Molecular mechanisms of atomic layer etching of cobalt with sequential exposure to molecular chlorine and diketones

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The mechanism of thermal dry etching of cobalt films is discussed for a thermal process utilizing sequential exposures to chlorine gas and a diketone [either 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hexafluoroacetylacetone, hfacH) or 2,4-pentanedione (acetylacetone, acacH)]. The process can be optimized experimentally to approach atomic layer etching (ALE); a sequential exposure to Cl₂ and hfacH dry etchants at 140 °C is shown to proceed efficiently. The use of acacH as a diketone does not result in ALE with chlorine even at 180 °C, but the decrease of surface chlorine concentration and chemical reduction of cobalt is noted. However, thermal desorption analysis suggests that the reaction of chlorinated cobalt surface exposed to the ambient conditions (oxidized) with hfacH does produce volatile Co-containing products within the desired temperature range and the products contain Co³⁺. The effect of adsorption of ligands on the energy required to remove surface cobalt atoms is evaluated using the density functional theory. *Published by the AVS.*

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I. INTRODUCTION

Atomic layer etching (ALE) has emerged as a necessary approach to fabricate magnetic random access memory (MRAM) devices. In order to be efficient, the removal of commonly used magnetic metal layers consisting of alloys containing Fe, Co, and Ni has to be performed with atomic level precision and without leaving residues. Cobalt and its alloys have attracted recent attention as components of MRAMs both because of their magnetic properties¹ and their high magnetoresistance.² Although some of the cobalt deposition methods, specifically based on atomic layer deposition (ALD), exhibit atomic level precision, they also generally show slow nucleation rate and increasing roughness of the resulting surface with thickness.³ Thus, ALE consistent with industrial processing of cobalt films has been in demand. A number of methods combining sequential dosing chemical organic precursor molecules and plasma methods to remove metalorganic fragments from a surface have been used to approach a single atomic layer per cycle. In fact, the variation of cobalt removal rates from several angstroms to several nanometers per cycle has been reported.⁴ Despite practical knowledge and potential process optimization success, the mechanism of the process remains largely unknown.

The recently developed chemical dry etching schemes for cobalt ALE rely on thermal chemistry of cobalt surfaces with diketones, the compounds that have been shown to have high affinity to metals.^{5–7} A simple acetylacetone (2,4-pentanedione, acacH) and hexafluorinated version of this compound (1,1,1,5,5,5-hexafluoro-2,4,-pentanedione, hfacH) have been

used successfully to etch oxidized cobalt surfaces,^{8,9} however, it was also shown recently that the proposed volatile product, Co(hfac)₂, does not form on a clean cobalt surface¹⁰ and that the presence of surface oxygen is required for this product to form. Even when Co(hfac)₂ is formed on the oxidized cobalt surface in a self-limited reaction, it was not observed to desorb until approximately 350 °C,¹⁰ the temperature substantially higher than the industrial processing conditions and experimentally observed etching. Thus, the etching mechanism proposed previously for nickel, where surface metal diketonates are formed and desorbed as Ni(hfac)₂ in a self-limiting reaction,¹¹ is not appropriate for cobalt, and further understanding of the process is needed.

The work described here uses the results of a working etching process for cobalt thin films exposed to sequential doses of Cl₂ and acacH (or hfacH) as a function of surface temperature¹² to uncover the mechanism of the process. Conceptually, the overall etching process is summarized in Scheme 1 for hfacH reacting with the chlorine-covered cobalt surface. As will be shown below, the overall process is substantially more complicated.

The surface is activated with a dose of Cl₂ as it is expected that chlorinated species are less thermodynamically stable than oxides or pure metals. The coverage of Cl on the surface is to be controlled kinetically. After the surface is activated, it is reacted with a diketone, and the products of this overall synergistic process are desorbed. *In situ* studies with x-ray photoelectron spectroscopy (XPS) and the thermal desorption observation of the products formed within the target temperature range suggest that optimal conditions for ALE of cobalt require the presence of both surface chlorine and surface oxygen, that the hfacH is much more efficient etchant than acacH, and that the products of the etching process contain Co³⁺ with multiple ligands.

