Growth and structure of Ag on bilayer Co nanoislands on Cu(111)



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# Growth and structure of Ag on bilayer Co nanoislands on Cu(111)

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**Abstract**

We have studied the growth of Ag on bilayer high Co nanoislands on Cu(111) using scanning tunneling microscopy. Noble metal capping of magnetic nanostructures is known to influence the magnetism and knowledge of the growth is therefore important. We find that Ag preferentially nucleates on the Co nanoislands, initially leaving the free Cu sites clean. Furthermore we observe that those Co islands which are capped with Ag are almost completely capped, thus making a perfect multilayered system of Ag/Co/Cu(111). We observe a $(9 \times 9)$ reconstruction of the Ag overlayer on Co/Cu(111).

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The properties of metallic thin films and nanostructures on crystalline surfaces are strongly interlinked with the morphology and chemical composition of the structures. Epitaxial growth of, in particular, homoepitaxial and bimetallic systems have therefore been studied extensively [1–3]. When growing multilayered heterostructures of several materials it becomes more complicated to control the growth and ensure that the desired structures are fabricated during deposition of the constituents of interest. Besides diffusion on terraces interlayer mass transport also becomes decisive for the growth [4–8]. Multilayered systems of magnetic and non-magnetic metallic layers, which we have studied, are interesting in particular for their technological applications in the area of data storage and processing [9–11]. It has recently been shown that capping a ferromagnetic thin film with a noble metal can influence the magnetic properties [12–17].

We report here on the capping of ferromagnetic Co nanoislands with Ag, thus producing Ag/Co/Cu(111) nanostructures. The growth of Co on Cu(111) is well known and the structural, electronic and magnetic properties have been studied in great detail [18–25]. It is important for the work presented here that, for lower coverages at room temperature, Co forms bilayer high islands of triangular shape and a width of 3–25 nm [18, 25]. We have deposited Ag on top and found that there is a preference for covering the Co islands before the Cu terraces and we observe that the Ag-capped Co islands, with few exceptions, are always fully covered with Ag. We conclude that interlayer mass transport plays an important role where Ag atoms, which have landed on the Cu terrace, must be allowed to ascend the bilayer high step edges of the Co island.

## 2. Experiment

Experiments have been performed in an ultrahigh vacuum system ($5 \times 10^{-11}$ mbar) using a scanning tunneling microscope (STM) operated at room temperature and low energy electron diffraction (LEED). We have used WSxM to analyze and display STM images [26]. A Cu(111) crystal was cleaned by sputter/anneal (500 °C) cycles. Co was deposited with a flux of 0.14 ML $\text{min}^{-1}$ at $T = 27$ °C. Next, Ag was deposited at room temperature (or 70 °C in one case) with a flux of 0.44 or 3.6 ML $\text{min}^{-1}$. The Co area coverage in all experiments is 0.15–0.36 ML and the Ag overlayer coverage is varied from 0 to ∼1.6 ML. Note that for the Co islands the term 'monolayer' (ML) is used for the visible area coverage, meaning that the deposited amount of Co is twice the visible coverage since the Co islands are of bilayer height.

## 3. Results and discussion

### 3.1. Growth

After depositing Co on Cu(111) we observe the well-known bilayer high (3.9 Å) islands [18, 19, 22–25], mostly of triangular shape as well as star-shaped islands (which is known

 

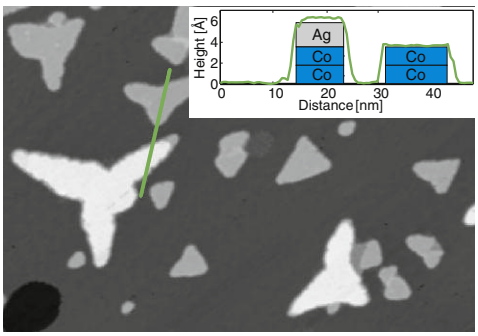


**Figure 1.** STM image after depositing 0.07 ML Ag on 0.2 ML Co/Cu(111). The image is taken at a bias voltage of 0.35 V, the size is 157 nm × 108 nm and the $z$ scale spans 0.91 nm. The inset shows a linescan.

