論文題目　　　　　Process development of Hot-Wire-assisted ALD
　　　　　　　　　dedicated to High Quality Ni/Ru Thin Films for
　　　　　　　　　Microelectronic Devices

　　　　　　　　　(微細電子デバイス用高品質Ni/Ru薄膜形成を目指し
　　　　　　　　　たホットワイヤーALDプロセスの開発)

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　This dissertation focused on high quality nickel and ruthenium thin films deposition that can be applied for ULSI and memory devices using hot-wire-assisted atomic layer deposition (HW-ALD). To achieve high quality Ni and Ru films, I have set 4 steps; (1) design of HW-ALD including precursor and reactant selection, (2) nickel deposition and its kinetic studies, (3) application of the kinetics to step coverage analysis, (4) ruthenium deposition under non-oxidization ambient, and its electrical property evaluation. By realizing each step, I have demonstrated successful high quality Ni and Ru deposition by HW-ALD based on the kinetics studies and electrical property analysis.

　Ni and Ru were selected as representative materials, because it will be used and promising for contact in metal-oxide-semiconductor field-effect transistor (MOSFETs), electrode in metal-insulator-metal (MIM) capacitor, and seed layer in Cu interconnect. With the ULSI and memory devices shrinking, their structure have changed from two-dimensional to three-dimensional structure and the required aspect ratio of features tends to be more than 5. There are several requirements for contact, gate electrode and nucleation layer fabrication process; (1) highly-purity deposition, (2) conformal deposition on high-aspect-ratio features, (3) damage-free process to avoid the plasma damage to the underlayer and reliability problem, and (4) low process temperature to avoid thermal damage to logic circuit.　In these senses, process development of Ni and Ru deposition is

necessary for various microelectronic devices. HW-ALD, which will be discussed in detail, is the most promising method, since it allows to achieve highly-purity, conformal Ni/Ru films and avoid the plasma/thermal damage.

In the HW-ALD, the metallocene (nickelocene, $NiCp_2$, and ruthenocene, $RuCp_2$) and NH_2 radicals were selected as the precursor and reactant. The hot wire was used to decompose the NH_3 gas, instead of substrate temperature and plasma. Similar to hot-wire chemical vapor deposition (HW-CVD), HW-ALD produces no plasma damage and has low deposition temperature ($<250^{\circ}C$). Moreover, the process is not limited to a specific substrate size, and the decomposition efficiency of the NH_3 gas is high. For the precursor and reducing agent selection, metallocenes was chosen as the precursor because they are oxygen-free/halogen-free, easy to be handled due to thermal stability, and less toxic. NH_2 radicals were chosen as the reactant because it efficiently reduces the metallocenes.

As it is difficult to form the high pure Ni films using thermal ALD and PE-ALD, the HW-ALD was used to examine the feasibility of highly-purity Ni deposition using nickellocene and NH_3. NH_2 radicals produced by cracking the NH_3 with the aid of HW. After deposition, highly pure and low resistive Ni films were acquired by HW-ALD, at low deposition temperature of $250^{\circ}C$. Negligible amount of nitrogen, oxygen or carbon contamination was detected by XPS at a sensitivity limit of 0.10 at%, even though I used NH_2 radicals as the reactant and nickelocene as the precursor. The lowest resistivity of Ni film was about 28 $\mu\Omega$ cm without a post-annealing. There was no change in resistivity for NH_3 feeding period longer than 20 s, where the GPC, material composition, and properties saturated. According to the total cycles of incubation period, it suggested that 10 nm continuous nickel film could be formed by HW-ALD on Si and SiO_2. These results confirmed the advantage of HW-ALD, compared with thermal ALD and PE-ALD.

For the in-depth study of HW-ALD, its kinetics was analyzed using Ni deposition. A Langmuir-type model was defined in this research and applied for the kinetic study. Unlike remote-plasma-enhanced atomic layer deposition, HW-ALD does not lead to plasma-induced damage. This is a significant advantage, because we can supply sufficient NH_2 radicals to deposit high-purity metallic films by adjusting the distance between the hot wire and the substrate. NH_2 radicals have a short lifetime, and it was important to use a short distance between the radical generation site and substrate. Furthermore, the impurity content of the nickel films was independent of the deposition temperature, which is evidence of the temperature-independent nature of the reaction between NH_2 radicals and adsorbed precursors. The relationship between the saturated GPC and deposition temperature can be explained by the steric hindrance and the sticking probability of physisorption. The gas-phase flux of NH_2 radicals near the surface was reduced considerably as the FSD

increased due to the finite lifetime of the NH_2 radicals, which react with other species before arriving at the surface. After roughly calculation, the value of the reaction probability of NH_2 radicals, η', was calculated to be about 1.6×10^{-5} in the Ni HW-ALD deposition, which has the similar range of some reactive gas, such as ozone.

