▼ Journal of Research (Science), Bahauddin Zakariya University, Multan, Pakistan.
Vol.14, No.2, December 2003, pp. 139-146 ISSN 1021-1012

STUDY OF THE EFFECT OF ATMOSPHERE AND WATER VAPOR ON THIN DEPOSITS OF ALKALI HALIDES ON CARBON

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Abstract: Thin continuous carbon film for use as substrate has been prepared by using a new technique. Thin layers of CsBr, CsI, CsF and LiF on carbon substrate from the vapor phase has been deposited, exposed to atmosphere or water vapor and then studied by transmission electron microscope. Thin layers of alkali halides absorb water to make tiny droplets of their solution. The water evaporates in the electron microscope leaving behind a number of oriented small crystals or a quite large single crystal depending upon the thickness of unexposed deposit and time of exposure. The perfection and the shape of the crystals depend on the rate of crystallization.

Keywords: Alkali halides, carbon film, crystallization, exposure to atmosphere, exposure to water vapor, unexposed deposit, vacuum evaporation.

INTRODUCTION

Thin films are prepared most frequently by vacuum evaporation in which the source material is transformed into gaseous state by raising its vapor pressure through an increase in temperature. The vapors of source material condense on the substrate. A comprehensive review, the theory and practice of vacuum evaporation has been published by Glang [1970]. The substrate used was a thin continuous carbon film. A thin carbon film has greater mechanical strength and stability under electron bombardment than some other amorphous thin films and for high resolution work a very thin film of the order of 2 nm in thickness can be made easily. The very fine background structure present was of low contrast and did not interfere significantly with the over growth structure.

The method for vacuum evaporation of carbon thin films, used by Bradley [1954], was modified as follows: A microscope glass slide was held vertically in the solution of 1% w/v of formvar in equal parts of ethylene dichloride and dioxane and then transferred to a jar, which contained some ethylene dichloride or chloroform. The slide was kept there for 10 minutes and then transferred to a dust free place and kept there for 20 minutes or so to dry thoroughly. At this stage the formvar films on the lateral sides of the slide were stripped off with a sharp knife. Then the film on one side of the slide was floated on to the surface of distilled water in a bowl. After putting 10 to 20 electron microscope grids on to the film it was picked up with a dry glass slide in such a way that the grids were sandwiched between the formvar film and the slide. The grids with formvar film on them were then placed in a carbon-evaporating unit and coated with 2 to 5 nm carbon. Placing them in the vapor of ethylene dichloride for 3 to 4 hours washed the formvar substrate away. The carbon film prepared in this way was quite uniform and adhered well to the grids.

MATERIALS AND METHODS

An electron microscope grid with a thin carbon film on it was placed in the specimen holder so that the carbon film side of the grid faces downward. The holder was attached to the manipulating system in the transport chamber [Muhammad 1984 and 2002]. The transport chamber was inserted into intermediate chamber and fixed on a stainless steel jar, which was then placed on the vacuum deposition system. A schematic diagram in Fig. 1 shows the whole assembly. A simple boat of folded tungsten sheet was used to evaporate the alkali halides. The system was then evacuated to 10^{-9} bar by a diffusion pump backed by a rotary pump. A liquid nitrogen trap was used between the diffusion pump and the system to prevent the pump oil back streaming to contaminate the evaporated film.

