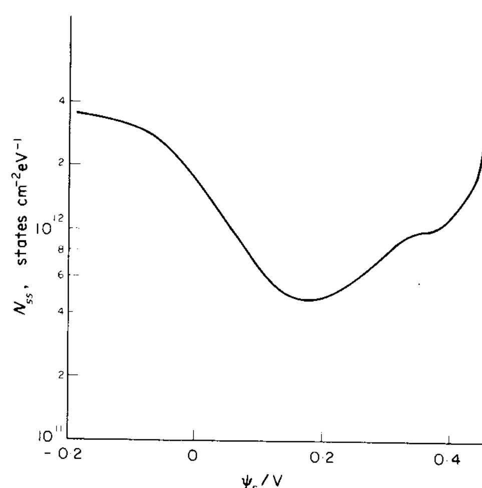

Fig. 4. Surface state density vs surface potential for n-Si sample plasma-anodized at 16·5 $mAcm^{-2}$ and annealed at 450°C in dry N_2 for 15 min. Oxide thickness 1060 Å.

*The authors thank one of the referees for pointing out this possibility.

1000°C. No such high temperature anneals were performed in this work even though some improvement in surface state density could be expected.

From the capacitance measurements corresponding to the case of Si in strong accumulation, the relative permittivity of the plasma-grown SiO_2 films was calculated and always found to be in the range 3·6–4·0, with the variation being most likely due to discrepancies in estimating gate area, rather than to a dependence on process variables.

Using theoretical curves[25] of normalized minimum capacitance vs oxide thickness and experimental values from the present work it was found that the silicon doping density was unchanged from that computed to exist in wafers prior to processing. Hence no redistribution of impurities or uncontrolled doping through contamination appeared to have taken place, even though handling precautions taken were minimal. It follows that, in the determination of substrate doping profiles by anodic sectioning techniques, plasma anodization offers an alternative to the normally-used[26] solution anodization with potential advantages in control of contaminants.

3.2 *Insulating properties*

The breakdown field strength was computed from the voltage required to induce catastrophic breakdown in 120 MOS capacitors taken from four different samples in the 1000–1200 Å thickness range. The voltage polarity was such as to drive the Si into accumulation and the calculated average value of breakdown strength was $8{\cdot}85 \times 10^6\,Vcm^{-1}$, with a variance of $0{\cdot}85 \times 10^6\,Vcm^{-1}$.

MOS capacitors with guard rings were prepared by photolithographic etching techniques and bulk leakage currents were measured with a Keithley model 602 electrometer. The gate voltage polarity was such as to accumulate the silicon surface. The resistivity of the oxide was calculated to be about $1{\cdot}4 \times 10^{16}\,\Omega$ cm for samples at room temperature in the 1000–1200 Å thickness range.

During the electrical testing of the above MOS capacitor structures only one device was found to be shorted by pinholes.

3.3 *Etching properties*

Some plasma-grown anodic oxides apparently have poor etching characteristics, e.g. Al_2O_3 films have been reported[27] to soften and peel from the substrate before appreciable etching occurs, Nb_2O_5 films have been stated[28] to etch very non-uniformly. No such problems of adhesion or uniformity have appeared in the SiO_2 films prepared in this work using a standard buffered HF solution as etchant. Etch rates in this solution were around 200–300 Å/min. Fine patterns have been satisfactorily etched in the oxide and Schottky photodiodes[29] with plasma-grown guard-rings constructed.

3.4 *Infrared spectra*

Infrared spectroscopy is a valuable technique for evaluating the bonding characteristics, stochiometry, density and porosity of thin films, besides shedding light on possible impurities present[2]. SiO_2 films grown in this study were investigated using a Perkin–Elmer model 475 recording spectrophotometer and no differences were detected between samples anodized in the current density range 5–30 $mAcm^{-2}$. The Si–O stretching band occurred at 1075 cm^{-1}, which is within the range reported for thermally-grown oxides, and had a half-width of 85 cm^{-1}. This latter figure is slightly larger than that of the best thermally-grown films (78 cm^{-1}) and may be an indication of slight bond strain. For further comparison purposes[30] samples prepared by wet anodization showed a shift in band position (1040 cm^{-1}) and larger bandwidth (96 cm^{-1}), whereas reactively sputtered SiO_2 and oxide formed by the CO_2 process displayed spectra nearly identical to those found in this study.

No absorbed water, which would indicate a porous film, or any other contamination was detected in any of the samples.

3.5 *Stochiometry*

Films subjected to nuclear backscattering analysis at the Kellogg Laboratory in California yielded spectra that were indistinguishable from those reported[31] for thermally-grown SiO_2. Within the statistical errors involved in the analysis the plasma-grown oxides can be classed as stochiometric. For comparison purposes[31] solution-grown anodic oxide was found to have an oxygen–silicon ratio dependent on water content, sputtered oxides had an oxygen–silicon ratio of 1·9–1·95 while that for samples grown from SiH_4 in an oxygen atmosphere was about 1·85.

