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Atomic Layer Deposition of Ru Thin Films Using (2,4-dimethyloxopentadienyl)(ethylcyclopentadienyl)Ru and the Effect of Ammonia Treatment during the Deposition

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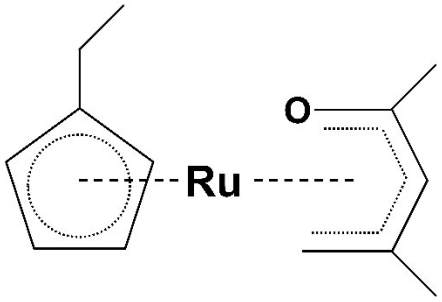

Fig. S1 The molecular structure of Rudense®

Fig. S1 shows the molecular structure of Rudense® ((2,4-dimethyloxopentadienyl)(ethylcyclopenta-dienyl)Ru, [Ru(DMOPD)(EtCp)]).

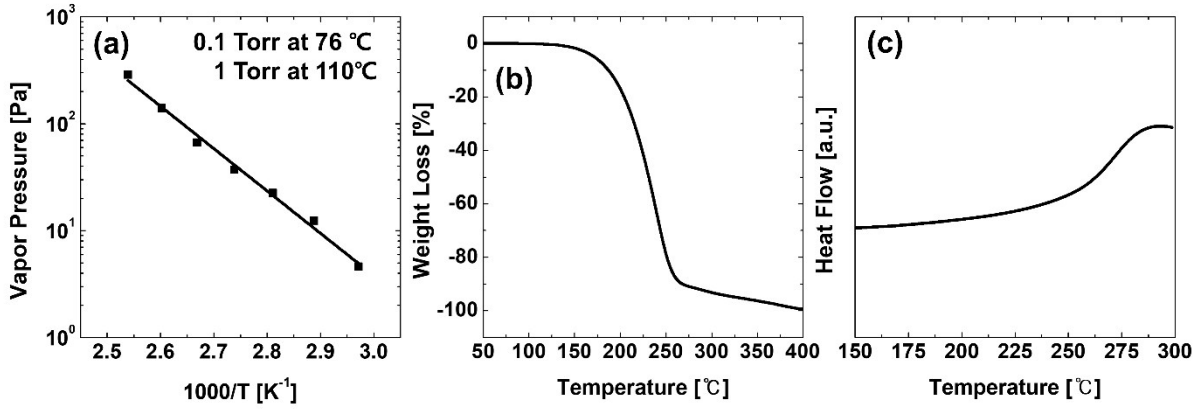

Fig. S2 (a) Vapor pressure of Rudense® as a function of reciprocal temperature, (b) TGA % weight loss of Rudense® as a function of temperature, (c) DSC data (heat flow) of Rudense® as a function of temperature.

Fig. S2 shows the physical properties of Rudense®. Fig. S2(a) shows the vapor pressure of Rudense® as a function of reciprocal temperature. Rudense® shows vapor pressures of 0.1 Torr and 1 Torr at 76 ℃ and 110 ℃, respectively. Thermal gravimetric analysis (TGA) was conducted with a heating rate of 10 ℃/min under Ar gas flow of 400 sccm, and Fig. S2(b) shows the result of the analysis. Figs. S2(a)-(b) present that Rudense® has enough volatility. Fig. S2(c) shows the DSC data of Rudense® as a function

of temperature. The analysis was conducted at the conditions of the heating rate of 10 ℃/min, N_2 gas flow rate of 50 sccm in the Ar atmosphere. The thermal decomposition of Rudense® occurred at ~230 ℃.