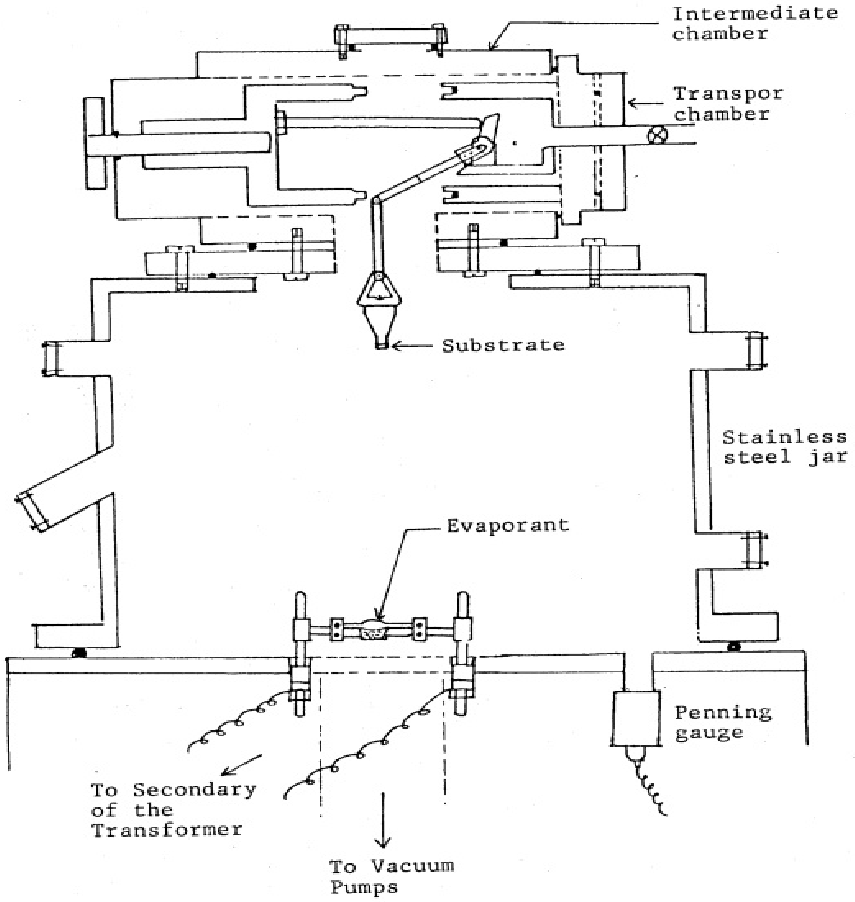

Fig. 1: Schematic diagram of vacuum evaporation assembly.

The evaporation of alkali halides were performed under the following conditions:

Temperature of the substrate = 20° C (Room Temperature)
Residual gas pressure = 10^{-9} bar
Rate of deposition = less than 1 nm sec^{-1}.

After evaporation specimen was transferred to the electron microscope via transport chamber and observations were taken without exposure to the atmosphere [Muhammad 2003]. The specimens were exposed to the atmosphere as follows: The small chamber in the transport chamber was closed, which isolate the specimen from the column of the electrons microscope and then the side valve of transport chamber was opened to allow the air into small chamber for prescribed time. The valve was then closed and an auxiliary vacuum pump was attached to the transport chamber for evacuating it. When the pressure in the transport chamber was near to the pressure of the column of the electron microscope, the side valve of the transport chamber was closed before opening the small chamber. This also allowed the specimen to be engaged in the plane of objective lens of the electron microscope and ready to observe.

RESULTS AND DISCUSSION

Fig. 2 is an electron micrograph showing a 10 nm thick deposit of CsI after exposure to atmosphere for 5 minutes. Clusters without any crystallographic shapes are formed with dimensions between 25 nm and 50 nm. A film of nearly same thickness exposed to atmosphere for 10 minutes forms fewer larger clusters, some of these are in contact and coalesce to form larger linked islands as shown in Fig. 3. The average diameter of these clusters is 150 nm.

