

Growth of Cr on Cu(001) studied by scanning tunneling microscopy

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The growth of ultrathin films of Cr on Cu(001) over the temperature range 285–575 K is reported. Film formation has been studied by scanning tunneling microscopy, Auger electron spectroscopy, and low-energy electron diffraction. The growth is found to be three dimensional in character with the formation of irregular multilayer high islands. The deposited chromium becomes more particulate and bulklike in nature with increasing deposition temperature, with the formation of high surface outgrowths. The films are metastable and agglomerate upon annealing at higher temperatures.

I. INTRODUCTION

The development of scanning probe microscopies has opened up new horizons for the study of surfaces and interfaces of materials. The field of surface magnetism is just one example where these new tools, coupled with the existing surface analysis techniques, have brought about an increase in interest and activity. Contiguous to this is the advent of more powerful computational facilities, which have been very successful in the calculation and prediction of new magnetic materials and other unusual phenomena.¹

Cr represents an interesting case since in its bulk form, though it is only a weak antiferromagnet, it possesses a half-filled $3d$ shell. The prospect of somehow stabilizing a high spin configuration yields the possibility of forming a large local moment.^{2,3} There are also important similarities to be drawn between Cr and Fe. Both have a body-centered-cubic (bcc) structure in their equilibrium room-temperature form. They have practically the same lattice parameters: 0.288 and 0.287 nm, respectively. Iron has been shown to grow on Cu(001) in metastable ultrathin films (≈ 11 monolayers) with a face-centered-cubic (fcc) form.^{4,5} Calculations also predict that the fcc Cr lattice constant would be within 1% of that of Cu.⁶

The growth of high-quality epitaxial thin films of Cr is also of interest because of the continued controversy about its surface magnetic properties. It has been proposed⁷ that Cr possesses an enhanced layered antiferromagnetic structure. In this scheme there is a sequence of (001) layers with alternating magnetization with the surface layer having a magnetic moment 3–4 times higher than in the bulk. This resulted in considerable effort to the determination of the surface magnetization of Cr. There is disagreement between the results of different measurement techniques as to whether an enhanced antiferromagnetic surface exists.^{8,9} Spin-polarized scanning electron microscope images of Cr wedges grown on iron¹⁰ have shown oscillations in the in-plane magnetization between successive atomic Cr layers, but are unable to determine values of it. Scanning tunneling microscopy (STM) measurements¹¹ have reported the observation of a change in polarization of the tunnel current when going

from one step to the next. This manifested itself as an effective periodic variation in the measured monatomic step height. One of the difficulties with this experiment was the cleaning of the Cr single crystal surface, a process that took several months. The growth of epitaxial Cr films with suitable orientation would greatly facilitate further study of this phenomenon.

The growth of Cr on Cu(001) has already been studied by a number of groups. An initial low-energy electron diffraction (LEED) investigation¹² of the system observed two orthogonal domains, with an apparently 3×1 structure visible for deposited thicknesses greater than 3 monolayer equivalents (MLE). One monolayer equivalent is assumed to be the amount of Cr necessary to form a single bcc layer on the copper surface. Magneto-optic Kerr effect measurements showed no evidence of any ferromagnetic behavior. Inverse photoemission measurements¹³ for the deposition of Cr on Cu(001) showed little or no magnetic splitting, though similar measurements on Cr/Ag(001) and Cr/Au(001) indicated the presence of a large magnetic moment. It was judged from this work that the results obtained for Cr deposited on Ag(001) and Au(001) were antiferromagnetic in origin due to fcc growth, while Cr on Cu(001) was considered to be bcc and paramagnetic. LEED, x-ray photoemission spectroscopy, and x-ray photoelectron diffraction studies^{14,15} and the full dynamical LEED study¹⁶ showed that Cr retains its bulk body-centered-cubic structure and grows in a multilayer fashion with four equivalent domain orientations. We report here the deposition of submonolayer Cr films on Cu(001) and the study of their initial growth stages as a function of temperature by STM, LEED, and Auger electron spectroscopy (AES) in the temperature range 285–575 K.

