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Rhenium Metal and Rhenium Nitride Thin Films Grown by Atomic Layer Deposition

Jani Hämäläinen,*[a] Kenichiro Mizohata,[b] Kristoffer Meinander,[b] Miika Mattinen,[a] Marko Vehkamäki,[a] Jyrki Räisänen,[b] Mikko Ritala,[a] and Markku Leskelä[a]

Abstract: Rhenium is both a refractory metal and a noble metal that has attractive properties for various applications. Still, synthesis and applications of rhenium thin films have been limited. We introduce here the growth of both rhenium metal and rhenium nitride thin films by the technologically important atomic layer deposition (ALD) method over a wide deposition temperature range using fast, simple, and robust surface reactions between rhenium pentachloride and ammonia. Films are grown and characterized for compositions, surface morphologies and roughnesses, crystallinities, and resistivities. Conductive rhenium subnitride films of tunable composition are obtained at deposition temperatures between 275 and 375 °C, whereas pure rhenium metal films grow at 400 °C and above. Already a 3 nm thick rhenium film is continuous and has a low resistivity of about 90 µΩcm showing potential for applications where also other noble metals and refractory metals have been considered.

The late discovery, complicated extraction from nature, and scarcity of the element have been limiting research and applications of rhenium. Still, rhenium is crucial in super-alloys for jet engines and in catalysis. As an example, Re-Pt catalysts are vital in making lead-free, high-octane petrol.[1] Rhenium has also been applied for ammonia synthesis[2,3] and hydrodenitrogenation,[4] and it is a potential photoelectrocatalyst for reduction of nitrate ions.[5] Rhenium has been suggested for hydrogen evolution reaction (HER) as well but with contradictory results.[6] Notably, Re should perform similarly as Co and Ni in HER, but rhenium oxides are even better and as good as Pt,[6] which is considered to be the most effective HER catalyst. One potential application is the use of rhenium as a liner material in gun tubes as Re coatings outperformed the commonly applied hard chrome plating in vented bomb combustor tests.[7] Microwave resonators have been made using epitaxial Re on sapphire.[8] Re and rhenium nitride barrier layers against Cu diffusion have been studied and found to inhibit Cu/Si interdiffusion and silicide formation effectively.[9,10] As rhenium has been used for preparation of Re/Al-Al_2O_3/Re Josephson tunnel junctions,[11] it could be of interest in superconducting quantum computing and quantum information applications too. Furthermore, 7 nm thick Re gate contacts in Re/HfO_2/Si(100) stacked structures have been previously evaluated[12] to prevent oxygen diffusion up to 500 °C in oxygen-containing atmosphere. For the electrode applications in metal-oxide-semiconductor field-effect transistors (MOSFETs) and various capacitors Re could be an interesting alternative to ruthenium as they have nearly identical work functions (Re 4.72 eV and Ru 4.71 eV). Importantly, Re costs currently substantially less and its annual production is about three times higher than that of Ru.

Rhenium has a rich nitride chemistry. Both crystalline subnitrides and nitrides of rhenium such as Re_3N, Re_2N, Re_3N_2, ReN_2, ReN_3, and ReN_4 have been noted to exist.[13] Rhenium nitrides can be used in several applications, although these have been limited due to the scarcity of the materials. Similar to Re metal, also Re_3N has been used as a catalyst for ammonia synthesis,[2,3] and it is active also for hydrodenitrogenation.[4] Both Re_3N and Re_2N are ultrastiff and hard materials, and in contrast to most other hard materials they also have good electronic mobility.[14] Thus, they could be considered as hard conductors for extreme conditions.

