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RADIATION AND CHARGE INJECTION IN Al$_2$O$_3$ USING NEW TECHNIQUES

Richard J. Powell

RCA LABORATORIES
Princeton, New Jersey 08540

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Optical transmission of unbacked thin films of thermally grown SiO$_2$ films was measured in the vacuum UV. The absorption data indicate a bandgap of 8.0 ± 0.2 eV for SiO$_2$, and this value is confirmed by measurements of electron and hole photoconductivity and positive charging thresholds in MOS samples. Coincidence of the absorption and hole photoconductivity thresholds provides evidence that the

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uppermost valence levels in SiO_2 form a band, perhaps quite narrow, and most likely are dominated by oxygen $2p\pi$ and silicon $3d$ atomic orbitals.

Vacuum ultraviolet radiation studies of steam-grown SiO_2 samples with different annealing temperatures show a rather sharp minimum in hole trapping at 1000°C. The results indicate the presence of at least two trap species whose densities vary oppositely with anneal temperature. A reasonable fit to the experimental results is obtained using a two-trap model, with trap cross sections of 1.04×10^{-13} cm^2 and $\ast$ 6.5×10^{-15} cm^2. The former is believed to be associated with a species that diffuses into the oxide, particularly at high anneal temperatures, and the latter is associated with intrinsic interface trapping. Corona discharge experiments are inconsistent with the VUV results in that a monotonic increase in hole trap density with anneal temperature is observed. This is tentatively explained by the possible inability of this technique to fill traps with certain energy levels and spatial locations.

Included in this report is a summary of previous work on Al_2O_3 which is described in earlier technical reports issued under this contract.

$\ast$ 1.04 × 10 to the -13th power sq cm and
6.5 × 10 to the -15th power sq cm

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PREFACE

This Final Report describes work done at RCA Laboratories, Princeton, NJ, under Contract No. F19628-74-C-0132 in the Integrated Circuit Technology Center, J. H. Scott, Director. The Project Supervisor is K. H. Zaininger and the Project Scientist is R. J. Powell. The Air Force Project Monitor is Sven A. Roosild.

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I. INTRODUCTION

The spectral dependence of optical absorption of SiO_2 through the fundamental absorption edge is important to interpretation of vacuum ultraviolet (VUV) transport and charging studies [1-3]. Accurate knowledge of the bandgap is important to analysis of electron bombardment experiments [4] and dielectric breakdown studies [5] in addition to its obvious importance to electronic structure studies. For these reasons, we have performed experiments on thin, unbacked films of thermally grown SiO_2 films. The results of these experiments, along with photoconductivity and charge accumulation spectra, are presented and discussed in Section II of this report.

It has recently been shown [6] that processing parameters play an important role in determining the trap structure near the $Si-SiO_2$ interface. Studies of well-characterized MOS structures with steam-grown SiO_2 films have been performed on samples with different post-oxidation anneal histories in order to determine the dependence on anneal temperature and ambient gas, hopefully to provide new insight into the nature of the hole trap. These results, which include current enhancement and flatband shift experiments, are presented and discussed in Section III.

Section IV contains the results of corona discharge experiments performed on the same series of samples used for the vacuum UV experiments. Similarities and differences are pointed out and discussed.

1. R. J. Powell and G. F. Derbenwick, IEEE Trans. Nuclear Science NS-19, 99 (1971).
2. A. G. Holmes-Siedle and I. Groombridge, Thin Solid Films 27, 165 (1975).
3. R. J. Powell, J. Appl. Phys. 46, 4557 (1975).
4. O. L. Curtis, J. R. Srour, and K. Y. Chiu, J. Appl. Phys. 45, 4506 (1974).
5. N. Klein, Advances in Electronics and Electron Physics 26, 309 (1971).
6. R. J. Powell, IEEE Trans. Nuclear Science NS-22, 2240 (1975).

II. OPTICAL PROPERTIES AND PHOTOCONDUCTIVITY
IN THERMALLY GROWN SiO_2

A. OPTICAL ABSORPTION

Transmission measurements on SiO_2 have previously been limited to thick ($\gtrsim 1$ mm) samples of fused silica [7] or crystalline quartz [8]. With such samples the absorption coefficient α cannot be determined accurately above 50 cm^{-1} because of experimental limitations such as scattered light. Philipp [9] has determined the optical properties of SiO_2 by means of a Kramers–Kronig analysis of his reflectance data. With this method, values of α are not expected to be accurate much below 10^5 cm^{-1} owing to the relative insensitivity of reflectance to absorption in this range. We have measured the optical transmission of thin unbacked films of SiO_2 to determine α through the fundamental edge. These data indicated an energy gap of 8 eV for thermally grown SiO_2. Measurements of the photoconductivity and positive charging thresholds confirm this value.

Transmisson samples were prepared in the following manner: <100> silicon wafers, 0.15 mm thick, were polished on both sides and processed to produce a thick (5000-Å) film on the backside for masking purposes and a thin (900 Å to 2000 Å) oxide on the front side. Apertures, 1 mm in diameter, were etched in the back oxide using standard photoresist masking. The silicon was then etched through from the backside using a solution of Ethylenediamine and Pyrocatechol [10] at 110°C. The front side of a typical sample is shown in Fig. 1(a), and a cross section is illustrated in Fig. 1(b). The aperture in the back oxide is circular, but in the silicon it approaches a square with sloping sides because of the strong anisotropy in the silicon etch rates. The etch rates are approximately 50, 30, and 3 μm/h for the <100>, <110>, and <111> directions, respectively [10]. Therefore, etching proceeds rapidly beneath the masking oxide until <111> planes are formed and then practically stops. The crystalline planes are indicated in the illustration. The samples

7. D. F. Health and P. A. Sacher, Appl. Optics 5, 937 (1966).
8. A. A. Ballman, et al., Appl. Optics 7, 1387 (1968).
9. H. R. Philipp, J. Phys. Chem. Solids 32, 1935 (1971).
10. R. M. Finne and D. L. Klein, J. Electrochem. Soc. 114, 965 (1967).
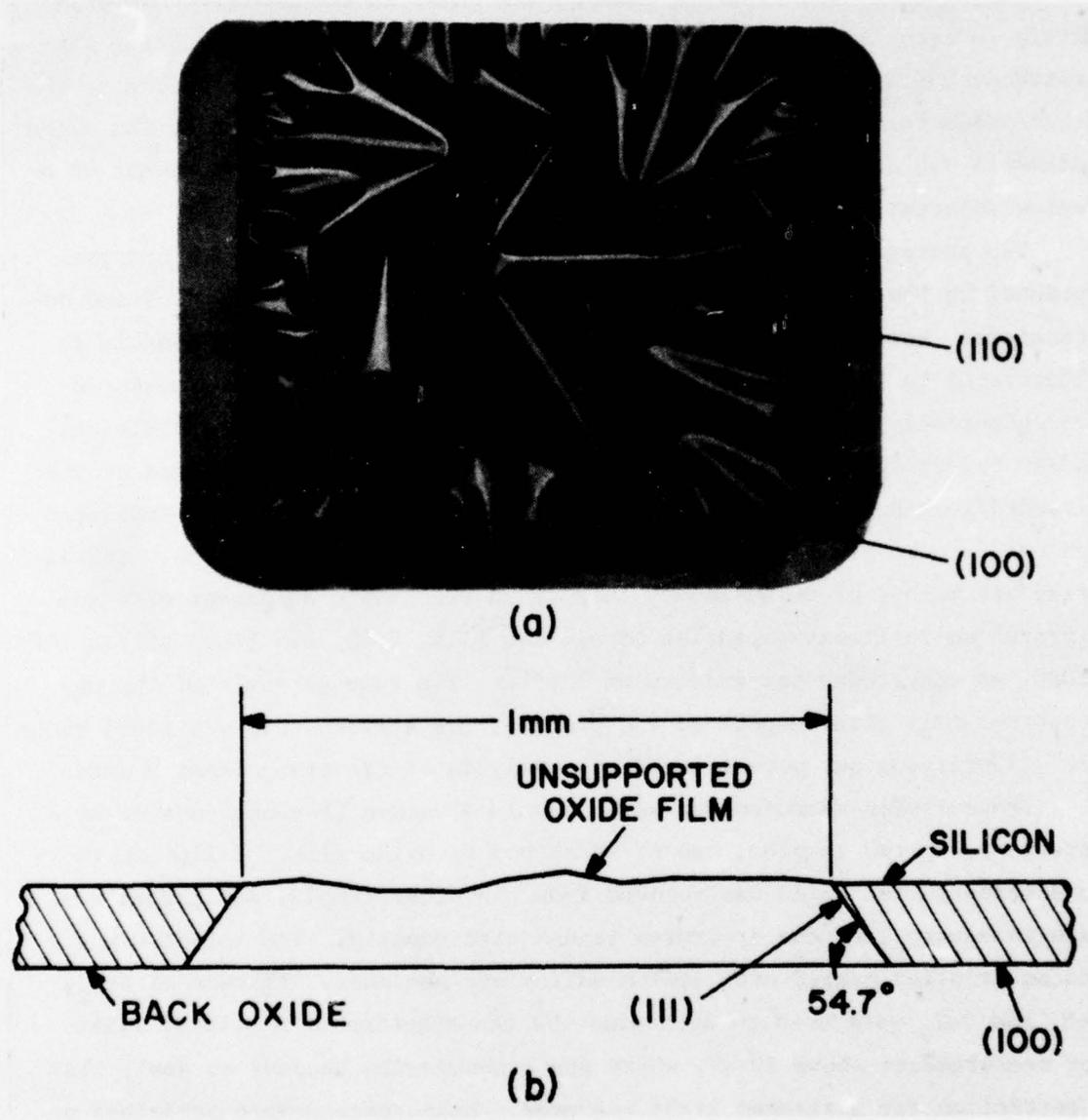
Figure 1. (a) Photograph of typical unbacked SiO$_2$ film, 580 Å thick, produced by etching through the silicon wafer. (b) Cross section of sample showing an actual measured oxide profile. The various crystalline planes are indicated.

