ALD Applications
Room 116-118 - Session AA2-MoA

Memory Device & Materials II
Moderator: Ji-Hoon Ahn, Korea Maritime and Ocean University

4:00pm **AA2-MoA-11 Effects of Fluorine in ALD W on Dielectric Properties**, ***Hyung Chul Kim***, *S Lee, H Cho, S Jin,* SK Hynix, Republic of Korea **INVITED**

Recently, it has been recognized that both achieving low resistivity at the gate electrode and suppressing poly-Si gate depletion are key factors for developing deep submicron metal–oxide–semiconductor field effect transistors (MOSFETs). The tungsten (W) metal gate electrode is a good candidate for solving simultaneously the problems mentioned above. However, it has been known that pure tungsten gate is unstable when it is deposited on the SiO_2 and that fluorine (F) diffusion into SiO_2 during the deposition and annealing process causes many undesirable effects . Little is known about the effect of the impurity present in the metal on the properties of the oxide . In this paper, we show the changes of the capacitance equivalent thickness (CET) by the F in atomic layer deposition (ALD) W on the oxide in the W / barrier metal / oxide / Si metal oxide semiconductor capacitor (MOSCAP) . The CET increased by 4 ~ 5 Å in ALD W compared to PVD W, and the change of oxide by F was confirmed. As the barrier metal thickness increases, the CET decreases. Also when the RTA proceeds after the W deposition, the CET increases . F reacts with SiO_2 in Al_2O_3/SiO_2 stack to increase CET. The SiO_2 reacted with F makes a defect source inside SiO_2, leading to the increase of the frequency dispersion and the leakage current. The results of this study can be usefully used as the basic data for metal development and oxide reliability in DRAM and Flash devices.

4:30pm **AA2-MoA-13 Low Temperature Atomic Layer Deposition of Ru for Copper Metallization**, *A Mane,* ***Yan Zhang,*** Argonne National Laboratory*; A Kumar, J Allgair,* BRIDG*; J Hryn, J Elam,* Argonne National Laboratory

Contact metallization in large-scale semiconductor devices such as logic, memory, MEMS, and SoC using 2.5D and 3D interposers requires a high quality and conductivity metal barrier/seed layer for subsequent metal electroplating. Ruthenium metal has a bulk resistivity of 7.1 μΩ cm, a work function of 4.7 eV, and a low solid solubility with strong adhesion to Cu, making Ru an attractive contact metal barrier metal or seed layer for Cu electroplating. There have been numerous reports of Ru ALD using a variety of precursors. However, technical challenges remain including the need for high growth temperature, very long nucleation delay, and the use of plasma that limits Ru conformality in high aspect ratio features. Currently, there is a strong desire and demand for 3D-devices where high quality, uniform, and conformal metal growth on high aspect ratio structures for ultra largescale integration (ULSI) process flow including for 2.5D and 3D interposer substrates creation.

Here we have developed a low temperature (200°C) Ru atomic layer deposition process using $Ru(DMBD)(CO)_3$ and O_2 precursors. To enhance the Ru nucleation and growth, especially at low temperature, we performed low temperature Pt ALD using $Pt(MeCp)Me_3$ and O_2 to deposit a sub-monolayer Pt seed layer that greatly accelerates the subsequent Ru nucleation. High quality Ru films were deposited on a variety of substrates including Si(100), fused silica, Al_2O_3 and TiN. The ALD Ru films were uniform across the 18" deposition zone of our tubular ALD reactor. Thin Ru films were characterized by XPS, SEM, TEM, four point IV measurements, XRD and XRF. We have also performed Cu electroplating on the ALD Ru layers and found that the Ru films deposited using the Pt seed layer exhibited excellent Cu electroplating. Here we will present details of the Ru ALD and Cu electroplating.

