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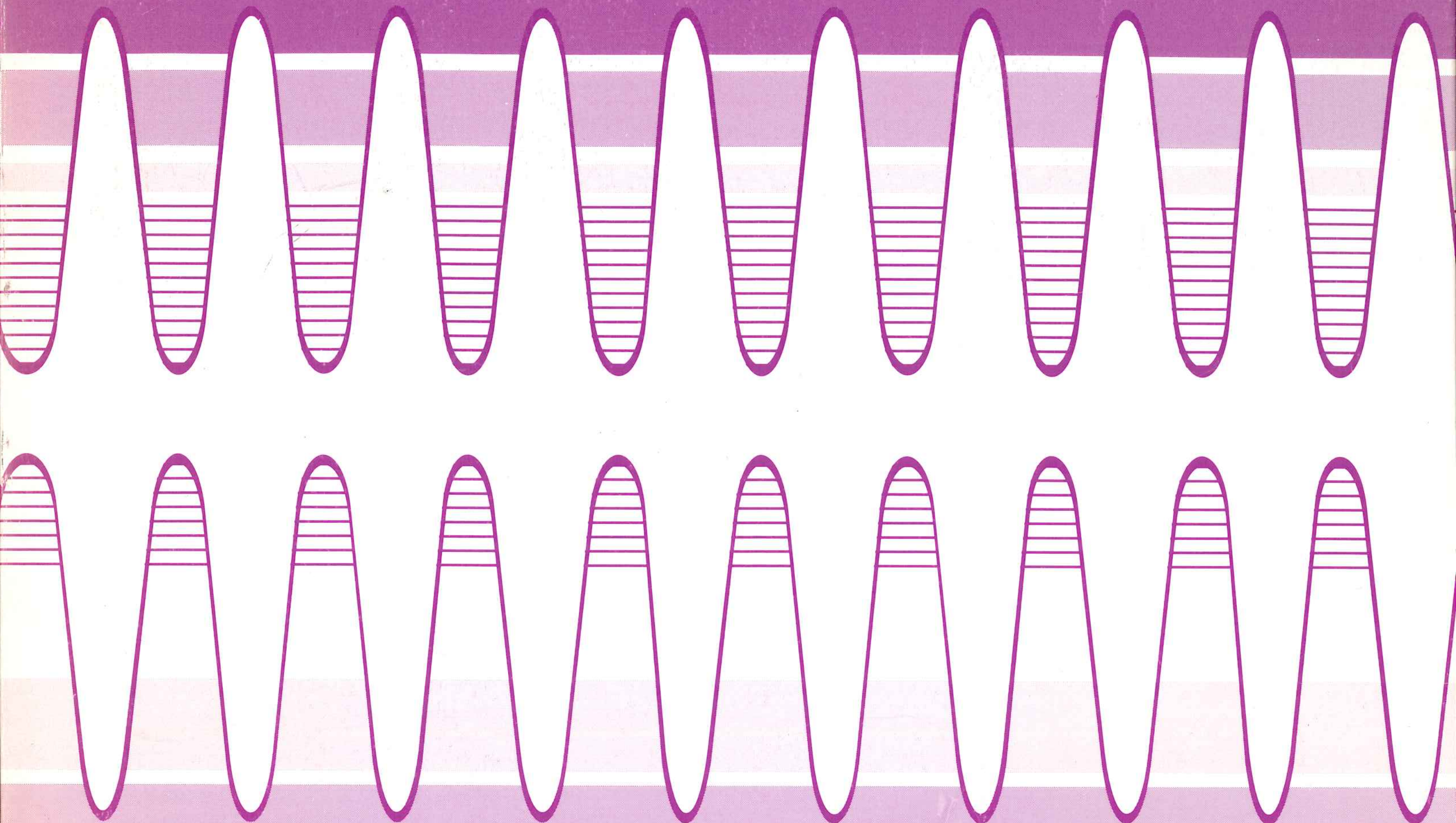

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Technical Program with Abstracts

Lionel C. Kimerling, Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

The steady decrease in the minimum feature size of commercial IC's has tightened the wafer cleanliness standards needed to achieve satisfactory device yields. While wet cleaning cycles continue to be used because of their excellent ability to remove particles, adsorption of trace amounts of metals from contaminated solutions is a growing concern.