3.6 *Refractive index*

During the routine growth experiments reported here the index of refraction at 6328 Å was measured[12] to always lie between 1·460 and 1·465. This can be compared to the figure of 1·45 generally quoted for thermally-grown oxides.

Films grown at very low current densities ($< 2{\cdot}5\,mA\,cm^{-2}$) and exhibiting some sputtering

damage similar to that shown in Fig. 2 had complex refractive indices with the real part generally falling within the range 1·30–1·42 and the imaginary part lying between 0·014 and 0·034.

4. CONCLUSIONS

The work reported here indicates that thin films of SiO_2 can be routinely grown by plasma anodization to a quality that is comparable with the best thermally-grown oxides. The low temperature ($\sim 200°C$) of the process is an added asset and, as the technique is compatible with other vacuum processing steps, complete MOS device fabrication in a vacuum environment appears an attractive possibility.

Acknowledgements—The authors sincerely thank Drs. C. A. T. Salama, W. Westwood and M.-A. Nicolet for respectively providing a computer program for analysing the quasi-static $C-V$ data, arranging the fabrication of thermally-grown SiO_2 films, performing nuclear backscattering experiments. The financial assistance of the National Research Council of Canada was also most appreciated.

REFERENCES

1. R. M. Burger and R. P. Donovan (Eds.). *Fundamentals of Silicon Integrated Device Technology*, Vol. 1, chapters 2–3, Prentice-Hall, New Jersey (1967).
2. L. I. Maissel and R. Glang (Eds.), *Handbook of Thin Film Technology*, chapter 11, McGraw-Hill, New York (1970).
3. J. D. E. Benyon, G. G. Bloodworth and I. M. McLeod, *Solid-St. Electron.* **16**, 309 (1973).
4. J. F. O'Hanlon, *J. Vac. Sci. Tech.* **7**, 330 (1970).
5. C. J. Dell'Oca, D. L. Pulfrey and L. Young, *Physics of Thin Films*, (edit. by G. Hass and R. E. Thun) Vol. 6, p. 1. Academic Press, New York (1971).
6. J. R. Ligenza, *J. appl. Phys.* **36**, 2703 (1965).
7. J. Kraitchman, *J. appl. Phys.* **38**, 4323 (1967).
8. M. A. Copeland and R. Pappu, *Appl. Phys. Letts* **19**, 199 (1971).
9. J. R. Ligenza and M. Kuhn, *Sol. Stat. Tech.* **33** (1970).
10. D. L. Pulfrey, F. G. M. Hathorn and L. Young, *J. Electrochem. Soc.* **120**, 1529 (1973).
11. J. J. H. Reche and D. L. Pulfrey, *Rev. Sci. Instr.* **44**, 914 (1973).
12. D. L. Pulfrey and J. J. H. Reche, *Appl. Opt.* **12**, 1577 (1973).
13. W. Kern and D. A. Puotinen, *RCA Rev.* **31**, 187 (1970).
14. S. Y. Wu and N. P. Formigoni, *J. appl. Phys.* **39**, 5613 (1968).
15. G. Olive, Ph.D. thesis, University of British Columbia, (1973).
16. L. I. Maissel, R. E. Jones and C. L. Standley, *IBM J. Res. Dev.* **14**, 176 (1970).
17. L. Young, *Anodic Oxide Films*, p. 126, Academic Press, New York (1961).
18. R. Morgan, *J. Mat. Sci.* **6**, 1227 (1971).
19. A. D. Lopez, *Rev. Sci. Instr.* **44**, 200 (1972).
20. M. Kuhn and E. H. Nicollian, *J. Electrochem. Soc.* **118**, 370 (1971).
21. D. V. McCaughan and V. T. Murphy, *J. appl. Phys.* **44**, 2008 (1973).
22. E. H. Snow, A. S. Grove and D. J. Fitzgerald, *Proc. IEEE* **55**, 1168 (1967).
23. M. Kuhn, *Solid-St. Electron.* **13**, 873 (1970).
24. P. L. Castro and B. E. Deal, *J. Electrochem. Soc.* **118**, 280 (1971).
25. A. Goetzberger, *Bell Syst. Tech. J.* **46**, 1097 (1966).
26. A. Manara, A. Ostidich, G. Pedroli and G. Restelli, *Thin Solid Films* **8**, 359 (1971).
27. F. B. Micheletti and S. H. McFarlane, Ext. Abstr. 22, Electrochem. Soc. Meeting Washington D.C., May (1971).
28. D. L. Pulfrey and L. Young, USAF Techn. Rept. AFAL-TR-70-328, March (1971).
29. J. J. H. Reche, MA.Sc. thesis, University of British Columbia, (1973).
30. W. A. Pliskin and H. S. Lehman, *J. Electrochem. Soc.* **112**, 1013 (1965).
31. O. Meyer, J. Gyulai and J. W. Mayer, *Surface Sci.* **22**, 263 (1970).