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Surface Science 377–379 (1997) 937–942

surface science

Formation of copper crystallites on a Cu/Fe/Cu(100) sandwich

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Received 1 August 1996; accepted for publication 15 October 1996

Abstract

The formation of copper microcrystallites on a Cu/Fe/Cu(100) sandwich due to annealing at temperatures between 500 K and 600 K was studied. For the crystallites to form, the iron film thickness must be more than 10 monolayers (bcc-Fe) and the copper film thickness must be in the range of 3–10 monolayers. The formation process of the crystallites was investigated using a newly developed apparatus allowing scanning electron, scanning Auger and scanning tunneling microscopy on the same sample position and repeated repositioning to a given position. The crystallites were found to form mainly at step bunches and predominantly oriented along the ⟨110⟩ directions of the copper substrate. A large number of screw dislocations are visible on top of the crystallites. The growth of the crystallites was observed by sequential measuring/annealing cycles. The results are discussed in terms of the structural transformation of the Cu/Fe/Cu sandwich.

Keywords: Copper; Iron; Scanning electron microscopy (SEM); Scanning tunneling microscopy (STM); Surface diffusion; Thin films

1. Introduction

The growth and morphology of iron (Fe) deposited on copper (Cu) and the correlation between morphology and magnetic properties is of current interest and the topic of many investigations [1–15]. For thin films up to approximately 10 monolayers (ML) the Fe matches the lattice of the Cu(100) substrate and grows in fcc structure. The film undergoes a martensitic structural transition from fcc to bcc above this thickness range [11–14], while the onset of the transformation strongly depends on the growth conditions and the presence of surfactants [5]. Domains of bcc-Fe may exist in the fcc film between 5 and 10 ML [11]. After the martensitic transformation of the film the surface is much rougher, with bcc Fe grains partly oriented along the ⟨110⟩ axis of the substrate surface [11,12]. Cu from the substrate migrates onto the Fe film upon annealing to minimize the surface energy [10]. Pinhole formation has been observed for a certain thickness range [6].

Multilayers of Cu/Fe/Cu are an interesting field for research from a magnetic point of view [16], but these sandwich structures are not yet well characterized. In particular, the behaviour upon annealing has not been investigated intensively before. Our aim is to understand the structure of these sandwiches and their behaviour upon annealing.

2. Experimental procedures

The experiments were carried out using a recently developed apparatus combining scanning

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PII S0039-6028(96)01525-7

electron, scanning Auger and scanning tunneling microscopy (SEM/SAM/STM), operated under ultra high vacuum (UHV) conditions [17]. This apparatus allows simultaneous SEM and STM measurements and the repeated relocation of a given position on the sample with a high accuracy. The analysis equipment of the apparatus consists of an STM with a maximum scan area of 10 μm, an SEM with a resolution of 20 nm, an Auger analyzer (cylindrical sector analyzer), as well as RHEED and LEED facilities. All this equipment is fitted into a single analysis chamber. Preparation and annealing of the sample were performed in a preparation chamber. The base pressure of the apparatus during the SEM, SAM and STM measurements was better than 1×10^{-10} mbar.

The Cu(100) crystal was oriented within an accuracy of 0.2°. The UHV cleaning procedure consisted of repeated 1 kV argon ion bombardment and annealing at 870 K. After this procedure no contamination could be detected using Auger electron spectroscopy (AES). STM shows a clean surface with terrace widths of up to 1000 nm. The Cu/Fe/Cu(100) sandwich structure was prepared by thermal evaporation of Fe and Cu. During evaporation and annealing the pressure inside the preparation chamber never exceeded 5×10^{-10} mbar. No contamination of the as prepared sandwich could be detected with AES. Annealing of the sample was performed by radiation heating.

3. Results

We investigated several combinations of Fe and Cu layer thicknesses: 3,8,10 and 18 ML of Fe and 1,2,3,4,6,8,10,18 and 25 ML of Cu. LEED measurements show that the Fe film grows in the fcc structure up to 10 ML, while above this thickness the film undergoes a martensitic transformation and grows in bcc structure. Before annealing, a diffuse pattern can be observed on an 8 ML Cu/18 ML Fe/Cu(100) sandwich, which sharpens after annealing at 420 K. This pattern is similar to that of 18 ML Fe/Cu(100) and is attributed to bcc-(110) domains in 4 different orientations [14].

