Thursday Morning, November 6, 2003

Electronic Materials and Devices
Room 321/322 - Session EM-ThM
Materials for Interconnects and Contacts to Semiconductors

Moderator: S.E. Mohney, The Pennsylvania State University

8:20am **EM-ThM1 Self-aligned Silicides for Ohmic Contacts in CMOS Technology: TiSi@sub 2@, CoSi@sub 2@ and NiSi*, S.-L. Zhang,*** KTH, Sweden **INVITED**

Metal silicides have played an indispensable role during the remarkable developments of microelectronics since PtSi was first used to improve the rectifying characteristics of diodes in early 1960's. Along with several other technological innovations, the implementation of the self-aligned silicide (SALICIDE) technology has paved the way for rapid and successful miniaturization of device dimensions for metal-oxide-semiconductor field-effect transistors (MOSFETs) keeping in pace with the Moore's law. The primary use of silicides has also evolved from creating reliable contacts for diodes, to generating high-conductivity current paths for local wiring, and lately to forming low-resistivity electrical contacts for MOSFETs. With respect to the choice of silicides for CMOS technology, a convergence has become clear with the self-alignment technology using only a limited number of silicides, namely TiSi@sub 2@, CoSi@sub 2@ and NiSi. The present work discusses the advantages and limitations of TiSi@sub 2@, CoSi@sub 2@ and NiSi with the development trend of CMOS technology as a measure. Specifically, the reactive diffusion and phase formation of these silicides in the three terminals of a MOSFET, i.e. gate, source and drain, are analyzed. This work ends with a brief discussion about future trends of metal silicides in micro/nanoelectronics with reference to the potential material aspects and device structures outlined in the International Technology Roadmap for Semiconductors.

9:00am **EM-ThM3 Ni-Si Thin Films Reactions at Low Temperatures: Phase Identification and Sequence Characterization*, C. Coia,*** École Polytechnique de Montréal, Canada*; C. Lavoie,* IBM Research*; M. Tremblay,* École Polytechnique de Montréal, Canada*; C. Detavernier, F.M. d'Heurle,* IBM Research*; P. Desjardins,* École Polytechnique de Montréal, Canada

The phase formation sequence upon thermal annealing of 5 to 20-nm-thick Ni layers on Si(001) has been investigated using a combination of in-situ synchrotron x-ray diffraction (XRD), diffuse elastic light scattering, and electrical resistance complemented by post-annealing transmission electron microscopy and XRD analyses. In addition to the generally reported Ni@sub 2@Si, NiSi, and NiSi@sub 2@ phases, we observe the formation of several metal-rich silicide compounds at low temperatures. The complete sequence is identified as Ni-Ni@sub 31@Si@sub 12@-Ni@sub 2@Si-Ni@sub 3@Si@sub 2@-NiSi-NiSi@sub 2@ with the possible brief appearance of Ni@sub 3@Si preceding Ni@sub 31@Si@sub 12@. The sequence observed for Ni reaction with B- and P-doped Si(001) starts at higher temperatures and occurs over a narrower range in temperature than for undoped Si(001), n-doping having a stronger influence thus showing the larger increase in temperature. Quantitative analyses of XRD peak intensities during isothermal anneals are used to determine rate limiting mechanisms and reaction kinetics. In complementary experiments, 200-nm-thick single-phase layers were obtained for each of the stable phases present in the Ni-Si binary phase diagram in order to determine their physical and chemical properties. The phase formation sequence in these thicker layers of fixed composition suggests that the phases still grow sequentially with the first phase being the Ni@sub 31@Si@sub 12@.