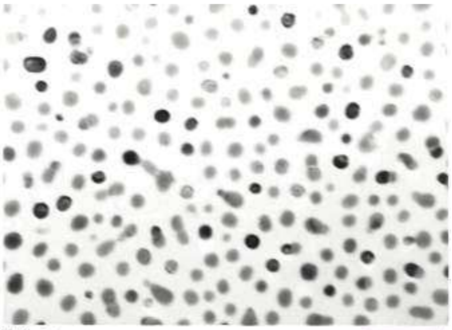

Fig.2

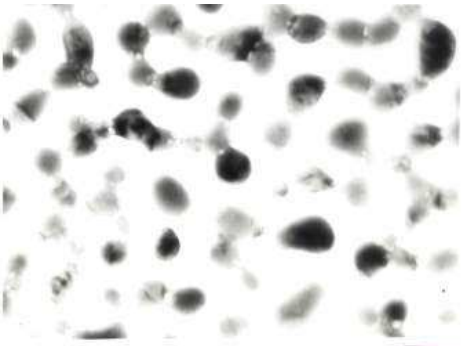

Fig.3

Fig. 2: Thin deposit of CsI after exposure to the atmosphere for 5 minutes.
Fig. 3: Thin deposit of CsI after exposure to the atmosphere for 10 minutes.

After atmospheric exposure of 1 hour, the 50 nm thick deposit of CsI formed the large dendritic single crystal as shown in Fig. 4. Deposit with this thickness formed a relatively thick continuous film on the substrate and having nearly the bulk density. The thin deposits are less dense, according to Raether [1976] and Muhammad [2003] less than 10 nm thick film has only 10% of the bulk density and more than 50 nm film has nearly the bulk density. A thick deposit absorbs water from atmospheric humidity and forms few large drops of concentrated solution on the substrate. During evacuation the water evaporates very quickly and due to the high concentration of the material in the solution, rapid growth occurs and forms dendrites. The dendrites are formed due to rapid crystallization from super saturated solution. The central part of the crystal is thicker than the edges; the edges are fairly transparent to the electrons and show some bending contours due to variation in thickness. There are some small holes in the transparent areas, which arise from the sublimation of material by electron bombardment in electron microscope. Its diffraction pattern is shown in Fig. 5, which indicates that the crystal is normal to $[\bar{1}33]$, i.e., the $(\bar{1}33)$ plane of crystal is parallel to the substrate surface.

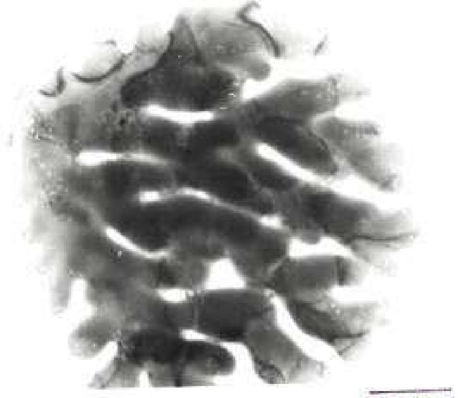

Fig.4

Fig.5

Fig. 4. A 50 nm thick deposit of CsI after exposure to the atmosphere for 1 hour,
Fig. 5. Diffraction pattern of crystal shown in Fig. 4.

Fig.6

Fig,7

Fig. 6: Evaporated CsI exposed to the atmosphere for 1 hour with decreased rate of crystallization.

Fig. 7: Diffraction pattern of crystal shown in Fig. 6.

Fig. 6 shows another large single crystal formed when a nearly 20 nm thick deposit of CsI was exposed for one hour and crystal growth rate decreased by covering the specimen to slow down the evaporation of water. The diffraction pattern, Fig. 7, shows the crystal has a $[\bar{1}11]$ orientation normal to substrate surface and some extra spots in the pattern indicate the presence of some disoriented fragments. The micrograph in Fig. 8 shows a10 nm thick deposit of CsBr after exposure to the atmosphere for 20 minutes. A number of clusters, with diameter between 40 and 50 nm, are formed. Some of them are nearly square shaped with average side length about 30 nm. These crystals are situated randomly on the carbon substrate as indicated by its diffraction pattern shown in Fig. 9. As CsF is more hygroscopic than any other alkali halide, it reacts with the atmospheric moisture very rapidly. Fig. 10 is a micrograph of a 20 nm thick deposit of CsF after exposure to the atmosphere for just 3 minutes; triangular shaped single crystals were formed. The diffraction pattern of one of these crystals is shown in Fig. 11, which indicates that the crystal is oriented with $[\bar{1}12]$ normal to the substrate surface.

