

Defect Generation at SiO₂/Si(100) Interfaces by Metal Contamination

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The effect of structural defects and impurities, e.g. metal contamination, on the integrity of gate oxide layers is investigated using a high temperature anneal in vacuum. Stacking faults are found to enhance defect formation in the oxide via the presence of metals gettering in the faults. Metals, especially near-noble transition metals, are shown to be catalysts for the oxide decomposition reaction $\text{Si} + \text{SiO}_2 \rightarrow 2 \text{SiO}$ at the Si/SiO₂ interface. This catalytic behavior causes nucleation of voids in the oxide at defect sites, after which the voids grow laterally with time. At lower temperatures a reaction product closely related to SiO is believed to remain in the vicinity of the SiO₂/Si interface, thus creating electrical defects in MOS structures.

INTRODUCTION

A major challenge for advanced integrated circuit technology is the identification and control of low density defects at surfaces, interfaces, and thin films. Identification of low density ($\approx 1\text{-}1000/\text{cm}^2$) defects is a substantial challenge even before the nature and origin of the defects can be investigated. High temperature annealing of thin SiO₂/Si structures has previously been shown [1] to effectively decorate existing defects because the oxide decomposition reaction $\text{Si} + \text{SiO}_2 \rightarrow 2 \text{SiO}$ is nucleated at defect sites, from which oxide voids are formed, grow laterally, and become readily observable by optical microscopy, etc.. This oxide degradation process is important also because annealing at lower temperatures activates existing defects electrically, as evidenced in low field breakdown and hole trapping phenomena [2]. In order to better understand what kinds of defects can be decorated by the oxide decomposition process, we have investigated the role of substrate defects (stacking faults) [3] and impurities [4] (mainly metal atoms) in the formation

of oxide voids, using in-situ annealing and observation in a scanning Auger electron microscope.

EXPERIMENT

Gate quality oxide films of 200Å thickness were furnace grown in dry oxygen with 4.5% HCl at 900°C on lightly doped p-type and n-type Si(100) wafers. Before vacuum anneal the wafers were cleaved into 0.7 cm² large pieces and inserted into the vacuum system without any further chemical cleaning. Wafers were annealed in-situ in the temperature range from 400°C to 1000°C by direct current flow through the samples either in vacuum or under nitrogen atmosphere. The experiments were performed in a scanning Auger microscope (SAM) Phi 590 with a base pressure of 5×10^{-9} Pa. Anneals were done continuously, monitoring the surface in vacuum with secondary electron microscopy (SEM mode) and Auger electron spectroscopy (AES) during sample anneal. Auger mapping (SAM mode) images were obtained after cooldown of the sample.

RESULTS AND DISCUSSION

As a prototype for structural defects, we have purposely introduced stacking faults into Si(100) by boron implantation [5] and subsequent high temperature steam oxidation. The presence of stacking faults was verified by flat-on transmission electron microscopy. For comparison, two sets of samples were prepared with implants of phosphorus and silicon, both of which create implant damage that can be removed by annealing. All samples were annealed in vacuum to 1000°C while taking SEM pictures.

A plot of void density vs. implant dose for the three different implants (P, B, Si) is shown in Figure 1.