II. EXPERIMENT

The experiments took place under UHV conditions in a system that has been described previously.¹⁷ The substrate was a mechanically polished Cu(001) single crystal, with a miscut of less than 0.5° . The surface was cleaned by repeated cycles of Ar ion bombardment [1 keV at 620 K (Refs. 17 and 18)] and annealing at 800 K. The substrate

heater uses an indirect electron beam, which impinges on the back of the sample holder. Prior to deposition the substrate was given a final ion etching and then allowed to cool radiatively from 620 K to the required deposition temperature, in order to anneal out any remaining surface damage. The cleaned Cu(001) crystal exhibited a clearly defined (1×1) LEED pattern and impurity levels were below the detection limit of the AES. The surface consisted of a series of broad terraces (≈ 400 nm) separated by monatomic steps or clusters of steps. On the terraces atomic resolution of the copper surface was clearly evident.

The Cr (99.995%) was sublimed from a Knudsen cell held at 1423 ± 0.5 K providing a stable deposition rate of 0.25 MLE/min. This was calibrated using a quartz crystal microbalance as well as with AES data, which are in good agreement with the estimates of the island surface coverage determined from the STM images.

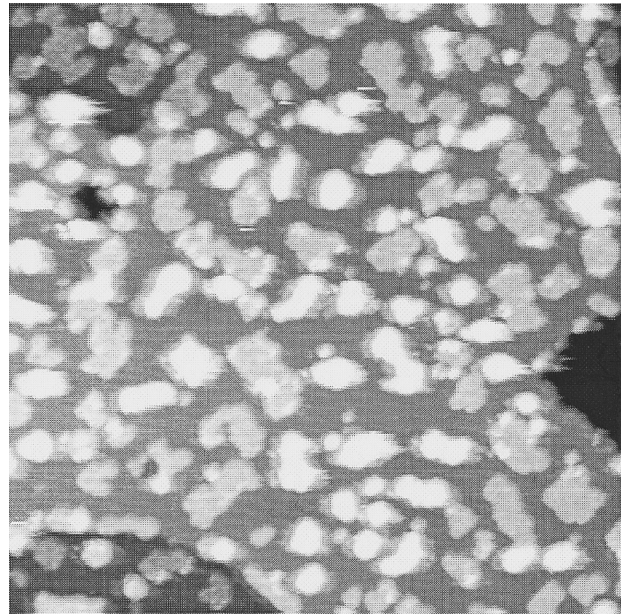
III. RESULTS AND DISCUSSION

Films of Cr on Cu(001) were grown for nominal thicknesses of typically less than 1 MLE and for substrate temperatures between 285 and 573 K. Thicker films (≈ 3.0 MLE) were also deposited at room temperature in order to investigate the evolution of the growth. The STM and LEED results will be discussed in relation to the conclusions of other studies of this system using other techniques.

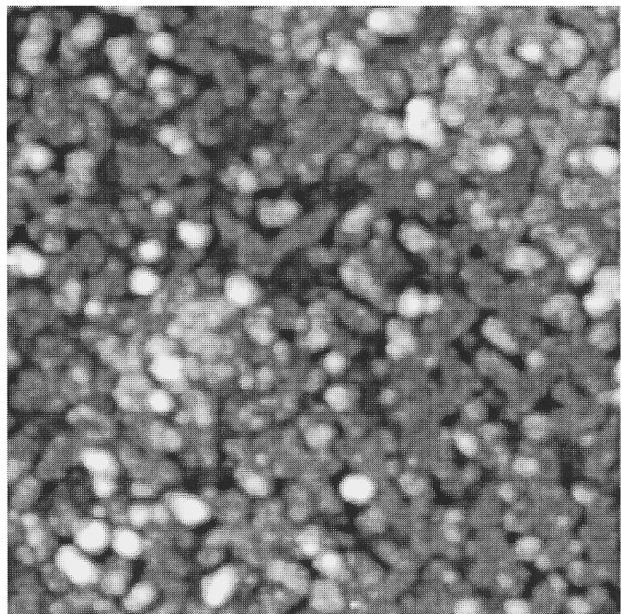
LEED patterns of all the films showed only the presence of a (1×1) surface structure. We ascribe these to the Cu(001) reflections as the spots become weaker with increased Cr coverage and were accompanied by the emergence of a diffuse background. This is indicative of a highly disordered surface structure. The fact that no obvious reflections from the Cr are visible up to thicknesses of 3 MLE is in contrast to other studies of this system.^{16,14,15}

