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STUDY OF ELECTRONIC TRANSPORT AND BREAKDOWN IN THIN INSULATING FILMS

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An overview is given of progress in the study of high-field electronic transport and dielectric breakdown in thin (1000-5000 Å) insulating films on silicon. The principal results to date are on SiO_2; also under study are Al_2O_3, Si_3N_4, and layered composites. The studies include corona-induced nondestructive breakdown, self-quenched breakdown, effects of electron irradiation, study of charge-carrier trapping, study of lateral nonuniformities, electron-beam probing of the insulator-semiconductor interface, and theoretical modeling of hot-electron distributions and of localized breakdown.

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I. INTRODUCTION

The purpose of this report is to provide an overview of progress in a research program directed toward a basic understanding of electronic transport, charge trapping, and dielectric breakdown in the thin insulating films used in integrated circuits. The films being studied are silicon dioxide, aluminum oxide, silicon nitride, and their layered composites, on silicon substrates. The purpose of the program is to provide a correct and quantitatively accurate understanding of the physical processes leading to breakdown of the films, with the ultimate objective of providing a rational basis for the choice of materials, processing methods and treatment of insulating films for increased yield in manufacturing and greater reliability in use. The results obtained in each of the various aspects of this program are being presented in a series of Special Reports, some of which have already been issued and others of which are in various stages of preparation.

The program consists of a number of coordinated investigations which include studies of transport and trapping in which charge injection is accomplished by corona charging of the surface of the insulator; the use of UV and vacuum UV excitation for charge injection and trap depopulation, combined with corona charging for inducing transport; the study of insulator breakdown by the self-quenching technique; the probing of trapping centers in insulating films by charge-discharge techniques using equipment which we have developed especially for this purpose; studies of charge transport and trapping using an electron beam for carrier injection; studies of lateral nonuniformities in MIS structures by electronic measurement techniques and by the use of a scanning electron microscope and theoretical modeling of hot-electron distributions and of localized breakdown. A summary of overall progress in each of these areas is given in subsequent sections of this report, together with brief descriptions of some recent results.

II. CORONA-INDUCED NONDESTRUCTIVE BREAKDOWN OF INSULATING FILMS

(Z. A. Weinberg and H. S. Lee collaborating)

The use of a corona discharge at atmospheric pressure to contact the unmetallized surface of an insulating film provides a convenient means of inducing charge injection and transport without danger of catastrophic

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breakdown. The procedures employed, together with some of the earlier results, were described in a previous report.[1] Two techniques that we developed during the course of this work have been described in journal papers and in Special Reports on this contract, one a p-n junction technique for determining the sign of the principal charge carrier in the insulator[2] and the other a comparison method for measuring the potential difference across an insulating film during steady-state corona charging.[3] A comprehensive paper describing the corona technique and giving the results of a study of high-field effects in thermally grown SiO_2 is being prepared in preprint form as a Special Report on this contract and will appear subsequently in a journal.

The neutralization of an ion at the surface of the insulator will depend on the species of ion being used. Our original work was done in dry air, and we are currently investigating the effects produced by ions obtained from corona discharges in other gases. The experimental equipment has been altered to provide sample current densities greater than those obtainable previously, and we are studying the effects obtained over a wide range of current densities. One of our most important recent findings has been the generation of electron trapping centers in thermally grown SiO_2 under the very high field conditions produced by negative charging of the insulator surface. A typical result is shown in Fig. 1. The sample here consists of a 1000Å film of SiO_2 grown in dry oxygen on a p-type silicon substrate with a resistivity of 1-2 Ω-cm. The C-V curves of Fig. 1 were taken at 1 MHz after temporary metallization of the surface by use of a mercury probe. Curve 1 shows the initial C-V curve. The flatband voltage is nearly zero, indicating negligible storage of charge in the insulator. Curve 2 was taken after a 6-minute exposure of the insulator surface to negative corona, using a current density of 3×10^{-7} A/cm^2. The average electric field in the insulator under these conditions was very large, about 1.3×10^7 V/cm.[1] The leftward shift of Curve 2 indicates positive charge storage in the insulator. The important effect, however, is seen when negative corona charging is followed by positive corona charging. Curve 3 of Fig. 1 shows the effect of an additional 10 minutes of exposure to positive corona at a current

