Hole traps and trivalent silicon centers in metal/oxide/silicon devices

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We report electron spin resonance (ESR) measurements of E'-center (a "trivalent silicon" center in SiO_2) density as well as capacitance versus voltage (C-V) measurements on γ-irradiated metal/oxide/silicon (MOS) structures. We also report a considerable refinement of earlier ESR measurements of the dependence of radiation-induced P_b-center (a "trivalent silicon" center at the Si/SiO_2 interface) occupation as a function of the Fermi level at the Si/SiO_2 interface. These measurements indicate that the P_b centers are neutral when the Fermi level is at mid-gap. Since the P_b centers are largely responsible for the radiation-induced interface states, one may take $\Delta V_{mg} C_{ox}/e$ (where ΔV_{mg} is the "mid-gap" C-V shift, C_{ox} is the oxide capacitance, and e is the electronic charge) as the density of holes trapped in the oxide. We find that radiation-induced E' density equals $\Delta V_{mg} C_{ox}/e$ in oxides grown in both stream and dry oxygen. Etch-back experiments demonstrate that the E' centers are concentrated very near the Si/SiO_2 interface (as are the trapped holes). Furthermore, we have subjected irradiated oxide structures to a sequence of isochronal anneals and find that the E' density and ΔV_{mg} annealing characteristics are virtually identical. We conclude that the E' centers are largely responsible for the deep hole traps in thermal SiO_2 on silicon. This observation coupled with observations regarding the P_b center indicates that two intrinsic centers, both involving silicon atoms lacking one bond to an oxygen atom, are largely responsible for the two electrically significant aspects of radiation damage in MOS devices: charge buildup in the oxide and interface-state creation at the Si/SiO_2 interface.

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I. INTRODUCTION

The effects of ionizing radiation on metal/oxide/silicon (MOS) field-effect transistors (MOSFET's) have been intensively investigated since the early 1960s.[1–23] These effects are so damaging in some technologically significant applications, for example, MOS integrated circuitry in satellites, that enormous effort has been invested in both the study of radiation effects and the development of radiation-tolerant ("radiation hard") MOS devices.[24,25] Two decades of study have established that irradiation results in the trapping of holes (generated by the radiation) in the SiO_2 and the creation of interface states at the Si/SiO_2 boundary.[2–7] Both the trapped holes and interface states contribute to shifts in threshold voltage; the interface states also degrade channel conductance.[3] Numerous models have been proposed to account for both the hole traps in the oxide and the interface states.[8,10–18] However, until recently very little direct evidence existed regarding the chemical and structural nature of these defects.

Recently, we reported the observation of three radiation-induced paramagnetic centers in MOS structures.[20–23] One center, termed P_b, was first observed by Nishi[26,27] and was later identified by Caplan *et al.* as a "trivalent silicon" bonded to three silicon atoms at the Si/SiO_2 interface.[28,29] The radiation-induced P_b resonance g values and anisotropy ($g_{\parallel} = 2.0014$, $g_{\perp} = 2.008$) are, as discussed in earlier publications[20,23] identical (within experimental error) to those reported by Caplan *et al.* (The g factor is defined by the expression $g = h\nu/\beta H$ where h is Planck's constant, ν is the microwave frequency, β is the Bohr magneton, and H is the magnetic field at which resonance occurs.) A second radiation-induced center, termed E', is also a "trivalent silicon" but in this case the silicon is bonded to three oxygens and is in the SiO_2.[30–33] The radiation-induced MOS oxide E'-center resonance "zero-crossing" g value ($g = 2.0004$) and line shape are identical to that of E'-center resonances observed in bulk amorphous SiO_2.[21,30–33] A third center resonance resembles that of a nonbridging oxygen center.[21,34,35]

In our earlier work we demonstrated that the density of radiation-induced P_b centers is roughly equal to the density of radiation-induced interface states,[20–23] and also anneal out in the same temperature range as the interface states.[23] Furthermore, by varying the position of the Fermi level at the interface, we were able to change the population of paramagnetic P_b centers by about a factor of 3.[22,23] The fact that the P_b population is minimized when the Fermi level is near either the valence- or conduction-band edge allowed us to identify the P_b center as an amphoteric interface-state defect.[22,23] We thus were able to conclude that the P_b center levels were largely responsible for the radiation-induced interface states.[22,23] (The results of our earlier P_b versus bias experiment were recently reproduced on unirradiated samples by Johnson *et al.*,[36] who arrived at essentially identical results and conclusions regarding processing-induced P_b centers.) Furthermore, in earlier work we also noted that the density of radiation-induced E' centers was of the same order of magnitude as that of holes trapped in the oxide.[21]