Although rhenium is rare and can be difficult to synthesize, various methods have still been employed to grow particles, powders, thin films, and coatings. These techniques include chemical vapor deposition (CVD),[7,12] chemical vapor infiltration (CVI),[15] pulsed laser evaporation (PLE),[16] electron-beam evaporation,[12] electrodeposition,[5] molecular beam epitaxy (MBE),[8] and magnetron sputtering.[17] Even more limited has been the preparation of rhenium nitrides which have been synthesized by sputtering,[18,19] ion implantation,[20] pulsed laser deposition,[21] and high-pressure solid-state metathesis.[22,23] There is thus still room for introducing new methods for preparing these intriguing refractory/noble metal materials to make them more widely available for various applications using highly controllable methods with moderate deposition conditions.

Atomic layer deposition (ALD)[24,25] has become a crucial industrial technique to deposit thin films and nanoparticles, especially in the semiconductor industry. ALD is similar to CVD as thin films are deposited chemically from a vapor phase, but inherent to ALD is the alternate supply of the precursors and thus the films grow in uniform and conformal manner over large and complex substrates with precise control on film thickness and excellent repeatability. These properties make ALD an unrivaled thin film deposition method for microelectronics and nanotechnology where the dimensions are continuously shrinking and device designs becoming more complex and three-dimensional. This has led into

[a] Dr. J. Hämäläinen, M. Mattinen, Dr. M. Vehkamäki, Prof. M. Ritala, Prof. M. Leskelä
Department of Chemistry
University of Helsinki
P.O. Box 55, FI-00014 Helsinki, Finland
E-mail: jani.hamalainen@helsinki.fi
[b] Dr. K. Mizohata, Dr. K. Meinander, Prof. J. Räisänen
Division of Materials Physics, Department of Physics
University of Helsinki
P.O. Box 64, FI-00014 Helsinki, Finland

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a growing academic and commercial interest in ALD, and an industrially driven necessity to develop new ALD processes and materials. The inherent properties of ALD also provide straightforward scalability in terms of number and size of substrates which narrows the gap between fundamental and applied research, and industry. Fundamental research on ALD process development is still needed to provide new materials, perspectives, and tools for the high-technology applications of the future.

Here we report the deposition of rhenium and rhenium nitride (ReN_x) thin films for the first time by ALD using ammonia as the co-reactant and the same $ReCl_5$ precursor as recently exploited[26] for the ReS_2 ALD. The Re metal growth relies on fully reductive chemistry in contrast to typical noble metal ALD. Simple and robust precursors are used and the growth proceeds via fast saturative surface reactions. Deposition of low resistivity rhenium nitride is also demonstrated by lowering the deposition temperature. These Re and ReN_x ALD processes that do not use oxidizing or oxygen-containing precursors are very attractive for applications where the oxidation of the underlying material must be avoided. Volatile metal halides have excelled in many industrial applications of ALD ranging from electroluminescent displays to gate oxides in microprocessors because of their high-temperature stability, sufficient volatility, and small size of the ligands, *i.e.* high metal content in the compound. That in mind, we report here another simple ALD metal halide process that can be used to deposit thin, conductive films of either metal or metal nitride of tunable composition.

Re and ReN_x thin films were deposited from $ReCl_5$ (99.9 %) and NH_3 (99.9999 %) in a commercial ALD reactor operated under a reduced nitrogen pressure (5–10 mbar). The films were grown on about 5–10 nm thick Al_2O_3 films on top of native oxide covered silicon (100) substrates (5 × 5 cm^2). The solid $ReCl_5$ precursor was sublimed from an open boat inside the reactor at 110 °C and pulsed with inert gas valving. The flow rate of NH_3 was 5 sccm unless otherwise stated. Additional experimental details can be found from the Supporting information.

Thin film growth is successfully obtained pulsing $ReCl_5$ and NH_3 alternately at deposition temperatures above 250 °C (Figure 1). For crystalline rhenium nitride films deposited at 325 and 375 °C (Figure 1b) the growth rate is 0.4–0.5 Å/cycle as determined by x-ray reflectivity (XRR) measurements (Figure 1a). Films deposited at 400 °C and above are metallic Re instead of ReN_x (Figure 1b) according to the grazing incidence x-ray diffraction (GIXRD) patterns and the growth rate decreases to 0.3 Å/cycle (Figure 1a). The film morphology seen in field emission scanning electron microscope (FESEM) images changes distinctively between 375 and 400 °C, i.e. at the same time when the film composition changes from ReN_x to Re (Figure 1c). The film roughness remains about 2–3 nm for the films grown using 1000 cycles as measured by atomic force microscope (AFM).