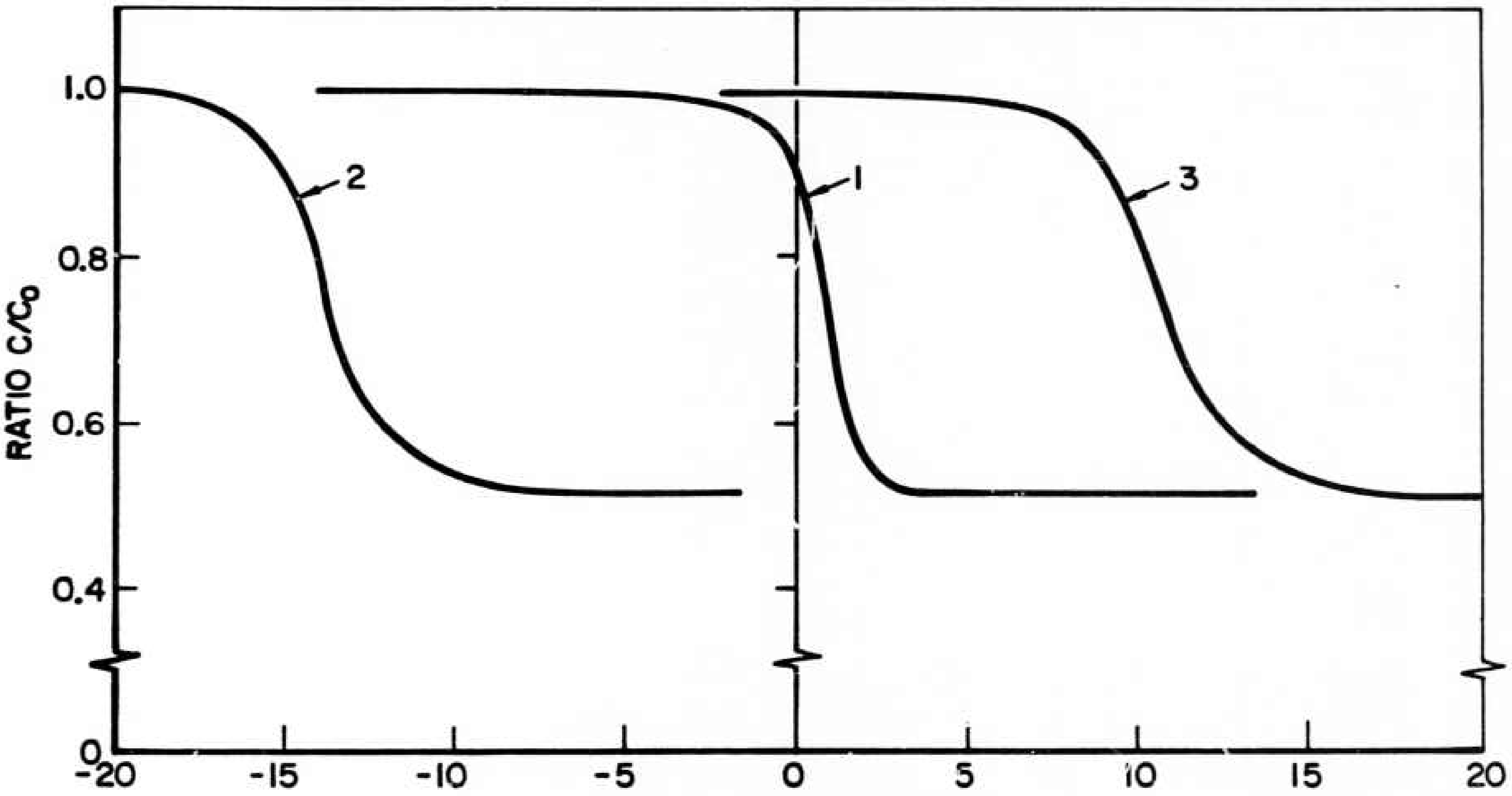


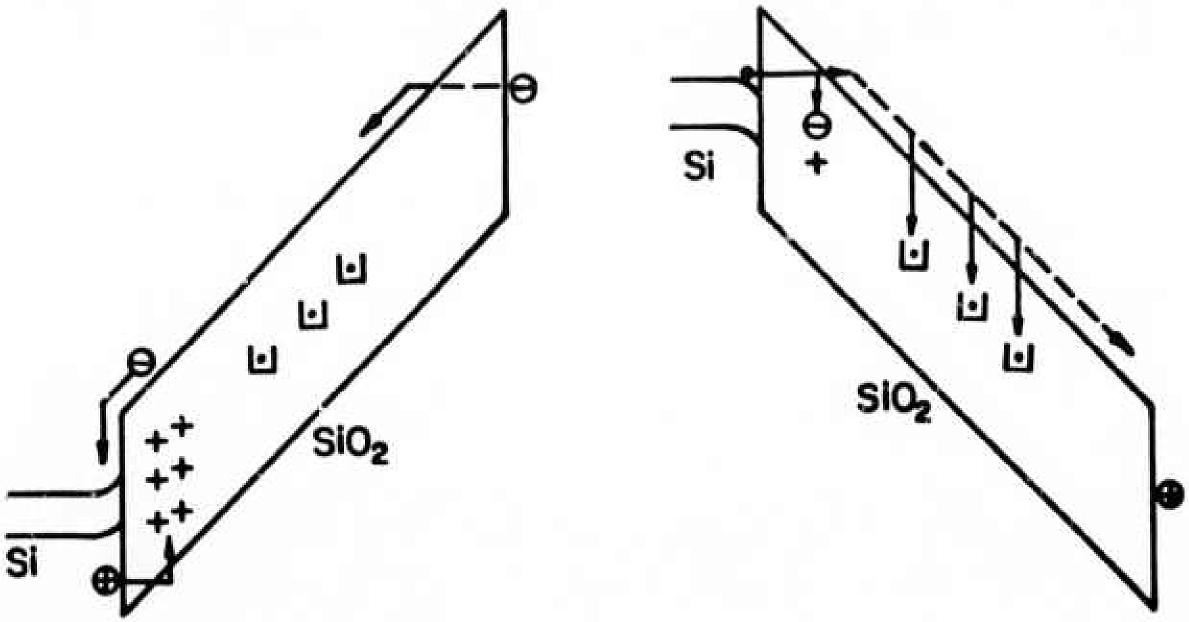
Fig. 1. Effect of Positive Corona After Negative Corona. 1000Å SiO_2 on p-Si, 1-2 Ω-cm. 1) Initial Curve. 2) After 6 min. Negative Corona, $J = 3 \times 10^{-7}$ A/cm^2. 3) After 10 additional min. in Positive Corona, $J = 2 \times 10^{-7}$ A/cm^2.

density of 2×10^{-7} A/cm^2. This shifts the C-V curve to a positive flatband voltage, indicating the storage of negative charge. Control samples that have been subjected to positive corona of this intensity do not show any appreciable storage of charge, either positive or negative, and, in fact, thermally grown SiO_2 normally possesses very few electron trapping centers. The conclusion here is that electron traps have been generated in the SiO_2 by exposure to the negative corona.

Diagrams showing our interpretation of this effect are shown in Fig. 2. During exposure to negative corona, electrons tunnel from the surface into the conduction band of the SiO_2 and drift toward the silicon substrate. The electrons, upon entering the silicon substrate, generate hole-electron pairs,[2] and holes (possibly hot holes) enter the oxide where they are trapped.[4] The trapped holes give rise to the negative flatband shift observed after negative corona charging. At the same time, electron traps, whose nature and characteristics have yet to be explored, are generated in the oxide, but the negative charge stored in these cannot be observed because their effect is overshadowed by the positive trapped holes. If the sample is now exposed to positive corona, as is shown in Fig. 2(b), electrons tunnel into the oxide from the substrate.[2] Some of these electrons recombine with the trapped holes, thus gradually reducing the trapped positive charge to zero and allowing the negative charge in the electron traps to be observed.

The significance of electron-trap generation under high-field conditions is that when the newly generated traps fill with electrons, the resulting space charge produces a nonuniform electric field distribution within the oxide, and this results in an enhancement of the electric field intensity in the region between the trapped electrons and the positive electrode. The mechanisms of breakdown are very sensitive to the magnitude of the electric field, and a localized enhancement can affect the breakdown properties of the insulating film in a major way.