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SCHEME 1. Summary of the proposed process of the etching chlorinated cobalt surface by hfacH.

II. EXPERIMENT

A. Samples and compounds used

The cobalt films used in this work were prepared by standard physical vapor deposition of cobalt (50 nm) onto an SiO_x covered single-side polished 300 mm silicon wafer (Advantiv Technologies Inc.) using either 10 nm Ta or 10 nm Ti as the adhesion layer. The thickness of the films was verified by SEM of cross sections.

Chlorine gas (98%, Matheson) was used as received. 2,4-pentanedione (acacH) (99.5%, Aldrich) and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfacH) (98+%, Alfa Aesar) were used after several freeze-pump-thaw cycles as described in the procedures below. Scheme 2 shows chemical structures of acacH and hfacH in their diketone forms.

B. Description of the etching reactor and process

The custom-built etching system used in the experiment is shown in Fig. 1. The main reaction chamber is made of stainless steel. The chamber walls are heated to 80 °C to minimize gas adsorption on the chamber walls. Mass flow controllers are used on all gas lines to control the flow rates except for the organic precursor. Since the organic precursors hfacH/acacH are liquid at room temperature, they were stored in stainless-steel vessels and dosed by evaporation. A needle valve in this gas line is used to adjust the partial pressure of organic compound in the chamber. This gas pressure rather than flow rate was used as the control parameter in these experiments. The processing pressure is controlled by a downstream throttle valve, which is positioned over the vacuum pump. The base pressure of the chamber is 0.05 Torr. A mass spectrometer (MKS, Cirrus 2) is used to monitor the background of the chamber and purity of precursors. All the pneumatic valves in the gas line are connected to a computer and controlled by a LABVIEW program. The etching process uses cyclic exposures of Cl_2 and acacH/hfacH in the gas phase. Only thermal etching was performed, except as indicated in the text for selected experiments which utilized a chlorine plasma. The plasma experiments utilized reactive ion etching using a capacitively coupled

plasma source. The setup with the RF generator (ENI, ACG-6B) could deliver a maximum power of 500 W at a frequency of 13.56 MHz with the matching network (ENI, 25D) and impedance matching network controller (Advanced Energy, ATX-600).

There are two steps in each etching cycle. In the first step, a mixture of 60 sccm Ar and 15 sccm Cl_2 was dosed for 20 s. In the second step, a mixture of 60 sccm Ar and 30 mtorr acacH/hfacH was dosed for 45 s. Between the two steps, the chamber is pumped down to base pressure then purged by N_2 for 30 s. Before introducing acacH/hfacH, the chamber is pumped down to base pressure again. Ar was used as the carrier gas for the dosing in order to compare directly with selected experiments using plasma reactants. There is a heater underneath the substrate to control temperature, and a thermocouple is attached to the heater block with a metal clip. The surface temperature was calibrated using a feed-through thermocouple in the same position as used during the process. A JSM-7400F SEM was used to measure the cross section of the films and surface morphology before and after the gas exposure. The accelerating voltage is 5 kV for the measurement. The samples have been cleaved to fit the SEM holder for cross-sectional imaging.

An NX20 model atomic force microscope (AFM) from Park Systems and non-contact tips (OMCL-AC160TS, Park Systems) were used to analyze metallic samples in non-contact mode, and a scan size of $10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$ was chosen for each experiment. Each sample was tested three times.

C. In situ XPS setup

Our *in situ* XPS spectrometer features a temperature-monitored reaction chamber directly connected to the XPS-characterization main chamber. Utilizing a sample transfer arm, metal films investigated in our ALE experiments are transferred in and out of the XPS-characterization main

SCHEME 2. Chemical structure of acacH (left) and hfacH (right) in their diketone (as opposed to enol) forms.

FIG. 1. Custom-built etching chamber for ALE experiments.

