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# Uptake of Copper Acetamidinate ALD Precursors on Nickel Surfaces

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The adsorption and thermal activation of copper(I)-*N*,*N*′-di-*sec*-butylacetamidinate on a Ni(110) single-crystal surface were characterized in connection with the use of that compound as a precursor for the growth of copper films via atomic layer deposition (ALD) processes. Studies were carried out under ultrahigh vacuum (UHV) conditions by using a combination of X-ray photoelectron spectroscopy (XPS), low-energy ion scattering (LEIS), and temperature-programmed desorption (TPD). A temperature window between approximately 350 and 450 K was identified for the clean deposition of the precursor on the surface: lower temperatures are insufficient for activation of the dissociative adsorption, and higher temperatures lead to continuous decomposition beyond Cu monolayer saturation. Approximately three ALD-like cycles are required to reach full Cu monolayer saturation, the equivalent of a film growth rate of approximately 0.75 Å/cycle. Preadsorption of hydrogen on the surface does not modify any of this behavior because of its rapid desorption at temperatures above 350 K once the gas-phase $H_2$ is removed. A discussion is provided on how hydrogen pressures above the mbar range are required to maintain significant steady-state coverages of hydrogen on the surface. Copper precursors leading to relatively stable organic surface intermediates are required in ALD because their clean removal can only happen in the second half-cycle of processes that rely on hydrogenation reactions.

## 1. Introduction

Because of the decrease in size and increase in topographic complexity of newer microelectronic devices, there has been an increased interest in developing chemical means for the deposition of thin films.[1−3] Key to these applications is the need to deposit thin films conformally, that is, uniformly over the peaks and valleys of the underlying structures. A variation of chemical vapor deposition (CVD) known as atomic layer deposition (ALD) has proven particularly promising for achieving such conformality while controlling the film thickness at the monolayer level.[4−6] In ALD, two self-limiting and complementary reactions are used sequentially and in alternating fashion to slowly build up solid films one monolayer at the time. The ALD approach brings a number of advantages over conventional CVD methods, including higher control over film thickness, the use of lower temperatures, and less stringent requirements in terms of reactor design.[5,7] On the other hand, like other chemical-based methods, it adds some complexity to the surface processes involved, and tends to lead to the incorporation of impurities within the growing films via undesirable side reactions. Ideally, ALD precursors should follow a clean surface chemistry that deposits only the element of interest.[8,9]

In particular, ALD offers great promise in the growth of electrical interconnects.[10] In the past those have been made out of aluminum, but more recently copper has drawn much attention because of its lower bulk resistivity and superior electromigration resistance.[11,12] Copper interconnects are typically made by electrodeposition, but a thin seed layer is required for that process to work optimally, free of the void spaces or seams responsible for surface-like fast Cu diffusion.[13,14] It has been suggested that the seed layer is perhaps best grown by ALD,[7,15,16] but unfortunately, there are at present no copper precursors available for the deposition of seed copper layers

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by CVD or ALD with acceptable adhesion to the surfaces of current devices.[17] Although quite a few copper compounds have been developed for Cu CVD processes, including carboxylates, oxalates, and acetonates,[18−20] only a few have ever been tested for ALD,[4,7,21−25] and, in general, those have proven to lead to films with high resistivities and poor growth.

One of the most promising families of precursors for copper ALD is copper acetamidinates.[26−29] The advantages of metal acetamidinates for ALD include their relative resistance to reactions with air and their reasonable vapor pressure (about 0.1 Torr at 85 °C for copper(I)-*N*,*N*′-di-*sec*-butylacetamidinate). Past work has indicated that, although Cu acetamidinates appear not to chemisorb onto clean metals at the temperatures needed for ALD, somewhere around 450−500 K, they may be activated on hydrogen-presaturated surfaces. Under those conditions the deposition appears to be self-limited, and to leave a clean copper layer of about 0.5 Å in thickness on the surface.[27] However, the surface chemistry involved in this process is virtually unknown, and many questions remain.

In this report we summarize results obtained from surface-science studies designed to pin down the optimum conditions under which copper acetamidinates may be used for ALD and to investigate the role of hydrogen as the second reactant in these processes. It is shown here that, with copper(I)-*N*,*N*′-di-*sec*-butylacetamidinate, activated adsorption on nickel surfaces is possible only above 300 K. Also, at least on nickel substrates and under vacuum conditions, the optimum deposition temperature was identified to be around 350 K, because by 400 K deposition past the monolayer is possible, and by 450 K decomposition and Cu multilayer deposition is rapid; the adsorption is no longer self-limiting, as required for clean ALD processes. It is also reported that approximately three ALD cycles are required to deposit a full copper monolayer. No detectable changes in deposition rates or surface chemistry were observed upon presaturation of the substrate with hydrogen. A discussion is provided to justify this latter observation.