to be a kinetic effect [25]). An STM image of 0.07 ML Ag deposited on a Cu surface with a low coverage of Co islands ($\Theta_{\mathrm{Co}} = 0.20$, where only bilayer high Co islands are formed) is shown in figure 1. The bright islands consist of 2 ML Co with 1 ML Ag on top. Although Co islands of 3 ML height are never observed at these Co coverages we note for comparison that the height of islands consisting of 2 ML Co + 1 ML Ag is 1 Å larger than 3 ML Co. Furthermore the Ag cap layer shows a reconstruction (discussed later). The less bright islands are 2 ML Co islands that are not capped with Ag. The heights are illustrated by the inset in figure 1. It is remarkable that those Co islands which *do contain* Ag on top are almost *completely covered* with an Ag layer. On the other hand, the amount of Ag on the Cu surface is minimal although Ag has been deposited homogeneously. Ag thus accumulates on top of some of the Co islands, leaving the other Co islands and the Cu terrace clean. We note that occasionally it might happen that narrow corners of islands are not filled with Ag (as observable at the upper right corner of the largest star-shaped island in figure 1). As the Ag coverage is increased to 0.35 ML we observe, besides fully capped Co islands, that some of the Co islands are surrounded by Ag instead (figure 2(a)). At 0.8 ML Ag (figure 2(b)) most of the Cu surface and all Co islands are filled with Ag, except from some of the smaller Co islands. In figure 2(c) we have plotted the fraction of Co islands that are capped with Ag as a function of island size and see that larger islands have a higher probability of being capped.

Before analyzing the data in more detail we will briefly discuss the growth in the areas containing Cu step edges. Co deposition on clean Cu(111) leads to islands on the terraces as well as a decoration of both sides of the Cu step edges [18]. On the other hand, deposition of Ag on clean Cu(111) at room temperature never leads to nucleation on the terraces but only to decoration of the lower side of the Cu step edges, resulting in 'step flow growth' [27]. In agreement with this we find here that Ag deposited on a partially Co-covered Cu(111) surface nucleates at step edges but also on top of Co islands. This is shown in an overview STM image in figure 3. We avoid the complexity at the Cu step edges and concentrate our further analysis on Cu terraces.

We will now quantify the preference of Ag nucleating on top of Co islands versus nucleating on Cu. For fabrication of

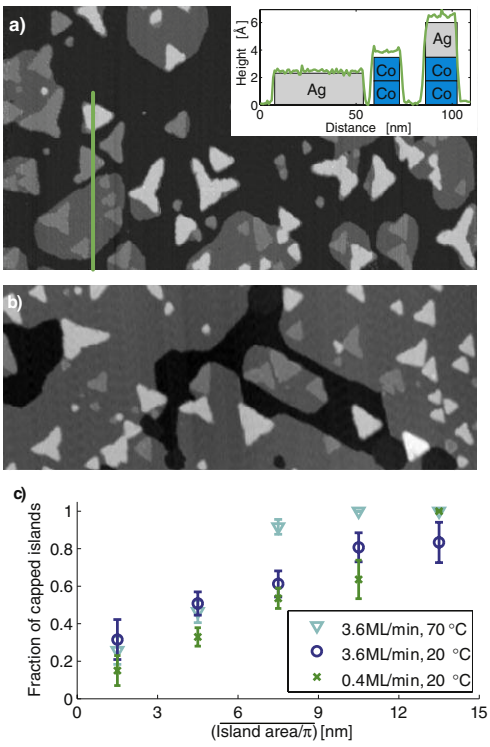


**Figure 2.** STM images for (a) 0.35 ML Ag on 0.2 ML Co/Cu(111). The image is 300 nm × 167 nm and the $z$ scale spans 0.94 nm. The linescan runs through an Ag-capped Co island, an uncapped Co island and a layer of Ag directly on Cu(111). (b) 0.80 ML Ag on 0.2 ML Co/Cu(111). The image is 300 nm × 118 nm and the $z$ scale spans 0.94 nm. (c) The fraction of capped islands as a function of approximate island radius grouped in 3 nm bins for two Ag deposition rates and two temperatures. $\Theta_{\mathrm{Co}} \approx 0.17$ and $\Theta_{\mathrm{Ag}} \approx 0.4$. In total 598 islands were analyzed to produce the three datasets.