4:45pm **AA2-MoA-14 Conformal Growth of Low-resistivity Ru by Oxygen-free Thermal Atomic Layer Deposition**, ***Guo Liu,*** *J Woodruff, D Moser,* EMD Performance Materials

Ru has been widely investigated as an alternative material for metallization applications in semiconductor devices to replace the Co adhesion layer or as a filling material to replace Cu without the need for a barrier layer. ALD deposition of low resistivity Ru is typically achieved using O_2 as the co-reactant or by plasma enhanced ALD using N_2/H_2 or NH_3 in an oxygen-free process. However, for certain semiconductor applications, the strongly oxidizing O_2 co-reactant can cause damages to other layers especially metal films, while a PEALD process has limited capability for step coverage. An oxygen-free thermal ALD process for Ru would be desirable. Current oxygen-free thermal ALD processes for Ru generally suffer from low growth rate and high resistivity problems due to high impurity levels and/or low film density because of limited reactivity of common O_2-free co-reactants with most Ru precursors below their thermal decomposition temperatures.

In this work, we present an oxygen-free thermal ALD process that can deposit low-resistivity Ru thin films down to a few nm thick with a short nucleation delay of less than 30 cycles as shown in Fig. 1. The methods include ALD growth of a ruthenium film at lower temperatures using an oxygen-free co-reactant and post-deposition annealing at higher temperatures. The deposition step was carried out in the temperature range of 150-250°C using a thermally stable high vapor pressure precursor, dimethylbutadiene ruthenium tricarbonyl or $(DMBD)Ru(CO)_3$. The annealing step was performed at 300°C or higher in an oxygen-free atmosphere. The deposition and annealing conditions have been optimized for high growth rate and low resistivity. Under optimal deposition and annealing conditions, low resistivity of about 20 μΩ-cm comparable with the O_2 ALD process of the same precursor (1) has been achieved. Conformal step coverage has also been demonstrated as shown in Fig. 2.

References:

(1). Dustin Z. Austin, Melanie A. Jenkins, Derryl Allman, Sallie Hose, David Price, Charles L. Dezelah, and John F. Conley, Jr.Chem. Mater., **2017**, *29* (3), pp 1107–1115.

5:00pm **AA2-MoA-15 Plasma Enhanced Atomic Layer Deposition of Nickel and Nickel-based Alloy Thin Films for High-quality and Thermally Stable Nickel Silicide**, *S Kim,* ***Shunichi Nabeya,*** Yeungnam University, Republic of Korea

Metal silicides are silicon compounds with metals, and they have low resistivity like metals as well as good compatibility with Si and metals. So, metal silicides, which have been formed by metal deposition on Si followed by post silicidation annealing, have been used for contact materials in Si devices. $TiSi_2$ have been widely used for contacts, however NiSi and $CoSi_2$ are applied to sub-100 nm Si devices since $TiSi_2$ shows narrow line width effect that is increase in $TiSi_2$ resistivity with decreasing linewidth. In order to overcome limitations of current Si devices in downscaling, emerging nanodevices have been intensively studied, and their structures are moved from 2D planar to 3D structure. So, the schemes of contact fabrication used for 2D devices are changed in 3D emerging nanodevices, and conformality of metal thin films is the most important requirement to be achieved. In view of this, ALD is a good alternative to conventional PVD techniques for fabricating the silicide contact. Earlier, there are few reports on nickel deposition by thermal ALD process due to the lack of suitable Ni precursors for it [1, 2]. Though ALD of nickel oxide processes are relatively easy to develop, a rather complex step is needed to obtain nickel silicides from this oxide. In our previous research, we successfully obtained metallic Ni film by using thermal ALD process using a Ni metalorgarnic precursor and H_2 or NH_3 molecules as reactants. One drawback of thermal ALD Ni process is that much amount of impurities of O and C are included in as-deposited film, leading to a relatively high resistivity of ~1700 μΩ-cm and a post annealing process at 480˚C was needed to obtain high-quality Ni film. In order to obtain NiSi with a simpler process, it is necessary to realize a high-purity Ni film by ALD. Generally, plasma enhanced ALD (PEALD) is a better method for obtaining high-quality metal thin films as compared to the thermal ALD. In this study, PEALD Ni processes are developed by using various reactants including N_2, H_2 or NH_3 plasma. The properties of PEALD-Ni films depending on the reactants used are compared using various analysis such as XRD, XPS, 4-point probe, TEM etc. We also evaluate the silicidation behavior of PEALD-Ni films deposited with optimized condition. Finally, Ni-based alloy films where a noble metal is incorporated in them are also prepared using PEALD for improving the thermal stability of the nickel silicide film.

