Material Characterization
Room Exhibit Hall C & D - Session MC-TuP
Poster Session

MC-TuP1 Quantitative Detection and Mapping of SiOH Groups on Si using Chemically Labeled TOF-SIMS Method*, T. Mitsuoka,* *M. Ikai, T. Ohwaki, Y. Taga,* TOYOTA Central Research and Development Laboratories Inc., Japan

This paper first demonstrates an accurate quantitative detection and mapping of SiOH by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) combined with phenyldimethylchlorosilane (PDMCS) treatment to detect the amount of SiOH on a Si wafer. We found that we can detect the quantity of SiOH on a Si wafer without the influence of adsorbed water by the labeled TOF-SIMS method. Furthermore, we could map the 2D distribution of SiOH on the Si surface. The quantitative analysis of SiOH by TOF-SIMS was confirmed as follows. H and OH terminated surfaces were prepared by dipping a Si wafer into hydrofluoric acid (HF) solution and H@sub 2@O@sub 2@:H@sub 2@SO@sub 4@=4:1 solution, respectively. Contact angles of the SiOH surface became smaller with dipping time in deionized water. Surface chemical characteristics and adhesion force of the surfaces thus treated were examined by attenuated total refraction (ATR) of IR and Atomic Force Microscopy (AFM). The yields of characteristic ions (C@sub 6@H@sub 5@Si@super +@, C@sub 6@H@sub 5@(CH@sub 3@)@sub 2@Si@super +@)emitted from the labeled SiOH surfaces were compared with the data of contact angles, ATR and AFM. There was a good correlation between the amount of these fragment ions and contact angles. In conclusion, quantitative detection and mapping of SiOH groups on Si were demonstrated by the sophisticated labeled TOF-SIMS method.

MC-TuP2 Secondary Ion Emission from Well Defined Molecular Overlayers Under Molecular Primary Ion Bombardment*, D. Stapel,* *A. Benninghoven,* University of Muenster, Germany

Molecular primary ions have been shown to enhance the yield Y(X@sub i@@super q@) of organic secondary ions considerably. The simultaneous increase in the corresponding damage cross section @sigma@(X@sub i@@super q@) is much smaller. This holds in particular for thick molecular samples like LB multilayers or polymers. For LB multilayers we found yield increases up to a factor of 1000, when changing from Ar@super +@ to SF@sub 5@@super +@ bombardment. This phenomenon is important for practical analytical applications of TOF-SIMS, because yields, damage cross sections, and the resulting ion formation efficiencies E=Y/@sigma@ determine the achievable sensitivity as well as the achievable lateral resolution. In recent years we have investigated in some detail this secondary ion emission behavior for a variety of LB layers under atomic and molecular primary ion bombardment. Basic studies were performed with three series of LB layers (n = 1, 3, 5, 7, 9; n : number of monolayers) under 0.5 - 11 keV Ne@super +@, Ar@super +@, Xe@super +@, O@sub 2@@super +@, CO@sub 2@@super +@, SF@sub 5@@super +@, C@sub 7@H@sub 7@@super +@, C@sub 10@H@sub 8@@super +@, C@sub 6@F@sub 6@@super +@ and C@sub 10@F@sub 8@@super +@ bombardment. Y(X@sub i@@super q@) as well as @sigma@(X@sub i@@super q@) were determined. We found a more pronounced Y and E enhancement for multilayers (n>1). Y, @sigma@ and E increases with increasing mass of atomic primary ions and with growing number of constituents up to 6 heavy atoms. Y, @sigma@ and E features a saturation behaviour for molecular primary ion species containing more than 6 atoms. We could not find an influence of the chemical composition of the primary ion on this enhancement under static SIMS conditions. We found that the molecular secondary ions are emitted from the 1@super st@ and 2@super nd@ layer and a pronounced decrease in Y and E was determined for 1 keV SF@sub 5@@super +@ bombardment.

MC-TuP3 A SIMS Study on the Negative Boron Cluster Secondary Ion Yield Change in Boron Implanted Silicon*, S. Hayashi,* Nippon Steel Corporation, Japan*; Y. Okamoto,* SHARP Corporation, Japan*; F. Toujou,* Matsushita Technoresearch Inc., Japan*; Y. Homma,* NTT Basic Research Laboratories, Japan

To establish standard protocols in depth profiling, the linearity of the ion intensity using the ion-implanted silicon specimens with a variety of ion dose have been investigated. In these round-robin test, we have been studying secondary ion emission mechanism and found the irregularity of the production of negative boron cluster in boron implanted silicon specimens. These phenomena have been reported only the positive secondary ion emission in the high dose specimen.@footnote 1@ In this study we applied the boron implanted silicon wafer to quantify the amounts of boron in silicon with a wide concentration range. Cs@super +@ ion beam was used to detect negatively charged boron cluster ion signals, ie, B@super -@, B@sub 2@@super -@, B@sub 3@@super -@ ,etc.. The dependency of negative secondary ion yields on a variety of ion doses was estimated in order to compare with the detection of boron cluster ion counts. The higher dose of boron was implanted into silicon, the larger production efficiency of boron cluster ion was. Especially, the efficiency of B@sub 2@@super -@ exceeded the one of boron atomic ion in the high dose, 1x10@super 17@ions/cm@super 2@ specimen which was implanted B@super +@ with 50keV as an accelerating voltage. Such an enhancement of negative dimer ion emission yield cannot be explained on the basis of the recombination mechanism because B@sub 2@@super -@ yield is larger than the B@super -@ ion yield. The emission mechanism of boron negative cluster ion will be discussed, comparing with the dependence of the boron negative cluster ion yields on the implanted doses, the shape of the implanted depth profile, and boron positive secondary ion emission. @FootnoteText@ @footnote 1@M. Tomita, F. Takahashi and Y. Homma, Nucl. Instrum. Methods Phys. Res., B85(1994), 399.