## 2. Experimental Details

The experiments were conducted in an ultrahigh vacuum (UHV) system turbo-pumped to a base pressure of $1 \times 10^{-10}$ Torr and equipped with an UTI mass quadruple for temperature programmed desorption (TPD), a concentric hemispherical analyzer (VG 100AX) for X-ray photoelectron (XPS) and low-energy ion scattering (LEIS) spectroscopies, an Al Kα/Mg Kα dual anode X-ray source for XPS, and a Kratos rasterable rare-gas ion gun for sample cleaning and LEIS.[30,31] The XPS data reported here were taken by using the Al Kα X-ray source ($h\nu = 1486.6$ e V), and correspond to averages of 25 scans (a total data acquisition time of 7.5 s per point) recorded in 0.1 eV increments. An electron-energy-analyzer pass energy of 50 eV was used, which in our system corresponds to an analyzer resolution of 0.6 eV and a total resolution of approximately 1.0 eV once the natural width of the Al Kα line is taken into consideration. Most of the LEIS studies were carried out by using $Ne^+$ ions to better discriminate between copper and nickel surface atoms, but $He^+$ was also used in some instances to identify lighter elements such as carbon, nitrogen, and oxygen. An incident energy of 2000 eV was used in the experiments reported below.

A polished Ni(110) single-crystal was used as the substrate. Nickel was chosen as a convenient representative of the metal surfaces used as diffusion barriers for copper; typical barriers are made out of metal nitrides, but those interfere with the nitrogen signals of the copper acetamidinate precursor in XPS experiments. The Ni(110) single crystal used was in the form of a disk 10 mm in diameter and 1 mm in thickness, and it was mounted on a vacuum manipulator via 0.5 mm Ta-wires spot-welded to the edge of the crystal and fixed to the ends of copper vacuum feedthroughs. Cooling was accomplished by using a liquid-nitrogen reservoir in direct contact with the copper feedthroughs, and resistive heating was used to reach any desired temperature between 90 and 1200 K. A K-type thermocouple was spot-welded to the edge of the crystal to monitor the temperature of the surface, and a homemade temperature controller was used to provide linear temperature ramps for the TPD experiments and to maintain the crystal to within ±1 K of any specified temperature. The heating rate for the TPD measurements was set to 10 K/s.

The copper(I)-*N*,*N*′-di-*sec*-butylacetamidinate precursor was synthesized by reaction of *N*,*N*′-di-*sec*-butylacetamidine first with methyl-lithium and then with CuCl; the free acetamidine was prepared by reaction of acetonitrile with *sec*-butylamine. Details of the synthesis and full characterization of the final product are provided elsewhere.[26,27] The precursor proved quite stable against thermal decomposition: its half-life in a hydrocarbon solution in a sealed glass NMR tube was measured to be 33 days at 465 K, and no detectable decomposition was observed in a glass bubbler used for over 500 ALD depositions at 295 K, each lasting several hours, over a period of approximately 3 years. Only when containers made out of metals such as stainless steel were used was rapid initial decomposition observed.

All gases were purchased from Liquid Carbonic (Research Purity, >99.995%), and used without further treatment. The Ni(110) crystal was cleaned before each experiment by repeated cycles of $Ar^+$ ion sputtering and annealing at 1100 K until the surface was deemed clean by XPS. Dosing of the sample was done by backfilling of the chamber using appropriate leak

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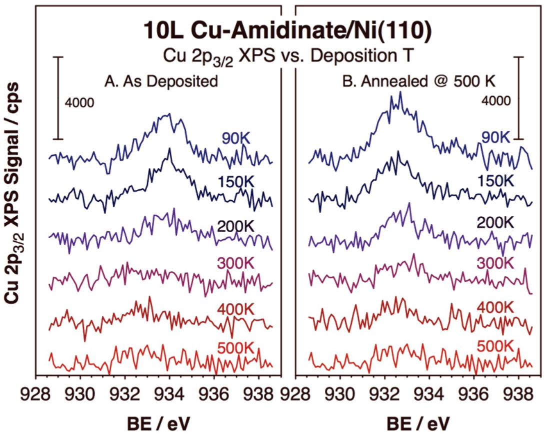

**Figure 1.** Cu $2p_{3/2}$ X-ray photoelectron spectra (XPS) obtained after exposures of a Ni(110) single-crystal surface to 10.0 L of copper(I)-*N*,*N'*-di-*sec*-butylacetamidinate. Two sets of data are shown, for surfaces dosed at the indicated temperatures (left panel), and after annealing those to 500 K (right). Adsorption at low temperatures is molecular, but decomposition and deposition of metallic copper is seen around 300 K. The conversion is direct from Cu(I) to Cu(0) species; no Cu(II) was ever detected at any stage of the deposition or annealing.

valves; in the case of the copper acetamidinate precursor, the gas lines behind the valve were kept at approximately 330 K in order to minimize condensation. The pressure in the main UHV chamber was measured using a nude ion gauge. Gas doses are reported in Langmuirs ($1\ L = 1 \times 10^{-6}$ Torr·s), uncorrected for differences in ion gauge sensitivities. All exposures were performed at the constant surface temperatures indicated in the corresponding figures.

