ALD Fundamentals
Room Hall 3A - Session AF2-WeM

Growth and Characterization: Low Temperature ALD

Moderators: John Conley, Oregon State University, **Henrik Pedersen**, Linköping University, Sweden

10:45am **AF2-WeM-12 Low-Temperature ALD of Metallic Cobalt for 3D Structures**, ***Mathias Franz***, *L. Kaßner,* Fraunhofer ENAS, Germany; *C. Thurm,* University of Technology Chemnitz, Germany; *X. Hu,* Fraunhofer ENAS, University of Technology Chemnitz, Germany; *M. Daniel,* scia systems GmbH, Germany; *F. Stahr,* Forschungs- und Applikationslabor Plasmatechnik GmbH, Germany; *S. Schulz,* Fraunhofer ENAS, Center for Microtechnologies (ZfM), University of Technology Chemnitz, Germany

Atomic Layer Deposition (ALD) of metallic films is a broad and ongoing topic of research. The conformal deposition of metallic cobalt is relevant for modern interconnects[1], seed layers for electroplating[2], and antibacterial coatings[3]. One of the essential process parameters is the deposition temperature. Here, we present the development of a low temperature ALD process for the deposition of metallic cobalt on integrated 3D structures in silicon substrates.

We base our process development on a set of previously developed precursors of the form $[Co_2(CO)_6(RC{\equiv}CR')]$ published by Georgi et al.[4]. We evaluated a set of these precursors for ALD using density functional theory (DFT) calculations. According to these calculations the precursor $[Co_2(CO)_6(HC{\equiv}CC_5H_{11})]$ was identified as the most favourable precursor for deposition via ALD. It adsorbs with remaining ($HC{\equiv}CC_5H_{11}$) group which can be easily removed by use of activated hydrogen. The process development was done on a novel *scia Atol 200* reactor. The depositions took place on 200 mm Si wafers with a preliminary SiO_2 layer of 100 nm thickness. The precursor was evaporated via the bubbling method. A full ALD cycle consists of a cobalt precursor pulse, an Ar purge, an H_2 plasma pulse, and a second Ar purge. The deposited cobalt films were analysed by *in-vacuo* ellipsometry to determine in-line the film growth rates. Figure 1 shows the growth per cycle in the temperature range from 35 °C to 125 °C showing the ALD window for this process within the range of 50 °C to 110 °C.[5] The process was optimised regarding pulse and purge duration times to ensure stable saturation conditions. *Ex situ* measurements with XPS confirm that cobalt is in metallic state. The optimised ALD process has been applied to silicon trench structures. Figure 2 shows a SEM image of cobalt deposited to the sidewalls of a silicon trench.

We demonstrated the successful development of a low temperature ALD process for metallic cobalt. This process was successfully applied to 3D structures.

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References

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[2] Liu *et al.*, doi: https://doi.org/10.1149/1945-7111/ac862d

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11:00am **AF2-WeM-13 Towards Deposition of Metallic Molybdenum Films from Molybdenum Hexacarbonyl in a Process Involving an Intermediate ALD Step and Subsequent Reduction**, ***Kees van der Zouw***, *M. Sturm, T. Aarnink, A. Kovalgin,* University of Twente, the Netherlands

Atomic layer deposition (ALD) is expected to be essential for future CMOS back-end-of-line (BEOL) applications. Due to its electrical and thermal properties, molybdenum (Mo) is among the metals that have gained significant interest [1]. The research into ALD of metallic Mo has been limited to halide-based processes [2-5], in which corrosive byproducts like hydrogen fluoride or hydrogen chloride can be formed. A process for Mo ALD from a metalorganic precursor remains to be identified. This work investigates the feasibility of Mo ALD using molybdenum hexacarbonyl [$Mo(CO)_6$] as the precursor.

Films of metallic Mo were produced by the atomic hydrogen (at-H) reduction of ALD MoO_3 films obtained from $Mo(CO)_6$ and ozone (O_3). The reduction of MoO_3 with molecular hydrogen (H_2) at temperatures beyond the BEOL limit is well-known and commercially utilized [6]. This work investigated the feasibility of bringing the temperature well below the BEOL limit by replacing H_2 with at-H.

