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GROWTH AND SURFACE CHEMISTRY OF PASSIVATING INSULATORS FOR SILICON TECHNOLOGY

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Recapitulation of Accomplishments

Below are summarized the significant findings of research carried out under the contract. References refer to journal articles published and listed in the following section.

1. **Surface Cleaning and Passivation Chemistry** [2, 6, 7, 9]

The role of HF cleaning to remove SiO_2 from Si has been studied for both aqueous and vapor reactant. The resulting hydrogen passivation is valuable for subsequent epitaxial growth. Hydrocarbons adsorb onto the H-passivated surface and lead to surface carbide formation upon annealing since H desorption occurs before all hydrocarbons are volatilized.

UV/ozone treatment of the surface is effective in oxidizing hydrocarbons to volatile CO and CO_2, but the surface is then oxidized. This oxide passivation turns out valuable for pre-oxidation cleaning. Furthermore, small concentrations of F left in the surface region (especially subsurface) are incorporated into the UV/ozone-grown oxide and lead to reliability enhancement.

2. **Integrated Processing of MOS Structures** [3, 8, 14, 16, 17]

Using ultraclean, multichamber processing it has been possible to combine the pre-oxidation cleaning step with UHV wafer transfer, subsequent thermal oxidation and annealing, and polySi deposition for the gate electrode. From Al-gate MOS capacitors (and verified by integrated polySi gate structures) it is clear that oxide surface passivation is an essential element in fabricating device-quality MOS structures by integrated processing. Without oxide passivation, roughening of the Si surface occurs while the surface is at high temperature in oxygen-deficient conditions, leading to Si etching by oxygen species and thereby statistical roughening which produces asperities, field enhancement, and low field breakdown in MOS structures. The importance of surface cleaning and its consequent chemical surface passivation properties is strikingly demonstrated.

3. **Integrated Processing for Research and Manufacturing** [3, 12, 20, 21]

The experiences achieved under this contract have significantly defined the appropriate strategies for exploiting multichamber, integrated, ultraclean processing in research and in manufacturing. For example, results and insights from the study of MOS integrated processing provide clear recipes for how to utilize multichamber processing tools which have become a dominant trend in microelectronics manufacturing. Such exercises also open the door to addressing the consequences and benefits of ultraclean processing and real-time, in-situ diagnostics and process control.

4. **Mechanisms of Low Temperature UHV/CVD Si Epitaxy** [11, 19]

UHV-based rapid thermal CVD has been used to combine UHV/CVD epitaxy conditions with in-situ thermal desorption to assess growth mechanisms. Reaction quenching and subsequent H desorption shows for the first time that at low temperatures the growth surface is H-passivated (H desorption is rate-limiting), while at higher temperatures the surface is H-free (reaction and/or supply limited). These details are crucial in the success of low temperature epitaxy and the profound applications demonstrated in devices in the past few years.

5. Nucleation and Growth of Si on SiO_2 [4]

Thermal desorption of H has been exploited to titrate the amount of exposed Si present on the SiO_2 surface during SiH_4 CVD as used for polySi deposition or as relevant in selectivity loss for selective Si deposition. Kinetics have been measured with sensitivities well under 1% of a monolayer of Si on SiO_2 and show that new nucleation sites are generated spontaneously by heterogeneous reaction. Control of the initial nucleation/growth leads to an ability to modify growth morphology and microstructure, e.g. to produce rough polySi for DRAM capacitor applications or to control polySi gate properties.

6. Low Temperature CVD Oxide Growth [5]

The CVD deposition of SiO_2 from SiH_4 and O_2 has been shown to be a fast gas phase reaction at pressures from 1 mtorr to 3 torr. Hydroxyl group products are incorporated into the film and are detrimental to oxide quality. Although the deposition occurs at low temperature (400C), the gas phase dominance makes the process hard to control for manufacturing, while the inferior dielectric quality restricts it range of application.

7. Anomalous Diffusion of Fluorine in Silicon [1]

To understand how halogens are best incorporated and distributed in MOS structures for reliability enhancement, the diffusion of F in Si has been measured. Following F implantation well below amorphization threshold, annealing studies show the F redistribution to be highly anomalous and not explained by conventional diffusion models.

8. Interfacial Oxide Decomposition at the Si/SiO_2 Interface [13, 18, 20, 23]

Further work has extended our understanding of high temperature oxide decomposition at the Si/SiO_2 interface. In particular, metal impurities at the interface, reacting with the oxide, or in stacking faults which penetrate to the interface have been shown effective in initiating or accelerating the interfacial oxide decomposition reaction.

9. Advanced Diagnostics for Insulator Materials and Processes [10, 15, 20, 22, 23]

The utilization of in-situ diagnostics for this work has led to several advances in diagnostic techniques. High resolution electron energy loss spectroscopy has proven valuable for in-situ characterization of thin insulators. High temperature vacuum annealing of thin SiO_2 on Si reveals some classes of point defects, in particular metal impurities which lead to lateral growth of essentially circular voids in the oxide as a consequence of interfacial oxide decomposition. Positron annihilation depth profiling has been shown very sensitive to interfacial defects, e.g. to microvoids which exist in the as-grown thermal oxide as well as to interface states which respond to chemical treatments like H_2 annealing.

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