## 3. Results

The adsorption and activation of the copper acetamidinate on the Ni(110) surface was first investigated by XPS. Figure 1 displays the Cu $2p_{3/2}$ XPS data obtained after adsorption of 10.0 L of the acetamidinate at different temperatures. Two sets of data are shown, one for the surface immediately after the adsorption at the indicated temperatures (left), and another obtained after annealing each of the surfaces of the first set to 500 K. The 10 L exposure was chosen to reach surface coverages close to one monolayer (see below). The data show that adsorption at temperatures below 200 K results in the appearance of one XPS peak centered at 934.0 eV. This value is typical of Cu(I) species[32] and close to that reported for a copper acetylacetonate complex deposited onto a K10-montmorillonite clay,[33] and is therefore indicative of molecular adsorption. The +1 oxidation state of the metal centers was further confirmed by the kinetic energy of the $L_3VV$ Auger electrons, which was determined to be 913.7 eV (the Auger parameter amounting to 361.1 eV; data not shown).[34]

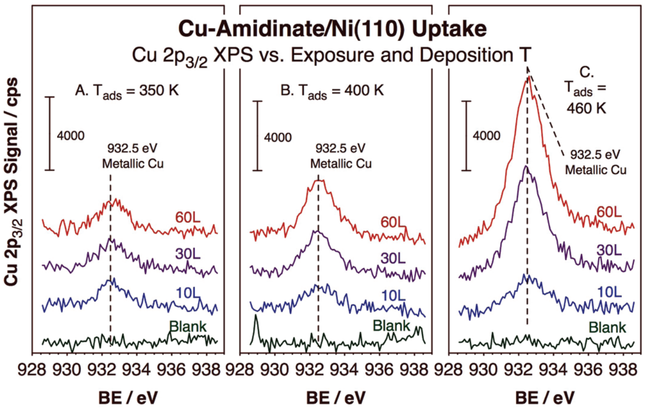

**Figure 2.** Cu $2p_{3/2}$ XPS uptake for copper(I)-*N*,*N'*-di-*sec*-butylacetamidinate on Ni(110) at 350 (left), 400 (center) and 460 (right) K. All peaks are centered at 932.5 eV, a value typical for metallic copper. Also, the uptake is faster at higher temperatures, as more clearly illustrated in Figure 5.

Annealing at 500 K of the copper acetamidinate initially adsorbed at temperatures below 200 K results in a clear shift in the binding energy of the Cu $2p_{3/2}$ XPS peak of the adsorbed copper species, to 932.5 eV. The Auger $L_3VV$ line shifts even more, to a kinetic energy of 919.0 eV (Auger parameter = 364.9 eV), consistent with the reduction of the copper atoms to a metallic state.[32,34] In fact, dosing of the copper acetamidinate on surfaces kept at temperatures of 300 K or above directly leads to the formation of adsorbed copper metal. This means that there is a switch in adsorption mode between 200 and 300 K from molecular to dissociative. Under no circumstances were other oxidation states identified for the copper-containing surface species; no disproportionation reactions or formation of Cu(II) species were detected. Finally, the dissociative adsorption of copper acetamidinate takes place with a lower effective sticking coefficient than that seen for molecular adsorption at lower temperatures, a fact indicated by the lower copper uptake (smaller Cu XPS peak) seen above 300 K. Clearly, activation and adsorption of the copper acetamidinate on the surface competes with molecular desorption at these higher temperatures. Such kinetic competition may explain why high doses of the precursor are required in ALD processes: at the high temperatures used in those, most of the incoming molecules simply desorb molecularly before having the opportunity to react and bond to the surface.