STM images of an 8 ML Cu/5 ML Fe/Cu(100) and an 8 ML Cu/18 ML Fe/Cu(100) sandwich after annealing are shown in Fig. 1. Upon annealing of sandwiches with Fe layers thinner than 10 ML (fcc-Fe) the Cu overlayer remains a closed film. Between 470 K and 570 K no break-up of the overlayer is observed, irrespective of the Cu layer thickness. At a Fe film thickness of 18 ML a structural transformation of the Cu overlayer takes place. The film breaks up and large structures with a spatial size of several hundred nm are observed. The annealing temperature needed for this transformation strongly depends on the Cu layer thickness, the thicker the layer the higher the temperature. For a Cu layer of more than 10 ML even at 570 K no transformation was observed. For the following experiments we chose a sandwich structure of 8 ML Cu/18 ML Fe/Cu(100). With these film thicknesses the structural transformation of the Cu layer can be observed within a temperature range of 520–570 K using total annealing times of several hours.

Figs. 2a and 2b show SEM images of the sandwich after annealing for 30 min at 520 K. Large 3D structures are visible which are oriented predominantly along the ⟨110⟩ axis of the substrate surface (see Fig. 2b). For all images the ⟨110⟩ axes are oriented at 45° to the image boundaries. The islands have an approximate size of 350×650 nm. Due to their large height of 25–70 nm, these islands will be called crystallites in the following text. The crystallites are separated from each other by several micrometers and seem to be oriented in lines (see Fig. 2a). Dark regions (halos) are visible around the crystallites, while bright regions exist where no crystallites have formed. In Fig. 2c and 2d STM measurements at two subareas, indicated in Fig. 2a, are shown, Fig. 2c is taken in the dark region and Fig. 2d in the bright one. Both images show a slab-like structure, the slabs in Fig. 2d are much more elongated than in Fig. 2c. In Fig. 2c, islands of monoatomic height on a smoother slab-like structure are visible. Auger electron spectra (AES) show that for the bright region, compared to the dark ones, the intensity of the Cu peaks is increased while the Fe peak intensity is decreased. AES from the crystallites shows only a negligible intensity of

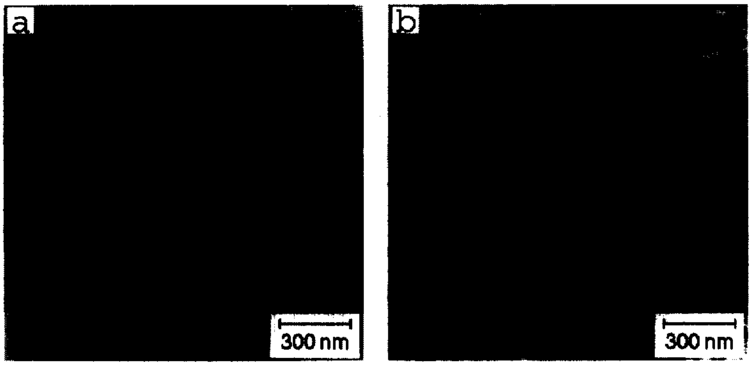

Fig. 1. (a) STM image of a sandwich structure of 8 ML Cu/5 ML Fe/Cu(100) after annealing for 30 min at 470 K. The steps are monoatomic. (b) Sandwich of 8 ML Cu/18 ML Fe/Cu(100) for the same conditions.