In this paper we greatly extend our earlier semiquantitative observations with regard to the E' center. We present results of ESR and C-V measurements which, within experimental error, indicate that the concentration of radiation-induced E' centers is equal to the concentration of holes trapped in the SiO_2, that the distribution of E' centers and trapped holes in the oxide is identical, and that annealing characteristics of E' centers and trapped holes are also iden-

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tical. Furthermore, we also extend earlier observations with regard to the P_b center which allow us to measure the density of holes trapped in the oxide (and thereby make the comparisons regarding trapped holes and E' referred to above). It is possible to determine the concentration of holes trapped in the SiO_2 from a C-V measurement, if one can determine the Fermi-level position at the interface which corresponds to charge neutrality of the interface states.[37] Since it is known[38] that nearly all of the hole traps are very near the Si/SiO_2 interface, $C_{ox}\Delta V/e =$ trapped hole density, where C_{ox} is the oxide capacitance, e is the electronic charge, and ΔV is the radiation-induced shift in voltage of the capacitance curve taken at the Fermi-level position corresponding to charge neutrality of the interface states. As discussed below we argue that one may reasonably suppose this Fermi level to be that at which the population of paramagnetic P_b centers is maximized.

II. EXPERIMENTAL PROCEDURES

The samples utilized in measurements reported in this paper were in the form of 4×30 and 4×50 mm^2 bars cut from 100-mm-diam silicon wafers ($\rho \sim 30$–$100\ \Omega$ cm) with (111) surface orientation. Oxides were grown in steam at 900 °C and in dry oxygen at 1000 °C, in both cases to a thickness of approximately 1200 Å. Sets of both types of samples (steam and dry) were softened by an anneal in nitrogen at 1100 °C. A polysilicon gate approximately 0.6 μm thick was deposited on all samples except those utilized in a corona biasing experiment. Sample preparation was carried out in the processing facility of the Center for Radiation Hardened Microelectronics at Sandia National Laboratories. Samples were subjected to Co^{60} γ irradiation while the gates were under positive bias ($+20$ V).

After irradiation, the polysilicon gates were removed from the structures to facilitate electron spin resonance (ESR) measurements. (The polycrystalline silicon contains a very high concentration of "trivalent silicon" centers[39,40] which would greatly complicate measurement of far lower concentrations of radiation-induced centers in the oxide.)

The electron spin resonance measurements were made using a Varian E Line Century Spectrometer with a TE_{104} "double" cavity. The spin concentrations were determined by comparison of (unsaturated) E' and P_b absorption spectra with the spectrum of a calibrated weak-pitch standard. High-frequency C-V (1-MHz) measurements were made using a mercury probe. We estimate that the absolute spin concentration measurement of P_b and E' are accurate to somewhat better than a factor of 2; the relative spin concentrations are much more accurately determined ($\pm 10\%$). We estimate electrical measurements (C-V) reported in this work to be accurate to about $\pm 10\%$.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Relationship of Fermi level at the interface to P_b occupation probability

To obtain P_b population as a function of the Fermi level at the interface, a potential was applied to irradiated bare oxide Si/SiO_2 structures utilizing a corona-discharge apparatus.[41] This potential was measured with a commercial Kelvin probe electrostatic voltmeter (Monroe 170). The charged bare oxide structures were placed in the TE_{104} cavity of a Varian E Line Century spectrometer. The concentration of paramagnetic P_b centers was determined from unsaturated P_b absorption spectra.