The work of Refs. 14 and 15 conclude that Cr grows with its bulk (bcc) lattice parameters for thicknesses greater than 3 MLE. For lower coverage this lattice is distorted from its bulk parameters to produce epitaxy, i.e., pseudomorphic growth. There are four equivalent domain orientations, aligned with the (110) plane parallel to the Cu (001) surface and the Cr[111] direction parallel to the Cu[110]. Similar LEED patterns have been observed¹⁶ for thicker films annealed at temperatures up to 570 K. The low coverage films in our study are probably insufficiently thick to obtain this LEED pattern. However, we also only observe the 1×1 Cu(001) reflections in our thicker films (3.0 MLE), unlike the other studies^{16,14,15} that show the four domain LEED pattern at these deposition levels. The question of deposition temperature and its effect on film morphology must be considered when discussing these results and this will be done later in conjunction with the STM data.

We present here a series of images of the Cu(001) surface after the deposition of Cr over the temperature range 285–575 K. These are chosen to show the variation in topography for similar amounts of Cr deposited with increasing temperature. Figures 1(a) and 1(b) display STM images of the Cu(001) surface after deposition of 0.6 and 3.0 MLE of Cr respectively at 285 K. In both images the growth of irregular multilayer islands is clearly evident. The size of the islands varies over a large range (2–15 nm). Even with only 0.6



(a)



(b)

FIG. 1. STM images of the Cu(001) surface after deposition of Cr at 285 K (a) 0.6 MLE ($100 \times 100 \times 0.8$ nm³) ($V_t=1.5$ V, $I_t=100$ pA) and (b) 3.0 MLE ($100 \times 100 \times 0.9$ nm³) ($V_t=10.0$ V, $I_t=110$ pA). The islands are irregular and multilayer and vary greatly in size (2–15 nm). The step heights are characteristic of the Cr(110) interlayer spacing; there are also some similar to the predicted fcc Cr(001) spacing. The lack of atomic resolution on the islands is indicative of surface disorder.

MLE deposited [Fig. 1(a)] three-layer-high islands are observed. The copper terrace is clearly visible between the islands at these lower coverages. The STM image in Fig. 2 shows a small-scale atomically resolved image of the Cu terrace. The measured corrugation on the Cu(001) surface was as up to 0.6 nm. From the beam widths of their LEED pattern Ref. 14 estimates the size of the islands to be about

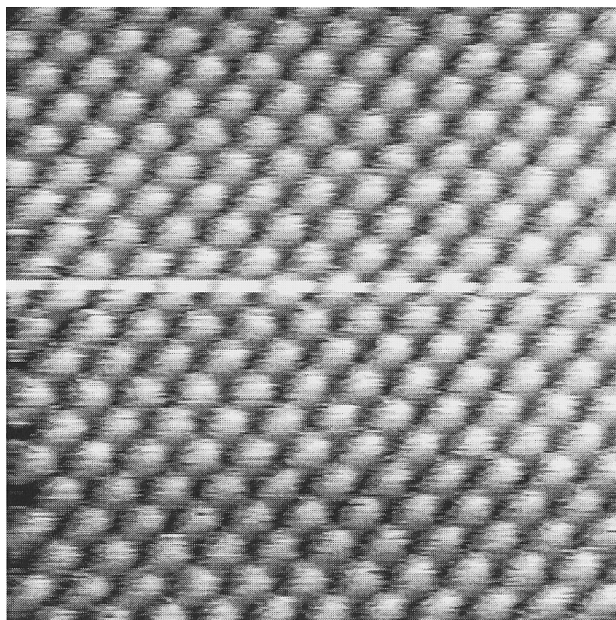


FIG. 2. Small-scale STM images of the Cu(001) terrace between the Cr islands ($4.3 \times 4.3 \times 0.13 \text{ nm}^3$). The atomically resolved images had measured corrugations up to 0.06 nm high. While it was possible to obtain atomic resolution on the Cu surface, this was not the case on any of the islands. ($V_t=110 \text{ mV}$, $I_t=474 \text{ pA}$.)

ten lattice spacings. This is an order of magnitude smaller than those that we observe. Highly disordered islands may be responsible for this anomalous value, implying that they consist of segregated small ordered regions ($\approx 2 \text{ nm}$).