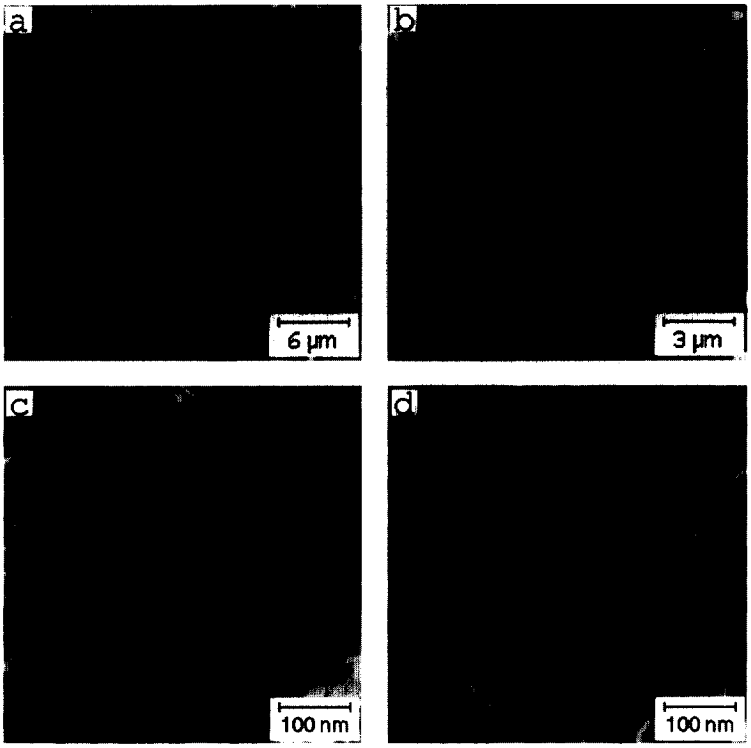

Fig. 2. (a) SEM image of 8 ML Cu/18 ML Fe/Cu(100) after annealing for 30 min at 520 K. Dark regions are visible around the crystallites. (b) The crystallites are mainly oriented along the ⟨110⟩ directions of the substrate. (c),(d) STM images of the surface, the white squares in image (a) mark the scan positions. (c) Near to the crystallites, showing the structure of bcc-Fe with at least 1 ML of Cu on top. Islands of monoatomic height on a slab-like structure are visible. The gray scale covers 1.5 nm. (d) Far away from the crystallites. Elongated structures with two main directions are visible. The gray scale covers 2.5 nm.

the Fe peaks. On top of the crystallites a large number of screw dislocations are visible (see Fig. 3f).

The formation of the crystallites and the change of the surrounding surface was investigated by STM. At an annealing temperature of 520 K the

