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STUDY OF THE NUCLEATION AND GROWTH OF CESIUM IODIDE AND CESIUM CHLORIDE ON CESIUM IODIDE SUBSTRATES

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Abstract: Single crystals of cesium iodide with reasonable flat surfaces are produced in the holes of carbon film and have been used as substrates. Lattice structure of cesium iodide with its diffraction patterns has been discussed. Two kinds of experiments have been carried out. In the first, the film of CsI and CsCl grown by evaporation was transferred into the electron microscope without exposing it to the atmosphere, by means of transport chamber. In the second type of experiments the grown film was exposed to the atmosphere before being observed in the electron microscope. The micrographs and diffraction patterns of overgrowth together with substrate reveal that unexposed deposits of CsI on CsI do not show any orientation. Exposed deposits are well oriented with simple cubic lattice structure, indicating poor homo-epitaxy from the vapor but good epitaxial growth from solution. Unexposed and exposed deposits of CsCl on CsI are well oriented in all cases with there axes parallel to those of the substrate.

Keywords: Cesium chloride, nucleation and growth, single crystal, substrate.

INTRODUCTION

The most commonly used process that leads to the growth of thin monocrystalline films is based on the phenomenon of epitaxy. The word epitaxy comes from the Greek ‘epi’ + ‘taxis’, the former means outer, upon or attached to, and the latter means arrangement or order. Thus, epitaxy is the growth of a crystalline layer on a single crystalline substrate where the atoms in the growing layer mimic the arrangement of the substrate. Royer [1928] carried out extensive and systematic studies of a wide variety of overgrowths and introduced the term epitaxy. He put forward some rules of epitaxy, the most important of which was that the oriented growth occurs only when it involves the parallelism of two lattice planes that have network identical or quasi-identical form and of closely similar spacing. The experiments indicate that epitaxy occurs only if the misfit is no more than 15%. The misfit is defined as 100(b-a)/a, where a and b are the corresponding network spacing in the substrate and overgrowth, respectively. Numerous examples showed epitaxy with quite large misfits was possible [Schulz 1951 and 1952].

Most of the published work on the nucleation and growth of alkali halides on another alkali halide deals with the common halides of sodium, potassium and lithium. The substrates used have usually been NaCl, KCl and LiF. Very little work has been reported on the growth of cesium halides: Royer [1928] (CsF on NaCl and KCl), Schulz [1950] (CsBr on LiF), Schulz [1951] (CsCl, CsBr and CsI on LiF, NaCl and KBr) and Ludeman [1957] (CsCl on LiF and CsBr on KCl). CsI has not been used as a substrate before the present work. CsI can be produced with reasonable flat surface. The experiments of gold decoration on alkali halides show that CsI has the flattest surface of all the halides of cesium [Muhammad 2002a] and is, therefore, the best substrate for nucleation and growth of other alkali halides.

LATTICE STRUCTURE OF CsI

X-ray crystallographic data shows the lattice structure of CsI to be body-centered cubic as shown in Fig. 1.

Fig.1

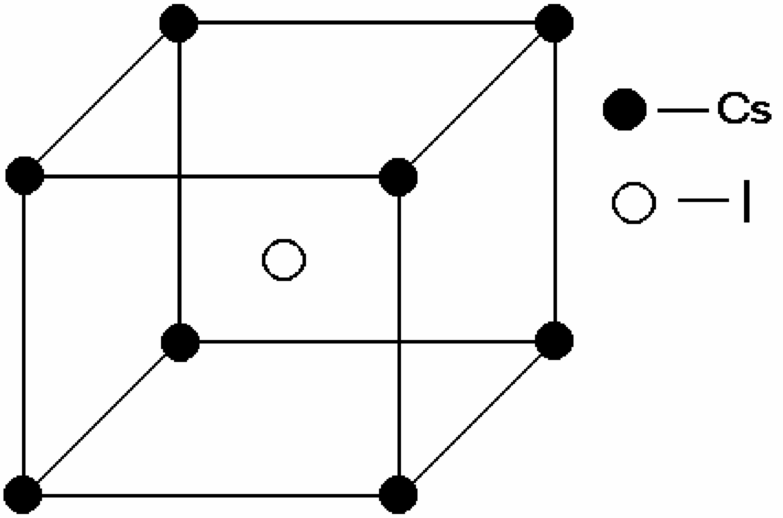


Fig.1: Unit cell of Cesium Iodide.