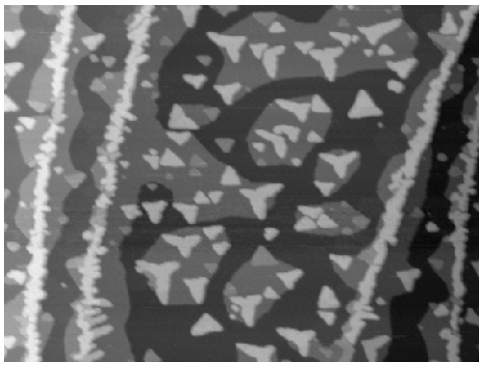

**Figure 3.** Overview STM image of 0.48 ML Ag deposited on 0.25 ML Co on Cu(111). For the analysis only terrace sites are used and the areas around Cu steps are neglected. The image size is 400 nm × 300 nm.

Ag/Co/Cu structures, nucleation on top of Co islands would be preferred. We have determined the partial coverage of Ag on Co islands, $Y_{\mathrm{AgCo}}$, and Ag directly on Cu(111), $Y_{\mathrm{AgCu}}$, from STM images of surfaces with variable Ag coverage and a Co coverage of $0.25 \pm 0.1$ ML. The partial coverage of Ag on Co (Cu) is defined as the relative area of Co (Cu) that is covered with Ag. In this way we normalize the Ag coverage to the

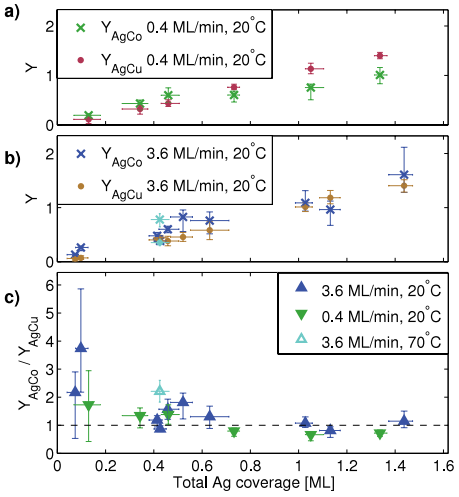


**Figure 4.** (a) The partial coverage (Y) of Ag on Co and Cu, respectively, at low Ag deposition rate (0.44 ML min$^{-1}$). (b) The partial coverage (Y) of Ag on Co and Cu, respectively, at high Ag deposition rate (3.6 ML min$^{-1}$). (c) The ratio of the partial coverages of Ag on Co islands and Ag on Cu(111) as a function of deposited Ag for the two Ag rates. At a ratio above 1, indicated by the horizontal dashed line, there is preference for Ag nucleation on Co. All data are for deposition at $T = 20\,^{\circ}$C except for the light-blue data point ($T = 70\,^{\circ}$C).