MC-TuP4 Fabrication and Characterization of Boron-Doped Silicon Thin Film as a Reference Material for Secondary Ion Mass Spectrometry Quantification*, K.J. Kim,* *D.W. Moon, H.K. Kim,* Korea Research Institute of Standards and Science, Korea*; C.J. Park,* Korea Research Institute of Standards and Science

Secondary ion mass spectrometry(SIMS) is one of the most powerful techniques for the determination of the concentration of minor impurities in solid materials. Ion implanted reference materials are generally used for the quantification of impurities by SIMS. In this study, we will present a new type of reference material for the quantification of minor impurities by SIMS. Uniformly-doped silicon thin films with three levels of boron concentrations were fabricated by ion beam sputter deposition. A Si target with a small BN was sputter deposited simultaneously on a Si(100) and a polyester substrate by 1 keV Ar ion beam. The boron concentration was determined by inductively coupled plasma mass spectrometry (ICP-MS) using the isotope dilution method. The boron concentration measured by ICP-MS was compared with that by SIMS using a boron ion implanted standard reference material.

MC-TuP5 Development of Secondary Ion Mass Spectrometry Methodology for the Film Thickness Measurement of Sub-2nm SiO@sub 2@ Interlayers, *C.M. Jones,* ***J. Zhao,*** Advanced Micro Devices

Film thickness of interfacial SiO@sub 2@ in poly-emitter devices and thickness of gate oxide in transistors is crucial to device performance and speed. The thickness regimes (0-1nm and 1.5-2.5 nm, respectively) are too thin to allow for accurate measurement by electron microscopic techniques. In the present work, we report the development of secondary ion mass spectrometry (SIMS) methodology for the film thickness measurement of sub-2nm SiO@sub 2@ interlayers. The SiO@sub 2@ interlayer structure is polycrystalline Si / SiO@sub 2@ / Si substrate. The polycrystalline Si layer can be up to a few hundred nano-meters thick. The sample is analyzed by SIMS and a concentration depth profile of oxygen is acquired. High-energy Cs bombardment is used, so that the thin SiO@sub 2@ layer is diluted by ion beam mixing. A 14.5 kV net impact energy provides sufficient mixing to change the composition of the interface from that of stoichiometric SiO@sub 2@ to Si with a high dose of oxygen. The areal density of the interfacial oxygen peak may be calibrated against a SIMS oxygen ion implant standard with a precision of better than 3%. The SiO@sub 2@ thickness is then calculated with equal precision, using the formula derived. A statistical measurement of the same sample over a period of several weeks demonstrated a superior reproducibility.

MC-TuP6 Analysis of Delta Multilayer Profiles Measured by Secondary Ion Mass Spectrometry*, A. Takano,* *Y. Higashi,* NTT Advance Technology Corporation, Japan*; Y. Homma,* NTT Basic Research Laboratories, Japan*; J. Kikuma, S. Soga, Y. Okamoto, R. Oishi, S. Hayashi, R. Saito, M. Tomita, Y. Ueki, S. Seo, F. Toujou, S. Yoshikawa, J. Kinoshita,* SIMS-Depth Profiling WG, Japan*; D.W. Moon,* Korea Research Institute of Standards and Science, Korea

Delta-doped multilayers are potential reference materials for the evaluation of depth resolution in secondary ion mass spectrometry (SIMS). For this purpose establishing standard procedures of depth resolution evaluation is necessary, as well as developing reliable delta multilayers. We tested a theoretical model, mixing-roughness-information depth (MRI) model@footnote 1@ for extracting depth resolution parameters from the measured profiles in the round-robin study using a delta-multilayer specimen that includes five GaAs-doped delta layers separated by amorphous Si layers. The measured arsenic profiles were analyzed using the MRI model. For SIMS, information depth in the model can be regarded to be very small, so we used the only two parameters concerning mixing and roughness. The mixing parameters showed very little in-depth variation but dependence only on primary-ion energy and impact angle, irrespective of the instrument types used. This means that the mixing parameter may be regarded as a physical quantity. The roughness parameter and its in-depth dependence, on the other hand, varied among participating laboratories, reflecting the measurement conditions and surface roughening. @FootnoteText@ @footnote 1@ S. Hofmann, Surf. Interface Anal. 21 (1994) 673

MC-TuP7 Comparison of Improved Spreading Resistance Profiling and Secondary Ion Mass Spectrometry in the Characterization of Ion Implanted Dopant Profiles*, **L.C.P. Tan**,* The National University of Singapore, Republic of Singapore*; L.S. Tan, M.S. Leong,* The National University of Singapore*; C.W. Lee,* ST Microelectronics Ltd.

Spreading resistance profiling (SRP) is a well-established technique for the determination of dopant profiles in silicon wafers. The dopant profile can then be recovered from the spreading resistance profile by using an iterative algorithm. It has been noticed that for certain dopant profiles, especially shallow ion implanted profiles, the junction depth determined from SRP often do not agree with those predicted by process simulators such as SUPREM3. In addition, the sheet resistance as measured using four-point probes is also sometimes different from that deduced from dopant profiles recovered by SRP. The discrepancy may arise if the algorithm used to convert the spreading resistance profile into the dopant profile does not take into an account a phenomenon known as the carrier redistribution effect. In this work, we describe the results of a set of experiments carried out to compare the dopant profiles obtained from SRP and secondary ions mass spectrometry (SIMS) as well as those predicted by SUPREM3. SRP is an electrical characterization technique that responds to the presence of electrons and holes. The p-n junction indicated by the spreading resistance profile is the electrical junction, where the electron concentration is equal to the hole concentration. SIMS, on the other hand, is a physical characterization technique that measures the profile of dopant atoms, and the junction obtained by SIMS is the metallurgical junction where the donor concentration is equal to the acceptor concentration. The electrical junction and the metallurgical junction do not necessarily coincide because of the carrier redistribution effect, especially in shallow ion implanted profiles. However, we shall show that by using a new algorithm that correctly models the carrier redistribution effect, the disagreement in the dopant profiles obtained by SRP, SIMS and SUPREM3 can be significantly reduced.

