Thursday Morning, October 5, 2000

Dielectrics

Room 312 - Session DI+EL+MS-ThM

Ultrathin Dielectrics and Interfaces

Moderator: Y.J. Chabal, Bell Laboratories, Lucent Technologies

8:20am DI+EL+MS-ThM1 Oxidation of Clean and H-passivated Silicon by Molecular and Atomic Oxygen, X. Zhang, Rutgers University; Y.J. Chabal, Bell Laboratories, Lucent Technologies; E. Garfunkel, Rutgers University; S.B. Christman, E.E. Chaban, Bell Laboratories, Lucent Technologies

The need for uniform and ultra-thin silicon oxides in microelectronics requires a fundamental understanding of the initial oxidation of both clean and H-passivated (HF-etched) silicon in oxygen. We have undertaken a systematic infrared absorption study of molecular O@sub 2@ and atomic O oxidation of H-passivated flat and vicinal Si(111) and Si(100) surfaces. Using an IR transmission geometry for full access to Si-O stretch (900-1250 cm@super -1@) and Si-H bending (600-850 cm@super -1@) modes, we can directly observe the incorporation of oxygen even after H-desorption under ultra-high vacuum conditions. Furthermore, hydrogen at steps can be spectrally distinguished from H on terraces, thus making it possible to correlate the kinetics of H elimination with oxide formation as a function of surface structure. We find that upon 1 Torr exposure at 300@super o@C, the bonding of step hydrogen is preferentially altered on the H/Si(111) surface, with dihydride steps being the most reactive. Yet, the rate of oxidation does not scale with the step density, indicating that direct oxidation of terraces takes place simultaneously. For the Si(100) surface, we contrast the oxidation of the HF-etched (atomically rough surface) with that of the smooth H-Si(100)-(2x1) surface prepared in HHV and that of the clean Si(100)- (2x1) surface in order to extract the mechanism for molecular O@sub 2@ dissociation.

8:40am DI+EL+MS-ThM2 New Oxidation Process Using Collimated Hyperthermal Ozone Beam, T. Nishiguchi, Y. Morikawa, M. Miyamoto, Meidensha Corporation, Japan; H. Nonaka, A. Kurokawa, S. Ichimura, Electrotechnical Laboratory, Japan

As the electronic devices are scaled down, using more reactive process gas than molecular oxygen is required to fabricate an ultra-thin highly reliable Si dioxide film for the gate oxide in MOSFET. We used ozone as an oxidant gas and achieved the enhanced initial oxidation rate, resulting in lower temperature oxidation process. In our experiments using highly concentrated ozone gas, more than 3nm Si dioxide film was obtained within 30 minutes under the conditions of 873K of Si temperature and 10Pa of ozone pressure, where the oxidation hardly proceeds by molecular oxygen. In the present study, we carried out the laser ablation of solid ozone in order to obtain collimated ozone beam on the purpose of applying ozone beam to new oxidation processes such as local oxidation of patterned Si surface (e.g. oxidation of a bottom part of a trench). We irradiated a KrF pulsed excimer laser light to highly concentrated solidified ozone that was adsorbed on the sapphire plate cooled down to 30-60K by cryocooler in an UHV chamber. We could obtain collimated ozone beam (within 20° spread) whose supply (typically 10@super 16@ molecules per laser pulse), concentration (typically 70%) and translational energy (3eV maximum) were controlled through the laser ablation conditions such as the laser fluence. Not only the local oxidation but also even lower temperature process is expected using this high-translational-energy (hyperthermal) ozone beam. We will demonstrate the initial oxidation profile for the first 1000 laser shots by Auger Electron Spectroscopy and discuss the applicability of this ozone beam to the semiconductor process.