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are 5-mm square chips with the unsupported oxide in the center. Approximately 20 identical samples are formed simultaneously, the chip being separated during formation of the apertures. Since the exposed surface of the front oxide is etched somewhat (200 to 300 Å) during the process, the oxide thickness was determined after etching by an ellipsometer measurement of a region adjacent to the aperture.

The photograph of Fig. 1(a) is deceiving in that the strong contrast produced by the microscope gives the impression of large elevations and depressions. However, this is not the case, and a typical oxide profile is illustrated to scale in Fig. 1(b). Several oxide profiles were measured microscopically using a focusing stage with 1-µm vertical scale divisions and an objective which produced a 1-µm depth of focus. Calculation of the extended length of the oxide from such piecewise linear profiles indicated the oxide to be about 0.5% larger than the opening in the silicon. Considering our method of measurement, this is in reasonable agreement with the differences in linear expansion of silicon [11], 0.4%, and fused silica [12], 0.05%, at the growth temperature of 1000°C. The average angle of the unsupported film with respect to the plane of the silicon chip was found to be 4.5°, justifying our normal incidence analysis of the transmisssion data.

Transmission measurements were made in a vacuum UV monochromator by interchanging two samples, one of which had no oxide film. Following the measurements, the oxide was removed from the other sample, and checks were made to ensure that the apertures transmitted equally. The detector was a photomultiplier coated with sodium salicylate phosphor. Filters of BaF_2, NaF, and CaF_2 were used to determine the contribution of scattered light for measurements above 10 eV, where the transmission becomes so small that a correction for scattered light was made. Measurements were performed on several samples with thicknesses of 580 Å and 2045 Å. The transmission of an unsupported film is given by [13]

$$T = \frac{(1-R)^2(1+k^2/n^2)}{e^{\alpha d}-2R\cos(\phi-\theta)-R^2 e^{-\alpha d}} \tag{1}$$

11. *Handbook of Thermophysical Properties of Solid Materials*, Vol. 1, (MacMillan Co., New York, 1961).
12. T. A. Hahn and R. K. Kirby, *Thermal Expansion 1971 - AIP Conference Proceedings*.
13. O. S. Heavens, *Optical Properties of Thin Solid Films*, (Dover Publications, Inc., New York, 1965).

where R is the reflectance $[(n-1)^2 + k^2]/[(n+1)^2 + k^2]$, n and k are the real and imaginary parts of the complex refractive index, $n-ik$, $\phi = 4\pi nd/\lambda$, $\theta = 2\tan^{-1}[2k/(1-n^2-k^2)]$, d is the film thickness, and α the absorption coefficient. In the usual range of transmission measurements $k^2 \ll n^2$, $e^{\alpha d} \gg R^2 e^{-\alpha d}$, and $\theta \simeq 0$. Including these approximations, and solving Eq. (1) for α we get

$$\alpha \simeq \frac{1}{d} \ln \left[\frac{(1-R)^2}{T} + 2R\cos\phi \right] \tag{2}$$

The second term in the brackets results from interference in the film and is important where the transmission is large. Equation (2) was used to calculate α from our transmission data from 8 eV to 10 eV, although above 9.5 eV the interference term has little effect. Values of R and n were obtained from the reflectance data of Philipp since it was previously established [1] that the reflectance of thermally grown SiO_2 and fused silica are identical within experimental error. It should be noted that Philipp's values of n over this range should be quite accurate since k is small and $R \simeq (n-1)^2/(n+1)^2$. Since the absorption coefficient α is $4\pi k/\lambda$, we can determine k for each photon energy to check the assumptions made in deriving Eq. (2) from Eq. (1). The approximations were found to be excellent except above 10.2 eV, where a correction was made for the factor $(1+k^2/n^2)$ in Eq. (1). In this range α was determined from a two-step iteration of

$$\alpha \simeq \frac{1}{d} \ln \left[(1-R)^2 (1+k^2/n^2)/T \right] \tag{3}$$

and n was taken from the data of Philipp. This correction has a maximum effect of increasing α about 5% at the 10.5-eV peak.

The absorption coefficient of SiO_2 determined from transmission measurements on a 580-Å film is given in Fig. 2. It is seen that the absorption is still quite strong well below 9 eV, and just on the basis of magnitude the absorption above about 8.3 eV may be safely attributed to fundamental absorption. The data indicate an absorption threshold of 8 eV, which we interpret to be the bandgap of SiO_2.

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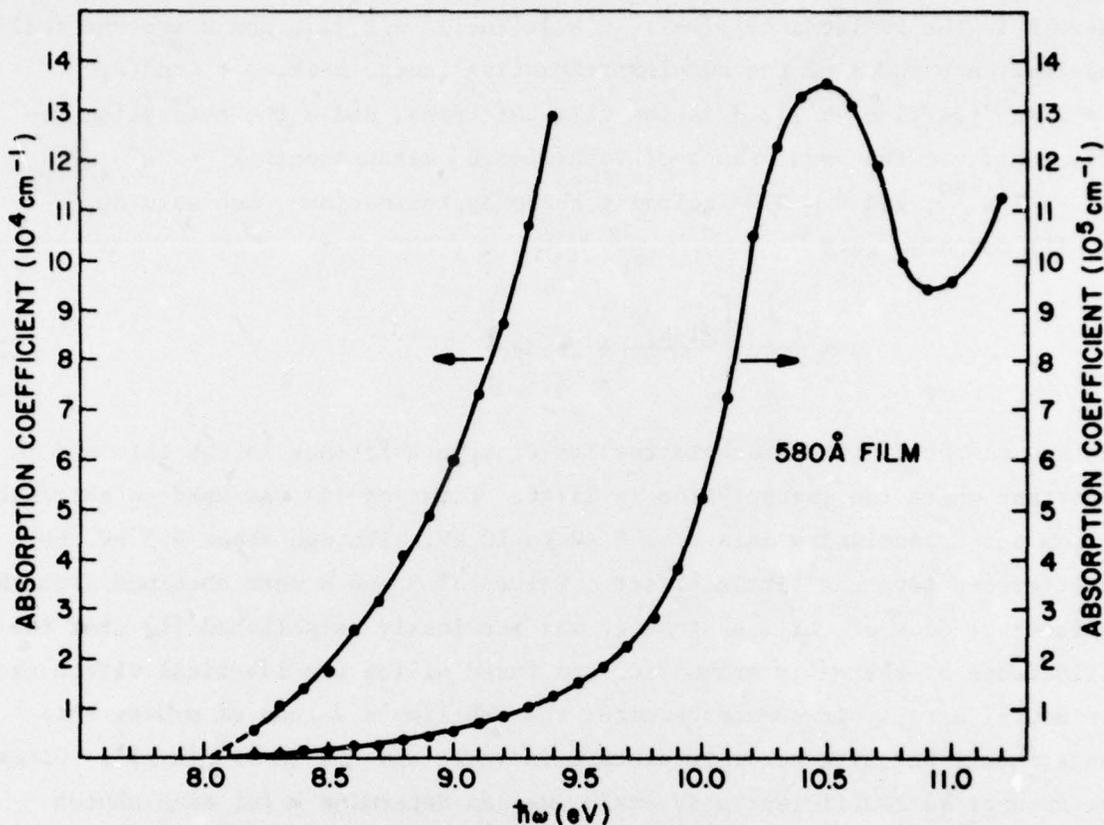
Figure 2. Optical absorption coefficient of a thermally grown SiO_2 film as determined from transmission measurements. The expanded curve on the left corresponds to the scale on the left side of the illustration.

B. PHOTOCONDUCTIVITY AND CHARGE ACCUMULATION SPECTRA

It has recently been shown that hole trapping in SiO_2 films varies widely with growth and anneal temperatures [6]. Using this fact, we have prepared samples with negligible hole trapping and large hole trapping for photoconductivity and charge accumulation spectra, respectively. The photoconductivity spectrum depicted in Fig. 3 was measured on a 1200-Å-thick MOS sample. With both positive and negative gate polarities, photocurrents were time-independent, and negligible charge accumulation was observed. The photoconductive yield shows a shape similar to the absorption, and the threshold is about 7.9 eV. In another 1200-Å sample, which was annealed to produce
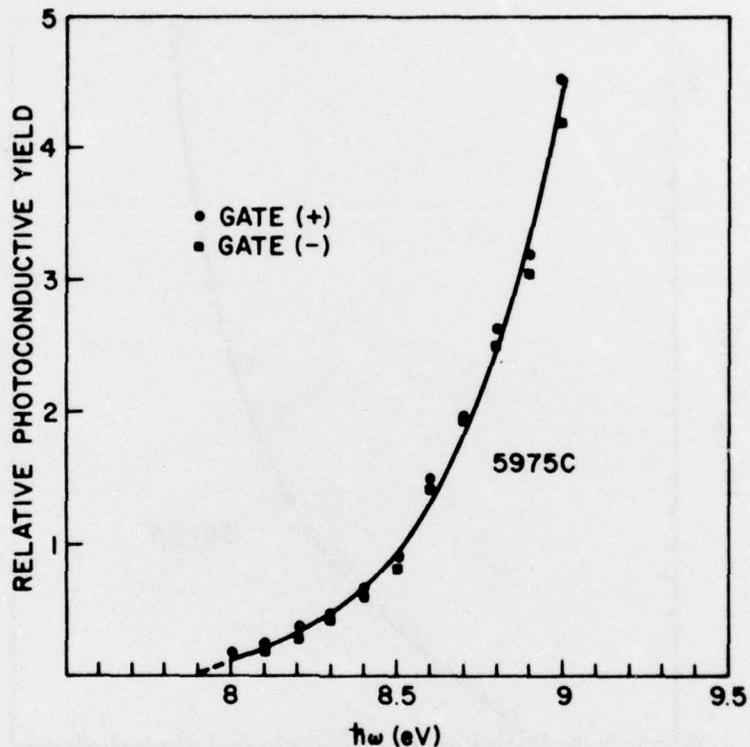
Figure 3.   Photoconductivity spectra measured near threshold on
an MOS structure with a 1034-Å SiO_2 film and a
semitransparent Al-gate electrode. The yields for
both bias polarities are given.