It is of interest to note that we also observe the generation of electron traps within thermally grown silicon dioxide under conditions of shallow electron-beam irradiation of the insulator (Section VI).



a) NEGATIVE CORONA

b) NEGATIVE CORONA FOLLOWED BY POSITIVE CORONA

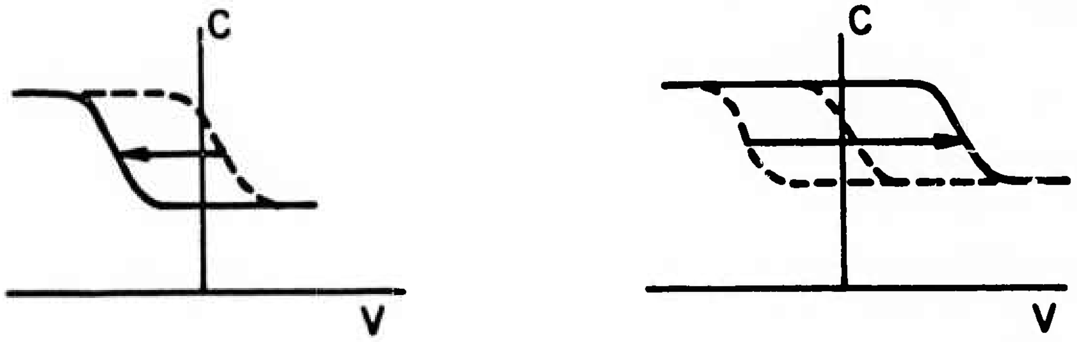


Fig. 2· Explanation of the Curves of Fig. 1.
(a) J ∿ 3 x 10^{-7} A/cm^2, E ∿ 1.3 x 10^7 V/cm.
(b) J ∿ 2 x 10^{-7} A/cm^2, E ∿ 6 x 10^6 V/cm.

The relationship, if any, between the electron traps generated under these two conditions has yet to be established.

An important controversy in recent years has been concerned with the role of impact ionization in the breakdown of insulators. Clearly the breakdown of the insulator terminates in thermally produced damage, but the initiating mechanisms are in question. Evidence exists that thermal damage is preceded by an instability, perhaps purely electronic in origin, in which at least two separate processes reinforce each other to provide the effect of a positive feedback. Impact ionization is a likely candidate for the initiating process, but experiments on thermally grown SiO_2 have indicated that free electrons, which are the principal charge carriers in this material, are not, <u>on the average</u>, substantially heated even at large electric field intensities.[2] There remains the question of whether a small but sufficient fraction of the free electrons may reach large enough kinetic energies to produce impact ionization. Two separate studies in our laboratories indicate that this is so. One of these, which employs the self-quenching technique, is discussed in Section IV. The other study utilized a positive corona to produce current densities greater than those employed in previous studies. As was indicated in Fig. 2, a positive corona which produces current densities of the order of 10^{-7} A/cm^2 (and which requires fields of about 6 x 10^6 V/cm) results only in the tunneling of electrons from the substrate with the subsequent neutralization of positive charge stored previously and the filling of any electron traps that may be present. Note that the charge storage proceeds in the <u>negative</u> direction. However, an increase in the magnitude of the positive-corona-induced current by a factor of ten to 10^{-6} A/cm^2 (which requires a field of about 7 x 10^6 V/cm), is found to result in <u>positive</u> charge storage within the oxide. Our interpretation of this is shown in Fig. 3. The main current is carried by electrons which tunnel from the substrate into the conduction band of the oxide. At these higher electric fields a few electrons leave the well behaved energy distribution and gain enough kinetic energy to cause hole-electron pair production by impact ionization.