available area of Co (Cu). Whereas $Y_{\mathrm{AgCo}}$ is sensitive to $\Theta_{\mathrm{Co}}$, it is notable that the free Cu area plays a less important role for how much of the Ag nucleates on Cu sites since nucleation of Ag never occurs on Cu terrace sites away from Co island steps. We have used the Flooding function of the WSxM program [26] to determine coverages. The images used for the analysis are sized approximately 200 nm × 200 nm. For each data point in figure 4 we have analyzed 1–4 different areas on the surface for a given preparation. In figures 4(a) and (b) we plot $Y_{\mathrm{AgCo}}$ and $Y_{\mathrm{AgCu}}$ as a function of $\Theta_{\mathrm{Ag}}$ for two different Ag deposition fluxes of 0.44 ML min$^{-1}$ and 3.6 ML min$^{-1}$, respectively. At low Ag doses $Y_{\mathrm{AgCo}}$ increases faster than $Y_{\mathrm{AgCu}}$. This preference disappears above $\Theta_{\mathrm{Ag}} \sim 0.7$ ML. The effect is more clearly demonstrated by plotting the ratio $\frac{Y_{\mathrm{AgCo}}}{Y_{\mathrm{AgCu}}}$ (figure 4(c)), which thus is a measure of the preference of Ag nucleating on Co versus on Cu[1]. In agreement with the qualitative discussion earlier we observe indeed that at low Ag coverage there is an increased preference of Ag nucleating on Co islands. At higher Ag coverage this decreases since Co islands which are already capped and those with an Ag rim are no longer available and the ratio approaches unity. Furthermore we note that a higher Ag flux initially leads to a slightly increased preference for nucleation on Co (see figure 4(c)). We observe no significant dependence on $\Theta_{\mathrm{Co}}$ in the range we have used ($\Theta_{\mathrm{Co}}$: 0.15–0.36 ML).

There have been a number of studies investigating nucleation on a surface with pre-grown islands [4–8]. Atoms landing directly on an island will diffuse around until they either descend and disappear from the island or meet other adatoms, finally forming a stable cluster. This can then act as a nucleation site for further adatoms. The additional Ehrlich–Schwoebel barrier at the step edge [28, 29] increases the time an adatom stays on the island and thereby the probability of meeting another adatom. With this in mind we can rationalize our experimental findings. We observed that larger Co islands have a larger probability of being capped with Ag (see figure 2(c)). This has also been seen in other systems [5] and is due to a larger probability of finding two adatoms at the same time on a larger island. There was a more sharp transition between capped and uncapped islands, compared to the results presented here, and it was possible to identify a so-called critical radius ($R_{\mathrm{c}}$), where islands having a radius larger than $R_{\mathrm{c}}$ would experience two-layer nucleation on top [4, 5]. The varying and, in part, irregular shape of the Co islands makes it difficult to identify the radius but we used $\sqrt{A/\pi}$, where $A$ is the island area[2]. We found that a higher Ag flux led to increased nucleation on top of the Co islands. This is seen as a slight shift towards smaller islands in figure 2(c) but more clearly in figure 4(c), where the trend is that the ratio $\frac{Y_{\mathrm{AgCo}}}{Y_{\mathrm{AgCu}}}$ (and thereby the preference for nucleation on Co) is largest for the high Ag deposition rate, 3.6 ML min$^{-1}$. A higher Ag flux makes it more likely that another atom necessary for making a stable cluster lands on the island in time. We also studied the effect of increased surface temperature. The simple expectation would be that a higher temperature leads to a higher diffusivity of Ag adatoms on the island and a higher descent rate, thus reducing the residence time and the chance of nucleation [4, 5] (especially visible in the experimental data presented in [5]). We find, on the contrary, that $T = 70\,^{\circ}$C results in an *increased* nucleation rate on the islands compared to $T = 20\,^{\circ}$C. This can be seen in figure 2(c) (as a function of island size) and in the ratio of relative coverages (figure 4(c)). The explanation presented in [4, 5] does not take into account that atoms landing on the bare surface (not on the islands) may *ascend* the islands and thereby lead to an increased nucleation probability on the islands. Apparently this is a prerequisite in this case and is very surprising since the Ag atoms need to ascend steps of 2 ML height. In contrast, Ag atoms never ascend monatomic Cu steps [27] or steps at Ag islands. This peculiarity is illustrated in figure 5. The reason is likely to be found in Co being chemically more reactive than the more noble Cu [35] and the binding of Ag is therefore expected to be stronger to Co than to Cu. This could give rise to asymmetric rates of step edge crossing, i.e. the diffusion rate for atoms moving up is higher than for moving down, but also to a smaller critical cluster size on Co than on Cu. Both effects lead to a preference for nucleation and an accumulation on Co compared to Cu as observed.