MC-TuP8 Characterization of Si Distribution at the Tungsten / Titanium Nitride Interface Using Secondary Ion Mass Spectrometry - An Investigation of the Dynamic Response of a Chemical Vapor Deposition Chamber*, **C.M. Jones**, J. Zhao,* Advanced Micro Devices

In sub-micron MOS IC processing, tungsten lines or contact (via) plugs are formed by blanket chemical vapor deposited tungsten thin film fill into the narrow SiO@sub 2@ trenches or small contact openings on the titanium nitride (TiN) layer with the underlying structure. The blanket CVD tungsten thin film is typically accomplished as the following: a thin nucleation layer (~50nm) is grown by silane (SiH@sub 4@) reduction of tungsten hexafluoride (WF@sub 6@), and the bulk deposition is accomplished via hydrogen (H@sub 2@) reduction of WF@sub 6@. The TiN layer serves as an adhesion layer that promotes uniform W growth as well as a diffusion barrier between W and underlying Si or silicide layers. For the common CVD deposition chamber, such as a batch-processing machine, the deposition process parameters, such as gas flow, temperature and pressure, are monitored in the inlets of the chamber usually at a distance from the wafer surface where the reaction takes place. The small SiH@sub 4@ gas flow that controls the Si concentration in the nucleation layer, in particular, will have certain modulating effects from the chamber, in terms of time and concentration, in the course of transport. In the present work, simultaneous SiH@sub 4@ and H@sub 2@ reduction of WF@sub 6@ formed the tungsten nucleation layer with a nominal thickness of 60nm. A two-step SiH@sub 4@ gas flow scheme was used to determine the effects of magnitude and duration of SiH@sub 4@ flow on the Si concentration at the W/TiN interface. The results amply demonstrate that SIMS analysis can be used to evaluate the deposition process so as to meet the fill and barrier protection requirements for narrow trench or small via. Issues of SIMS analysis such as depth resolution, interference from molecular ions, memory effect, and quantification are discussed.

MC-TuP9 SIMS/XPS Depth Profiling of a Fluoride-Modified Epoxycoating*, **W.J.H. Van Gennip**, R.D. Van de Grampel, R. Van der Linde,* Eindhoven University of Technology, The Netherlands*; P.C. Zalm,* Philips Research, The Netherlands*; J.W. Niemantsverdriet,* Eindhoven University of Technology, The Netherlands, Netherlands

The surface of an epoxy resin has been modified by the addition of a small amount of a polymerizable monomeric surfactant. The difference between the surface free energy of the epoxy and surfactant caused the surfactant, by definition the component with the lower surface free energy, to segregate preferentially to the solid/air interface. Curing caused the surfactant to bind to the crosslinking agent, thus permanently modifying the surface of the epoxy. Initial XPS measurements showed that the surface is indeed fluoride-modified. This was confirmed by contact angle measurements. Only a small amount of surfactant is necessary to saturate the surface. These exploratory measurements were used as reference to study, explain and confirm the depth profiles we subsequently acquired using depthprofiling SIMS. Although depth profiling of semiconductors has become a widely used technique, the application of depthprofiling SIMS to polymers is much less common. The preliminary results obtained thus far indicate that depthprofiling through polymers can deliver useful results unobtainable by other techniques.

MC-TuP10 Strategies for Reducing the Effects of Topography in Depth Profile Analysis of Polycrystalline Thin Film CdTe/CdS Photovoltaic Materials and Devices*, **S.E. Asher**, M.R. Young, H. Moutinho, T. Gessert, R.G. Dhere, P. Sheldon,* National Renewable Energy Laboratory

Polycrystalline thin film materials are promising for low-cost, large area manufacturing of photovoltaic modules. Surface analysis methods are critical tools to measure the distribution of contaminants and dopants in these materials. However, the native t opography and heterogeneity can present significant challenges for depth profile analysis, particularly by SIMS. We have developed several methods that have proved useful for SIMS examinations of CdTe/CdS solar cells made by different thin film depositio n methods. Depth profile results obtained after chemical etching, controlled polishing and back-side analysis show strengths and limitations of each method. These methods have allowed us to study diffusion and composition in 100 nm CdS layers buried under up to 10 µm of CdTe. In the films studied, the CdTe may have an initial average surface roughness of @>=@ 200 nm or more. The depth profile results from sample preparation methods listed above will also be compared to depth profiles obtained with sample rotation. We find that sample rotation in these materials is complicated by lateral inhomogeneities, even when the rotation speed is well matched to the cycle time of the analysis.