FIG. 2. Schematic of the *in situ* XPS spectrometer used in this work. The reaction chamber in which multiple reactive gas precursors are located is directly connected to the XPS spectra-characterization main chamber.

chamber following ALE processing. Our *in situ* XPS setup configuration specifically monitors and probes surface chemistry and chemical bonding types of all possible elements in metal films without any interference resulting from surface contamination. Figure 2 shows a schematic representation of the *in situ* XPS spectrometer used in this work. The reaction chamber in which multiple reactive gas precursors are located is directly connected to the XPS spectra-characterization main chamber with a base pressure of 5×10^{-9} Torr. All measurements are carried out under high vacuum to limit surface contaminations due to exposure to air.

D. Thermal desorption investigation

The ultrahigh vacuum (UHV) chamber used for temperature programmed desorption (TPD) studies has a 10^{-9} Torr base pressure. It is equipped with a differentially pumped mass spectrometer (Hiden Analytical, HAL 511/3F) with a detection range from 0 to 510 amu. The chlorinated and partially oxidized cobalt film samples, prepared in a different laboratory (as described above), were attached to a button heater with a tantalum collar and placed in UHV with minimal exposure to ambient conditions. After the initial preparation by annealing at 440 K (165 °C) for 40 min to remove possible surface contaminants, the exposure to hfach was performed at the desired sample temperature, read by the thermocouple attached to the tantalum shield of sample mounting. Following the dose, the sample was allowed to cool to room temperature, and thermal desorption spectrum was collected at a linear heating rate of 2 K/s up to 700 K (425 °C) controlled by the dedicated temperature controller (Eurotherm, Model 818). The liquid samples (acach and hfach) were prepared by a standard freeze-pump-thaw procedure, and the purity of the dosing liquid was confirmed *in situ* by mass spectrometry. Only one sample was used for TPD experiment at a time, and it was removed from the chamber following the collection of the TPD and replaced by a fresh sample.

III. MODELING

The modeling of surface etching on different Co(100) surfaces has been carried out by means of periodic density functional theory (DFT) calculations. All DFT calculations were

performed using the Vienna *Ab initio* Simulation Package (VASP) computational code.^{13,14} The VESTA software has been used to visualize and represent the structures of these models.¹⁵ In all the slab models, a 5×5 supercell of metallic cobalt with a vacuum layer (>15 Å) on the top was constructed using the optimized lattice parameter of 3.53 Å, which is in good agreement with the experimental value of 3.54 Å.¹⁶ The top two layers of 50 cobalt atoms were set to relax while the third to the fifth layers of 75 cobalt atoms were fixed to simulate the underlying atomic layers in the bulk system, which is sufficiently large to investigate the hfach moieties on a Co(100) surface. The energy values were calculated using generalized gradient approximation with correlation functional of Perdew and Wang (PW91) and a cutoff energy of 400 eV for the plane-wave basis set with a $3 \times 3 \times 3$ set of k-points for integrations over the Brillouin zone.^{17,18}

The calculated energy of removing cobalt atoms from two different Co(100) surfaces, the defect atom added Co(100) surface (shown as Co_{126} in the equation), and the plain Co(100) surface (shown as Co_{125} in the equation) has been compared under three different circumstances: unmodified Co(100) surfaces, chlorinated Co(100) surfaces (shown as Cl/Co_x in the equation), and hfach modified Co(100) surfaces (shown as hfach/Co_x in the equation). The energy comparison was made based on the balanced equations of these surface etching reactions as shown in Eqs. (1)–(6). In these equations, the subscripts x in Co_x show the total number of cobalt atoms in the model unit cell, $E[\text{Co}(\text{hfach})_2]$ and $E(\text{CoCl}_2)$ are the calculated energies of the respective compounds in the gas phase

$$E_{\text{Etching}} = E(\text{Co}_{125}) + E(\text{Co}_1) - E(\text{Co}_{126}), \quad (1)$$

$$E_{\text{Etching}} = E(\text{Co}_{124}) + E(\text{Co}_1) - E(\text{Co}_{125}), \quad (2)$$

