PROCEEDINGS OF THE SECOND INTERNATIONAL SYMPOSIUM ON VERY LARGE SCALE INTEGRATION SCIENCE AND TECHNOLOGY

MATERIALS FOR HIGH SPEED/ HIGH DENSITY APPLICATIONS

VLSI SCIENCE AND TECHNOLOGY/1984

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ELECTRONICS AND DIELECTRICS AND INSULATION DIVISIONS

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PREFACE

Materials for High Speed/High Density Applications is of critical interest to those of us involved in semiconductor processing today, and will be even more so as we move into one micron and submicron geometries with megabit and beyond densities.

This proceedings volume contains many of the papers presented at the Second International Symposium on very Large Scale Integration Science and Technology. "Materials for High Speed/High Density Applications." May 6-11th, 1984, Cincinatti, Ohio.

The symposium and volume have been organized into six sections as follows:

Materials Characterization and Defects
Chemical Vapor Deposition and Dopant Control
Silicon on Insulator
Dielectrics and Isolation
Metallization and Contacts
Silicon Molecular Beam Epitaxy

We wish to thank the - Authors, the Session Chairmen, their Assistants and secretaries for their cooperation, patience and many hours of hard work in preparing the volume and the symposium. We also thank the entire National headquarters staff of the Electrochemical society, Dr. Bruce Deal and Divisional Officers of the Electronics and Dielectrics and Insulation Divisions for their support.

Ken Bean *George Rozgonyi*

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ELECTRONIC PROPERTY-RELATED DEFECT INTERACTIONS IN SILICON ON A MICROSCALE

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Abstract

Defect interactions in Si with pronounced consequences on its carrier concentration and minority carrier lifetime have been recognized for some time. It has been also speculated that the invariably present oxygen and carbon impurities as well as dopant atoms play important roles in such point- and micro-defect interactions. However, only in the case of oxygen it became possible, and only in the last few years, to identify impurity-induced defect interactions and relate them directly to the degradation as well as to the enhancement of the electronic properties. Oxygen-induced defect interactions leading to electron donors, electron traps and carrier recombination centers are discussed in the light of VLSI technology demands.

General Remarks

For about 30 years it has been known that heat treatment of single crystal Si over a broad temperature range (from close to its melting point down) changes its electronic characteristics (e.g., carrier concentration and excess carrier lifetime). A tremendous amount of work has been devoted to the study of these changes since heat treatments are indispensable in device fabrication. As a result, various heat treatment schemes have been developed to minimize undesirable changes and to optimize desirable ones, however, a detailed account of their causes has not emerged as yet; it has become clear, nevertheless, that interactions of defects (point defects, including impurity atoms, their complexes and clusters) are involved. Oxygen-related defect interactions have attracted by far the greatest attention because oxygen is always present at very high concentrations (particularly in CZ-grown crystals) because it is inherently a very reactive element, and perhaps more importantly, because it became possible to determine reliably its concentration on a macroscale and more recently on a microscale. Actually, in the present report only defect interactions related to oxygen and their effects on the electronic properties of Si will be discussed.

Thermal Donors - Origin and Formation Kinetics

It was shown 25 years ago that interstitial oxygen in Si is responsible for the formation of donors upon low temperature heat treatment (450°C) (1). The formation of these donors has been attributed to various, experimentally unconfirmed, processes leading to a variety of oxygen-related complexes including Si-O (1) and Si-vacancy

complexes (2).

A quantitative assessment of electronic property-related defect interactions became possible about four years ago when the distribution of oxygen in Si on a microscale was achieved by scanning IR absorption. Thus, it was shown that the distribution of thermally-induced microdefects correlates directly with the oxygen distribution (3). It was also found, by relating directly oxygen concentration and carrier concentration microprofiles, that the low temperature (450°C) generated donor is indeed associated with oxygen as seen in Fig. 1 (4). In contrast to the prevailing belief (1), however, the thermal donor distribution is not consistently related to the oxygen concentration, as seen in Fig. 2 (5).

These findings provided the first evidence of important factors other than the oxygen concentration affecting the thermal donor formation processes. As will be pointed out below, we have identified a state of oxygen in the Si lattice and acceptor impurities as contributors to these complex processes.