Further copper acetamidinate uptake experiments were carried out at surface temperatures between 300 and 460 K, a temperature range more in tune with those of interest for ALD. The Cu $2p_{3/2}$ XPS data obtained as a function of exposure for 350 (left panel), 400 (center), and 460 (right) K are provided in Figure 2. First to notice in this figure is the fact that, again, all peaks are centered at 932.5 eV, the binding energy identified with metallic copper atoms. Moreover, a larger uptake is seen at higher temperatures, an observation indicative of the activated nature of the adsorption. In fact, at 350 K the copper surface coverage reaches saturation after exposures on the order of 10 L, after which no further uptake is possible. At 460 K, by contrast, the uptake appears to be unlimited, and certainly continues well past the first

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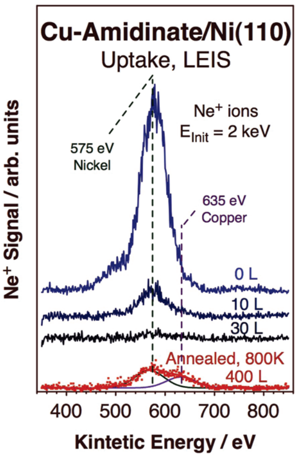

**Figure 3.** $Ne^+$ low-energy ion scattering (LEIS) data from a Ni(110) single-crystal surface dosed at 90 K with copper(I)-*N*,*N*′-di-*sec*-butylacetamidinate as a function of exposure. Monolayer saturation, indicated by the disappearance of the signal at 575 eV, occurs after exposures of about 12 L. The bottom trace corresponds to a surface dosed with 400 L of the copper acetamidine at 90 K and then annealed to 800 K. A fraction of the nickel surface (~10%) becomes exposed again, and a new feature due to the deposited copper is seen at 635 eV.

monolayer. Based on the attenuation of the Ni 2p XPS signal (data not shown) and on comparisons with LEIS data (see below), a coverage of approximately three monolayers is estimated for the case of the 60 L exposure at 460 K (the term monolayer is used here relative to a value of one for monolayer saturation). A summary of the copper uptake derived from these data is provided in Figure 5 in connection with our discussion on the effect of coadsorbed hydrogen (see below).

Calibration of the exposures required for the buildup of a monolayer coverage of the adsorbed copper acetamidinate is better accomplished by LEIS, because that technique is sensitive to the composition of the topmost layer (as opposed to XPS, which provides a weighted average of the composition of several layers, down to a depth of a few nanometers).[35] Figure 3 displays results from LEIS experiments on the uptake of copper acetamidinate on a Ni(110) single-crystal surface at 90 K. It shows that most of the signal seen at 575 eV, which corresponds to $Ne^+$ scattering from the nickel surface atoms, is already suppressed after a 10 L exposure: only approximately 15% of the nickel surface remains uncovered at this stage of the uptake. Exposures of approximately 12 L are sufficient to saturate the surface at these low temperatures, and by 30 L no nickel atoms are any longer exposed. It should be noted, though, that the adsorbed monolayer under these conditions is comprised of molecular copper acetamidinate, and that those molecules have a large footprint, much larger than that of the surface species obtained upon activated adsorption at higher temperatures. Indeed, the bottom trace of Figure 3 shows that annealing of saturated monolayers of adsorbed copper acetamidinate to high temperatures leads to some adsorbate decomposition and to the re-exposure of some nickel atoms. Two additional observations are worth highlighting from the data obtained after annealing: (1) a new peak develops in the LEIS data at 635 eV, associated with surface copper atoms, and (2) the combined signal from nickel and copper at this stage is much smaller than that of the clean surface. The latter observation is at least in part justified by the codeposition of carbon- and/or nitrogen-containing species on the surface upon thermal activation of the adsorbed copper acetamidinate, a fact that was corroborated by additional LEIS experiments using $He^+$ ions (data not shown). It should be pointed out, however, that differences in scattering cross section may also contribute to the overall decrease in LEIS signal intensity once the nickel is covered with copper.

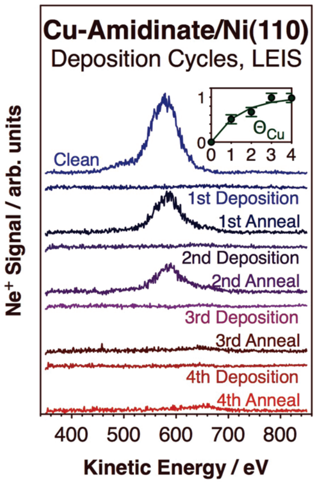

**Figure 4.** $Ne^+$ LEIS data obtained during the deposition of copper on Ni(110) using copper(I)-*N*,*N*′-di-*sec*-butylacetamidinate. Shown are the traces obtained after each dosing, performed at 90 K (50 L for each of the first two cycles, 100 L for the latter two), and after each subsequent annealing of the surface at 465 K. The inset shows the coverage of copper obtained after each cycle estimated from the data. Approximately three cycles are required to deposit one monolayer.

