A SPONTANEOUS MORPHOLOGY CHANGE ON THE SURFACE OF ELECTRODEPOSITED SINGLE-CRYSTAL COPPER FILMS DURING ROOM-TEMPERATURE AGING

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Room-temperature annealing effects in nanoscale copper metallization are the subject of considerable interest and investigation. We have previously reported real-time atomic force microscopy (AFM) observations of spontaneous morphology changes[1] (SMC) in electrodeposited copper films that occurred suddenly during room temperature aging after an incubation period typically in the range of 30 – 120 minutes. We have proposed[2] that outdiffusion of excess vacancies causes a volume contraction in the near-surface region leading to the development of the SMC. A systematic study[3,4] of the effects of annealing time and temperature on the incubation period for SMC yielded an activation energy of 0.48 eV for the incubation process. This value is comparable to the (grain boundary) migration energy of excess vacancies in copper. Additional experimental evidence supporting the SMC phenomenon in electrodeposited copper films has been obtained from differential scanning calorimetry and *in situ* electrical resistance measurements[5].

In this paper, we report an extension of our study to electrodeposits on single-crystal copper. Two types of substrates were used: 1-mm thick <001> single-crystal copper plate and cold-rolled copper annealed at 800ºC for 1 hour in hydrogen to give large-grained (20~40 µm) <001>-textured sheets. The substrate surface was electropolished prior to copper deposition. Copper was galvanostatically electrodeposited at 15 mA cm^{-2} from a stirred room-temperature bath of 0.25 mol dm^{-3} $CuSO_4$ and 1 mol dm^{-3} H_2SO_4. AFM images were taken repeatedly over the same area during room-temperature aging.

Fig. 1(a) is an AFM image a 30-nm thick film taken between 1,835 and 2,255 seconds after the end of electrodeposition. The surface topography clearly indicates that the film has grown epitaxially on the substrate which has a well-defined pyramidal structure characteristic of the {001} surface. The crystal faces are seen to be very smooth and featureless, except for some small round particles distributed uniformly over the surface. All AFM image taken from the end of deposition up to 1,835 s had a similar appearance.

An AFM image taken between 2,300 and 2,720 s is shown in Fig. 1(b). It reveals a dramatic change in the surface structure, closely-spaced fine lines having appeared suddenly (within ~45 s) around each pyramid in the form of a contour. Similar results were also observed for copper films grown on the surface of large-grained <001>-textured copper substrates.

We will discuss a proposed mechanism for the appearance of these periodic contour lines. As in the case[2] of SMC in polycrystalline copper films, the most plausible mechanism is outdiffusion of excess vacancies trapped in the deposit. The volume of freshly-deposited films is slightly expanded, because such films often contain a high (up to few atomic percent[6]) concentration of excess vacancies. These excess vacancies are highly mobile at room temperature and thus they are rapidly annihilated at the film surface and grain boundaries. This can cause preferential shrinkage inducing a gradient of tensile stress in the near-surface region. Thus the contour lines are thought to represent periodic surface relief patterns in the form of cracks/steps, which are formed to relieve tensile stress developed as a result of surface annihilation of excess vacancies trapped in the film.

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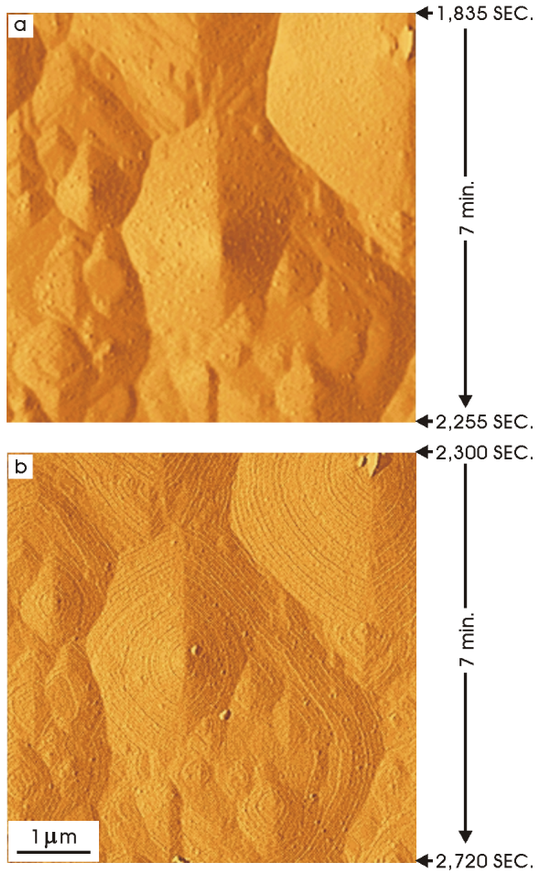

Fig. 1. AFM images showing a spontaneous morphology change (SMC) in a 30-nm copper film electrodeposited epitaxially on a {001} single-crystal copper substrate. Both images show the same area. The image in (a) was taken at 1,835 - 2,255 s and the image in (b) at 2,300 - 2,720 s after the end of electrodeposition.