Spontaneous Morphology Change in Electrodeposited Copper Films during Room-Temperature Aging

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Electrodeposited thin metal films, especially those grown at high deposition rates, contain a high concentration of excess vacancies. The reason for the inclusion of such a high concentration of vacancies in these films is that low-temperature and high-deposition-rate conditions often cause crystal growth to occur with a limited atomic mobility, thus leaving a number of unfilled lattice sites (excess vacancies). These non-equilibrium vacancies are generally unstable at ambient temperatures and are gradually annihilated over a period of time. Room-temperature aging phenomena are particularly prominent in Group IB metal films (copper, silver, and gold), because the activation energy for migration is sufficiently low for excess vacancies to migrate and eventually annihilate at the film surface. We propose a new mechanism that explains how these excess vacancies leaving the film surface will affect the surface morphology of thin films. It will be shown that our model can explain, using a concept of stress relaxation, the spontaneous morphology change observed in electrodeposited copper films [1].

As-deposited thin films are generally expanded due to the presence of excess vacancies. Based on this fact, we illustrate our model in Fig. 1. An as-deposited film is expanded laterally by an amount, ΔL, from the original vacancy-free value, L (see Fig. 1(a)). As the vacancies leave the film surface, a vacancy-depleted layer (VDL) will develop in the near-surface region. The VDL will tend to contract. This contraction, however, will be countered by the underlying thicker expanded layer, which exerts a tensile stress on the VDL. As long as the VDL thickness is sufficiently small, the tensile stress will be accommodated elastically and thus the VDL will remain expanded (see Fig. 1(b)). With increasing aging time, however, the VDL thickness increases and, at the same time, the elastic strain energy stored in the VDL continues to increase. At some critical thickness, the VDL can no longer sustain the increasing strain energy. At this stage, a stress relaxation of the VDL will occur by introducing surface cracks or islands (see Fig. 1(c)). We found that this stress relaxation model can satisfactorily explain the spontaneous appearance of small features [1] observed on the surface of electrodeposited copper films (Fig. 2).

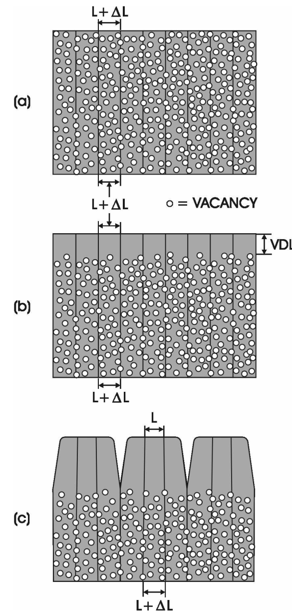

Fig.1. Schematic diagram showing how the surface of a thin film can be modified due to out-diffusion of excess vacancies.

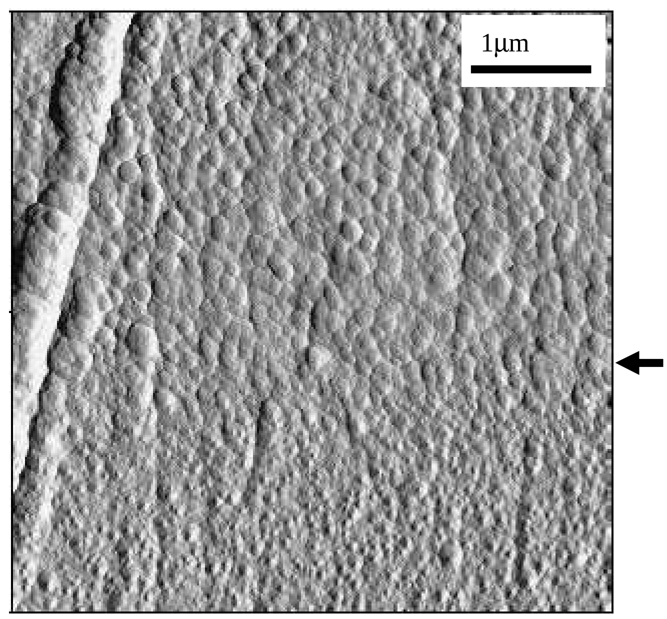

Fig. 2 AFM image of the surface of a 30 nm copper film electrodeposited on a polished gold foil at 1.6 mA cm^{-2} from 0.05 mol dm^{-3} $CuSO_4$ in 1 mol dm^{-3} H_2SO_4 with 1.3x10^{-4} thiourea as an additive. The scan was begun 7.6 minutes after the end of electrodeposition and the scan time from top to bottom was 7 minutes. It can be seen that a spontaneous morphological change occurred suddenly about ~ 4.2 minutes after the beginning of the scan (indicated by arrow).

REFERENCES

[1] D. N. Buckley and S. Ahmed, *Electrochemical & Solid-State Letters* **6**, C33 (2003).