The role of the state of the oxygen was addressed in our extensive study of the oxygen thermal donor generation kinetics in as-grown and in high temperature (1100°C for 30 minutes) preannealed Si (6). It was found that high temperature preannealing decreases significantly (by a factor of 5 to 6) the maximum donor concentration, and also decreases the 450°C heat treatment time (by about a factor of 50) necessary for thermal donor concentration to reach saturation.

We analyzed the thermal donor generation results employing the phenomenological Johnson-Mehl equation (7) which is often used to describe solid state phase transformations and recently it has been used to analyze the "new donor" generation at 700°C (8). The Johnson-Mehl equation can be written as:

$$\log[(1-\gamma)] = (kt)^n/2.3 \qquad (1)$$

where k is a rate constant, t is the time, and n is the time exponent; here, $\gamma = c(t)/c_{max}$, where c(t) is the concentration of the generated donors at time t and c_{max} is the maximum thermal donor concentration. The time exponent n normally ranges from 0.5 to 2.5 and is used to identify the type of reaction kinetics.

Experimental results from our study on as-grown and high temperature preannealed crystals are shown in Fig. 3, together with results from ref. 9. It is seen that for as-grown crystals $n \simeq 0.9$, whereas for high temperature preannealed crystals $n \simeq 1.5$. This large change in n represents major differences in thermal donor formation kinetics between as-grown and preannealed crystals. A value of $n = 1.5$ characterizes a diffusion-controlled process with a constant number of nucleation sites, whereas a value of $n \simeq 0.9$ indicates that more than one reaction is involved.

A detailed analysis of the results of Fig. 3 revealed that in as-grown crystals thermal donor nucleation sites are already present,

apparently formed during crystal growth (post-solidification cooling); at 450°C, growth (donor formation) continues on these sites but reaches saturation while growth on nuclei formed during 450°C treatment continues. Thus, the value of the time exponent $n \simeq 0.9$ is an apparent composite of two processes. When the late stages of donor formation are subtracted from the early stages of the overall donor kinetics, in as-grown crystals, it is found that the thermal donor generation on nuclei present in as-grown crystals proceeds with $n \simeq 1.5$, indicative of diffusion-controlled kinetics, as shown in Fig. 4. It should be pointed out that during high temperature preannealing the nuclei sites present are dissolved (the concentration of stable nuclei decreases with increasing temperature); upon 450°C treatment nucleation takes place from the supersaturated matrix and growth proceeds under oxygen diffusion control.

The above results are a striking demonstration of the strong dependence of the nucleation process, and thus of the low temperature thermal donor formation, on the thermal history of the crystals. As is discussed elsewhere (6), the above results also account for all mechanisms proposed to explain low temperature thermal donor formation.

Oxygen-Induced Recombination Centers

The approach to the microprofiling of the interstitial oxygen distribution in Si (IR scanning employing a CO_2 laser tuned to the oxygen absorption band at about 9 μm) (4,5) was extended to correlate the oxygen microdistribution with corresponding microprofiles of the minority carrier lifetime (10). This correlation was made possible by incorporating scanning with a YAG laser which can excite excess carriers in Si. Having obtained the oxygen profile, the CO_2 laser is tuned at 10.3 μm, i.e., outside the oxygen absorption band. At this wavelength optical absorption is a measure of the free carrier concentration. The variations in the excess carrier concentration generated by the YAG laser become a direct measure of the variations in the excess carrier lifetime. Some results on the correlation of the oxygen concentration and the excess carrier lifetime are shown in Fig. 5.

It is seen that the spacial variations of the lifetime correlate well with variations in concentration of the interstitial oxygen, i.e., lifetime maxima (minima) occur where the oxygen concentration exhibit minima (maxima). These findings show that oxygen in CZ-Si as-grown crystals is involved in the formation of recombination centers. However, these recombination centers cannot be directly assigned to interstitial oxygen. As shown in Fig. 5, the central and the peripheral regions of Si crystals exhibit significant quantitative differences. Near the center of the crystal the lifetime microprofile shows minima coinciding with oxygen concentration maxima, however, the relative magnitude of lifetime variations ($\Delta\tau/\tau_{av} \simeq 10\%$) is relatively low (much lower than the corresponding magnitude of oxygen concentration variations, $\Delta[O_i]/[O_i]_{av} \simeq 20\%$).