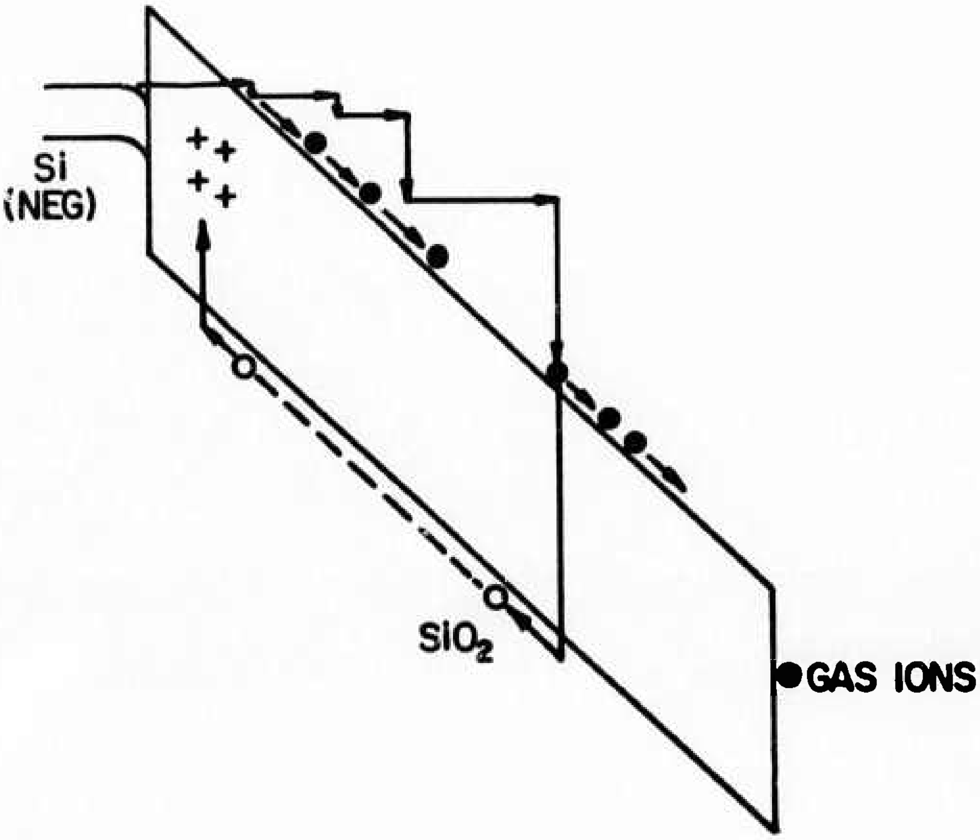


Fig. 3. Effect of Greater Current Density (Impact-Ionization Model). $J \sim 10^{-6}$ A/cm^2, $E \sim 7 \times 10^6$ V/cm.

The holes drift toward the substrate, and some of them are captured by the hole traps which are known to exist in large concentrations near the Si-SiO_2 interface. A competing process is the neutralization of trapped holes by incoming electrons in the manner shown in Fig. 2(b); thus positive charge will accumulate only when hole production and trapping dominates over recombination. The importance of the processes shown in Fig. 3 is that positive charge which accumulates near the Si-SiO_2 interface will sharpen the electric field in this region and will result in easier tunneling of electrons from the substrate. We have, therefore, three processes which are linked together in a positive-feedback relationship: tunneling of electrons from the substrate, hole-electron pair production under sufficiently high fields, and the trapping of holes near the Si-SiO_2 interface with the result that tunneling of electrons from the substrate is made easier. Actual runaway can not take place in the corona-charging experiment because the corona acts as a current source; thus the results obtained in this way are complementary to those discussed in Section IV, where the self-quenching technique was used and localized breakdown took place.

III. UV AND VACUUM UV EXCITATION COMBINED WITH CORONA CHARGING

(H. H. Chao collaborating)

We have designed and constructed apparatus for the simultaneous use of corona charging with UV and vacuum-UV excitation. The use of ions from a corona discharge to provide the electric field in the insulator eliminates the need for a metallic field plate. Thus (a) the absorption of light in a metallic field plate is avoided, and (b) charge carriers can be photoinjected from the substrate without simultaneously injecting carriers of the opposite sign from a surface metallization. The latter removes a fatal ambiguity that has plagued such experiments in the past. A similar experiment with this degree of sophistication has not, to our knowledge, been set up previously. This apparatus offers the possibility of injecting holes into the insulating film without recombining them with electrons simultaneously injected from a metallic electrode. The injection of holes from the substrate by sub-bandgap photons and the injection of holes from the front surface by bandgap photons provides convenient means for studying hole trapping and recombination in insulating films.

Preliminary experiments using this equipment are now under way and the results of these studies will be reported from time to time.

IV. STUDIES OF INSULATOR BREAKDOWN BY THE SELF-QUENCHING TECHNIQUE

(D. Y. Yang collaborating)

The self-quenching technique employs a thin (200-1000 Å) metallization so that when a local breakdown occurs in the insulator, the localized heating causes the metal to be vaporized in the vicinity of the fault; thus the damage is self limiting. There are several advantages to this procedure: (1) The remainder of the sample is preserved for further experimentation. (2) The location of the breakdown can be correlated with other information concerning the sample, for example with the location of faults in the insulator or in the metallization. (3) The physical appearance of the breakdown region can provide information about the mechanisms and progress of the breakdown. (4) If the sample originally has weak spots, these can be "blown out" at the start of the experiment and the intrinsic properties of the insulating film can then be observed.