The lattice complex for CsI is as follows:

(i) Cs^+ at (0, 0, 0)
I^- at (½, ½, ½)

(ii) With alternate choice of origin,
I^- at (0, 0, 0)
Cs^+ at (½, ½, ½)

The lattice parameter $a_o = 0.4562$ nm and the Cs-I contact distance lies along the body diagonal of the cube, giving an effective radius sum.

$$r_{Cs} + r_I = \sqrt{3}\ a/2 = 0.395 \text{ nm}$$

The structure-factor equation for CsI can be written as:

$$F_{hkl} = f_{Cs}\, e^{2\pi i(o)} + f_I\, e^{2\pi i(\frac{1}{2}h+\frac{1}{2}k+\frac{1}{2}l)}$$
$$= f_{Cs} + f_I\, e^{\pi i(h+k+l)}$$

which means, if

$$h + k + l = \text{even number}$$

then

$$F_{hkl} = f_{Cs} + f_I$$

and, if

$$h + k + l = \text{odd number}$$

then

$$F_{hkl} = f_{Cs} - f_I$$

The atomic number of Cs is 55 and of I is 53 which means Cs^+ has 54 electrons and I^- also has 54 electrons. So electronically the ions are identical and their scattering factors are similar. In diffraction pattern of CsI the reflection from a plane whose indices' sum is odd has zero intensity. The diffraction pattern of CsI derives only from planes whose indices' sums are even. It makes the diffraction pattern of CsI relatively easy to index and helps to locate the spots reflected from overgrowth.

Fig. 2 shows the diffraction pattern from a single crystal of CsI made by the technique explained in Muhammad [2002a]. It is shown from indexing that the crystal is normal to $[\bar{1}11]$, (the crystal is said to be normal to $[\bar{1}11]$ means that plane $(\bar{1}11)$ of crystal is normal to electron beam), and all the spots have indices whose sum is even. Fig. 3 is from a polycrystalline film of CsI grown on continuous carbon film [Muhammad 2003a]. The indexing shows the rings correspond to {110}, {200}, {211}, {310}, {222}, ------- and so on.

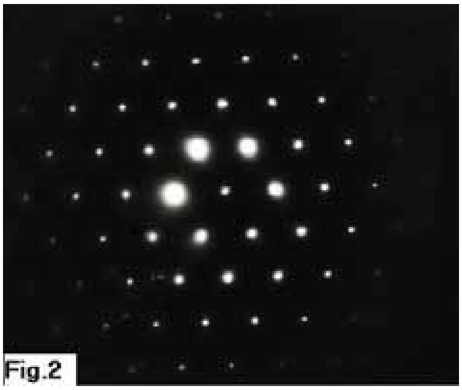


Fig.2

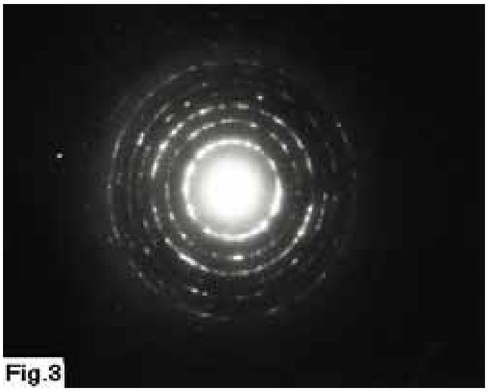


Fig.3

Fig. 2: Electron diffraction from a $[\bar{1}11]$ single crystal of CsI.

Fig. 3: Ring pattern from a polycrystalline film of CsI grown from vapor phase on continuous carbon film.

MATERIALS AND METHODS

The single crystals of CsI were produced in the holes of carbon films on electron microscope grids [Muhammad 2002a] and used as substrates. A tungsten boat was used for evaporation of CsI and CsCl in a vacuum unit. Two kinds of experiments have been carried out. In the first the film grown by evaporation was transferred into the electron microscope without exposing it to the atmosphere, by means of transport chamber [Muhammad 2002b]. These kinds of deposits are referred as "unexposed deposits". In the second type of experiments the film was exposed to the atmosphere before being observed in the electron microscope. These kinds of deposits are referred as "exposed deposits" [Muhammad 2003c].

