

Modifying diffusion anisotropies: Cap layer induced changes in spreading anisotropies

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We have studied the spreading of Fe, Co, and Ni from a dot deposited onto a W(110) substrate. A Cu cap layer covering dot and surface is found to change the fast spreading directions for all three metals to $\langle 100 \rangle$. This is in contrast to the spreading without a cap layer where the fast spreading direction is either along $\langle 110 \rangle$ in the case of Fe or influenced by the step directions on the substrate surface for Co and Ni. The cap layer induced spreading anisotropy is proposed to be caused by the structure in the alloy layer formed during the spreading process. © 1997 American Institute of Physics. [S0021-8979(97)02623-6]

INTRODUCTION

The diffusion of atoms on a surface, i.e., surface diffusion, is an important phenomenon in many areas of surface science, e.g., heterogeneous catalysis and thin-film growth and has, therefore, been a field of extensive research in the past.¹ One way to study surface diffusion processes is to perform so-called “spreading experiments,” i.e., to analyze the spreading of material from a defined source region on the surface. Usually, the source region is prepared by depositing through a mask. Often, anisotropic spreading is observed and so far two reasons for this behavior have been reported. On the one hand, the crystallographic structure of the substrate or of the spreading overlayer can determine the anisotropy,² and on the other hand, the substrate step direction can be the fast spreading direction.^{3,4} The temperature-dependent competition between these two types of anisotropies has also been observed.⁵ So far, no reports on spreading experiments with metal cap layers have been published.

In this article, we present results concerning the spreading of Fe, Co, and Ni on W(110) with a Cu cap layer of various thicknesses. It will be shown that Cu cap layers induce a change of the fast spreading direction from the $\langle 110 \rangle$ -directions for Fe, or the step direction for Co and Ni, to the $\langle 100 \rangle$ -directions of the W(110) substrate. A model that explains this strong modification of the anisotropy by changes in the crystallographic structure of the spreading overlayer is proposed.

The ferromagnetic metals on W(110) are interesting systems for spreading experiments for the following reasons: Growth and electronic, as well as magnetic properties, of ultrathin Fe,^{6–8} Co,^{9,10} and Ni (Refs. 11–14) films on W(110) have been extensively studied, and neither alloy formation between film and substrate nor diffusion of adsorbate atoms into the bulk was reported for temperatures up to 1200 K. Therefore, the spreading should be controlled only by surface diffusion processes. Because of the twofold symmetry of the W(110) surface, spreading anisotropies due to the crystallographic structure of the substrate are expected to be found under certain experimental conditions. Cu as cap layer material was chosen because it neither forms an alloy with

the substrate nor diffuses it into the bulk of the tungsten crystal.¹⁵ The influence of the bulk miscibilities between the spreading material and cap layer material on the spreading behavior was also investigated. Ni and Cu are 100% miscible in the bulk, whereas Co and Fe are nearly immiscible with Cu in the bulk,¹⁶ so one could expect that these differences in bulk miscibilities are reflected in the spreading behavior. As discussed below, this is not the case.

EXPERIMENTAL ASPECTS

The spreading experiments were performed under ultra-high vacuum conditions. Fe, Co, or Ni were deposited at a substrate temperature of 340 K through a mask with a hole (\varnothing 100 μm), thus, producing circular dots, which were analyzed with scanning electron and scanning Auger microscopy. Then, the sample was annealed and analyzed again after cooling. For the experiments with a cap layer, the dot together with the substrate surface was covered by a Cu layer immediately after the preparation of the dot. Cu cap layer thicknesses between 0.5 and 5 monolayers (ML) were investigated. The ferromagnetic metals were evaporated from disks of high-purity material, which were heated by electron bombardment. Cu was evaporated from a W25%Re wire basket, which was resistively heated. The film thickness for all materials was controlled by a quartz microbalance. The cleanliness of substrate and deposit were checked by Auger electron spectroscopy (AES), and the impurity concentration was found to be below 3% of an atomic layer. The sample was heated by electron bombardment and its temperature was measured using a W–W26%Re thermocouple.

