### Monday Afternoon, October 25, 1999

#### Applied Surface Science Division Room 6A - Session AS2-MoA

#### Applied Surface Science for Microelectronics Moderator: C. Magee, Evans East

# 2:00pm AS2-MoA1 Determination by XPS of the Reactions Taking Place at the Semiconductor/'Heteropolyanion Solution' Interface, A. Quennoy, A. Rothschild, A. Etcheberry, CNRS - France; C. Debiemme-Chouvy, CNRS - France, FRANCE

When semiconductors (SC) are immersed in a solution containing oxydizing species they could undergo an oxidation/dissolution process. Therefore their surface chemical composition can evolve. The knowledge of the SC surface composition after the treatment allow sometimes to determine the reactions which had taken place at the SC/solution interface. In this communication, an example will be shown. The heteropolyanions (HPA) based on oxometallate compounds can undergo multiple one- or twoelectron reduction of the metallic atoms. @footnote 1@ Thus depending on their oxidizing power they could oxidize SC. We studied the behavior in acidic solution of two HPA species with a Keggin structure H@sub 4@SiW@sub 12@O@sub 40@ (SiW@sub 12@) and H@sub 4@SiMo@sub 12@O@sub 40@ (SiMo@sub 12@) toward GaAs. The XPS analyses shown that after immersion in the HPA solution a deposit is formed on the GaAs surface. For immersion longer than one hour the substrate is no more detected. The deposit obtained in the presence of SiW@sub 12@ is composed of WO@sub 3@.@footnote 2@ Concerning SiMo@sub 12@, the HPA structure seems conserved in the deposit. Moreover the peak fitting of the Mo3p XPS spectrum indicates that some Mo atoms have remained at the oxidation state (VI) and that others have reached the oxidation state V. Otherwise, whatever the HPA studied As atoms are present in the deposit. They are at an oxidation state higher than that of As atoms inside the substrate. All these results indicate that in the presence of SiW@sub 12@ or SiMo@sub 12@ GaAs is oxidized while the HPA species are reduced. The conclusions obtained just on the basis of the XPS analyses were confirmed by electrochemical studies and profilometry. @FootnoteText@ @footnote 1@ M.T. Pope, Heteropoly and Isopoly Oxometalates, Springer, Heidelberg, 1983. @footnote 2@ A. Rothschild, C. Debiemme-Chouvy, A. Etcheberry, Applied Surface science 135 (1998) 65.

# 2:20pm AS2-MoA2 Sputter Deposition and Annealing of Ta, TaSi and Ta@sub 4@B Composite Films and Their Application in Next Generation Lithography Masks, *K. Racette*, *C. Brooks*, IBM

Ta and Ta composites with other elements have been developed by several researchers as low stress absorbers for x-ray mask technology. These thin films are often produced in small quantities by sputter deposition from targets of pure Ta with chips of the minor elements placed on the target to create the composites. For membrane-mask manufacturing it is important that absorber films have uniform composition, thickness and low stress to assure that image size and pattern placement errors are minimal. Since sputter deposited films containing Ta have highly compressive stress, several methods have been used to reduce the final stress, including careful control of sputtering conditions, deposition of layered films with different stresses, and thermal annealing. Much data has been reported on the effects of thermal annealing of Ta films but less information is available on multiple element films such as TaSi and Ta@sub 4@B. Reports have generally been developmental in nature and not discussed behavior of these films under longer term, higher volume manufacturing conditions. During the last several years IBM has been engaged in development and fabrication of refractory x-ray membrane-masks using TaSi and Ta@sub 4@B as absorber materials. Films were sputter deposited from hot isostatically pressed powder targets of Ta, Si, and B using an S-gun cluster deposition system. This paper will report on the deposition and annealing of these films and their application to membrane-mask fabrication in a manufacturing environment. The effects of deposition parameters such as dc power, argon gas flow (pressure) and substrate on film stress, composition and density will be dicsussed. The results of air and nitrogen annealing on thick and thin films of TaSi and Ta@sub 4@B will be presented. Absorber film quality data and its impact on image size, pattern placement and defect density of some fabricated x-ray masks will be presented.