9:20am **EM-ThM4 Development of Ohmic Contact Materials for Compound Semiconductors*, M. Murakami,*** *M. Moriyama, S. Tsukimoto,* Kyoto University, Japan **INVITED**

Compound semiconductors have been extensively used in a variety of devices which Si semiconductor cannot function. Although wide gap compound semiconductors are attractive for light emitting diodes, ultra-violet laser diodes, and high frequency and/or high power devices, lack of reliable, low resistance ohmic contact materials for these compound semiconductors hinders development of these devices. Our studies on ohmic contacts for GaAs, SiC, and diamond (although not compound semiconductor) indicated that formation of an intermediate semiconductor layer (ISL) which reduced the barrier height and/or the width of the depletion region (formed at an interface between the contact metal and the semiconductor) was essential to prepare low resistance ohmic contacts. Thus, once key materials for ISL formation was found, reduction of the contact resistance was obtained in these contacts by annealing at an optimum temperature. However, materials to form ISL could not be found for InP, ZnSe, GaN, and InGaN. For these semiconductors, not only search of materials to form ideal ISL's by reacting with these compound semiconductors should be continued, but also another contact formation mechanism should be explored. Our recent activities for ohmic contact formation mechanisms for various compound semiconductors will be reviewed.

10:00am **EM-ThM6 Indium-Based Ohmic Contacts to n-Type Gallium Antimonide*, J.A. Robinson,*** *S.E. Mohney,* The Pennsylvania State University

Antimonide based compound semiconductors are promising for a variety of optoelectronic and electronic devices. For some of these devices, shallow ohmic contacts to n-type GaSb are required. Among the ohmic contacts that have been developed for this semiconductor, indium-bearing contacts have provided the lowest specific contact resistances. These contacts offer the possibility of lowering the bang gap of the semiconductor and the barrier height at the metal/semiconductor interface through the formation of InGaSb near the metal/semiconductor interface. However, no studies have been reported demonstrating indium-bearing contacts that remain very shallow, penetrating only tens of nanometers into the semiconductor. Furthermore, the surface morphology of these contacts can be poor due to In agglomeration. Using Pd and In, we are engineering shallow In-based contacts with improved surface and interfacial morphology. To achieve this goal, we are combining an investigation of the phase equilibria in the relevant multi-component systems and an understanding of the kinetics of reaction at the Pd/GaSb interface. In this presentation, we describe the formation of newly identified ternary phases in the Pd-Ga-Sb system, the kinetics of reaction at the Pd/GaSb interface, and the formation of ohmic contacts containing Pd and In on n-type GaSb (n = 2.8 x 10@super 18@ cm@super -3@). By choosing the proportions of Pd and In with guidance from multi-component phase diagrams and by minimizing the sheet resistance of the metallization itself, we have achieved to date contact resistances as low as .085 ohm-mm and specific contact resistances as low as 2 x 10@super -6@ ohm-cm@super 2@.

10:20am **EM-ThM7 Long and Short Term Thermal Stability of Gate Metallizations on GaN/AlGaN/GaN Heterostructures*, E.D. Readinger*,** *S.E. Mohney,* Penn State University*; R. Therrien,* Nitronex Corp.

The III-nitride family of semiconductors is expected to provide devices for a variety of high power/high temperature applications, but only a few reports have addressed the thermal stability of gate metallizations for high electron mobility transistors (HEMTs) designed for these applications. This study examines two different forms of thermal stability. First, high temperature rapid thermal processing (RTP) commonly used for ohmic contact formation is used to identify candidates for gate metallizations that could be deposited prior to the anneal of source and drain ohmic contacts. Second, long-term anneals at moderate temperatures to accelerate the aging of HEMTs have been performed. A GaN capped Al@sub 0.23@Ga@sub 0.77@N/GaN heterostructure was used; the metallizations Re, Pt, Au, Ni, Ni/Au, Ni/Ga/Ni and Co were tested; and current-voltage curves were evaluated. Aside from Au and Pt which begin degrading above 400°C, the contacts exhibited neither improvement nor degradation after annealing for 60 s at 600°C. All the metallization schemes degrade above 600°C; however, Re showed marked improvement at 800°C for 60 s, returning to the as-deposited condition. The same metals were evaluated for long times at 425°C and 550°C. Although the commonly used Ni/Au contacts did not provide the lowest reverse currents among the metals tested, they do provide great stability at either temperature for at least 4 weeks. Rhenium exhibits improvement with respect to reverse currents after long times at 425°C, whereas most other contacts either degrade or remain stable. Materials characterization of the contacts will also be presented.