RESULTS

Before presenting our results for the cap layer modified spreading, we will briefly summarize the observations for the spreading of the ferromagnetic metals on the W(110) surface without the cap layer. A detailed discussion of these results may be found elsewhere.⁵ For Fe, Co, and Ni on W(110) without a cap layer, a 1 ML thick film spreads across the surface.⁵ This behavior can be explained by the “unrolling carpet” model.^{3,4,17} In this model, it is assumed that the first ML is immobile and that the atoms diffuse on top of the first layer. As soon as they reach the edge of the first layer they

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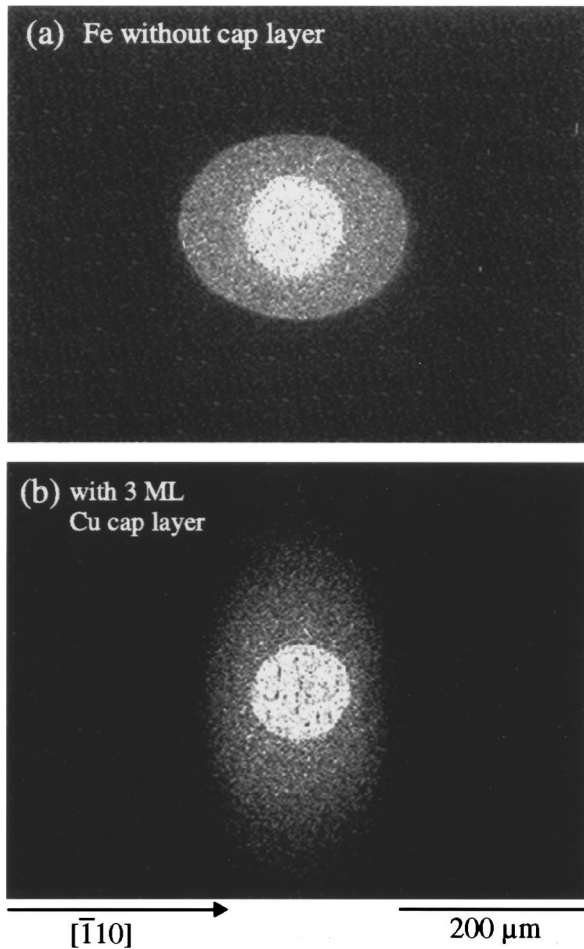


FIG. 1. Fe Auger maps showing the Fe spreading without (a) and with (b) the Cu cap layer after 18 min at 970 K.

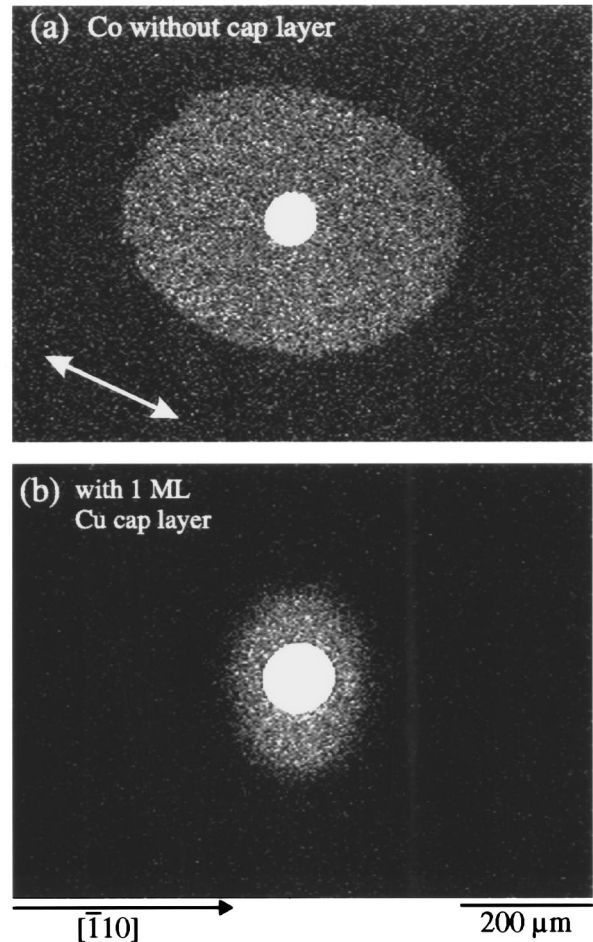


FIG. 2. Co Auger maps showing the Co spreading without (a) and with (b) the Cu cap layer after 6 min at 970 K. The white arrow indicates the direction of the steps on the substrate surface.

