Thin Films
Room 123 - Session TF-WeM

Fundamentals of Deposition

Moderator: J. Colligon, Manchester Metropolitan University, U.K.

8:40am **TF-WeM2 Molecular Dynamics Simulations of Self-bombardment of Compact Clusters on Pt(111)**, ***D. Adamovic***, *E.P. Münger, V. Chirita, L. Hultman,* Linköping University, Sweden*; J.E. Greene,* University of Illinois, Urbana

Studies of low-energy bombardment of two-dimensional (2D) close-packed clusters are of great importance and strongly related to thin film growth. We use embedded-atom method molecular dynamics simulations to monitor the kinetics characterizing the self-bombardment of Pt@sub 3@, Pt@sub 7@ and Pt@sub 19@ clusters on Pt(111) at 1000K. Atoms incident perpendicular to the surface with energies between 5 and 50 eV are followed in separate simulations of ~ 20 ps each. Clusters are divided into different sections, outer, rim and core area respectively. Our simulations reveal three major classes of events. They are cluster preservation, i.e. no change in shape or position, cluster reconfiguration, involving edge-diffusion and/or concerted dimer/trimer gliding and cluster disruption (rim atom scattering and/or total disintegration). Two of the most commonly observed events are the formation of three-dimensional (3D) clusters and the hopping and/or push out/exchange mechanism with rim atoms. Other typical processes observed are the permanent or temporary dislodgement of cluster atoms onto the surface as well as the creation of surface vacancies. For Pt@sub 3@ our results suggest that cluster preservation and reconfiguration events primarily occur with incident atom energies below 25 eV, while cluster disintegration prevails at higher energies. Similar effects are observed for larger clusters, however the energy threshold is not as sharply defined.

9:00am **TF-WeM3 On the Relative Motion of Thermal Gas Atoms In the Monte Carlo Simulation of Sputtering**, ***T. Nakano***, *S. Baba,* Seikei University, Japan

In this study, we have developed the treatment of gas motion in the Monte Carlo (MC) simulation of sputter deposition process. It has been known well that the mean free path of the sputtered particle depends on the speed of the particle, but the distribution function of colliding gas has been assumed to be the Maxwellian, which is independent of the particle speed.@footnote 1@ We show here that the distribution also depends on it. The collision frequency of the sputtered particle with those gases which belong to some volume in the velocity space is proportional to the product of the density of the gas, the cross section and the relative speed between the sputtered particle and the gas atoms. Therefore, the colliding gas velocity does not obey the stock Maxwellian but the one weighed by the relative speed. This distribution function can be integrated by using the relative speed and the gas speed (in laboratory system) as integrating parameters, hence it is applicable to the MC simulation. Using this method, time evolutions of velocity and positional distributions of sputtered particles are calculated and demonstrated. It is shown that the speed distribution of the sputtered particles after some period of time is described well by the Maxwellian of the same temperature with the gas. It is also shown that this method has enabled the accurate calculation of the resident time of sputtered particles in the chamber, which leads the spatial density of the particle. @FootnoteText@ @footnote 1@G. M. Turner, et al., J. Appl. Phys. 65 (1989) 3671.

9:20am **TF-WeM4 Self-Similar Structure Evolution and Surface Reaction Kinetics in Low Temperature Silicon Deposition**, ***G.N. Parsons***, *K.R. Bray, A. Gupta,* North Carolina State University

A current challenge in low temperature thin film deposition is to analyze energetics and kinetics of surface processes to control growth reactions and improve material properties. In this work, surface transport kinetics during silicon plasma deposition are determined by analyzing time and temperature dependent surface topography in comparison to dynamic scaling models. For plasma deposition of silicon using silane or silane/helium mixtures at 25 - 350Â°C, static and dynamic scaling parameters determined from atomic force microscopy are consistent with self-similar fractal geometry. Comparing parameters with those expected from linear continuum models indicates indicate that surface transport is dominated by adspecies diffusion with a diffusion activation barrier of 0.2eV, consistent with previous empirical estimates. However, the elementary steps associated with initial film growth are still not clear. The observed increase in diffusion length with increasing temperature contradicts some current published growth models, and ab-initio analysis of precursor adsorption reactions indicate that silyl radicals do not directly adsorb onto Si-H bonds to form 3-centered bonds, as is commonly proposed. When helium is replace by argon, significant departure from self-similar structure is observed, consistent with excess energy from surface bombardment of heavier Ar ions. Diluting silane with hydrogen results in significant changes in scaling coefficients, indicating that an additional non-linear term is needed in the continuum model to describe surface diffusion. All of the results suggest that atomic hydrogen generated in the plasma plays an important role in assisting surface transport. Possible elementary surface reactions consistent with observed results will be presented and discussed.