10:40am **EM-ThM8 Compositional Shift in Al@sub x@Ga@sub 1-x@N Induced by Reaction with Metallic Thin Films*, B.A. Hull,*** *E.D. Readinger, S.E. Mohney,* The Pennsylvania State University*; U. Chowdhury, R.D. Dupuis,* The University of Texas at Austin

The increasing use of AlGaN in group III nitride devices calls for further advances in our understanding of the chemistry of contacts to this alloy semiconductor. Interfacial reactions between the metals Ni, Pd or Au and Al@sub x@Ga@sub 1-x@N (0.15 < x < 0.6) have been studied for annealing temperatures of 250 to 900°C. X-ray photoelectron spectroscopy indicates that the Al to Ga ratio within the Al@sub x@Ga@sub 1-x@N directly beneath the contact metal increases, in some cases dramatically. Elemental profiles across the interfaces of annealed Ni/Al@sub 0.47@Ga@sub

0.53@N samples obtained by scanning transmission electron microscopy confirm the Al-enrichment near the interface. The Al-enrichment is consistent with thermodynamic modeling, which indicates that the AlGaN composition is favored to shift towards the more stable of the two binary nitride components (AlN). Less severe annealing conditions result in smaller compositional shifts; however, a very narrow annealing temperature range (750°C to 825°C) was required to induce extensive compositional shifts (greater than 5% increase in x), regardless of the initial Al@sub x@Ga@sub 1-x@N composition, indicating that extensive reaction is limited by the slow diffusion of Ga and Al within the AlGaN rather than the thermodynamic driving force for reaction. These compositional shifts can be expected to significantly impact the electrical properties of contacts annealed at high temperature due to the strong dependence of the band gap and Schottky barrier height on the AlGaN composition. We have correlated these reactions to the electrical characteristics of annealed ohmic contacts to p-type AlGaN as well as the thermal stability of Schottky contacts to n-type AlGaN.

11:00am **EM-ThM9 Low Temperature Chemical Vapor Deposition and Characterization of Ultra-thin Ruthenium for Copper Diffusion Barriers in ULSI Interconnects***, **Q. Wang**, Y.-M. Sun, D. Gay, J.M. White, J.G. Ekerdt,* University of Texas at Austin

Ultra-thin ruthenium (Ru) films covering Ta were investigated as part of a Cu diffusion barrier with enhanced adhesion of Cu that potentially enables seedless Cu plating on the barrier surface in ULSI interconnect processes. A low temperature thermal chemical vapor deposition (CVD) of ultra-thin Ru films on Ta and SiO@sub 2@ surfaces using ruthenium carbonyl [Ru@sub 3@(CO)@sub 12@] as a precursor was developed. Films deposited at substrate temperatures between 423 and 593 K were characterized using in-situ X-ray photoelectron spectroscopy (XPS), atomic force microscopy and in-situ four-point probe resistance measurements. A pure Ru ultra-thin film with low resistivity of ~50 µ@Ohm@@super .@cm was deposited without any reactive gas at temperatures as low as 423 K. In-situ ion scattering spectrometry and Ta 4f XPS peak attenuation indicated that the minimum thickness to form a continuous Ru film on Ta is ~2.5 nm. The pure Ru film also showed good thermal stability at elevated temperatures (up to 593 K). This Ru film also inhibited oxidation of the Ta film when the sample was exposed to air. Compared with poor wettability of Cu on Ta, only ~0.3 nm of Cu fully covers Ru indicating excellent wetting.