get trapped. For Fe [Fig. 1(a)], the fast spreading direction is along $\langle 110 \rangle$ for the entire temperature range investigated (870–1070 K). This anisotropy is caused by the crystallographic structure of the first Fe layer, which is pseudomorphic to the substrate, i.e., it has a bcc(110) structure, leading to an anisotropy in the diffusion coefficient. This anisotropy is due to the fact that on a bcc(110) surface the atoms move in a zig-zag-like manner along closed-packed $\langle 111 \rangle$ directions, which results in a diffusion coefficient that is twice as large along $\langle 110 \rangle$ as along $\langle 100 \rangle$.¹⁸ For Co, the fast spreading is along the step direction (indicated in Fig. 2 by a white arrow) at low temperatures (≤ 820 K), while for $T \geq 1070$ K the anisotropy is determined by the crystallographic structure (fast spreading along $\langle 110 \rangle$). For Ni, the influence of the steps is stronger than for Co. Even after annealing at 1070 K, the step direction is reflected in the shape of the diffusion zone. A detailed discussion of the observed spreading anisotropies of all three metals, their temperature dependence, and a model to describe the influence of steps are given in Refs. 4 and 5.

Figure 1(a) shows an Auger map of an Fe dot after 18 min at 970 K. The elliptical shape of the area covered by Fe (“diffusion zone”) shows that the fast spreading direction is obviously along $\langle 110 \rangle$. The dramatic influence of a Cu cap layer on the spreading behavior can be seen in Fig. 1(b),

which shows an Fe dot with a 3 ML Cu cap layer heated for the same time at the same temperature. Now, the elliptically shaped diffusion zone is rotated by 90° with respect to Fig. 1(a), indicating the cap layer induced change of the fast spreading direction from $\langle 110 \rangle$ to $\langle 100 \rangle$. Figure 2(a) shows that for uncapped Co at 970 K, steps have a strong influence on the fast spreading direction indicated by the deviation of this direction from $\langle 110 \rangle$ favored by the crystallographic structure in the diffusion zone. As Fig. 2(b) shows, a 1 ML Cu cap layer induces fast spreading along $\langle 100 \rangle$, i.e., the same direction as for capped Fe. These two examples show that Cu cap layers can change spreading anisotropies determined by the crystallographic structure (Fe) as well as spreading anisotropies influenced by step directions (Co). Also for Ni, where the step influence is even stronger than for Co, a 1 ML Cu cap layer induces fast spreading along $\langle 100 \rangle$. The big difference between Fe on the one hand and Co and Ni on the other hand is that for Co and Ni, 1 ML Cu is sufficient to induce fast spreading along $\langle 100 \rangle$, whereas for Fe a minimum of 2 ML Cu is required.

Before a model is proposed to explain the changes in the fast spreading direction induced by Cu cap layers, one has to discuss the concentration profiles for the spreading metal and Cu, i.e., the composition, in the diffusion zone. This discus-

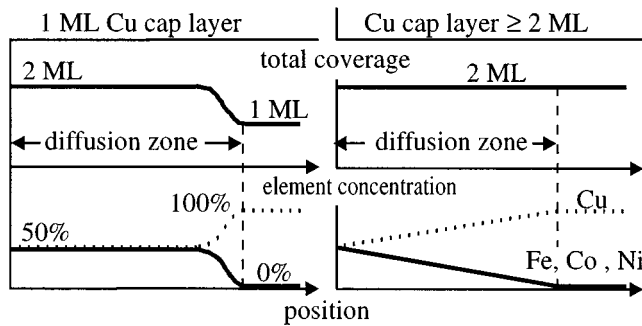


FIG. 3. Schematic sketch of the concentration profile for Cu and the respective ferromagnetic metal in the diffusion zone. The upper part shows the total coverage, and the lower part the fraction of the two elements.

