Surface Engineering
Room 132 - Session SE-MoA

Surface Engineering I: Graded, Multicomponent, and Complex Coatings

Moderator: A. Inspektor, Kennametal Inc.

2:00pm **SE-MoA1 Multi-Level Control for Reactive Sputtering***, **W.D. Sproul**, B.E. Sylvia,* Reactive Sputtering, Inc.

Pulsed dc power combined with partial pressure control of the reactive gas has made it possible to reactively sputter deposit non-conducting films such as aluminum oxide at relatively high deposition rates. Most reactive sputtering control systems rely on a single feedback signal for process control. However controlling on a single variable can affect the quality and repeatability of the deposited films. For example when the target voltage is used as the feedback signal, it can change for reasons other than a change in the reactive gas partial pressure such as outgassing or a disappearing anode. Another signal is needed to remove the ambiguity in the control process. Similarly if a mass spectrometer is used to provide the primary feedback control signal, the control signal can change with time due to drift in the mass spectrometer. A new system has been built that overcomes the problem of controlling on a single feedback signal. This new system, called IRESS, controls on a primary signal and then makes on-line adjustments to this primary signal based on secondary feedback signals. Examples of how this works for aluminum oxide and aluminum oxynitrides coatings will be given.

2:20pm **SE-MoA2 The Influence of Sputtering Conditions on Microstructure and Mechanical Properties of Zr-Si-N Films Prepared by r.f.- Reactive Sputtering***, **M. Zhou**,* Osaka University, Japan*; M. Nose,* Takaoka National College, Japan*; Y. Deguchi,* Toyama University, Japan*; T. Mae,* Toyama National College of Technology, Japan*; K. Nogi,* Osaka University, Japan

ZrN and ZrSiN films were prepared in an r.f. sputtering apparatus which has a pair of targets facing each other (referred to as the Facing Target -type r.f. Sputtering). Si content in the ZrSiN films was changed by using different number of Si tips during deposition. Films were deposited on silicon wafer. During the deposition, substrate was heated from room temperature to 473K, 573K and 673K in order to investigate the influence of substrate temperature on the microstructure and properties of transition metal nitride films. The microstructure of the deposited films was studied by XRD. The chemical contents of zirconium, nitrogen and silicon of the films were determined by EPMA with ZAF method. In order to investigate the relationship between mechanical properties and microstructure of films, the hardness and Young's modulus were measured by a nano-indentation system at room temperature. The load was selected to produce an impression depth below 60nm (not more than 5% of film thickness) so that the influence from the substrate can be neglected. The surface morphology of as-deposited films was also observed by AFM. A study of their microstructure and mechanical properties has provided as follows: (1) As-deposited ZrSiN films were consist of nano-crystals and the crystal size was in the range of 5-10 nm; (2) With increasing substrate temperature from room temperature to 673K during deposition, the crystal size of as-deposited ZrSiN films did not show obvious increase; (3) The hardness of ZrSiN films increased with small amount of Si reaching maximum hardness value of 35GPa, regardless of substrate temperature; (4) AFM results show that the surface morphology have obvious change with increasing Si content and substrate temperature.

3:00pm **SE-MoA4 Characterization of Ternary Nitride Films using Spectroscopic Ellipsometry***, **S.M. Aouadi**, T.Z. Gorishnyy,* University of Nebraska - Lincoln*; F. Namavar,* Spire Corporation*; N. Finnegan,* University of Illinois at Urbana-Champaign*; S.L. Rohde,* University of Nebraska - Lincoln