In this paper, the thermodynamics of metals in solutions is used as a tool for understanding metal removal and contamination in wet wafer processing. A quantitative description of contamination effects in peroxide solutions is possible by means of E-pH (E = redox potential, pH = $-\log([H^+])$ diagrams. These diagrams define a thermodynamic driving force for adsorption on the substrate, reflecting the tendency of a metal in the cleaning solution to adsorb and contaminate the wafer. Calculated values of this driving force are in excellent agreement with data for the relative adsorption tendencies of Al, Fe, Ni, Cu, Zn and Cr from APM (Ammonium hydroxide - Peroxide Mixture), as previously reported. We developed a kinetic model for metal removal and contamination processes in peroxide solutions, based on the assumption that the metal oxide forms as an impurity in the chemical oxide. Due to etching and contaminant depletion effects, the saturation surface concentration of contaminant will deviate from the equilibrium value predicted by thermodynamics. For HF solutions, the driving force for adsorption is dependent on the standard reduction potential of the ion and the final bonding state of the metal on the silicon surface. Implications of these results for optimizing the performance of wet cleaning systems will be discussed.

To illustrate our analysis, we shall present the results of controlled adsorption measurements on silicon in APM, HPM (Hydrochloric acid - Peroxide Mixture) and HF, using RF-PCD, DLTS, TXRF and EBIC analyses. Vanadium, which is commonly used as a catalyst in polymerization processes, was observed to deposit from HF, after being leached out of a polypropylene beaker. This adsorption behavior was predicted by our thermodynamic treatment. Fe exhibits a strong adsorption tendency in APM, in agreement with the strong positive driving force as determined on thermodynamic grounds. Meanwhile, in HPM and HF, the driving force is negative and no adsorption is observed.

1:50PM, O2

Kinetics of Silicon Surface Reaction with Germane at Low Temperature in Atmospheric Pressure Chemical Vapor Deposition System: Wen-Sheng Wang, and Ishwara Bhat, Electrical Computer & Systems Engineering Department, Rensselaer Polytechnic Institute, Troy, NY 12180-3590

Several workers have shown that Ge or germane gas can reduce native Si surface oxide in a UHV or low-pressure CVD systems. We have shown earlier that single crystal CdTe can be grown on Si substrates in an atmospheric pressure CVD reactor without using the high temperature de-oxidation step, if germane gas is passed over Si prior to CdTe growth. Without this germane cleaning step, only poly-crystalline layers could be obtained. We have carried out a more detailed study of this "in-situ cleaning step" at low temperature (<500°C) in order to understand the mechanism and will present our detailed results to show that germane gas reduces SiO_x. We also show that it is germane gas, rather than elemental Ge, that is responsible for this reduction reaction.

We have carried out growth of Ge on Si using germane gas in an atmospheric pressure CVD reactor[3]. We observed that when we pass germane gas over H-passivated Si at 450°C, the growth of Ge starts almost immediately, without any "induction" period. On the other hand, if we grow a thin layer (8Å) of oxide on Si, it takes over 20 minutes before Ge growth starts. If we use a 1000Å thick thermally grown SiO_2, no continuous layer was observed even after 1 hour of growth. From these and additional experiments led us to believe that germane gas first reduces native SiO_x on Si, and when all the SiO_x is desorbed, Ge growth starts.