$$E_{\text{Etching}} = E(\text{Co}_{126}) + E(\text{Co}_{125}) + E(\text{CoCl}_2) - 2 \times E(\text{Cl}/\text{Co}_{126}), \quad (3)$$

$$E_{\text{Etching}} = E(\text{Co}_{125}) + E(\text{Co}_{124}) + E(\text{CoCl}_2) - 2 \times E(\text{Cl}/\text{Co}_{125}), \quad (4)$$

$$E_{\text{Etching}} = E(\text{Co}_{126}) + E(\text{Co}_{125}) + E(\text{Co}(\text{hfach})_2) - 2 \times E(\text{hfach}/\text{Co}_{126}), \quad (5)$$

$$E_{\text{Etching}} = E(\text{Co}_{125}) + E(\text{Co}_{124}) + E(\text{Co}(\text{hfach})_2) - 2 \times E(\text{hfach}/\text{Co}_{125}). \quad (6)$$

IV. RESULTS AND DISCUSSION

In order to understand the mechanism of cobalt ALE, it is important to compare the industrially relevant processing and the molecular-level interrogation of the elementary steps of

the process set in ideal controlled conditions. First, this section describes the cobalt etching processing in a set of reactor studies, where the conditions can be optimized for ALE. Then, the elementary steps that can be proposed based on these findings are investigated in a controlled environment of ultrahigh vacuum, where spectroscopic techniques can be applied to describe molecular surface processes and intermediates. Finally, selected findings of these detailed studies will be supplemented and explained by computational DFT investigations.

A. Reactor studies of ALE of cobalt films

A summary of the investigation of dry etching of cobalt films by cyclic exposure to Cl_2 followed by hfach is shown in Fig. 3 as a function of the number of cycles for four different surface temperatures compared to the exposures to hfach at 170 °C without exposure to Cl_2 . In the first step, a mixture of Ar (60 sccm) and Cl_2 (15 sccm) was dosed for 20 s. In the second step, hfach was dosed for 45 s at

30 mTorr partial pressure. (Pressure was used as the control variable rather than the flow rate in the second step.)

Single gas exposures of hfach conducted at 170 °C showed no change of metal thickness as a function of the number of these half-cycles, indicating that hfach by itself does not etch the cobalt film under these conditions. When the cycle is completed by predosing Cl_2 , the Co film can be etched even at 140 °C, as confirmed by cross-sectional SEM imaging. The etching rate is 0.2 nm/cycle at 140 °C, which indicates the atomic scale etching control. However, the etching rate is highly temperature dependent, reaching 1.6 nm/cycle at 185 °C, the highest surface temperature studied. This set of investigations confirms that etching of cobalt films can be performed by a two-step cycle of Cl_2 and hfach exposure and that the temperature control of the process allows us to optimize it to follow atomic layer etching.

AFM is used to compare surface roughness of the pristine and etched Co samples to see if the ALE process changes the surface morphology. Figure 4 shows AFM images for pristine Co sample and etched Co sample following 45 ALE cycles at 140 °C. The root mean square (RMS) roughness for pristine Co is 4.8 nm. The RMS roughness does not change substantially after 15 cycles etching and remains nearly constant after 45 cycles, at 5.2 nm. Thus, ALE process does not substantially increase the surface roughness compared with the pristine sample, which is a good indication that ALE leads to conformal etching. In fact, although the surface roughness is not the focus of the present work, the observation that the ALE process does not increase the roughness of the cobalt film surface is consistent with the previous observations of surface “smoothing” in ALE processes.^{10,19–21}

We also evaluated another beta-diketone precursor, acacH, for the Co ALE process. However, the Co film did not show a significant thickness change with sequential doses of Cl_2 and acacH at 140 °C. No etching was observed after 50 etching cycles even when dosing with a 100 W RF Cl_2 plasma. The removal of Co can only be observed with a sequential dose of Cl_2 plasma (RF power 100 W) and acacH at 200 °C. However, the etching at 200 °C is not self-limiting, because the Co film can also be etched by Cl_2 plasma at 100 W RF power without dosing acacH. As a result, hfach is a better choice than acacH for achieving Co atomic layer etching.