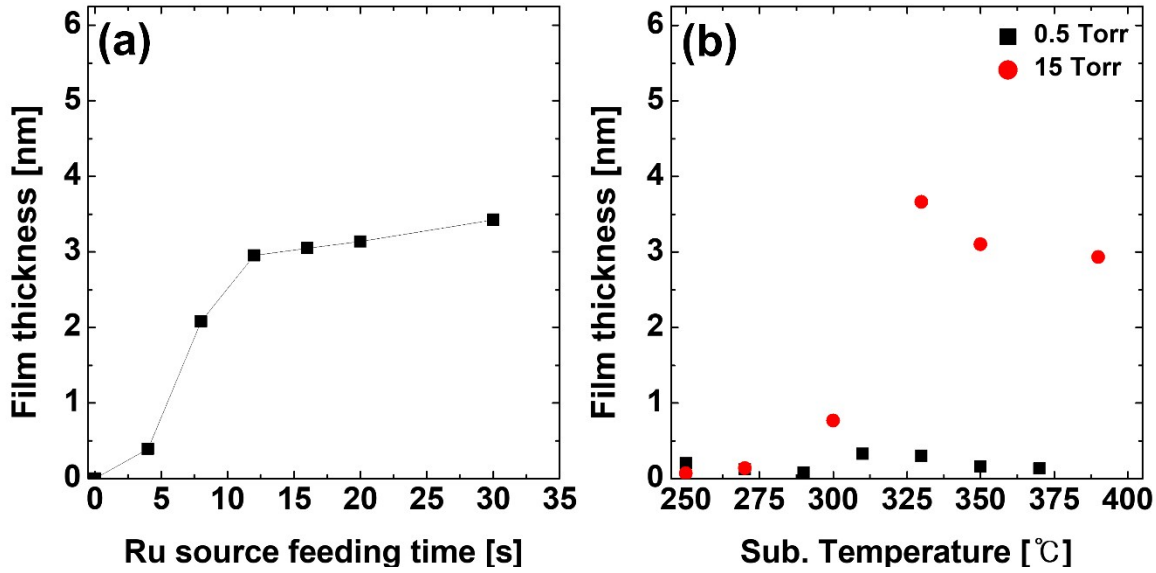

Fig. S3 (a) The variations in the film thickness of a Ru film grown on Ta_2O_5 substrates as a function of the Ru source feeding time at 270 ℃, (b) The variations in the film thickness of a Ru film grown on Ta_2O_5 substrates as a function of the substrate temperature at the different process pressure, where only Ru-precursor was delivered for 50 cycles without O_2 gas supply.

It has been reported that the Ru-precursor started to thermally decompose at 230 ℃. The thermal property data of the Rudense® (Fig. S2 of S.I.), provided by the manufacturer, however, showed that the thermal decomposition was not serious up to 270–280 ℃. To prove that the Rudense® can be used as a facile ALD precursor without the thermal decomposition, the saturation experiment regarding the Ru-precursor pulse time was performed at 270 ℃, under the identical conditions as Fig. 1(a), of which results were summarized in Fig. S3(a). The ALD-specific self-saturation behavior was observed even at this elevated temperature too. Also, additional experiments are performed as follows. Only Ru-precursor was pulsed by 50 times without the O_2 gas pulse according to 10 s – 5 s – 0 s – 10 s sequence, where the chamber pressure was controlled to 0.5 or 15 Torr, and the results were summarized in Fig. S3(b). At 0.5 Torr, which is the process pressure in this study, there was almost no film growth, suggesting that the thermal decomposition of the Ru precursor did not occur. However, at 15 Torr, significant film growth has occurred from ~300 ℃. At the higher chamber pressure, the precursor molecules remained adsorbed on the substrate for a longer time compared with the case with the lower

pressure, which may enhance the thermal decomposition. Therefore, the thermal decomposition of the Ru-precursor at 250 ℃ must be negligible in this study.

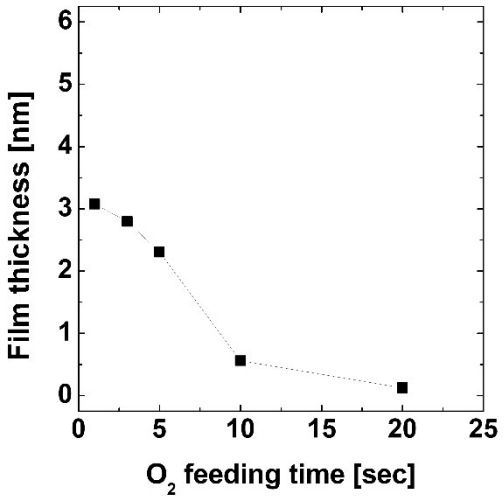

Fig. S4 The variations in the film thickness of Ru film grown on a Ta_2O_5 substrate as a function of O_2 feeding time at 330 ℃.

Fig. S4 shows the variation in the thickness of the Ru films deposited on a Ta_2O_5 substrate as a function of the O_2 feeding time at 330 ℃. The ALD sequence was fixed at 10 s – 5 s – X s – 10 s, where "X" is the variable of the O_2 feeding time. The number of cycles was fixed at 50. The thickness of the film decreased significantly from ~3 nm to ~0 nm. This result might be due to the etching effect by high activeness of O_2 gas, as well as the easy desorption of the Ru precursor due to the high process temperature.[1]

