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Analysis of thickness distribution and the crystal structure in a Wehner spot

The first observations of anisotropic distribution of sputtered material were reported by Wehner [1] during his investigation of the effects of controlled single crystal sputtering by low energy Hg^+ ions. The same effect was later observed by other authors with different ion–atom pairs at different energies [2, 3]. Silsbee [4] explained this effect by the fact that in the crystal lattice the impulse is better transferred in the close-packed direction of the crystal. Focussing collision sequence efficiently transferred in the close-packed direction is responsible for anisotropic distribution of the material obtained on the collector during sputtering. On further investigation, by photometry of the collector with the sputtered material, it has been found that the material distribution in the spot is subcosinusoidal, which is indicative of higher deposition in the central part of the spot decreasing towards the periphery.

In the present paper the sputtering of Cu monocrystal by Ar^+ ions has been investigated and the distribution of the material in the obtained spots and structural characteristics in their particular zones have been determined. For this investigation the spots lying in the $\langle 1\,1\,0 \rangle$ direction obtained by sputtering the $(1\,0\,0)$ plane of the monocrystal have been used.

An electromagnetic isotope separation with well defined ion beam energy and incidence angle was used for ion bombardment. Copper monocrystals were sputtered by Ar^+ ions at 10 to 30 keV energy. An ion current density up to $1\,mA\,cm^{-2}$ and an interaction chamber pressure during bombardment of 6 to 8×10^{-6} Torr was used. The beam diameter was 4 mm and the distance between the target and the collector was about 40 mm. Prior to bombardment, the targets were polished in orthophosphoric acid. The Cu monocrystals were positioned on a separator collector so that the incident ion beam was normal to the $(1\,0\,0)$ plane of the crystal.

Sputtered material was deposited on to a sphere or a plane glass collector. The sphere collector was used only for the investigation of the anisotropic distribution of the material sputtered from the monocrystal target. To determine the distribution of the material in the spot, the material was deposited onto a plane glass collector which enabled measurement of the spot profile (using a Talystep* profilometer) and sample (thin film) separation from the substrate for electron microscopic investigation. Fig. 1 shows a schematic diagram of the collector arrangement (Fig. 1a) and the zones in the Wehner spot (Fig. 1b).

In order to obtain well separated zones in the spot, many different attempts were made. The best results, which actually made the investigation of the crystal structure possible in particular zones of the spot, were obtained by winding radially 6 to 8 coils of 0.5 mm copper wire at 5 places on the collector plate (Fig. 1b). Thus on the collector, during the bombardment of $(1\,0\,0)$ planes, several zones were usually obtained with minimum one spot, the structure and thickness of which could be investigated.

The investigation of the spot profile has shown the thickness distribution of the deposited material to be inhomogeneous. The cross-section of the spot was elliptical in form, with the axis $a = 12\,mm$ and $b = 10\,mm$. The thicknesses were measured in the direction of the longer axis at a distance of 3 and 5 mm from the centre. The thickness is highest in the central part of the spot and decreases towards the periphery. The Wehner spot in the $\langle 1\,1\,0 \rangle$ direction, obtained by bombarding a Cu
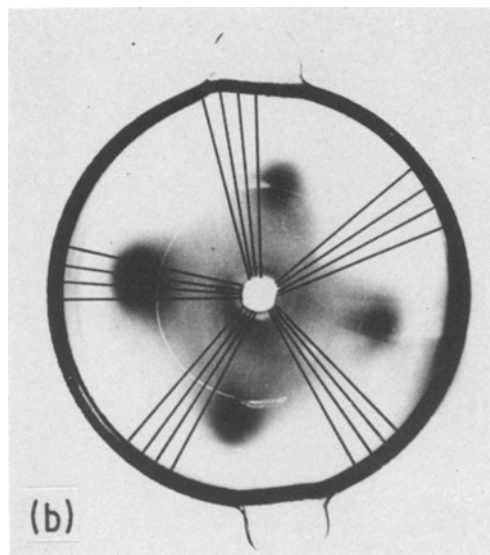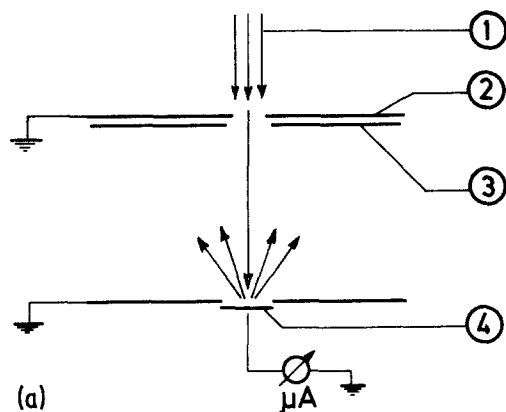
*Trademark of Johnson Matthey Ltd.

