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STUDY OF ELECTRONIC TRANSPORT AND BREAKDOWN  
IN THIN INSULATING FILMS

Walter C. Johnson  
Wilmer R. Bottoms

Princeton University  
Department of Electrical Engineering  
Princeton, New Jersey 08540

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Principal Investigator and phone no.  
Prof. Walter C. Johnson/609 452-4621

AFCRL Project Scientist and phone no.  
Dr. John C. Garth/617 861-4051

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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 comprehensive and detailed manner in a series of Special Reports, some of which have already been issued and others of which are in various stages of preparation.

Separate sections in this report are devoted to corona-induced nondestructive breakdown, studies of breakdown by the self-quenched technique, charge-discharge studies of charge-carrier trapping in insulating films, investigation of the effects of low-energy electron irradiation of insulating films, electron beam studies of semiconductor-insulator interfaces, a study of lateral nonuniformities in metal-insulator-semiconductor structures, and theoretical modeling of hot-electron distributions and of localized breakdown.

## II. CORONA-INDUCED NONDESTRUCTIVE BREAKDOWN OF INSULATING FILMS

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

The use of a corona discharge in a gas at atmospheric pressure to contact the unmetallized surface of an insulating film provides a convenient means of inducing charge transport across the insulating film, and the virtual absence of lateral surface conduction allows the use of very high field intensities - tantamount to breakdown - without destruction of the films. We have developed the corona-charging technique together with auxiliary new techniques such as the use of the charge-separating property of a PN junction to identify the principal charge carrier in the insulator and the use of a

comparison method for measuring the steady-state surface potential of the insulator during charging, and have applied these to a study of charge injection, transport, and trapping in  $\text{SiO}_2$  films on Si. In support of the experimental work, a theoretical study has been made of the tunneling of electrons into the insulator from the thin potential well formed in the semiconductor by strong band bending under high-field conditions. The PN junction technique has been described in a Special Report on this contract<sup>1</sup> and in a published paper.<sup>2</sup> A manuscript on the comparison method for measuring insulator surface potential is being issued as Special Report No. 5 on this contract, and has been accepted for journal publication.<sup>3</sup> A paper on the corona technique and results obtained by this method on  $\text{SiO}_2$  has been submitted for journal publication and will soon be submitted to AFCRL for permission to publish and distribute as a Special Report on this contract.<sup>4</sup> Also prepared for journal publication and soon to be submitted as another Special Report is a paper on the theory of the tunneling of electrons from a semiconducting substrate into an insulator.<sup>5</sup>

Because the corona technique has proved to be remarkably convenient and productive in the study of high-field effects in thin insulating films, we are enlarging the scope of this study. Mr. H. S. Lee is studying transport and trapping in  $\text{SiO}_2$  films at current densities that are considerably greater than those investigated previously, using both positive and negative polarities of corona, and he is also studying the use of gases other than dry air. Deep electron traps, not previously present in the oxide, are observed after exposure of the  $\text{SiO}_2$  to sufficiently intense positive corona. The generation of deep electron traps under high-field conditions has important implications in regard to the spatial concentration of electric field under breakdown conditions.

Mr. H. H. Chao is preparing equipment for the simultaneous use of corona charging with UV and vacuum UV excitation. The use of corona ions to provide the electric field in the insulator eliminates the need for a metallic field plate and should remove the ambiguity arising from the photoelectric emission of carriers from a metallic electrode. A similar experiment with this degree of sophistication has not, to our knowledge, been set up

in the past. Sub-bandgap UV excitation will be used to produce internal photoemission of carriers from the substrate, and vacuum UV excitation will be used to produce hole-electron pairs in the insulator itself.

### III. SELF-QUENCHED BREAKDOWN OF INSULATING FILMS (D.Y. Yang collaborating)

In these studies we use metal-oxide-semiconductor structures in which the metallization is very thin (200-1000 Å). When a voltage is applied to the structure and a localized breakdown occurs in the insulating film, the Joule heat evolved in the immediate vicinity of the breakdown results in the removal of the thin metal about this point; thus the breakdown, although locally destructive, is self-quenching. The time evolution of the breakdown, the charge storage after breakdown, the effect of substrate type (p or n) and of polarity, and the physical features as observed by optical microscope and scanning electron microscope, all furnish information regarding the mechanisms and parameters relevant to the breakdown.