MC-TuP11 Comparison of Sputter Rate and Interfacial Resolution in a Multi-instrument Surface Science Laboratory*, **M.H. Engelhard**, A.S. Lea, D.J. Gaspar, G.C. Dunham, T. Thevuthasan, D.R. Baer,* Pacific Northwest National Laboratory

A multi-instrument, multi-technique laboratory faces a wide variety of analysis needs. Although much is known about the parameters that influence sputtering and the ability of a technique to resolve an interface, variations among different instruments reflect the geometry and design of each instrument, as well as the conditions convenient for operation and actual performance of an ion gun. Each instrument has advantages and limitations for specific types of analyses. In order to determine the actual performance of various instruments found in the Environmental Molecular Sciences Laboratory, we have measured interfacial resolution and sputtering rates produced for common operating and a few optimized sputter conditions for several instruments. The capabilities of these instruments include X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), time-of-flight secondary ion mass spectrometry (TOF-SIMS), and accelerator based materials analysis. Samples used for these studies included Si/SiO@sub 2@, Ta/Ta@sub 2@O@sub 5@ and Ni/Cr multilayer standards. For instruments with sample rotation capability, data has been collected with and without rotation. Using this data, we have developed a matrix describing the performance of the various techniques and instruments. We utilize this matrix to choose the appropriate instrumentation to acquire the desired information at the required accuracy for a wide range of scientific studies in the minimum time.

MC-TuP12 XPS Investigation of Counterion Exchange in SiO@sub 2@ Sol-gel Films Doped with Tris(2,2'-bipyridine)Ruthenium(II)*, **X. Wen**, M. Sykora, T.J. Meyer, R.W. Linton,* University of North Carolina at Chapel Hill

SiO@sub 2@-based sol-gels provide an attractive matrix for doping a variety of molecules. Ru complexes are among the most attractive dopant molecules for SiO@sub 2@ sol-gels due to their unique photophysical and redox properties. Applications of sol-gel films doped with Ru complexes are mostly based on the properties related to the metal-to-ligand charge transfer (MLCT) excited state of the complex. The MLCT excited states are very sensitive to not only the physical nature but also the compositions of the sol-gel matrix. This research work investigates the possible new method of tailoring the compositions of SiO@sub 2@ sol-gel thin films doped with [Ru(bpy)@sub 3@]Cl@sub 2@, which involves the exchange of the original counterions of Ru complexes with new counterions. SiO@sub 2@ sol-gel films doped with [Ru(bpy)@sub 3@]Cl@sub 2@ were prepared by spin-coating from sol/[Ru(bpy)@sub 3@]Cl@sub 2@ mixtures. XPS coupled with Ar@super +@ sputtering was used to study both the surface compositions and depth profiles of the sol-gel films before and after the counterion exchange experiments. The results indicated the original counterion, Cl@super -@, of Ru(II) complex completely leached out of the film after exposing the film to water. Cl@super -@ ion could be reintroduced into the film by putting the Cl@super -@ deprived film back in HCl solution. New counter ions, such as PF@sub 6@@super -@, were incorporated into the sol-gel film by immersing the Cl@super -@ deprived film in HPF@sub 6@ solution. The incorporation of PF@sub 6@@super -@ ions was both time and pH dependent. In addition, cations such as Na@super +@ could also be incorporated into the film by putting the sol-gel film in basic solutions such as Na@sub 2@HPO@sub 4@/NaH@sub 2@PO@sub 4@. This approach was used to calculate the ratio of total Si to the number of SiO@super -@H@super +@ sites that can be exchanged in the SiO@sub 2@ sol-gel films.

MC-TuP13 SiO2 Growth on Si(100) and (111) Investigated by QUASES-XPS Analysis*, B. Semak, C. Gundlach, P. Morgen,* University of Southern Denmark*; S. Tougaard,* University of Southern Denmark, Denmark

It is well known that the growth of SiO2 on Si is an activated process. It must involve heating and it may be strongly influenced by the presence of small amounts of catalysts like alkali metals. A fundamental problem for the growth of very thin SiO2 films with heating is the formation of oxide islands and trenches at their perimeters. The parameters of oxide growth are varied in a series of experiments to determine their influence on the morphology and interface structure of silicon oxide on Si(111) and Si(100). Here we have used the QUASES-XPS technique@footnote 1@ to analyze the surface morphologies of 0 to 10 nm thin SiO2 films. The SiO2 growth is determined for different cycles of alkali-metal evaporation-, oxygen exposure- and annealing- procedures. @FootnoteText@ @footnote 1@ http://www.quases.com.

MC-TuP14 Influence of Ar@super +@ Ion Bombardment on the Chemical States of SrBi@sub 2@Ta@sub 2@O@sub 9@ Thin Films Fabricated by Metal-Organic Decomposition*, **Y.B. Park**, K.Y. Min, S. Heo, C.H. Lim, M.K. Lee, H.J. Kim, S.Y. Lee,* Hyundai Electronics Industries Co., Ltd., Korea

SrBi@sub 2@Ta@sub 2@O@sub 9@(SBT) belongs to a Bi-layered perovskite structure where double Ta-O octahedron layers are sandwiched between (Bi@sub 2@O@sub 2@)@super 2+@ layers were analyzed for the characterization of chemical states with the help of x-ray photoelectron spectroscopy (XPS) during the depth profiling analysis. When the sputter etching was performed to SBT films by Ar@super +@ ion bombardment, the chemical states of constituents were changed as a function of the applied Ar@super +@ ion beams energy from 1kV to 4kV. Among the constituents of SBT film, the Sr 3d peak was slightly changed by the change of Ar@super +@ ion beams energy. On the other hand, the change of Ta 4f and Bi 4f peak were obviously dependent on the applied Ar@super +@ ion beams energy. In particular, Bi 4f peak was dramatically changed from Bi@sub x@O@sub y@ oxide states to Bi metallic states by the lower Ar@super +@ ion energy than the cases of Sr and Ta. These changes of chemical state within SBT film resulted from the preferential sputtering of oxygen atoms. Following out present study, Preferential sputtering of oxygen atoms was found to depend on thermal stability and mass difference between oxygen and each constituent within SBT film.