In recent years, there is some reports on Ni films using PE-ALD, but they could not achieve conformal deposition on high-aspect-ratio (HAR) features (AR>5). Therefore, the HW-ALD was used to examine the feasibility of conformal Ni deposition on HAR features. Similar to conventional plasma-enhanced ALD processes, conformal deposition was less straightforward for HW-ALD on high aspect-ratio features. The mechanism of HW-ALD was thus investigated focusing on the dependencies of step coverage (SC) on precursor feed period, purge period after precursor supply, deposition temperature, and NH_3 feeding period. The SC was improved by extending the precursor feed period due to realizing enough precursor adsorption at the bottom of features. Two deposition species were found in HW-ALD. At low temperature below 300°C, the two deposition species are physisorbed species and chemisorbed species of precursor, respectively. The sticking probability and contribution of physisorbed species is larger than that of chemisorbed species. At temperature higher than 350°C, thermal decomposition of precursor i.e. "chemical vapor deposition (CVD) mode" dominates the growth, and its sticking probability and contribution change to be larger than that of physisorbed species. Deposition via "CVD mode" led to degraded surface morphology and also reversely affected the SC, suggesting temperature should be below 300°C. Below 300°C, the sticking probability and contribution of physisorption could be reduced to improve the SC by increasing the temperature. Besides, to reduce the physisorption and improve the SC at the low deposition temperature of 250°C, longer purge period was chosen because of the higher desorption rate of physisorbed species, compared with chemisorbed species. Step coverage was also dependent on the amount of supplied NH_2 radicals arriving at the trench bottom. Poor step coverage was closely related to an inadequate amount of NH_2 radicals near the bottom of the trenches, which was mainly caused by its surface loss probability on the Ni surface. However, its value was less than 0.0028, which was small and allowed HW-ALD easily achieve good step coverage of metal films, compared with the PE-ALD. Finally, conformal Ni films were successfully fabricated using HW-ALD at a low deposition temperature of 250°C using a long precursor feed period, long purge period after precursor supply, and long NH_3 feeding period (i.e., a 20/20/30/10 s cycle). The acquired SC was 0.92 and 0.85 when the AR of the trenches was 5 and 9, respectively. These results confirmed the feasibility of conformal meal deposition on HAR features, mainly because of the low surface loss probability of NH_2 radicals on the metal surface, which was different in PE-ALD process.

Previously, despite many papers reported the Ru deposition using thermal ALD and PE-ALD, they suffered from the oxygen contamination in formed Ru films, the oxidization at the interface between Ru film and dielectric, or plasma damage to the underlayer. In this dissertation, I succeeded in depositing ruthenium films by HW-ALD under non-oxidization ambient using ruthenocene and NH_3, respectively. NH_2 radical was generated with the assist of hot-wire and reduced the adsorbed ruthenocene. XPS datas suggest that highly-purity Ru films were achieved at the low deposition temperature of 250^oC. Besides, the effective work function of HW-ALD Ru films were analyzed by C-V measurement. Results using two methods were almost the same and EWF of HW-ALD Ru film was similar to the reported PVD-Ru, which was about 4.85 eV. Generally, the achieved EWF of Ru film was about 5.1 eV using thermal ALD, because the formed film had the oxygen contamination. It suggests that for HW-ALD Ru film, there almost had no oxygen contamination in deposited films and the interface between the Ru and SiO_2 might have almost no RuO_x, because the effective work function of RuO_x was much higher than that of Ru. Therefore, the thermal stability of Ru gated capacitors could be improved using the HW-ALD under the non-oxidation ambient. Furthermore, the similar EWF value of HW-ALD Ru with PVD-Ru confirmed that the acquired HW-ALD was high-purity.

In this dissertation, the deposition processes for Ni and Ru were established by kinetic studies. The formed Ni and Ru films had highly-purity, crystallinity, low electrical resistivity and good step coverage. Numerical simulation based on kinetics study for step coverage analysis of HW-ALD using Ni deposition demonstrated that HW-ALD had good performance of conformal film deposition. Finally, the effective work function of Ru films was calculated and confirmed the high purity of acquired Ru films. The results of this dissertation revealed that HW-ALD has a high potential for Ni and Ru deposition in the three-dimensional device fabrication.