Reduction of ReN_x to Re at 400 °C and above can be explained by the instability of rhenium nitrides, even if ammonia is used here as a co-reactant. Interestingly Alexander et al.[27] have shown Re_3N to lose close to 90 % of its nitrogen under H_2 atmosphere at 350 °C. That is close to the deposition temperature (400 °C) where the ALD growth of Re begins instead of ReN_x (Figure 1b). The depositions at 450 and 500 °C resulted in defective Re films and the flaking of the film was most dominant at 500 °C. The film flaking at the highest deposition temperatures could be likely avoided by the proper choice of the starting surface. It is noted that despite the flaking the Re films grown at 450 and 500 °C have relatively low film resistivities (Figure 1a) and impurity contents (to be discussed below).

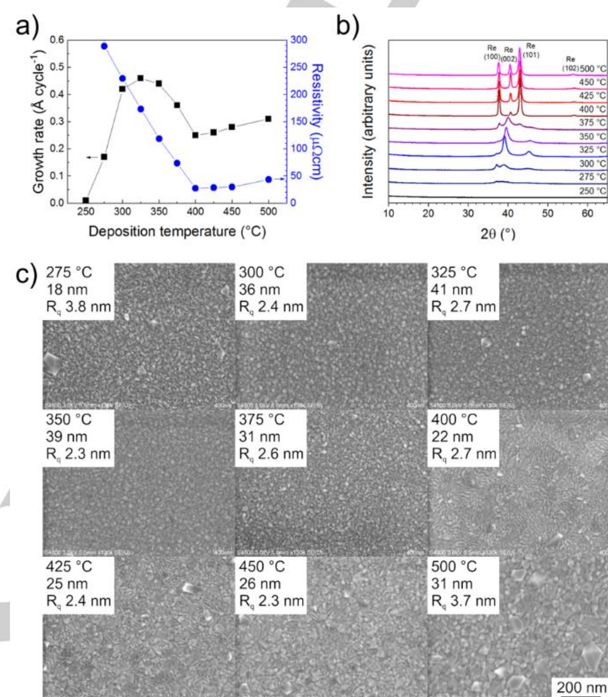

Figure 1. Re and ReN_x films grown on Al_2O_3 films at various deposition temperatures. a) Growth rates (XRR) and resistivities, b) GIXRD patterns, and c) FESEM images with deposition temperatures, film thicknesses (EDX; density corrected by XRR), and surface roughnesses (R_q, AFM). The pulse and purge lengths were 2 s and 1 s, respectively. The total number of deposition cycles was 1000.

As analyzed with time-of-flight elastic recoil detection analysis (TOF-ERDA) the deposited Re (≥400 °C) and ReN_x (<400 °C) thin films are pure (Table S2). The total impurity content of Cl, N, and H in the Re thin films grown at 400 and 425 °C is only about 2 at. %. As the nitrogen content is 1 at. % in all the Re metal films deposited below 500 °C and the films are phase-pure metal in GIXRD (Figure 1b), complete reduction to Re can be concluded. It should be emphasized that this reductive metal ALD process uses one of the simplest metal ALD chemistries in terms of the number of elements and the size of the ligands, *i.e.* only Re, Cl, N, and H are involved in reactions between $ReCl_5$ and NH_3 under reduced N_2 pressure. The N/Re ratios (~0.2–0.5) of the rhenium nitride films grown between 275 and 350 °C are close to the Re_3N (0.33) and Re_2N (0.50) stoichiometries (Table S2).

