

## Looking Back, Charging Ahead

by Dennis W. Hess

The silicon-silicon dioxide (Si-SiO<sub>2</sub>) interface system is the heart and soul of silicon microelectronic devices and integrated circuits. The importance of this interface system for device fabrication and operation began with the recognition that a thermally-grown SiO<sub>2</sub> layer on silicon can serve as both a diffusion barrier to dopants<sup>1</sup> and a means to reduce the silicon surface state density.<sup>2</sup> In the early to mid 1950s, Brown<sup>3</sup> and Kingston<sup>4</sup> recognized that transport of adsorbed ions could cause instabilities in (germanium) bipolar devices; Kingston felt that similar effects would be operative in silicon-based devices. Due to their design, operation of metal-oxide-semiconductor (MOS) devices was even more sensitive to surface stability problems than were bipolar designs, which delayed the wide-spread manufacture and use of MOS devices relative to the more structurally complex bipolar devices.

Despite an appreciation for the advantages of passivating silicon with an SiO<sub>2</sub> layer during device manufacture and

In 1964, Snow *et al.*, invoked capacitance-voltage (C-V) characteristics to experimentally and theoretically establish that alkali ions (*e.g.*, Na<sup>+</sup>, K<sup>+</sup>) resulting from processing chemicals, processing atmospheres and materials, device metallization, and personnel handling the wafers were a major cause of the instabilities observed in the Si-SiO<sub>2</sub> system.<sup>7</sup> Control of these mobile charges subsequently facilitated the investigation of other charges in the Si-SiO<sub>2</sub> system. Balk, *et al.*<sup>8</sup> measured the surface state charge on different orientations of silicon after growth of SiO<sub>2</sub> by thermal oxidation and reported that the charge decreased in the order <111> > <110> > <100>. Balk, *et al.*<sup>8</sup> correlated these observations with the relative oxidation rates on these same surfaces according to their and Deal's data<sup>9</sup> and concluded that "The strong dependence of the built-in charge on the crystal face orientation in silicon is of fundamental significance for understanding the nature of surface charge." Thus in the mid 1960s it was evident that oxide and interface

FROM:  
B. Deal, M. Sklar, and A. Grove, "Surface-State Charge of Thermally Oxidized Silicon," JES, **114**, 266 (1967).

### Characteristics of the Surface-State Charge (Q<sub>ss</sub>) of Thermally Oxidized Silicon

B. E. Deal, M. Sklar, A. S. Grove, and E. H. Snow

Research and Development Laboratories, Fairchild Semiconductor, Palo Alto, California

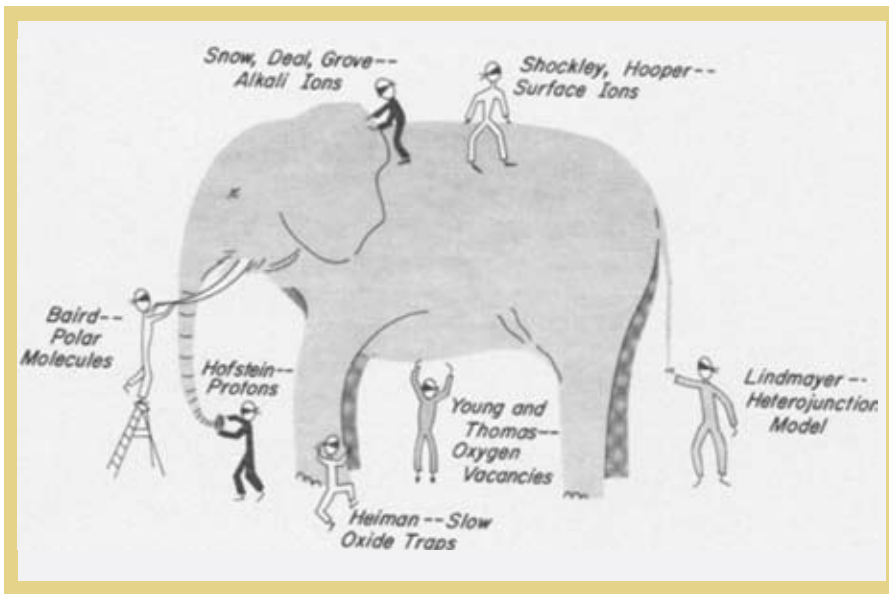
#### ABSTRACT

The nature of the surface-state charge (Q<sub>ss</sub>) associated with thermally oxidized silicon has been studied experimentally using MOS structures. The effects of oxidation conditions, silicon orientation, annealing treatments, oxide thickness, and electric field were examined, as well as the physical location of the surface-state charge. The results indicate that the surface-state charge can be reproducibly controlled over a range 10<sup>10</sup>-10<sup>12</sup> cm<sup>-2</sup>, and that it is an intrinsic property of the silicon dioxide-silicon system. It appears to be due to an excess silicon species introduced into the oxide layer near the silicon during the oxidation process.

