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A TECHNIQUE FOR PREPARING ELECTRON TRASPARENT SUBSTRATES OF ALKALI HALIDES

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Abstract: A new technique of preparing alkali halides electron transparent substrates has been developed. The substrate crystals are formed inside the holes of a carbon support film, so that each crystal has two free faces for deposition and study. The mechanism of formation of transparent crystals and the important factors involved have been discussed.

Keywords: Alkali halides, crystal growth, deposition, electron transparent substrates, epitaxial films.

INTRODUCTION

The most important basic requisite for transmission electron microscopic (T.E.M.) studies of the nucleation and growth of a film from the vapours phase is a suitable substrate. For epitaxial films the preparation of the substrate surface is very important, as it is here where the film-substrate interaction occurs. Ideally the surfaces should be extremely smooth, flat and free from contamination.

Either cleaving or mechanically polishing a single crystal usually prepares the substrate surfaces. Surface of an epitaxial grown film is also used as substrate [Pashley 1959]. These substrates have been used for metal films and after deposition the overgrowth is usually covered by a support film. The substrate is then dissolved in a suitable solvent and only the overgrowth is examined. The problem in this method is that the support film obscures the original fine structure and small particles of the deposit can be lost during dissolution of the substrate. This disadvantage can be eliminated by not detaching the deposit film from its substrate. To examine the substrate and overgrowth simultaneously, imposes new substrate material requirements of electron transparency and good stability under the imaging electron beam. It also has the advantage that it could be possible to assess the epitaxial relationship between substrate and overgrowth directly.

For the application of T.E.M to the study of matter, thin foil producing techniques have been developed. These include rapid vacuum drying technique used by Hibi and Yada [1960], the sandwich technique developed by Mollenstedt [1964], the electron beam flashing thinning technique used by Yagi and Honjo [1962] and others.

MATERIALS AND METHODS

The method developed is based on the use of an emulsion made with farmvar solution and glycerol. After casting on glass the film is steamed and then transferred to 10 to 15 electron microscope grids. The grids are then covered with 20 nm carbon film and farmvar film is dissolved. Kay has described this method of preparing perforated carbon film.

A grid with perforated carbon film is held horizontally by a pair of tweezers. A drop of 10% salt solution in distilled water is poured on the grid using a fine dropper. The size of the drop should be smaller than the diameter of the grid to avoid the grid to stick to the tweezers. The drop is then drained gently from beneath the grid by a clean filter paper. The grids so prepared are now ready for examination.

RESULTS

The T.E.M observations of grid prepared show that crystals are formed inside the hole of carbon film (Fig.s1-3). In case of KCl, NaCl and KBr the crystals appear darker while others are either fully or partially transparent. For the same size crystals, different transparency is sometimes observed.

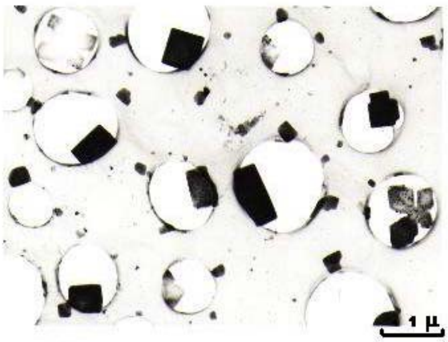


Fig.1

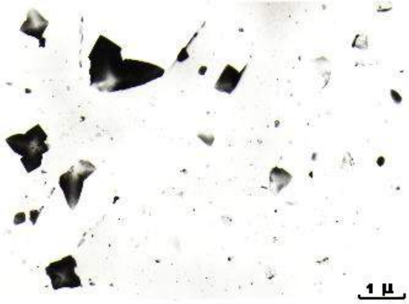


Fig.2

Figs. 1 and 2: KCl and NaCl crystals in the holes of carbon film.

