
Surface Reaction Mechanisms of Hexafluoroacetylacetone (HFAC) on a Nickel or Nickel Oxide Surface for Atomic-Layer Etching (ALE)

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Atomic layer etching (ALE) is a promising technology for and a prospective solution to a challenging problem of the formation of nano-scale structures on a material surface used in modern semiconductor manufacturing processes. In ALE, a transition step to form a reactive thin layer on the material surface is followed by a removal step to take off only this modified layer and this cycle is repeated until the desired amount of the surface material is removed. ALE offers low damage and atomically controlled etching processes. For a metal surface, one may be able to achieve ALE by the formation of volatile organic metal complexes. It has been shown that hexafluoroacetylacetone (hfac) may be used effectively to etch some magnetic materials [1,2]. When gas-phase hfac is exposed to a Ni surface, it may form organometallic compounds on the surface first. Then with the increase of the Ni surface temperature, nickel hexafluoro-acetylacetonates $\text{Ni}(\text{hfac})_2$ are formed and evaporated, which remove Ni atoms from the surface. Other magnetic materials such as Fe and Co may also be removed in a similar way with different organic molecules such as acetylacetone by the formation of metal acetylacetonates (acac) [3]. As an earlier study [2] indicated, when gas-phase hfac is exposed to a pre-oxidized nickel (Ni) surface and the substrate temperature is increased, $\text{Ni}(\text{hfac})_2$ can be desorbed from the surface whereas, when gas-phase hfac is exposed to a metallic Ni surface, hfac tends to break down on the surface. The goal of this study is to understand why and how a pre-oxidized Ni surface and a metallic Ni surface interact differently with hfac molecules incident on them. To achieve this goal, we have used the first principles calculation or quantum mechanical (QM) numerical simulation to study interactions of a hfac molecule with Ni or NiO surfaces. Our simulation results have so far suggested that the transfer of a proton from an enol hfac molecule to the Ni or NiO surface generates its deprotonated anion, whose oxygen atoms strongly interact with a positively charged Ni atom on the surface and thus form a precursor of a highly volatile metal complex. Difference in charge distribution between Ni and NiO surfaces affects the likelihood of the formation of such precursors. Surface roughness may also affect such surface reactions.

[1] Chen J. K., Altieri N. D., Kim T., Chen E., Lill T., Shen M., and Chang J. P., "Direction etch of magnetic and noble metals. II. Organic chemical vapor etch," *J. Vacuum Sci. & Tech. A* **35**, 05C305 (2017).

[2] Nigg H. L. and Masel R. I., "Surface reaction pathways of 1,1,1,5,5,5-hexafluoro-2,4-pentandione on clean and pre-oxidized Ni(110) surface," *J. Vacuum Sci. & Tech. A* **17**, 3477 (1999)

[3] Chen J. K., Kim T., Altieri N. D., Chen E., and Chang J. P., "Ion beam assisted organic chemical vapor etch of magnetic thin films," *J. Vacuum Sci. & Tech. A* **35**, 031304 (2017).