The magnitude of lifetime variations increases drastically toward the periphery of the crystal. About 5 mm from the periphery of the crystal $\Delta\tau/\tau_{av}$ approaches a factor of 10, while $\Delta[O_i]/[O_i]_{av}$ does not exceed 1.5 (Fig. 5b). 0.6 mm from the periphery the lifetime changes by as much as a factor of 20. It is also of interest to note that the average value of τ decreased from the center of the wafer to the edges by a factor of 2, while the average concentration of the interstitial oxygen decreased by 30%. In all instances, however, the lifetime minima (maxima) coincided with maxima (minima) of the oxygen concentration.

These results indicate that lifetime limiting recombination centers in as-grown CZ-Si are due to complexes involving oxygen rather than to interstitial oxygen. Thus, it has been shown (11) that in as-grown Si a certain amount of oxygen is present in the form of precipitates. This amount increases toward the periphery of the crystal. It has also been suggested recently that certain types of oxygen precipitates in Si act as recombination centers (12).

Oxygen-Induced Electron Trap

In p-type CZ-Si we have identified a new electron trap (acceptor level) by employing current transient spectroscopy (13). The p-n junctions required for minority-carrier trap investigation were fabricated using low-energy ion implantation and pulsed electron beam annealing in order to preserve the defects as close to their "as grown" state as possible. This new electron trap (ET) behaves very similar to the oxygen thermal donors. Thus 450°C heat treatment increases the trap concentration, while high temperature annealing (1100-1200°C) leads to the virtual elimination of the trap (13) as seen in Fig. 6. ET is not observed in oxygen-free float-zone Si nor is it found in n-type CZ-Si containing oxygen. Furthermore, the energy position of the trap depends on the group III acceptor element (Fig. 7). These findings indicate that ET is not only oxygen-related, but it is also associated with the acceptor impurity as well. In this context it should be pointed out that oxygen thermal donor activation rates were found to be different from the acceptor elements B, Ga and In (14).

Internal Gettering

In contrast to the above adverse effects, oxygen-induced defect interactions have been widely exploited in Si technology for achieving internal gettering of carrier lifetime including recombination centers. Thus, heat treatments schedules have been developed whereby oxygen outdiffuses from the surface region, while internal gettering takes place at some distance from the surface leading to the formation of a "denuded zone" with superior electronic characteristics and particularly high excess carrier lifetime. The effects of the oxygen microdistribution on the characteristics of the denuded zone as well as the electronic characteristics of the denuded zone on a microscale remain unexplored.

Concluding Remarks

The above discussion of some recent results is intended to illustrate some salient issues bearing on the all-important materials property-electronic property relationships.

Unintentional impurities at quite high concentrations (e.g., oxygen and, to a lesser extent, carbon) continue to be present in device quality Si (thirty years later).

The complexity of the oxygen-induced defect interactions in Si and their effects on its electronic characteristics have only been identified; they have not been resolved and are not understood. Carbon-induced defect interactions and their effect on the electronics of Si are still virtually a total unknown.

Reliable and reproducible characterization of materials and electronic characteristics is the only means of establishing materials property-electronic property relationships without which the development of Si (and other semiconductors) and processing for device fabrication will continue to be more of an art than a science.