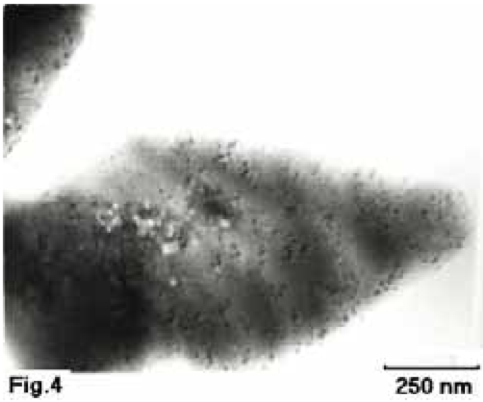
Evaporation of alkali halides was performed under the following conditions:

Residual gas pressure = 10^{-9} bar
Temperature = 20 °C (room temperature)
Average deposition rate = 1 nm sec^{-1}

The diffraction patters are indexed by using the camera constant technique [Muhammad 2003d].

RESULTS AND DISCUSSION

Fig. 4 shows a micrograph of an unexposed deposit of CsI on $[\bar{1}11]$ CsI crystal. It shows a number of small crystallites situated randomly on the substrate. The sizes of these crystallites vary from 7.5 nm and 15 nm. As the overgrowth is on the lower surface of the substrate, the strong reflected beams from the substrate act as primary beams with respect to the overgrowth. As a result there are a number of secondary electron diffraction patterns as seen in Fig. 5. The displacement of these patterns relative to one another is the same as the separation of the corresponding reflections from the substrate. Schulz [1950] had observed the two secondary diffractions patterns in examining the CsBr on LiF. Some more intense spots on the rings related to a very weak [111] orientation.



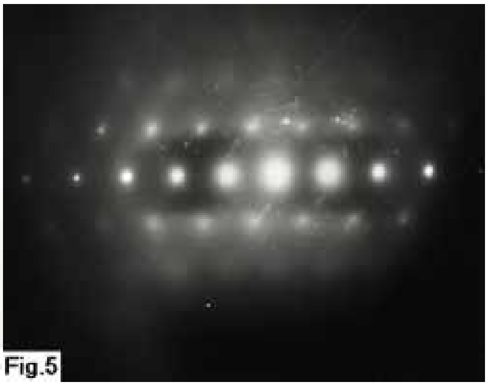
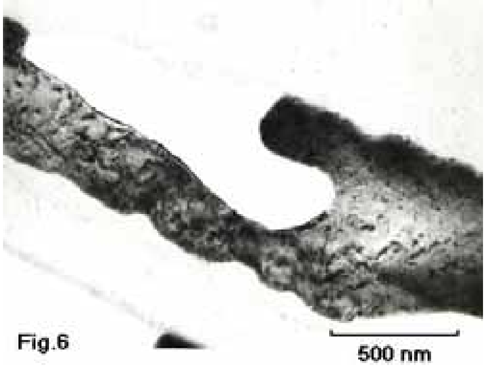


Fig. 4: Unexposed deposit of CsI on CsI.
Fig. 5: Diffraction pattern from an unexposed deposit of CsI on $[\bar{1}11]$ CsI.

Fig. 6 shows another unexposed deposit of CsI on CsI. Its diffraction pattern is shown in Fig. 7 in which the more intense spots are from the substrate and indicates that it is normal to $[\bar{1}12]$. The overgrowth gives two very weak rings correspond to {211} and {321}, which indicates the randomness of the crystallites on the substrate. Two relatively weak orientations $[\bar{1}11]$ and $[\bar{1}13]$ were also been observed. So the unexposed deposits of CsI on a single crystal of CsI show either no orientation or very weak orientation.



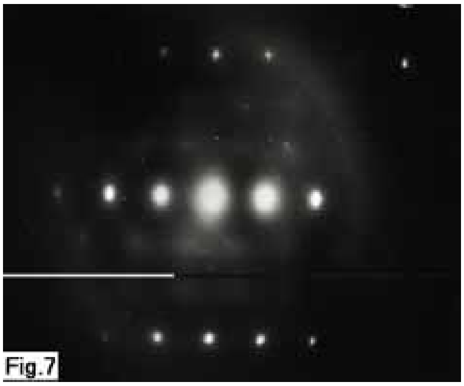
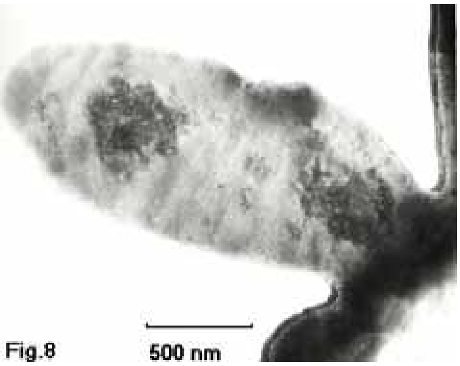


Fig. 6: Unexposed deposit of CsI on CsI.
Fig. 7: Diffraction pattern from an unexposed deposit of CsI on [$\bar{1}$12] CsI.