This paper reports on the first attempt to quantitatively analyze the chemical and phase composition of ternary nitride nanocrystalline films using spectroscopic ellipsometry (SE). Coatings of CrBN, TiBN, TiZrN, and TiCrN were deposited at low temperatures (<200 Â°C) on silicon substrates using ion beam assisted deposition (IBAD) and/or unbalanced magnetron sputtering. These coatings were developed for the protective and decorative coating industries, which require very precise compositions to obtain the desired mechanical properties and/or color. The deposited films were characterized post-deposition using x-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), Rutherford Backscattering (RBS), infrared spectroscopic ellipsometry (IR-SE), and visible-light spectroscopic ellipsometry (VIS-SE). The primary phases in the films were identified using XRD. The chemical composition and phase composition of the samples were determined from XPS, AES, and RBS measurements, as appropriate. VIS-SE and IR-SE data were analyzed using two different approaches to obtain the chemical and phase composition of these samples. The first approach relies on the identification of the optical constants for a few samples of known compositions (from RBS, AES or XPS data) and the use of these optical "standards" in the interpolation of the optical constants of unknown materials to deduce the corresponding chemical composition. The second approach is based on the effective medium approximation, which requires the knowledge of the optical constants of each of the constituent phases. The chemical compositions obtained by SE using both the above approaches were compared to the results obtained from traditional chemical analysis techniques (RBS, XPS, and AES).

3:20pm **SE-MoA5 Structural and Chemical Interplays in Hard Coatings Properties: Multinary Transition Metal Nitrides***, **F. Lévy**,* Swiss Federal Institute of Technology in Lausanne - EPFL, Switzerland*; P. Hones, P.E. Schmid, R. Sanjinés, M. Diserens,* Swiss Federal Institute of Technology in Lausanne - EPFL **INVITED**

Transition metal nitrides are useful as hard, resistant and protective coatings. Both film composition and film morphology have an influence on the functional properties like hardness, wear and corrosion resistance or colour. Physical vapour deposition techniques are flexible enough to allow a control of the chemical and structural characteristics. In turn, targeted or new coating properties can be obtained. In particular new coating chemistries can be explored by reactive sputtering, which is a clean, polyvalent process, compatible with elemental metal sources. Property improvements may be driven by structural and morphological features, as discussed for example in (CrMo)N ternary sputtered thin films. In contrast, the effects of electronic structure and chemical bonding are illustrated in (CrW)N. In single-phase refractory thin films, the hardness often increases with increasing substrate temperature T@sub s@. This effect has been related to an increase of the grain size d (e.g. in TiN, H@sub m@ = 23...35 GPa with d = 300...600 nm for T@sub s@ = 200...650 @degree@C). In CrN@sub y@, however, the increase in hardness from 8 to 19 GPa observed with increasing substrate temperature T@sub s@ = 330...680 @degree@C was not related to the grain size in a straightforward manner. For this material the grain size was always of the order of 40 nm. The porosity of the film, however, was reduced by substrate heating as demonstrated by an increase of the density. In the ternary compounds, for example in Cr@sub 1-x@Mo@sub x@N@sub y@, the grain size increases significantly in comparison with the binary end compounds. This grain size increase is accompanied by a loss of hardness. The morphology of the films remains columnar and the apparently increasing porosity can be held responsible for the deterioration of the mechanical properties. The chemical composition is determining for most properties, even if often masked by the morphological features. Such effects are present in binary compounds (CrN@sub y@) and are amplified in ternary systems ((Cr,M)N@sub y@ with M = Mo, W).

4:20pm **SE-MoA8 Formation of Voids and its Influence on the Thermal Stability of Co Silicide***, **N.S. Kim**, H.S. Cha, N.G. Sung, H.H. Ryu, W.G. Lee,* Hynix Semiconductor, Korea

We investigated the voids formation during Co silicidation and its influence on the thermal stability of CoSi@sub 2@ on boron or BF@sub 2@-doped poly-Si in ULSI device. The sheet resistance of as-formed CoSi@sub 2@ has been slightly higher on BF@sub 2@ doped poly-Si than boron doped poly-Si, but the sheet resistance of CoSi@sub 2@ on boron doped poly-Si after thermal process increased abruptly. Cross-sectional TEM has shown local voids at the interface between CoSi@sub 2@ and BF@sub 2@ doped poly-Si, but no void on boron doped poly-Si. Furthermore, as pre-cleaning time in diluted HF before Co deposition increased, sheet resistance of as-formed CoSi@sub 2@ decreased and void formation on BF@sub 2@ doped poly-Si was suppressed, but thermal stability of CoSi@sub 2@ after following thermal process was aggravated. From those results, It was thought that the thermal agglomeration of CoSi@sub 2@ was suppressed by stress release at the interface with local voids formed by remained oxide and some florine compounds on the surface of BF@sub 2@ doped poly-Si.

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