large hole trapping, the spectral dependence of charge accumulation was de-
termined by measuring the high-frequency capacitance-voltage shift ΔV_{FB} versus
photon energy for the same number of absorbed photons. This spectrum is illus-
trated in Fig. 4, and it also shows a threshold at 7.9 eV. Hence, we have
shown in three separate experiments that the bandgap of SiO_2 thermally grown
on silicon is 8.0 ± 0.2 eV. This value agrees with a previous estimate by
Williams [14] based on transmission data of Groth and Weyssenhof [15]. How-
ever, such estimates were previously subject to question because the small
absorption coefficients measurable with thick samples might be interpreted as
absorption due to impurities or imperfections. Other previous estimates have

14. R. Williams, Phys. Rev. 140, A5669 (1965).
15. W. Groth and H. v. Weyssenhof, Z. Naturforsch. 11a, 165 (1956).

13
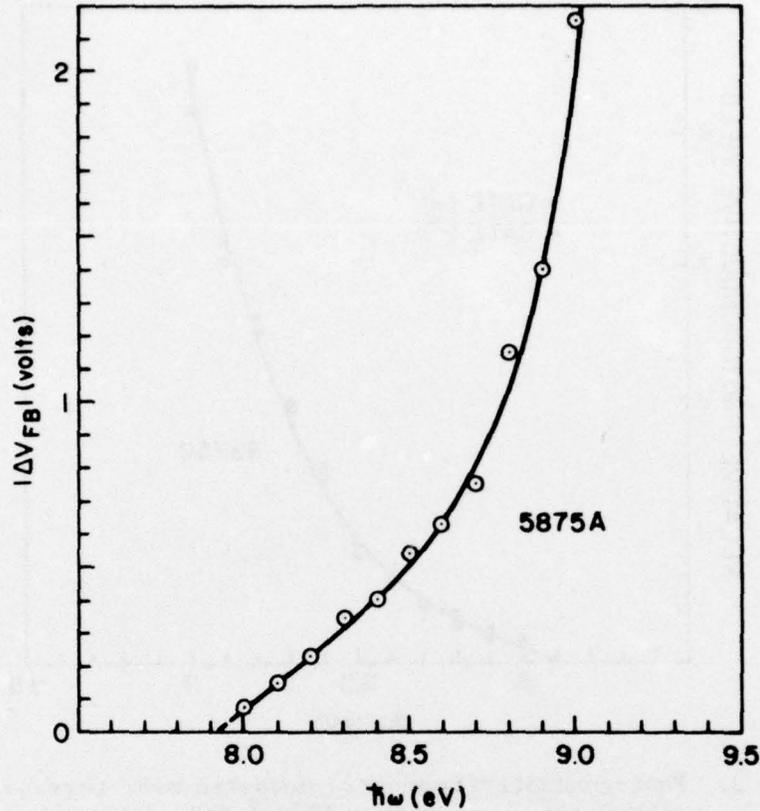
Figure 4. Charge accumulation spectrum measured near threshold on an MOS structure with a 1034-Å SiO$_2$ film and a semitransparent Al-gate electrode. The flatband shift produced by trapped charge is the measured quantity.

placed the SiO$_2$ bandgap as high as 11 eV. However, those estimates [16-19] were based on the assumption that the 10.5-eV peak in Fig. 2, which corresponds to the reflectance peak [9] at 10.3 eV, is due to an excitonic transition. The first band-to-band transition was assumed to lie energetically above the exciton. It is obvious from our results that if the 10.5-eV peak is

16. E. Loh, Solid State Commun. 2, 269 (1964).
17. A. R. Ruffa, Phys. Stat. Sol. 29, 605 (1968).
18. M. H. Reilly, J. Phys. Chem. Solids 31, 1041 (1970).
19. K. Platzöder, Phys. Stat. Sol. 29, K63 (1968).

14

excitonic, it is degenerate in energy with band-to-band transitions. Furthermore, since the photoconductivity near 10.5 eV shows no strong excitonic effects [20], it would seem that the only evidence for the interpretation is the temperature dependence reported by Platzöder [19].

C. DISCUSSION AND INTERPRETATION

It is useful to consider the results of our experiments in light of the various theoretical predictions regarding the electronic energy levels in SiO_2. There have been a number of molecular orbital-type calculations of the energy levels in SiO_2 and its polymorphs with tetrahedral coordination [21-24]. There is general agreement that the uppermost filled levels are associated with the 2p lone pair, or π, orbitals of oxygen (i.e., those orbitals not involved in the σ-bond with Si) and that the σ-electrons, being more strongly bonded, will have lower energy levels. However, there is a long-standing controversy regarding the importance of π bonding, which results from the overlap of the oxygen $2p\pi$ orbitals and the originally empty 3d orbitals of silicon. Pauling [25] postulated the $3d-2p\pi$ bonding to reduce the ionic nature of the Si-O bond below 50% to satisfy his electroneutrality principle. Recent positron annihilation experiments [26,27] support Pauling's argument, particularly for amorphous SiO_2, in which the effective charge of the oxygen atom is found to be about -0.6, in electronic units (50% ionicity corresponds to a charge of -1). The experimental and theoretical papers supporting $3d-2p\pi$ bonding are too numerous to summarize here, and for a review the reader is referred to a paper by Revesz [28] and the references contained therein. On the other side of the argument are calculations by Gilbert, et al. [21], and Bennett and

20. T. H. DiStefano and D. E. Eastman, Solid State Commun. 9, 2259 (1971).
21. T. L. Gilbert, et al., Phys. Rev. B8, 5977 (1973).
22. A. J. Bennett and L. M. Roth, J. Phys. Chem. Solids 32, 1251 (1971).
23. G. A. D. Collins, D. W. J. Cruickshank, and A. Breeze, J. Chem. Soc., Faraday Trans. II 68, 1189 (1972).
24. K. L. Yip and W. B. Fowler, Phys. Rev. B10, 1400 (1974).
25. L. Pauling, J. Phys. Chem. 56, 361 (1952).
26. V. P. Prjanishnikov, et al., *Proc. IX International Congress on Glass*, Versaille, Vol. 1, pp. 119-131 (1971).
27. G. M. Bartenev, et al., Izvestiya Akademii Nauk SSSR, Neroganicheskie Materialy 6, 1553 (1970).
28. A. G. Revesz, J. Non-Crystalline Solids 11, 309 (1973).

Roth [22] based on an SiO_2 fragment and the β-crystobalite structure, respectively, which indicate relatively small 3d hybridization in the valence molecular orbitals. The calculations of Reilly [18] and the more extensive work of Yip and Fowler [24] unfortunately provide no direct evidence since these authors neglect d orbitals at the outset. However, the latter authors have noted that their poor agreement with experimental x-ray emission intensities may be due to their neglect of the silicon 3d orbitals. It seems likely that this may have contributed to the large ionicity they calculated for the SiO_4 cluster.

The optical transitions involved in the absorption and photoconductivity spectra reported here must originate from the oxygen 2p lone pair (π) orbitals, since it has been shown by ample experimental [21,29] and theoretical [18,21, 24] evidence that the oxygen 2p σ-bonding band lies at least 5 eV below the uppermost filled level. The observation of hole photoconductivity over this range of $\hbar\omega$ with a threshold coincident with that of the optical absorption compels us to conclude that the upper valence levels are broadened into a band with sufficient orbital overlap that holes readily transport. The bonding in the uppermost band is most likely due to π bonding, which we have discussed above, since the 2pπ(O) - 3d(Si) interaction is quite strong [23], whereas the overlap integral for π orbitals on neighboring oxygen atoms is much smaller even than that of their σ orbitals [21]. Also, holes are found to be trapped mostly near the $Si-SiO_2$ interface [1,30], and the density of hole traps is strongly dependent on oxide growth and anneal temperatures [6]. These observations are inconsistent with models in which holes are presumed to be self-trapped in localized valence levels. As a final observation, the transmission of our 2045-Å sample is well below 0.05% for $\hbar\omega > 10$ eV. Hence, we must conclude that the photoluminescent efficiency in these films is less than 0.05%, and, therefore, the recombination in these films with the excitation levels of our experiments is dominated by nonradiative processes.

29. T. H. Distefano and D. E. Eastman, Phys. Rev. Letters 27, 1560 (1971).
30. R. Williams and M. H. Woods, J. Appl. Phys. 46, 695 (1975).

III. VACUUM ULTRAVIOLET RADIATION STUDIES

A. CURRENT ENHANCEMENT EXPERIMENTS

It has been shown [3,6] that during irradiation of SiO_2 MOS structures, holes travel in the SiO_2, and some are trapped in the vicinity of the negative electrode. This accumulation of space charge augments the average (applied) field, and when the interface field reaches 6 to 7 MV/cm, current enhancement is observed as electron tunneling from the electrode contributes to the current. This current enhancement phenomenon proves to be a very sensitive measure of the number and location of traps near the Si-SiO_2 and gate-SiO_2 interfaces. Furthermore, it also provides a sensitive method for comparing radiation sensitivity between samples with differing processing histories. In this section we present and discuss the results of experiments on well-characterized samples. The samples were grown on 1 ohm-cm n-type <100> silicon at 900°C in steam. Following oxidation, the samples were annealed for 15 minutes in ultrapure helium at temperatures ranging from 850° to 1100°C. In addition, one set of samples was also given a 15-min 500°C anneal in hydrogen. The wafers were then divided and metallized with 1-mm-diameter, 100-Å-thick (semitransparent) Al-gate electrodes for VUV experiments. No metallization was used for the corona discharge experiments. All samples were tested for mobile ion contamination using the bias-temperature stress technique, and contamination was found to be negligible.

The current enhancement phenomenon and its experimental implementation have been described in detail previously [1]; thus, it will only be outlined briefly here. The MOS sample under test is placed in a vacuum monochromator, biased with an appropriate gate bias, either positive or negative, and irradiated with VUV light of a photon energy that is strongly absorbed* in the oxide film. One measures the time dependence of the total current flowing through the MOS device. The current measured at the initiation of radiation is just the electron or hole photocurrent flowing through the oxide. If the applied field is sufficient, eventually a current enhancement will be observed as

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*This is not essential, and the device may be irradiated with penetrating radiation as well.

