

Monday Evening Poster Sessions, November 2, 1998

Applied Surface Science Division Room Hall A - Session AS-MoP

Aspects of Applied Surface Science Poster Session

AS-MoP1 Auger Depth Profile Analysis of Ba@sub x@Sr@sub 1-x@TiO@sub 3@ Thin Films, M.L. Kottke, Motorola, Inc.

High dielectric constant sputtered thin films of Ba@sub x@Sr@sub 1-x@TiO@sub 3@ are being developed for use in the storage capacitors of high density microelectronic memory circuits. The correlation of the electrical characteristics of such capacitors with the compositional and structural properties of the Ba@sub x@Sr@sub 1-x@TiO@sub 3@ films is key to optimizing device and circuit performance. This paper gives a detailed description of the methodology developed to provide quantitative Auger depth profiles with high resolution and high precision. Data will be shown giving the optimum angles of incidence for best depth resolution when sputtering with both Ar and Xe ions. Sputter rates versus angle of incidence will be provided for both Ar and Xe at 1.0 keV. Variations in sputter rate and Auger sensitivity factors with variations in composition between x=0 and x=0.7 will be presented. The Auger analysis provides insight into the accuracy of BST thin film stoichiometry measurements made by x-ray fluorescence and Rutherford backscattering techniques, and a discussion of the issues involved will be provided.

AS-MoP2 Characterization of Shallow Implants with SIMS using Electron Beam Oxidation, M. Puga-Lambers, P.H. Holloway, University of Florida, Gainesville

Secondary ion mass spectrometry (SIMS) depth profiles of boron shallow implants in silicon have been measured with a quadrupole Perkin-Elmer 6600 PHI SIMS system. Oxygen backfill from the base pressure (10@super -10@ Torr) to 10@super -6@ Torr was applied in conjunction with oxygen bombardment. Silicon wafers implanted with 8 keV As and 5 keV and 0.5 keV B to doses of 3, 5 and 1 x10@super 15@ cm@super -2@, respectively were analyzed. Maximum peak concentrations were about 2.5x10@super 21@ cm@super -3@ for As, and 1.5x10@super 21@ cm@super -3@ and 1.0x10@super 21@ cm@super -3@ for B, respectively. The peak maxima were located at 10 nm, 22 nm and 3 nm for As at 8KeV and B at 5 KeV and 0.5 keV, respectively. Oxygen backfill improved the depth resolution but degraded the dynamic range of 0.5 keV B implants by about half an order of magnitude. Simultaneous electron bombardment during oxygen backfill and during depth profiling further improved the depth resolution while maintaining the dynamic range of the SIMS analysis as measured both by the surface transients in the Si@super +@ and SiO@super +@ substrate as well as the B@super +@ signal. In addition, analysis of both the Si@super +@ and SiO@super +@ transients demonstrated that the extent of surface oxidation during oxygen backfill was accelerated by simultaneous electron bombardment. The prospects for further improvement in this technique for shallow implant profiles will be discussed.

AS-MoP3 Total Sputtering Yield of Ag/Cu Alloys Versus Composition and Temperature for 260 eV Ar+, K.W. Pierson, C.D. Hawes, M.S. Vogel, N.C. Harris, P.J. Gustafson, G.C. Falkenberg, University of Wisconsin, Eau Claire

The results of recent sputtering yield experiments have important implications concerning depth profiling of the Ag/Cu alloy system. The total sputtering yield of a range of Ag/Cu alloy compositions for various target temperatures has been measured for normally incident 260 eV Ar+ and a dose of 5.4x10@super 19@ ions/cm@super 2@. At temperatures between -50 C and +40 C the yield of all compositions between 20/80 (% atomic Ag/Cu) and 80/20 is approximately equal to pure Cu. For targets with an increased Ag percentage above 80/20 the yield climbs toward the value of pure Ag. At temperatures above 40 C, micron size cones develop on the target surface and the yield decreases dramatically in an unpredictable manner due to redeposition of ejected material. We hypothesize that the relatively sharp transition to cone development is due to the exponential nature of surface diffusion, which is believed to be necessary for cone development. The low transition temperature to cone development and unpredictable yields is important for depth profiling, as these temperatures are easily attainable for improperly heat-sunked targets, high ion energy, or high ion beam flux. The fact that yield of a large range of compositions becomes approximately equal to pure Cu at low temperatures for properly heat-sunked targets is important for predicting depth scales.