operation, control of the electrical properties of the silicon surface to allow reliable, reproducible device fabrication was not possible, at least throughout the early 1960s. Indeed, investigators realized by the mid-1960s, that a variety of phenomena could cause the instabilities observed in the Si-SiO<sub>2</sub> system; the range of possibilities was cleverly presented by Donovan in his cartoon of "the blind men and the elephant" as shown in Fig. 1.<sup>5</sup> Revesz<sup>6</sup> summarized a number of possible origins of charges and instabilities present in the Si-SiO<sub>2</sub> system, wherein he focused on the defect structure of grown silicon dioxide films including oxide vacancies and interstitials, metal ions injected from electrodes, alkali ions in the glass structure, and the inhomogeneous distribution of such defects across the oxide layer. In his Conclusion Section, Revesz stated, "One of the main problems in MOS device technology is the establishment of the required silicon surface potential in a controllable manner. This problem cannot be solved without a proper understanding of the interactions between the oxide, silicon, and gate electrode, and this implies a knowledge of the defect structure of the oxide."

charges for the Si-SiO<sub>2</sub> system needed to be controlled if reliable reproducible silicon-based devices were to be fabricated. To accomplish this task, a more fundamental understanding of the relationship of these charges to the Si-SiO<sub>2</sub> materials and processing parameters was needed. It is within this background, framework, and critical need that the pioneering work of Deal, Sklar, Grove, and Snow was performed.<sup>10</sup>

"Characteristics of the Surface-State Charge (Q<sub>ss</sub>) of Thermally Oxidized Silicon"<sup>10</sup> was the first report to unequivocally characterize surface state charge in the Si-SiO<sub>2</sub> system, and describe detailed processing approaches to control and minimize this charge. Up to this point in time, only the mobile charges due to alkali and possibly hydrogen ions were understood reasonably well. However, a host of other effects that altered the silicon surface potential and that depended upon processing conditions and silicon properties were to date, undefined, unexplained, and uncontrolled. Specifically, so-called "fast states" (subsequently termed interface states), which were in communication with the silicon surface and so could charge and discharge (trap and release electrons or holes)



**Fig. 1.** Indication of early confusion regarding source of MOS instability as represented by Donovan's "blind men and the elephant."<sup>5</sup>

as the silicon surface potential was swept across the band gap, had been described by a number of other investigators, although their origin was unclear. Similarly, "slow states" were believed to be due to ionic contamination within the SiO<sub>2</sub> layer, but removed from the interface with silicon so that they were not in direct electrical communication with the silicon surface potential. In this classic paper,<sup>10</sup> the authors described numerous experiments and processing sequences that altered Si-SiO<sub>2</sub> interface and bulk SiO<sub>2</sub> properties and established that the surface state charge was an integral part of this interface system, independent of unintentional impurities, silicon doping type (at ~10<sup>16</sup> cm<sup>-3</sup>), and fast/slow states. Rather, the surface state charge properties were established by oxidation and subsequent heat treatment (annealing) conditions. They also suggested likely physical and chemical bonding configurations that could lead to the charge observed; with relatively little modification, these speculations on the fundamental cause of the charge held up to further scrutiny in succeeding years. Brief summaries of the findings reported in this paper are given below.