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holes accumulate near the negatively biased electrode, and electron tunneling current from this electrode becomes comparable to and exceeds the photocurrent.

The results of many experiments on steam-grown oxides, which were annealed in helium at various temperatures, are summarized in Fig. 5 for positive gate bias. The current flowing initially, as shown in this figure, is
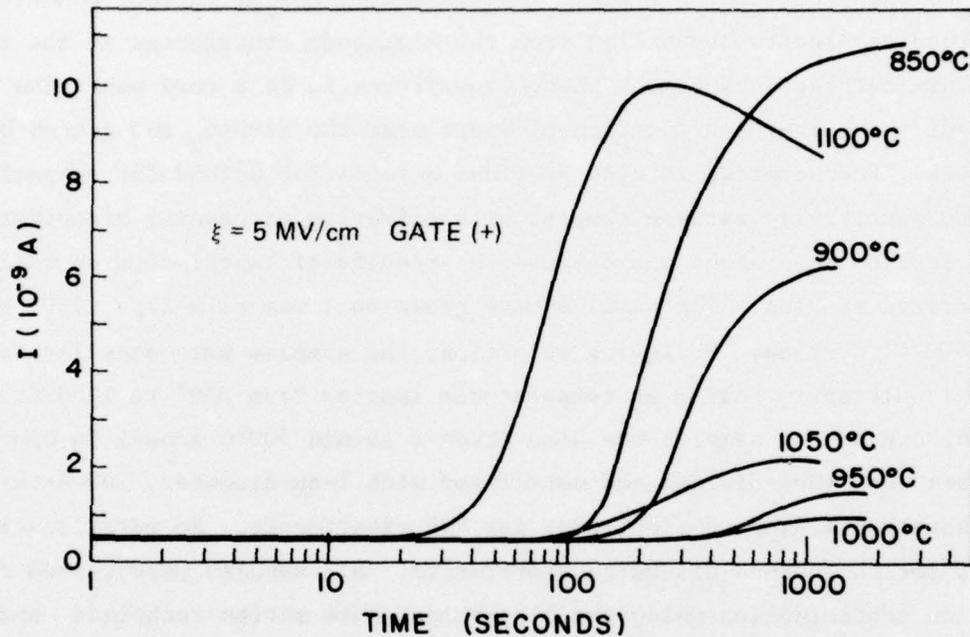
Figure 5. Time dependence of current during VUV irradiation for steam-grown samples with different helium anneal temperatures. Positive gate bias was used to produce an average field of 5 MV/cm. The photon energy was 10.2 eV and the SiO_2-absorbed photon flux was 4×10^{11} cm^{-2}s^{-1}.

the hole photocurrent produced by the 10.2-eV photons, which are strongly absorbed in the SiO_2 near the gate electrode. When sufficient space charge accumulates to raise the Si-SiO_2 interface field to the vicinity of 7 MV/cm, the current begins to increase. The curves of Fig. 5 show the time dependence of total oxide current for different helium anneal temperatures. It is important to point out that all of these samples have relatively few traps compared with those previously studied since no current enhancement is observed with applied fields less than about 4 MV/cm, whereas in previously reported results [6]

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current enhancement was observed with applied fields as small as 1 MV/cm. Furthermore, one should recognize that the differences in the amount of space charge accumulation between the samples is magnified in the current enhancement by the strong current-field dependence of the tunnel-injection mechanism. The most striking observation to be made from the data of Fig. 5 is that there is a very strong and definite minimum in the current enhancement as a function of anneal temperature. Minimum enhancement is observed at 1000°C anneal temperature, and the temperature extremes at 850°C and 1100°C are about equally effective in current enhancement. These results indicate that the low- and high-temperature anneals have markedly increased the number of traps near the Si-SiO$_2$ interface which are effective* in producing current enhancement. This statement is confirmed by the C-V curve flatband voltage shift data shown in Fig. 6. These data show that the flatband shifts at 10^3 s for the 850° and 1100°C samples are nearly twice as large as that of the 1000°C sample. Since there is ample evidence [1, 2] that charge is located mostly near the Si-SiO$_2$ interface following positive bias irradiation, this result implies that the amount of charge trapped in the 850° and 1100°C samples is about twice that of the 1000°C sample. The data of Fig. 6 show the same trends with temperature as the current enhancement data of Fig. 5. After 10^3-s exposure, there is a definite minimum in the $|\Delta V_{FB}|$ at 1000°C, and it increases markedly for lower and higher anneal temperatures. There is some crossing of curves at earlier times, and similar crossing is observed near 10^2s in the current enhancement data. It appears that for short exposures the minimum $|\Delta V_{FB}|$ is obtained with a 950°C anneal temperature.

There are two unusual effects to be noted regarding the differences between the 850° and 1100°C samples. First, focusing our attention on Fig. 5, we see that the 1100°C curve begins rising above the photocurrent about four times earlier than the 850°C sample. In addition, examination of the $|\Delta V_{FB}|$ curves in Fig. 6 for t $\gtrsim$ 100 s reveals that for the same $|\Delta V_{FB}|$ the 850°C sample has been irradiated about four times longer than the 1100°C sample.

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*The actual number of traps is difficult to ascertain because some may be so near to the silicon interface that they immediately empty by tunneling. It is suggested that the variation in temperature changes the density of traps which are either sufficiently far from the interface or have energy levels unfavorable for direct tunneling.
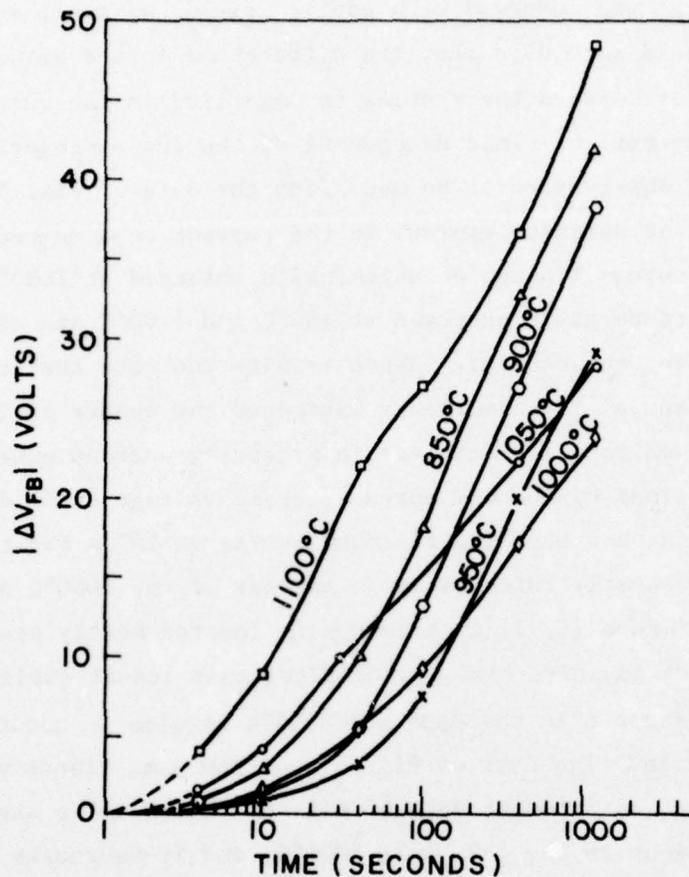
Figure 6. High-frequency (1 MHz) capacitance-voltage
flatband shift versus time during VUV
irradiation with positive gate bias and an
average oxide field of 5 MV/cm. The samples
are the same as used in the experiments
illustrated in Fig. 5, and the same irradia-
tion conditions were used.

If we consider that approximately equal hole photocurrents were used in the two
experiments, this result indicates that the 1100°C sample is initially about
four times more effective in trapping holes than the 850°C sample. An even
larger difference is noted between the 1100° and 950°C samples in Fig. 6,
where it is noted that the 950°C sample requires about ten times the exposure
of the 1100°C sample in order to accumulate the same interface charge. It is
also important to note that the final shifts obtained at 1000 s differ by only
about a factor of two for all samples. We take this to be evidence that the

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density of fillable traps does not vary much with anneal temperature. The large difference in trapping rate must then be attributed to differences in the capture cross section for holes. There is no reason to expect that the capture cross section of a specific trap should vary with anneal temperature; it is proposed that there are at least two different species of traps involved. Suppose, for example, that there is one trap species near the interface whose density decreases with temperature and a second trap with a much larger cross section whose density increases with temperature. The first trap might be associated with excess silicon near the interface [31], which, if associated with interface fixed charge, is known to decrease with increasing oxidation temperature [31]. The large cross section trap might be associated with a species which diffuses into the oxide much more rapidly at 1100°C than at 850°C. There is additional evidence that different trap species are involved, but before considering it further let us determine the approximate density and cross section of the traps.

B.   TRAPPING KINETICS

Consider a distribution of traps located in a narrow region near the $Si-SiO_2$ interface. Let there be N_T traps per cm^2 of which N_T^+ traps per cm^2 are filled with holes. Then the probability that a hole reaching the interface is trapped is $(N_T - N_T^+) \cdot S$, where S is the capture cross section. Letting J be the constant hole current density flowing through the interface, we can write

$$\frac{dN_T^+}{dt} = \frac{J}{q} \cdot (N_T - N_T^+) \cdot S \tag{4}$$

This equation has the solution:

$$N_T^+ = N_T \left(1 - e^{-\frac{J}{q} \cdot S \cdot t}\right) \tag{5}$$

and if we express the densities of traps in terms of flatband shift, Eq. (5) becomes

$$d\Delta V_{FB} = \Delta V_{FBF} \left(1 - e^{-\frac{J}{q} \cdot S \cdot t}\right) \tag{6}$$

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31.   B. E. Deal, et al., J. Electrochem. Soc. 114, 266 (1967).