In a published paper[5] and in a Special Report on this contract[6] we have previously reported on the strikingly different appearance of the breakdown regions observed in Al-SiO_2-(100)Si structures for the four different combinations of n-type and p-type substrates with positive and negative field-plate polarities. The shape of removal of field-plate material showed an anisotropy reflecting the underlying (100) silicon structure when the substrate was p-type and when the field plate was positive. We found methods of enhancing this effect, and the results of a further study of this anisotropy are being prepared as a Special Report on this contract and for journal publication.[7] A comprehensive report of results obtained on thermally grown SiO_2 films by the self-quenching technique has been issued as a Special Report on this contract.[8]

A review of some of the salient results of these studies will be presented at the 1975 International Reliability Physics Symposium and will be published in the Proceedings of this Symposium.[9] During the course of this work we observed and investigated a slow instability which leads to breakdown in Si-SiO_2-Al structures. This seems clearly to be related to the positive charging phenomenon observed under intense positive corona, which is described in Section II of this report. Our observations and conclusions are being prepared as a Special Report on this contract and will also be submitted for journal publication.[10] A brief account of the phenomenon is given below.

We find that when we subject a Si-SiO_2-Al structure to a voltage just below breakdown, using either polarity, a small current initially flows which is evidently caused by the tunneling of electrons from whichever electrode is negative. The current gradually increases over a period of time whose duration is critically dependent on the exact value of the applied voltage: it can be minutes, hours, or longer. This long-term instability eventually results in some self-quenched breakdowns and finally terminates in a series of rapid breakdowns which destroy the sample if the voltage is not removed. Two further observations are of great importance. First, positive charge storage is found to build up in the insulator as the instability progresses. Second, if the sample is cooled (toward liquid nitrogen temperature) the instability progresses at a faster rate; in fact, a sample that is biased just below instability at room temperature will become unstable as the temperature is reduced. The latter result is striking because it would seem to rule out both thermal processes and impurity ion effects.

The observed results can be explained as shown in Fig. 4, which, it will be seen, has elements in common with Fig. 3. In Fig. 4 we show the aluminum field plate to be positive, but entirely similar results are obtained with the reverse polarity. Electrons tunnel from the negative electrode. A few of these gain a large enough kinetic energy in the high field to cause hole-electron pair production in the oxide. Some of the holes are trapped near the interface of the insulator