MC-TuP15 XPS Analysis of Plasma-Modified Polymers for Enhanced Cellular Response*, **R. White**,* VG Scientific, UK*; R.L. Williams, T. Markkula,* University of Liverpool, UK*; G. Jones, J. Wolstenholme,* VG Scientific, UK

Gas plasmas are a convenient way of modifying the surface properties of polymers without significantly altering their bulk properties. As such they have been proposed as a means of modifying the surface properties of polymers to enhance the cellular response to the materials for particular applications. XPS has been used to determine both the elemental composition and chemical state functionality of PET and PTFE polymers modified using two different RF plasma systems (Capacitor Plate and Inductive Coil) with nitrogen and ammonia gases. Initial results indicate significant differences in modification of the polymers with the respective treatments.

MC-TuP16 Surface Potential Measurement with High Spatial Resolution using a Scanning Auger Electron Microscope*, Y. Sakai, M. Kudo,* JEOL Ltd., Japan*; **C. Nielsen**,* JEOL USA Inc.

The microscopic surface potential distributions were measured from the onset energies of secondary electron spectra using a scanning Auger electron microscope. An equipment used in this experiment was a scanning Auger electron microscope (JEOL Model JAMP-7830F) attached with a hemispherical electron energy analyzer with an input focusing lens system and a secondary electron detector to take SEM images. The electron gun is a Schottky field emission type and electrons emitted from a cathode tip are focused onto the specimen surface. The hemispherical electron energy analyzer with a high detection efficiency in the region lower than several ten eV was used at an ultra-high vacuum pressure. Such a technology makes possible to measure the work function change caused by different crystal orientations, the surface potential profile depending on micro-electronic structures of semiconductor devices, etc. The typical applications of the work function measurement are presented in this paper. The four grains of poly-crystal Ni (99.9% purity) with different crystal orientation were prepared for testing a spatial resolution of work function mapping. The initial rises of secondary electron emission for the four grains of Ni are observed by the primary electron beam at 10 keV and 1.3 n A., and the onset energies are 5.55, 5.60, 5.65, and 5.50eV, respectively. If we put the work function of the analyzer equal to 5.60 eV, the work functions of Ni are 4..95, 5.04, 5.22 and 5.35 eV, respectively. The mapping of work function distribution was carried out by measuring intensities of secondary electron emission at the fixed point of. 5.70eV. The observed work function images show a spatial resolution of several tens nm estimated from the image contrast. The measurement of work function and imaging of the surface potential at a spatial resolutions of several tens nm and a sensitivity of 0.05V have been established by using a scanning Auger electron microscope of ultra-high vacuum.

MC-TuP17 Satellite Structure of KLL Auger Spectra in Fluorides*, **L. Kövér**,* Institute of Nuclear Research of the HAS, Hungary*; M. Uda,* Waseda University, Japan*; I. Cserny, J. Tóth,* Institute of Nuclear Research of the HAS, Hungary*; K. Ogasawara, H. Adachi,* Kyoto University, Japan

Considerable chemical effects have been found on the satellite structures of the F KLL Auger spectra in fluorides recently,@footnote 1-3@ which could be important for surface chemical identification and could provide information on the origin and the atomic or molecular character of the particular Auger satellite lines. In the case of the alkali fluorides unassigned satellites were found and interpreted on the basis of a new concept,the resonant orbital rearrangement.@footnote 3@ In the present work we study the structure of the Auger satellites induced from rutile-type fluorides. F KLL Auger spectra were excited by Al K@alpha@ and Cu L@alpha@ X-rays from polycrystalline powder samples of MgF@sub 2@, ZnF@sub 2@, NiF@sub 2@ and CoF@sub 2@ and measured by a high luminosity electron spectrometer.@footnote 4@ Excitation by Cu L@alpha@ increased the peak to background ratio in the spectra significantly. Similarly to the alkali fluorides, a satellite has been found in the high kinetic energy part of the measured F KLL spectra. From the satellite intensities the fluorescence yield for the doubly ionized states in MgF@sub 2@ has been determined. An inverse proportionality has been found between the satellite/diagram X-ray and the corresponding Auger intensity ratios, while the latter ratios have been found to be proportional to the energy width of the new Auger satellites. These observations indicate the resonant nature of the Auger transition identified. For determining the energy difference between the molecular orbitals in resonance, Discrete Variational X@alpha@ cluster molecular orbital calculations have been performed. This work was supported by the projects OTKA T026514, MTA-JSPS 24/1998. @FootnoteText@ @footnote 1@ O. Benka and M. Uda, Phys. Rev. Letters, 56 (1986) 1667, @footnote 2@ H. Aksela, E. Kukk, S. Aksela, A. Kikas, E. Nommiste, A. Ausmees and M. Elango,Phys. Rev. B 49 (1994) 3116,@footnote 3@ M. Uda, T. Yamamoto and T. Takenaga, Adv. in Quant. Chem. 29 (1997) 389,@footnote 4@ L. Kövér, D. Varga, I. Cserny, J. Tóth and K. Tökési, Surf. Interface Anal. 19 (1992) 9.