In the ReN_x films the nitrogen content increases with decreasing deposition temperature (Table S2). The increase in the nitrogen content is accompanied with the increase in resistivity (Figure 1a) and changes in the GIXRD patterns from hexagonal Re to other crystalline materials (Figure 1b). Reliable x-ray diffraction reference patterns for rhenium nitrides are not available, and thus the identification of the ALD grown ReN_x films is limited from the

measured GIXRD patterns. However, the two main peaks in the GIXRD pattern of the $Re_{0.7}N_{0.3}$ film (N/Re ratio 0.37) deposited at 325 °C could be assigned to the (111) and (200) orientations of the cubic $Re_{0.69}N_{0.31}$ (N/Re ratio 0.45; 00-037-0852; "Blank" quality mark where the pattern does not meet the "Star", "Indexed", or "Low-Precision" criteria). The peak around 37° could not be identified with the rhenium nitride reference XRD patterns available. Furthermore, the GIXRD pattern of the $Re_{0.8}N_{0.2}$ film (N/Re ratio 0.19) grown at 350 °C does not show this peak, but the two peaks are close to the reference (111) and (200) orientations found in rhenium nitrides.

Surface x-ray photoelectron spectroscopy (XPS) results are presented in Tables S3 and S4. The XPS analysis corroborate the TOF-ERDA results in that at 400 °C and above majority of the Re on the surface is at an oxidation state 0 whereas below 375 °C other oxidation states dominate (Table S4). The transition from the rhenium nitride to metal films is also seen in the surface N/Re ratios (Table S3) in line with the TOF-ERDA (Table S2) and XRD (Figure 1b) results. The film composition appears to be uniform through the film thickness as TOF-ERDA (the whole film) and XPS (the surface) give similar N/Re ratios for the rhenium nitride films (Tables S2 and S3).

The Re ALD process was examined at 400 °C to confirm the saturative self-limiting surface reactions of both $ReCl_5$ and NH_3 precursors (Figure 2). Self-limiting growth is obtained already with very short precursor pulses of 0.2 and 0.5 s for NH_3 and $ReCl_5$. The film growth is also independent of the NH_3 flow rate at 2 sccm and above. The Re film grown using 0.2 s $ReCl_5$ pulses was not uniform across the substrate indicating insufficient $ReCl_5$ dose because of the low source temperature chosen to minimize the precursor consumption. It should be emphasized that here the process is not optimized for the fastest cycle times. A bit higher source temperature should have been enough to ensure uniform film growth across the substrate also with the shortest 0.2 s $ReCl_5$ pulses. The short pulses being enough for the saturative growth indicate that this ALD process is robust which is beneficial for upscaling and commercial applications.

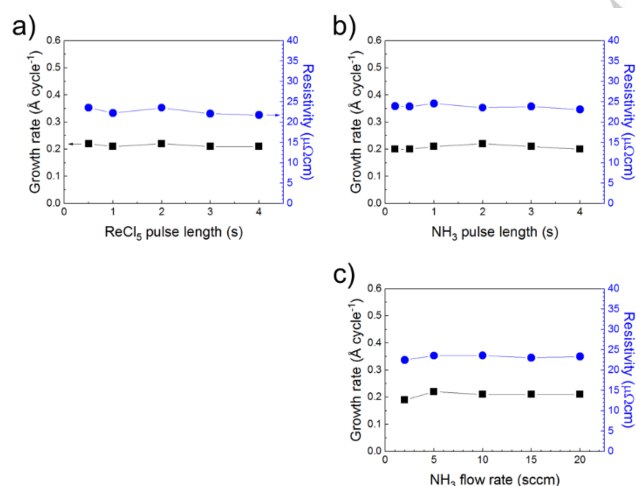

Figure 2. Re films grown on Al_2O_3 films at 400 °C. Film growth rate (EDX) and resistivity as a function of a) $ReCl_5$ pulse length, b) NH_3 (5 sccm) pulse length, c) NH_3 flow rate. The total number of deposition cycles was 1000 while all the purges were 1 s. In a) the NH_3 (5 sccm) pulse length was 2 s, in b) the $ReCl_5$ pulse length was 2 s, and in c) both precursor pulses were 2 s.

