Two-carrier nature of interface-state generation in hole trapping and radiation damage

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In hole trapping and radiation damage in silicon dioxide, a characteristic interface-state peak is present. It is shown by the present work that the interface peak is due to trapping of holes at the silicon-silicon dioxide interface and the subsequent capture of injected electrons by the holes. It is postulated that dipolar complexes are formed, which give rise to electronic states at the interface. Similar dipoles may be responsible for neutral traps in the bulk of oxides after irradation.

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It has been reported that one of the results of radiation damage and hole trapping in silicon dioxide is the generation of interface states at the silicon-silicon dioxide interface.[1–8] The process of interface-state generation can actually be divided into two steps.[3–8] The first step involves the transport to and the trapping of holes at the interface.[3–8] Holes can be generated by electron beam,[1,9] gamma ray,[2] x-ray,[10] vacuum ultraviolet light,[2,9–12] or any form of radiation that has sufficient energy to generate electron-hole pairs in oxides. They can also be generated by high-field stress in oxides.[6,10,13] Holes in the bulk of the oxide are transported to the silicon-silicon dioxide interface through some form of hopping process characterized by very low mobility.[14] Part of the holes recombine, while a fraction of them are trapped near the interface.[6,9–12] These trapped holes give rise to a positive-charge distribution near the interface and are reflected by a shift of the *C-V* curve in the direction of negative voltages.

Once the holes are trapped near the interface, there is the much slower second step of interface state generation.[3–8] The generation has been studied in two different ways. Hu *et al.* generated and trapped holes by high-field stress at liquid-nitrogen temperature.[6] They then measured the generation of interface states when the samples were warmed to room temperature or above. They observed a one to one relationship between interface states generated and holes trapped over a very long time. Winokur *et al.* measured the buildup of interface states as a function of electric field and temperature after oxides were irradiated by electron pulses from an electron linear accelerator.[3–5,7] They observed that the generation of interface states was enhanced by both higher field and higher temperature. They explained the effect by the release of energy by trapped holes. The released energy was sufficient to break bonds to give rise to interface states.[5] Recently, McLeon proposed a different model of ion transport for the generation of interface states.[8] The interface-state spectrum was not reported in the above experiments, but the interface states generated after radiation damage had a broad peak approximately 0.25 eV above midgap towards the conduction band.[1] These interface states were usually measured by the quasistatic capacitance technique.[1,3] The peak was observed in oxides that were damaged by different kinds of radiation larger than a certain dosage,[1] and it was believed to be characteristic of radiation damage.[15]

In the present work, the processes of hole trapping and interface-state generation are studied. Instead of using high-energy radiation which generates both holes and electrons, only holes are injected into the oxide by avalanche injection from the silicon substrate.[16] By this technique, only the effect of hole trapping is studied, avoiding complications due to electrons. The process of hole injection is similar to the first step of hole generation described above. After hole injection and trapping, the interface-state peak described above was *not* observed. There was only an increase in the background interface states. These interface states were due to holes at the interface only, and they may be part of the interface states that were observed to build up in the other experiments.[3–5,7] An attempt was made to neutralize the holes by injecting electrons by internal photoemission.[10] As the holes were neutralized, the *C-V* curve were shifted in the positive voltage direction. Unexpectedly, however, as electrons were injected, the interface-state density was increased, and the peak characteristic of radiation damage appeared. These results indicate that both trapped holes and trapped electrons are necessary to give rise to the build up of interface-state peak and that the holes are not simply neutralized. In fact, part of the previous experimental observation of field and temperature dependence of interface-state generation might be explained by the electron injection model.

The wafers used in the present experiments were *n* type, ⟨100⟩ in orientation and had resistivities of 0.1–0.2 Ω cm. The oxides were all dry oxides. Some of them were pulled from the furnace in oxygen to ensure radiation hardness.[16] Others were annealed in nitrogen or argon for times ranging from 20 min to 17 h to give oxides with different degrees of radiation hardness.[16–18] The oxide thicknesses were in the range of 10–100 nm, and oxidation temperatures were from 800 to 1000 °C depending on the oxide thickness. Aluminum, 13.5 nm thick, was used as the top transparent electrode in simple metal oxide semiconductor (MOS) capacitors for all the measurements. The transparent electrodes were necessary for internal photoemission experiments. The system used for avalanche injection of holes was the same one used for avalanche injection of electrons and holes described previously.[16,19] A deuterium lamp was used for electron injection and a Corning glass filter was used to limit the light energy to less than 5 eV. The filter was necessary to prevent the injection of holes. The dependence of the density of hole

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traps on processing followed the dependence of radiation hardness on processing.[16–18] The present reported results were observed on *all* the oxides.