MC-TuP18 XPS and XRD Characterization of CuO-TiO2-CeO2 Catalyst System*, M.S.P. Francisco,* Universidade de Sao Paulo, Brazil*; **P.A.P. Nascente**,* Universidade Federal de Sao Carlos, Brazil*; V.R. Mastelaro,* Universidade de Sao Paulo, Brazil*; A.O. Florentino,* Universidade Estadual Paulista, Brazil

The CuO-TiO@sub 2@ system has been widely studied due to its catalytic properties on methanol oxidation. However, disadvantages are related to TiO@sub 2@ as support: thermal instability, its sintering and the sintering of the active phase. The cerium addition to this system is known to stabilize the active phase in a fine dispersed state and to improve both the resistance to thermal loss of surface area and the catalytic activity of supported catalysts. The influence of loading cerium and cooper to TiO@sub 2@ on its superficial composition and on its structure have been studied by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). The analyses revealed that with increasing amount of cerium on titania, cerium occurs mainly in a dispersed superficial specie and just a little as CeO@sub 2@ phase (cerianite). At higher loading of cerium, the CeO@sub 2@ phase increases and the Ce/Ti atomic rate is smaller than the bulk rate, as a consequence of cerium agglomeration. We have concluded that a limited amount of cerium can be spread on the titania surface. The Cu/(Ce+Ti) atomic rate showed no influence from cerium on the dispersion of cooper. For CuO-TiO@sub 2@ samples with low concentration of cerium, we could observe that cerium is found as Ce@super 3+@, at least partly. Also the XPS spectra confirmed the presence of a second titanium specie with a spin-orbit component at higher binding energy than the one presented by Ti@super 4+@ in CuO-TiO@sub 2@ samples rich in cerium. The structural results obtained by XAS were in good agreement with those obtained by XRD and XPS.

MC-TuP19 Structural Characterization of V@sub 2@O@sub 5@/TiO@sub 2@ Catalysts*, C.B. Rodella,* Universidade de Sao Paulo, Brazil*; **P.A.P. Nascente**,* Universidade Federal de Sao Carlos, Brazil*; V.R. Mastelaro, M.R. Zucchi, R.W. Franco, C.J. Magon, J.P. Donoso,* Universidade de Sao Paulo, Brazil*; A.O. Florentino,* Universidade Estadual Paulista, Brazil

Vanadia supported on titania constitutes a well-know catalytic system for selective oxidation of o-xylene, ammoxidation of hydrocarbons and selective reduction of NO@subx@ with NH@sub3@. A series of V@sub2@O@sub5@/TiO@sub2@ samples was synthesized by sol-gel and impregnation method with different contents of vanadia and treated in different calcination temperature. The samples were characterized by X-ray diffraction (XDR), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and electronic paramagnetic resonance (EPR). XDR detected rutile as the predominant phase for pure TiO@sub2@ prepared by the sol-gel method when calcined at 450@super0@C. The structure changed to anatase when the vanadia loading was increased. Also anatase was the predominant phase for samples obtained by the impregnation method. XPS results indicated that the Ti ions were surrounded tetrahedrally by oxygen ions. The V/Ti atomic ratios showed that V ions were highly dispersed on the vanadia/titania surface obtained by sol-gel method. Raman measurements identified three species of surface vanadium: monomeric vanadyl (V@super4+@), polymeric vanadates (V@super5+@) and V@sub2@O@sub5@ crystalline. EPR analysis detected three V@super4+@ ion types: two of them were located in axial symmetry sites substituting the Ti@super4+@ in the rutile structure, and the third one was constituted by a magnetically interacting V@super4+@ ions in the form of pairs or clusters. For the materials with higher concentrations of vanadium, a partial oxidation of V@super4+@ to V@super5+@ was evident from EPR analysis.

MC-TuP20 Investigation of Oxide Layers Formed on NiTi Shape Memory Alloys at Elevatated Temperatures*, **R.G. Vitchev**, G. Firstov, H. Kumar,* Katholieke Universiteit Leuven, Belgium*; Y. Liu,* Nanyang Technological University, Singapore*; B. Blanpain, J. Van Humbeeck,* Katholieke Universiteit Leuven, Belgium

NiTi shape memory alloys have attracted considerable attention as materials for medical implants. It is known that the biocompatibility of the implants fabricated from NiTi depends on their surface composition since nickel often causes allergic and toxic effects. The purpose of this study is to characterise the thermally grown oxides on the surface of an NiTi alloy (50 at. % Ni). The samples were heat treated in air in the temperature range 473-1073 K. Thermo-gravimetry measurements were carried out to investigate the kinetics of oxidation. X-ray photoelectron spectroscopy and Auger electron spectroscopy combined with sputter depth profiling were used to investigate the surface composition and chemical state of the constituent atoms and their depth distribution. X-ray diffraction was used to determine the phases formed in the oxide layers. The influence of the surface treatment of the alloy on the oxidation process was also studied. Thermodynamic calculations were carried out to explain the oxidation behaviour of the NiTi alloy.

MC-TuP21 Reduction of Artifacts in Temperature Programmed Desorption Measurements of Field Generated, Real-Life, Powdered Samples*, **V.S. Smentkowski**, A.L. Linsebigler,* General Electric Corporate Research and Development Center

Temperature programmed desorption (TPD) is a powerful surface analytical technique used for studies of adsorbate systems under controlled, high vacuum, conditions. Even under controlled, high vacuum, conditions background events such as desorption from the mounting wires and/or the heater assembly can contribute to the TPD signal and complicates data analysis. Researchers often need to determine the desorption characteristics of field generated, real-life, samples that have been prepared under ambient conditions and TPD measurements are often utilized to provide the desorption characteristics. Since real-life samples are generated under ambient conditions, the potential for background effects is significantly enhanced. In many cases, background effects and their implications on data analysis are not considered. It will be demonstrated that background effects are very significant for real-life, field generated samples when traditional TPD measurements are performed. We have devised a novel experimental protocol to reduce background effects during TPD measurements of field generated, real-life, powdered samples. The novel experimental apparatus and procedures will be described. TPD spectra measured using the new protocol will be compared with spectra measured using traditional protocol.