A large spread in step heights was measured from the STM images of films grown at 285 K [Fig. 1(a)]. Nevertheless, two characteristic island step heights could be determined and these correspond closely to that for the bcc Cr(110) interlayer spacing (0.204 nm) and the predicted fcc Cr(001) spacing (0.180 nm). The occurrence of this latter spacing was only for a minority of one-monolayer islands. The height histogram in Fig. 3 is of several monolayer-high Cr islands on the Cu(001) surface shown in Fig. 1(a). The large peak is the Cu surface and the Cr islands while having

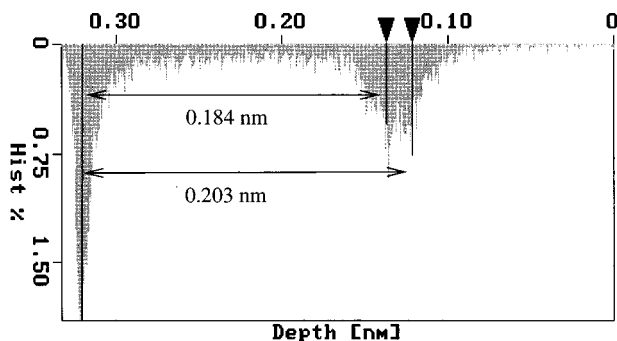


FIG. 3. Height histogram of a several monolayer-high islands from Fig. 1(a). The large peak on the left represents the Cu surface. Though there is a spread in the step heights of the islands, there appear to be two distinct components at heights of $\sim 0.18 \text{ nm}$ and $\sim 0.20 \text{ nm}$ above the surface.

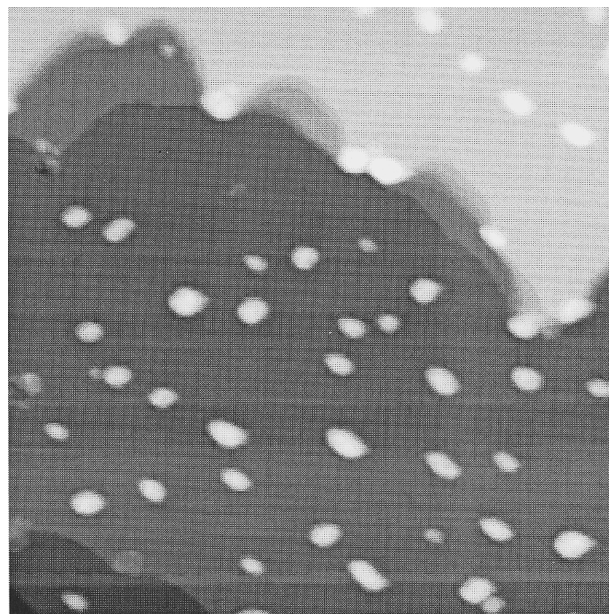


FIG. 4. STM image ($200 \times 200 \times 2.5 \text{ nm}^3$) after deposition of 0.55 MLE Cr at 425 K on the Cu(001) surface. The islands are typically 4–8 monolayers high and more regular in form than on films grown at lower temperatures. Interlayer mass transport must increase for the islands to grow to these heights. ($V_t=4.3 \text{ V}$, $I_t=100 \text{ pA}$.)

a spread in step heights appear to have two distinct components at heights of $\sim 0.18 \text{ nm}$ and $\sim 0.20 \text{ nm}$ above the surface. The layer spacing of $\sim 0.20 \text{ nm}$ supports the assignment of the (110) plane growth parallel to Cu(001),^{14,15} but the inability to obtain atomic resolution does not allow any confirmation of an epitaxial relationship. Determination of actual heights above the terrace is difficult because in contrast to the flat copper surface where atomic resolution was readily obtained, we were unable to image individual atoms on the islands. The surfaces of the islands appear somewhat irregular even at the nominally one-atomic-step height and in particular the edges are quite indistinct. The blurred Cr surface could be due to movement of atoms in the islands. Another explanation could be a small contamination of the Cr surface changing the tip while scanning over the surface or it could be an intrinsic property of the chromium surface as none of the STM reports on chromium have shown atomic resolution.^{11,19}

Figures 4 and 5 show the effect of depositing at elevated temperature, 425 K and 575 K, respectively. The most marked change between these images and the films grown at 285 K is the reduced number of islands and the increase in their size and height. The higher temperatures augment this process. This produces a reduced effective coverage for similar amounts of material deposited. The AES data also show a large decrease in the Cr signal (529 eV) for this higher temperature deposition. Films deposited at 285 K and subsequently annealed at elevated temperature also showed a reduction in their AES signal. Cr is immiscible in Cu at these temperatures, so the signal reduction must be due to a decrease in the coverage of the substrate surface. This is confirmed by the STM images, which show the agglomeration of the islands that appear similar in form to those pro-