The film thickness follows linearly the number of deposition cycles at 400 °C (Figure 3a) and after 300 cycles metallic Re is identified in GIXRD (Figure 3b). Already a 3 nm thick Re film (200 cycles) is continuous and highly conductive (~90 μΩcm). The film resistivity stabilizes to about 22 μΩcm in thicker films. The bulk resistivity of Re is 18.7 μΩcm. Interestingly, one of the rhenium oxides, ReO_3, possess metallic conductivity and even lower bulk resistivity (~10 μΩcm) than the metal itself. MBE grown epitaxial Re films on sapphire were reported[8] to have resistivities of about 21 μΩcm (25–100 nm) when deposited at 700–770 °C. The resistivities of the polycrystalline Re films grown here on amorphous Al_2O_3 stabilize close to similar resistivities as the MBE films.

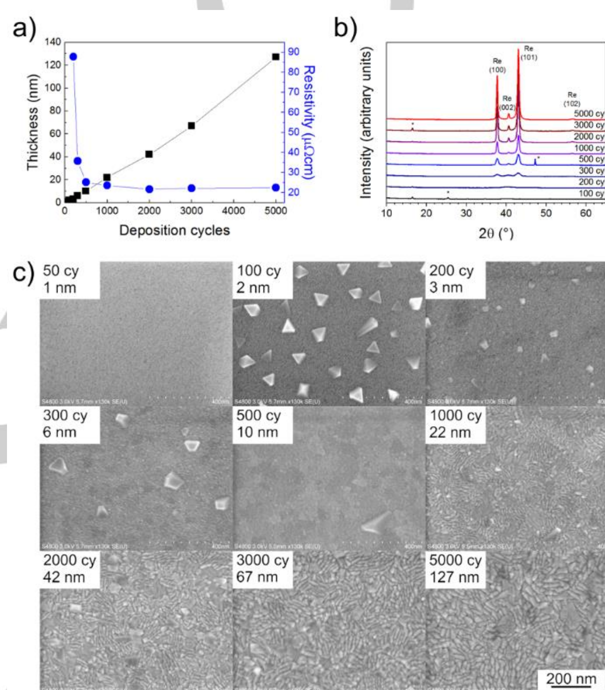

Figure 3. Re films grown on Al_2O_3 films at 400 °C as a function of the number of deposition cycles. a) Film thicknesses (EDX) and resistivities, b) GIXRD patterns, and c) FESEM images with the number of deposition cycles and corresponding film thicknesses. The pulse and purge lengths were 2 s and 1 s, respectively. The peaks denoted by an asterisk could not be reliably identified.

The reactive nature of the thinner films under the ambient can be seen from the FESEM images (Figure 3c). The GIXRD patterns reveal the films to be nearly x-ray amorphous (Figure 3b), although the FESEM images show large crystallites on the film surface. Surfaces of amorphous Re films deposited by PLE have been noted[16] to naturally age in air leading to the formation of ReO_3. It is most probable that similar aging is occurring also here with the ALD grown Re films (Figure 4a). The aging is especially dominant on the Re films grown with a small number of deposition cycles (Figures 3b and 3c) as the films were susceptible to ambient for prolonged period of time. The thicker Re films have quite distinctive crystalline surface morphology (Figure 3c). The transmission electron microscope (TEM) images reveal differences in film morphology between the $Re_{0.6}N_{0.3}$ (N/Re ratio 0.48; stoichiometric Re_2N ratio 0.5) (Figure 4b) and Re metal (Figure 4a). Notably the oxidized surface layer is absent on the ReN_x film indicating higher long-term stability in the ambient. The

Re and ReN_x film thicknesses determined from the TEM images are 25 and 43 nm, respectively, which correspond well with the XRR film thicknesses (Figure 1a).