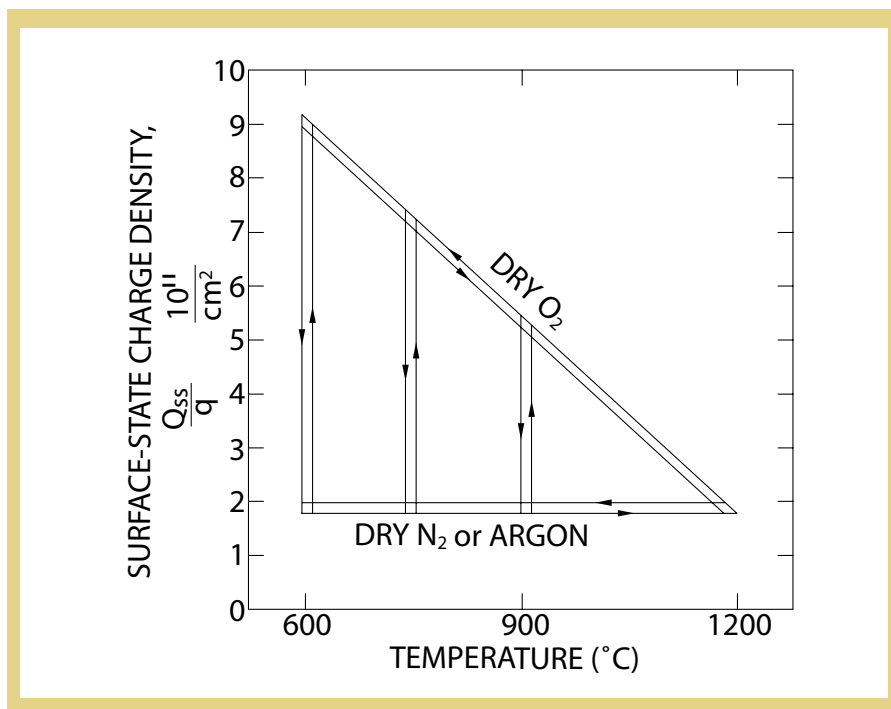
Primarily through the use of C-V characteristics, the surface state charge ( $Q_{ss}$ ) was measured. The value was designated as  $Q_{ss}/q$ , where  $q$  is the electronic charge, so that the units were (# charges)/cm<sup>2</sup>, although the symbol  $Q_{ss}$  is the generally accepted term. Variation in the value of  $Q_{ss}$  was primarily dependent upon oxidation conditions; previous studies had indicated that thermal oxidation of silicon occurred by diffusion of oxygen moieties across the growing oxide to the Si-SiO<sub>2</sub> interface so that the oxygen concentration decreased from the Si-oxidant interface to the Si-SiO<sub>2</sub> interface.<sup>11</sup> With respect to oxidation conditions, the charge level decreased as the oxidation temperature in dry O<sub>2</sub> increased at a constant pull rate from the furnace; a slight decrease with increasing temperature was observed in wet O<sub>2</sub> (O<sub>2</sub> bubbled through 95°C H<sub>2</sub>O) oxidation, although the dependence on temperature was considerably less than that for dry O<sub>2</sub>. The pull rate affected the length of time that the Si-SiO<sub>2</sub> interface was subjected to lower temperatures, and so represented

another parameter that required control; a decrease in  $Q_{ss}$  resulted from higher pull rates. Although  $Q_{ss}$  could be controlled by oxidation temperature and pull rate from the furnace, post-oxidation annealing treatments in nitrogen or argon minimized the charge irrespective of the anneal temperature between 920° and 1200°C as shown in Fig. 2, and thus allowed  $Q_{ss}$  control independent of oxidation temperature. This discovery alone opened the door to the routine fabrication of stable, reproducible electronic devices.

Oxide thickness variation between 0.01-0.6 μm showed essentially no change in  $Q_{ss}$ , indicating that the surface state charge was an integral part of the interface structure rather than being dependent upon charge or impurity distribution within the oxide. Indeed, analogous results were demonstrated by etching back the oxide and determining  $Q_{ss}$  for these thinned oxides, which thus determined that the charge resided near (< 200 Å) the Si-SiO<sub>2</sub> interface. Since alteration in silicon surface potential did not change the value of  $Q_{ss}$  as established by oxidation/

annealing conditions, this charge is not in direct electrical communication with silicon. In addition, silicon orientation had a profound effect on  $Q_{ss}$  wherein the charge decreased in the order <111> > <110> > <100>, as reported earlier.<sup>8</sup> Deal, *et al.*<sup>10</sup> also first reported that  $Q_{ss}$  and interface state density were increased by the application of negative electric fields across the SiO<sub>2</sub> at elevated temperature, an effect known as the negative bias temperature instability (NBTI). This phenomenon caused accelerated aging, especially in p-channel MOSFETs, and is intrinsically associated with the Si-SiO<sub>2</sub> interface.