When a thin deposit of CsI on CsI is exposed to the atmosphere before examining in the electron microscope, recrystallization occurs and usually the overgrowth is well oriented on the substrate surface, as seen from its diffraction pattern. Fig. 8 shows an electron micrograph of a ≈ 10 nm thick deposit of CsI on CsI after exposure to the atmosphere. There are a number of small crystallites, 5 to 10 nm in size, and well oriented on the [$\bar{1}$11] CsI substrate as indicated by the diffraction pattern in Fig. 9. There are two fairly large and a few small clusters formed by coalescence of the small crystallites during recrystallization [Muhammad 2003c].



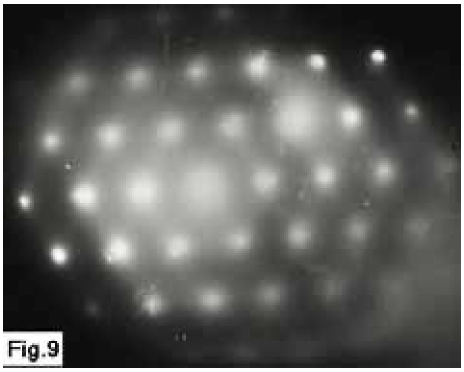
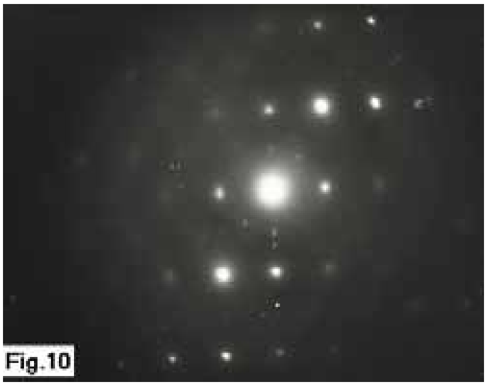


Fig. 8: Exposed deposit of CsI on CsI.
Fig. 9: Diffraction pattern from an exposed deposit of CsI on [$\bar{1}$11] CsI.

The diffraction pattern in Fig. 10 is from a thin deposit (< 5 nm) of CsI on CsI after exposure. The substrate is normal to the [011] and overgrowth has a simple cubic lattice structure, oriented with its axes parallel to those of the substrate as seen from the indexing of the pattern. CsI has normally a bcc lattice structure, which is stable below the melting point. Some polymorphic transitions occur in CsI in certain conditions. Schulz [1950] has reported thin deposits of CsI were found to have the NaCl-type structure, when grown from vapour phase on appropriate single crystal substrates. Much work has been reported on ultrahigh speed polymorphic transitions in alkali halides, induced by preliminary heat treatment or heterogeneity of the pressure medium. The most important observations are by Sizova and Urusouskaya [1977] on the micro plasticity of CsI crystals. Urusouskaya [1979] has explained the slip geometry of the {110} <100> slip system in CsI crystals. According to Schulz [1949] the evaporated films of alkali halides are rather porous and are composed of relatively independent crystals. CsI is a comparatively loosely packed lattice. Impurities, even in very low concentrations, usually occur between the atoms in CsI. All these properties of CsI crystals favor the observed polymorphic transitions.



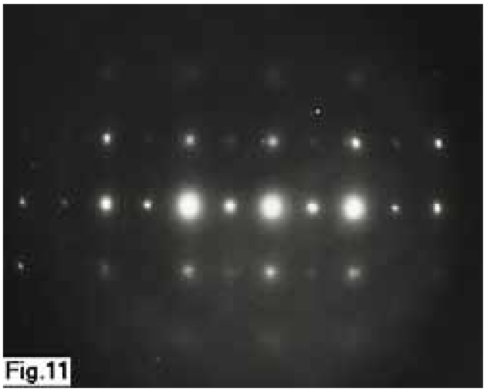
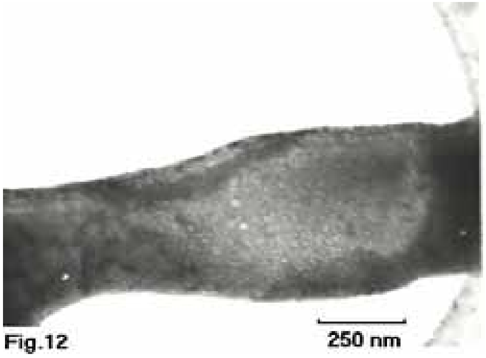


Fig. 10: Diffraction pattern from an exposed deposit of CsI on [011] CsI.
Fig. 11: Diffraction pattern from a very thin exposed deposit of CsI on [011] CsI.