Figure 1 shows the high-frequency and quasistatic capacitance curves before and after injection of $10^{15}/cm^2$ holes and then after a subsequent injection of $6\times10^{14}/cm^2$ electrons for a 50-nm oxide. The result is typical of what was observed in ten oxides of different thicknesses and prepared different ways. After hole injection, the high-frequency curve is shifted in the negative voltage direction and this voltage shift is proportional to the density of trapped holes. There is also some interface-state generation as can be seen from the quasistatic curve. After the injection of electrons, the high-frequency curve is shifted back in the positive voltage direction to almost the original curve. This is complicated by the distortion in the curve because of interface states. There is a distinct feature in the quasistatic curve indicated in the figure by an arrow. That is due to the interface-state peak observed in radiation damage. The interface-state spectrums can be calculated from the capacitance curves, and the results are plotted in Fig. 2. There is increase in interface states after hole injection but the characterictic peak is not present. The falloff in interface-state density close to the conduction band is due to limitations of the measurement in that region. After electron injection, a distinct interface-state peak appears, the same that is observed in radiation damage. The peak height is a monotonic function of number of trapped electrons. The kinetics of electron trapping were analyzed and were shown to be due to capture by coulombic attractive positive-charge centers. The capture cross section is very large, and it decreases with increasing electric field in the oxide.[10,20] The only positive-charge centers present in the oxide are the holes. Thus the shifting of the *C-V* curves is due to the capture of electrons by the holes, compensating the charge. The electrons can be injected from either the aluminum or the silicon, and the same results were obtained. The simple conclusion is that electrons are captured by the holes. It is *not* the simple recombination process that is observed in crystalline silicon. Instead, electrons and holes may recombine, releasing energy in such a way as to induce structural

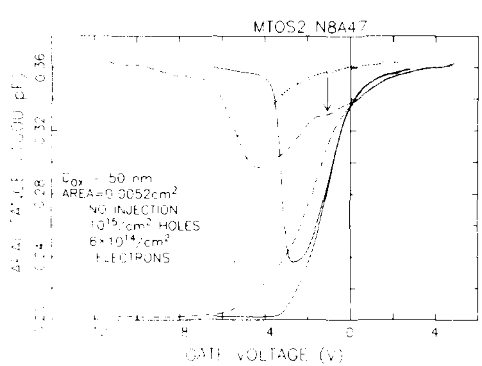

FIG. 1. High-frequency (1 MHz) and quasistatic capacitance curves for before and after hole injection and then after subsequent electron injection. The hole injection was by avalanche of the silicon substrate at a current level of 5.4×10^{-8} A/cm^2 for 3000 sec giving a total of $10^{15}/cm^2$ holes. The electron injection was by internal photoemission at a current level of approximately 4.8×10^{-8} A/cm^2 under a negative oxide field of about 2 MV/cm. The injection time was 2000 sec giving a total of $6\times10^{14}/cm^2$ electrons. The feature in the third quasistatic curve marked by an arrow is due to an interface-state peak.

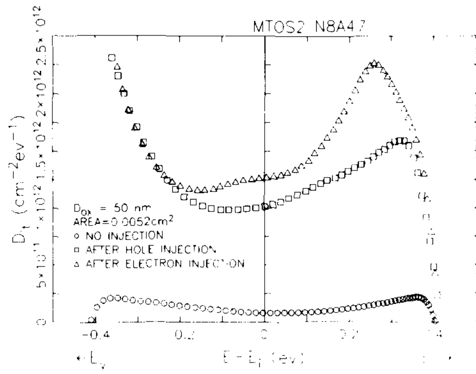

FIG. 2. Interface-state spectrums calculated from the high-frequency and quasistatic capacitance curves in Fig. 1. The feature in the quasistatic curve after electron injection shows up as an interface state peak at 0.25 eV above midgap.

change at the interface to give rise to interface states. This is the reverse of what Ma *et al.* proposed as the mechanism for rf annealing.[21] Another possible explanation is that electrons may be bound to holes in dipolar complexes to give electronic states at the interface.