sion can be restricted to cap layer thicknesses up to 2 ML because Cu in excess of 2 ML forms large three-dimensional islands¹⁵ so that the spreading material “sees” essentially 2 ML Cu. The concentration profiles in the diffusion zone were derived from Auger line profiles and laterally resolved AES. It was found that the concentration profiles in the diffusion zone do not depend on the spreading material but strongly on the Cu cap layer thickness. In Fig. 3, the observed concentration profiles for Cu and the ferromagnetic metal are shown schematically. For a 1 ML Cu cap layer, a 2 ML thick alloy layer is formed. The Cu concentration in nearly the entire diffusion zone is 50%, and Cu atoms are present in both layers. Also, for a Cu cap layer thickness of 2 ML, a 2 ML thick alloy layer is found in the diffusion zone but with a different concentration profile. In the direct vicinity of the dot, the concentration of Cu and of the ferromagnetic metal is 50%, respectively. The concentration of the ferromagnetic metal decreases nearly linearly to zero towards the edge of the diffusion zone, while the Cu concentration increases correspondingly, so that the total coverage remains at 2 ML. The main difference in the concentration profiles for the two cap layer thicknesses is, that for the 1 ML cap layer the Cu concentration is 50% in most of the diffusion zone whereas for the 2 ML cap layer thickness the Cu concentration is significantly higher than 50%.

DISCUSSION

We propose the following model for the spreading process to explain the different concentration profiles in the diffusion zone for the two cap layer thicknesses: In the initial stage of the spreading process, atoms of the spreading material move away from the dot and diffuse on top of the Cu layer. Leaving the dot and going to the top of the Cu layer is possible despite the Cu cap layer covering the dot, since due to alloy formation, ferromagnetic metal atoms should be present in the top layer of the dot. While diffusing on top of the Cu layer, the atoms exchange with the Cu atoms of the cap layer and in this way a 2 ML thick alloy layer is formed. In the case of a 2 ML cap layer, the expelled Cu atoms attach to the three-dimensional Cu islands. The driving force for the exchange is the higher binding energy for the ferromagnetic metals on W(110) compared to the Cu–W(110) bond.^{6,9,11,15} The formation of a 2 ML thick alloy layer in the diffusion

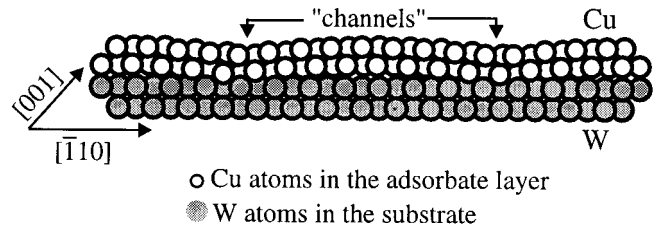


FIG. 4. Schematic “side” view of the structure of 2 ML Cu on W(110). Due to pseudomorphism along $\langle 100 \rangle$ and an additional periodicity along the $\langle 110 \rangle$ surface, buckling occurs and “channels” along $\langle 100 \rangle$ are formed (Ref. 15). The influence of the channels on the spreading is discussed.

zone indicates the strong influence of the Cu and agrees well with the fact that 2 ML Cu on W(110) are thermally stable against formation of three-dimensional islands,¹⁵ whereas for Fe, Co, and Ni, in contrast, only 1 ML is thermally stable.^{6,9,11} After the initial stage of the spreading, which results in an alloy layer, the atoms diffuse on top of the alloy layer. The diffusing atoms become incorporated into the alloy layer only if the concentration of the ferromagnetic species is below 50%. The spreading of a certain concentration with a sharp boundary will only occur if the incorporation probability strongly increases below this concentration. For a 1 ML cap layer, the value of this concentration is obviously 50%, whereas for 2 ML no significant change in the incorporation probability is indicated by the observed concentration profiles (see Fig. 3). This difference can be understood if one takes into account that for a 1 ML cap layer thickness a concentration of the ferromagnetic metal below 50% corresponds to a total coverage of less than 2 ML. In this case, the driving force for incorporation of diffusing atoms, i.e., the gain in binding energy, is enhanced, because the atoms can be incorporated without expelling a Cu atom into the third layer. This results in a higher incorporation probability for concentrations below 50%. For a 2 ML cap layer, the total coverage is constant and, therefore, this enhancement in the incorporation probability does not occur.