AS-MoP4 Study on Reaction Mechanism of Aluminum Chemical Vapor Deposition with In-situ XPS and TOF-SIMS Measurements, K. Tanaka, H. Yanashima, Sumitomo Chemical Co., Ltd., Japan; T. Yako, Sumika Chemical Analysis Service Ltd., Japan; K. Kamio, Sumitomo Chemical Co., Ltd., Japan; K. Sugai, S. Kishida, NEC Corporation, Japan

Chemical vapor deposition (CVD) of Al is one of the most promising methods for multilevel metallization of ultra-large-scale integration (ULSI) circuits as it can fill via holes that have sub-half-micron diameters and high aspect ratios with superior step coverage. However, the surface morphology of CVD Al films deposited on oxidized Si surfaces is generally unsatisfactory. The CVD Al films deposited on TiN barrier layers, on the other hand, show much smoother surfaces due to higher Al island density in the early stage of growth. In the present work, the reactions of dimethylaluminum hydride (DMAH; (CH@sub 3@)@sub 2@AlH) with slightly oxidized TiN and Si surfaces were investigated in situ with x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS). Si substrates with/without TiN surface layer were introduced into a UHV chamber. After evacuation H@sub 2@ gas was introduced at a pressure of 1x10@super -3@ Pa and the substrates were heated to 200°C, following the introduction of DMAH vapor at partial pressures of 1x10@super -6@ to 1x10@super -4@ Pa. After CVD reaction, the chamber was evacuated to UHV again and the specimens were transferred to XPS and TOF-SIMS spectrometers in vacuum. It was observed that the native oxide layer formed on TiN surface was reduced when exposed to DMAH vapor and a clean TiN surface became to appear. The reduction of oxide and deposition of Al on TiN surface were enhanced with increase of DMAH exposure. In contrast with the TiN surface, no reduction of native oxide layer by DMAH was observed on Si surface except the uppermost surface analyzed by TOF-SIMS. The amount of Al deposited on Si surface was also decreased and substantially equal independent of DMAH exposure. The reduction of oxide and appearance of clean TiN surface must be important to account for the nucleation mechanisms of Al film growth on TiN during CVD. The difference of chemical states of adsorbed DMAH molecules on TiN and Si surfaces will also be discussed. @FootnoteText@ @footnote 1@K. Sugai, H. Okabayashi, T. Shinzawa, S. Kishida, T. Kobayashi, N. Hosokawa, T. Yako, H. Kadokura, M. Isemura, and K. Kamio, Proceedings of the 10th International IEEE VLSI Multilevel Interconnection Conference, 1993 (IEEE, New York, 1993), p. 463.

AS-MoP5 The Orientational Relationship in Epitaxial Rocksalt(001)/Rocksalt(001) and Rocksalt(001)/Perovskite(001), G. Chern, National Chung-Cheng University, Taiwan; C. Cheng, National Cheng Kung University, Taiwan

We have grown several different oxide thin films, including MgO, SrO, NiO, and Fe@sub 3@O@sub 4@ on single crystalline MgO(001) and SrTiO@sub 3@(001) substrates by molecular beam epitaxy. These oxides have either rocksalt or perovskite structure which are two of the most standard crystalline structures in ionic crystals. By using high energy electron diffraction (RHEED) we observed some specific orientation relations between these two structures. The interface of a rocksalt/rocksalt only shows a direct matching configuration. However, the interface of rocksalt(001)/perovskite(001) shows at least two different matching configurations, direct on and 45-degree rotation of the film relative to the substrate. These results imply:(1) SrTiO@sub 3@ (or other perovskite substrate) is a "better" substrate candidate for a hetero-epitaxial thin film growth. The grown material may or may not need to be closely lattice matched to the substrate because there are two stable interface matching possibilities for an epitaxial growth. (2) Since the matching configurations are originated from the interfacial energy, a simple "electrostatic matching" instead of "geometrical matching" may be constructed for the ionic systems with different structures.

AS-MoP7 Optical and Structural Characterization of Copper-based Colloidal Particles in SiO@sub 2@ Coatings, R. Bernal, CICESE, Mexico; F.J. Garcia-Rodriguez, Univ. Autonoma de Queretaro, Mexico; J.F. Perez-Robles, F.J. Espinoza-Beltran, CINVESTAV-IPN, Mexico; R. Ramirez-Bon, Univ. de Sonora, Mexico; Y.V. Vorobiev, J. Gonzalez-Hernandez, CINVESTAV-IPN, Mexico

By using the sol-gel method were produced coatings having colloidal copper-based particles embedded in a SiO@sub 2@ matrix. The particle composition in each sample depended on the amount of copper added to the starting solutions, the atmosphere in which the samples were annealed and the annealing temperature. The optical properties of the colloidal system were determined by transmission and photoacoustic spectroscopies. X-ray diffraction, Raman scattering, and infrared

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measurements were used to characterize the structure of the composite glass. The model proposed by Mie was used with effective values for the optical constants of the colloidal particles to determine characteristic parameters of the colloidal system and the particle composition.