The above result can be used to explain the rapid relaxation in the trapped charge in a similar hole trapping experiment.[16] When there is positive charge trapped near the silicon-silicon dioxide interface, electrons in silicon can tunnel directly into the charge centers depending on the relative energy levels and the applied electric field. The application of positive fields of 5 MV/cm[16] enhanced the injection of electrons by making more of the trapped hole levels available to tunneling electrons and by lowering of the tunneling barrier. This would result in the shifting of the flatband voltage in the positive-voltage direction. This is similar to injection by internal photoemission. The interface-state spectrum was not measured in those experiments,[22] but when they were repeated, the interface-state peak was observed after the charge relaxation under bias. The same tunneling injection model may also be used to explain part of the interface-state generation observed previously.[3–5,7] It takes about 1 min to stop the avalanche injection of holes and to start the slow ramp quasistatic measurement of interface states. Some buildup of interface states as reported in other experiments[3–5,7] would have already taken place. This is shown in Fig. 2 by the increase in background interface state density. Any further buildup to give the peak will depend on the injection of electrons. The time for the buildup cannot be measured in detail because of the long time it takes for a quasistatic measurement. The injection of electron is enhanced by a positive electric field or an increase in temperature but is suppressed by a negative electric field. Such field and temperature dependence is similar to what was reported[3–5,7,8] and electron injection may be responsible for further buildup of interface states after the initial phase.

Under normal conditions in radiation damage, there are electrons and holes generated. Some of the electrons are captured by the trapped holes to give the interface-state peak. The same process may also occur in the bulk of oxides. Aitken proposed that radiation-induced neutral traps in the bulk of oxides were due to dipoles.[23,24] It was based on the experimental observation that densities and location of both neutral electron and hole traps in the bulk of irradiated oxides were the same, and that they might be the same traps but dipolar in nature.[24] This can be explained by the following simple model. Intrinsic hole traps exist in the bulk of oxide or at the interface as strained bonds. In a simple-minded picture, a hole is a broken bond in an amorphous oxide network. Holes can move from one unstrained bond to the next under an electric field if there is no change in the unstrained bonds in the process. But if a hole gets to a strained bond and enters into a lower-energy metastable state by deforming it further, the hole may be trapped. These trapped holes have very large capture cross section for the capture of electrons, which are also generated and present in the oxide. When the trapped holes capture electrons, the deformed bonds cannot be restored to original states. In this way neutral traps are formed in the bulk and interface states are generated at the interface. The properties of the neutral traps thus favor the model of an electron and hole forming a dipolar complex to give an electronic state. However, the model for recombination-induced structural change cannot be ruled out completely. From previous work on damaged oxides, the interface states at the peak are acceptor states.[25] This means that they are neutral when empty and negative when occupied by electrons. This may have some significance in the study of the nature of the interface state.

It must be pointed out that there may be two kinds of positive charge at the interface. The first are the holes trapped at the interface as described above. The second is the anomalous positive charge that was observed in electron trapping experiments.[19,26] All evidence so far indicates that the anomalous positive charge is generated as a result of trapping of electrons at water related centers in the bulk of the oxide.[19] After the trapping, some transport process, which may be exciton or hydrogen,[12,27] causes the generation of slow interface states at the interface. The slow interface states are donors and are positively charged when empty.[19,28] The properties of the anomalous positive charge have been investigated and will be reported in a future paper.[28] In the process of high-field stress or radiation damage, there are electrons as well as holes flowing in the oxide and the interaction of the electrons with water related centers, which are present even in dry oxides, may give rise to some anomalous positive charge. The water related centers have small capture cross sections in the 10^{-17}–10^{-18}-cm^2 range[16] and densities $\geqslant 10^{11}/\text{cm}^2$. The anomalous positive charge is observed after passage of $10^{16}/\text{cm}^2$ of electrons.[28] Weinberg *et al.* have shown that positive charge appeared at the silicon-silicon dioxide interface even when the applied field opposed the transport of holes to the interface and that the effect was enhanced in wet oxides.[27] So, in most of the reported results in the literature it must be understood that both trapped holes and anomalous positive charge may be present at the interface. The effect may be more significant when wet oxides are used. In the present experiments, no electrons are injected during the first step of hole injection. Too few electrons are injected by internal photoemission to interact with water related centers. Therefore, there is no generation of anomalous positive charge.