Figure 1 (a) The collector arrangement and (b) the Wehner's spots from Cu (1 0 0) bombarded plane; (1) ion beam, (2) collimator, (3) glass collector and (4) Cu specimen.

monocrystal with Ar^+ ions of 18 keV energy and a dose of 1.6×10^{18} ions cm^{-2}, has a thickness of 2000 Å in the central part of the spot (Fig. 2a). The two other regions investigated, in the direction from the centre of the spot to the periphery, had an average thicknesses of 1600 and 900 Å. The thickness distribution and the crystal structure in a Wehner spot are presented in Fig. 2.

Structural characteristics of the spot as a function of the distance from the centre are shown on the microphotographs (Fig. 2b). The crystallization of the spot was studied by transmission electron microscopy. Crystal structure in the central portion of the spot was quite pronounced. Crystals are irregular in form, with a high concentration of defects. In this region the mean grain size is about 800 Å; grains are inhomogeneous in size, in some places up to 0.2 μm. In the second zone with a spot thickness of about 1600 Å the grain size is more homogeneous and the mean crystal size is 450 Å. The structure at the periphery of the spot, with a thickness of 900 Å, is composed of very small crystal grains. The mean grain size in this region is about 200 Å. This small grain size structure (150 to 200 Å) is present in the whole spot. Even in its central part where the concentration of large irregular grains is high, fractions with a highly expressed small grain size

structure of 150–200 Å mean grain size are present and they take up to 20% of the surface.

A similar increase in the mean crystal grain size, with increasing thickness was also observed on the deposition of Cu thin films by vacuum evaporation [5]. Two explanations of this phenomenon have been given: (1) deposition temperature increases with increasing thickness, (2) geometric factors (hill and valley topography of the thin films) cause retarding crystallization of the films, with the thickness less than 1000 Å.

These explanations may be applied to the structures of particular zones of the investigated spot but neither of them is applicable to the whole region of thicknesses obtained in the spot. It is also possible that the deposition rate contributes to different amount of recrystallization in different zones [6]. Though the mean deposition rate (calculated from the thickness and deposition time) is about 20 Å min^{-1} it changes in different zones of the spot. In the central part of the spot, the deposition rate of the thin film is 2 to 3 times higher than at its periphery. Furthermore, the kinetic energy of atoms falling in the centre of the spot is most likely to be higher than the kinetic energy of atoms falling at the periphery. Both effects (deposition rate and energy of sputtered atoms) are important for nucleation and growth of thin films
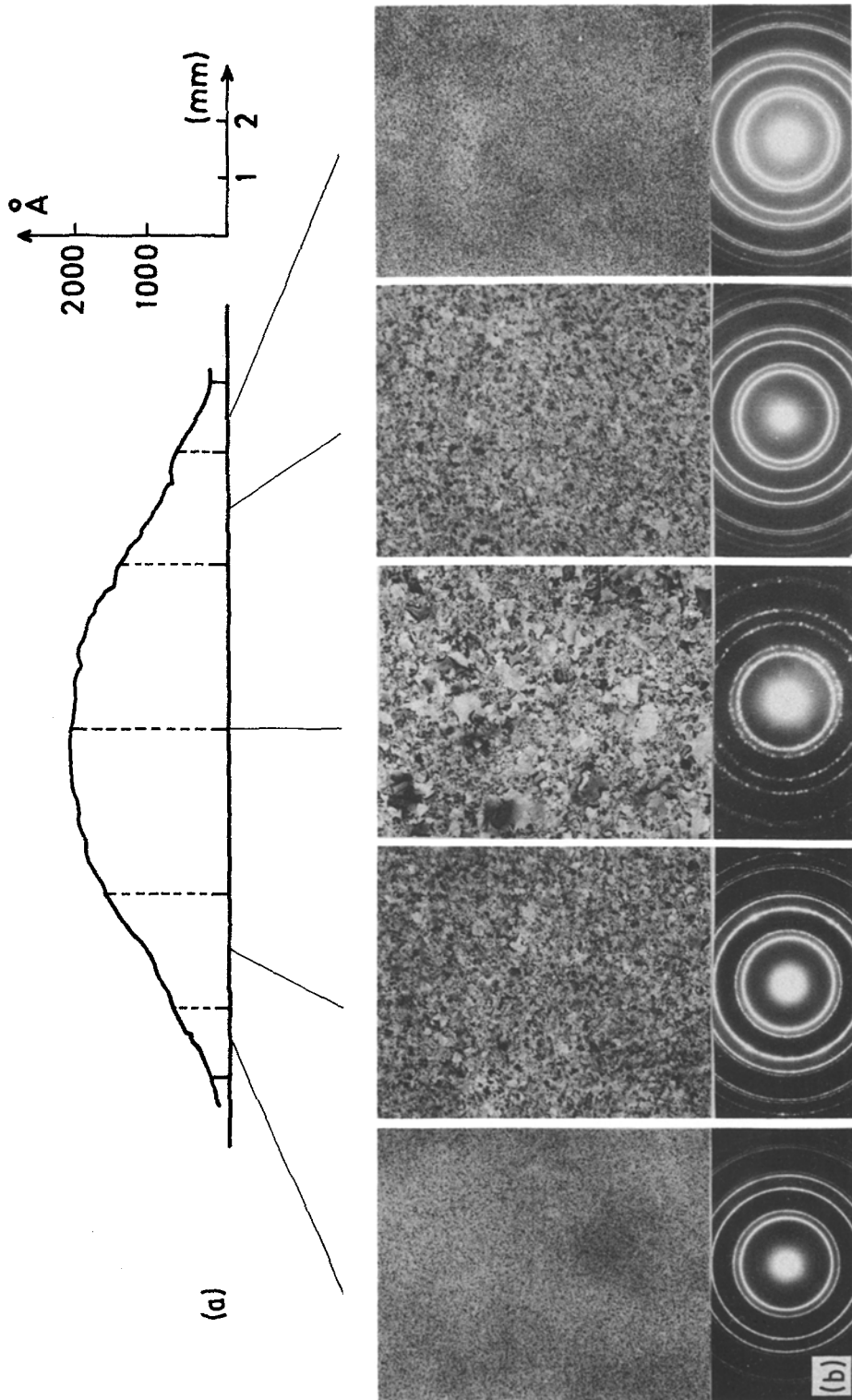
Figure 2 (a) Thickness distribution of the material deposited on the spot and (b) the corresponding crystal structure in the separated zones.