9:00am DI+EL+MS-ThM3 Nondestructive Investigation of the Si/SiO2 Interface by Spectroscopic Ellipsometry, Reflectance Difference Spectroscopy, Second Harmonic Generation, and X-ray Photoelectron Spectroscopy, J.F.T. Wang, J.W. Keister, Y.M. Lee, G. Lucovsky, J.E. Rowe, D.E. Aspnes, North Carolina State University

We report results of a systematic study with various nondestructive techniques of buried interfaces between Si and thin gate oxides thermally grown at 700C and rapid-thermal-annealed at temperatures to 900C. The objectives are to understand the optical properties, the step structure, and the nature of the chemical bonding of the interface and to determine the limits to which the various nondestructive probes, alone and in combination, can provide this information. We examine in particular data obtained as a function of heat treatment and surface orientation (miscuts 2, 4, 8, 10 degrees off (001) toward the nearest (111); (113); (111); and (110)), with emphasis on the vicinal (001) orientations. The RD spectra of

all as-oxidized vicinal (001) samples decrease by nearly a factor of 5 for the 900C RTA, indicating step-density reduction and a net smoothing of the interface. Except for the 2 deg sample, which shows basically no signal, these spectra become essentially identical to the spectra of chemically etched, H-terminated vicinal (001) surfaces. All such spectra have the appearance of RD lineshapes obtained on (113) surfaces, which are nominally dominated by double-height steps. The ellipsometric data differ mainly in overlayer thickness, but interface information can be extracted through least-squares analysis assuming interface spectra of Si in amorphous and +1 and +2 charge states. To assist in this analysis we orthogonalize the fitting parameters to determine which combinations are best determined by the data. The results indicate that the best reference data are those obtained on H-terminated (111) surfaces. The interface XPS spectra become much more consistent after rapid thermal annealing, with the (001) and (111) spectra being dominated by Si in +2 and +1 charge states, respectively, as expected. This provides further evidence of a reduction in roughness with annealing.

9:20am DI+EL+MS-ThM4 Core-level Photoemission of Interface States on SiO@sub 2@/Si: Substrate Orientation Effects, *J.E. Rowe*, Army Research Office; *J.W. Keister, J.F.T. Wang*, North Carolina State University; *G.J. Jackson, T.E. Madey*, Rutgers University; *D.E. Aspnes*, North Carolina State University

High resolution soft X-ray photoelectron spectroscopy (SXPS) with synchrotron radiation is used to study the interface of mis-cut SiO@sub 2@/Si(100) [i.e. stepped interface] of device quality ultrathin gate oxides. Our studies were performed on thin oxides grown by thermal oxidation in pure O@sub 2@ at a temperature of 600@degree@C and pressure of ~760 Torr. Our data can be well described by five different Si species due to Si in different oxidation states which are usually labeled Si@super 0@, Si@super +1@, Si@super +2@, Si@super +3@, and Si@super +4@. We have studied a number of samples prepared as described above and find that the energies relative to the SiO peak are 0.95 eV, 1.80 eV, 2.50 eV, and 4.00 eV for the Si@super +1@, Si@super +2@, Si@super +3@, and Si@super +4@ peaks respectively. For this study, we define the transition region as the region containing Si in intermediate oxidation states (Si@super +1@, Si@super +2@, Si@super +3@). We find a transitionregion Si suboxide concentration of 1.3 x 10@super 15@ cm@super -2@ assuming an escape depth of ~7 @Ao@ at a photon energy of 200 eV for samples annealed after growth at temperatures of ~900 @degree@C . This transition region is that in excess of the density ~1 monolayer of Si@super +1@ expected for the most abrupt SiO@sub 2@/Si(111) interface in terms of the Si(111) layer density of 7.8 x 10@super 14@ cm@super -2@. The I@sub 1@ interface peak is largest for (111) and decreases substantially for (113), (110), and for stepped (100) substrates. The total interface density appears to be lowest for Si(100) with a modest step density introduced by a 2@degree@ mis-cut. The step-dependent behavior is consistent with that reported using second harmonic generation. The total concentration of suboxide derived from SXPS data is dependent on the uniformity of SiO@sub 2@ films as well as data modeling, i.e., fitting of the data; both will be discussed.