FIG. 3 (a) ALE of cobalt thin films as a function of the number of two-step cycles of Cl_2 and hfach exposures for the temperatures indicated (error bars represent three separate sets of experiments); (b) comparison of the etching rates of cobalt as a function of temperature.

FIG. 4. AFM images for (a) pristine Co sample and (b) etched Co under 140 °C after 45 ALE cycles.

FIG. 5. XPS spectra of chlorinated cobalt thin film before (a) and after (b) acach exposure (1 Torr for 3 min). Dashed line indicates the expected position of the Co(0) peak reported in Ref. 22.

B. *In situ* XPS investigations of cobalt etching

In order to understand the differences between acach and hfach described in Sec. IV A, the *in situ* experiments in an ultrahigh vacuum chamber were performed to target the elementary steps of the process. As briefly summarized in Fig. 5 and Table I, the surface of a cobalt film that is free of adventitious oxygen (prepared by Ar^+ sputtering in a vacuum chamber) does react with Cl_2 gas and then, upon exposure to acach, reduction of the cobalt oxidation state simultaneously with partial chlorine removal is observed; however, no etching (a decrease of film thickness) was observed. There is no observed difference between the chlorinated cobalt surface in Fig. 5(a) and the same surface briefly heated to 180 °C. An important conclusion from this observation is that the surface reactions may lead to adducts suggesting the possibility of ALE; however, these findings must be combined with the independent verification of etching. Thus, since acach appears to have limited use in the ALE of cobalt films within the conditions investigated here,

TABLE I. Estimated relative surface concentration of species indicated based on the XPS investigation of the reaction of chlorinated cobalt film with acach.

	Sputter-cleaned cobalt film chlorinated by exposure to 100 mTorr of Cl_2 gas at room temperature for 3 min	Chlorinated cobalt film exposed to 1 Torr of acach at 180 °C for 3 min
$\text{Cl}/\text{Co}^{0+} + \text{Co}^{2+/3+}$	4.1	3.8
$\text{Co}^{2+/3+}/\text{Co}^0$	3.16	1.63

FIG. 6. XPS spectra of a chlorinated cobalt thin film following its treatment with hfach (1 Torr for 3 min) at (a) 140 °C and (b) 100 °C, compared to the starting chlorinated cobalt surface (c). Dashed line indicates the expected position of the Co(0) peak reported in Ref. 22.

the rest of this work will focus on hfach application for cobalt etching.

With the efficiency of the use of hfach and Cl_2 in mind, the rest of the studies will be dedicated to the mechanism of the cobalt etching process observed, focusing specifically on the first cycle of the process. As shown in Fig. 6 and Table II, for the dosing conditions ($T = 140$ °C) and sequence verified above for ALE of cobalt, the *in situ* XPS investigation confirms the chlorination of the cobalt film surface by Cl_2 . Following the second half-cycle, hfach exposure, the amount of the chlorine on the surface is reduced by 15% and

TABLE II. Estimated relative surface concentration of species indicated based on the XPS investigation of the reaction of chlorinated cobalt film with hfach.

	Sputter-cleaned cobalt film chlorinated by exposure to 100 mTorr of Cl_2 gas at room temperature for 3 min	Chlorinated cobalt film exposed to 1 Torr of hfach at 100 °C for 3 min	Chlorinated cobalt film exposed to 1 Torr of hfach at 140 °C for 3 min
$\text{Cl}/\text{Co}^{0+} + \text{Co}^{2+/3+}$	3.13	2.92	2.64
$\text{Co}^{2+/3+}/\text{Co}^0$	2.82	2.63	0.94

the oxidation state of cobalt is changed, leading to the metallic cobalt formation. There is no adsorbed fluorine as observed by XPS following this step.