9:40am **TF-WeM5 Atomic-Scale Processes in the Growth of Transition-Metal Nitrides**, ***D. Gall***, *C.-S. Shin, M.A. Wall, I. Petrov, J.E. Greene,* University of Illinois, Urbana

Polycrystalline and epitaxial layers of NaCl-structure transition-metal (TM) nitrides -- TiN, ScN, CrN, and TaN -- were grown on oxidized Si and MgO(001) at 450-1000 °C by ultra-high-vacuum magnetically-unbalanced magnetron sputter deposition in pure N@sub 2@ and N@sub 2@+Ar discharges at 3-20 mTorr. Polycrystalline layers grown under low ion-irradiation conditions exhibit a columnar microstructure with strong 111 preferred orientation which evolves in a kinetically-limited competitive growth mode due to a large anisotropy in adatom mobilities and binding energies. Surface diffusion energies E@sub s@ were obtained from T-dependent nucleation length measurements using STM and by ab-inito density functional calculations. E@sub s@ for (001) and (111) TiN surfaces are 0.8 and 1.7 eV. The much smaller 111 adatom mobility results in preferential 3D growth and, ultimately, in the observed 111-preferred orientation. However, increasing the energy of incident N@sub 2@@super +@ ions during deposition to 20 eV results in layers with purely 001-texture. The high anisotropy in adatom mobilities gives rise to another unique microstructural feature: epitaxial 001-oriented layers exhibit self-organized arrays of 1-nm-wide nanopipes which are formed as a result of periodic kinetic surface roughening and subsequent atomic self-shadowing. While the microstructures of different NaCl-structure TM-nitrides are similar, their electronic and optical properties vary widely. TiN has metallic conductivity, ScN is semiconducting, and CrN is an antiferromagnetic insulator. The color of Ti@sub 1-x@Sc@sub x@N varies continuously with x from golden yellow to orange to burgundy to blue-green to transparent. Measured hardness of single crystal 001-oriented layers are 20, 21, 28, and 31 GPa for TiN, ScN, CrN, and TaN, respectively.

10:00am **TF-WeM6 Low Temperature Synthesis of Fully Textured Highly Oriented AlN Films by RF and Pulsed DC Reactive Sputtering**, ***G.F. Iriarte***, *F. Engelmark, I.V. Katardjiev,* Uppsala University, Sweden*; H.P. Loebl,* Philips GmbH, Germany

Textured as well as epitaxial thin AlN films are of great interest for a wide range of electro-acoustic and optoelectronic applications. Reduction of the deposition temperature is of vital importance in a number of applications due to thermal budget limitations. In this work we study systematically the influence of the process parameters on the film properties and identify the mechanisms leading to improved film quality as well as reduced deposition temperature with both RF and pulsed DC sputtering in an Ar/N@sub 2@ atmosphere. It is demonstrated that fully textured (0002) films are grown under a wide range of conditions. At the same time the FWHM of the rocking curve of the (0002) XRD peak is found to vary systematically with process conditions - depostion rate, process pressure and gas composition, substrate temperature and bias. The best films show a FWHM of 1.2@super o@. By comparing RF and pulsed DC sputtering we have identified the major mechanisms leading to the synthesis of high quality films. Thus it has been found that by far the most important factor is the arrival energy of the sputtered Al atoms which is primarily controlled by the process pressure. We report for the first time that fully textured AlN films with a FWHM of under 2@super o@ can be grown at room temperature. Other important factors are the ion and electron bombardment of the films, substrate temperature as well as gas composition, although their influence is not as dramatic. Generally, the film quality increases with temperature. Bias and electron bombardment within a certain range also lead to better films. Low Ar/N@sub 2@ ratios also result in improved film quality although the mechanisms are not fully understood.

10:40am **TF-WeM8 A Theoretical Study of the Chemical Vapor Deposition of (100) Silicon from Silane**, ***J.K. Kang***, *C.B. Musgrave,* Stanford University

