## Monday Morning, October 2, 2000

### Semiconductors Room 306 - Session SC1+EL+SS-MoM

#### Chemistry of Silicon Oxides and Nitrides Moderator: E. Cartier, IBM

# 8:20am SC1+EL+SS-MoM1 Atomic-Order Thermal Nitridation of Si(100) and Subsequent Epitaxial Growth of Si, *T. Watanabe*, *M. Sakuraba*, *T. Matsuura*, *J. Murota*, Tohoku University, Japan

Atomic-order nitridation by NH@sub 3@ on Si(100) and subsequent Si growth by SiH@sub 4@ were investigated using an ultraclean low-pressure CVD system with a Xe flash lamp. Thermal nitridation on Si(100) at 400°C in an NH@sub 3@ environment with and without the flash lamp light irradiation is explained by Langmuir-type physical adsorption of NH@sub 3@ and nitridation by the adsorbed NH@sub 3@. The nitridation can be enhanced by Xe flash lamp light irradiation, and the N atom concentration tends to saturate to about 2.7x10@super 15@ cm@super -2@. In the Si deposition on the ultrathin silicon nitride, it is found that N desorption from the Si nitride films hardly occurs, and Si grew on silicon nitride, whose N atom concentrations are from about 2x10@super 14@ cm@super -2@ to about 2.7x10@super 15@ cm@super -2@, at 385°C in an SiH@sub 4@ environment with and without the flash lamp light irradiation. The incubation period of Si growth is observed and increases with increasing N atom concentration of the silicon nitride film. On the silicon nitride of N atom concentration of about 2x10@super 14@ cm@super -2@, the incubation period is hardly observed and it is found by RHEED measurements that Si epitaxially grew. Layer-by-layer growth control of silicon nitride is proposed by combining atomic-order nitridation on Si and atomic-layer growth of Si on the silicon nitride.

# 8:40am SC1+EL+SS-MoM2 The Role of Inter-dimer Interactions in NH@sub 3@ Dissociation on Si(100) - (2 x 1), K.T. Queeney, Smith College; K. Raghavachari, Y.J. Chabal, Bell Laboratories, Lucent Technologies

The chemistry of gas-phase precursors to film growth on the Si(100) surface in ultrahigh vacuum is often well-described by localized interaction of the adsorbate with a single Si-Si dimer.@footnote 1@ However, our combined experimental and theoretical studies of the dissociation of NH@sub 3@ to form NH@sub 2@-Si-Si-H on this surface reveal that this reaction is in fact governed by a complex set of inter-dimer interactions involving both bare and adsorbate-covered Si dimers. External transmission FTIR spectroscopy allows us to probe both the lower-frequency @delta@(NH@sub 3@) modes of metastable, undissociated NH@sub 3@ and the higher-frequency @nu@(SiH) modes resulting from dissociation. By comparing our experimental results with density functional calculations describing two-dimer clusters, we find that the vibrational spectra can only be interpreted when inter-dimer effects are considered. Specifically, while hydrogen bonding between undissociated NH@sub 3@ and dissociated NH@sub 2@ species renders coupling of adjacent nitrogen-containing groups thermodynamically favorable, kinetic control of the dissociation process yields a predominance of the opposite configuration, resulting from the influence of dissociated species on the buckling of neighboring bare dimers during adsorption. We propose that such adsorbate-induced effects on the electronic structure of neighboring dimers may have general implications for controlling the two-dimensional ordering of reactions on the dimerized Si(100) surface. @FootnoteText@ @footnote 1@ See for example: R. Konecny and D. J. Doren, J. Chem. Phys. 1997, 106 (2426); B. B. Stefanov and K. Raghavachari, App. Phys. Lett. 1998, 73 (824).

9:00am SC1+EL+SS-MoM3 Quantum Chemical Study of Silicon Nitride Deposition Using Ammonia, Y. Widjaja, C.B. Musgrave, Stanford University Density functional theory is used to examine the reaction mechanisms of nitridation of the Si(100)-2x1 surface by NH@sub 3@. The surface is modeled using the cluster approximation. A detailed reaction mechanism is investigated including ammonia adsorption and decomposition, insertion of N into Si-Si bonds, and H@sub 2@ desorption. We find that nitrogen prefers to be in the subsurface layer, bonded to three Si atoms. The energy barriers leading to the nitridation of the Si(100) surface are also calculated. The activation barrier of the rate limiting step is found to be higher than the activation barrier for NH@sub 3@ desorption. This confirms the experimental observation that a large fraction of the NH@sub 3@ that dissociates on adsorption will recombine and desorb. Furthermore, we have also calculated the vibrational frequencies of various surface nitride structures. The computed frequencies are then compared with the experimental HREELS spectra. The comparison further allows the

unambiguous characterization of the surface species. Using the calculated barriers and frequencies we use transition state theory to estimate a rate for nitridation of the (100) silicon surface. We investigate the validity of the cluster approximation and find that bigger cluster models are necessary to describe the nonlocal electronic effects.