C. Thermal desorption investigations

The reactor studies described in Sec. IV A and the *in situ* XPS investigations outlined in Sec. IV B indicate that sequential doses of Cl_2 and hfacH at temperatures above 140°C result in cobalt ALE and that each cycle results in cobalt reduction and removal of surface chlorine upon exposure to hfacH. However, the formation of a similar surface species was recorded for the Cl_2/acacH sequence and that sequence did not result in any cobalt removal. Thus, in addition to analyzing the species present on the surface during each step of the ALE cycle, it is imperative to understand which species are responsible for metal removal during the process. In order to achieve this goal, thermal desorption studies were conducted in a separate UHV chamber. For this work, a cobalt film exposed to chlorine gas in a UHV setup described in Sec. II C was transferred with minimal exposure to ambient conditions into a UHV chamber designed specifically for thermal desorption studies, described in Sec. II D. This step resulted in surface oxidation; however, chlorine loss was less than 30%, as confirmed by XPS, when the sample prepared by the identical procedure was removed from UHV and then reintroduced back into the chamber. Thus, the TPD experiments focused on the second half of the ALE cycle at the conditions that are determined from the work summarized in Fig. 3. The process may seem to be resulting in a poorly prepared surface; however, the same surface is probably realistic in the ALE process described above, where the background pressure of the ALE setup is 0.05 Torr, which obviously leads to surface oxidation.

For thermal desorption experiments, the chlorinated (and partially oxidized) cobalt film sample was loaded into the TPD chamber at UHV conditions, dosed with hfacH (1×10^{-6} Torr for 5 min) at several different surface temperatures, and the thermal desorption spectra were recorded at 2 K/s heating rate, stopping at approximately 425°C . As has been shown previously,¹⁰ heating substantially above this temperature results in surface pitting of the film. Figure 7 compares the traces collected for selected representative Co-containing species desorbing from the surface. As was shown previously, exposure of clean (sputtered with argon and briefly annealed to 425°C) cobalt surface to hfacH at room temperature results in hfacH adsorption followed by decomposition during the course of thermal desorption. In contrast to this observation, the oxidized cobalt surface does react with hfacH forming volatile Co-containing compound $[\text{Co}(\text{hfac})_2]$; however, this compound only desorbs from the surface at 352°C , a temperature 200°C higher than during observed ALE of cobalt, as shown in Fig. 2. Finally, if the chlorinated and partially oxidized cobalt surface is exposed to hfacH at 165°C , there is observed desorption of cobalt-containing species within the desired temperature range (between approximately 160 and 320°C). As also shown in Fig. 7, this low-temperature process does not take place if

Fig. 7. Summary of the thermal desorption studies of ALE of cobalt: (a) desorption of $\text{Co}(\text{hfac})_2$ from oxidized cobalt surface following room temperature dose of hfacH; (b) the absence of $\text{Co}(\text{hfac})_2$ desorption following room temperature dose onto a clean (Ar^+ sputtered) cobalt surface pre-annealed to 165°C ; (c) desorption of the $\text{Co}(\text{hfac})_2$ fragment ($m/z = 473$) from the chlorinated and partially oxidized cobalt surface exposed to hfacH at 165°C ; (d) desorption of the $\text{Co}(\text{hfac})\text{Cl}_2$ fragment ($m/z = 337$) from the chlorinated and partially oxidized cobalt surface exposed to hfacH at 165°C ; (e) absence of $\text{Co}(\text{hfac})_2$ fragment desorption from the chlorinated and partially oxidized cobalt surface exposed to hfacH at room temperature.

the exposure of the chlorinated and partially oxidized Co surface to hfacH is done at room temperature [Fig. 7(e)] or at 100°C (not shown). Although the *ex situ* XPS following this TPD experiments indicated the presence of surface fluorine following the TPD process, it also clearly indicated the reduction of cobalt, fully consistent with the rest of the studies presented above. The next important step is to actually characterize the Co-containing product desorbing from the surface. Although the $\text{Co}(\text{hfac})_2$ fragment does seem to be desorbing in the 160 – 320°C range, examination of other possible fragments suggests that the desorbing species may be much more complex. For example, $m/z = 337$ trace presented in Fig. 7(d) suggests the presence of $\text{Co}(\text{hfac})\text{Cl}_2$ fragment. This fragment is not present in the mass spectrum of $\text{Co}(\text{hfac})_2$,²³ meaning that other Co-containing species must be responsible for the process of ALE of this material. Finally, it is worth mentioning that the presence of such species as $\text{Co}(\text{hfac})\text{Cl}_2$ implies that at least part of the cobalt removal occurs via the formation of Co^{3+} species consistent