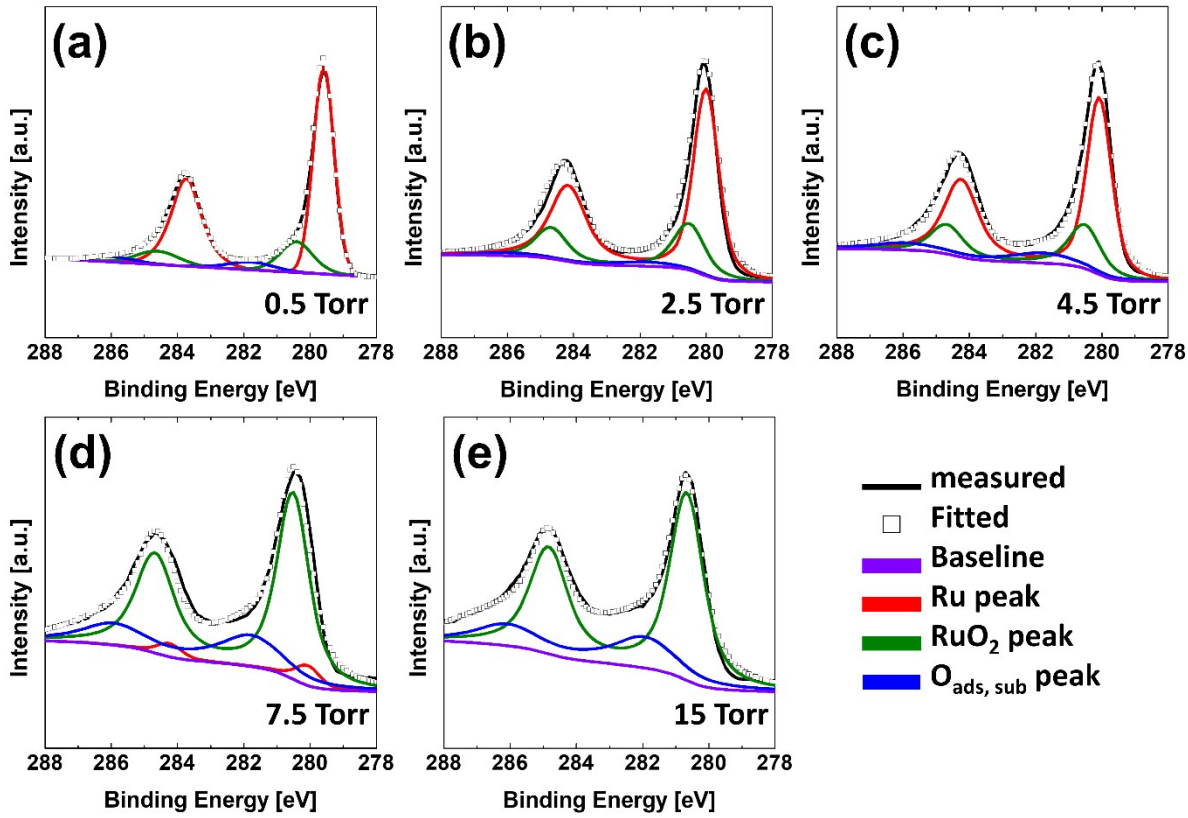

Fig. S5 Deconvoluted XP spectra of Ru 3d of grown films at various pressures (at 270 ℃). (a) 0.5 Torr, (b) 2.5 Torr, (c) 4.5 Torr. (d) 7.5 Torr, (e) 15 Torr

Fig. S5 shows the deconvoluted XP spectra of Ru 3d deposited at various pressures, under process temperature of 270 ℃. The films were deposited on Ta_2O_5 substrates, the thickness of the films was ~8 - 10 nm, and in-situ etching of the surface was conducted before the analysis. As the pressure increased, the portions associated with the oxygen component (RuO_2, $O_{ads,\ sub}$) also increased. It might be as a result of the larger number of oxygen molecules during the O_2 feeding step. Kim et. al reported that a large number of oxygen components caused incomplete oxygen consumption for the oxidation of incoming Ru precursor ligands, which induced the formation of an oxygen-containing Ru phase (RuO_2).[2] From 0.5 Torr to 4.5 Torr, the portions of RuO_2 and $O_{ads,\ sub}$ increased gradually. However, the portions of RuO_2 and $O_{ads,\ sub}$ increased abruptly at a pressure of 7.5 Torr, which might be due to the catalytic effect.[3]