We obtained the position of the Fermi level at the interface from a high-frequency capacitance versus voltage measurement on the same sample utilized in the ESR measurement. Results of both measurements are illustrated in Fig. 1. In Fig. 2(a) we plot the distribution of paramagnetic P_b centers versus the position of the Fermi level at the interface; in Fig. 2(b) we plot the density of interface states determined by the Terman technique[42] utilizing the C-V results of Fig. 1. The distribution of paramagnetic P_b centers is broadly peaked slightly below mid-gap. In the lower part of the gap, the P_b center is a *donorlike* interface-state defect ($P_b \rightleftharpoons P_b^+ + e$, $P_b + h \rightleftharpoons P_b^+$). As the Fermi level moves toward mid-gap, the positively charged P_b centers accept an electron and become paramagnetic and neutral ($P_b^+ + e \rightarrow P_b$.) As the Fermi level moves from the vicinity of the mid-gap towards the conduction-band edge, the P_b center picks up another electron, becoming negatively charged and again diamagnetic ($P_b + e \rightarrow P_b^-$). In the upper part of the band gap the P_b center is thus an *acceptorlike* interface-state defect ($P_b + e \rightleftharpoons P_b^-$, $P_b^- + h \rightleftharpoons P_b$). The P_b center is paramagnetic only when it has an unpaired spin (one electron); the paramagnetic P_b center is thus converted to a diamagnetic state by either *donating* or *accepting* an electron. The "spin states" of the P_b center are schematically illustrated in Fig. 2(c). Since our earlier[20–23] observations demonstrate that the P_b centers are largely responsible for radiation-induced interface states, we take the Fermi-level position corresponding to neutral P_b centers (about mid-gap) to be that of net zero charge in the interface states.

Our conclusions (regarding mid-gap neutrality of inter-

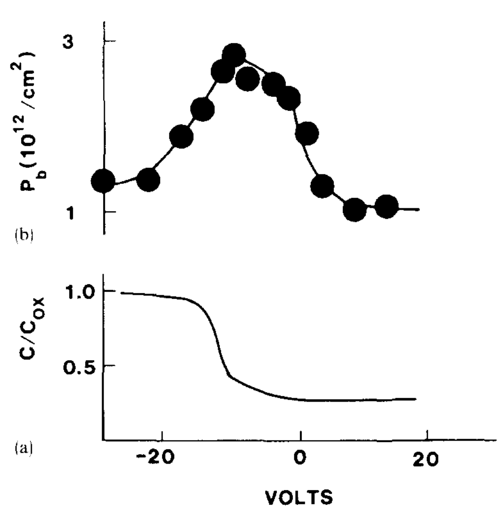

FIG. 1. (a) High-frequency capacitance vs voltage measurement on γ-irradiated (10 Mrad) oxide. (Unlike samples utilized in the E' measurements, this oxide was irradiated bare.) (b) Concentration of paramagnetic P_b centers plotted vs bias.

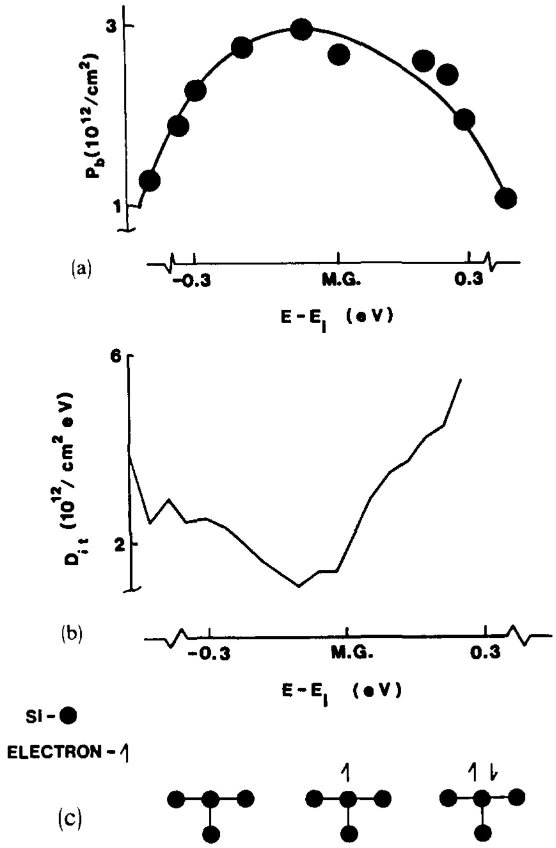

FIG. 2. (a) Population of paragmagnetic P_b centers vs Fermi level. (b) Distribution of interface states. Results were obtained from the data of Fig. 1. (c) Schematic illustration of P_b occupancy.

face states) are consistent with assumptions made by several workers that states in the upper part of the gap are acceptorlike, states in the lower part of the gap donorlike,[43] and that the Fermi level at mid-gap corresponds to net zero charge in the interface states.[44] Our observations are also consistent with the qualitative observations of Brunstrom and Svensson regarding processing-induced P_b centers.[45] Furthermore, the distribution of P_b levels is consistent with the generally "U"-shaped distribution of interface states in the band gap.[9,17,46–48] (The P_b interface-state distribution would roughly correspond to the absolute value of the P_b population derivative with respect to energy in the gap.) As Fig. 2(b) indicates, we observe such a "U"-shaped distribution of interface states in these samples.