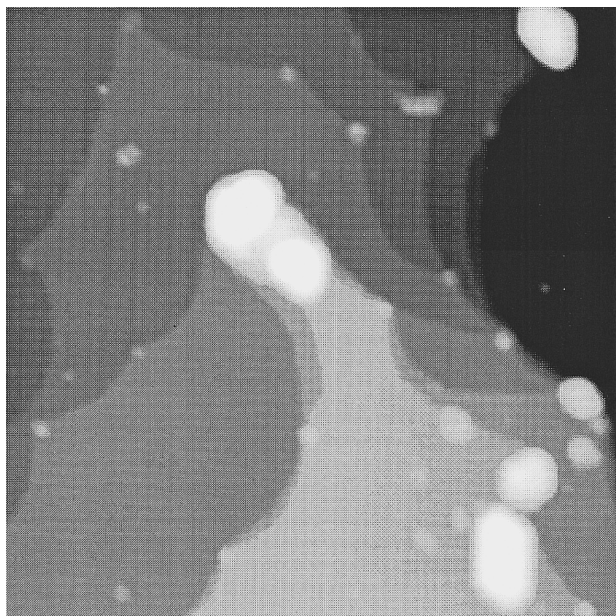


FIG. 5. STM image of the Cu(001) surface ($200 \times 200 \times 1.5 \text{ nm}^3$) after deposition of 0.5 MLE Cr at 575 K. The large islands tend to form at the apices of step bunches on the Cu surface. This may be due to diffusion of Cr along the step edges and their agglomeration in these positions. ($V_t=10.0 \text{ V}$, $I_t=137 \text{ pA}$.)

duced by depositing at higher temperature.

The presence of monolayer-high islands with a step height of $\sim 0.18 \text{ nm}$ in the films grown at 285 K and also at 425 K is surprising. In both cases their numbers are few and at the higher temperature the rest of the Cr has agglomerated into particulates. The reason why these monolayer islands are stable and the similarity of their height to the interlayer spacing of Cu or that predicted for fcc Cr are unclear. The lack of atomic resolution would seem to preclude the possibility that they are Cu adislands, so other explanations such as alloying may be considered.

Figure 5 shows a 0.5-MLE film deposited at 575 K. The surface has a small number of large outgrowths. These are positioned close to the apex of step bunches on the Cu substrate. There are other particulates on the surface, but these are much smaller when compared with the film deposited at 425 K. There is also evidence, in small-scale images, of slight protrusions at the Cu step edges. These may be due to the presence of Cr at the step edge. If this is the case, then it may explain the preferential growth of the large grains at these positions on the surface. The Cr adatoms could diffuse to these step edges and then travel along them and subsequently agglomerate at the apex of the step bunches and form the larger particulates. The fact that on the film grown at 425 K the islands next to the step edges are generally larger than those on the terrace would support this hypothesis.

From the STM data it is clear that the growth is by no means layer by layer, as had been originally suggested,¹² and appears to be better described by a three-dimensional growth system. Reference 15 observed the evolution of the Cu(001) Tamm state as a function of increased deposition to determine the surface coverage. Their results show a lower surface coverage than would be expected from a random depo-

sition model.²⁰ In this type of growth the arriving condensate atoms are able to stick anywhere on the surface regardless of the previous topography (hit and stick). They interpret this smaller than expected coverage as evidence of significant mobility and surface diffusion of the Cr on the Cu(001) at room temperature. This results in a more particulate, three-dimensional growth of the Cr. Our STM images display higher island coverage than these estimates using the Tamm state. For our case of 3.0 MLE deposited we see 95% coverage of the Cu surface, while Tamm state measurements give 80%. There is a more marked difference in the submonolayer range: the values at 0.6 MLE are 50% and 30%, respectively. The amounts derived from the STM bear a closer relation to the random deposition model. One possible explanation for this disparity is if the films are deposited at different temperatures. When films deposited at 285 K were annealed to roughly 500 K, we observed a dramatic clustering of the Cr islands to form particulates. A similar effect is achieved by depositing at elevated temperature; Fig. 4 shows a film of 0.5 MLE deposited at 425 K. So even though both sets of films are deposited nominally at room temperature, a slightly higher deposition temperature in the case of Ref. 15 could bring about this apparent difference in the two measurements. The lack of a distinct LEED diffraction pattern for our Cr films is further evidence of lower temperature growth, as the full dynamical LEED study¹⁶ obtained the sharpest diffraction patterns for higher deposition temperatures or after annealing the films.