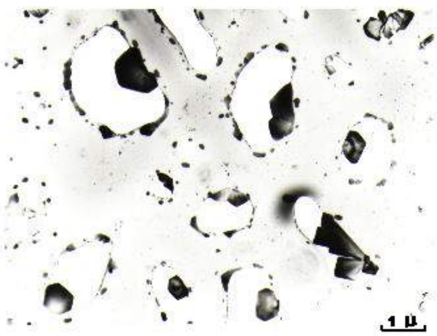


Fig.3

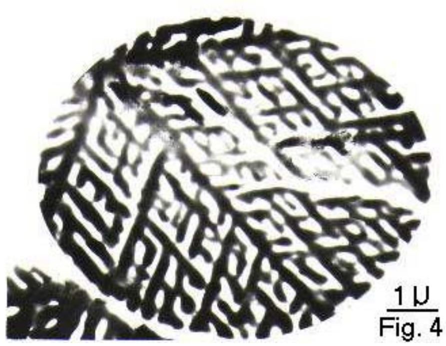
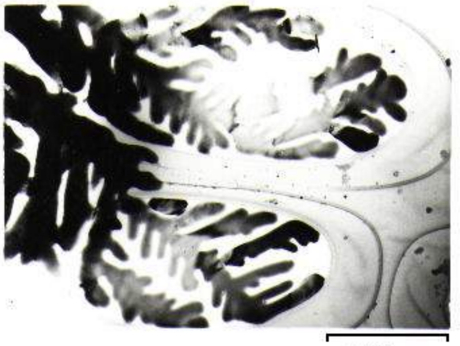


Fig. 4

Fig. 3: KBr crystals in the holes of carbon film.
Fig. 4: Dendritic crystals of CsI in the holes of carbon film.

CsI, CsCl and CsBr form dendrites i.e. tree like growth. It is observed that some of the crystals form entirely inside the holes (Fig. 4), while some of them start growing on the support film and extend into the holes (Fig. 5). It is further noticed that, as in (Fig. 6), some of the crystals are grown all over the support film and fill the holes as well. Some large crystals of CsI are also observed (Fig. 7), it is suggested that some crystals are suitable to be used as substrates.



0.5 μ

Fig. 5

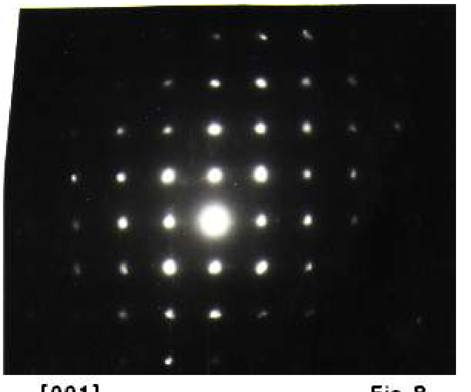
Fig. 6

3 μ

Figs. 5 and 6: Dendritic crystals of CsI in the holes of carbon film.

Fig. 7

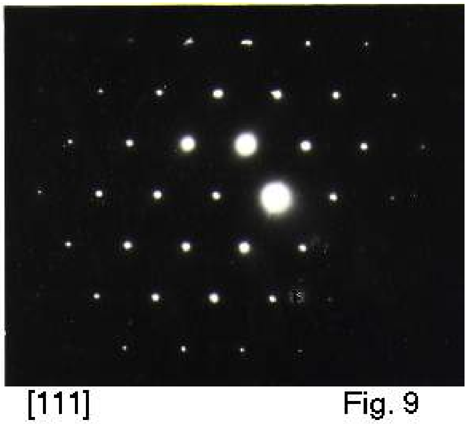
0.5 μ



[001]

Fig. 8

Fig. 7: A large crystal of CsI.
Fig. 8: Electron diffraction pattern of a [001] single crystal of KCl.



[111]

Fig. 9

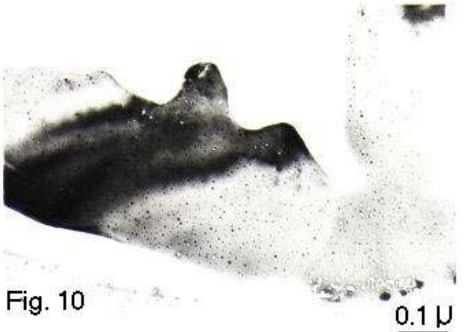


Fig. 10

0.1 μ

Fig. 9: [111] diffraction pattern of CsI.
Fig. 10: Thin deposit of gold on a large crystal of CsI.