We use quantum chemistry to investigate the chemical vapor deposition of (100) silicon from silane. The CVD reaction proceeds through four sequential steps. The first step is activation of surface sites through H2 desorption from the Si (100)-2x1 monohydride surface. We find that H2 desorption proceeds through a two-step pathway. The barrier for the first step is 35.1 kcal/mol while the second step proceeds with a barrier of 31.1 kcal/mol. Next, dissociative adsorption of SiH4 occurs, where SiH3 and H fragments add to two surface dangling bonds. We find the barrier to adsorption to be 4.3 kcal/mol. Then, adsorbed SiH3 transforms directly to SiH2 through simultaneous H migration from adsorbed SiH3 to the dimer and through a dimer-opening and ring-closing reaction with a barrier of 70.7 kcal/mol. We also find an alternative path where adsorbed SiH3 transforms to SiH2 through two sequential steps in the presence of atomic H. One pathway proceeds through hydrogen abstraction from the adsorbed SiH3 on the surface with a barrier of 0.4 kcal/mol followed by a dimer-opening and ring-closing step with a barrier of 23.3 kcal/mol. An alternative path proceeds through abstraction of H from the dimer and has a barrier of 0.2 kcal/mol followed by dimer-opening and ring-closing steps with a barrier of 32.9 kcal/mol. Finally, a dihydride surface with SiH2(a) formed through dimer-opening and ring-closing reactions transforms to a monohydride surface with SiH(a) through two-sequential steps of H2 desorption from one side of dimer followed by H migration from the other side of the dimer. The predicted barrier for this H2 desorption is 47.1 kcal/mol while that for H migration is 2.8 kcal/mol. In addition, we find that the overall theoretical barrier of 60.6 kcal/mol for H2 desorption is in a good agreement with the experimentall barrier (58.2 +/- 2.3 kcal/mol).

11:00am **TF-WeM9 Gas and Surface Reactions of Radicals in Hot Wire CVD of Amorphous Silicon**, ***H.L. Duan***, *G.A. Zaharias, S.F. Bent,* Stanford University

Hot wire chemical vapor deposition (HW-CVD) is a relatively new growth method that has been shown to produce amorphous and microcrystalline silicon materials of superior quality in comparison to the more conventional plasma enhanced chemical vapor deposit ion (PECVD). By using this technique, the precursor molecule such as silane is dissociated on a metal filament (wire) heated to high temperature. Radical species produced from the filament subsequently either diffuse to the substrate to form the film or react to form secondary products. In this study, a laser-based soft ionization method utilizing the ninth harmonic of a Nd:YAG laser has been applied for the first time to probe various silicon-containing species simultaneously during the growth process. In addition to the detection of gas phase radicals, multiple internal reflection infrared spectroscopy is used to characterize the hydride bonding and film structure. Surface and gas phase species are followed as a function of important growth parameters such as filament temperature, filament material and substrate temperature. It is shown that Si, SiH@sub 3@, and Si@sub 2@H@sub 6@ are the major silicon-containing species evolved upon activating silane with the hot wire. However, even at low gas pressure the filament condition and chamber history are found to influence the radical species produced. Further study of the gas species generated by W and Re filaments at wire temperatures between 1000@super o@C and 2000@super o@ C indicates that heating the fil ament to higher temperatures increases the flux of Si, SiH@sub 3@, and Si@sub 2@H@sub 6@ differently. Above 1800@super o@C, the Si intensity saturates, while SiH@sub 3@ and Si@sub 2@H@sub 6@ show a monotonic increase without saturation up to 2000@super o@C. A growth mechanism consistent with these observations will be discussed.

11:20am **TF-WeM10 In-Situ Determination of the Deposition Chemistry During BPSG Dielectric Thin Film Growth**, ***L.D. Flores***, *J.E. Crowell,* University of California, San Diego

Dielectric thin film growth of boron and phosphorus doped silicate glass (BPSG) has been studied using the atmospheric pressure reaction between trimethylborate (TMB), triethylphosphite (TEPi), tetraethoxysilane (TEOS) and ozone (O@sub 3@). In-situ gas-phase transmission FTIR spectroscopy was performed between 400-600°C by probing the variable region between the injector, heated Si wafer and exhaust zones. These studies involve low temperature ozone initiated deposition of dielectric thin films using a new atmospheric-pressure chemical vapor deposition (APCVD) reactor utilizing a commercial monoblok vent assembly. We compare the products of N@sub 2@ / O@sub 2@ / O@sub 3@ reactions with BPSG film forming precursors while varying their reactant ratios and corresponding flow rates. The products produced during the reaction of TEOS and ozone are compared to those products measured during dopant reaction and incorporation from TMB and/or TMPi addition. Absorbances due to isolated silanol species (3737 cm@sup -1@) have been quantitatively followed as a function of input reagent concentration and distance from the injector inlet. The silanol groups and their reactions with boron and phosphorus dopant sources has been investigated in order to clarify their role in the oxidation process and to determine the reaction mechanism. Chemical pathways unique to elemental B-P-Si-O-C containing species will be presented with an emphasis placed on their role during the hydrolysis and polycondensation process leading to siloxane formation and BPSG network film growth.

Author Index

Bold page numbers indicate presenter