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Controlled Oxygen Doping in Silicon

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Conventional silicon wafers grown from SiO_2 crucible is well known to contain 10-20 ppm oxygen. Oxygen-related phenomena such as precipitation, intrinsic gettering and donor formation comes important in LSI itself and its manufacturing processes. Oxygen concentration must be optimized and be precisely controlled, both in as-grown crystal and in LSI manufacturing processes, to get maximum gettering effects and recombination at the defects while getting rid of degradation of device electrical performance and of activation of thermal slip. In addition to oxygen, carbon and nitrogen play an important role in the above phenomena. We will discuss the control of oxygen doping in the single crystal growth and LSI processes.

Oxygen comes from erosion of crucible. It is possible to control it by fine tuning the crystal growth conditions such as crucible/seed rotation rate, crucible size and temperature distribution in the crucible/1/. Another method are crystal growth under magnetic field/2/or crystal growth from double crucible/3/. All of these method use SiO_2 crucible so that oxygen-free crystal cannot be grown. Alternative method is intentional doping of oxygen into essentially oxygen-free crystal. Conventional oxygen-free crystal grown by float zone method is seldom used in LSI due to troublesome microscopic resistivity distribution and low resistance to thermal slip. The latter may be overcome by nitrogen doping/4/.

Our new oxygen doping is based upon oxygen-free single crystal growth using Si_3N_4 crucible/5/, instead of SiO_2 crucible. The Si_3N_4 crucible was made by depositing dense well developed α-Si_3N_4 crystalline layer by the reaction

$$SiCl_4 + NH_3 \rightarrow Si_3N_4$$

on a reaction-sintered Si_3N_4 or carbon crucible-shaped substrate. The CVD Si_3N_4 layer was chemically inactive to the molten silicon and mechanically strong enough to grow single crystal. Oxygen in a crystal grown from it was not detected by infrared absorption measurement. The detection limit was $2 \times 10^{16}/cm^3$. However, nitrogen about $6\text{-}8 \times 10^{15}/cm^3$ was detected by infrared absorption and radioactivation analysis using $N^{14}(p,\alpha)C^{11}$ reaction. Oxygen was doped by adding a small piece of fused quartz in the molten silicon. Oxygen concentration depended primarily on surface area of the fused quartz piece so that the oxygen concentration could be controlled to any level. An example is shown in Fig. 1. The oxygen concentration was calculated from infrared absorbance according to ASTM F-121 (1978); $\alpha \times 4.81 \times 10^{17}/cm^3$. Nitrogen was also detected in the oxygen doped crystal. Nitrogen is group V element, but almost electrically inactive. 800 ohm-cm crystal ($N_D-N_A = 7 \times 10^{12}/cm^3$) could be grown even though $7 \times 10^{15}/cm^3$ nitrogen was dissolved in it.

Oxygen concentration near the wafer surface can be controlled in LSI processes, however, this is complicated because of two competing phenomena;

(i) out-diffusion of oxygen from surface even if the surface is covered with oxide film.

(ii) precipitation of oxygen whenever oxygen concentration is well over its solid solubility limit at the process temperature and there are nuclei of the precipitate.

These depend on oxygen and carbon concentration, thermal history from crystal growth to LSI manufacturing processes, device geometry and so on. There is no simple way to optimize these to design the best fit wafer to each LSI and its manufacturing processes. Then, one has to make computer simulation of the oxygen-related phenomena. Wide selection of oxygen level by our new growth method makes the wafer design much easier than one in case of the conventional wafer from SiO_2 crucible. Nitrogen might be able to improve some single crystal properties. Oxygen-free or controlled oxygen crystal from Si_3N_4 crucible will be suitable not only for LSI but also for discrete devices such as power transistor and thyristor.

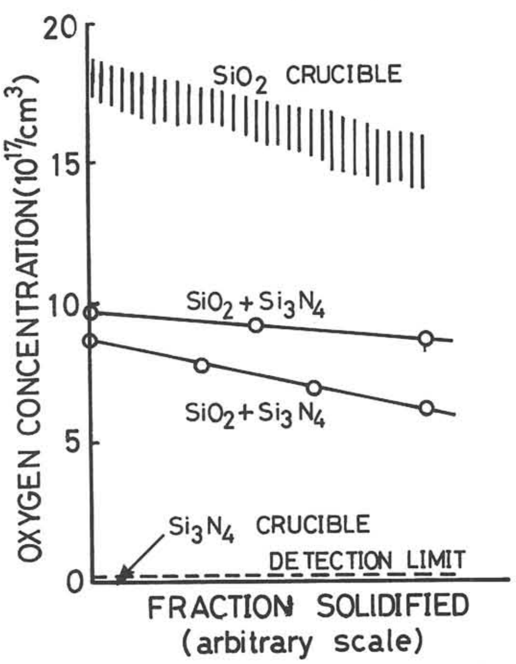

Figure 1 Oxygen concentration in crystal grown from SiO_2 crucible, Si_3N_4 crucible with fused quartz piece and Si_3N_4 crucible.

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