Increasing the concentration of salt solution gradually increases the size and thickness of crystals. It is observed that a 15% concentration is adequate for KCl, NaCl and KBr while for CsI a 10% concentration yields good crystals. The orientation of KCl, NaCl and KBr crystals is mostly [001] normal to the plane of the holes (Fig. 8). The crystals of CsI are mostly oriented with [111] (Fig. 9), some [001] and [011] orientations have also been observed. The micrograph in Fig.10 shows a thin deposit of gold on CsI where small crystallites are evenly distributed indicating the flatness of the surface.

DISCUSSION

Most of the micrographs included here show that a variety of crystals are formed inside the holes of carbon film. This leads to assumption that when a drop of alkali halide solution is poured on to a grid with a perforated carbon support film and is drained from beneath with a filter paper a large number of small droplets are formed and captured by the holes. Due to small volume of these droplets the water evaporates rapidly and solution becomes supersaturated. The crystal nucleus is formed somewhere in the hole and as the evaporation continues, further growth occurs until the entire solid in the drop crystallizes.

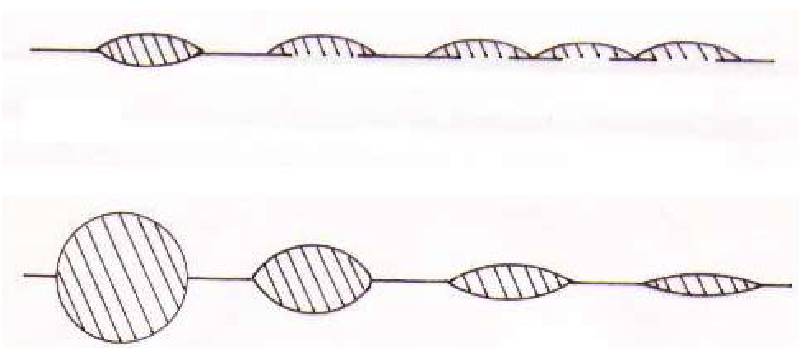


Fig. 11

Fig. 11: Some of the possible profiles for the droplets captured by the holes.

The formation of droplets and the growth of crystals are sensitive to the surface tension of the solution and the interface energy between the drop and film itself. For alkali halide solution the surface tension, γ, is about 80 x 10^{-3} Nm^{-1}, this gives a pressure of 8 x 10^4 Pa for a droplet of radius R = 2 μm. Under such a high pressure the droplets are mostly spherical. The mass, m, of the dissolved substance inside the hole is

$$m = (4/3)\, C\, \pi\, R^3$$

Hence thickness, t, of the crystal is

$$t = (4/3)\,\pi\, C\, R^3 / (\rho\, S)$$

where C is the concentration, ρ is the density and S is the surface area of the crystal. For cube-shaped thick crystals of KCl with C=15% the thickness comes out to be 3 μm, while for others it is of the order of 1.2μm. These calculations indicate that dark crystals are formed from spherical droplets. Hence, for transparent crystals the idea of spherical droplets should be discarded. Most of the droplets in the holes of the carbon support film are not in a minimum state of energy or they are not spherical or so. Due to different energy states, the droplets even in the same size holes may be in the shape of lenses of various thicknesses as shown in Fig. 11.

Although the surface tension tends to reduce the energies of the droplets by rendering them spherical, but evaporation result in super saturation and crystallization starts before this could happen.

For droplets of the size of the order of microns the effect of gravity can simply be ignored and all directions in a spherical droplet would be equivalent, so that the crystal can have any orientation. In lens-shaped droplet all directions are not equivalent and the fastest mode of transition, from solution to crystal, determines the directions of the fast growth of the crystal nuclei in the plane of the droplet. It has been suggested by Brice [1965] that the directions of the fast growth in alkali halide crystals are <110>, which has been confirmed in the present work (Fig.12).

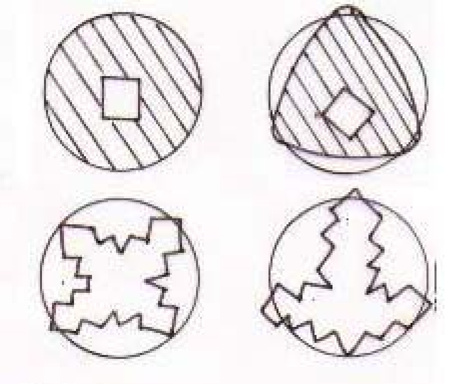


Fig.12

Fig. 12: Some of the crystals and suggested shapes of their droplets and nuclei at the beginning of crystallization.

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