An estimate of the number of cycles needed for the build up of one monolayer of copper atoms on the surface was obtained by performing several exposure-and-annealing cycles in sequence. Figure 4 reports the LEIS traces recorded after four of such cycles, in which the surface was first saturated with copper acetamidinate at 90 K and then annealed to 465 K to decompose the adsorbates and desorb the excess molecules of the precursor. A lower temperature than that used in the experiments in Figure 3 was used here for the annealing to minimize the dehydrogenation of the organic ligands in the hope to better reproduce the conditions seen in ALD. As expected, the LEIS peak associated with the nickel surface atoms decreases in size, by about a factor of 2 after each of those cycles, and disappears almost completely after the third. Quantitation of the uptake, shown as a function of the number of cycles in the inset, indicates an exponential decrease in the amount of nickel atoms exposed as a function of the number of cycles performed, the result expected if new deposition occurs with constant probability on the uncovered nickel substrate. Also evident from the data in the mainframe of Figure 4 is the appearance of the peak due to surface copper, which,

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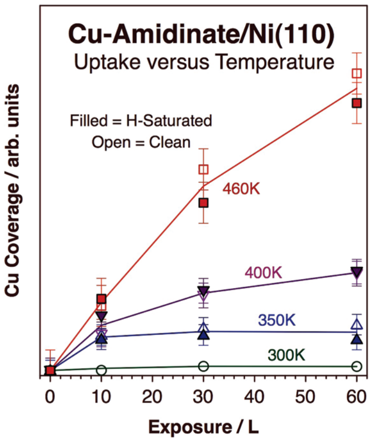

**Figure 5.** Copper uptake estimated from Cu $2p_{3/2}$ XPS experiments such as those shown in Figure 2 for copper(I)-*N*,*N*′-di-*sec*-butylacetamidinate on clean (open symbols) and hydrogen presaturated (150 L $H_2$ at 90 K; filled symbols) Ni(110) as a function of surface temperature. No significant differences are observed between the surfaces with versus without preadsorbed hydrogen.

again, is small because of a combination of codeposition of carbon- and/or nitrogen-containing species and changes in LEIS cross section. A deposition rate of ~ 0.33 monolayers/cycle, or 0.75 Å/cycle, was calculated from these LEIS data.

In order to investigate the effect that coadsorbed hydrogen exerts on the adsorption and decomposition of copper acetamidinate on Ni(110), experiments similar to those reported in Figure 2 were carried out on surfaces previously saturated with hydrogen (by dosing 150 L $H_2$ at 90 K). The resulting uptake curves are compared to those obtained by integration of the data in Figure 2 for the clean surface in Figure 5. No significant changes are apparent from these data: a slightly slower deposition rate may have been seen on the H-presaturated surface at 460 K, but the difference is most likely within the experimental error of the experiments. No appreciable differences were seen in the XPS peak shapes, and no differences were detected in the XPS signals for carbon and nitrogen either (data not shown). It appears that, at least under vacuum, preadsorptrion of hydrogen does not lead to any appreciable changes in the surface chemistry of copper acetamidinates in the temperature range relevant to ALD processes.

The latter conclusion is quite important, and at first sight surprising given that $H_2$ has been successfully used as the second reactant in ALD processes with copper acetamidinates.[28] However, our observation can be easily explained by the fact that hydrogen recombination and desorption from metal surfaces typically occurs at low temperatures, lower than those being considered here.[36,37] A more detailed discussion of this point is offered in the Discussion section. This is certainly true with Ni(110), where all adsorbed hydrogen desorbs by approximately 350 K as indicated by the $H_2$ TPD trace from H-saturated Ni(110) shown at the bottom of Figure 6 (our data, which are in good agreement with reported spectra).[38] Also shown in that figure are the $H_2$ TPD data obtained from monolayers of *N*,*N*′-di-*sec*-butylacetamidine and copper(I)-*N*,*N*′-di-*sec*-butylacetamidinate for comparison. Note that in those cases the traces extend to higher temperatures, indicating that the surface chemistry of both compounds is complex and involves several dehydrogenation steps. Clean ALD processes aim to avoid the high-temperature reactions implied by the $H_2$ TPD signals seen here above 400 K, in particular if those lead to the formation of dehydrogenated surface species that cannot removed in the second half-cycle of the ALD process with $H_2$. We are at present investigating the details of the surface chemistry of both the copper acetamidinate and the free acetamidine to better understand the implications of these results, but that subject is beyond the scope of the present report.

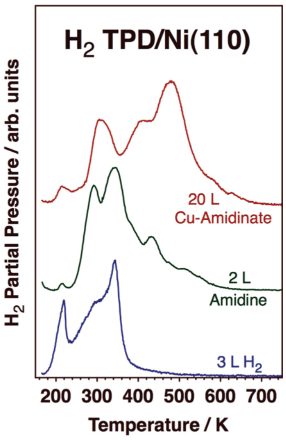

**Figure 6.** $H_2$ (2 amu) temperature programmed desorption (TPD) traces from a Ni(110) single-crystal surface dosed with 3.0 L $H_2$ (bottom trace), 2.0 L disec-butylacetamidine (middle), and 20.0 L copper(I)-*N*,*N*′-di-*sec*-butylacetamidinate (top), all at 100 K. These doses correspond to coverages slightly above monolayer saturation in all three cases. All the hydrogen from the $H_2$-dosed surface desorbs below approximately 380 K. On the other hand, higher $H_2$ TPD peaks are seen with the other two compounds, indicative of stepwise dehydrogenation chemistry.

