Supplemental Information

As described in the main text, we investigated the surface reaction processes in Nb PE-ALD by performing molecular dynamics (MD) simulations using Matlantis™. As shown in Fig. 1, $NbCl_5$ readily dissociatively adsorbs on the Nb surface, and more extensive ligand dissociation is observed at elevated temperatures. When $NbCl_5$ molecules were sequentially supplied to the surface at 187 °C, a second Nb layer formed and an Nb cluster emerged at the point where the 10th molecule was introduced, as shown in Fig. 2. With further $NbCl_5$ supply, chain-like $NbCl_4$ species began to form, which is considered a possible origin of increased residual chlorine in the film. As noted in the main text, our simulations suggest that the $NbCl_4$ chains can be efficiently removed when the Ar ion energy is kept at or below 10 eV. To examine this experimentally, we compared two plasma-bias conditions and found that the process using a lower bias power (30 W) resulted in a lower residual chlorine concentration, as shown in Fig. 3.

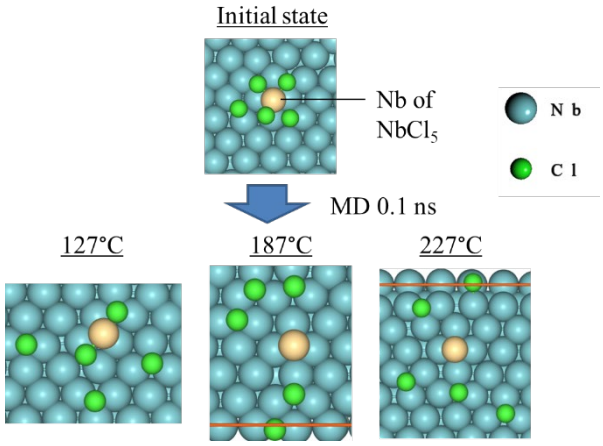

Fig. 1. NNP-MD snapshots of $NbCl_5$ dissociative adsorption on Nb. At 127 °C, Nb-containing species remained partially chlorinated (e.g., $NbCl_2$), possibly due to limited simulation time and/or incomplete equilibration. At 187 °C and above, the Cl ligands initially coordinated to $NbCl_5$ were fully dissociated in the simulation.

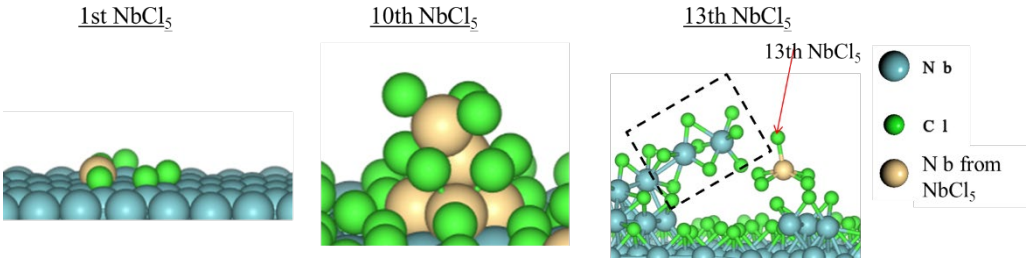

Fig. 2. NNP-MD results for sequential $NbCl_5$ supply at 187 °C. Nb-containing species adsorb and subsequently aggregate, leading to the formation of a second Nb layer and Nb clustering upon continued dosing. At higher coverage, chain-like $NbCl_4$ species are formed.

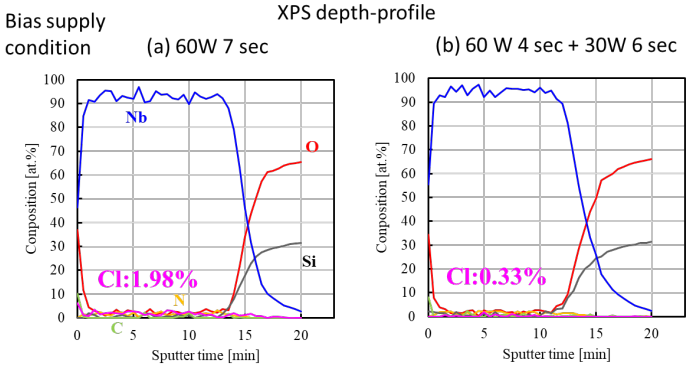

Fig. 3. Dependence of film composition on substrate-bias conditions (XPS depth profile). A two-step bias sequence (high bias followed by lower bias) reduced the residual Cl concentration compared with a single high-bias condition. Impurity concentrations were low in all samples.