Another reason for the preference of capping Co with Ag can possibly be found in the gain of free energy [1]. Most

[1] Although the absolute error bars in figures 4(a) and (b) are comparable, the relative errors are larger for low Ag coverage. This explains the large error bars seen at low coverage of the ratio between $Y_{\mathrm{AgCo}}$ and $Y_{\mathrm{AgCu}}$ in figure 4(c).

[2] The geometry of the step in general influences diffusion barriers [25] and the island shape may therefore play a role in the interlayer mass transport. It was therefore necessary to use relatively large bin sizes to achieve reasonable statistics and could explain why the capping fraction versus island size in figure 2(c) is so broad compared to the more step-like distribution seen, for example, in [5], where the islands varied in size but were much more uniformly shaped. We note that the size distribution of the Co islands ranges from 3 to 25 nm in width, showing a smooth and broad distribution, peaking at approx 10 nm width.

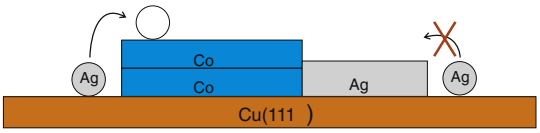


**Figure 5.** We illustrate here the peculiar growth, where Ag atoms ascend bilayer high Co islands but do not ascend monolayer high Ag islands (or Cu step edges).

simply, there are three free energy parameters to take into account, where $\gamma_S$ is the surface free energy of the substrate (Cu or Co), $\gamma_D$ is the surface free energy of the deposit (Ag in this case) and $\gamma_i$ is the interface free energy. The values for the surface energies are $\gamma_{Ag(111)} = 1.17\ J\,m^{-2}$, $\gamma_{Cu(111)} = 1.95\ J\,m^{-2}$ and $\gamma_{Co(0001)} = 2.78\ J\,m^{-2}$ [36]. Note that the latter value is for Co(0001) and not for 2 ML Co/Cu(111), where it may be different due to the strained Co adlayer, which has adapted to the Cu lattice. The criterion for layer growth, $\gamma_D + \gamma_i < \gamma_S$, seems to be fulfilled for both Ag on Cu(111) and Ag on Co/Cu(111) since in both cases a complete adlayer of Ag is formed. The change in free energy, $\Delta\gamma = (\gamma_D + \gamma_i) - \gamma_S$, is difficult to evaluate exactly since, to our knowledge, $\gamma_{i,Ag/Co}$ is not available for Ag on Co/Cu(111). The interface energy is strongly interlinked with the lattice mismatch and there is therefore reason to believe that $\gamma_{i,Ag/Co}$ and $\gamma_{i,Ag/Cu}$ are similar in this particular case and the gain in free energy will therefore be larger for capping the Co islands, since $\gamma_{Cu} < \gamma_{Co}$. This argument is in agreement with our finding of increased preference for capping Co.

Although the mobility of single-atom diffusion on (111) surfaces is very high it does not always lead to Ag-covered Co islands. This can be explained by an apparently high critical cluster size for nucleation, i.e. only if a sufficient number of Ag atoms meet and form a stable immobile cluster on top of the Co island will the Ag adlayer be formed. Otherwise, Ag atoms diffuse down onto the Cu surface. If, on the other hand, a stable cluster has been formed, attachment of further Ag atoms occurs frequently due to the high mobility of Ag atoms and a complete adlayer is formed. At very low Ag coverages it might happen that there is not sufficient Ag to form a complete capping layer on an island, but the Ag coverages used here (all above 0.07 ML) lead either to capped or empty Co islands. This is in contrast to findings for Au or Cu growth on Co/Cu(111), where only part of a Co island is capped [30]. Those Co islands which are not capped are mostly completely surrounded with Ag (see figures 2(a) and (b)). This can be due to a simple blocking effect, where an Ag rim at the Co island border prevents further atoms from ascending the island or that the rim reduces the Ehrlich–Schwoebel barrier and the confinement of Ag atoms landing on top of an island is then less effective. It is known that Co islands on Cu(111) grow in two general orientations [18]. We note that this had no influence on the Ag capping.