9:40am DI+EL+MS-ThM5 Spectroscopic and Electrical Characterization of the Evolution of Chemical Oxides Into Ultrathin Gate Oxides, J. Eng, Jr., R.L. Opila, J.M. Rosamilia, J. Sapjeta, Y.J. Chabal, B.E. Weir, P. Silverman, T. Boone, R.L. Masaitis, T. Sorsch, M.L. Green, Bell Labs, Lucent Technologies The goal of this study is to understand how the structure of wet chemical oxides change during oxidation, and to determine whether the quality of ultrathin oxides is sensitive to the type of of wet chemical treatments. Four wet chemical treatments were examined: 1. standard RCA, with an SC1 step (ammonium hydroxide and peroxide) followed by an SC2 step (hydrochloric acid and peroxide), 2. modified RCA, with an HF etch between the SC1 and SC2, 3. ozonated water, and 4. HF. X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy (IR) have been used to probe the structure and composition of the wet chemical oxides. IR probes the long range order in the films, while XPS probes the local Si stoichiometry. Both techniques show that the ozone oxide has the highest quality. Despite large differences in the initial quality of the wet chemical oxides, rapid thermal oxidation of the chemical oxides produces oxide films that are spectroscopically similar. Electrical properties of the oxides will correlated with the spectroscopic studies.

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10:00am DI+EL+MS-ThM6 Studies on Accurate Determination of the Physical Thickness of nm Gate Oxides and its Correlation with the Electric Thickness, *D.W. Moon, H.K. Kim, H.J. Lee, H.M. Jo*, Korea Research Institute of Standards and Science, Korea; *H.S. Jang, H. Hwang,* Kwangju Institute of Science and Technology, Korea

Accurate Determination of nm gate oxides is critical for the development of nanoelectronic devices as well as for CMOS device scaling beyond 100 nm. In semiconductor industries, the thickness of gate oxides has been measured by ellipsometry. However, the accuracy has been not evaluated especially for gate oxides thinner than 10 nm. Recently, TEM and spectrometric ellipsometry(SE) have been used to measure the physical thickness of nm gate oxides and the electric methods such as I-V an C-V have been modified to include quantum effects. In this work, to estimate the uncertainty and improve the accuracy of the methods used for gate oxides thickness determination, TEM, SE and Medium Energy Ion Scattering Spectroscopy(MEIS) were used to determined the physical thickness of 6 gate oxides from 9 nm thick to 1.5 nm native oxide thick. MEIS can analyze the composition and structure of ultrathin films with atomic layer depth resolution. It was investigated that MEIS can be a reference for gate oxide thickness determination down to 1-2 nm. The difference of the physical thickness determined with TEM, SE and MEIS were discussed and compared with the electric thickness determined by I-V and C-V methods. For the gate oxides studied, the thickness determined by the Si MEIS peak was 1.5 nm thicker than that by the O MEIS peak. The thickness determined by SE and TEM was between the two values, while SE gave ~0.5 nm higher thickness than TEM. However, with the interlayer thickness, TEM thickness approached that of Si MEIS peak thickness. The electric thickness determined with I-V and C-V was close to that of Si MEIS peak thickness within 0.2nm. The thickness by SE is quite sensitive to the refractive index value used for fitting, especially for gate oxides thinner than 5nm. Based on this multi-disciplinary approach, it will be discussed how to provide standards for nm gate oxides approaching the limit of CMOS and how to transfer the standards to SE which is widely used in semiconductor process lines.

10:20am DI+EL+MS-ThM7 Bonding of Nitrogen in Silicon Oxynitride Films, *R.L. Opila*, J. Eng, Jr., Y.J. Chabal, K.T. Queeney, Bell Laboratories, Lucent Technologies; J.P. Chang, University of California, Los Angeles

Silicon oxynitride is a promising candidate to replace silicon dioxide in the next generation of microelectronic devices, but key aspects of the nitrogen chemistry in this material remain unresolved. This talk describes a twofold approach for understanding nitrogen bonding in these materials. The first approach employs surface analytical techniques, including photoelectron spectroscopy, infrared spectroscopy and near edge x-ray absorption fine structure, to study how oynitride precursors, suchas as nitric acid, nitromethane, and ammonia, react with silicon surfaces. The second approach uses the previous analytical techniques, along with electron spin resonance spectroscopy, to compare the nitrogen bonding states in silicon oxynitride and silicon nitride films prepared by thermal growth and ion implantation. Significant differences in the distribution of nitrogen bonding states and point defects are observed and correlated with the method of film preparation.