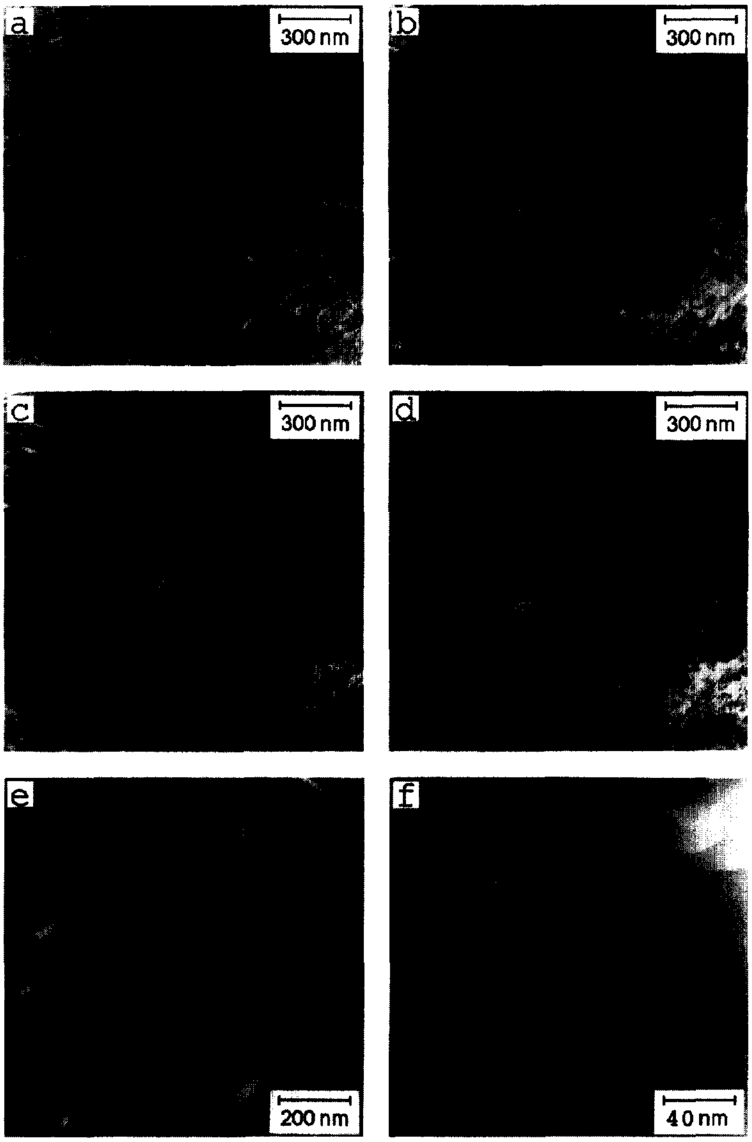

Fig. 3. STM images of a selected crystallite between several annealing cycles at 520 K. (a) After 20 min annealing. (b) After additional 20 min. (c) After additional 30 min. (d) After additional 50 min. For the STM images we used two colour tables, one for the surrounding surface and a second for the top of the crystallite. Both gray scales cover a range of about 3 nm. The regions where the gray scale is not defined are in a distinct colour. (e) STM image of the edge of a halo. Needles with a height up to 2.5 nm are visible. (f) Surface on top of a crystallite. Monoatomic steps are visible.

formation of the crystallites takes several hours. Several annealing cycles at this temperature were performed and after each one STM images were taken at the same sample position, see Figs. 3a–d. The increase of the crystallite size is obvious. After the first annealing step the surrounding surface shows a net-like structure formed from elongated slabs. The net-like structure opens during further annealing while needle-like structures remain partly stable for a long time (see Fig. 3e). After the last annealing step these needles have completely disappeared.

4. Discussion

From our measurements we conclude that the formation of microcrystallites only takes place if the Fe layer is in its bcc structure. LEED measurements show similar patterns for Fe/Cu(100) and Cu/Fe/Cu(100) for the layer thickness used. We believe that the Cu layer on top of the bcc-Fe layer grows in a bcc or a distorted bcc structure up to a certain thickness. This Cu layer is obviously strained. The driving force for crystallite formation is, therefore, stress relaxation and minimization of the surface, bulk and interface energies. In view of their large size it is expected that the crystallites grow in fcc structure. AES indicates that the crystallites consist of pure Cu. This is expected as Cu and Fe are only miscible to a few percent in bulk at the temperatures used [18,19]. For crystallites which have grown on a rough, slab-like surface, it is clear that they incorporate a large number of dislocations, which can be seen on top of the crystallites.

In Fig. 2a it can be seen that the crystallites tend to form in chains. A more detailed analysis shows that these chains correspond to step bunches. We can therefore conclude that the crystallites form predominantly at step bunches and other large crystal defects. Nuclei are formed very quickly at these positions while the nucleation rate in regions without large crystal defects is comparatively low. We attribute the dark regions around the crystallites to the diffusion zone where material transport from the Cu layer to the crystallites takes place. The Cu layer breaks up while the crystallites increase their volume. As seen from the STM images, long needles remain on the surface for a long time. These needles are probably domains of fcc-Cu which are expected to be more stable. Taking the ratios between the Cu and the Fe Auger signals we estimate that after the crystallite formation only 1–2 ML of Cu remain on the Fe layer between the crystallites. On the assumption that the edges of the crystallite are approximately orthogonal to the substrate surface we can estimate the volume of a crystallite from the STM measurements. The estimated total volume of the crystallites is consistent with a remaining coverage of 1–2 ML, the same result as determined from the Auger signal ratio. Thus, no migration of substrate material to the surface is necessary to explain the crystallite formation. The crystallites are formed from the material of the Cu overlayer only.

The crystallite volume was estimated for several stages of their growth (see Figs. 3a–d). For a long time the volume increases linearly, but the linearity breaks down at the end of the growth when the halos coalesce and the material from the Cu layer can be found completely in the crystallites. A more detailed description and a model for the formation process will be published elsewhere.

5. Conclusion

We demonstrate that a sandwich structure of Cu/Fe/Cu(100) shows new interesting features upon annealing. Cu-crystallites form from the Cu overlayer if the underlying Fe layer is in bcc structure. This happens only for a Cu layer thickness between 3 and 10 monolayers. For this thickness range at room temperature the Cu layer grows mainly in bcc or distorted bcc structure. The crystallites form at annealing temperatures between 500 and 600 K; at 520 K the growth is complete within about 2–3 h. While the material diffuses to the crystallites and increases their volume, the diffusion zones (halos) around the crystallites increase their area and coalesce. Inside the halos a structural transformation of the surface takes place, which reaches a final state with a slab-like structure of bcc-Fe. The volume of the crystallites increases linearly in time until the the halos coalesce. No migration of Cu from the substrate was observed.

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