AS-MoP8 Role of Surface Chemistry on the Nature of Passive Oxide Film Growth on Fe-Cr (Low & High) Alloys at High Temperatures, S. Seal, R. Nardelli¹, A. Kale, K. Casey, V. Desai, University of Central Florida

High temperature material degradation or protection of Fe-Cr alloys are often related to the nature of their oxide scale formation. Breakdown of passive oxide films leads to localized corrosion. Many a times, various alloying elements are incorporated in these alloys to prevent high temperature degradation. Addition of selected alloying elements is cumbersome and not always cost effective. In this paper, we investigate the role of rare earth oxide coatings on high temperature corrosion prevention of both low and high Cr steel at various temperatures. An in-situ high temperature oxidation set up has been built to study the oxidation kinetics of both coated and uncoated alloys under ambient pressure and dry air. Reduction in reaction rate constants is observed in the presence of coating. While SEM and XRD are employed to study the structure and morphology of the films, XPS, AES are used to study the surface chemistry of the oxide layer. This paper relates some of these data to explain the linear, para-linear and parabolic growth kinetics observed in both low and high Cr steels.

AS-MoP9 Surface Microchemistry of Roman and Etruscan Bronzes of the Vatican Museums, E. Paparazzo, L. Moretto, Consiglio Nazionale delle Ricerche, Italy; M. Sannibale, Vatican Museums, Vatican City

The main objective of this work is to find out how a given burial site affects the surface chemistry of archaeomaterials lying in it. To accomplish this task we have explored the surface chemical composition of Roman and Etruscan bronzes of the Vatican Museums using x ray photoemission spectroscopy (XPS) and scanning Auger microscopy (SAM). The Roman bronze, a statue of the 1st century AD found in seawater, contains copper sulfides as the main corrosion products, along with minor amounts of copper chlorides. We relate the former to both the presence of sulfide ions formed in seawater via bacteria-assisted chemical reduction of sulfates and to the solubility products of copper sulfides being much lower than those of copper chlorides. Conversely, the Etruscan bronze, a helmet of the 6th century BC found in the soil, contains a mixture of copper chlorides and copper oxides which we explain as being due to corrosive attack of sodium chloride from the soil. We find that the tin, always entirely present as SnO₂, plays a beneficial role in limiting the corrosion of copper, since it is about twice as abundant, as is metallic copper, in the Etruscan bronze than in the Roman one. This beneficial role of tin is directly shown by way of SAM imaging at the surface of the two objects. Indeed, the regions that are rich in this element are virtually free of either sulfides (Roman bronze) or chlorides (Etruscan bronze), and these lateral inhomogeneities are highlighted with a spatial resolution ~ 200 nm. Our results are compared with the findings of other studies on "modern" Cu-Sn systems, as well as with the reports of historical sources.

AS-MoP10 Surface Analysis Studies of Bidri Archaeomaterials from the Collection of the British Museum, M. Anderle, M. Bersani, M. Fedrizzi, ITC-IRST, Italy; L. Moretto, E. Paparazzo, Consiglio Nazionale delle Ricerche, Italy

Bidri ware is a class of inlaid Indian archaeological metalwork, made from Zn-Cu alloy, and characterized by a black patina which contrasts strikingly with the shiny metallic inlays. While the chemical composition of the patina is well known, the reason for its black color is not, knowledge of such a reason being an essential pre-requisite for devising appropriate schemes for both restorative and conservative purposes. In order to ascertain whether the surface microchemistry of the patina is responsible for the black color, we undertook a thorough study of Bidri samples (courtesy of the British Museum) using XPS, scanning Auger microscopy, SIMS, and EDS as a means of analysis. We find that the patina, about 0.5 micrometers thick, contains Zn, Cu, O, Cl, and C along with trace amounts of Pb and Sn. The Zn/Cu atomic ratio is about 7 in the patina and increases considerably in the alloy, whereas the interface is high in Cl and poor in Cu. Both the copper and zinc are entirely oxidized at the patina, and laterally separated from each other to a few microns, whereas Cl lateral segregation is lower than 0.5 microns. The SIMS analyses has been performed using a magnetic sector mass spectrometer (CAMECA 4f) in depth profile and imaging mode to obtain elemental maps. SEM/EDS were also carried out to obtain

morphological and elemental information from the surface samples and from the bottom of the SIMS craters. We propose a model which explains the black color of the patina as originating from a highly-dispersed ZnO-like phase which features a broad range of light absorption coefficients.