with *in situ* XPS results for cobalt, which makes the mechanism of etching of chlorinated cobalt surface substantially different from that of the surface of the same material that is simply oxidized. In fact, there is a precedent of using a similar mixed precursor, $\text{CoCl}_2(\text{N,N,N',N'}\text{-tetramethylethylenediamine})$ for successful deposition of cobalt oxide films by ALD with further reduction producing cobalt metal films.²⁴ A mixed Cl-containing compound was also proposed as a possible desorbing product in ALE of chlorinated iron surface.²⁵ Thus, the role of mixed Co^{3+} -containing metalorganic species in ALE processes may need to be explored further.

D. Computational investigation and potential for surface smoothing in ALE

Several conclusions reached in the experimental investigation described above can be tested in a computational investigation. Specifically, a set of simple computational studies was performed on a $\text{Co}(100)$ surface model surface to explore the energetics of a Co atom removal with the help of Cl or hfac ligands. Figure 8 summarizes the results of this computational work. The energy needed to remove a Co from a $\text{Co}(100)$ terrace is predicted to be 300.2 kJ/mol; however, this number is reduced to 279.8 kJ/mol if the atom is connected to an hfac ligand. It is further reduced to 258.6 kJ/mol if instead of hfac, a chlorine atom is attached to the same cobalt atom of the surface. The trend is very similar

if instead of the cobalt atom from a $\text{Co}(100)$ terrace, a cobalt *adatom* is removed from the same $\text{Co}(100)$ face. However, the absolute numbers are substantially smaller, as would be expected: The energy required to remove the adatom is 109.1 kJ/mol, but it is only 86.3 kJ/mol if hfac ligand is attached to it and 69.7 kJ/mol for chlorine atom attached to the same cobalt atom. The details of the calculations are described in Sec. III.

Two main conclusions can be inferred based on this computational work. First, the attachment of a ligand (chlorine or hfac) decreases the energy required to remove a cobalt atom from the film. Second, the energy needed to remove a cobalt *adatom* is drastically lower than that needed to remove a cobalt atom from the (100) surface. This simple exercise proposes the way to analyze energy requirements for the removal of metal atoms bound to a ligand, which in addition to thermal processing could be achieved by other means, including sputtering or plasma. This study also implies that removing a metal *adatom* is substantially less energetically demanding than removing an atom from a smooth surface, which is fully consistent with the previous observations of surface smoothing during ALE.^{10,19–21}

As shown above, the mechanism of ALE of metals can be very complex, so further experimental work is needed to identify and sort all the possible desorbing products containing metals and then to propose energetic diagrams for the identified processes. This last step could be correlated with

FIG. 8. Summary of the DFT investigation of the effects of surface chlorine and hfac species on the energy required to remove a cobalt atom from a (100) terrace and to remove a cobalt adatom from the same surface.

computational investigations; however, much more complex models, starting with oxidized and partially chlorinated surfaces, will be needed.

V. SUMMARY AND CONCLUSIONS

The combination of the experimental and computational work at a variety of conditions suggests that the ALE of cobalt films can be tuned to allow truly atomic layer etching for oxidized and chlorinated cobalt surfaces. This process is temperature dependent. The most efficient etching protocol was shown to involve hfacH (as opposed to acacH) combined with Cl₂ in a two-step thermal process. The mechanism of thermal dry etching of chlorinated and partially oxidized cobalt films is complex. It appears that it involves multiligand organometallic compounds as desorbing Co-containing products, with at least some of cobalt removed likely being in a +3 oxidation state.

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