## 4. Discussion

The surface-science studies reported here corroborate and expand on some of the knowledge on the chemistry associated with the deposition of copper films using copper acetamidinates, copper(I)-*N*,*N*′-di-*sec*-butylacetamidinate in particular, as precursors. In general, the work reported here attests to the power of using a surface-science approach to look into the details of the surface chemistry involved in ALD processes.[9,39−41] In this particular case, it was shown that the copper acetamidinate adsorbs dissociatively on nickel surfaces only above

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approximately 300 K. Moreover, the build up of a copper-containing monolayer was deemed possible only at temperatures of 350 K or above. These temperatures are slightly lower than the onset of the thermal decomposition of the pure compound,[26,27] indicating that the metal substrate plays a role in promoting adsorption. On the other hand, our value agrees reasonably well with the ~390 K threshold reported in ALD experiments.[28] The adsorption is not only dissociative but also activated, since it is faster at higher temperatures. Moreover, the effective sticking probability reflected by the copper uptake is quite high even at 350 K. It appears that ALD processes using copper acetamidinates can, at least in principle, be designed to operate at fairly low temperatures (at least as far as the need to activate the copper precursor is concerned), and to require small copper acetamidinate exposures per cycles (for film deposition on metal substrates).

Perhaps more important is the establishment of an upper limit for the temperatures that can be used in ALD. The main criterion for this is the need to promote the desired self-limiting dissociative adsorption while avoiding further decomposition and uptake beyond a monolayer coverage. In that regard, our data indicate that, under UHV conditions, some slow decomposition occurs on the surface at temperatures as low as 400 K, and that a fast and continuous copper deposition is achieved by 460 K, well beyond the saturation of the first layer. These temperatures are somewhat lower than those reported in ALD kinetic studies: most ALD-grown Cu films have typically been deposited at temperatures between approximately 425 and 465 K, and significant carbon codeposition (> 10%) appears to occur only above 575 K.[28]

A number of issues are worth discussing in connection with the apparent discrepancy between the surface-science and ALD experiments. First, the possibility of competing CVD processes taking place during ALD film growth has not been fully ruled out, and is quite likely given the high deposition rates seen on some substrates (see below). In fact, increasing the temperature used in ALD results in the deposition of rougher and less conductive films, an observation suggestive of side reactions associated with nucleation and further copper acetamidinate decomposition. On the other hand, our uptake data in Figure 5 indicate reasonably slow CVD-like processes even at 460 K, a competing pathway that could in fact be minimized by minimizing the total copper acetamidinate dose used per cycle in the ALD process (ideally by reducing the cycle time in well-designed ALD reactors). Next, it is quite possible for the dissociative adsorption and surface decomposition of copper acetamidinate to be slowed down by the competitive adsorption of the carrier gas in ALD applications, a factor not relevant in the UHV environment used for our surface-science studies. Finally, after the deposition of the first layer of the metal, Cu deposition in ALD processes effectively occurs on the growing copper film, not on the original substrate; given the generally mild surface chemistry exhibited by copper,[42-44] that is likely to result in slower hydrocarbon decomposition, and therefore a wider temperature window for ALD. Based on all these points, it can be concluded that, from the point of view of the cleanliness of the surface chemistry of the copper acetamidinate precursor, although low temperatures are preferred in ALD processes, temperatures around 470 K are still acceptable.

From a practical point of view, the high reactivity of the copper acetamidinate precursor on nickel (and presumably other metal) surfaces has important implications in terms of the handling of the compound for its delivery in ALD reactors. As stated in the Experimental Details section, the copper acetamidinate proved quite stable in glass bubblers but decomposed rapidly in bubblers made out of stainless steel. It is easy to conclude that metal surfaces may aid in the decomposition of the precursor within the gas handling and/or reactor hardware at relatively low temperatures. In fact, the temperatures typically used in ALD bubblers (395 K) are quite close to those reported here for the onset of decomposition on the nickel surface (400 K). The take-home lesson is that an effort must be made to expose the precursor only to noncatalytic surfaces such as glass. Fortunately, there are simple ways to coat stainless steel surfaces with silica, as done regularly on fittings and tubing in gas chromatography in order to avoid the catalytic destruction of the compounds being analyzed.