The diffraction pattern in Fig. 11 is from a very thin (<2.5 nm) exposed deposit of CsI on [011] CsI single crystal. There is few reflections from the overgrowth, two small spots correspond to {110} and four spots nearest to the center have d-spacing 0.425 nm, since lattice parameter of CsI is 0.4562 nm, so they do not correspond to any particular planes. The possible explanations of these extra reflections are either due to some kind of impurities or some extra planes are formed due to various kinds of defects caused by electron irradiation in the electron microscope [Muhammad 2003b].

The diffraction patterns of unexposed and exposed deposits of CsCl on CsI show good orientation in all cases (Fig. 12 to 19). Fig. 12 shows an unexposed deposit of a 10 nm thick deposit of CsCl on a [011] single crystal substrate. The white specks in the micrograph are due to the point defects (vacancies) caused by the electron irradiation in the electron microscope [Muhammad 2003b]. The diffraction pattern in Fig. 13 indicates that the overgrowth crystals are well oriented with their axes parallel to those of the substrate.



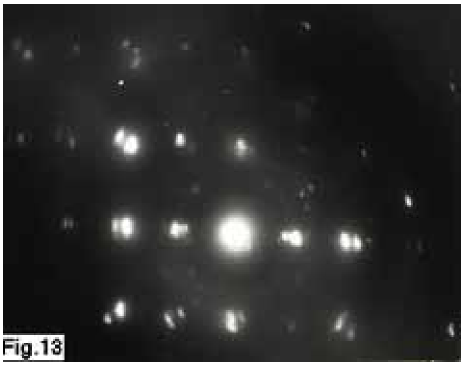
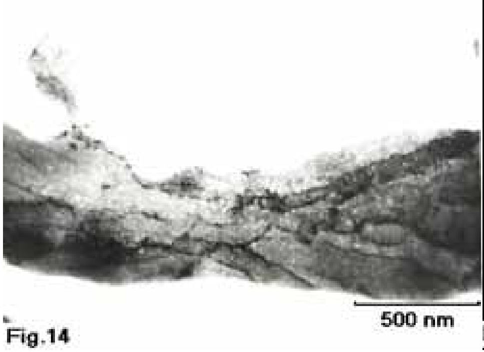


Fig. 12: Unexposed deposit of CsCl on CsI.
Fig. 13: Diffraction pattern from an unexposed deposit of CsCl on [011] CsI.

Fig. 14 shows another unexposed deposit, ≈ 5 nm thick, of CsCl on [012] CsI. The indexing of its diffraction pattern, shown in Fig. 15, indicates that the lattice structure of overgrowth to be simple cubic. CsCl is said to occur in two polymorphic forms at atmosphere pressure: the CsCl type and the NaCl type. The former is stable below 445 °C and the latter between 445 °C and the melting point 646 °C [Wagner and Lippert 1936]. Schulz [1951] had observed the CsCl → NaCl transition in very thin deposits of CsCl grown from vapour phase on NaCl – type substrates. This transition occurs with an increase in lattice parameter.



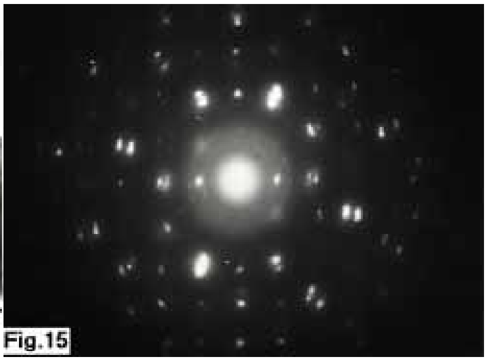
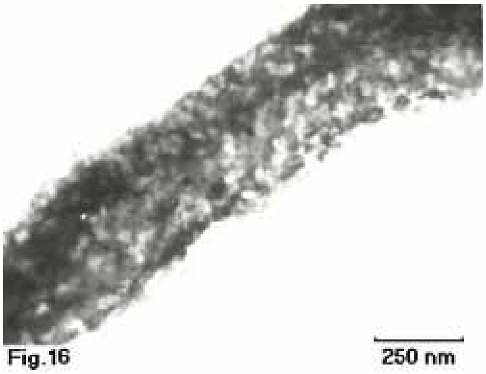


Fig. 14: Unexposed deposit of CsCl on CsI.
Fig. 15: Diffraction pattern from an unexposed deposit of CsCl on [012] CsI.