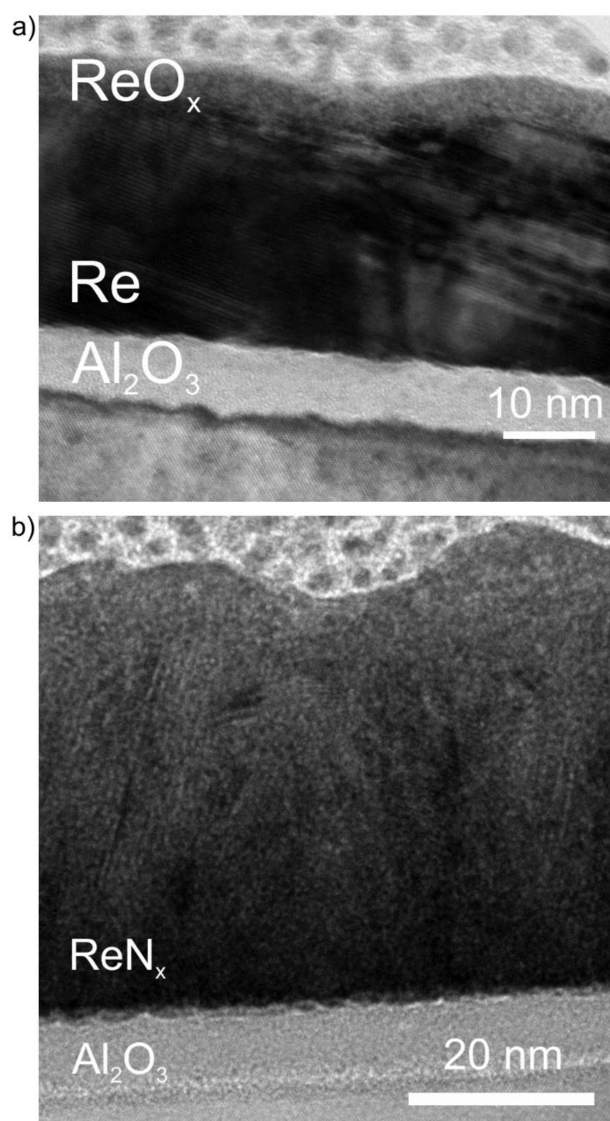

Figure 4. TEM images of the a) Re and b) ReN_x films grown at 400 and 300 °C, respectively. The TEM images are from the same samples as seen in Figure 1.

To summarize, ALD was applied to deposit both ReN_x and Re thin films from $ReCl_5$ and NH_3 precursors over a wide temperature range between 275 and 500 °C. The films grown at 400 °C and above were Re metal whereas at lower temperatures conductive rhenium nitrides with tunable stoichiometry and resistivity (70–290 µΩcm) were obtained. A very thin, 3 nm, Re film was shown to be already continuous and to have a low resistivity of about 90 µΩcm. The resistivities of the thicker Re films were as low as 22 µΩcm and the amounts of impurities (N, H, Cl, C) were down to about 2 at. % in total. Additionally, the Re ALD process was shown to proceed via fast surface reactions between the precursors. The simple and robust process presented here using only a metal halide and ammonia to produce conductive rhenium-based films in a highly controlled manner serves as an interesting opening to bring this intriguing element more widely available for various applications, starting with semiconductor industry.

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Keywords: atomic layer deposition • ALD • rhenium • rhenium nitrides • thin films

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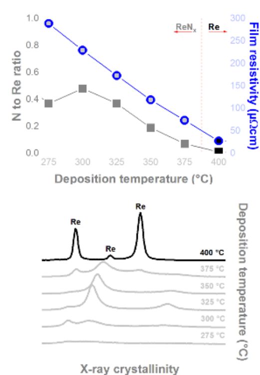
Highly conductive rhenium and rhenium nitride thin films are deposited at moderate temperatures. The films grow in a highly controllable manner from ammonia and rhenium pentachloride at temperatures up to 500 °C by atomic layer deposition. As thin as 3 nm rhenium film is already continuous and has a low resistivity of 90 µΩcm.



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