We may now estimate the density of holes trapped in the oxides utilizing the expression trapped hole density $= C_{ox} \Delta V_{mg}/e$, where ΔV_{mg} is the shift in the capacitance versus voltage curve for the Fermi level at mid-gap.

B. Correlation of E′ density and trapped hole density

1. Post-irradiation comparison of E′ density and $C_{ox}\Delta V_{mg}/e$

In Fig. 3(a) we illustrate the electron spin resonance spectrum of the E' resonance in a MOS structure irradiated to 10 Mrad while a + 20-V bias was applied. (The polysilicon gate was etched off the sample prior to the resonance measurement.) In Fig. 3(b) we illustrate the absence of any measurable E' spectrum in an identical sample (from the same

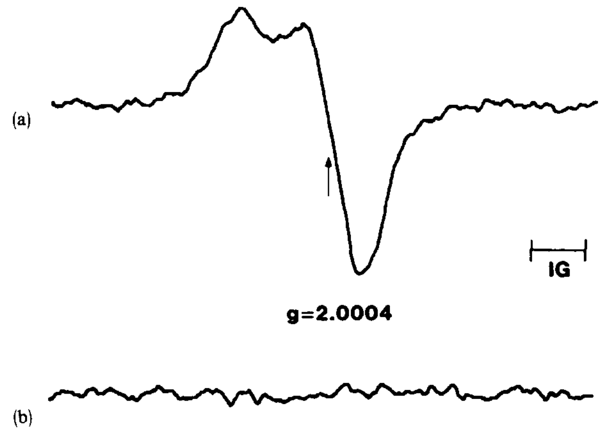

FIG. 3. ESR traces of identical samples (a) after exposure to 10 Mrad of Co^{60} γ-irradiation and (b) before exposure. The sample gates were positively biased to 20 V during irradiation. The E' center resonance is observed in (a).

wafer) which has not been irradiated. The narrow (2 G wide) "double-humped" line shape with $g \simeq 2.0004$ is characteristic of the E' centers. It is a "trivalent silicon" center in the SiO_2.[30–33] Marquardt and Sigel[19] first observed E' centers in heavily irradiated (up to 220 Mrad), rather thick (up to 11 000 Å) oxide films on silicon. Although they did not report results of electrical measurements, they suggested (we believe correctly) that E' centers were the hole traps in the oxide.

Post-irradiation E' density as well as $\Delta V_{mg} C_{ox}/e$ are plotted in Fig. 4. The dry MOS oxides utilized in these measurements had been subjected to a 1100 °C nitrogen anneal to render them relatively radiation intolerant.

In order to determine whether or not the correlation between E' and ΔV_{mg} is the case for a wide range of processing conditions, we subjected four sets of oxides prepared quite differently to a 10-Mrad dose of γ radiation. Two oxides were grown in steam at 900 °C and two in dry oxygen at 1000 °C. One of the steam-oxide structures and one of the dry-oxide structures were subjected to an 1100 °C anneal in dry nitrogen.

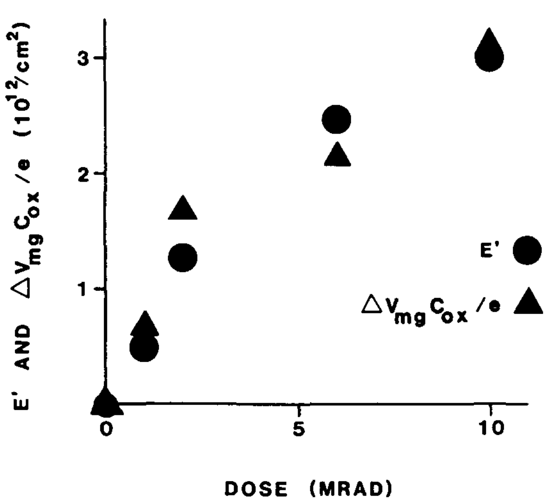

FIG. 4. Distributions of E' and $\Delta V_{mg} C_{ox}/e$ vs irradiation dose for MOS structures with oxides grown in dry oxygen and subjected to a nitrogen anneal.