In conclusion, it was shown that the generation of an interface-state peak in radiation damage and hole trapping is due to the injection of electrons. They are captured by trapped holes. One possible result is the formation of dipolar complexes which give rise to electronic states at the interface. Another possibility is the recombination of the electrons and holes releases energy to form defect interface states. The result may be used to explain some of the field and temperature dependence reported by other workers. It is also very important for the understanding of the electronic states at the interface and may contribute to solving the problem of degradation in devices due to radiation damage. Further experiments are now being planned to study the process and the interface states in more detail.

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[1] T. P. Ma, G. Scoggan, and R. Leone, Appl. Phys. Lett. **27**, 61 (1975).
[2] P. S. Winokur, and M. M. Sokoloski, Appl. Phys. Lett. **28**, 627 (1976).
[3] P. S. Winokur, H. E. Boesch, Jr., J. M. McGarrity, and F. B. McLean IEEE Trans. Nucl. Sci. **NS-24**, 2113 (1977).
[4] J. M. McGarrity, P. S. Winokur, H. E. Boesch, Jr., F. B. McLean, *Proc. of Intl. Conf. on Physics of SiO$_2$ and its Interfaces* (Pergamon, New York, 1978), p. 428.
[5] P. S. Winokur, H. E. Boesch, Jr., J. M. McGarrity, and F. B. McLean, J. Appl. Phys. **50**, 3492 (1979).
[6] G. Hu, W. C. Johnson, Appl. Phys. Lett. **36**, 590 (1980).
[7] P. S. Winokur and H. E. Boesch, Jr., IEEE Trans. Nucl. Sci. **NS-27**, 1647 (1980).
[8] F. B. McLean, IEEE Trans. Nucl. Sci. **NS-27**, 1651 (1980).
[9] G. W. Huges, R. J. Powell, and M. H. Woods, Appl. Phys. Lett. **29**, 377 (1976).
[10] D. J. DiMaria, Z. A. Weinberg, and J. M. Aitken, J. Appl. Phys. **48**, 898 (1977).
[11] R. J. Powell, J. Appl. Phys. **46**, 4557 (1975).
[12] Z. A. Weinberg, and G. W. Rubloff, Appl. Phys. Lett. **32**, 185 (1978).
[13] M. Shatzkes, M. Av-Ron, J. Appl. Phys. **47**, 3192 (1976).
[14] F. B. McLean, G. A. Ausman, Jr., H. E. Boesch, Jr., and J. M. McGarrity, J. Appl. Phys. **47**, 1529 (1976).
[15] P. V. Dressendorfer (private communication).
[16] J. M. Aitken and D. R. Young, IEEE Trans. Nucl. Sci. **NS-24**, 2128 (1977).
[17] G. F. Derbenwick and B. L. Gregory, IEEE Trans. Nucl. Sci. **NS-22**, 2151 (1975).
[18] R. R. Razouk, B. E. Deal, *Electrochemical Society Fall Meeting, Hollywood, Florida*, Extended Abstract 553, 1980 (The Electrochemical Society, New York, 1980).
[19] D. R. Young, E. A. Irene, D. J. DiMaria, R. F. DeKeersmaecker, and H. Z. Massoud, J. Appl. Phys. **50**, 6366 (1979).
[20] T. H. Ning, J. Appl. Phys. **47**, 3203 (1976).
[21] T. P. Ma, M. R. Chin, J. Appl. Phys. **51**, 5458 (1980).
[22] J. M. Aitken (private communication).
[23] J. M. Aitken, D. R. Young, and K. Pan, J. Appl. Phys. **49**, 3386 (1978).
[24] J. M. Aitken, J. Non-Crystal. Solids **40**, 31 (1980).
[25] G. A. Scoggan and T. P. Ma, J. Appl. Phys. **48**, 294 (1977).
[26] D. J. DiMaria, R. Ghez, and D. W. Dong, J. Appl. Phys. **51**, 4830 (1980).
[27] Z. A. Weinberg, D. R. Young, D. J. DiMaria, and G. W. Rubloff, J. Appl. Phys. **50**, 5757 (1979).
[28] S. K. Lai, and D. R. Young (unpublished).