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The Deposition and Redistribution of Gold During the Thermal Oxidation of Silicon

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Metal impurities Au, Cu, Fe, Mn, Ni and their effect on devices have been the subject of several studies (1,2-6). Au is a particularly significant impurity in Si because of its pronounced effects on the properties of that material. Controlled Au concentrations in Si can have desirable effects, particularly on high speed switching devices. Alternately, undesirable Au contamination can critically effect device operation. This work considers the adsorption of Au^{198} from HF solutions onto Si surfaces and its subsequent redistribution during thermal oxidation between 1000°C and 1100°C.

High purity .001" diameter Au^{197} wiere supplied by Sigmund Cohn Corporation, Mt. Vernon, New York, was used as the gold source. The Au was activiated in a neutral flux of 10^{13} per cm^2 per sec. Activation times were varied to obtain the most desirable activity for the particular Au concentration being studied. A primary solution of 10% hydrofluoric acid containing 10 ppm of gold by weight was diluted down to produce solutions of nominally 3, 1, 0.3, 0.1, .03 and .01 ppm Au contaminated etchant. To ensure reproducible results particularly at low contamination levels, the solutions were thoroughly mixed at all times with a magnetic stirrer, and all losses of gold from solution to surfaces touched by the solution were accounted for. Gold standards were obtained by pipetting 0.1 cc. of solution onto a standard quartz slide and evaporating to dryness. Standards were always made from the 10 ppm solution where losses to beakers and pipette were negligible.

Clean, polished silicon wafers (.008" thick) were contaminated for 15 minutes in disposable polythene dishes containing 10 cc. of solution. Contamination levels on (111), (110), and (100) orientations of both N and P silicon with resistivities between 1 and 10Ω cm were measured using both radio tracer techniques. Autoradiographs confirmed that the gold plated uniformly on the samples and was not depositing preferentially at defect sites or at the wafer edges.

Following contamination, the samples were thermally oxidized between 1000°C and 1100°C under different ambient conditions. SiO_2 layers were grown in a dry oxygen ambient. During thermal treatment a number of the Au atoms:

(1) evaporated and were lost to the furnace, and gas ambient;

(2) remained on the oxide surface;

(3) were incorporated into the oxide layer; or

(4) diffused into the silicon.

The redistribution of Au between these four areas was investigated for three systems, $Si-SiO_2$, $Si-SiO_2$-PSG and Si-PSG. Figure 1 shows the distribution as a function of contamination level at 1050°C for the $Si-SiO_2$-PSG system. That obtained for the $Si-SiO_2$ system is similar. At the 10 ppm level, excess gold rejected by the system remained on the glass surface. Where PSG was grown directly on the silicon such that phosphorous diffused into the semi-conductor, the Au concentration in the N+Si layer was greatly enhanced. Au concentrations in PSG and SiO_2 layers were comparable suggesting that the N+ layer rather than PSG itself accounts for the gettering properties attributed to PSG.

Au concentration profiles in the oxide layers were determined by an etch back technique where approximately 100A° layers of oxide were etched off in a buffered HF solution. The etch steps were determined on a Talysurf or an ellipsometer. The integral of the concentration profile was first obtained by determining the thickness of oxide removed and measuring the Au^{198} activity before and after etching. This result is than differentiated to obtain the gold profiles. Figure 2 shows the profiles obtained for the 10 ppm contamination level obtained in the $Si-SiO_2$ system. The quantity of Au in the glass was very small except for a region within 300A° of the glass/Si interface where the gold concentration was about 1% by volume and 10% by surface atom density. This accumulation of Au at the interface occurred on all silicon/glass systems investigated. By complete removal of the glass, it was determined that the Au concentrations in the oxide were several orders of magnitude greater than the Au concentrations in the silicon.

As a final check upon the role of diffused n+ layers in gettering gold from Silicon, studies are reported that show a convenient method of making solid solubility studies in the Silicon systems. The results of solubility measurements on a range of phosphorous doped specimens are compared with the values predicted from theory (7), using an accurate analysis of high-temperature fermi-level data.

Some of the conclusions that may be drawn from this investigation are:

(1) When a gold contaminated silicon surface is oxidized, the gold is redistributed between the silicon and the oxide layer. Excess gold is rejected by the system to the oxide surface where some gold evaporates and is lost.

(2) Gold redistributions in the $Si-SiO_2$ and $Si-SiO_2$-PSG systems are similar. PSG does not effect the redistribution when not in contact with the semi-conductor.

(3) Gold in the oxide layers consists of a region of high concentration within 300A° of the Si/Oxide interface and a region of low gold centration in the bulk oxide.

(4) PSG grown in intimate contact with a silicon surface does not absorb more gold than SiO_2.

(5) Interfacial gold appears to exist at low energy sites in the oxide and does not diffuse into the silicon from the oxide.

(6) The N+ layer due to phosphorous diffusion getters Au in Si.

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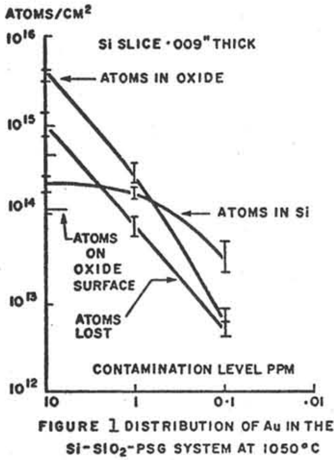

FIGURE 1 DISTRIBUTION OF Au IN THE $Si-SiO_2$-PSG SYSTEM AT 1050°C

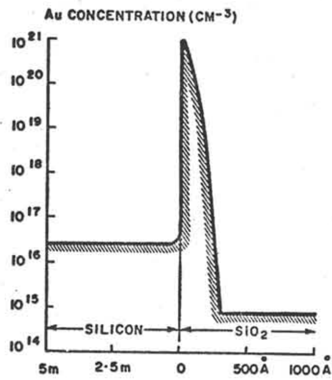

FIGURE 2 Au DISTRIBUTION IN $Si-SiO_2$ STRUCTURE