### *3.2. Structure*

Finally, we will address the atomic structure of Ag on Co/Cu(111) by STM and LEED measurements. Figure 6(a)

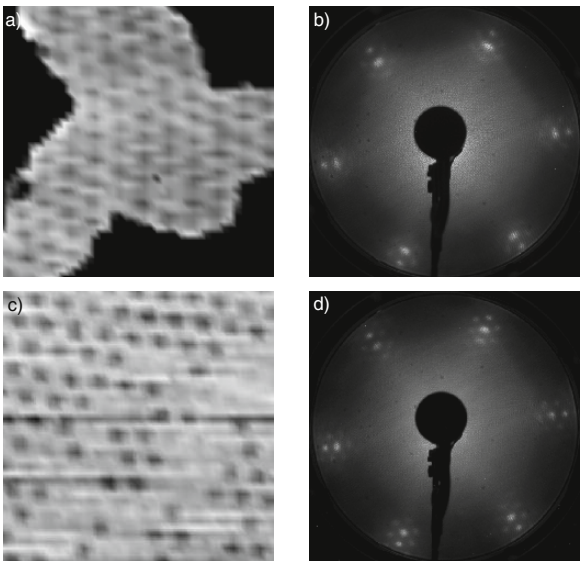


**Figure 6.** (a) Close-up STM image of an Ag-capped Co island on Cu(111) with (b) the corresponding LEED pattern. The observed moiré pattern has a corrugation of 25 pm and a periodicity of approx. 24 Å taken with a bias voltage of 0.35 V. (c) Close-up STM image of the (9 × 9) reconstruction of Ag grown directly on Cu(111) with a bias voltage at 0.23 V and (d) corresponding LEED pattern. The image size is 24 nm × 24 nm in both (a) and (c). The electron energy used for the LEED images was 65 eV.

shows an STM image of a bilayer thick Co island which subsequently has been capped with Ag. We observe a moiré pattern with a periodicity of approx. 24 Å and an apparent corrugation of 25 pm. For the diffraction experiments we deposited 3 ML Co and subsequently 1.3 ML Ag at room temperature. The LEED image in figure 6(b) shows six main spots from the Cu(111) substrate (or the Co islands which grow pseudomorphically [22]). At each main spot there are six satellites due to the Ag layer. This symmetry is identical to what is seen for an Ag overlayer on Cu(111) [31, 32, 27, 33, 34], where the atomic structure depends on deposition temperature [27, 34], but in any case the periodicity is approx. (9 × 9) originating from the lattice mismatch between Cu and Ag. For comparison we have deposited 1.3 ML Ag on Cu(111) and recorded an STM and a LEED image (shown in figures 6(c) and (d)). Since Co grows pseudomorphically on Cu a similar reconstruction is expected for Ag grown on Co/Cu(111). This is indeed observed here, although the Ag-related LEED pattern is more blurry for Ag/Co/Cu(111) compared to Ag/Cu(111). We believe this is due to edge effects at Co islands where the periodicity of the Ag moiré pattern may change and the relatively smaller 'coherence areas' for LEED are taken on Ag/Co/Cu(111) than on the much larger Ag areas directly on Cu(111), since Ag grows almost layer by layer on Cu(111) [27] and the size of Ag domains is therefore only limited by the terrace size of the Cu(111) crystal. The moiré pattern of Ag on Co/Cu(111) has recently been shown to exhibit interesting electronic properties, where the electronic structure of the Co islands is modulated with the same periodicity as the Ag overlayer moiré superstructure [37].

## 4. Conclusion

We have studied the growth of an Ag overlayer on Co nanoislands on Cu(111) at room temperature. The atomic structure of Ag on Co/Cu(111) shows a $(9 \times 9)$ periodicity due to the mismatch of the lattice parameter. We find that there is a preferred nucleation for Ag on top of Co compared to Cu(111) terrace sites, especially at low Ag doses. This is quite remarkable since the Co islands are all of bilayer height and an accumulation on top of the islands thus involves ascending steps of 2 ML height. We furthermore find that Co islands are either completely free of Ag or almost completely capped with Ag. These nearly perfect multilayers can be expected to act as a model system for magnetic multilayer studies.

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