Integration and consolidation of the results of this study led to a picture of the surface state charge in the Si-SiO<sub>2</sub> system: "...the surface-state charge ( $Q_{ss}$ ) can best be explained as being due to excess silicon ions in a narrow region next to the silicon, which are introduced into the oxide...during the process of oxidation."<sup>10</sup> It is difficult to imagine that the authors of this paper foresaw the enormous impact that this work would have



**Fig. 2.** Illustration of the reversibility of heat treatment effects on the surface-state charge density  $Q_{ss}$ .<sup>10</sup>

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on the young semiconductor industry. Clearly, results from these studies made possible the large-scale manufacture of reliable and reproducible silicon-based ICs. Furthermore, this work played a major role in moving semiconductor processing technology onto a more fundamental foundation upon which an entire industry was based. This conclusion was expounded only a few years later in the Conclusions section to a paper on the Si-SiO<sub>2</sub> system by Paul Gray at General Electric:<sup>12</sup> "The development of the processing art to a processing science has been responsible for the spectacular growth of the semiconductor industry as a whole and, in particular, the MOSFET and integrated circuit industry."

As a result of the improvements and successes made possible by these initial efforts to control and understand the fundamental origin of surface state charge in the Si-SiO<sub>2</sub> interface system, studies trying to unravel the variety of charges and instabilities in this vital interface system have continued to the present. In fact, these efforts have probably been more focused and extensive than those on any interface system ever investigated. Although there are many questions still remaining, particularly with respect to a fundamental understanding of interface states, the progress has been remarkable. The 1967 paper by Deal, *et al.*<sup>10</sup> paved the way to controlled fabrication of ICs and allowed the semiconductor industry to take the next leap forward—it has never looked back. ■

### Acknowledgments

I would like to express my gratitude to the late Bruce E. Deal, who ensured that all those who interacted with him appreciated and were educated in the finer qualities and importance of charges, instabilities, and "drifts" in the Si-SiO<sub>2</sub> interface system. I also want to thank Durga Misra and Katalin Voros for their helpful and insightful comments and suggestions on the initial draft of this article.

### About the Author

**DENNIS W. HESS** is the Thomas C. DeLoach, Jr. Professor of Chemical and Biomolecular Engineering and Director of the NSF Materials Research Science and Engineering Center for New Electronic Materials at the Georgia Institute of Technology. His research interests are in the area of thin films, surfaces, interfaces, and microelectronic devices. He is a Fellow of the American Association for the Advancement of Science, the American Institute of Chemical Engineers (AIChE), and ECS. He has served as Editor-in-Chief for *Electrochemical and Solid-State Letters* since 2004, and as Associate Editor for *Chemistry of Materials* from 1988-1996. He may be reached at 404.894.5922 and dennis.hess@chbe.gatech.edu.

### References

1. J. C. Frosch and L. Derick, *J. Electrochem. Soc.*, **104**, 547 (1957).
2. M. M. Atalla, E. Tannenbaum, and E. J. Schiebner, *Bell Sys. Tech. J.*, **30**, 749 (1959).
3. W. L. Brown, *Phys. Rev.*, **91**, 518 (1953).
4. R. H. Kingston, *J. Appl. Phys.*, **27**, 101 (1956).
5. From B. E. Deal, *J. Electrochem. Soc.*, **121**, 198C (1974), as obtained from R. P. Donovan, Research Triangle Institute, NC.
6. A. G. Revesz, *IEEE Trans. Elect. Dev.*, **ED-12**, 97 (1965).
7. E. H. Snow, A. S. Grove, B. E. Deal, and C. T. Sah, *J. Appl. Phys.*, **36**, 1664 (1964).
8. P. Balk, P. J. Burkhardt, and L. V. Gregor, *Proc. IEEE*, **53**, 2133 (1965).
9. B. E. Deal, *J. Electrochem. Soc.*, **110**, 527 (1963).
10. B. E. Deal, M. Sklar, A. S. Grove, and E. H. Snow, *J. Electrochem. Soc.*, **114**, 266 (1967).
11. B. E. Deal and A. S. Grove, *J. Appl. Phys.*, **36**, 3770 (1965).
12. P. V. Gray, *Proc. IEEE*, **57**, 1543 (1969).

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