An issue related to that of activation temperatures is that of the deposition rate expected in copper ALD processes. The relevant information from our work on this issue comes from the LEIS data summarized in Figure 4. Those experiments do not exactly reproduce the situation encountered in ALD, where a second reactant is used to clean up the surface from the byproducts, but still provide a rough estimate for the expected growth rate. This is so because the film growth rate measured in our LEIS studies is controlled by the large footprint of the original copper acetamidinate precursor, which limits the density of copper atoms deposited on the first monolayer. After thermal activation of the precursor-saturated monolayer, the conversion of the initial acetamidinate into the final surface species does free some surface sites and makes them available for further Cu deposition, but that occurs afterward; the new sites can be filled with more copper only in the next deposition cycle.

As long as the rate of the ALD is also determined by the adsorption of the original precursor, the same argument should hold true there as well, and the deposition rate in both cases should be the same. Such an analogy provides an estimate for the rate of film growth in pure ALD mode of approximately 0.75 Å/cycle. Moreover, because in the experiments in Figure 4 the surface was heated to temperatures similar to those in ALD between adsorption cycles, the same organic side species are likely to form on the surface. It is worth remembering that in ALD the

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surface produced after the first half-cycle is also expected to be covered with a combination of copper and organic surface species. The extra organic species are allegedly removed by $H_2$ in the second half-cycle of the ALD, but that is not what controls the maximum amount of copper deposited in each cycle; the uptake of the acetamidinate is. According to our data, the fraction of the surface covered by copper in each cycle is constant and determined by the amount of copper that can be fit in a monolayer by using the copper acetamidinate precursor; the same argument is likely to apply to ALD.

Another difference to consider between the LEIS experiments and ALD processes is that under ALD conditions the adsorption of the precursor is done at higher temperatures, and may therefore be accompanied by partial decomposition. In the case of the copper acetamidinate, one desirable possibility is for one of the two acetamidinate ligands to be hydrogenated as it dissociatively bonds to the surface, and for it to desorb as a free acetamidine molecule. In that case, additional sites would be freed during the copper acetamidinate dosing for further copper uptake, and a somewhat higher deposition rate per cycle could be possible. However, this chemistry is not likely to occur, at least on metals, because there are no obvious chemical pathways for the clean elimination of the organic ligands in the copper precursor without the deposition of irreversibly adsorbed moieties. In particular, given that no significant hydrogen from the second half-cycle remains on the surface once the $H_2$ is pumped away (see below), hydrogenation of the acetamidinate ligands would require surface hydrogen from decomposition of other organic moieties, and that would be likely to deposit other irreversibly adsorbed species, which would end up as impurities in the growing films. If no ligand elimination takes place during the first half-cycle, the metal uptake rate in ALD may be similar to that seen in the LEIS experiments. The deposition rate value obtained here is certainly within the range reported in many ALD studies.[28]

Hydrogen from specific surface groups in nonmetallic substrates such as hydroxyl moieties in oxides may aid in promoting the type of hydrogenation reactions mentioned above during the initial stages of deposition. Higher deposition rates may therefore be seen in those types of substrates.[28] They are certainly expected to have a higher density of reactive sites (hydroxyl groups in oxides, for instance), and to facilitate the removal of at least one ligand from the precursor as it dissociatively adsorbs on the surface (the hydroxyl groups may provide the hydrogen needed to hydrogenate acetamidinate ligands to the free acetamidine). If this is the case, there would be fewer bulky ligands left on the adsorbed species, and more space for further copper acetamidinate uptake within a given cycle. However, although such reaction would lead to the existence of more nucleation sites on the initial surface and perhaps to the ability to grow smoother films as a result, it would still not be able to account for faster film growth rates once the surface is covered with the first layer of metallic copper. Consistent high deposition rates, even in this case, are likely to be indicative of a CVD component.

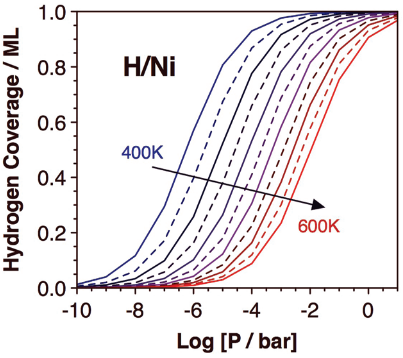

**Figure 7.** Estimated steady-state hydrogen surface coverages on Ni(110) as a function of hydrogen pressure and surface temperature, as calculated using adsorption and desorption parameters from the literature.[36] Traces are shown in 20 K intervals from 400 to 600 K, the temperature range of interest in ALD. At these temperatures, significant hydrogen coverages are only possible in the presence of relatively high $H_2$ pressures, above approximately $10^{-6}$ bar.