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where $\Delta V_{FB} = qN_T^+ d_{ox}/\varepsilon_{ox}$ is the flatband shift at time t, d_{ox} is the oxide thickness, ε_{ox} is the dielectric constant, and $\Delta V_{FBF} = qN_T d_{ox}/\varepsilon_{ox}$ is the flatband shift with all the traps filled. This simple model assumes that emission from traps is unimportant. It is well known that some hole traps near the silicon interface retain their charge for very short times so that they make no contribution to ΔV_{FB}, which is measured typically minutes after each irradiation. Thus, the density N_T refers to the density of fillable interface traps, i.e., those which retain their charge for minutes or hours without appreciable detrapping. One can determine the trap density N_T and the capture cross section S by fitting Eq. (6) to experimental data. Unfortunately, it is not always possible to measure ΔV_{FBF} directly because tunnel injection may prevent complete filling of traps, and the highest value of ΔV_{FB} reached may be appreciably less than ΔV_{FBF}. There is an alternate method for determining N_T and S from the data. Consider the derivative of Eq. (6):

$$\frac{d\Delta V_{FB}}{dt} = \Delta V_{FBF} \, e^{-\frac{JSt}{q}} \, \frac{J}{q} \, S \tag{7}$$

Evaluate the derivative at t = 0 and some other convenient value of t, e.g., t = q/JS; then we get

$$\frac{d\Delta V_{FB}}{dt} \bigg|_{t=0} = \Delta V_{FBF} \, \frac{J}{q} \, S = \frac{Jd_{ox}}{\varepsilon_{ox}} N_T S \tag{8}$$

$$\frac{d\Delta V_{FB}}{dt} \bigg|_{t=q/(JS)} = \Delta V_{FBF} \, \frac{J}{q} \, S \, e^{-1} = \frac{Jd_{ox}}{\varepsilon_{ox}} N_T S \, e^{-1} \tag{9}$$

Clearly, we can determine the products $N_T \cdot S$ from the initial slope of the experimental curve, and the time for which the slope is 1/e of its initial value is just t = q/JS; so we get S from this time. Hence, N_T and S are both determined. Using this technique, it was found that a good fit to the 1100°C curve in Fig. 6 was obtained for $t \lesssim 100$ with $\Delta V_{FB} = 28(1 - e^{-t/28})$. Since this equation saturates at $\Delta V_{FB} = 28$, the implication is that there are other traps with smaller S which account for the continued increase of ΔV_{FB} for t > 100. Since there is reason to expect that there are at least two trap species involved, one should try to fit the data with an extension of Eq. (5), which applies for two noninteracting trap species:

$$N_T^+ = N_{T1}\left(1-e^{-\frac{J}{q}S_1 \cdot t}\right) + N_{T2}\left(1-e^{-\frac{J}{q}S_2 \cdot t}\right) \tag{10}$$

An approximate fit of Eq. (10) to some of the experimental data of Fig. 6 is shown in Fig. 7 for the 1100°, 950°, and 850°C samples. The fit was obtained
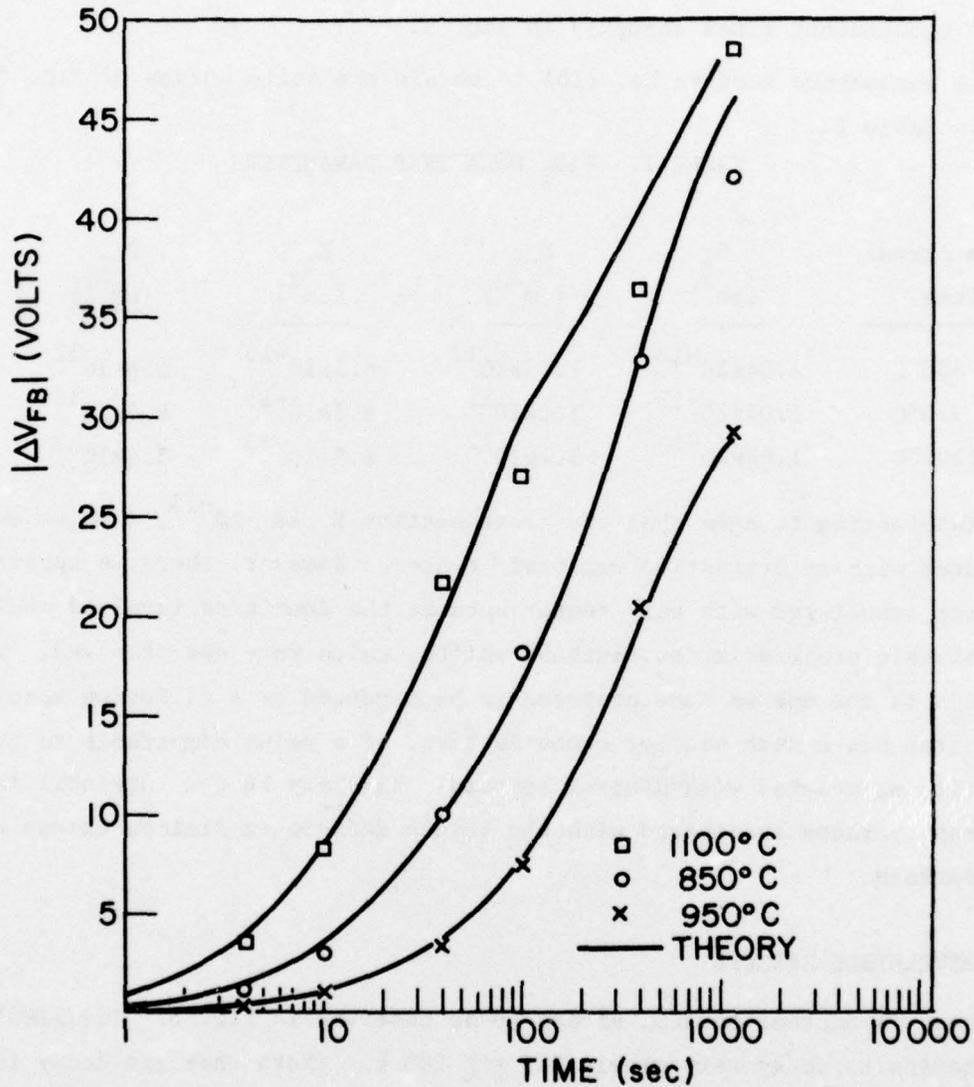

Figure 7. Illustration of the fit of some of the experimental data of Fig. 6 with a theoretical model using two species of hole traps. The solid curves are theoretical and the points experimental. The trap parameters used are given in Table I.

within the constraint that the same values of S_1 and S_2 are used for all three curves, and only the densities N_{T1} and N_{T2} were varied. The agreement is quite good, considering the simplicity of the model. Some of the discrepancy might be accounted for by the trap neutralization caused by the tunneling currents, especially for the 850° and 1100°C samples. In this regard, it should be noted that the kink in the 1100°C curve of Fig. 6 begins at about 40 s, where the current enhancement rises abruptly in Fig. 5.

The parameters used in Eq. (10) to obtain the solid curves of Fig. 7 are given in Table I.

TABLE I. SiO_2 HOLE TRAP PARAMETERS

He Anneal Temp.	S_1 (cm^2)	N_{T1} (cm^{-2})	S_2 (cm^2)	N_{T2} (cm^{-2})
850°C	1.04×10^{-13}	1.73×10^{12}	6.5×10^{-15}	8.6×10^{12}
950°C	1.04×10^{-13}	3.0×10^{11}	6.5×10^{-15}	6.3×10^{12}
1100°C	1.04×10^{-13}	5.4×10^{12}	6.5×10^{-15}	5.4×10^{12}

It is interesting to note that the cross section S_1 is $\sim 10^{-13}$, a value usually associated with an attractive coulombic center. However, there is apparently no charge associated with this center because the densities involved would require sizable preirradiation flatband shifts, which were not observed. This trap (S_1) is the one we have proposed to be produced by a diffusing species. The S_2 trap has a much smaller cross section, of a value comparable to those ordinarily associated with neutral centers. This may be the intrinsic interface trap, perhaps associated with the oxygen deficit or silicon excess near the interface.

C. IRREVERSIBLE EFFECTS

There is another unusual effect to be observed in Fig. 5. The 1100°C curve begins to decay very slowly for $t \gtrsim 200$ s. (Note that the decay is much slower than the rise since the time scale is logarithmic.) This decay in the total current might be explained by a decrease in the number of trapped holes, causing a corresponding reduction in the field. However, this is not confirmed by the data of Fig. 6, which show a monotonic increase in $|\Delta V_{FB}|$ during this

interval. It would appear that we have a dilemma: an increase in interface field and $|\Delta V_{FB}|$ with a decrease in tunneling current. There are at least two possible explanations for this effect: (1) If some atomic species is ionized by the UV radiation, it could contribute a portion of the total current until depleted in the UV absorbing region. So an ionic component of current could decay with time. If the ions accumulate very near the $Si-SiO_2$ interface, they will not increase the tunneling current, although they will increase the flatband shift. The difficulty with this explanation is that it requires an ionic current of $\sim 3 \times 10^{-9}$A or $\sim 3 \times 10^{-7}$A/cm^2 to decay over several hundred seconds. This would result in the accumulation of more than 10^{14} ions/cm^2 at the interface and unless some neutralization mechanism exists, this would produce a flatband shift of more than 500 volts. (2) When holes are trapped more than ~ 40 Å from the $Si-SiO_2$ interface, they are effective in producing current enhancement and flatband shifts. On the other hand, charge trapped very near the interface has a much reduced effect on current enhancement. The effect of charge location on current enhancement is illustrated with the aid of Fig. 8(a), which shows the calculated shape of the conduction band edge near the $Si-SiO_2$ interface with an applied (average) field of 5 MV/cm and a sheet charge density of 10^{13}q cm^{-2} located at various distances from the interface. It is seen that the tunneling distance χ_t from the silicon accumulation (or inversion) layer to the SiO_2 conduction band is markedly influenced by the location of the charge when it is within about 40 Å of the interface. In Fig. 8(b) we have plotted χ_t versus charge location for two different charge densities. It is clear that charge located about 40 Å or more from the interface produces the largest current enhancement with only a small reduction in effectiveness with increasing distance up to 100 Å or more. However, since the tunneling current is exponentially dependent on χ_t, its effectiveness is drastically reduced as charge moves nearer the interface. For example, increasing χ_t from 40 Å to 50 Å will reduce the tunneling current by a factor of more than 1000.