First, a reliable ALD process for MoO_3 growth was developed by determining an appropriate ALD cycle (Fig. 1) and process temperature (Fig. 2). According to spectroscopic ellipsometry, the resulting films showed a 2-3% film thickness non-uniformity across the 100 mm wafer (Fig. 3). X-ray photoelectron spectroscopy (XPS) confirmed the MoO_3 stoichiometry (Fig. 4a). The as-deposited MoO_3 films were then exposed in situ to a steady supply of (hot wire generated) at-H for 30 min at 150 °C. A shift in the peak position of the Mo3d doublet from 234/237 eV to 228/231 eV showed a transition from an oxidized to a metallic state of Mo (Fig. 4b). The existence of satellite peaks corresponding to Mo in a non-zero oxidation state indicated the need to increase the reduction temperature. Another sample was reduced for 30 min at 350 °C, significantly lowering the satellite peak intensity (Fig. 4c). Performing angle-resolved XPS measurements on the samples revealed a gradual increase of the metallic Mo phase at the surface compared to that in the bulk (Fig. 5).

Implementing super cycles by introducing an at-H pulse during each ALD cycle resulted in highly oxidized films, indicating the importance of applying a final at-H reduction step to obtain metallic Mo films. Similarly, an ALD cycle that excluded O_3 oxidation but solely included at-H reduction resulted in a non-self-limiting deposition of Mo films with significant shares of carbon (15-25 at%) and oxygen (10-20 at%). Based on these findings, we conclude that the formation of pure Mo from $Mo(CO)_6$ below the BEOL limit requires an oxidation route to remove carbon efficiently; the intermediately formed MoO_3 can then be reduced in at-H to metallic Mo.

11:15am **AF2-WeM-14 Growth of Metallic Ru Film by Oxidant-Free Atomic Layer Deposition Below 100 °C**, ***Kyeongmin Min***, *H. Lee,* Incheon National University, Republic of Korea; *C. Nguyen,* Incheon National University, Viet Nam

Ru is one of the very well-known metals in atomic layer deposition (ALD) researches because of its potential applications in the interconnect technology of Si devices. The main drawback of Ru ALD processes reported so far, however, is the oxidant counter reactants, such as O_2, O_3, and H_2O. In ALD, most of the noble metals, including Pt, Ir, and Ru, could be deposited by using oxygen counter reactant through their combustion reactions, so the oxidation of substrate underneath of the noble metal films could not be avoidable. The oxidation of substrate increases contact resistance of Ru, so it is not desirable in the interconnect applications. In this study, we deposited a high purity Ru film through thermal H_2 plasma ALD at low deposition temperature below 100 °C without any oxidant counter reactants. The thermal plasma was generated by exposing the H_2 counter reactant gas to a filament with high temperature over 1600 °C. By the high thermal energy of the filament, the H_2 gas molecules are dissociated into high energy radicals, and the radicals play an important role as a reactant in the thermal plasma ALD process. A high purity and conformal Ru film was obtained, and the resistivity of Ru film was 25 μΩcm. The metallic Ru films could be formed even at the low temperature, 80 °C. The resistivities of Ru films were X-ray photoelectron spectroscopy (XPS) and auger electron spectroscopy (AES) showed very low impurity levels below 5% in carbon and oxygen spectra. From the results of this work, we believe that the thermal plasma ALD could be widely applied to many applications which have critical issues in the oxidation of bottom layer and increase of contact resistance.