First, we carried out GE growth on Si covered with various thicknesses of native oxide.These native oxides were grown by dipping the wafers in $HCl:H_2O_2:H_2O$ solution for different time periods. The "induction" periods required for the start of continuous Ge layer were determined from these experiments. The thickness of the native oxide layers was independently measured using spectroscopic ellipsometry. The observed induction time increased monotonically with the oxide layer thickness, indicating that this period was related to the time required to desorb the native oxide. For a fixed oxide layer thickness, the induction period decreased exponentially with increase in temperature. For example, the induction time for a 8Å thick oxide was about 5 min. at 480°C, whereas it was about 110 min. at 350°C. From these experiments, the activation energy associated with the SiO_x reduction by germane gas was determined to about 21 kCal/mole. The activation energy associated with the decomposition of germane to Ge was also determined and was found to be 38 kCal/mole. These studies indicate that germane gas, rather than elemental Ge may be responsible for the reduction of native SiO_x. Further studies are underway by SIMS to confirm that native oxide desorption indeed takes place. Detailed experimental results to explain the reaction mechanism with correlations to previous works will be presented at the talk.

2:10PM, O3

Scattering Studies of Hyperthermal Cl_2 on the Si(100) Surface with Implications to Collision Dynamics and Etching Product Formation: Gabriela C. Weaver, and Stephen R. Leone, Joint Institute for Laboratory Astrophysics, National Institute of Standards and Technology and Dept. of Chemistry, University of Colorado, Campus Box 440, Boulder, CO 80309-0440

The scattering behavior of a beam of Cl_2 and Cl neutrals with Si(100) is studied at transitional kinetic energies of 0.5 eV to 6.5 eV and 0.2 eV to 3.5 eV, respectively. By comparing the scattering behavior from a silicon (100) crystal surface with a non-reactive quartz standard we can observe differences in uptake for a two species over the continuum of kinetic energies. For both Cl_2 and Cl species, significant sticking occurs at all energies on a clean Si surface. As coverage increases to approximately 6% of a monolayer, sticking all occurs for Cl_2 energies up to 1 eV, but particles above that energy are almost completely scattered.

There is less scattering overall for beams with energy distributions which have significant flux above 2.5 eV. We previously observed that these beams contribute to increased etching of the silicon surface, as evidenced by the production of $SiCl_3$ etch product. By comparison of the scattered fraction to Auger coverage data, it can be shown that these higher energy beams do not merely stick on the surface. The decrease in the scattering fraction for these beams is thus believed to e a result of increased reactivity with the surface leading to etchant product formation. As a general trend, we see that sticking decreases with increasing energy.

Investigation of the angular distribution of the scattered products shows a strongly peaked elastic contribution and a more isotropic $\cos^3$ Q contribution along the spectral angle. The elastic contribution is seen to reflect the gaussian spatial distribution of the incoming beam. The isotropic portion represents interaction with the corrugations of the attractive surface potential. However, since the distribution is not a purely cos Q distribution, it demonstrates incomplete accommodation to the surface.

The ratio of Cl to Cl_2 in the beam is monitored by scattering from the quartz standard. Scattering with silicon shows an increase in the Cl/Cl_2 ratio which indicates two possibilities for the scattering dynamics. The Cl_2 may be preferentially taken up with respect to the Cl on the surface. Additionally, Cl_2 may undergo collision dissociation upon striking the surface and subsequently scatter as Cl.

2:30PM, O4

Oxygen Incorporation During Low-Temperature Chemical Vapor Deposition Growth of Epitaxial Silicon Films: P.V. Schwartz, Department of Electrical and Computer Engineering, University of Iowa, Iowa City, IA 52242, and J.C. Sturm, Department of Electrical Engineering, Princeton University, Princeton, NJ 08540

We have studied the incorporation kinetics of oxygen during the low temperature chemical vapor deposition (CVD) growth of epitaxial silicon films in the temperature range of 700°C to 750°C. For any crystalline growth technique, a clean, defect free surface is needed for epitaxial growth. During silicon epitaxy, surface oxide formation can break the pattern of the silicon surface and cause non-crystalline growth

THURSDAY PM

and highly defective films through the formation of stacking faults and hillock structures. Ultrahigh vacuum (UHV) experiments performed to determine the stability of oxygen on clean silicon surfaces, found the sticking coefficient of oxygen on the clean silicon surface to be approximately 0.01. Historically, the UHV experimental results have been used to determine the operating points of epitaxial reactors and the constraints placed on gas purity for growth at low temperatures. In our work we find that the sticking coefficient for oxygen on the surface of silicon during CVD growth conditions is reduced by almost two orders of magnitude from the UHV experiments. The main focus of this paper is to show that the UHV experimental conditions are overly pessimistic in the case of growth by chemical vapor deposition because of hydrogen passivation of the silicon surface, and a boundary layer established during CVD growth.