10:40am DI+EL+MS-ThM8 Photoemission Investigation of Nitrogen Incorporation at the Si/SiO@sub 2@ Interface, J.E. Rowe, Army Research Office; J.W. Keister, North Carolina State University

Monolayer incorporation of nitrogen at the Si/SiO@sub 2@ interface enhances the reliability and electrical characteristics of this nearly perfect interface for ultrathin SiO2 layers.@footnote 1@ In this paper we demonstrate that the Si(100)/SiO@sub 2@ interface is chemically sensitive to the nitrogen concentration. The nitrogen (1s) Soft X-ray Photoemission Spectroscopy (SXPS) peak was measured for varying degrees of N incorporation using the Advanced Light Source synchrotron at LBL National Lab. The broad width of the N(1s) SXPS peak lineshape is consistent with a large degree of final-state, Gaussian phonon broadening, and is comparable to O(1s) line. However, unlike the O(1s) line which is not especially chemically sensitive, the N(1s) line shows a clearly measureable, interface peak shift@footnote 2@ with increasing N incorporation. The average interface peak binding energy is ~0.75 eV greater than that recently reported for thick "bulk" films of Si3N4 with Al-K" XPS. To a lesser degree, the peak shape is seen to change as well. In particular, the peak width minimizes near to the value ~1.0 ML N incorporation, which is also the level at which devices interfaces perform best electrically. @FootnoteText@ @footnote 1@ G. Lucovsky, A. Banerjee, B. Hinds, B. Claflin, K. Koh, H. Yang. J. Vac. Sci Technol. B 15(4) 1074-1079 (1997).

@footnote 2@ J. W. Keister, J. E. Rowe, J. J. Kolodziej, H. Niimi, H.-S. Tao, T. E. Madey, G. Lucovsky. J. Vac. Sci Technol. A 17(4) 1250-1257 (1999).

11:00am DI+EL+MS-ThM9 Investigation of Fluorine in Dry Ultrathin Silicon Oxides, *G. Vereecke*, *E. Röhr, R.J. Carter, T. Conard, H. Dewitte, M.M. Heyns*, IMEC, Belgium

As critical dimensions of integrated circuits continue to decrease, insulators with dielectric constants higher than silicon dioxide will be introduced in capacitors and transistors. However an ultrathin (< 1 nm) silicon oxide layer will generally be needed at the interface between Si and high-k layers. In cluster tools integrating surface preparation and dielectric deposition, vapor HF chemistries are envisaged to etch the native oxide prior to oxide growth. This HF etch leaves F on the surface of the Si wafer, which gets incorporated into the growing oxide. In addition, the silicon subsurface has also been proposed as a source of the F found in these oxides. The presence of F may be beneficial or detrimental for the properties of these layers depending on application, F location, and layer thickness. We have evaluated the sources of F in ultrathin oxides grown by UV/O2 at room temperature in an experimental vapor phase cleaning tool. Surface pretreatment was either by in-situ HF/methanol vapor process or by ex-situ wet HF dip followed by a DIW rinse. Evidence was found for F crosscontamination from the tool gaspanel when the HF etch step was performed in-situ. After correcting for this, F atomic concentrations in oxides grown on vapour HF and wet HF treated surfaces were of about 5 % and 2 %, respectively. The former would lower the dielectric constant of the layer if homogeneously distributed. The level of F contributed by the subsurface was estimated with oxides grown on wet HF treated surfaces in a specially built quartz chamber with no F contamination. No F was detected in these oxides, which indicates that the level of subsurface F is lower than previously reported. Ultrathin oxides continued to grow when exposed to air. This raises concern about their stability during the deposition and annealing of high-k layers. XPS results suggest that this is related to the exchange of labile F groups in the films.