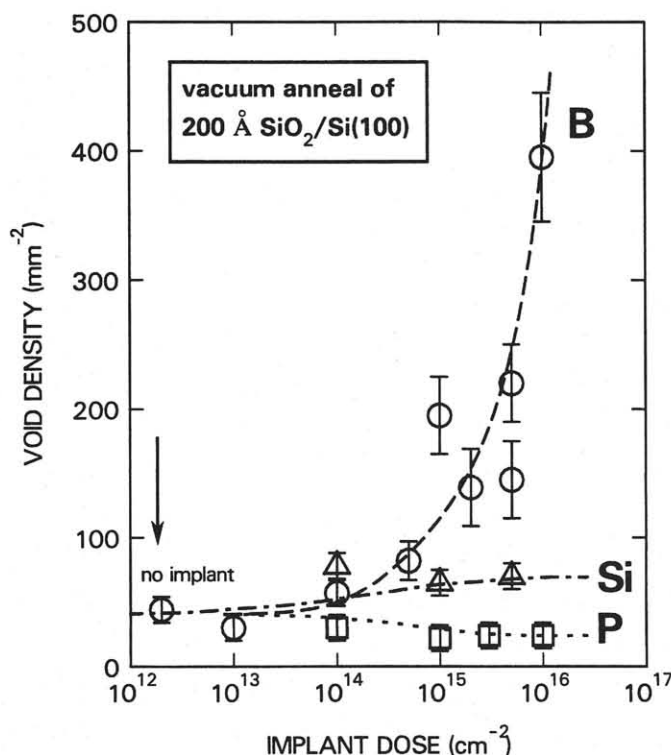


Fig. 1: Void density in 200Å SiO₂/Si(100) after vacuum anneal to 1000°C for 420 min vs. implant dose with silicon, phosphorus, and boron.

Whereas the density of voids stays approximately constant over the full implant range for

phosphorus and silicon, a clear increase in density is observed for boron implants above 10¹⁵/cm². This increase is almost exclusively due to growth of a second population of voids that form after an incubation time. This second population of voids is caused by a higher density of nucleation centers for the formation of volatile SiO. By comparing implanted wafers with wafers intentionally doped to identical levels it was found that the position of the Fermi level (i.e. the doping level itself) has no significant influence on the void density. Thus it appears that the activity of the nucleation center originates in the particular bond configuration at the structural defect site, in this case the stacking fault produced by B implantation. Stacking faults in the Si substrate can therefore contribute to enhanced oxide decomposition and void formation/growth.

Wafers have also been prepared with 3000 Å of polycrystalline silicon deposited on sample backside before oxidation. The polycrystalline silicon is known [6,7] to be an efficient getter for several metal impurities and to remain efficient even after prolonged anneals or oxidations. No additional population of smaller voids is detected on a wafer implanted with boron when a polysilicon backside getter was present. By offering a competing and more efficient getter for metals, this procedure has reduced the amount of metal which may have been getterred by the stacking faults. We conclude that it is the metals getterred in the stacking faults which are the prime candidate for catalytic initiation of the SiO₂ decomposition reaction. The lattice defect structure present at the stacking fault thus acts only indirectly as nucleation center, namely by acting as a getter for metallic impurities in the Si lattice.

In order to investigate the influence of impurities and particles, monolayer amounts of material were deposited on the SiO₂ surface of oxide/Si structures. Decomposition of the oxide is strongly enhanced by presence of such impurities.

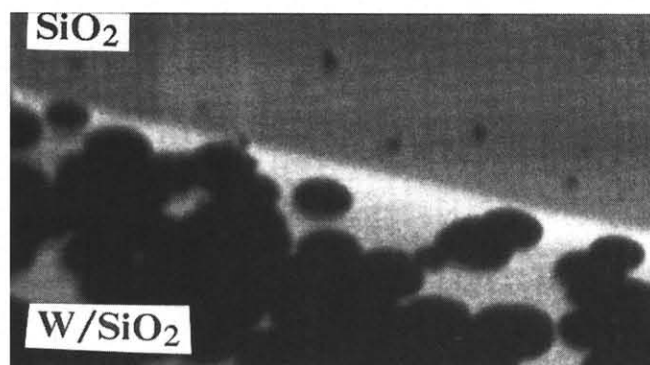


Fig. 2: A scanning electron microscope picture taken during ultrahigh vacuum anneal of a 200Å SiO₂ layer on Si(100). The field of view is ≈ 1 mm by 1 mm (the sample being tilted by $\approx 60^\circ$ giving circular voids an elliptical shape). The pictures were taken at 3 keV electron energy and 50 nA beam current in secondary electron mode. The dark areas represent clean Si areas, the bright background the SiO₂ layer. Metal (W) has been evaporated only on the lower half of the samples to allow comparison with "clean" conditions.

Figure 2 shows, as an example, a scanning electron micrograph after vacuum anneal (1000°C for several minutes) for an oxide/Si structure with a very thin layer of W (3Å effective thickness) having been deposited on the oxide surface prior to annealing. Very clearly enhanced decomposition of the oxide layer is seen on the lower half of the sample, where W had been deposited before vacuum anneal. For the case of W, the oxide decomposition rate is enhanced primarily by a strong increase in the void growth rate, rather than by creation of higher density of nucleation centers. Details of the decomposition rates or defect densities are determined largely by the diffusion properties of the deposited material [4].