MC-TuP22 A New Look at the Steel Cord-Rubber Adhesive Interphase by Chemical Depth Profiling*, **G.E. Hammer**,* The Goodyear Tire & Rubber Company

The adhesive interphase formed between brass plated steel cord and sulfur crosslinked rubber is known to be a complex layer of metal oxides, sulfides, and rubber. Hostile aging of this system produces changes in the structure, morphology, thickness and mechanical properties of this layer. In a previous publication it has been shown that the overall thickness of the sulfide layer as measured by depth profiling with Auger electron spectroscopy could be used to characterize the degradation of the adhesive bond.@footnote 1@ In this work multivariate statistical analysis of the sulfur Auger electron spectra was used to produce chemical depth profiles of the individual copper and zinc sulfide layers. These chemical depth profiles give new insight into the adhesion degradation mechanism on the nanometer scale. Particularly, the percentage of copper sulfide in the layer was found to be an accurate predictor of adhesion degradation. @FootnoteText@ @footnote 1@G. E. Hammer, R. M. Shemenski, J.Vac. Sci. Technol. A, 12(4), 2388 (1994).

MC-TuP23 Electrical Property of TiN@sub x@/SiO@sub 2@/Si Structure for Metal Gate Electrodes*, **K.S. Kim**, Y.C. Jang, K.J. Kim,* Sungkyunkwan University, South Korea*; N.-E. Lee, S. Youn, K. Roh, Y. Roh,* Sungkyunkwan University, South Korea, Korea

Recently, there have been growing research interests in the gate structures utilizing metal gate electrode materials including W in Si MOS devices. In order to avoid the strong interactions of F during W CVD with gate oxide layer leading to the destruction of gate oxide integrity, TiN@sub x@ diffusion barrier layer has been employed between the metal electrode and the gate oxide due to its excellent electrical property and structural stability. In this work, we investigated the interface formation between TiN@sub x@ and SiO@sub 2@ and electrical properties of TiN@sub x@/SiO@sub 2@ as a function of annealing temperature. Thermal gate oxide with the thickness of 110 Å was grown at 850 °C in the O@sub 2@ atmosphere by RTP on p-type Si. Then, TiN@sub x@ layers with the film thickness of 1000 Å were deposited at room-temperature by reactive d.c. magnetron sputtering with the Ar and N@sub 2@ gas mixture ratios of 6:1, 6:3, and 6:6. To minimize the radiation-induced damage of thermal gate oxide, plasma power was kept as low as 100 W during sputtering. Annealing of TiN@sub x@/SiO@sub 2@/Si structures was performed for 180 sec at 600, 700, and 800 °C by RTA in order to investigate the structural and chemical stability. AES and 4-point probe were performed to measure the chemical composition and sheet resistance (R@sub s@) of TiN@sub x@/SiO@sub 2@ films, respectively. The results of R@sub s@ measurements as a function of annealing temperature indicated that the R@sub s@ values of TiN@sub x@ films decreased at the annealing temperature below 600 °C but started to increase above 700 °C compared to those of as-deposited films. Increased R@sub s@ of the samples annealed at elevated temperature above 700 °C was attributed to the increased oxygen concentration in TiN@sub x@ layers, judged from the AES results. Microstructures of TiN@sub x@/SiO@sub 2@ interfaces investigated by cross-sectional TEM showed a good structural integrity.

MC-TuP24 The Observation of Ferroelectric Domains using Scanning Capacitance Microscope*, M.K. Lee,* Hyundai Electronic Industries Co. Ltd., Korea*; P. DeWolf, R. Alvis,* Digital Instruments, Veeco Metrology Group*; W.S. Yang, C.H. Lim, S. Heo, T.K. Lee, Y.B. Park, H.J. Kim, K.Y. Min, S.Y. Lee,* Hyundai Electronic Industries Co. Ltd., Korea

The ferroelectric domain structure affects the ferroelectric properties like as hysteresis loop characteristic that is of importance in manufacturing of ferroelectric random access memory (FeRAM). However, the domain images cannot be easily seen using a general analytic method. We have investigated the ferroelectric domain structure of SrBi@sub 2@Ta@sub 2@O@sub 9@ (SBT) using a scanning capacitance microscope (SCM) combined with an atomic force microscope (AFM). The ferroelectric domains were imaged by optimizing AC and DC bias between sample and cantilever tip. Integrating a dc/dv signal from single domain makes a microscopic ferroelectric hysteresis loop that corresponds well with a macroscopic one obtained from the same film. We also try to image the leakage current of SBT film by means of tunneling AFM (TunA). As the result, the weak point passing by the high currents was observed. Further study on the chemical composition or the structure of the weak point will be helpful to understand the leakage current mechanism of ferroelectric materials.

MC-TuP25 Improved Local Capacitance Detection and a Quantitative 1-D Carrier Profile Extracted from the Scanning Capacitance Microscopy dC/dV versus V Curves*, E.-S. Kang**, J. Kang, H.-J. Hwang,* Chung-Ang University, Korea

We have quantitatively extracted 1-dimensional carrier profile from the scanning capacitance microscope (SCM) dC/dV versus V curves using the SCM modeling and an inversion modeling. This is based on the spherical capacitor model, not the common parallel-plate capacitor model. We physically analyzed the spherical capacitor and calculated the rate of capacitance change with bias. Our modeling data have resulted in the capacitance-voltage (C-V) curves different from the conventional C-V curves. The method for a quantitative carrier profiling can be applied directly th the 2- or 3-dimensional dopant profile extractions. Since the current SCM system has a poor reproducibility and sensibility for obtaining the local dC/dV curves, this problem will prevent us from acquiring carrier depth information. For a better quantity of the carrier profiling, for example, to obtain a carrier profile more than 10x18 cm@super -3@, we have designed a new capacitance detector operating at 1.8GHz voltage-controlled oscillator. It consists of an vco, a microstrip resonator, and a peak detector. It will bring a greater enhancement for the SCM sensitivity and performance.