11:20am **EM-ThM10 Evaluating Ruthenium Thin Film Deposited on Silicon as a Directly Plate-able Cu Diffusion Barrier***, **O. Chyan**,* University of North Texas*; T.G. Hurd,* Texas Instruments*; R.M. Wallace, M.J. Kim, R. Chan, T. Arunagiri,* University of North Texas

Tantalum (Ta) and tantalum nitride (TaN) bilayer diffusion barrier is currently used in the fabrication of 130 nm integrated circuits to ensure the electrical integrity of the copper interconnects. Thin Ta/TaN are too resistive to plate Cu effectively, additional Cu-seed layer is deposited on Ta/TaN to carry the required current for copper electrofill. However, the Cu-seed/Ta/TaN tri-layer configuration will encounter severe scaling difficulties at the 45 nm node where ultra-thin barrier is need to minimize effects on interconnect resistivity. In this paper, we explore using ruthenium (Ru) as a new Cu diffusion barrier to afford direct Cu plating without the additional Cu-seed layer. Ru is an air stable transition metal with high melting point (2310 C) and is nearly twice as thermally and electrically conductive as Ta. More importantly Ru, like Ta, shows negligible solid solubility with Cu even at 900 C. The preparation and interfacial characterization of Cu thin film on both Ru metal surface and Ru thin film (<10 nm) sputtered on silicon wafer substrate will be discussed. Both dry (magnetron sputtering) and wet (electrodeposition) preparation routes were employed to deposit Cu on Ru. We will present un-published results that demonstrate efficient Cu plating (over 95% efficiency) was achieved on a ~8 nm an ultra-thin film of Ru metal deposited on silicon wafer. The nucleation and growth of Cu deposited layer on Ru was studied by the current transient techniques. The Cu deposited Ru thin film samples (Cu/Ru) were characterized by XPS, SEM, AFM. XRD and SIMS depth profiling. The observed direct Cu-plating on the ultra thin Ru film with excellent adhesion and the effective barrier performance properties based on SIMS depth-profiling and sheet resistance measurements underscores the potential of Ru as an effective direct plate-able Cu diffusion barrier for the advanced 65 and 45 nm nodes.

11:40am **EM-ThM11 ZrB@sub 2@ Diffusion Barriers: Conformal CVD Below 400 °C***, **E.J. Klein**, D.-Y. Kim, S. Jayaraman, G.S. Girolami, J.R. Abelson,* University of Illinois at Urbana-Champaign

Transition metal diborides are classified as "metallic ceramics" due to their high mechanical hardness, chemical stability, melting temperature > 3000 °C and low electrical resistivity. This combination of properties makes them attractive as diffusion barrier materials for the contact metallization in next-generation microelectronics or to wide bandgap semiconductors. We report the low temperature and fully conformal chemical vapor deposition of ZrB@sub 2@ thin films with essentially bulk properties. The ZrB@sub 2@ films are deposited at substrate temperatures of 200-500 °C using the single-source precursor Zr(BH@sub 4@)@sub 4@ and a concurrent flux of atomic hydrogen produced by a remote hydrogen plasma source. The films have a B/Zr atomic ratio of 2 and electrical resistivity < 40 µm@ohm@-cm; those produced at < 400 °C appear amorphous in X-ray diffraction. By contrast, films grown without the use of atomic hydrogen are B-rich, oxidize rapidly in air, and have high resistivity; these problems were typical of previous attempts to deposit ZrB@sub 2@ films reported in the literature. In this work, we study the diffusion barrier characteristics of ZrB@sub 2@ by annealing a sandwich structure of evaporated Cu (50 nm) / amorphous ZrB@sub 2@ (20 nm) / c-Si(100) [both n- and p-type]. For various annealing temperatures, we report the contact resistivity, stress, and micromorphology. Initial results show that no Cu diffuses into Si during annealing up to 650 °C for 30 minutes; the onset of Cu in-diffusion correlates with the appearance of crystalline X-ray diffraction peaks for ZrB@sub 2@. We will discuss the failure mechanism of the barrier material.

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