Acknowledgement

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References

[1] J. Chae, H.-S. Park, S.-W. Kang, Electrochem. Solid State Lett. 5 2002 C64-66.

[2] K.-W. Do, C.-M. Yang, I.-S. Kang, et al., Jpn. J. Appl. Phys. 45 2006 2975-2979.

5:15pm **AA2-MoA-16 Ternary Thin Film Alloys of Ti-Si-N as Low Resistance Diffusion Barrier for Memory Applications**, ***Somilkumar Rathi,*** *J Mack, Z Karim, N Mukherjee,* Eugenus, Inc.

The rapid advances in memory technology, coupled with decreasing feature sizes and increasing aspect ratios, have imposed stringent

requirements on the physical and electrical properties of metal-to-semiconductor interfaces. This has resulted in several integration and material challenges for low-resistance contacts and diffusion-barrier films. Reactively-sputtered titanium nitride (TiN) is widely used as diffusion-barrier layer due its high thermal and chemical stability, low electrical resistivity, and process maturity. However, the columnar and polycrystalline grain structure provides a pathway for diffusion during higher-temperature anneal steps. This undesirable effect, which leads to device degradation and failure, has led to the search for alternative films. In this work, we report recent advancements on the amorphous ternary alloy films composed of titanium, silicon and nitrogen (TSN), an excellent alternative to TiN films. These TSN films were grown using Atomic Layer Deposition (ALD) technique on the Eugenus 300mm QXP commercial reactor. In order to understand the feasibility and tunability for a variety of applications, the films were grown over a wide temperature window of 400-620°C and using several different chlorine-based Si precursors. Film thickness and silicon content were varied and corresponding electrical characterization was performed. X-ray photoelectron spectroscopy and Rutherford Back Scattering techniques were utilized for compositional analysis. The results indicate that ALD-based TSN films are not only high volume manufacturing compatible, but have excellent mechanical, thermal and electrical properties and are scalable to the next technology nodes.

5:30pm **AA2-MoA-17 Atomic Layer Deposition of Mixed Phase TiN_xC_y using Highly Reactive Substituted Hydrazines and Tetrakis(dimethylamido)Titanium***, **Jaime DuMont**, M Knez,* CIC nanoGUNE, Spain

Tribology, in spite of being one of the most traditional industrial sectors, is in great demand of innovation. At over 6% of the worlds GDP, corrosion and wear represent significant expenses in the global economy and yet they seldom receive the attention they require. The development of protective coatings that can suppress both factors at the same time is therefore of great economic interest. Among the materials which have demonstrated superior hardness, strength and chemical stability are titanium nitride (TiN) and titanium carbide (TiC). The protective capability of these materials is not, however, without limitation. When exposed to high temperature applications or high-speed machining these coatings can become brittle and easily fracture because of poor resistance to high temperature oxidation. Inclusion of carbon atoms in the TiN lattice has been shown to substantially increase the hardness and lower the friction coefficient. These beneficial properties are a result of the TiN_xC_y composition and can be adjusted by controlling the material's C-N ratio to a precise level. When tuned correctly, TiCN films can display anti-wear capabilities and higher hardness that far surpass those of TiN and TiC alone.

Next generation TiN_xC_y coatings will require a deposition strategy that 1) functions at temperatures low enough to keep critical tool dimensions within tolerance 2) circumvents corrosive hydrogen halide by-products 3) maintains a strong chemical binding of the coating to the substrate and 4) can be easily scaled for large-area applications. Atomic layer deposition is a technique primed to meet these requirements. In this work we develop a new low-temperature, halide-free, mixed phase TiN_xC_y thermal atomic layer deposition (ALD) process. We exploit the high reactivity of substituted hydrazines, including tertiary butyl hydrazine (TBH) and monomethylhydrazine (MHH), together with the amide based precursor, TDMATi. These superior precursor combinations circumvent the corrosive hydrogen halide by-products of conventional metal nitride ALD processes, provide the required C and N atoms and further lower the deposition temperature through transamination-like exchange reactions. We will discuss process parameters (substrate temperature and precursor exposure times) as well as ex situ characterization studies (X-ray diffraction (XRD) and reflectivity (XRR) and scanning electron microscopy (SEM)) of the TiN_xC_y materials deposited as well as their effectiveness as next generation protective coatings.

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