Monday Morning, October 2, 2000

Thin Films
Room 203 - Session TF-MoM
Atomic Layer Chemical Vapor Deposition I

Moderator: S.M. George, University of Colorado

8:20am **TF-MoM1 Atomic Layer Deposition of Microelectronic Materials: The Present Status and Future Challenges***, M.K. Ritala,* University of Helsinki, Finland **INVITED**

As the evolution towards increasing integration densities continues in the integrated circuit manufacturing, new materials and thin film deposition methods will inevitably be needed. Atomic Layer Deposition (ALD) is one of the most promising film deposition techniques capable of meeting the strict requirements in future generation IC manufacturing. The self-limiting film growth mechanism of ALD ensures excellent conformality and uniformity over large areas, and atomic level composition and thickness control. In this paper, the present state of ALD of materials of an interest to microelectronics will be reviewed, including also the current understanding of the related chemistry, and challenges for the future research will be outlined. At present, there already exist many potential ALD processes for the following microelectronic materials: dielectrics (e.g. SrTiO@sub 3@, BaTiO@sub 3@, Ta@sub 2@O@sub 5@, Nb@sub 2@O@sub5@, ZrO@sub 2@, HfO@sub 2@ and Al@sub 2@O@sub 3@, and their multilayers and mixtures) for gate oxides and DRAM capacitors, and nitride (e.g. TiN, TaN, NbN, W@sub 2@N) diffusion barriers for metallizations. In addition, some metal (W, Ti, Ta, Cu) ALD processes have been reported as well. Further development of ALD will require increasing efforts in precursor chemistry supported by improved understanding of the growth mechanisms. For the latter, different approaches may be taken. Here a recently developed ALD-QMS-QCM setup enabling in situ characterization of ALD processes under the practically important flow type reactor conditions will be briefly introduced.

9:00am **TF-MoM3 Atomic Layer Deposition of BN Using Sequential Exposures of BCl@sub 3@ and NH@sub 3@***, J.D. Ferguson, S.J. Ferro, S.M. George,* University of Colorado

BN is an inert insulating material with a very high thermal conductivity that is desirable for many applications. Atomic layer deposition (ALD) is a useful method for growing ultrathin and conformal films. BN ALD was accomplished by separating the binary reaction BCl@sub 3@ + NH@sub 3@ --> BN + 3 HCl into two half-reactions: A) BNH* + BCl@sub 3@ --> BNBCl@sub 2@* + HCl; B) BCl* + NH@sub 3@ --> BNH@sub 2@* + HCl. BN films were grown on high surface area SiO@sub 2@ particles using alternating exposures of BCl@sub 3@ and NH@sub 3@ at 700 K. The sequential surface chemistry was monitored in a vacuum chamber using in situ transmission Fourier transform infrared (FTIR) vibrational spectroscopy. The initial SiO@sub 2@ surface contained SiOH* surface species. The first BCl@sub 3@ exposure reacted with the SiOH* species to form SiOBCl@sub x@* species. The subsequent NH@sub 3@ exposure converted the surface species to BNH@sub 2@*. The following BCl@sub 3@ and NH@sub 3@ exposures converted the surface to BCl@sub x@* and BNH@sub 2@* species, respectively. By repeating the sequential surface reactions, BN bulk vibrational modes on the SiO@sub 2@ particles increased versus number of AB cycles. In addition, spectroscopic ellipsometry studies of BN ALD on Si(100) measured BN growth rates of ~2.5 Å per AB cycle. Transmission electron microscopy also examined the conformality of the BN films on the SiO@sub 2@ particles.

9:20am **TF-MoM4 Thermal Stability of Si and C Atomic Layers Formed on Ge(100) in Silane and Methylsilane Reactions***, M. Fujiu, M. Sakuraba, T. Matsuura, J. Murota,* Tohoku University, Japan

In order to realize an atomic layer superlattice of group IV semiconductors, self-limited control of adsorption and reaction of reactant gases and suppression of the mutual diffusion at the hetero interfaces are essential. In this work, thermal stability of Si and C atomic layers formed on Ge(100) in SiH@sub 4@ and CH@sub 3@SiH@sub 3@ reactions was investigated using XPS by an ultraclean low-pressure CVD system. With CH@sub 3@SiH@sub 3@ reaction on Ge(100) at 18Pa, the concentration of Si deposited on Ge(100) was nearly the same as that of C during the reaction at the temperature of 550@super o@C or lower. Especially at 450@super o@C, single atomic layers of Si and C were formed self-limitedly on Ge(100). When the single atomic layers were subsequently annealed for 60 min at 600@super o@C, the C atom concentration decreased from the single atomic layer to about half of the atomic layer, although the Si atom concentration hardly changed. The result suggests that the Si-C bond is gradually broken by annealing at 600@super o@C, and the C atom desorbs. On the other hand, with SiH@sub 4@ exposure on Ge(100) at 120Pa, the deposited Si concentration saturated to that of the single atomic layer at 300@super o@C. After formation of the Si single atomic layer on Ge(100) followed by further annealing for 60 min at 500@super o@C and subsequent SiH@sub 4@ exposure for 30 min at 300@super o@C, the deposited Si concentration increased and reached to 120% of the Si single atomic layer. It is suggested that atomic order mixing occurs even at 500@super o@C at the interface between the Si atomic layer and the Ge substrate, and the segregated Ge atom enhances the further SiH@sub 4@ reaction on the surface. The above results reveal that the atomic order mixing is greatly suppressed by the existence of C atoms on the surface. The dependence of the growth and annealing temperatures on the thermal stability of Si and C atomic layers on Ge(100) will be presented.