Most metals aggregate on the SiO₂ surface because of a lack of reactivity between the metal and SiO₂ [8], e.g. W, thus simulating the presence of particles of these materials. These metals need to

diffuse to the SiO₂/Si interface in order to cause enhanced decomposition of the oxide at isolated defect centers (inhomogeneous decomposition). Behavior similar to that for W is also seen for Ag, Au, Cu, Ni, Pd, and Pt. We have found a linear relationship between the rate of oxide decomposition and the quantity of deposited metal. We conclude that, as long as the coverage is not continuous, results for thin metal coverages may well serve as a model for surface contamination by small metal particles.

We have compared the reactivity of several void-forming metals. As a measure of the efficiency of the metal in enhancing the oxide decomposition process, we have chosen the product of the void diameter growth rate and the number of voids.

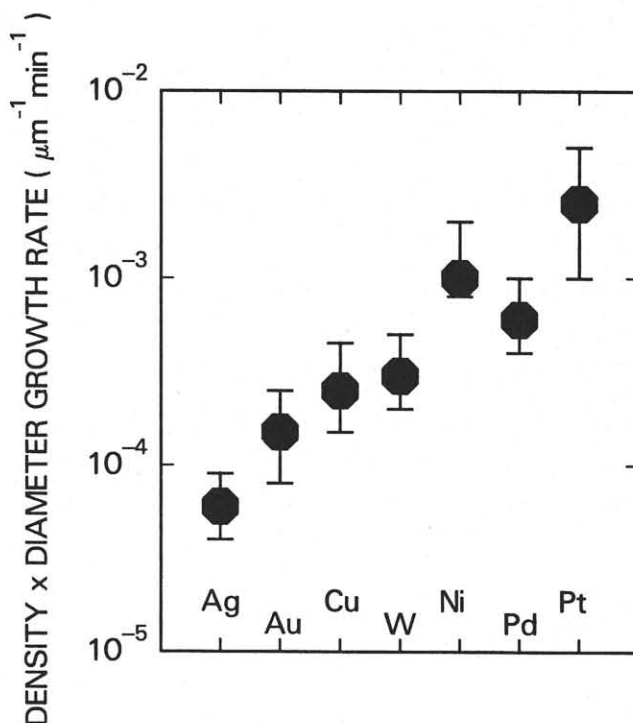


Figure 3: Comparison of oxide decomposition rates for different metals that decompose the oxide via void formation. The product of void diameter growth rate and void density is chosen as parameter. The rates are for a metal layer thickness of one monolayer. All samples have been annealed in nitrogen atmosphere before high temperature vacuum anneal to enhance diffusion of the metal to the interface.

Figure 3 shows the comparison of this measure for Ag, Au, Cu, W, Ni, Pd, and Pt. The near-noble metals appear in this comparison as the most reactive elements with respect to oxide decomposition. From these results we infer that transition metal particles should be efficient in degrading gate oxide layers, both by generation of electrically active defects and by chemical/physical decomposition and removal of the oxide through void growth.

CONCLUSIONS

We have shown that structural defects at the SiO_2/Si interface, such as stacking faults, act as nucleation centers for oxide decomposition and SiO production, which leads to void growth and likely to electrical defects at an early stage of the interfacial reaction. The activity of the defect was found to originate primarily from the metal gettered in the defect, rather than from the structural irregularity associated with the stacking fault itself. Very thin layers or particles of metal on SiO_2/Si structures were also shown to degrade the integrity of the oxide layer during vacuum anneals. Contamination with noble and near-noble elements enhances oxide decomposition via void growth (highly non-uniform laterally), where the reaction requires metal diffusion to the SiO_2/Si interface and catalytic formation of the SiO reaction product. The formation of SiO has previ-

ously been shown [2] to be responsible for electrical degradation of MOS structures during vacuum anneal to temperatures below $\approx 850^\circ\text{C}$, where a form of SiO seems to be trapped in the oxide.

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