We first determine experimentally the incorporation rate of oxygen in the growing films as a function of growth conditions. The growth experiments were performed in a load-locked rapid thermal chemical vapor deposition system. The base pressure of the system is approximately 10^{-8} Torr which ensures that the background oxygen contamination in the reactor is much less than the concentration introduced to the gas stream during growth. The oxygen is introduced into the growth environment in an argon carrier through a calibrated mass flow controller such that the oxygen concentrations in the epitaxial films are in the range of 6×10^{19} cm^{-3} to 6×10^{-20} cm^{-3}. The oxygen concentration in the films were determined by Fourier Transform Infrared Spectroscopy and calibrated by SIMS. We then model this incorporation taking into account both the boundary layer mass transport effects and the effects of hydrogen surface coverage on the sticking probability.

We develop a model of oxygen incorporation that is linear with oxygen concentration in the growth environment described by a simple kinetic limit for the oxygen incorporation. Although the experimental levels of oxygen are far above those acceptable in high-quality epitaxial layers, we assume that the results can be extrapolated to low oxygen concentrations as well. For example, we find, experimentally, the oxygen incorporation flux for 10 ppm O^2 in the gas flow at 6 Torr is 1.1×10^{13} atoms cm$^{-2} \cdot$ s^{-1}. (The oxygen concentration in a film grown under these conditions at 750°C is approximately 2×10^{20} cm^{-3}.) If the effective sticking coefficient were 10^{-2}, as in the UHV clean surface condition, we would have expected the oxygen incorporation flux to be approximately 10^{15} atoms cm$^{-2} \cdot$ s^{-1}, which is almost a factor of 100 larger than our experimental data. This reduction of the oxygen incorporation is extremely fortuitous for chemical vapor deposition and explains why conditions for epitaxy inferred from UHV experiments are overly pessimistic for CVD. We explain the reduction in oxygen incorporation by two important effects which are determined by CVD growth kinetics *1)* the slow nature of mass transport across a CVD boundary layer and *2)* the hydrogen passivation of the silicon surface.

Within the boundaries of our model, we determine the maximum oxygen concentration which can be tolerated in a CVD growth environment to allow for the growth of epitaxial silicon (and silicon-germanium) films with oxygen concentration below the solid solubility limit. The limitation placed on the amount of oxygen which can reach the silicon surface during CVD growth enables the low-temperature growth of high-quality epitaxial layers with gases purified to the level available from commercial gas purifiers.

2:50PM, O5

Selective Silicon Epitaxy by Photo-CVD at a Very Low-Temperature of 160∞C: Akira Yamada, Takayuki Oshima, Masashi Sano, *Makoto Konagai and Kiyoshi Takahashi, Department of Physical Electronics, *Department of Electrical and Electronic Engineering, Tokyo Institute of Technology, O-okayama 2-12-1, Meguro-ku, Tokyo 152, Japan

The development of the low-temperature Si epitaxy has been required for further reduction of the lateral dimension of the Si devices and the selective growth of silicon has attracted attention to realize the submicron-scale MOS devices. In this paper, we have grown epitaxial silicon films using SiH_4, SiH_2Cl_2 and H_2 gas mixture at a growth temperature of 160°C by photo-chemical vapor deposition (photo-CVD). Furthermore, the selective silicon epitaxy has been successfully demonstrated by the photo-epitaxy followed by photo-etching.