Most of our experiments have been performed on films of SiO<sub>2</sub> thermally grown on (100) Si substrates to a thickness of approximately 2500 Å. Both p and n substrates were used. The metallization was of aluminum, about 1000 Å in thickness. Upon the occurrence of a breakdown event, the rate of discharge of the capacitor energy corresponded to a series resistance of about 100 ohms when the substrate was in accumulation, and to several thousands of ohms when the substrate was in inversion, indicating that the discharge was controlled by the spreading resistance offered by the substrate. Each of the four possible combinations (p or n substrate, + or - field-plate polarity) showed its own distinctive properties and its own distinctive configuration of breakdown damage. Some properties correlated with the nature of the substrate surface channel (inversion versus accumulation); other properties correlated with the field-plate polarity. With a p-substrate and positive field-plate polarity, the region of removal of metal tended to be square, with the sides of the square parallel to the (100) axes of the substrate. This effect is attributed to the anisotropy of hot-electron conduction in the (100) plane of the substrate, a conclusion which has been confirmed by further studies using other samples with different

oxide thicknesses and therefore having different breakdown voltages. As the breakdown voltage was made greater, the breakdown pattern evolved from round to square and finally to the form of a four-pointed star with the points along the [110] directions.

In order to study the initiation mechanisms of the breakdown, electrical measurements were made in the pre-breakdown region. The results of steady-state I-V and C-V measurements were consistent with the conclusion that the pre-breakdown currents in the SiO<sub>2</sub> were caused by Fowler-Nordheim tunneling. Electric field intensities in excess of about  $7.6 \times 10^6$  V/cm resulted in current instabilities which were found to be closely related to the appearance of positive charges in the SiO<sub>2</sub>. An instability in the current could be induced by cooling the sample at a constant bias voltage. This can be interpreted as due to the larger mean free path of electrons at the reduced temperature, resulting in a greater production of hole-electron pairs through impact ionization. Trapping of the holes near the electron-tunneling contact enhances the electric field at this contact and increases the tunneling current. We believe that these experiments provide the first direct evidence of the role of impact ionization in the runaway process at the onset of breakdown.

A paper describing some of the results of these studies has been published<sup>6</sup> and has also been issued as Special Report No. 3 on this contract.<sup>7</sup> A second paper<sup>8</sup> is almost ready for submission. A comprehensive report on the results of these studies will be issued as Special Report No. 4 on this contract.<sup>9</sup>

#### IV. CHARGE-DISCHARGE STUDIES OF CHARGE-CARRIER TRAPPING IN INSULATING FILMS\*

(N. M. Johnson and J. Clement collaborating)

We have designed and constructed apparatus for the convenient exploitation of charge-discharge techniques for the probing of deep traps in thin insulating films, and we have used this equipment and these techniques in a study of the electron traps produced in silicon dioxide by the implantation of aluminum and neon ions. The equipment includes a high-vacuum sample chamber, a sample holder arranged for convenient manipulation from the outside and

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\*This work was also supported in part by DNA under sponsorship of NRL (ONR Contract N00014-67-0151-0035).

provided with means for heating and for cooling to liquid nitrogen temperature, a soft X-ray generator for excitation of the insulator to produce hole-electron pairs, a high-intensity monochromator arranged for internal photoemission of carriers into the insulating film and for photon excitation of trapped carriers, and appropriate electronic instrumentation including provision for the exploitation of the MIS measurement techniques for determination of charge storage and density of interface states. This equipment makes a wide variety of trap-probing techniques conveniently available, and is used as an important adjunct in other experimental studies.

Our study of electron traps in ion-implanted  $\text{SiO}_2$  films was motivated by the observation that ion implantation can improve the radiation hardness of MOS structures under positive gate bias and from the speculation that the improvement is caused by increased electron trapping which balances the effect of the strong hole trapping that is always present in the metal- $\text{SiO}_2$ -Si structure. Our studies showed that thermally grown  $\text{SiO}_2$  that has been implanted with aluminum ions possess much larger concentrations of electron traps than are found in normal  $\text{SiO}_2$ . The traps are deep, requiring photon energies in excess of 4.0 eV for photodepopulation of trapped electrons. A thermal anneal at 600°C for 30 minutes substantially reduced the number of electron traps, leading to the conclusion that a large proportion of the traps were associated with displacement damage created by the ion implantation. A further indication of the correctness of this conclusion was obtained from preliminary measurements taken on neon-implanted samples, in which deep electron trapping was found to be approximately the same as in aluminum-implanted samples, indicating that the displacement damage, rather than the electronic activity of the implanted ion was the major factor.

A Special Report<sup>10</sup> has been issued on the foregoing work and a shortened version has been accepted for publication.<sup>11</sup> In addition to the work already reported, we have made a more careful study of the effect of neon implantation as compared with implantation with aluminum and have verified the similarity in electron trapping between the two. We have also found an important fluence-related effect in implanted  $\text{SiO}_2$ , i.e., there



appears to be an optimum concentration of trapping centers; too large a concentration leads to instability of the trapped charge. The instability is not sensitive to temperature and may be associated with charge-carrier hopping between adjacent centers. Further studies planned for the immediate future include: (a) Hole-trapping properties of the implantation-produced centers and the effectiveness of the centers in promoting hole-electron recombination. Although we have established the presence of large concentrations of electron traps in the implantation-hardened  $\text{SiO}_2$  films, the actual mechanism of hardening — whether by enhanced recombination or charge balancing by electron trapping — has not been established. (b) The effect of ion implantation on the dielectric breakdown properties of the insulating films. (c) A systematic study of the effects of heat treatment. This important subject has not yet received sufficient attention, both from a practical, phenomenological point of view and also from the basic aspect of the electronic activity of the implanted impurity atoms themselves.