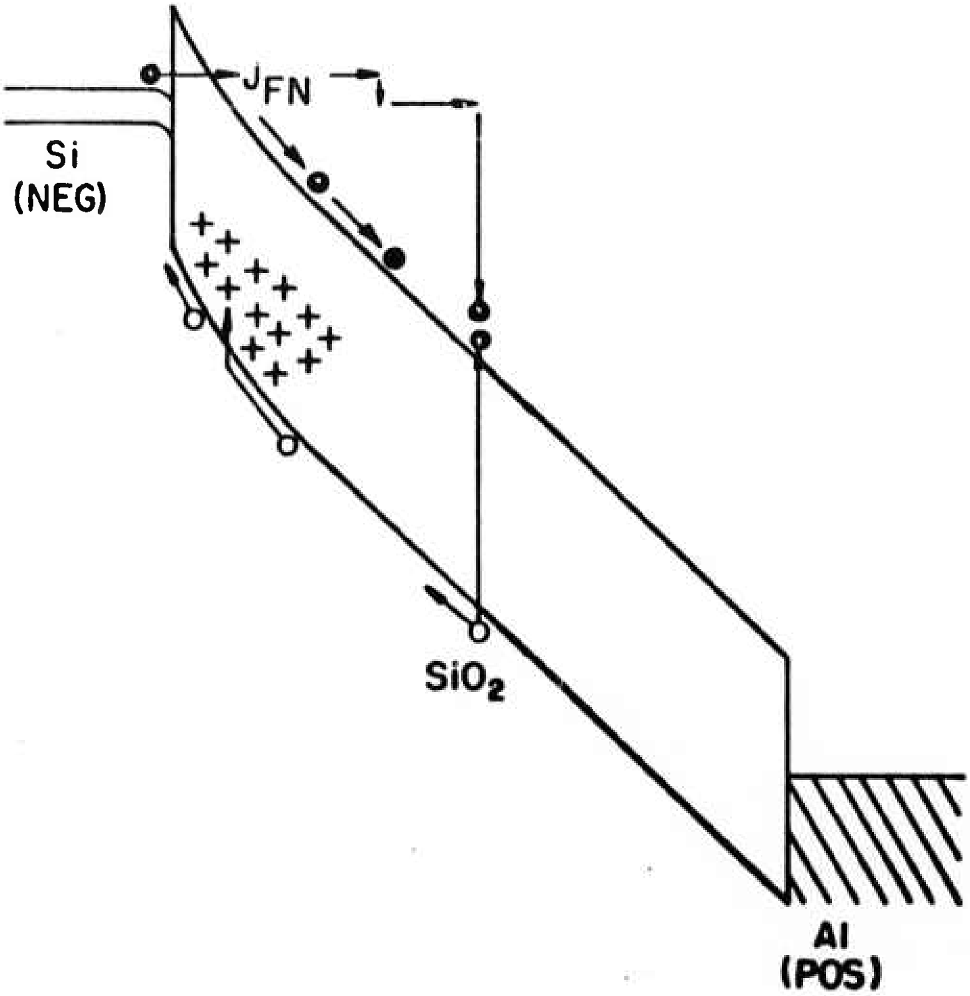


Fig. 4. Explanation of the Slow Instability.

with the negative electrode, thus enhancing the electric field in this region and increasing the tunneling of electrons. We estimate that only one in 10^3 or 10^4 electrons needs to get hot enough to produce impact ionization, the positive charge being the result of an integrated trapping of holes over a long period of time. Again, as in the corona experiment described in Section II, a competing process is the recombination of trapped holes with incoming electrons. As the temperature is lowered, the fraction of electrons that can reach the required large kinetic energy is increased and the instability is enhanced.

We have performed other experiments which indicate that the trapped positive charge is that of holes, not of ions. Bias-temperature stress does not remove the charge. On the other hand, the positive charge can be removed by an injection of electrons. The latter is a characteristic of trapped holes, not of ions.

Other possible sources of the holes are indicated in the diagram. At B and C holes are shown tunneling from the positive electrode. If electrons were trapped under this electrode, the tunneling of holes would be enhanced. However, we find essentially the same instability when the polarities are reversed, and C-V measurements show no storage of negative charge near the Si-SiO_2 interface under these conditions.

A more complete account of our experiments, results, and conclusions will be presented in a Special Report.[10]

V. CHARGE-DISCHARGE STUDIES OF CHARGE-CARRIER TRAPPING IN INSULATING FILMS (C. Jenq and J. J. Clement collaborating)

In these studies, trapping centers in the insulating films and at their interfaces are probed by charge-discharge techniques in which internal photoinjection is used to provide carriers to charge the traps and heat or photon energy is used to stimulate discharge of trapped carriers. The apparatus, which we designed and constructed specifically for the convenient exploitation of these techniques, also includes provision for the use of soft X-rays for the production of hole-electron pairs in the insulating films.

Using the abovementioned techniques, N. M. Johnson as completed one phase of a study of electron trapping in aluminum-implanted silicon dioxide films on silicon. His samples were 1400-Å dry-grown silicon dioxide films that were implanted with aluminum ions at 20 keV to a fluence of 10^{14} cm^{-3}. The photoinjection of electrons into the implanted, unannealed oxides resulted in the buildup of negative space charge. Data analysis indicated that all injected electrons had been trapped and that the observed transient responses of the photocurrent and flatband voltage were governed by the electric-field dependence of the photoinjected current. The negative space charge could be annealed either optically by photons of energy exceeding 4 eV or thermally at 350°C. A 600°C anneal for 30 min. considerably reduced the concentration of electron traps. From this it is concluded that a substantial fraction of the traps were associated with displacement damage created by the ion implantation.

In another study, the electron trapping in Ne-implanted SiO$_2$ was compared with that in Al-implanted SiO$_2$. The samples were 4700-Å dry-grown silicon dioxide, one set implanted with Ne at 10 keV to a fluence of 1.5×10^{15} cm^{-3} and the other implanted with Al at 10 keV to a fluence of 1.0×10^{15} cm^{-3}, both sets unannealed. The study showed that electron trapping was approximately the same for both species of implanted ions, again indicating that displacement damage is largely responsible for the observed electron trapping.

The foregoing experiments, together with the earlier results, have been described in a Special Report issued on this contract.[11] A paper summarizing the results of this report and giving additional results has been scheduled for journal publication.[12]

Messrs. C. Jenq and J. J. Clement, who are second-year Ph.D. candidates, collaborated with N. M. Johnson in his comparison studies of Al and Ne implants. In addition, they have performed a series of experiments to separate out the effects of ion migration from those of hole trapping in radiation damage. They find that the positive flatband shift produced by exposure to soft X-rays with field plate positive can be annealed out by photoinjecting electrons into the oxide, whereas the flatband shift produced by the migration of ions (presumably Na^+) under bias-temperature stress can not be so annealed, thus showing that the observed radiation damage is due to trapped holes, not to the migration of ions. C. Jenq and J. J. Clement are now studying the effect of high-temperature (1000°C) annealing on aluminum- and neon-implanted SiO_2, with the objective of separating out the effects of displacement damage from those produced by the presence of the aluminum atoms themselves.

