Thermal grooving in thin silver films

The phenomena of thermal grooving [1, 2], thermal faceting [3, 4] and scratch removing [5] by thermal heating in various atmospheres are well known in bulk materials. Recently thermal faceting in thin films of nickel and aluminium by thermal heating in vacuum has been observed by Gol'diner and Yagubets [6]. However, certain other phenomena such as hillock formation, hole growth and agglomeration in various metal films deposited on to the different substrates have been reported by Lahiri and Wells [7], Presland *et al.* [8] and Sharma and Spitz [9] under different conditions of treatments. As far as the authors know, there are no reports in the literature describing the phenomenon of thermal grooving at the grain boundaries in thin films, although one would expect to observe it in thin films also. In the present communication, the authors report the phenomenon of thermal grooving at grain boundaries in thin silver films as observed with a transmission electron microscope during heating.

Thin films of silver (500 to 1000 Å) were prepared on quartz substrates by cathodic sputtering in an argon atmosphere at a partial pressure of 1.3×10^{-1} Pa (10^{-3} torr). These films were removed from the substrates by dissolving quartz in 40% HF and, after washing the films a number of times in distilled water, the films were picked up on the copper grids. The films were examined by a high resolution transmission electron microscope JEM-200 installed with a specimen heating stage and operated at 200 kV.

On examination with a transmission electron microscope, as-deposited films showed a high density (10^{10} to 10^{12} cm^{-2}) of microvoids as reported earlier [10]. The films were heated inside the microscope at 400° C for 15 min and were cooled to room temperature before examination. The films showed an increase in the crystallite size by recrystallization and the void size and density were found as 50 Å and 10^{11} cm^{-2} respectively. Continued heating at 400° C for up to 1 h did not cause an appreciable change in the crystallize size and density of the voids. Later these films were heated to 700° C and cooled. The examination of the films showed a further increase in the crystallite size and at the same time it caused grooving at the grain boundaries. Fig. 1 shows an electron micrograph of a region of the film 500 Å thick which depicts thermal grooving just before grain separation. If heating is continued at 700° C for a few minutes the grains separate at the grain boundaries and finally agglomeration occurs. Fig. 2 shows an electron micrograph depicting agglomeration caused after thermal grooving. The agglomeration appears to occur due to surface diffusion of silver atoms and the difference between the surface energies acts as a driving force. It may be worth mentioning that the phenomenon of agglomeration in silver films reported by Presland *et al.* [8] and Sharma and Spitz [9] differs from the one reported here in the respect that, in the former case the joining of the holes with each other during hole growth processes at relatively lower temperatures causes island separation which leads to agglomeration, whereas, in the present case it occurs by thermal

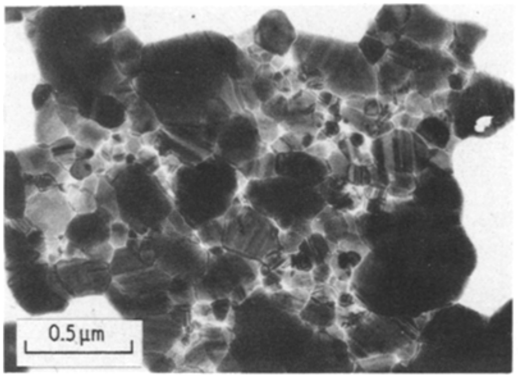

Figure 1 An electron micrograph of a silver film 500 Å thick heated to 700° C showing thermal grooving, just before grain separation.

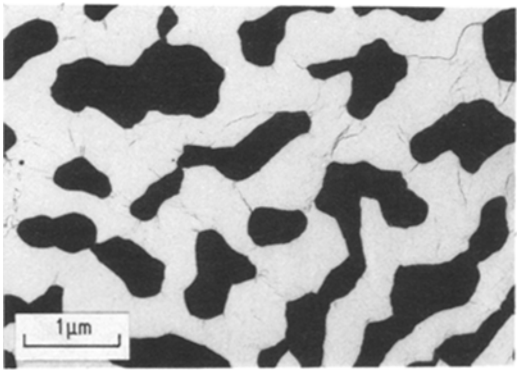

Figure 2 A micrograph depicting agglomeration in a film of silver 500 Å thick resulted after thermal grooving.

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grooving at the grain boundaries at relatively high temperatures, which causes grain separation and finally leads to agglomeration.

The process of thermal grooving can be explained as occurring as a result of local equilibrium being set up between the grain boundaries and the free surface. Thermodynamically the process may continue until the grain boundaries are eliminated completely. The transport processes which may be responsible for thermal grooving could be evaporation–condensation, volume diffusion or surface diffusion as described by Mullins [1, 2]. The contribution due to evaporation–condensation at the temperature involved in the present case under vacuum will be negligible while the contribution due to volume diffusion will be less important in solids, as pointed out by Mullins [2]. Hence the major atomic transport in the present case may occur by surface diffusion.

The theory of grain-boundary grooving by surface diffusion has been worked out by Mullins [1] and according to it the depth of the groove at the grain boundary can be given by

$$d = 0.973m(\beta t)^{1/4}$$

and

$$\beta = D_s \gamma \Omega^2 \rho / kT,$$

where D_s is the surface diffusion coefficient, γ is the surface energy, ρ is surface density of the atoms, Ω is the atomic volume, k is Boltzmann's constant, T is the absolute temperature, m is a factor on which the profile shape depends and t is the time needed to cause a groove of depth d. If we put the values of the various constants of the silver films 500 Å thick as $d = 5 \times 10^{-6}$ cm, $\Omega = 17 \times 10^{-24}$ cm^3, $m = 0.25$, and put other parameters at 700° C as $D_s = 2.0 \times 10^{-6}$ cm^2 sec^{-1} and $\gamma = 900$ ergs cm^{-2} [11], in the above equation one obtains $t = 26$ sec. Similarly one can calculate the time for causing a groove of the same depth at 400° C, $D_s = 3 \times 10^{-12}$ cm^2 sec^{-1}, $\gamma = 1400$ ergs cm^{-2} [11] the value of t comes out as 8×10^6 sec i.e. 92 days. Therefore one finds that at 400° C it would need 92 days for grain separation by thermal grooving while at 700° C it needs only 26 secs. Hence the phenomenon of thermal grooving in a few seconds as observed in the present case at 700° C can be explained very well on the basis of surface diffusion and it also explains why the grooving is not observed on annealing the films at 400° C for a few hours.

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