In the following, the anisotropy in the spreading behavior is discussed. Because the atoms diffuse on top of the alloy layer, its crystallographic structure determines the spreading anisotropy. Unfortunately, this structure cannot be determined with our experimental methods, but for a fast spreading along $\langle 100 \rangle$, the alloy layer cannot have a bcc(110) structure because this structure would cause a fast spreading along $\langle 110 \rangle$ as discussed above. Bauer and co-workers¹⁵ found that 2 ML Cu on W(110) are not pseudomorphic to the substrate but show a structure with surface buckling on a subatomic scale with “channels” along $\langle 100 \rangle$, as sketched in Fig. 4. It seems possible that such a structure would prefer diffusion along the channels compared to diffusion perpendicular to the channels because perpendicular to the channels, i.e., along $\langle 110 \rangle$, the binding sites are not equivalent, and therefore, it is probable that an atom faces an additional energy barrier if it tries to leave the channel. The preferred diffusion along the channels would result in a fast spreading along $\langle 100 \rangle$. Thus, if the alloy layer has a similar channel structure as 2 ML Cu on W(110), the fast spreading along the $\langle 100 \rangle$ direction could be explained. So far, only very few

bimetallic alloys on single-crystal substrates have been studied, so that little is known about the structures of these alloys.¹⁹ It seems, however, possible that the Cu has a strong influence on the structure of the alloy layer even at a concentration of the ferromagnetic metal of 50%. An indication for the strong influence of the Cu is the formation of a 2 ML thick film in the diffusion zone.

A model is proposed here to explain why for Co and Ni 1 ML Cu is sufficient to induce a fast spreading along $\langle 100 \rangle$, whereas for Fe the Cu thickness must be at least 2 ML. We suppose that this is due to the fact that the channel structure, which causes the fast spreading along $\langle 100 \rangle$, is formed for Co and Ni concentrations of 50% in the alloy layer but not for an Fe concentration of 50%. For an Fe concentration of 50%, it is assumed that the structure in the diffusion zone is bcc(110) as it is without a cap layer and, therefore, the same spreading anisotropy is observed as for uncapped Fe. Only if the Fe concentration is below 50% a channel structure is formed, because in this case, the influence of the Cu should determine the structure of the alloy layer. However, an Fe concentration below 50% in large parts of the diffusion zone only occurs for at least a 2 ML Cu cap layer, and therefore, only in this case a fast Fe spreading along $\langle 100 \rangle$ is observed. The assumption of different resulting structures for Fe and Co/Ni seems plausible if one takes into account that the channel structure is a distorted fcc(111) structure, which is closer to the Co(0001) and the Ni(111) structure than to the Fe(110) structure.

As mentioned in the introduction, Ni and Cu are 100% miscible in the bulk, but Co and Fe are nearly immiscible with Cu in the bulk.¹⁶ However, the differences in the bulk miscibilities are not reflected in the spreading behavior so that the concept of bulk miscibility is of no significance in our experiments. If the bulk miscibilities were reflected in the spreading behavior, Fe and Co should behave similarly and Ni should show a different spreading behavior. This contradicts our experimental findings, especially the fact that for all three ferromagnetic metals an alloy formation in the diffusion zone is observed. This can be understood if one takes into account that in thin films even those elements, which are immiscible in the bulk, can form alloys. This behavior has been observed for both, Fe/Cu (Ref. 20) and Co/Cu.²¹

SUMMARY

We have shown that metal cap layers can significantly alter the spreading behavior of metals on single-crystal surfaces compared to the spreading without cap layers. For Fe, Co, and Ni on W(110), Cu cap layers induce a change of the fast spreading direction from the $\langle 110 \rangle$ direction for Fe or the step direction for Co and Ni, respectively, to the $\langle 100 \rangle$ direction of the W(110) substrate. The anisotropy in the spreading behavior for all three ferromagnetic metals is determined by the crystallographic structure of the 2 ML thick alloy layer, which is formed during spreading.

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