VI. ELECTRON-BEAM INJECTION STUDIES

(C. T. Shih and P. Roitman collaborating)

A low energy (1-5 kV) electron beam can be used to inject electrons through a thin metallization and shallowly under the surface to provide carriers for transport and trapping studies of the insulator. Mr. C. T. Shih studied the electron-beam-induced conductivity of thin films of thermally grown SiO_2 and found evidence that the shallow electron irradiation generated electron traps throughout the oxide, well beyond the range of the electrons themselves. Charge-discharge probing of the electron trapping centers in the electron-irradiated oxides and in control samples confirmed this. It is of interest to note that electron traps of apparently a similar nature are observed to be generated in samples that have been subjected to negative corona (Section II of this report).

Mr. Shih conducted a further study of the effect of electron beam energy on charge trapping in his MOS structures. He found that electron trapping dominates at the lower beam energies but that the effect is obscured by positive charge trapping at higher energies where the beam penetrates to the semiconductor-insulator interface. This aspect of the investigation is incomplete at the present time, and will be carried forward by P. Roitman, using a scanning electron microscope for precise electron irradiation of the samples.

A full report on the results of Mr. Shih's studies is now in the final stages of preparation and will be issued as a Special Report on this contract.[13]

VII. STUDIES OF LATERAL NONUNIFORMITIES IN MIS STRUCTURES

(C. C. Chang, D. Guterman and P. Roitman collaborating)

The flatband voltage of an MIS structure, as obtained by a C-V measurement, provides a convenient measure of the charge stored in the insulating layer. (A mercury probe can be used for temporary metallization of the insulator surface if the sample is normally unmetallized, as is true in corona studies.) However, many of our experimental procedures, such as bias-temperature stressing, exposure to corona, application of large electric fields, and irradiation by electrons, produce a stretch-out of the C-V curve. This can be caused by either of two quite different phenomena: the generation of fast interface states or the laterally nonuniform storage of charge. It is important to the interpretation of the experimental results to identify the cause of the C-V stretch-out correctly and to characterize the results accurately.

The separation of the effects of lateral nonuniformities from those of fast interface states is not an easy matter. Several proposals have been made in the literature, including the use of the voltage dependence of the high-frequency conductance or the calculation of an effective doping profile of the semiconducting substrate which is compared before and after C-V stretch-out. Mr. C. C. Chang is evaluating the various proposals both theoretically and experimentally and is developing alternate methods such as the frequency dependence of the C-V curves. For the characterization of lateral nonuniformities, he has developed a computer program which extracts the distribution of flatband voltages from the high-and low-frequency C-V curves. We expect that a Special Report on the results of his studies will be available by mid-summer of this year.

Mr. D. Guterman has conducted a series of experiments in which he has employed a scanning electron microscope for the high-resolution study of lateral nonuniformities in the insulator and at the interface of

MOS capacitors. Images of internal structure are formed by variations in interface barrier height, by defects within the oxide or at the interfaces, and by localized high fields. These mechanisms give rise to small a-c signals in electron-beam-induced currents. Use of this technique has revealed several different types of structure at the interfaces of MOS capacitors. Electrical measurements and bias-thermal stressing are used to determine the nature of the observed nonuniformities. The results of preliminary studies have been published and will be issued as Special Reports on this contract.[14,15] The studies are being continued by Mr. P. Roitman.

VIII. THEORETICAL MODELING

(Professors M. A. Lampert and Brian K. Ridley collaborating)

Professor Lampert is preparing a Special Report on Monte Carlo calculations of hot-electron distributions produced by high electric fields in insulating films. The results of this study shows that when the mean free path of the electrons increases with increasing energy, some electrons escape from the well behaved part of the distribution and gain large energies. This is of importance in impact ionization (Sections II and IV).

Professor Ridley has analyzed a model of insulator breakdown based on Fowler-Nordheim injection from a cathodic protuberance, filamentary Joule heating, and activation of positive ions which drift to the cathode and enhance the injecting field. A paper based on this work is scheduled for publication[16] and will soon be issued as a Special Report on this contract.

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