Structural, Elemental, and Chemical Complex Defects in Silicon and Their Impact on Silicon Devices

by A. A. Istratov and E. R. Weber

Silicon materials science is largely an area of knowledge about defects—silicon native defects (self-interstitials and vacancies), intentionally introduced impurities (shallow dopants), and unintentional contaminants (oxygen, carbon, transition metals). This review provides a brief summary of the current understanding of the origin of defects and their impact in silicon. The inherent difficulty in understanding the properties and mechanisms of the formation of each particular defect is that a silicon wafer is a complicated structure in which native defects, dopants, unintentional impurities, and structural defects all interact with each other and affect each other in a variety of ways. These complex interactions are sketched in Fig. 1. The circle in the middle of the figure represents the interactions between the defects. It is difficult or impossible to fully understand one defect without understanding the complex defect environment in which it exists in a wafer; on the other hand, understanding the properties of one type of defect helps in understanding the others. The examples presented below show how one type of defect can be engineered or understood through the control over the other types of defects.

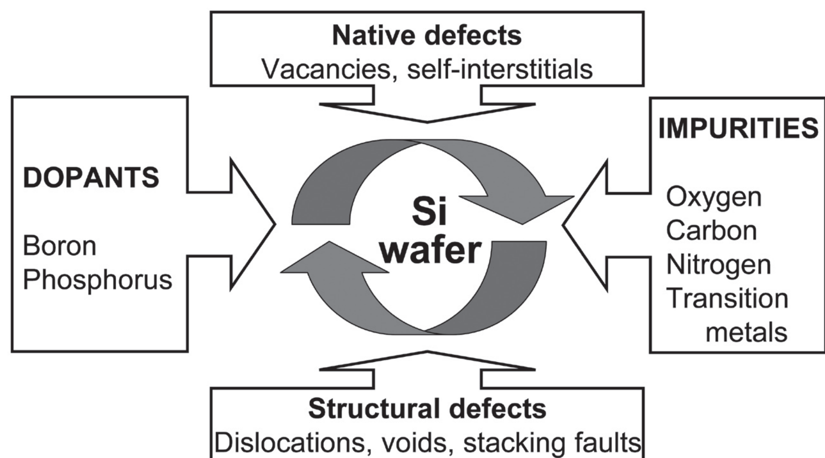

Fig. 1. Schematic representation of the complex interaction of different types of defects in silicon wafers.

Defects in Silicon

Native defects (vacancies, self-interstitials, and their complexes)—The origin of A-defects (now interpreted as clusters of silicon self-interstitials); D-defects (clusters of silicon vacancies); oxidation-induced stacking fault (OSF) ring (a ring formed during thermal oxidation of silicon wafers at the boundary that separates the vacancy-rich area near the center of the wafer and the interstitial-rich area near its edges; the radius of the ring is determined by the growth conditions of the ingot); swirl defects (microscopic dislocation loops arranged in swirl-like pattern); and crystal originated pits (COPs, which turned out to be voids formed through agglomeration of vacancies) have been important research topics in the past, when it was found that these defects could affect gate oxide integrity and device performance, yield, and reliability. Starting from the early report of Seeger and Chik,[1] it eventually became clear that all these defects are either complexes of vacancies or self-interstitials, or formed via interaction of vacancies and self-interstitials with oxygen, and that their formation is determined by the growth conditions of the ingot.

Progress in understanding the properties of native defects was hindered by the small concentrations of native defects, which precluded their direct measurement. Therefore, data on the properties of native defects had to be extracted from indirect studies (such as the analysis of defects in ingots grown using different pulling parameters, kinetics of diffusion of shallow dopants, heavy metals, and precipitation of oxygen), combined with theoretical modeling (a good historic perspective is given by Bergholz and Gilles[2]). The 1982 study of Voronkov[3] established that the growth parameter V/G (where V is the ingot growth velocity, and G is the temperature gradient near the melt-solid interface) determines whether the crystal is grown with vacancies or with silicon self-interstitials as the dominant native point defect. Typically, the concentration of native defects also varies along the radius of the crystal, and for certain values of V/G ratio, the crystal may contain both vacancy-rich and interstitial-rich areas. Falster *et al.*[4,5] modeled defect equilibrium between vacancies and self-interstitials and identified the processing conditions that lead to the formation of relatively defect-free crystals and allow one to avoid the formation of OSF rings and reduce the density of native defect clusters. Another implication of their model is a means to control precipitation of oxygen by engineering vacancy profiles, which is discussed below.

Oxygen is introduced into Czochralski-grown silicon from the quartz (SiO_2) crucible as it is slowly etched off by the silicon melt. A large fraction of the interstitial oxygen incorporated into the crystal from the liquid silicon melt (typically in the 10^{18} cm^{-3} range) precipitates out during cooling of the ingot or during subsequent anneals of the wafers. Oxygen has a relatively low electrical activity in silicon and has a beneficial impact on the mechanical strength of the wafers. Additionally, oxygen precipitates in the bulk of the silicon wafer provide sinks for transition metals (internal gettering sites), thus keeping the metals away from the devices.[6] However, oxygen precipitates formed in the near-surface area of the wafers are detrimental for the device yield. This can be prevented by the formation of near-surface denuded zones by the controlled out-diffusion of oxygen from the wafer. The width of the denuded zone formed via oxygen out-diffusion is extremely dependent on the growth conditions of the silicon ingot, the initial oxygen content in the wafer, and the detailed device fabrication thermal processes.