The space lattice for CsCl is simple cubic, although it is usually said to be bcc and sometimes behaves like bcc, as observed in the diffraction patterns in Figs. 13 and 15. In the crystal lattices each atom is at the center of a cube of the atoms of opposite kind, so the coordination number is eight. In other words a simple cubic lattice is inserted into another simple cubic lattice. Since Cs^+ and Cl^- ions have different number of orbital electrons, it is also possible that CsCl has reflections from planes whose indices sums are odd numbers; therefore, it gives a diffraction pattern of simple cube without any change in its lattice parameter.

Fig. 16 shows a micrograph of a 20 nm thick deposit of CsCl on $[\bar{1}11]$ CsI observed in the electron microscope before exposure to the exposure. The crystallites of the overgrowth are well oriented on the substrate as shown in the diffraction pattern of Fig. 17.



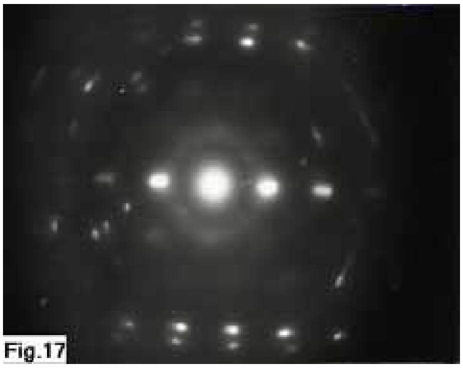
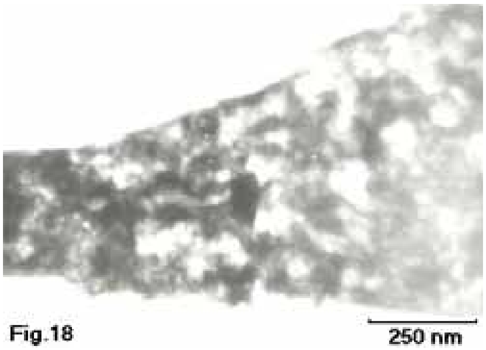


Fig. 16: Unexposed deposit of CsCl on CsI.
Fig. 17: Diffraction pattern from an unexposed deposit of CsCl on $[\bar{1}11]$ CsI.

When thin deposits of CsCl on CsI are exposed to the atmosphere, large crystals without any geometrical shapes are formed during recrystallization. The micrograph in Fig.18 is from a 20 nm thick deposit of CsCl on CsI after atmospheric exposure. Its diffraction pattern is shown in Fig.19 indicates that the substrate is normal to [001] and the overgrowth crystals, with simple cubic lattice structure, are oriented with their axes parallel to the corresponding axes of the substrate.



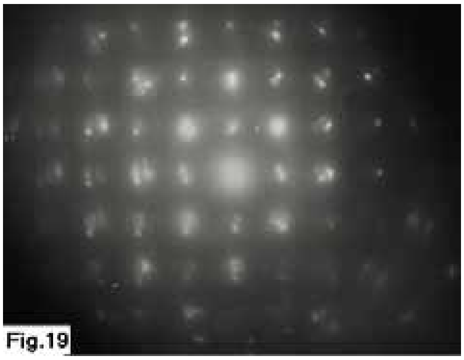


Fig. 18: Exposed deposit of CsCl on CsI.
Fig. 19: Diffraction pattern from an exposed deposit of CsCl on $[\bar{1}12]$ CsI.

CONCLUSIONS

Single crystals of cesium iodide in the holes of carbon film have reasonable flat surfaces and very useful substrates for epitaxial growth of other alkali halides. The micrographs and diffraction patterns of overgrowth together with substrate reveal that unexposed deposits of CsI on CsI do not show any orientation. Exposed deposits are well oriented with simple cubic lattice structure, indicating polymorphic transition. This also indicates that CsI shows poor homo-epitaxy from the vapor but good epitaxial growth from solution. Unexposed and exposed deposits of CsCl on CsI are well oriented in all cases with there axes parallel to those of the substrate.

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