Lastly, we turn our attention to the role of hydrogen in the surface chemistry of Cu ALD using copper acetamidinates. As indicated above, no significant effect was observed in our surface-science experiments upon preadsorption of hydrogen on the surface; similar copper deposition rates were measured on the clean versus H-pretreated surfaces at all temperatures (Figure 5). The reason for this was traced back to the early desorption of the hydrogen from the surface, which occurs at temperatures below those used for the Cu film growth (Figure 6). A more comprehensive argument in this respect can be made by using kinetic data available in the literature for hydrogen adsorption and desorption from metal surfaces.[36] Figure 7 displays the steady-state H coverages expected on Ni(110) surfaces as a function of both temperature and $H_2$ pressure estimated from such kinetic data. It can be clearly seen there that increasing temperatures and/or decreasing pressures result in a decrease in steady-state hydrogen surface coverage, and that, in the temperature regime of interest (400−600 K), significant H surface coverages can only be maintained under $H_2$ pressures above approximately $10^{-6}$ bar. Our calculations rely on kinetic parameters measured under UHV conditions, but recent in situ coverage measurements under atmospheric pressures have confirmed their validity.[45] It is also worth pointing out that the results reported here for nickel are quite representative of the chemistry that takes place on most transition metals, and that the kinetic parameters for hydrogen adsorption on cobalt, a substrate of interest in the microelectronic industry,[15,46] are almost identical to those on nickel. In fact, our preliminary surface-science data from experiments on a cobalt foil suggest adsorption behavior for the copper acetamidinate quite similar to that seen on nickel surfaces.

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The implication from the fast and reversible nature of hydrogen adsorption on transition metal surfaces is that any adsorbed hydrogen generated by exposure of the substrate to $H_2$ in the second half-cycle of the copper acetamidinate + $H_2$ ALD cycles is rapidly lost upon pumping or flushing of that gas. Consequently, any organic intermediates formed on the surface upon activated adsorption of copper acetamidinate need to be sufficiently stable under the temperatures used for ALD to survive the purging typically done in between half-cycles so they can be hydrogenated once the hydrogen gas is introduced in the system. Otherwise, they are likely to dehydrogenate and form irreversible adsorbates, and ultimately incorporate carbon and/or nitrogen impurities in the growing films. Both the temperatures used for ALD and the nature of the copper acetamidinate (or any other organometallic precursor used in ALD processes based on reduction with $H_2$) need to be tuned to fulfill this requirement. Unfortunately, the surface chemistry of copper acetamidinates is virtually unknown. We are, at present, exploring the details of this chemistry to be able to better evaluate the viability of organometallic precursors such as these as ALD precursors in cycles that rely on hydrogenation reactions.

## 5. Conclusions

The adsorption and thermal activation of copper(I)-*N*,*N*′-di-*sec*-butylacetamidinate on Ni(110) single-crystal surfaces was studied under ultrahigh vacuum conditions by using a combination of X-ray photoelectron spectroscopy, low-energy ion scattering, and temperature-programmed desorption. Two adsorption modes were identified, molecular at low temperatures, and dissociative above 300 K. The latter is activated, and leads to the reduction of the copper atoms directly to a metallic state. Monolayer saturation is seen when the deposition is carried out at 350 K, but some additional decomposition and copper deposition is seen over time at temperatures as low as 400 K, and almost a linear dependence of copper growth on exposure is observed by 460 K.

Because of the large footprint of the original adsorbed copper acetamidinate, the maximum uptake of copper atoms per cycle in ALD is limited by the initial dissociative adsorption of the precursor, even if its subsequent thermal treatment on the surface leads to the opening of some additional sites (presumably via the desorption of some organic byproducts). It was determined that approximately three cycles of low-temperature surface saturation and annealing are needed to reach a monolayer coverage of copper on the surface, the equivalent of a film growth rate of ~0.75 Å/cycle. It is likely for similar growth to define pure ALD processes, and for significantly larger values to be a reflection of additional CVD.

Finally, it was established that, under the conditions of these experiments, pretreatment of the nickel surface with hydrogen does not result in any significant changes in the deposition of copper via copper acetamidinate dissociative adsorption. The absence of any effect here was ascribed to the low temperatures needed for hydrogen desorption ($\leq$350 K), below those typically used in ALD processes. Based on calculations using published kinetic parameters, it was determined that significant steady-state hydrogen surface coverages above ~400 K are possible only under pressures of gas-phase hydrogen above approximately $10^{-6}$ bar. This suggests that the organic intermediates that may form on the surface upon thermal activation of adsorbed copper acetamidinate need to be stable at the temperatures used in ALD in order to be available for hydrogenation and removal from the surface in the second half-cycle rather than decomposing and incorporating as impurities in the growing films.

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