2:40pm AS2-MoA3 XPS Sputter Depth Profiling at the Pd/Y Interface@footnote \*@, G. Neuert, R.J. Smith, Montana State University; J.A. Schaefer, Technische Universität Ilmenau, Germany

X-ray photoelectron spectroscopy (XPS) sputter depth profiling, Rutherford Backscattering Spectroscopy (RBS) and in situ resistivity measurements are used to study the Pd-Y interface. This interface is of interest because of recent work showing that Pd-capped Y films exhibit a reversible metal semiconductor transition as a function of H content in the film. The yttrium film was first evaporated on a glass substrate. A palladium layer was then evaporated on the top of the yttrium film. Both films are made by thermal evaporation using a tungsten basket with a boron-nitride crucible as heating shield. RBS is used to measure the thickness of the film and to calibrate the sputter rate for pure Pd and Y. Palladium 3d photoelectron peaks, measured by XPS, show a core level shift to higher binding energies with sputter depth. This chemical shift can be an indication of alloy formation at the Pd / Y interface. The resistance measurements are done in situ by a four probe measurement after van der Pauw. The resistance of the yttrium film is measured after finishing the yttrium evaporation. A palladium layer was then evaporated on the top of the yttrium and the resistance of the films was monitored during Pd evaporation. @FootnoteText@ @footnote \*@Work supported by NSF DMR 97-10092 and NASA EPSCoR NCCW-0058. Permanent address of G. Neuert : Institut für Physik, Technische Universität Ilmenau, P.O. Box 100565, D-98684 Ilmenau, Germany.

#### 3:00pm AS2-MoA4 Thin Film Characterization through combined X-ray Photoelectron Spectroscopy (XPS) and X-ray Diffraction (XRD), D.J. Surman, S. Bates, Kratos Analytical Inc.; C.J. Blomfield, A.J. Roberts, Kratos Analytical Inc., UK; J.E. Fulghum, Kent State University

Traditionally there has been a range of methodologies applied to the analysis of thin films, centering on the use of XPS combined with sputter profiling. This approach provides both elemental and chemical information for each of the layers within the film. Following calibration with standard materials, a measure of the sputter rate can be obtained allowing allowing film thickness estimations to be made. It is well known however that different materials sputter at different rates and therefore it is difficult to obtain accurate measurements of individual layer thickness without extensive calibration. X-ray Diffraction (XRD) offers new possibilities for the characterization of thin films. Recently developed poly-capillary optics enable the generation of intense parallel beams of X-rays. This X-ray beam can then be used at grazing angles to provide a range of additional information on the nature of the thin film. This methodology allows accurate film thickness measurements to be obtained from monolayer to approximately 2000Å. This can be applied to multi-layer structures, providing an accurate measure of the individual layers enabling in-situ callibration of the sputter profile. The X-ray diffraction pattern also allows the polycrytalline phases within the film to be identified and quantified, providing additional support information for the chemical information provided by XPS. Variation of the diffraction pattern with grazing angle can also be used to obtain a measure of film thickness' of greater than 2000Å. This paper will demonstrate the enhanced characterization that can be achieved through the combined use and interpretation of the XPS and XRD data on a series of different materials and combined thin films.

#### 3:20pm AS2-MoA5 Photoelectron Spectroscopic Investigation of Interfaces and Thin Layers for Microelectronics: Composition and Chemistry as a Function of Depth, *R.L. Opila*, *J.P. Chang*, *J. Eng*, *Jr.*, *M. Du*, Bell Labs, Lucent Technologies INVITED

As dimensions shrink in microelectronics, the role of interfaces between materials becomes more important and the characteristic dimensions of microelectronics approach the escape depth of photoelectrons. Two strategies to examine thin layers and their interfaces will be described. First, the overlayer will slowly be deposited, the specimen will be transferred in vacuo, after which the photoelectron spectrum is recorded. This strategy has proven to be particularly useful in determining how metals react with polymers, which are being considered as low dielectric constant interlayers between conductors. Because it is desirable to use copper despite its poor adhesion, barrier layers of more reactive metals and their nitrides must be incorporated. We have successfully used photoelectron spectroscopy to study the chemistry that occurs between a series of low dielectric constant materials, including fluoropolymers and aerogels, and titanium, tantalum and their nitrides. The relative reactivity at the interface controls the morphology of the growing overlayer. The interface between the barrier metal and the copper seed layer has been studied. In another application of photoelectron spectroscopy, the

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composition and chemistry of oxide layers for use as gates in transistors or as dielectrics in capacitors have been studied. The thickness of the dielectric layer is comparable to the escape depth of the photoelectrons. Thus, we have been able to identify certain chemical states as those likely to act as defects in the electronic device. Moreover, using angle resolved photoemission, the composition of the dielectric overlayer has been determined as a function of depth for silicon oxynitrides and tantalum pentoxide. A maximum entropy algorithm to transform the angle resolved data to elemental and chemical depth profiles will be described. Reactions that occur at the buried interfaces between the dielectic and the underlying electrode will also be described.