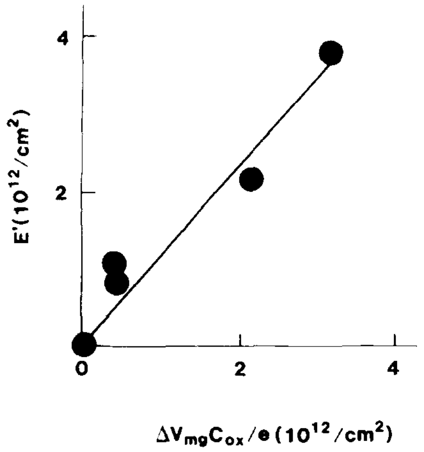

FIG. 5. Concentration of E' centers plotted vs trapped hole density in the oxide ($\Delta V_{mg} C_{ox}/e$) for MOS structure subjected to four sets of processing parameters. All structures were irradiated to 10 Mrad; thus differences in E' concentration here are due to processing variations.

In Fig. 5 we plot the concentration of E' centers in each of the (differently processed) γ-irradiated (10 Mrad, + 20-V gate) MOS structures versus $\Delta V_{mg} C_{ox}/e$. In all four cases the concentration of E' centers is (within experimental error) equal to $\Delta V_{mg} C_{ox}/e$, which we have argued above is the approximate concentration of positive charge in the oxides.

2. Etch-back experiment

It has long been well established that the trapped holes in irradiated MOS devices are concentrated near the Si/SiO_2 interface.[49] In order to determine whether or not the E' centers are also highly concentrated near the interface, we have subjected irradiated (10 Mrad Si nitrogen-annealed dry-oxide structures, identical to those described in Part 1, to a sequence of etches, gradually removing the oxide, monitoring the remaining E' centers. We utilized an etch of (70% HNO_3) nitric acid (70 parts), (49% HF) hydrofluoric acid (3 parts), and water (28 parts). This etch removes SiO_2 at a rate of about 5 Å/sec. Oxide thicknesses were determined utilizing an ellipsometer.

The results are illustrated in Fig. 6. Clearly, the E' centers are concentrated very near the Si/SiO_2 interface (all within about 100 Å). These results provide yet more evidence that the E' centers account for the hole traps since the trapped holes are similarly located.[49] Results *somewhat* similar to those of Fig. 6 were reported by Marquardt and Sigel in their pioneering study[19]; however, they observed rather large concentrations of E' centers in the bulk of the SiO_2. Perhaps the extremely thick (11 000 Å) oxide and extremely high level of γ irradiation (220 Mrad) utilized in their experiment accounts for this apparent discrepancy.

3. Isochronal annealing

In Fig. 7 we present results of a sequence of isochronal anneals (75 min in air) on an irradiated MOS structure. Within experimental error, the annealing characteristics of E' and ΔV_{mg} are identical.

Relationship of the Fermi level at the interface to E' occupation probability. In order to rule out any possibility that the E' centers might be interface-state defects, a potential was applied to irradiated bare oxide Si/SiO_2 structures while in an ESR-resonant cavity in a manner identical to that described in an earlier section of this paper regarding P_b centers. The concentration of paramagnetic E' centers was found to be independent of bias. Since bias values corresponding to the Fermi level near the valence-band edge, the conduction-band edge, and the mid-gap were utilized in this comparison, we conclude that E' occupation probability is *independent* of the Fermi level at the interface and that the E' centers do not exchange charge with the silicon.

IV. CONCLUSIONS

We find that, on the basis of ESR versus Fermi-level measurements of the P_b center, the mid-gap Fermi level rep-

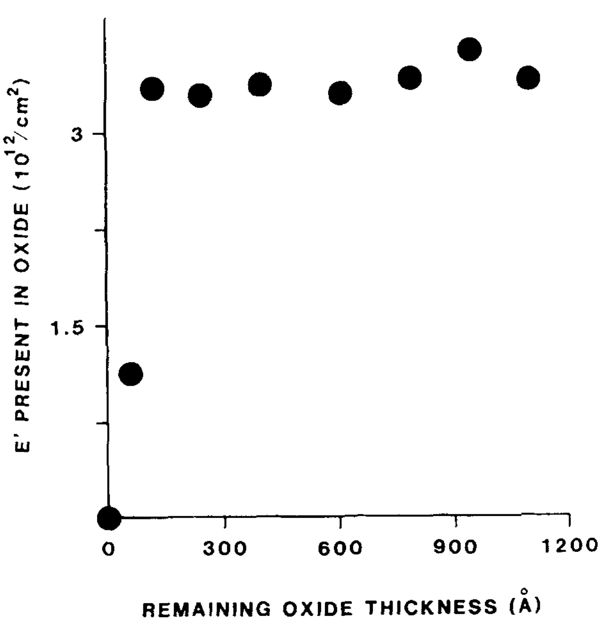

FIG. 6. Distribution of E' density in an irradiated oxide.