11:20am DI+EL+MS-ThM10 Studies on Electrical Properties of Ultrathin Oxides of Silicon Grown by Wet Oxidation at Low Water Vapor Pressure, *V.K. Bhat, K.N. Bhat, A. Subrahmanyam*, Indian Institute of Technology, India

The rapid downscaling of the device dimension has increased the interest in the ultrathin (< 5 nm) oxides of silicon. Ultrathin oxides with thickness uniformity and good electrical properties are required for the silicon submicron devices. In general, the dry oxidation is being followed to grow these ultarthin oxides. Wet oxidation is not considered for the growth of ultrathin oxides of silicon because of the following reasons: i) high growth rate associated with the conventional wet oxidation at 1 atm. water vapor pressure and ii) large density of electron trapping centres present in the wet oxide. In the present study we report the results on the electrical properties of ultrathin oxides of silicon grown by wet oxidation at low (0.04 atm.) water vapor pressure. Ultrathin oxide of silicon is grown at 900°C on n-type single crystal silicon, single side polished. (100) oriented and having 1-10 @ohm@ cm resistivity (procured from M/s Wacker GmbH, Germany). The grown ultrathin oxides are characterized for their electrical properties by fabricating MOS tunnel diodes (aluminum is thermally evaported with a metal mask on to the ultrathin oxide). The capacitance-voltage (C-V), conductance-voltage (G-V) and current-voltage (I-V) charcteristics of the MOS tunnel diodes are studied. The interafce state density (D@sub it@) and the density of the fixed oxide charge (Q@sub f@) are being calculated. The grown ultrathin oxide thickness is estimated from the measured C-V characteristics and are in the range 2.5-5.0 nm. The oxide growth rate is found to be linear. The charge trapping characteristics of the ultrathin oxides are studied by using consatnt current stress (CCS) technique. The decrease in the gate voltage is observed with the stress time. This observation may be attributed to the positive charge trapping in the oxide during the CCS. The charge trapping is found to be oxide thickness dependent and it decreases with the decrase in the oxide thickness.

11:40am DI+EL+MS-ThM11 Properties of SiO@sub 2@ Thin Films Deposited at Low Temperature on SiGe and Si Samples in O@sub 2@/TEOS Helicon Plasmas, A. Goullet, D. Goghero, V. Fernandez, A. Granier, Institut des Matériaux Jean Rouxel, France; F. Meyer, Université de Paris XI, France; G. Turban, Institut des Matériaux Jean Rouxel, France Silicon dioxide thin films are deposited at low pressure (< 5mTorr) and temperature (<200° C) on Si@sub 1-x@Ge@sub x@ epi-layers and silicon substrates in oxygen rich O@sub 2@/TEOS helicon plasmas. The growth of SiO@sub 2@ films and the evolution of the interfacial layer under applied radio frequency bias voltage (0, -100, -200 V) are investigated using a UV-

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Visible phase modulated ellipsometer (1.5-5 eV). The structural properties of the films are studied using infrared transmission spectroscopy, wet chemical etching and spectroscopic ellipsometry. Very thin (<10 nm) SiO@sub 2@ films deposited in the same conditions are investigated by Xray photoelectron spectroscopy and spectroscopic ellipsometry to gain better insight of the oxide/semiconductor interface. The ion energy is found to be a significant parameter both for film properties and deposition rate. Use of radio frequency bias is effective in producing high quality SiO@sub 2@ films but an amorphized transition layer is detected in this case as evidenced by ellipsometric data modeling. The increase in the ion energy is also responsible for the presence of an additional oxidation state which appears on the Ge 3d XPS peak. Complementary capacitive C(V) measurements of grown oxides have been performed using metal-oxidesemiconductor samples. An increase in the fixed oxide charge and interface state densities as a function of the applied bias voltage is observed for silicon substrates whereas the electrical properties of the films deposited on Si@sub 1-x@Ge@sub x@ are rather insensitive to the deposition conditions.

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