Falster *et al.*[7] have shown that the kinetics of nucleation of oxygen precipitates is, to a large extent, determined by the local vacancy concentration. They suggested using short anneals in a controlled ambient, followed by a rapid cool, to facilitate the formation of a vacancy profile in the wafer, which stimulates nucleation of oxygen precipitates in the bulk (high vacancy concentration) and suppresses it in the near-surface area (low vacancy concentration). This technique, called "Magic Denuded Zones",[7] gives highly reproducible results and depends neither on oxygen concentration nor on the growth conditions of the ingot.

Carbon is another impurity that is found in silicon in high concentrations, comparable to those of oxygen. Carbon has very low electrical activity, rarely forms precipitates, and has only weak or no impact on device performance for today's Czochraski-grown silicon. However, due to the small size of substitutional carbon compared to that of silicon, doping with carbon can be used for local strain compensation. For example, it was successfully used in SiGe MOSFET technology for strain control (see, *e.g.*, Ref. 8 and 9).

Transition metals, their complexes, and clusters—These are extremely detrimental in silicon due to their high generation- recombination activity and their ability to form precipitates. Even 10^{10}–10^{11} cm^{-3} of transition metals can decrease the device yield. Due to high diffusivity of transition metals (see Ref. 10 and 11 for a review) they can easily diffuse through the wafer to the devices. The devices contain heavily n-type and p-type doped areas, may include areas with high lattice strain, and therefore can provide efficient traps for transition metals via relaxation or segregation mechanisms. Since the device area thickness (less than a micrometer) is significantly less than the wafer thickness (525 or 725 μm), diffusion of metals dissolved in the substrate toward preferred sinks in the device area could lead to an increase in their local concentration by several orders of magnitude. The engineering of transition metals—trapping them at intentionally created sinks away from the devices—is generally referred to as "gettering." Recently, the notion of "competitive gettering" was introduced[12] to emphasize that devices compete for metals with the intentionally introduced gettering sites.

Development of efficient gettering techniques and metrology tools capable of detecting minute metal concentrations require solid understanding of the fundamental physical properties of transition metals. Some metals, such as iron, are very well understood (see, *e.g.*, Ref. 13 and 14). Comprehensive physical models for others, such as copper, have emerged in recent years (see Ref. 15 and references therein). Many other transition metals, particularly 4d and 5d, still require extensive studies.[16]

Previous generations of IC technologies relied on gettering sites in the bulk or at the back surface of the wafers. Novel device technologies require new approaches to gettering. As metal contamination levels get lower and device processing shifts to rapid thermal processing, substrate and backside gettering techniques get phased out in favor of proximity gettering techniques, which bring gettering sites into close proximity of devices. Some novel technologies, such as silicon-on-insulator (SOI),[17] require development of radically new approaches to gettering. Due to the low diffusion coefficients of transition metals in silicon dioxide, metals cannot diffuse through the buried oxide layer within a reasonable amount of time. This renders substrate and backside gettering techniques inefficient in SOI wafers.[18] On the other hand, a buried oxide protects the device area from contamination introduced from the backside and from metals dissolved in the substrate, which improves the device yield.

One possible gettering mechanism that is effective in SOI structures is gettering of metal impurities by heavily doped areas of the devices or specially fabricated heavily doped wells. These areas (whose electrical properties are weakly affected by metals as long as they do not form precipitates crossing the interfaces) act as proximity gettering sites and clean up the weaker doped contamination-sensitive areas and interfaces within the device structure. However, once their gettering capability is exhausted, devices degrade rapidly.

Extended defects—These defects, such as dislocations, cannot be tolerated in the device area. Crystals can be easily grown dislocation-free. However, dislocations can nucleate at the strained areas and interfaces in the device area during processing. Prevention of nucleation and propagation of dislocations in the device area was a serious problem in the 1960-1980s. Eventually, this problem was taken under control by the improved quality of silicon wafers, improved device design and lower temperature thermal budgets utilized in device processing. However, implementation of strained silicon structures have led to renewed interest in the nucleation and propagation of dislocations. Relaxation of strain occurs via propagation of misfit dislocations. The impact of various wafer parameters, such as doping level and impurity content (such as nitrogen) on the nucleation and propagation of misfit dislocations has yet to be fully comprehended.

Implications for Devices: Silicon Photovoltaics

This is another large market for silicon technology that is expected to surpass the value of the Si microelectronics market within the next 10-15 years. Solar cells are an excellent example of how large-scale devices are affected by nanoscale defects. A solar cell is a very simple device, a flat p-n junction with geometrical dimensions of 10 x 10 or 15 x 15 cm^2. The conversion efficiency of light to electricity in such a cell is strongly affected by metal-silicide precipitates with typical sizes in the range of several tens of nanometers, which, when present in sufficient density, decrease the minority carrier diffusion length, increase leakage current, contribute to shunt formation, and ultimately decrease the cell efficiency.[19,20] There is a clear correlation between the density and distribution of metal clusters and solar cell performance, despite a seven orders of magnitude difference between the size of the cell and the size of the precipitates.

In summary, in recent years we witnessed a great progress in understanding the physics of defects in silicon. It has become clear that silicon device performance, yield, and reliability are significantly affected by native defects and impurities, which can be successfully engineered on an atomic level. Improved understanding of silicon materials science has led to the development of novel defect engineering technologies. On the other hand, introduction of new technologies (such as silicon-on-insulator (SOI) or strained silicon) warrants in-depth investigations of materials science problems that were considered less important in the past. Some examples of such problems are strain relaxation and propagation and nucleation of dislocations in strained silicon structures; gettering in SOI wafers; behavior of nitrogen in nitrogen-doped silicon wafers and its interaction with native defects and other impurities; and mechanisms of hydrogen passivation of metal clusters in multicrystalline silicon used for solar cells. There is no doubt that defect science and engineering will remain one of the major directions of silicon research in the future. ■

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Istratov and Weber

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