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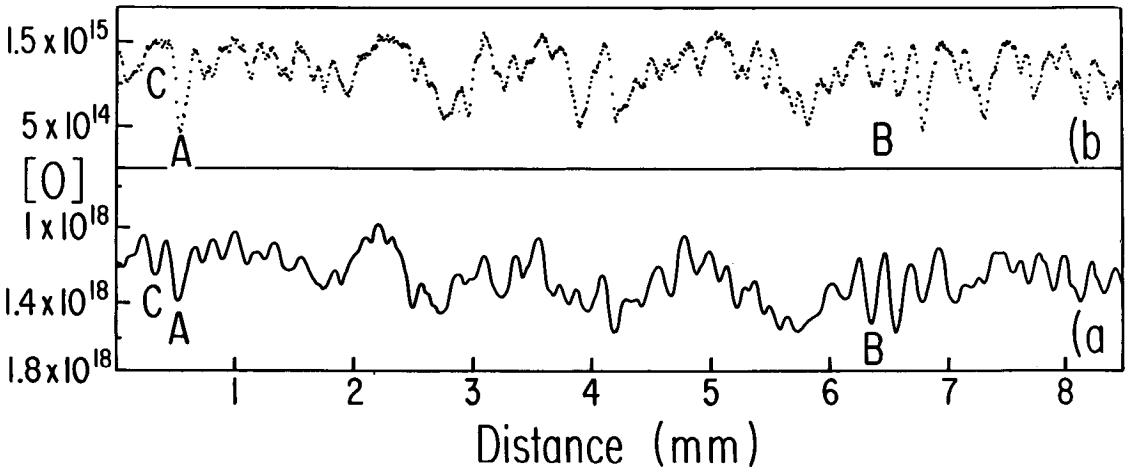

Fig. 1. (a) Oxygen concentration, [O], (O/cm^3) vs. distance parallel to the direction of growth at 6 mm from the periphery of the crystal. (b) Hole concentration [p], (p/cm^3) along the same locaction as in (a) after 4 hr heat-treatment at 450°C.

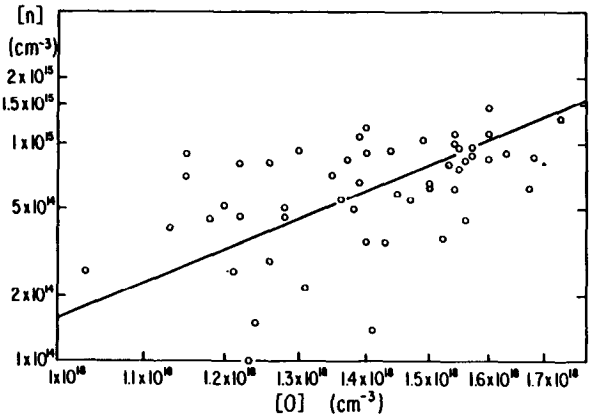

Fig. 2. Thermal donor concentrations (activated by a single heat-treatment at 450°C for 4 hr) as a function of oxygen concentration (see text). Straight line represents the proposed dependence of thermal donor concentration as the fourth power of oxygen concentration.

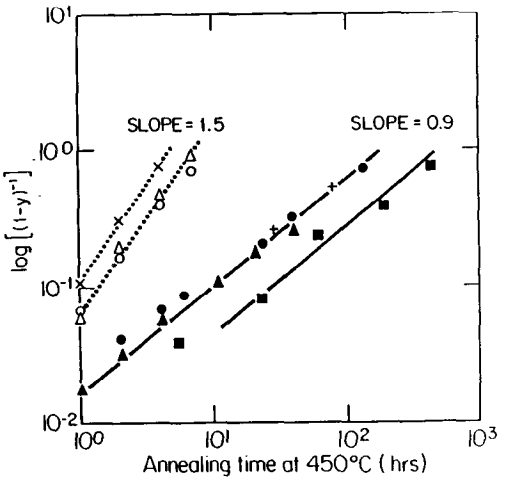

Fig. 3. log $[(1-y)^{-1}]$ as a function of heat treatment time at 450°C. Pre-annealed at 1100°C for 30 mins: × (B-doped); △ (B-doped); o (Ga-doped). As-grown: ▲ (B-doped); ● (Ga-doped); ■ (B-doped); + (Ref. (3)); $[O]_i = 0.9 \times 10^{18} cm^{-3}$.