#### 9:20am SC1+EL+SS-MoM4 Thermal Nitridation of Ultrathin Silicon Dioxide Films Using NH@sub 3@ Gas, O. Jintsugawa, M. Sakuraba, T. Matsuura, J. Murota, Tohoku University, Japan

Nitrided ultrathin SiO@sub 2@ film is attractive as the gate insulator of future MOS devices. In this work, thermal nitridation of thin SiO@sub 2@ films and transport of nitrogen species into SiO@sub 2@ films were investigated. A 30Å-thick SiO@sub 2@ film on Si(100) was formed by wet oxidation at 700°C , and was thermally nitrided for 90min at 750-850°C in NH@sub 3@ gas at 100Pa using an ultraclean low-pressure CVD system. The depth profile of N atom was obtained by the repetition of etching by a 1%-diluted HF solution and XPS measurements. By the thermal nitridation. most of the N atoms were present near the SiO@sub 2@ surface and the N atom concentration was remarkably lower (1/2 and 1/10 at 850 and 750°C, respectively) than that of the nitrided Si surface without the SiO@sub 2@ film. By 850°C nitridation. N atom diffused into the SiO@sub 2@ film and Si substrate nitridation were observed. The N atom concentration was estimated to be 4x 10@super 15@cm@super -2@ on the SiO@sub 2@ surface, 1x10@super 21@cm@super -3@ in the SiO@sub 2@ film, and 8x10@super 13@cm@super -2@ at the SiO@sub 2@/Si interface. Binding energy of N 1s at the SiO@sub 2@ surface and in the SiO@sub 2@ film was shifted 2eV-higher than that at the SiO@sub 2@/Si interface. By 750°C nitridation, the N atom concentration on the SiO@sub 2@ surface was 3x10@super 14@ cm@super -2@ and, in the SiO@sub 2@ film and at the SiO@sub 2@/Si interface, the N atom concentration was less than the detection limit (about 3x10@super 20@cm@super -3@ and 4x10@super 12@cm@super -2@, respectively). This result indicates that the existence of surface oxygen more greatly suppresses the reaction of NH@sub 3@ at the lower temperature. Pressure and time dependence of nitridation on the SiO@sub 2@ surface, in the SiO@sub 2@ and at the SiO@sub 2@/Si interface will be also presented.

#### 9:40am SC1+EL+SS-MoM5 Probing the Chemistry of Dielectric Thin Film Growth on Si Surfaces, L.D. Flores, J.E. Crowell, University of California, San Diego INVITED

The surface and gas phase chemistry involved during dielectric thin film growth of doped and undoped silicon dioxide has been studied using the atmospheric pressure reaction between tetraethoxysilane (TEOS) and ozone. The studies involve low temperature deposition of dielectric thin films using a new atmospheric-pressure chemical vapor deposition (APCVD) reactor utilizing a commercial injector / vent assembly. The APCVD reactor is coupled to a N@sub 2@-purged glovebox and a UHV surface analysis facility equipped with XPS, AES, TPD, and IR spectroscopy capabilities. Gasphase transmission FTIR spectroscopy measurements were performed insitu during deposition at 400°C by probing the variable gap region between the 400°C heated Si wafer and the injector. The primary products produced upon reaction of TEOS and ozone are acetic acid, formic acid, formaldehyde, carbon monoxide, carbon dioxide, and water. Reaction of TEOS and oxygen in the gas phase is negligible compared to reactions involving ozone at identical temperatures under these conditions. Potential TEOS / O@sub 3@ reaction products and their reaction with boron and phosphorus containing dopant sources has been investigated in order to clarify their role in the oxidation process and to clarify the chemical mechanism. This was accomplished by following the reaction with ozone of some possible and observed ozonation products in a flow reactor / gas cell using transmission FTIR spectroscopy. The products of acetaldehyde ozonation are shown to be different from pathways leading to acetic acid production during TEOS ozonation. Mechanistic pathways unique to Si-O-C containing species will be presented. The products formed upon introduction of boron and/or phosphorus containing precursors to the process flow will also be discussed.