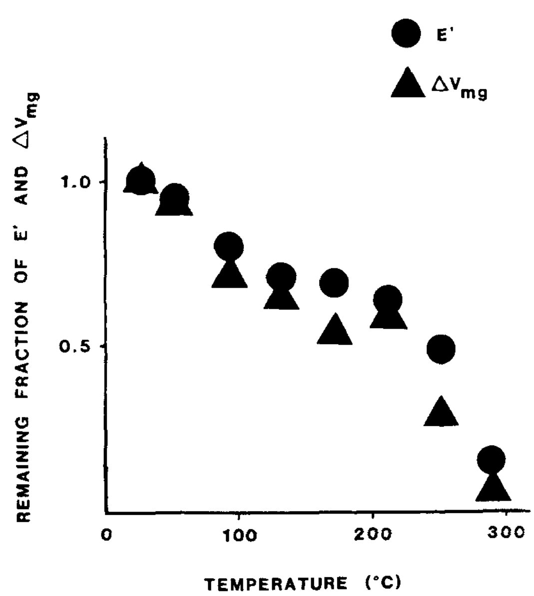

FIG. 7. Plot of remaining fractions of ΔV_{mg} and E' as a function of isochronal annealing time.

resents approximate net neutrality of the interface states. This observation allows us to determine the density of positive charge in the oxide from $\Delta V_{mg} C_{ox}/e$.

We find $\Delta V_{mg} C_{ox}/e$ to be, within experimental error, equal to the density of E' centers. The E' center ir a "trivalent silicon" center in the SiO_2 near the Si/SiO_2 interface.[30–33] We find that the densities of E' centers and holes trapped in the oxide are approximately equal. The annealing characteristics of E' and trapped holes are identical. The distribution of E' centers in the oxide is highly concentrated near the Si/SiO_2 interface, as is the distribution of trapped holes.[49] Furthermore, the population of E' centers is not dependent on the position of the Fermi level at the interface; this observation rules out the possibility that the E' center is an interface-state defect.

We believe that our findings convincingly establish the E' center, most likely as the point defect primarily responsible for hole traps in the thermal oxides of MOS devices. Our findings with regard to the E' center coupled with our findings with regard to the P_b center (described in other publications as well as this work) demonstrate that "trivalent silicon" point defects play a dominant role in the radiation-induced degradation of MOS devices.