Epitaxial Si films were grown by mercury-sensitized photo-CVD. A low-pressure mercury lamp was used as a ultra-violet light source. The growth temperature was 160°C and the total pressure was 1.0 Torr. The SiH_4, SiH_2Cl_2 and H_2 flow rates were 4.6 sccm, 0.5 sccm and 25 sccm, respectively. The epitaxial Si film was grown on a (001) Si substrate, which was confirmed by reflective high energy electron diffraction (RHEED) measurement. The growth rate was 430 nm/hr. From the Raman measurement, the full width at the half maximum of the film was 4.5 cm^{-1} and the value was comparable to that of the bulk Si, which showed the good crystallinity of the obtained films.

Amorphous-like films were deposited on the glass substrate and it was found that films easily peeled off. Since the etching rate of amorphous silicon is faster than that of the silicon against the H radicals, it was expected that the selective Si epitaxy could be realized by the photo-epitaxy followed by the photo-etching. The H radicals can be effectively produced by the photo-CVD technique.

To clarify above hypothesis, we have grown Si films on the thermally oxidized Si substrate which had rectangular window regions. After the growth of Si films, silicon epitaxy was confirmed on the window regions, while amorphous-like film was deposited on SiO_2 regions. Then the photo-etching with H radicals were carried out for 15 min. In the experiment, the etching rate of silicon was negligible. The amorphous-like film were completely removed by the etching and the perfect selective silicon epitaxy was realized.

3:10PM BREAK

3:30PM, O6

The Electrical Integrity of Oxides, Nitrides, and Oxynitrides During Dichlorosilane Exposure in RTCVD Reactor: C.C. Hobbs, B.E. Hornung, J.J. Wortman, M.C. Oznurk, North Carolina State University, ECE Dept,. Box 7911, Raleigh, NC 27695

In the fabrication of advanced MOSFET and BJT structures, selective silicon epitaxy can provide new degrees of freedom. Selective silicon epitaxy using dichlorosilane (DCS) and H_2 has been demonstrated and applied to several novel device structures. Chlorine from the DCS assists with the removal of adsorbed silicon atoms from oxide. However, this etching process can create damage to the surrounding oxide in the form of pinholes. This degrades the insulating quality and can weaken thin sidewall spacers. Sidewall spacer compatibility with chlorine based selective silicon epitaxy is crutial for thin oxides such as those that may be necessary for the raised source/drain MOSFET structure.

This paper presents research results on a selective RTCVD silicon epitaxy process window that could be required to maintain the electrical integrity of thin RTCVD oxides and oxynitrides for sidewall spacers applications. To determine this window, we initially focused upon the amount of oxide degradation occurring during 1000Å of silicon growth and selected an optimal epitaxy process. We used this process to study the integration of RTCVD oxides, nitrides, and oxynitrides.

Capacitors were fabricated using thermal oxides exposed to DCS silicon epitaxy gas ambients in a RTCVD reactor. The epitaxial growth temperature ranged from 750°C to 900°C at a pressure of 2 Torr using 5% DCS in H_2 and the capacitor oxide thickness was varied from 80Å to 375Å. Using unexposed oxides as a control, we computed the percent degradation in the electric field breakdown versus temperature. As an example, a 200Å thick film gave a percent degradation of 7%. For each oxide thickness exposed to DCS below 850°C, the degradation of the electric field breakdown remained below 10%. Above 850°C, the percent degradation showed a strong dependence upon the oxide thickness. In this temperature regime, the electrical field breakdown was observed to rapidly decrease as the oxide thickness decreased. Based on these experiments, it appears that one must remain below 850°C to maintain oxide integrity for thin oxides.

We have also investigated deposited oxides, nitrides and oxynitride dielectrics. Our 200Å thick RTCVD dielectrics were deposited at 800°C with a pressure of 9 Torr by holding the SiH_4/N_2O ratio constant at 2% and varying the NH_3/N_2O ratio from 0% to 50%. The deposition was followed by a 10 second 1000°C anneal in N_2 to densify the films. After exposing the films to 5% DCS in H_2 at 850°C, capacitors were fabricated for test purposes. Using similar electric field breakdown measurements as before, we observed no significant difference in electrical behavior