The increasing $|\Delta V_{FB}|$ in Fig. 6 proves that charge accumulation increases monotonically with time. In order to explain the decaying current in Fig. 4, we must hypothesize the motion of the charge centroid toward the $Si-SiO_2$ interface as accumulation continues. However, this motion of the centroid cannot be only the result of increased accumulation very near the interface; it must
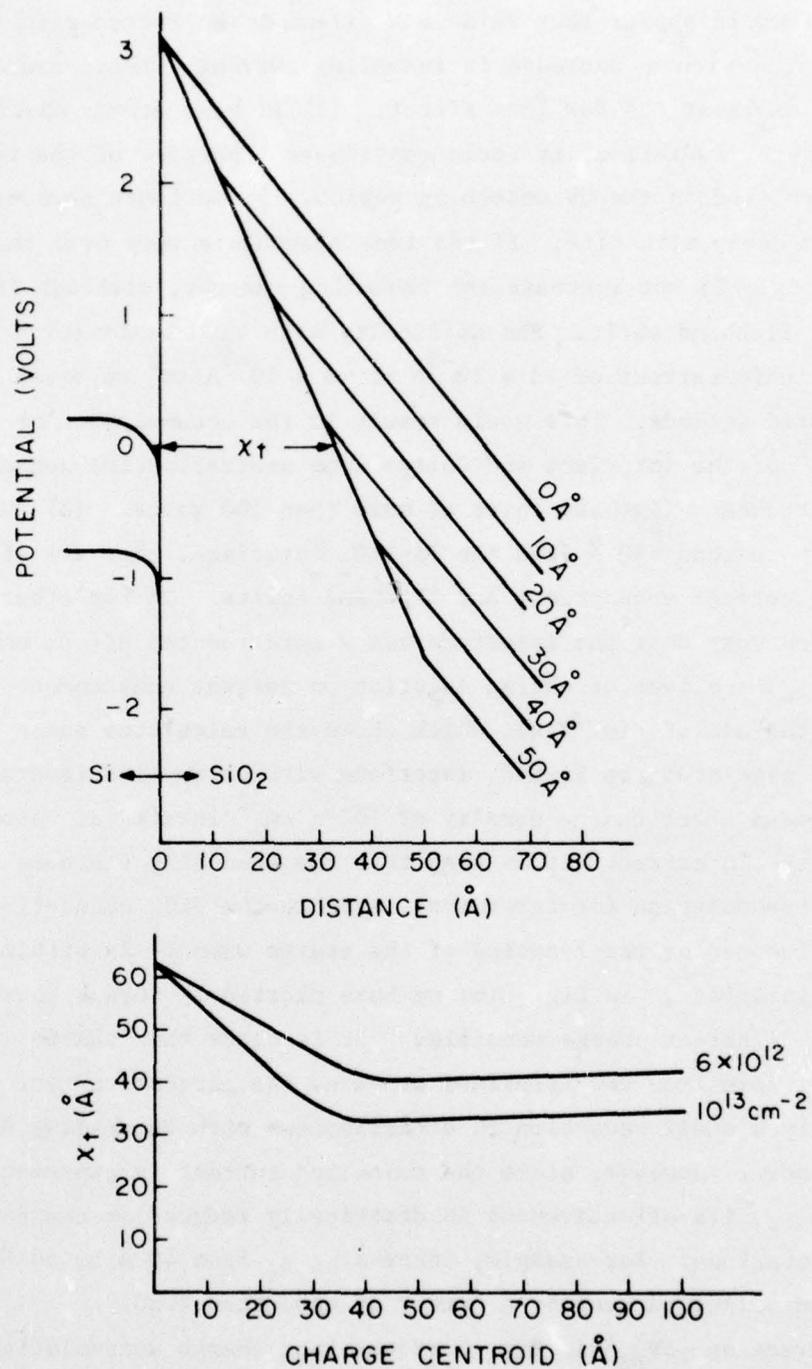
Figure 8. (a) Illustration of the shape of the Si-SiO$_2$ barrier with a sheet charge of 10^{13} q cm^{-2} located at various distances from the interface. (b) Variation of the tunneling distance χ_t with location of a charge sheet in the oxide for two different charge densities.

be accompanied by a <u>reduction</u> in charge density at more effective densities further than ~ 40 Å from the interface. This would appear to require some change in the trap structure of the oxide with continuing irradiation. Since our knowledge of the microscopic nature of the hole trap near the $Si-SiO_2$ interface is still quite meager, it would be premature to assign a specific chemical reaction to the effect at this time. However, it is not difficult to imagine that the continuous flux of holes through this disordered interface region might produce chemical reactions which are essentially irreversible at room temperature. One possibility that comes to mind is expressed in the reaction:

$$\equiv Si - OH + h^+ \rightarrow \equiv Si - O^+ + H_i \qquad (11)$$
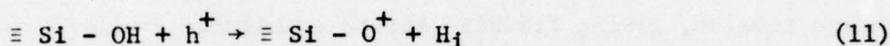
In this reaction, a hole interacts with an Si-OH bond to liberate the hydrogen which may diffuse out of the oxide. The positive charge may then be annihilated by the injected election flux leaving the center neutral.

$$\equiv Si - O^+ + e^- \rightarrow \equiv Si - O^\cdot \qquad (12)$$

The process is irreversible unless some source of hydrogen or protons is provided.

The current decay observed in Fig. 5 appears to be associated with the large cross section hole trap, since it is observed primarily in the 1100°C sample in which this trap predominates. This result provides further evidence that this trap is not intrinsic to the $Si-SiO_2$ interface but is associated with an impurity that has diffused in at the higher anneal temperatures.

IV. CORONA DISCHARGE EXPERIMENTS

In the corona discharge experiments, the surfaces of the unmetallized SiO_2 films on silicon are charged with a negative corona in air. The corona tip is about 5 cm away from the oxide surface. Negative ions form near the tip and are rapidly thermalized. They are transported through the air and land on the outer surface of the oxide with negligible kinetic energy. The field across the oxide reaches about 1.4×10^7 V/cm, which is sufficient to tunnel electrons from the hole trapping centers into the silicon directly or into the oxide conduction band [32]. When the corona is switched off the charge remains, giving flatband shifts comparable to those obtained with VUV irradiation. The flatband shifts are measured with a mercury probe.

The samples used in the experiments described here are portions of the same wafers used for the VUV experiments described in the previous section. The results are shown in Fig. 9, which displays the flatband shift versus helium anneal temperature. Since $|\Delta V_{FB}|$ is proportional to the number of traps filled by this technique, there is an apparent inconsistency between these data and the VUV data of Fig. 6. The 850°C sample shows very little trapping in the corona experiment, but quite large trapping effects with the VUV exposure, particularly associated with the small cross section trap, S_2. If one examines the flatband shifts obtained with the VUV exposure at $t = 10$ s in Fig. 6, he finds behavior qualitatively similar to that in Fig. 9, although the 850°C sample is out of place. These results suggest that the corona discharge experiment cannot fill certain traps available to holes, and these traps seem to be the ones with the small capture cross section. This disagreement between the two techniques might be explained if some traps are energetically near the SiO_2 valence band edge (within ~ 3 eV). Then it may be impossible for electrons to tunnel from these centers into the silicon because they may lie energetically opposite the Si- valence or forbidden bands even at 1.4×10^7 V/cm. This is particularly true for traps located near the Si-SiO_2 interface.

While the results shown here are preliminary and have not been duplicated, they are significant in illustrating the importance of this technique in

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32. M. H. Woods and R. Williams, to be published, J. Appl. Phys., Feb. 1976.
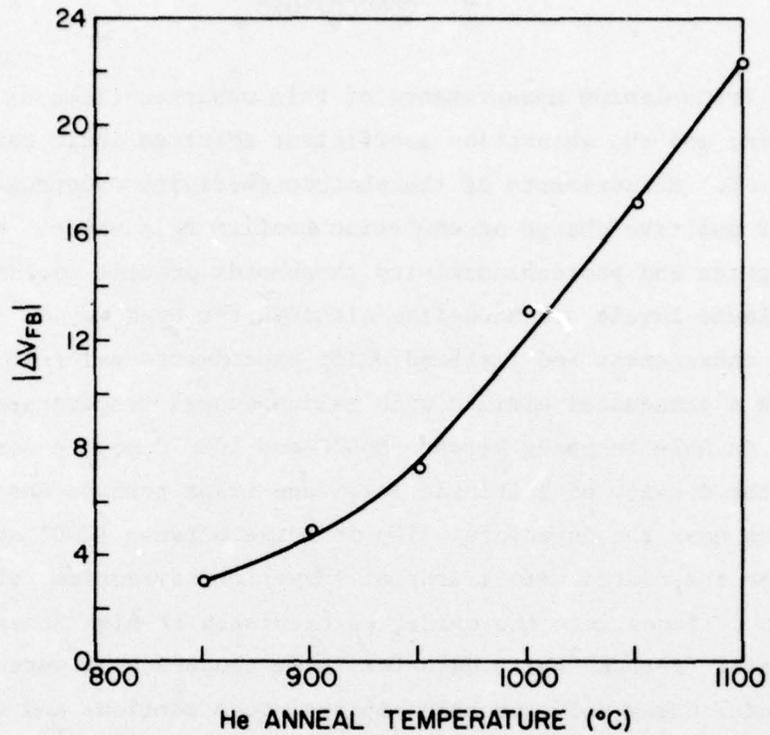
Figure 9. Flatband shift produced by negative corona
discharge exposure as a function of helium
anneal temperature. The samples are the
same as those used in obtaining the results
of Figs. 5 and 6.

sorting out the various characteristics of the hole traps. It is expected
that the combination of the VUV and corona techniques will prove useful to
future research in this area.