#### 4:00pm AS2-MOA7 Analytical Conditions for Semi-Quantitative Auger Analysis of TaN, C.F.H. Gondran, SEMATECH; D.C. Nelsen, SEMATECH, on assignment from Intel; D.A. Hess, Evans Texas

Historically, quantitative analysis of tantalum nitride (TaN) has been done by Rutherford backscattering spectroscopy (RBS), to avoid problems due to preferential sputtering effects seen in Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). Recently tantalum (Ta) and TaN have emerged as leading candidates for barrier layers in advanced metalization schemes for next generation semiconductor devices. The small size of the features in these devices, as small 0.25 micron and shrinking, necessitates the development of a procedure to perform at least semi-quantitative analysis of TaNx films by a technique with significantly higher spatial resolution than RBS. In this paper the preferential sputtering effects seen in TaN by AES and XPS are characterized as a function of ion beam energy and film composition. This data is used to determine the most favorable analytical conditions for semi-quantitative AES analysis and develop an understanding of the limitations.

4:20pm AS2-MoA8 Investigation of InP(110) Surface Damage Induced by Low Energy Ar and He Ion Bombardment, Q. Zhao, The Chinese University of Hong Kong, P.R. China; Z.W. Deng, Tsinghua University, P.R. China; R.W.M. Kwok, W.M. Lau, The Chinese University of Hong Kong, P.R. China High-resolution x-ray photoelectron spectroscopy (XPS) was employed to study the surface damage on n- and p-InP(110) caused by low energy ion bombardment in an ultrahigh-vacuum (UHV) system. The dynamic process of surface Fermi level shifting induced by ion bombardment as a function of ion dosage and ion energy was also measured. Two kinds of ion He@super +@ and Ar@super +@ at 10eV and 100eV energy with different ion dosages (from 10@super 12@ to 10@super 17@ ions/cm@super 2@) were chosen to investigate the performance of ion bombarded InP(110) surface. The results showed that the Fermi levels of both n- and p InP (110) surface moved to the midgap due to He@super +@ and Ar@super +@ ion bombardment, and ultimately pinned at about 0.95eV above the valence band maximum. More importantly, it was found that even at a bombardment energy of 10eV, ion fluence of 5x10@super 16@/cm@super 2@ was enough to cause an electrically active bandgap state density of 1x10@super 12@/cm@super 2@ which can detrimentally affect the device performance of the semiconductor.

4:40pm **AS2-MoA9** Phase Transformation of Cubic Boron Nitride Induced by Ion Bombardment, *B. Zheng*, The Chinese University of Hong Kong, P.R. China, Hong Kong, P.R. China; *R.W.M. Kwok*, The Chinese University of Hong Kong, P.R. China; *M.Y.Y. Hui*, The Chinese University of Hong Kong, P.R. China, Hong Kong, P.R. China; *W.M. Lau*, The Chinese University of Hong Kong, P.R. China

The effects of argon ion bombardment on cubic boron nitride in the energy range of 50-1000eV were studied by electron energy loss spectroscopy with a field emission scanning Auger microscope (PHI 670), and by Auger and photoelectron emission. The microanalysis capability of the microscope allowed data collection from a (111) facet of a cubic boron nitride crystal, which largely increased the accuracy in the determination of the ion bombardment effects. Through monitoring the conversion of the electron energy loss features of cubic boron nitride to those of hexagonal boron nitride with an incident electron beam energy of 250eV, we determined the cubic to hexagonal phase transformation as a function of ion fluence and ion energy with a sub-monolayer sensitivity. We found that even at the low end of our bombardment energy range, the cubic to hexagonal phase transformation was still evident.

5:00pm AS2-MoA10 Guided Ion-beam Studies of Low Energy Cu@super +@ and Cu@sub 2@@super +@ Ion Interactions with Ni(100), S.L. Anderson, A. Lapicki, K.J. Boyd, M. Aizawa, University of Utah

Low-energy (5-220 eV) Cu@super +@ and Cu@sub 2@@super +@ ions are deposited on Ni(100) under UHV conditions using the phase-space

compressing ion beam deposition system at the University of Utah. The nature of the deposited Cu is determined by variable angle XPS and XAES. The disposition of the Cu deposits is explored as a function of ion energy and species. The Cu-Ni system exhibits stable surface and bulk alloys, and thus provides an interesting comparison to the C metal systems previously studied by ion beam methods (Ag/Ni, Cu/Mo). The influence of system thermodynamics and ion energy effects are examined via experiments and computer simulations.

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