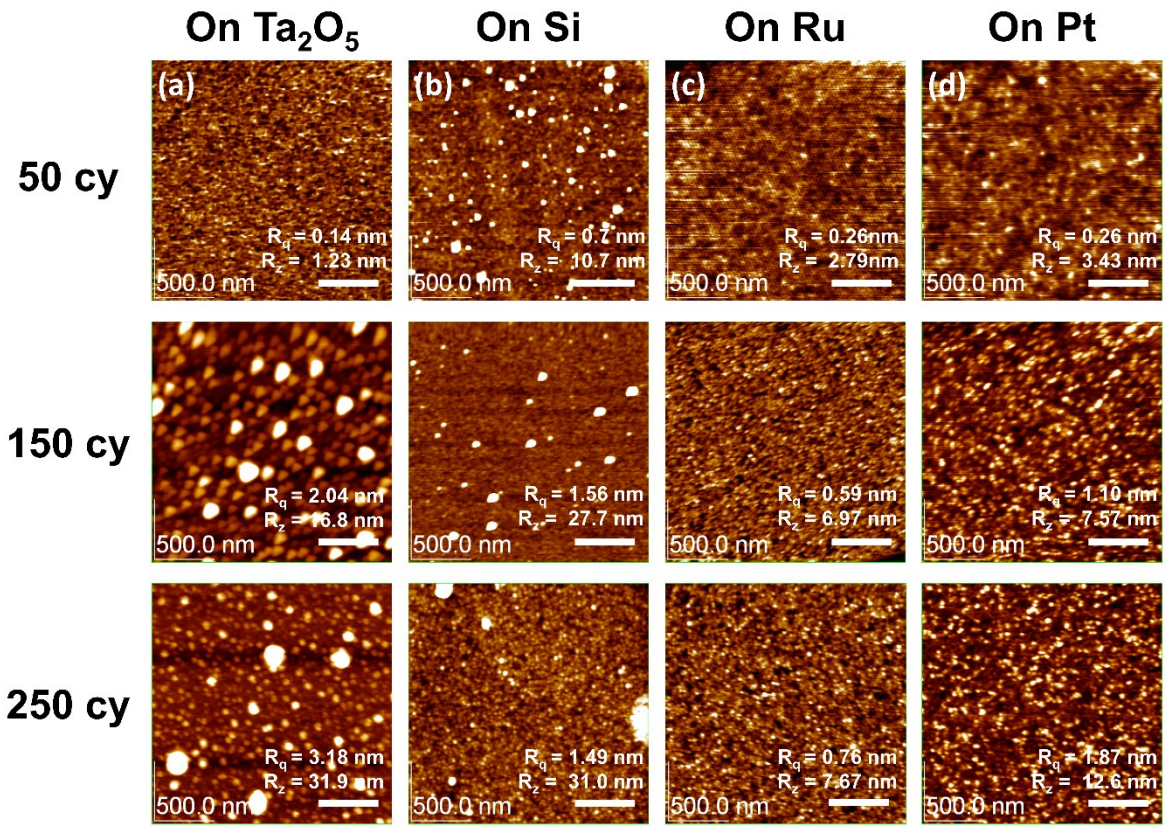

Fig. S6 AFM images of Ru films grown on (a) Ta_2O_5, (b) Si, (c) Ru, and (d) Pt substrates at the various deposition cycles (scale bar: 500 nm).

The surface morphologies of the Ru films at the various deposition cycles were investigated via AFM. Ru films as thin as ~3 nm (50 cy) show a significantly smooth surface for all substrates (R_q <1 nm). It suggested that the nucleation of Ru occurred fluently regardless of the substrates at the initial stage. However, the surface morphologies became rough with several local protrusions in the case of Ta_2O_5 and Si substrates.

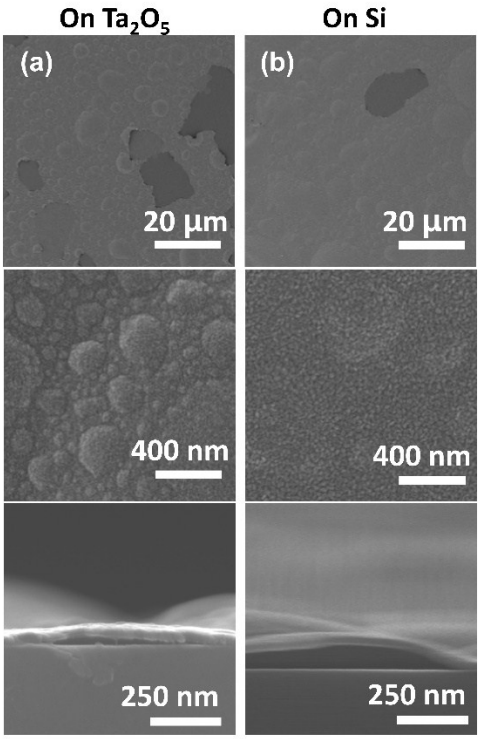

Fig. S7 SEM images of Ru films treated by NH_3 feeding time of 30 s grown on (a) Ta_2O_5 (b) Si substrates (planar and cross-section modes).

SEM images of Ru films on Ta_2O_5 and Si substrates treated by NH_3 feeding time of 30 s were investigated. The thickness of the Ru films was ~20 nm. Upper panels and middle panels consisted of low (× 1000) and high (× 50,000) magnification of planar images, respectively. Lower panels are cross-sectional images of the Ru films. Serious swelling of the Ru films occurred, while the swelling was more serious on the Ta_2O_5 substrate as compared to the Si substrate. In addition, some regions delaminated, leading to exposure of the substrates to the surface.

References

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