V. CONCLUSIONS

Optical transmission measurements of thin unbacked films of SiO_2 have been performed, and the absorption coefficient spectrum indicates a bandgap of 8.0 ± 0.2 eV. Measurements of the photoconductivity spectrum and the threshold for positive charge accumulation confirm this value. Coincidence of the absorption and photoconductivity thresholds provides evidence that the uppermost valence levels are band-like although the band may be quite narrow.

Current enhancement and flatband shift experiments using 10.2-eV vacuum UV light show a pronounced minimum with helium anneal temperature near 1000°C. The decrease in hole trapping between 850°C and 1000°C may be associated with a change in the density of intrinsic interface traps perhaps associated with excess silicon near the interface. The increase between 1000° and 1100°C is believed to be associated with a trap of larger cross section related to a species which diffuses into the oxide, particularly at high anneal temperatures. The experimental flatband shift data for three temperatures were fitted with a two-trap model using only two hole capture cross sections and varying the density of the two traps. The cross sections are 1.04×10^{-13} cm^2 and 6.5×10^{-15} cm^2, the first associated with a diffusing species, and the second with intrinsic interface trapping.

Some irreversible effects associated with the large cross section trap have been observed. A decay in the current enhancement with a corresponding increase in the flatband shift is believed to be the result of annihilation of some of the large cross section traps further from the interface during continued accumulation by the small cross section trap very near the interface. We have explained how such restructuring of the charge distribution can produce the experimental observation.

Corona discharge experiments on the same series of samples show a monotonic increase in ΔV_{FB} with anneal temperature. This result is not entirely understood at this time and has been tentatively explained by the possible inability of this technique to fill certain traps, depending on their energy and spatial location.

VI. SUMMARY OF EARLIER CONTRACT REPORTS

A. INTRODUCTION

In this section we briefly summarize the research on Al_2O_3 reported in earlier Scientific Reports; namely, in Technical Report No. AFCRL-TR-74-0330, dated 15 July 1974; Technical Report No. AFCRL-TR-75-0094, dated 16 January 1975; and Technical Report No. AFCRL-TR-75-0485, dated 17 July 1975.

The scientific work described in the aforementioned reports was undertaken with the purpose of applying new experimental techniques to develop models capable of explaining the phenomena of high-field charge injection and radiation-induced charging in pyrolytic Al_2O_3 films suitable for MOS-gate insulators. The use of vacuum ultraviolet (VUV) radiation has proved to be extremely valuable to an understanding of radiation-induced charging in SiO_2 films. Studies of SiO_2-MOS structures with bandgap light have revealed new information regarding the electronic processes in SiO_2. In particular, it has been shown that under positive gate bias holes transport to the vicinity of the Si-SiO_2 interface, where a significant number become trapped. The trapped charge enhances the interface field, resulting in electron tunneling currents that can be much larger than the photocurrents. These experiments have been extended to Al_2O_3 in an effort to provide further understanding of the electronic processes involved in this material. In these reports, we describe the results and give an interpretation of vacuum UV experiments on pyrolytic Al_2O_3 gate insulators.

Photoinjection of electrons has been used to provide information about three very important characteristics of the metal-Al_2O_3-Si system,

(1) The nature and location of electron trapping in the Al_2O_3.

(2) The barrier energy for electron injection from the silicon into the Al_2O_3.

(3) The scattering length for electrons in the Al_2O_3 near the Si-Al_2O_3 interface.

Finally, the technique of constant-current charging has been used to evaluate the effects of processing temperature and SiO_2 interlayers on the injection behavior of the Si-Al_2O_3 and Si-SiO_2-Al_2O_3 interface regions.

B. VACUUM ULTRAVIOLET RADIATION STUDIES

The energy threshold for electron-hole pair generation and radiation-induced positive charging was found to be approximately 7.8 eV. This value is significantly lower than previously predicted by others from interpretation of optical data. Our result indicates that their interpretation is probably incorrect. A decreasing flatband shift with photon energy was observed, and this is tentatively explained in terms of very small hole mobility, leaving holes trapped very near their birthsites.

The voltage dependence of flatband shift obtained under vacuum UV radiation shows a sharp maximum with voltage, and actually reverses sign for large gate voltages. This has been interpreted in terms of competition between electron-hole pair generation and electron injection from the electrodes at high interface fields.

Radiation-induced currents in aluminum oxide using strongly absorbed vacuum UV radiation have been measured. These currents show behavior similar to that which has been observed previously in SiO_2 films; namely, there is a photocurrent component and a dark current component that is apparently produced by the tunneling of electrons into the film from the silicon electrode. Several differences are noted between these results and those reported for SiO_2. First, the photocurrent component is much smaller than in the case of SiO_2, resulting in significantly less than 100% quantum efficiency. Secondly, the current enhancement mechanism occurs with a much lower applied field than in the case of SiO_2. The mechanism for the current enhancement in Al_2O_3 is believed to be the trapping of positive charge (holes) in the aluminum oxide film. Two possible models have been presented, one in which holes are mobile and one in which they are immobile. Either model can explain the presently observed experimental results. In either case, under irradiation the accumulation of positive charge in Al_2O_3 continues until the interface field is sufficient to produce tunnel injection from the silicon. This occurs at a much lower field in Al_2O_3 than in SiO_2, owing to the trap-assisted tunneling mechanism that has been described previously. Analyses of the photocurrents in this experiment have shown that it is not possible to distinguish between a model in which holes are immobile and the photocurrent results from merely the sweepout of electrons and a model in which holes are mobile and traverse the oxide. Interpretation of the results

in Al_2O_3 are complicated by the presence of large electron trapping and the relatively low injection threshold for electrons. The presence of both electron and hole trapping in Al_2O_3 and the difficulty in determining the location of the space charge by etching techniques make it very hard to distinguish between models involving mobile holes and immobile holes. Therefore, until some new experimental techniques are developed, it appears impossible to distinguish between the two models.

C. PHOTOINJECTION EXPERIMENTS

Photoinjection experiments have provided very useful information in several ways. Charge centroid measurements have shown that a large fraction of the charge injected into Al_2O_3 is trapped near the injecting electrode. Comparison of the experimental data with two limiting models shows that no conclusions can be drawn regarding the spatial distribution of *traps* but that *trapping* is localized to the interface region. Similar measurements on $Si-SiO_2-Al_2O_3$ structures have shown that trapping occurs in the Al_2O_3 near the SiO_2 interface.

Measurements of the voltage dependence of photocurrents have provided important information regarding barrier energies and electron scattering in Al_2O_3. The $Si-Al_2O_3$ barrier is approximately 4.2 eV, and the electron scattering length in the Al_2O_3 in the direction of the field is approximately 3 Å.

D. HIGH FIELD CHARGE INJECTION

Studies of high-field charge injection on Al_2O_3 MOS structures, with purposely introduced SiO_2 films between the Si and Al_2O_3, have shown that very thin SiO_2 ($\sim$40 Å) actually enhances the electron injection. Thicker films of SiO_2 ($\gtrsim$70 Å) can markedly reduce the electron injection for a given applied field in the Al_2O_3. Unfortunately, the SiO_2 layer, while reducing electron injection, increases the radiation sensitivity. Additionally, processing variables have an effect on the high-field injection process, but so far any reduction in the injection was accompanied by a corresponding reduction in hardness.

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GENERAL ELECTRIC COMPANY
ATTN JOHN W PALCHEFSKY JR
RE-ENTRY & ENVIRONMENTAL SYSTEMS DIV
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3198 CHESTNUT STREET
PHILADELPHIA, PA 19101

GENERAL ELECTRIC COMPANY
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GENERAL ELECTRIC COMPANY
ATTN JOSEPH J REIDL
ORDNANCE SYSTEMS
100 PLASTICS AVENUE
PITTSFIELD, MA 01201

GENERAL ELECTRIC COMPANY
ATTN DASIAC
TEMPO-CENTER FOR ADVANCED STUDIES
816 STATE STREET (P.O. DRAWER QQ)
SANTA BARBARA, CA 93102

GENERAL ELECTRIC COMPANY
ATTN ROYDEN R RUTHERFORD
TEMPO-CENTER FOR ADVANCED STUDIES
816 STATE STREET (P.O. DRAWER QQ)
SANTA BARBARA, CA 93102

GENERAL ELECTRIC COMPANY
ATTN M ESPIG
TEMPO-CENTER FOR ADVANCED STUDIES
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GENERAL ELECTRIC COMPANY
ATTN CSP 0-7 L H DEE
P.O. BOX 1122
SYRACUSE, NY 13201

GENERAL ELECTRIC COMPANY
ATTN JOHN A ELLERHORST E 2
AIRCRAFT ENGINE GROUP
EVENDALE PLANT
CINCINNATI, OH 45215

GENERAL ELECTRIC COMPANY
ATTN W J PATTERSON DROP 233
AEROSPACE ELECTRONICS SYSTEMS
FRENCH ROAD
UTICA, NY 13503

GENERAL ELECTRIC COMPANY
ATTN CHARLES M HEWISON DROP 624
AEROSPACE ELECTRONICS SYSTEMS
FRENCH ROAD
UTICA, NY 13503

GENERAL ELECTRIC COMPANY
ATTN DAVID W PEPIN DROP 160
P.O. BOX 5000
BINGHAMTON, NY 13902

GENERAL ELECTRIC COMPANY-TEMPO
ATTN WILLIAM ALFONTE

ATTN: DASIAC
C/O DEFENSE NUCLEAR AGENCY
WASHINGTON, DC 20305

GENERAL RESEARCH CORPORATION
ATTN ROBERT D HILL
P.O. BOX 3587
SANTA BARBARA, CA 93105

GENERAL RESEARCH CORPORATION
ATTN DAVID K OSIAS
WASHINGTON OPERATIONS
WESTGATE RESEARCH PARK
7655 OLD SPRINGHOUSE ROAD, SUITE 700
MCLEAN, VA 22101