#### V. LOW-ENERGY ELECTRON IRRADIATION OF INSULATING FILMS\* (C.T. Shih collaborating)

If a quasi-ohmic contact can be made to an insulator, the structure of the resulting I-V characteristic can serve as a powerful probe of traps in the insulator. We have used a low-energy (1-5 kV) electron beam to inject electrons through a thin metallization and shallowly under the surface of an insulator in order to provide a reservoir of free electrons which would serve as the desired contact. The silicon substrate, biased positively, serves as the anode. The electron beam, in addition to supplying electrons to the reservoir, creates hole-electron pairs throughout its range in the insulator and also generates photons with a wide spectrum of energies. The current-voltage characteristics that we have observed in thermally grown  $\text{SiO}_2$  under these conditions suggests a trap-dominated space-charge-limited current ( $J \propto V^2$ ) with detrapping of the electrons stimulated by beam-generated photons. The concentration of traps required in this interpretation is much greater than that observed in unirradiated thermally grown oxides, and furthermore the traps must be in the bulk rather than entirely at the interface. For this explanation to be correct, the electron irradiation must have been

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\* This work was also supported in part by DNA under sponsorship of NRL (ONR Contract N00014-67-0151-0035).

responsible for the generation of electron traps beyond the range of the beam itself.

In order to obtain independent evidence regarding the foregoing interpretation, we conducted a charge-discharge study of electron trapping both before and after electron-beam irradiation, using the apparatus described in Section IV. The results confirmed the generation in  $\text{SiO}_2$  of deep electron traps by irradiation with a nonpenetrating electron beam.

Inasmuch as relatively little had been reported in the literature regarding the effects of low-energy electron irradiation on  $\text{SiO}_2$ , and the results reported indicated positive, not negative, charge trapping, we conducted a study of the effect of beam energy in the range up to 15 kV. The results of this study show that electron trapping dominates at the lower energies but that positive charge trapping dominates at higher energies regardless of fluence.

An extensive Special Report on the results of these studies is in preparation.<sup>12</sup>

## VI. ELECTRON BEAM PROBE STUDIES OF SEMICONDUCTOR-INSULATOR INTERFACES

(D. Guterman and P. Rotiman collaborating)

An electron beam of diameter as small as 100 Å may be employed to study MOS structures providing information about the surface topography (secondary electron imaging), surface chemical composition (Auger electron spectroscopy), bulk chemical composition (X-ray fluorescence), as well as the structure of interface regions at high spatial resolutions. The penetration depth of the beam and therefore the excited volume can be altered by adjusting the accelerating voltage and the incident angle. Images of the internal surfaces of MOS structures are formed due to variations in the metal-insulator barrier height, the semiconductor-insulator barrier heights, defects within the oxide or at the interfaces, and topography causing localized high-field conditions. These mechanisms give rise to small ac signals in the current induced across the structure by the electron beam. The signals may be amplified and used to modulate the intensity on a CRT. Several different structures have been observed at the interfaces in MOS

systems using this technique. Electrical measurements and bias thermal stressing experiments have been used to determine the nature of the structures responsible for observed images.

A paper describing these studies has been accepted for publication and will be issued as a Special Report on this contract.<sup>13</sup>

#### VII. STUDY OF LATERAL NONUNIFORMITIES IN MIS STRUCTURES\* (C.C. Chang 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: fast interface states or laterally nonuniform charge storage. It is important to the interpretation of the experimental results to identify correctly the cause of the C-V stretch-out and to characterize the results accurately.

The separation of the effects of lateral nonuniformities from those of fast interface states is not a trivial 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. We are evaluating various proposals both theoretically and experimentally and are studying additional methods such as the frequency dependence of the C-V curves. For the characterization of lateral nonuniformities, we have written a computer program which extracts the distribution of flatband voltages from the high- and low-frequency C-V curves.

#### VIII. THEORETICAL MODELING (Professors M.A. Lampert and Brian Ridley collaborating)

Monte Carlo calculations have been made of hot-electron distributions produced by high electric fields in insulating films. The results show that when the mean free path increases with increasing energy, some electrons escape from the well behaved part of the distribution and gain large energies.

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A Special Report is planned on this subject.

A model of insulator breakdown has been explored. This is based on Fowler-Nordheim injection from a cathodic protuberance, filamentary joule heating, and activation of positive ions which enhance the injecting field. A mechanism for lateral spreading of the initial discharge and subsequent quenching by the substrate resistance gives the extent of the damaged area to be of the observed order in self-healing breakdowns. The breakdown field and its dependence on film thickness is in reasonable agreement with experiment. A Special Report on this work has been prepared and will soon be submitted.<sup>14</sup>

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