MC-TuP26 Dynamic Force Microscopy Investigations on Molecular Structures and Electrical Properties of Organic Ultrathin Films*, K. Kobayashi**, T. Fukuma, H. Yamada, T. Horiuchi, K. Matsushige,* Kyoto University, Japan

Dynamic force microscopy (DFM) was used to investigate the nanometer-scale structures and electrical properties of organic molecular films, which should be elucidated for their promising applications for molecular electronics. Frequency modulation (FM) detection method which can give high sensitivity especially in a vacuum environment was used in our DFM. The samples used in this study were organic ultrathin films such as self-assembled monolayers (SAMs) of alkanethiol molecules on Au(111) surface and fullerene crystalline islands deposited on Si(111) surface. On fullerene crystalline islands, we successfully obtained molecularly-resolved images, in which molecules were hexagonally packed. Local variation in surface potential (SP) was also mapped using Kelvin null method in DFM, which allowed us to study the local charge transfer between fullerene thin films and the substrate. In the SP image, a small contact potential difference (CPD) between the fullerene crystalline islands and monolayer-covered Si(111) surface was measured. In addition, we obtained molecularly-resolved images on both SAMs of short-chain alkanethiol molecule (octanethiol) and long-chain molecule (hexadecanethiol). The fact that the latter long-chain SAMs could not be imaged by scanning tunneling microscopy (STM) due to the poor electrical conductivity demonstrates a remarkable advantage of DFM for the studies of organic thin films.

MC-TuP27 Conservative and Dissipative Tip-sample Interaction Forces Reconstructed from Dynamic Atomic Force Microscopy Data*, B. Gotsmann**, H. Fuchs,* University of Muenster, Germany

The conservative and dissipative forces between a tip and a surface are characteristic for the materials involved and contain information on several material parameters. In order to determine these forces quantitatively at all tip-sample distances dynamic atomic force microscopy (AFM) can be used. We based our analysis on a combination of computer simulations and experimental AFM data obtained by the frequency modulation technique. In this way it became possible to reconstruct complete force versus distance curves and damping coefficient versus distance curves from experimental data (frequency shift and energy dissipation) without using free parameters and without using a predefined model for the interaction.@footnote 1@ As an example the interaction between an Al-tip and a Au(111)-sample under UHV conditions was analyzed. It turned out that the parts of the force curves that correspond to long range van-der-Waals-forces as well as strong repulsive contacts can be described well with known contact models. However in the transition regime between attractive and repulsive contact an additional short range force can be found. Similarly, the friction coefficient can be determined quantitatively up to a distance of several nanometers exhibiting an inverse power law. At closer contact both velocity dependent friction and adhesion hysteresis lead to energy dissipation. A strategy to distinguish between the two in AFM experiments will be discussed briefly. @FootnoteText@ @footnote 1@ B. Gotsmann, C. Seidel, B. Anczykowski, H. Fuchs, Phys. Rev. B 60 (1999) p.11051.

MC-TuP28 Challenges in Insulator Surface Analysis*, M. Reichling**, C. Barth,* Universit@um a@t M@um u@nchen, Germany*; M. Huisinga, R. Lindner,* FU Berlin, Germany

The application of high end ultraviolet optical materials as required for next generation optical lithography is extremely demanding in terms of preparing defect free surfaces. We report about major progress in insulator surface analysis with respect to both, characterizing the electronic and geometric surface structure. This is exemplified for crystals with the fluorite structure (CaF@sub 2@, SrF@sub 2@, BaF@sub 2@) that are important materials for advanced ultraviolet optical applications. Results from highest sensitivity ultraviolet photoelectron spectroscopy revealing defect states are presented. Supported by additional evidence from ultrafast laser spectroscopy, we demonstrate that for any preparation there are occupied and unoccupied states throughout the band gap where the density of states strongly decreases with energy above the valence band edge. The sources of the band gap states as well as their implications for optical absorption in the ultraviolet are discussed. We recently presented atomic resolution in imaging defects on a fluoride surface with scanning force microscopy in the ultra-high vacuum.@footnote 1@ With such measurements and controlled gas exposure we can show that chemical interactions between gas molecules and surface defects play a major role in the degradation of surfaces exposed to air. We, furthermore, demonstrate that it is now possible to resolve not only defects on terraces of cleaved surfaces but also features like step edges and kinks with atomic resolution and that we are able to locate positions of individual ions and vacancies along steps. We present recent results where we resolved individual atoms in regular nanometer-sized surface clusters that are a result of cleavage. @FootnoteText@ @footnote 1@ M. Reichling, C. Barth, Scanning force imaging of atomic size defects on the CaF@sub 2@(111) surface, Phys. Rev. Lett. 83(4), 768 (1999).

MC-TuP29 Controlled Surface Charging as an Analysis Tool in XPS of Mesoscopic Systems*, H. Cohen**, K. Shabtai, S.R. Cohen, I. Rubinstein,* Weizmann Institute of Science, Israel

A novel application of X-ray photoelectron spectroscopy (XPS) is presented, using controlled surface charging (CSC) in dielectric/conductive mesoscopic heterostructures. The method is based on the induction of well-defined potential gradients by means of the electron flood gun. The resultant local potential variations are projected on the photoelectron energy scale, directly detected as XPS line shifts, providing high-quality spatial information down to nanometer scale resolution. The method is applicable to a large variety of systems, offering important advantages over existing XPS-based techniques. Applications of the method will be demonstrated.

Author Index

Bold page numbers indicate presenter