GRUMMAN AEROSPACE CORPORATION
ATTN JERRY ROGERS DEPT 533
SOUTH OYSTER BAY ROAD
BETHPAGE, NY 11714

GTE SYLVANIA, INC.
ATTN LEONARD L BLAISDELL
ELECTRONICS SYSTEMS GRP-EASTERN DT.
77 A STREET
NEEDHAM, MA 02194

GTE SYLVANIA, INC.
ATTN CHARLES H THORNHILL LIBRARIAN
ELECTRONICS SYSTEMS GRP-EASTERN DIV
77 A STREET
NEEDHAM, MA 02194

GTE SYLVANIA, INC.
ATTN JAMES A WALDON
ELECTRONICS SYSTEMS GRP-EASTERN DIV
77 A STREET
NEEDHAM, MA 02194

GTE SYLVANIA, INC.
ATTN PAUL B FREDRICKSON
189 B STREET
NEEDHAM HEIGHTS, MA 02194

GTE SYLVANIA, INC.
ATTN H & V GROUP MARIO A NUREFORA

189 B STREET
NEEDHAM HEIGHTS, MA 02194

GTE SYLVANIA, INC.
ATTN HERBERT A ULLMAN
189 B STREET
NEEDHAM HEIGHTS, MA 02194

GTE SYLVANIA, INC.
ATTN CHARLES H RAMSBOTTOM
189 B STREET
NEEDHAM HEIGHTS, MA 02194

GULTON INDUSTRIES, INC.
ATTN ENGINEERED MAGNETICS DIV
ENGINEERED MAGNETICS DIVISION
13041 CERISE AVENUE
HAWTHORNE, CA 90250

HARRIS CORPORATION
ATTN T L CLARK MS 4040
HARRIS SEMICONDUCTOR DIVISION
P.O. BOX 883
MELBOURNE, FL 32901

HARRIS CORPORATION
ATTN CARL F DAVIS MS 17-220
HARRIS SEMICONDUCTOR DIVISION
P.O. BOX 883
MELBOURNE, FL 32901

HARRIS CORPORATION
ATTN WAYNE E CHARE MS 16-111
HARRIS SEMICONDUCTOR DIVISION
P.O. BOX 883
MELBOURNE, FL 32901

HAZELTINE CORPORATION
ATTN TECH INFO CTR M WAITE
PULASKI ROAD
GREEN LAWN, NY 11740

HONEYWELL INCORPORATED
ATTN RONALD R JOHNSON A1622
GOVERNMENT AND AERONAUTICAL
PRODUCTS DIVISION
2600 RIDGEWAY PARKWAY
MINNEAPOLIS, MN 55413

HONEYWELL INCORPORATED
ATTN R J KELL MS S2572
GOVERNMENT AND AERONAUTICAL
PRODUCTS DIVISION
2600 RIDGEWAY PARKWAY
MINNEAPOLIS, MN 55413

HONEYWELL INCORPORATED
ATTN HARRISON H NOBLE MS 725-5A
AEROSPACE DIVISION
13350 U.S. HIGHWAY 19
ST. PETERSBURG, FL 33733

HONEYWELL INCORPORATED
ATTN MS 725- STACEY H GRAFF
AEROSPACE DIVISION
13350 U.S. HIGHWAY 19
ST. PETERSBURG, FL 33733

HONEYWELL INCORPORATED
ATTN TECHNICAL LIBRARY
RADIATION CENTER
2 FORBES ROAD
LEXINGTON, MA 02173

HUGHES AIRCRAFT COMPANY
ATTN BILLY W CAMPBELL MS 6-E-110
CENTINELA AND TEALE
CULVER CITY, CA 90230

HUGHES AIRCRAFT COMPANY
ATTN DAN BINDER MS 6-D147
CENTINELA AND TEALE
CULVER CITY, CA 90230

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HUGHES AIRCRAFT COMPANY
ATTN KENNETH R WALKER M S D157
CENTINELA AND TEALE
CULVER CITY, CA 90230

KAMAN SCIENCES CORPORATION
ATTN ALBERT P BRIDGES
P. O. BOX 7463
COLORADO SPRINGS, CO 80933

HUGHES AIRCRAFT COMPANY
ATTN EDWARD C SMITH MS A620
SPACE SYSTEMS DIVISION
P.O. BOX 92919
LOS ANGELES, CA 90009

KAMAN SCIENCES CORPORATION
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P. O. BOX 7463
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HUGHES AIRCRAFT COMPANY
ATTN WILLIAM W SCOTT MS A1080
SPACE SYSTEMS DIVISION
P.O. BOX 92919
LOS ANGELES, CA 90009

LITTON SYSTEMS, INC.
ATTN JOHN P RETZLER
GUIDANCE & CONTROL SYSTEMS DIVISION
5500 CANOGA AVENUE
WOODLAND HILLS, CA 91364

IBM CORPORATION
ATTN FRANK FRANKOVSKY
ROUTE 17C
OWEGO, NY 13827

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ATTN VAL J ASHBY MS 67
GUIDANCE & CONTROL SYSTEMS DIVISION
5500 CANOGA AVENUE
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ROUTE 17C
OWEGO, NY 13827

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ATTN DEPT 81-01 G R MORRIS
P.O. BOX 504
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ION PHYSICS CORPORATION
ATTN ROBERT D EVANS
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IRT CORPORATION
ATTN MDC
P.O. BOX 81087
SAN DIEGO, CA 92138

LOCKHEED MISSILES & SPACE CO INC
ATTN EDWIN A SMITH DEPT 85-85
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MARTIN MARIETTA AEROSPACE
ATTN MONA C GRIFFITH LIB MP-30
ORLANDO DIVISION
P.O. BOX 5837
ORLANDO, FL 32805

MARTIN MARIETTA AEROSPACE
ATTN WILLIAM J MRAS MP-413
ORLANDO DIVISION
P.O. BOX 5837
ORLANDO, FL 32805

MARTIN MARIETTA AEROSPACE
ATTN JACK M ASHFORD MP-537
ORLANDO DIVISION
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MARTIN MARIETTA CORPORATION
ATTN PAUL G GAGE MATL 8203
DENVER DIVISION
P.O. BOX 179
DENVER, CO 80201

MARTIN MARIETTA CORPORATION
ATTN RESEARCH LIB 6617 JAY R MCKEE
DENVER DIVISION
P.O. BOX 179
DENVER, CO 80201

MARTIN MARIETTA CORPORATION
ATTN GEN T GRAHAM MS P0-454
DENVER DIVISION
P.O. BOX 179
DENVER, CO 80201

MARTIN MARIETTA CORPORATION
ATTN J L GOODWIN MATL 0452 (UNCL ONLY)
DENVER DIVISION
P.O. BOX 179
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ATTN L ROSSI DEPT 81-64
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LOCKHEED MISSILES & SPACE CO INC
ATTN PHILIP J HART DEPT 81-14
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3251 HANOVER STREET
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LTV AEROSPACE CORPORATION
ATTN TECHNICAL DATA CENTER
VOUGHT SYSTEMS DIVISION
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LTV AEROSPACE CORPORATION
ATTN TECHNICAL DATA CTR

P.O. BOX 5907
DALLAS, TX 75222

M.I.T. LINCOLN LABORATORY
ATTN LEONA LOUGHLIN LIBRARIAN A-082
P.O. BOX 73
LEXINGTON, MA 02173

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MITRE CORPORATION, THE
ATTN LIBRARY

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BEDFORD, MA   01730

MCDONNELL DOUGLAS CORPORATION
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POST OFFICE BOX 516
ST. LOUIS, MISSOURI 63166

NATIONAL ACADEMY OF SCIENCES
ATTN R S SHANE NAT MATERIALS ADVSY
ATTN, NATIONAL MATERIALS ADVISORY BOA
2101 CONSTITUTION AVENUE
WASHINGTON, DC   20418

MCDONNELL DOUGLAS CORPORATION
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POST OFFICE BOX 516
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MISSION RESEARCH CORPORATION
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SUDBURY, MA 01776

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ATTN RECORDS SUPERVISOR
201 VARICK STREET
NEW YORK, NY 10014

RCA CORPORATION
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GOVERNMENT & COMMERCIAL SYSTEMS
ASTRO ELECTRONICS DIVISION
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PRINCETON, NJ 08540

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2700 MERCED STREET
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CAMDEN COMPLEX
FRONT & COOPER STREETS
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POWER PHYSICS CORPORATION
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RENSSELAER POLYTECHNIC INSTITUTE
ATTN RONALD J GUTMANN
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ROCKWELL INTERNATIONAL CORPORATION
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5225 C AVENUE NE
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SANDERS ASSOCIATES, INC.
ATTN WM L ATTEL NCA 1-3236
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NASHUA, NH 03060

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SCIENCE APPLICATIONS, INC.
ATTN LARRY SCOTT
P.O. BOX 2351
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SCIENCE APPLICATIONS, INC.

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SIMULATION PHYSICS, INC.
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ATTN TECH INFO CENTER
150 TOTOWA ROAD
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SINGER COMPANY, THE
ATTN IRVIN GOLDMAN ENG MANAGEMENT
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LITTLE FALLS, NJ 07424

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SPERRY FLIGHT SYSTEMS DIVISION
ATTN D ANDREW SCHOW
SPERRY RAND CORPORATION
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SUNDSTRAND CORPORATION
ATTN CURTIS B WHITE (NO CLASS)
4751 HARRISON AVENUE
ROCKFORD, IL 61101

SPERRY RAND CORPORATION
ATTN JAMES A INDA MS 41T25
UNIVAC DIVISION
DEFENSE SYSTEMS DIVISION
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ST. PAUL, MN 55101

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1090 SAN MIGUEL ROAD
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ATTN CHARLES L CRAIG, E.
SPERRY DIVISION
SPERRY GYROSCOPE DIVISION
SPERRY SYSTEMS MANAGEMENT DIVISION
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SPERRY SYSTEMS MANAGEMENT DIVISION
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TEXAS INSTRUMENTS, INC.
ATTN DONALD J HANUS M S 72

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DALLAS, TX 75222