*Author for correspondence: hbrlee@inu.ac.kr

11:30am **AF2-WeM-15 Unveiling the Effect of the Starting Precursor on $Ge_2Sb_2Te_5$ Atomic Layer Deposition**, ***Jyoti Sinha***, KU Leuven, IMEC Belgium; *J. Innocent, A. Illiberi, M. Givens,* ASM, Belgium; *L. Nyns, A. Delabie,* IMEC Belgium

Chalcogenide materials like $Ge_2Sb_2Te_5$ (GST) are widely studied for application in memory devices [1]. To address the material needs resulting from the architectural device challenges within storage class memory (SCM), atomic layer deposition (ALD) has emerged as a prominent solution. Pore et al. have demonstrated a low temperature ALD process for GST using $GeCl_2.C_4H_8O_2$, $SbCl_3$, and $Te[(CH_3)_3Si]_2$ as precursors [2]. This process comprises the two binary ALD processes of GeTe and Sb_2Te_3 in a specific ratio to target the desired $Ge_2Sb_2Te_5$ composition, using either $GeCl_2.C_4H_8O_2$ or $SbCl_3$ as the first precursor pulse. This first pulse could affect the final film composition, and as such affect device performance.

In this work, we therefore study how the starting precursor influences the GST growth behavior and layer composition when deposited on SiO_2. The deposition on the SiO_2 substrate is initially Ge-rich, irrespective of the

starting precursor, and gradually evolves to the desired 2:2:5 Ge:Sb:Te ratio when the thickness increases. The ideal composition is reached after 36 cycles. The interfacial Ge content is slightly higher when the GST ALD process starts with a $GeCl_2.C_4H_8O_2$ reaction as compared to starting with a $SbCl_3$ reaction, according to X-ray Fluorescence (XRF).

The chemical reactions at the GST/SiO_2 interface are investigated more thoroughly through chemisorption experiments, where we apply a single precursor reaction and measure the surface concentration of either Ge, Te or Sb ex-situ by means of total reflection XRF (TXRF). The results indicate that $GeCl_2.C_4H_8O_2$ has a higher reactivity towards SiO_2 than $SbCl_3$, as the concentration of Ge is ~4 times higher than the concentration of Sb. Almost no Te was observed after a single $Te[(CH_3)_3Si]_2$ reaction, indicating very low reactivity. We also investigate the subsequent Ge, Te, and Sb precursor reactions after a first Sb, Te, or Ge precursor reaction on SiO_2 and analyze the results assuming that only ligand exchange reactions take place, according to the model in [3]. Based on the concentration of Ge, Te, and Sb, we propose that Ge could react with two surface hydroxyl groups on the SiO_2 surface. On the other hand, due to the lower reactivity of $SbCl_3$, we propose that there are still unreacted surface hydroxyl groups after the $SbCl_3$ reaction that can react with $GeCl_2.C_4H_8O_2$ during the next pulse. This model leads to an overall Ge-rich GST at the interface, irrespective of the starting precursor.

References:

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11:45am **AF2-WeM-16 Atomic Layer Deposition Equipment Vendors Market and Technology**, ***Taguhi Yeghoyan,*** Yole Group, France

From many years, Atomic Layer Deposition (ALD) and Atomic Layer Etch (ALE) have enabled subsequent generations of logic and memory. In 2024, ALD and ALE is again indispensable to drive innovation across patterning approaches, architecture change for transistor (FinFET to Gate All Around) and memory (DRAM to 3D DRAM or 3D NAND layer increase) as well as improve the performance of specialty devices (CMOS Image Sensors, BCD Power Si devices, SiC devices, integrated RF devices) .

These advancements are enabled by ALD and ALE equipment vendors who provide complete solutions that consider precursors, substrates, and processing problematics. Their efforts generate a collective 2023 market size of 3.3USDB for thermal and plasma equipment, representing 13% of the total deposition Wafer Fab Equipment (WFE) market. With further ALD and ALE needs, we expect this number to grow to 4.9USDB in 2029 with a 4.9% CAGR23-29, outperforming the overall WFE.

Via the market research, we aim to lay out the landscape of the industrial ALD and ALE equipment providers worldwide and highlight their innovative solutions proposed, which lead to specific market shares. Moreover, we draw a market forecast driven by mentioned CapEx hungry devices. Finally, we breakdown the market size to different device applications, wafer size, thermal and plasma ALD technologies.

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