9:40am **TF-MoM5 Selective Growth of ZnO Thin Film on Microprinted Si Substrate***, M. Yan, **R.P.H. Chang**, J. Ni, J.R. Babcock, T.J. Marks,* Northwestern University **INVITED**

ZnO is an inexpensive transparent conductive material that has already received intensive studies. Recently, its interesting optical property has made it a potential LED material. Various techniques, including chemical vapor deposition (CVD), sputtering, pulse laser deposition (PLD) and atomic layer epitaxy (ALE), have been used to deposit ZnO thin film onto different substrates. In order to make devices, patterned ZnO film has to be achieved. Typically, features can be fabricated using photolithography. For mass production, however, a low cost and high throughput method is needed. In this research, ZnO thin film was deposited onto microprinted Si substrate using ALE. 1-trichlorosilyl-docosane(CH@sub 3@(CH@sub 2@)@sub 21@SiCl@sub 3@) and perfluorodecyl-1H,1H,2H,2H-trichlorosilane(CF@sub 3@(CF@sub 2@)@sub 7@CH@sub 2@CH@sub 2@SiCl@sub 3@), both of which have a long hydrophobic alkyl chain, were used as ink in microprinting. The -SiCl@sub 3@ group in the above compounds can react with the -OH groups on the surface of Si substrate, thus the hydrophobic chain was fixed on the surface of Si. Water and diethylzinc (DetZn) were used as precursors in ALE. Since water can not stick to the areas that have been covered with ink, selective growth of ZnO can be achieved. Preliminary study shows that selective growth of ZnO has been realized on microprinted Si substrates, which has feature size of 50ï-m. Optical and Scanning Electronic Microscopy (SEM) observations show that features have satisfactory sharpness. Discussion of low temperature ALE of ZnO on different substrate, such as glass and flexible polyethylene terephthalate (PET), will be reported.

10:20am **TF-MoM7 Electrical Characterization of Ultrathin Al@sub 2@O@sub 3@ Films Grown by Atomic Layer Deposition in a Viscous Flow Reactor***, **M.D. Groner**, J.W. Elam, S.M. George,* University of Colorado

Al@sub 2@O@sub 3@ is an important insulator and is a candidate to replace SiO@sub 2@ as a gate dielectric in MOSFETS. Al@sub 2@O@sub 3@ films were deposited by atomic layer deposition (ALD) using alternating exposures of trimethylaluminum and H@sub 2@O on a variety of substrates. The films were grown in a custom viscous flow reactor employing a novel gas pulse switching method. The film growth was monitored in situ by a quartz microbalance and ex situ using ellipsometry. The electrical properties of the A l@sub 2@O@sub 3@ films were evaluated by performing I-V and C-V measurements with a mercury microprobe. The highest quality ALD Al@sub 2@O@sub 3@ films were obtained using ultraclean Si(100) substrates or molybdenum substrates. The ALD Al@sub 2@O@sub 3@ films exhibited extremely low leakage current levels. The electrical properties of the ALD Al@sub 2@O@sub 3@ films deposited on molybdenum were examined versus Al@sub 2@O@sub 3@ thickness from 30 Å to 2400 Å. The C-V measurements revealed that the dielectric constant was k=7.8 for Al@sub 2@O@sub 3@ films @>=@ 1200 Å. The dielectric constant decreased below 100 Å to k=4.0 at 25 Å. The I-V measurements showed that the Fowler-Nordheim (FN) tunneling onset voltage decreased with Al@sub 2@O@sub 3@ film thickness. The onset of FN tunneling occurred at >10 V for 600 Å films and at ~3.5 V for 60 Å Al@sub 2@O@sub 3@ films.

10:40am **TF-MoM8 A Study on the Characteristics of TiAlN Thin Film Deposited by Atomic Layer Chemical Vapor Deposition Method***, **H. Jeon**, J.W. Lee, J.H. Koo, T.H. Doh, Y.D. Kim,* Hanyang University, South Korea

Atomic Layer Chemical Vapor Deposition(ALCVD) method is one of the new deposition method to grow very thin films.@footnote 1@ Conventional PVD and CVD methods exhibit problems such as poor step coverage, impurity contamination and particle generation. ALCVD method has a lot of advantages over other CVD processes and these are excellent thickness uniformity, conformal step coverage, very low pinhole density, and complete elimination of particle generation by gas phase reaction.@footnote 2@ The sequential control of the growth in ALCVD system is based on saturating surface reactions between the substrate and each of the reactant needed for the compound to be grown. Each surface reaction adds full or partial fraction of monolayer of the material on the surface. Here we deposited TiAlN ternary diffusion barrier by ALCVD method. Ternary diffusion barrier is considered to be more efficient than binary diffusion barrier such as TiN. But ternary film of Ti-Si-N has high resistivity to apply for actual process. In this study we deposited TiAlN ternary diffusion barrier to study the diffusion barrier characteristics.@footnote 3@ TiCl@sub 4@ vapor, DMAH-EPP vapor, and NH@sub 3@ gas were alternatively introduced into reactor to form TiAlN by ALCVD. The physical and chemical properties of TiAlN films were analized by TEM, AES, RBS, and SEM. The growth mechanism will be discussed based on the results of characteristics of TiAlN. @FootnoteText@ @footnote 1@T. Suntola, Thin Solid Films, 216, 84-89(1992) @foontote 2@S. Yokoyama, H. Goto, T. Miyamoto, N. Ikeda, K. Shibahara, Applied Surface Science, 112, 75-81(1997) @footnote 3@ C. W. Kim, K. H. Kim, Thin Solid Films, 307, 113-119(1997).

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