#### 10:20am SC1+EL+SS-MoM7 Thickness Control of an Ultrathin Oxide Film on Si(100)2x1 Synthesized by Ozone: A Kinetic Study on Initial Oxidation, *K. Nakamura, A. Kurokawa, H. Itoh, S. Ichimura,* Electrotechnical Laboratory, Japan

One of the alternative oxidants for the fabrication of an ultrathin silicon oxide film is ozone. Using highly concentrated ozone, we have succeeded so far in synthesizing an oxide film of 2nm on Si(100) at lower substrate temperature (for example, at 350°C). This oxide film has high density equivalent to that of a thermally grown oxide, much smaller thickness of

## Monday Morning, October 2, 2000

structural transition layers, and can be obtained also by modifying and upgrading an already existing native oxide film.@footnote 1,2@ Moreover, the oxide thickness must be precisely and accurately controlled because of its practical use as a gate oxide film in MOSFET. In this paper, therefore, we will study growth kinetics of initial oxidation by ozone on silicon surfaces in detail. To fabricate an ultrathin silicon oxide film by ozone, clean Si(100)2x1 surfaces at between room temperature and 700°C were exposed to highly concentrated (>80%) ozone. Initial oxide growth was mainly monitored by x-ray photoelectron spectroscopy (XPS). The results indicate different kinetics on each oxide layer. Following to an adsorption on the surface investigated also by second harmonic generation (SHG), oxide growth on each of the first three oxide layers proceeded in accordance with Langmuir kinetics, indicating random adsorption on the active sites on each layer. Within this thickness, oxidation rates on the second and third layers possessed positive values of activation energy, while the growth rate on the first layer showed no activation barrier. Above this thickness, an oxide film by ozone grew in proportion to exposure time instead above the critical substrate temperature of 550°C. These suggest that control of film thickness should be optimized in the first three layers and above the fourth, respectively, due to different growth mechanisms. @FootnoteText@ @footnote 1@ K. Nakamura, S. Ichimura, A. Kurokawa, K. Koike, G. Inoue, and T. Fukuda, J. Vac. Sci. Technol. A 17 (1999) 1275. @footnote 2@ A. Kurokawa, K. Nakamura, S. Ichimura, and D. W. Moon, Appl. Phys. Lett. 76 (2000) 493.

10:40am SC1+EL+SS-MoM8 FTIR at Liquid/Solid Interfaces: In-situ Studies of HF Etching of SiO@sub 2@ on Si(100), *K.T. Queeney*, Smith College Department of Chemistry; *E.E. Chaban, Y.J. Chabal*, Bell Laboratories, Lucent Technologies

While much important semiconductor surface chemistry--cleaning, passivating and etching--takes place at the liquid/solid interface, the inherent difficulty of probing such interfaces has limited mechanistic understanding of these processes. We have developed a novel experimental setup that allows us to probe semiconductor/liquid interfaces with FTIR spectroscopy, circumventing the limitations of conventional multiple internal reflection spectroscopy to access the full frequency range of interest (850-4000 cm@super -1@), in particular the Si-O vibrational modes between 900 and 1250 cm@super -1@. We have used this capability to study in detail the etching in dilute hydrofluoric acid of SiO@sub 2@ on Si(100), lending new and valuable insight into the details not only of the chemical nature of the Si/SiO@sub 2@ interface, but also of structural aspects of the remainder of the film, including the SiO@sub 2@/air (water) interface. By analyzing spectra acquired sequentially during the etching process, we derive a layer-by-layer picture of the oxide spectral response; correlation of those spectra with changes in film structure are made via optical modeling. Varying the dielectric constant of the overlying medium (i.e. air versus water) allows quantification of spectral sensitivity to effects such as surface roughness. In addition, the in-situ nature of these studies allows us to evaluate the kinetics of the etching process and provides strong evidence for a structurally distinct layer near the Si(100) substrate, characterized by a marked change in vibrational signature, that is resistant to etching

### **Author Index**

#### - C --Chabal, Y.J.: SC1+EL+SS-MoM2, 1; SC1+EL+SS-MoM8, 2 Chaban, E.E.: SC1+EL+SS-MoM8, 2 Crowell, J.E.: SC1+EL+SS-MoM5, 1 - F --Flores, L.D.: SC1+EL+SS-MoM5, 1 - I --Ichimura, S.: SC1+EL+SS-MoM7, 1 Itoh, H.: SC1+EL+SS-MoM7, 1 - J --

Jintsugawa, O.: SC1+EL+SS-MoM4, 1

Bold page numbers indicate presenter

K –
Kurokawa, A.: SC1+EL+SS-MoM7, 1
M –
Matsuura, T.: SC1+EL+SS-MoM1, 1; SC1+EL+SS-MoM4, 1
Murota, J.: SC1+EL+SS-MoM1, 1; SC1+EL+SS-MoM4, 1
Musgrave, C.B.: SC1+EL+SS-MoM3, 1
N –
Nakamura, K.: SC1+EL+SS-MoM7, 1  Q - Queeney, K.T.: SC1+EL+SS-MoM2, 1; SC1+EL+SS-MoM8, 2
 R - Raghavachari, K.: SC1+EL+SS-MoM2, 1
 - S - Sakuraba, M.: SC1+EL+SS-MoM1, 1; SC1+EL+SS-MoM4, 1
 - W - Watanabe, T.: SC1+EL+SS-MoM1, 1
 Widjaja, Y.: SC1+EL+SS-MoM3, 1