Alternative Process Chemistries and Chemical Recycling

Personnel

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Decreasing feature size, low cost, and high yield continue to drive the silicon electronics industry. Perfect atomic surface silicon is therefore needed to manufacture high yield devices of submicron dimensions. In addition, there are rising environmental concerns, and EPA regulation is broadening its control over industrial environment. The solution to maintain traditional low cost wet cleaning is to investigate environmentally benign alternative chemistries and improve the effectiveness of this cleaning technology simultaneously.

To investigate atomistic perfection, our group has developed a measuring system, Radio-Frequency Photoconductance Decay, to measure surface defect *in-situ.* The sensitivity level of this measurement is 108 defects/cm^2, which is corresponded to approximately100 parts per billion of surface coverage. This highly sensitive device assists the development of contaminant control in dilute HydroFluoric acid (HF) bath, and an alternative method of passivation (protecting) the bare silicon surface.

To achieve low cost and environmentally benign semiconductor manufacturing, the industry has been exploring the use of dilute chemistries. However, our studies show that copper (Cu) deposition on silicon surfaces increase dramatically with dilute hydrofluoric acid. Our results indicate, for the same concentration of Cu, a seventeen and a half times increase in the deposition rate for a 500:1 bath as compared to a standard 100:1 bath. We therefore conclude that tight control over metal contamination is required for dilute hydrofluoric acid bath.

With our expertise in surface characterization, we expand our capability to measure metal contamination in HF bath with our collaborators at Millipore. Our bath monitor converts metal deposition rate to the level metallic contamination in solution. This technique allows i*n-situ* monitoring of the quality of HF bath with sensitivity about 20 parts per trillion (ppt) of Cu in 500:1 HF solution. This warns the operators when to change HF bath to meet the submicron technology environment.

The other problem with current industry standard using Dilute HydroFluoric acid (DHF) as the last cleaning step to create hydrogen terminated silicon (Si-H) surface is that a perfect hydrophobic hydrogen terminated surface will never be achieved in wet processing because the surface is always left with some fluorine terminations. The amount of fluorine terminated silicon is proportional to the concentration of hydrofluoric acid used. Secondly, although Si-H is non-polar in nature, it degrades in water to form Si-OH. This problem has been improved with the Marangoni drying technique. While it is relatively stable because of its high covalent bonding character, queuing times longer than 10 min. degrade the surface.

To restore the degraded surface, re-clean steps are needed before further processing. These series of re-cleaning steps cause increasing yield loss, time loss, and chemical wastage. Therefore, we have developed a new surface preparation technique, which utilizes alkoxy to protect the bare silicon surface. The current alkoxy passivation is compatible with current industrial processing technique. We have optimized the alkoxy passivation for stability and particle rejection. An alkoxy-passivated surface is 50 times more stable than a hydrogen passivated surface (see Figure 4). The alkoxy-passivated surface therefore resists degradation and oxidation 50 times longer, making expensive re-cleans unnecessary.

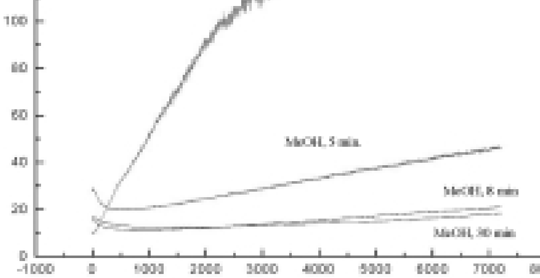

Fig 5. Stability of H- and MeO-passivated Si surfaces in air