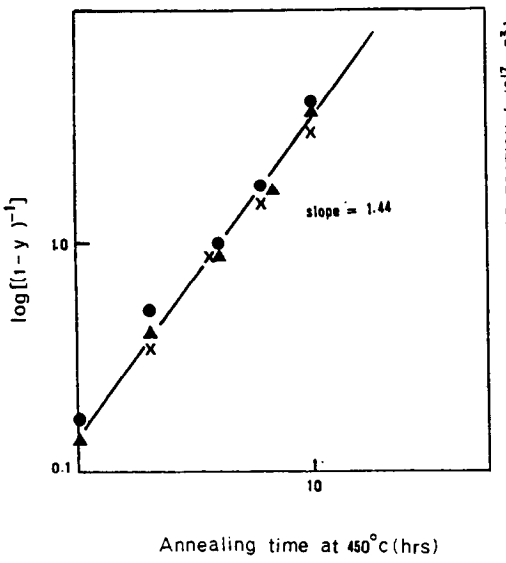

Fig. 4. log $[(1-y)^{-1}]$ as a function of heat treatment time at 450°C. For "as-grown" donors: ● Ga-doped; △ B-doped; ✕ B-doped.

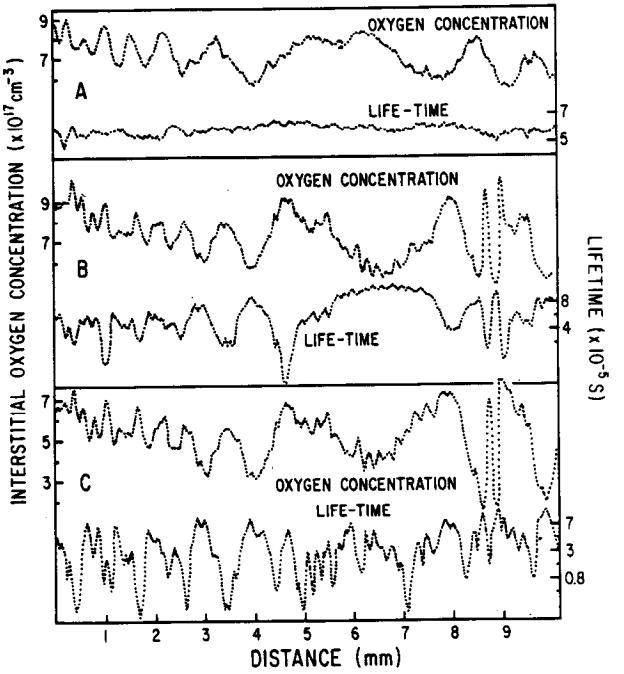

Fig. 5. Microscale distribution of the interstitial oxygen concentration and excess carrier lifetime. Profiles obtained along crystal growth direction. A, B, and C correspond, respectively, to distances of 13 mm, 5 mm, and 0.6 mm from the periphery of the crystal (B-doped crystal).

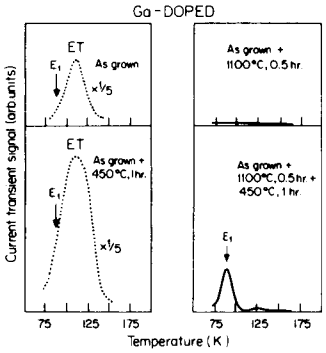

Fig. 6. Current transient spectra (emission time constant, τ = 90 μs) of Ga-doped Si. Only the position of one of the two oxygen thermal donor states (E_1) is indicated. The scale of the peak of ET on the lefthand side of the figure is reduced by a factor of 5.

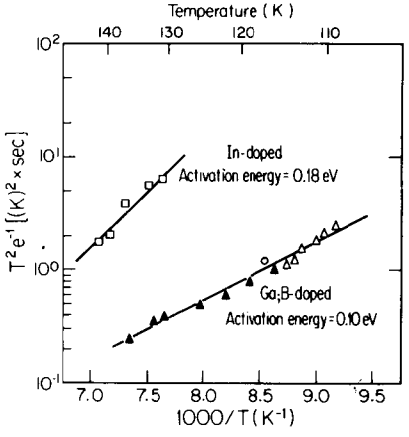

Fig. 7. Corrected emission rate vs (1/T) for ET level in boron and gallium-doped silicon (see text). Open symbols are from the peak position dependence on the rate window; closed symbols are from direct measurements of the time constant of the current transient.