and contribute to the increase in the mean grain size viewed from the periphery to the centre of the spot.

On the basis of the experimental results obtained by investigation of the Wehner spot in the $\langle 1\,1\,0\rangle$ direction obtained by bombarding the Cu monocrystal $(1\,0\,0)$ plane, the following conclusions can be made.

(1) Profilometric investigations show that the thickness distribution of the material deposited on the spot is inhomogeneous. For an energy of $18\,keV$ and a dose of 1.6×10^{18} ions cm^{-2} the thickness in the central part of the spot is about 2000 Å. This thickness is several (2 to 3) times higher than that on the periphery.

It is rather difficult to determine precisely the periphery and the edge of the spot. Because of the defocussing effects in the crystal lattice and surface diffusion of deposited material on the substrate, the spot is spread over a larger area.

(2) The crystal structure in the Wehner spot changes viewed in the direction from the periphery to the centre of the spot. Some of the reasons are probably the different deposition rate of the thin film which forms the spot and the distribution of kinetic energy of the sputtered atoms in the beam forming the spot. Although the fraction with the small grain size structure in the spot can be found, in the central part of the spot the crystallization of the deposited material is almost complete.

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Melting behaviour of Li_2TiSiO_5

Li_2TiSiO_5 is reported to be in that rare class of compounds which melts directly to a mixture of two liquids [1]. During a study of phase relations in the system $Li_2O-TiO_2-SiO_2$, the melting of Li_2TiSiO_5 was reinvestigated. It does not melt to two liquids but instead, melts incongruently to the high temperature polymorph of Li_2TiO_3 and liquid. This is shown in the diagram of the pseudobinary join $Li_2TiO_3-SiO_2$, Fig. 1, in which Li_2TiSO_5 melts incongruently at $1213 \pm 8°$ C. The diagram was determined by heating samples in a furnace, quenching them into Hg and analysing the products by optical microscopy and X-ray powder diffraction. Full details of the experimental methods used and the results for the

ternary system $Li_2O-TiO_2-SiO_2$ are given elsewhere [2, 3].

The join $Li_2TiO_3-SiO_2$ is not a true binary join because TiO_2 appears on the diagram over a small range of temperatures between ~ 1139 and $1180°$ C: since the composition TiO_2 does not belong on this join, as shown in the inset, Fig. 1, the join cannot be a true binary join. Li_2TiO_3 undergoes an order–disorder phase transition at $1213°$ C [4] and the high temperature polymorph has a disordered rock-salt structure with a very simple X-ray powder pattern, Table I. In stoichiometric Li_2TiO_3, it is apparently not possible to quench the high temperature polymorph to room temperature [4, 5]. On heating Li_2TiSiO_5 above $\sim 1220°$ C, however, the high Li_2TiO_3 polymorph which resulted could be quenched to room tem-