AS-MoP11 X-ray Photoelectron Spectroscopy of Ru@sub 3@(CO)@sub 9@(MeCN)@sub 3@ Modified Platinum Surfaces, C.R. Cabrera, E.R. Fachini, University of Puerto Rico

The ability to tailor surfaces is important in electrocatalysis. Furthermore, the interest in obtaining clean energetic systems has driven an additional effort on developing novel catalysts for fuel cells. An extensive study is being made with bimetallic Pt/Ru catalyst for methanol oxidation. This is because it combines the ability of platinum to oxidize methanol and the capacity of ruthenium to decrease the CO poisoning of the electrode surface. Different methods have been proposed to achieve the most economical way to prepare bimetallic catalyst. In the present work, we present a way to modify Pt surfaces with a Ru cluster by using surface organometallic coordination. The cluster used in our experiment is Ru@sub 3@(CO)@sub 9@(MeCN)@sub 3@ (1 mmol in CH@sub 2@C@sub 12@) (I). This cluster was used to modify a platinum foil (99.9%). The cluster (I) was synthesized from Ru@sub 3@(CO)@sub 12@ (II) following a procedure presented by Aime et al.¹ The purity and characterization of the product was confirmed by IR. The modified cluster (I) adsorbs on Pt surface, however, the original cluster, Ru@sub 3@(CO)@sub 12@, was unable to coordinate. The amount of platinum oxides on the surface did not seem change the amount of adsorption of the clusters, even when the platinum surface had a complete oxide layer. The platinum oxide was obtained by electrochemical procedures² and the amount of oxides was quantified by XPS. Despite of this, a very clean surface (certified by hydrogen adsorption on a CV of H@sub 2@SO@sub 4@ (0.5M)) was required to obtain good reproducibility on the adsorption of (I). After this, a reductive treatment was made by exposing the modified surface a H₂ atmosphere: 400°C at 15 min. was enough for the total reduction of the cluster to metallic Ru, either on a platinum surface or in crystalline form (this finding was confirmed by absence of CO and CN stretches in IR measurements). The presence of ruthenium at the platinum surface and its chemical environment was monitored very carefully by XPS analysis. This is necessary because Ru 3d peak overlaps with C 1s transition and is the unique signal for Ru chemical analysis by XPS.³ The binding energy of Ru were 281.7 ± 0.1 eV (cluster on Pt surface) and 280.3 ± 0.2 eV (Ru peak after H@sub 2@ reduction and corresponds to metallic Ru). No peak for Ru oxides was observed. The platinum presented peaks at 71.1 ± 0.2 eV (metallic Pt without Pt oxides), 71.9 ± 0.3 eV (metallic Pt when Pt oxides were present) and a single peak for Pt oxide at 74.7 eV. Just one peak for metallic platinum appeared after the reduction with H@sub 2@. The migration of the Ru atoms into Pt substrate was minimum or inexistant because with a slight sputtering with Ar was able to eliminate the Ru XPS peak.¹ S. Aime, W. Dastr, R. Gobetto, J. Krause, L. Violano, Inorg. Chim. Acta, 235, 357 (1995).² J.S. Hammond, N. Winograd, J. Electroanal. Chem. 78, 55 (1977).³ J.R. Felthouse, P.B. Framdorf, R.M. Friedman, C.L. Schoesser, J. Catal. 157, 421 (1991).

AS-MoP12 New SERS-Active Substrates Based on Thin Films of Noble Metals, L. He², S.P. Mulvaney, S.K. St. Angelo, M.J. Natan, Pennsylvania State University

A new approach to fabricating SERS substrates in which coats of Ag (or Au) are evaporated on Ag-coated Au colloid monolayers is described. The newly developed substrate circumvents the problems faced in previously reported techniques that use commercial plating solutions to chemically reduce Ag⁺ onto Au colloid monolayers. The optical properties of the resulting new substrates depend critically upon particle size and interparticle spacing in the initial monolayer as well as on the amounts of chemically deposited Ag and evaporated metal. Under certain condition, extremely large enhancement factors can be realized with excellent spot-to-spot and sample-to-sample reproducibility. This presentation will describe characterization of these novel substrates by AFM, field emission SEM, and other techniques, and will provide a rationale for the observed SERS behavior.

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