One problem with this argument is the size of the islands observed by the STM. For the case of the random deposition model a high nucleation density and many small islands are expected. Clearly this is not the situation shown in the STM images. This discrepancy is explained if we consider that there is a relatively high surface diffusivity upon the Cu terrace and on the Cr islands, but that interlayer mass transport is negligible at 285 K. Therefore the Cr forms larger islands, but the overall coverage resembles the random deposition model. As the shape of the islands is irregular the diffusion of Cr along the island edges should be small. No diffusion along the island edges would lead to the formation of dendritic islands, while a high diffusion rate produces more compact islands.²¹ The type of growth displayed at 285 K is an intermediary case between fractal and compact island formation. The transition between these two kinds is the source of some disagreement in the literature and has been the subject of recent theoretical calculations.²²

An argument against a very low interlayer mass transport is given by the observed height distribution. Figure 1(a) shows a large number of monolayer high islands, but also many islands with an almost completed second layer. This distribution should be very different in the case of random deposition and negligible interlayer mass transport. The process responsible for this discrepancy is unclear. A possible explanation is that the development of a second layer on top of a fcc first layer is unstable, while it is favored on top of a bcc Cr(110) oriented islands. These growth characteristics of monolayer and bilayer island formation at 285 K are similar to the case of Cr deposition on Ag(001).²³ The Cr/Ag(001) system also exhibits analogous behavior upon annealing or high-temperature deposition, though it is reported to have an antiferromagnetically driven stabilization of layer-by-layer

growth in a narrow temperature and deposition range. The particulate character of films grown at higher temperature (see Figs. 2 and 3) and the agglomeration of annealed films also support the hypothesis of a non-negligible mobility. However, in both these cases interlayer mass transport must become more significant than in the 285 K case. The film shown in Fig. 4 has a similar amount of Cr deposited (0.55 MLE) as the 285 K film, but has a lower island density. The heights of these islands are much greater, typically 4–8 monolayers, and are less irregular than those deposited at lower temperatures. Interlayer mass transport therefore must increase at higher temperatures for these higher particulates to form.

These growth characteristics may explain some of the effects observed by Ref. 16 in their LEED patterns. Their sharpest LEED patterns are achieved for films deposited at low temperature and annealed at 520 K. They attribute a reduction in their Cr AES signal upon annealing to the formation of a Cu overlayer on top of their Cr film. The formation of a floating top layer of substrate atoms can occur when the deposited material has a significantly higher surface free energy, as is the case here. Such a difference also tends to preclude wetting of the surface. The creation of a monatomic Au top layer during the deposition of Fe on Au(001) (Ref. 24) is one example of this. Our STM observations suggest that the reduction in their AES signal on annealing the films is most likely due to the agglomeration of the Cr. The deposition of their films at low temperature (200 K) should produce a high nucleation density due to the lower surface mobility, close to an ideal random deposition model. The subsequent annealing will form a surface covered with many small particulates. In contrast, deposition at higher temperature produces a surface with fewer growth centers but larger grains. This is because the arriving Cr atoms have a high

surface diffusion and can travel larger distances across the Cu terrace before they encounter an island.

IV. CONCLUSION

The growth and surface morphology of Cr deposited on Cu(001) have been studied as a function of temperature in the range 285–575 K. At 285 K the growth is by the formation of irregular multilayer islands. No atomic resolution has been obtained on the Cr, in contrast to the Cu terrace. The similarity of the surface coverage to the random deposition model suggests that interlayer mass transport remains negligible. However, this is not supported by the observed height distribution. Two distinct island step heights are measured: one similar to the bulk bcc Cr(110) plane separation, in agreement with the previous studies of this system, and the other can be ascribed to fcc Cr(001) steps. At higher deposition temperatures the Cr forms more particulate features due to an increase in interlayer mass transport. The nucleation density is also reduced at elevated growth temperatures due to larger diffusion rates. Annealing the films causes the agglomeration of the films to become more particulate in form.

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