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[1]H. L. Hughes and R. R. Giroux, Electronics **37**, 58 (1964).
[2]J. R. Szedon and J. E. Sandor, Appl. Phys. Lett. **6**, 181 (1965).
[3]E. H. Snow, A. S. Grove, and D. J. Fitzgerald, Proc. IEEE **55**, 1168 (1967).
[4]K. H. Zaininger, IEEE Trans. Nucl. Sci. **NS-13**, 237 (1966).
[5]R. J. Powell and G. F. Derbenwick, IEEE Trans. Nucl. Sci. **NS-18**, 99 (1971).
[6]P. W. Winokur, H. E. Boesch, Jr., J. M. McGarrity, and F. B. McLean, J. Appl. Phys. **50**, 3492 (1979).
[7]G. H. Hu and W. C. Johnson, Appl. Phys. Lett. **36**, 590 (1980).
[8]F. B. McLean, IEEE Trans. Nucl. Sci. **NS-27**, 1651 (1980).
[9]P. S. Winokur and M. M. Sokoloski, Appl. Phys. Lett. **28**, 627 (1976).
[10]A. G. Revesz, IEEE Trans. Nucl. Sci. **NS-18** 113 (1971).
[11]W. C. Johnson, IEEE Trans. Nucl. Sci. **NS-22**, 2144 (1975).
[12]C. T. Sah, IEEE Trans. Nucl. Sci. **NS-23**, 1563 (1976).
[13]C. M. Svensson, in *The Physics of SiO_2 and Its Interfaces*, edited by S. T. Pantelides (Pergamon, New York, 1978), p. 328.
[14]C. T. Sah, IEEE Trans. Nucl. Sci. **NS-23**, 1563 (1976).
[15]B. E. Deal, J. Electrochem. Soc. **121**, 198C (1974).
[16]A. G. Revesz, IEEE Trans. Nucl. Sci. **NS-24**, 2102 (1977).
[17]M. Pepper, Thin Solid Films **14**, 57 (1972).
[18]A. Geotzberger, V. Heine, and E. H. Nicollitan, Appl. Phys. Lett. **12**, 95 (1968).
[19]C. L. Marquardt and G. H. Sigel, IEEE Trans. Nucl. Sci. **22**, 2234 (1975).
[20]P. M. Lenahan, K. L. Brower, P. V. Dressendorfer, and W. C. Johnson, IEEE Trans. Nucl. Sci. **NS-28**, 4105 (1981).
[21]P. M. Lenahan and P. V. Dressendorfer, IEEE Trans. Nucl. Sci. **NS-29**, 1459 (1982).
[22]P. M. Lenahan and P. V. Dressendorfer, Appl. Phys. Lett. **41**, 542 (1982).
[23]P. M. Lenahan and P. V. Dressendorfer, J. Appl. Phys. **54**, 1457 (1983).
[24]K. Aubuchon, IEEE Trans. Nucl. Sci. **NS-18**, 117 (1971).
[25]G. F. Derbenwick and B. L. Gregory, IEEE Trans. Nucl. Sci. **NS-22**, 2151 (1975).
[26]Y. Nishi, Jpn. J. Appl. Phys. **5**, 333 (1966).
[27]Y. Nishi, Jpn. J. Appl. Phys. **10**, 52 (1971).
[28]P. J. Caplan, E. H. Poindexter, B. E. Deal, and R. R. Razouk, J. Appl. Phys. **50**, 5847 (1979).
[29]E. H. Poindexter, P. J. Caplan, B. E. Deal, and R. R. Razouk, J. Appl. Phys. **52**, 879 (1981).
[30]R. A. Weeks, J. Appl. Phys. **27**, 1376 (1956).
[31]R. H. Silsbee, J. Appl. Phys. **32**, 1459 (1961).
[32]F. J. Feigl, W. B. Fowler, and K. L. Yip, Solid State Commun. **14**, 225 (1974).
[33]D. L. Griscom, Phys. Rev. **22**, 4192 (1980).
[34]M. Stapelbroek, D. L. Griscom, E. J. Friebele, and G. H. Sigel, J. Noncryst. Solids **32**, 313 (1979).
[35]E. J. Friebele, D. L. Griscom, M. Stapelbroek, and R. A. Weeks, Phys. Rev. Lett. **42**, 1346 (1979).
[36]N. M. Johnson, D. R. Biegelsen, M. D. Moyer, S. T. Chang, E. H. Poindexter, and P. J. Caplan, Appl. Phys. Lett. **43**, 563 (1983).
[37]G. W. Hughes, J. Appl. Phys. **48**, 5357 (1977).
[38]E. H. Nicollian and J. R. Brews, *MOS Physics and Technology* (Wiley-Interscience, New York, 1982), p. 549, and references therein.
[39]N. M. Johnson, D. K. Biegelsen, and M. D. Moyer, Appl. Phys. Lett. **40**, 882 (1982).
[40]P. M. Lenahan and W. K. Schubert, Solid State Commun. **47**, 423 (1983).
[41]Z. E. Weinberg, D. L. Matthes, W. C. Johnson, and M. A. Lampert, Rev. Sci. Instrum. **46**, 201 (1975).
[42]E. M. Terman, Solid State Electron. **5**, 295 (1962).
[43]T. P. Ma, G. Scoggan, and R. Leone, Appl. Phys. Lett. **27**, 61 (1975).
[44]M. Knoll, D. Braunig, and W. R. Fahrner, IEEE Trans. Nucl. Sci. **NS-29**, 1471 (1982).
[45]C. Brunstrom and C. Svensson, Solid State Commun. **37**, 339 (1981).
[46]J. Singh and A. Madukar, Appl. Phys. Lett. **38**, 884 (1981).
[47]S. K. Lai, Appl. Phys. Lett. **39**, 58 (1981).
[48]E. H. Nicollian and J. R. Brews, Ref. 38, p. 882, and references therein.
[49]E. H. Nicollian and J. R. Brews, Ref. 38, p. 563, and references therein.