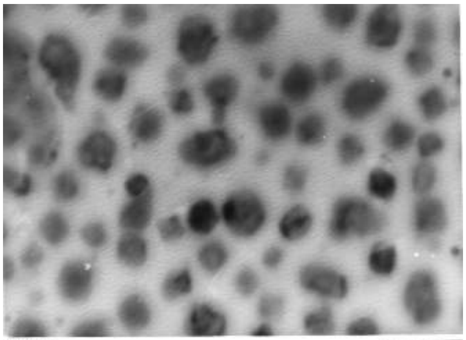

Fig.8

Fig.9

Fig. 8: A 10 nm thick deposit of CsBr after exposure to atmosphere for 20 minutes.
Fig. 9: Diffraction pattern of crystal shown in Fig. 8.

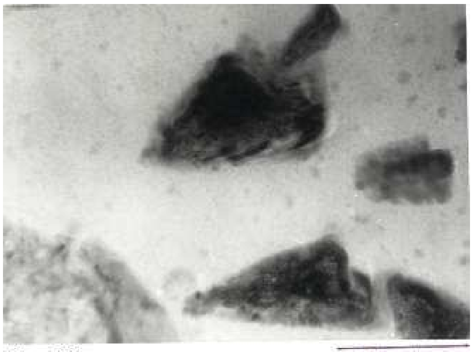

Fig.,10

Fig.,11

Fig. 10: Evaporated CsF after exposure to the atmosphere.
Fig. 11: Diffraction pattern of one of the crystal shown in Fig. 10.

Fig.12

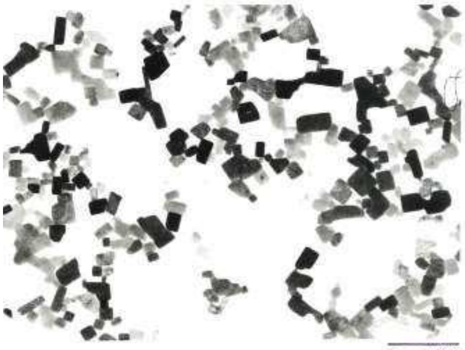

Fig.13

Fig. 12: A10 nm thick deposit of LiF exposed to water vapor for 1 minute.
Fig. 13: A 20 nm thick deposit of LiF exposed to water vapor for 3 minute.

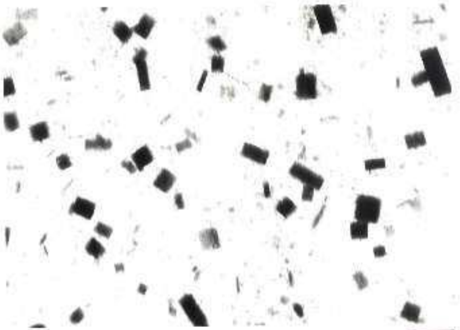

Fig.14

Fig.15

Fig. 14: A 5 nm thick deposit of LiF exposed to water vapor for 1/2 minute.
Fig. 15: Selected area diffraction pattern of one of the crystal shown in Fig. 14.

LiF is nearly insoluble in water at room temperature and, therefore, less reactive with atmosphere. There has not been observed any significant change in an initially unexposed deposit after exposure to the normal atmosphere for several hours. However, when a thin deposit of LiF was exposed to water vapor, the solution and recrystallization occurs. The experimental detail of this process of recrystallization is as follows: An electron microscope grid, with a 10 nm thick deposit of LiF on continuous carbon film substrate, was held horizontally over a bowl containing very hot water, for 1 minute and then observed in the electron microscope. The resulted micrograph is shown in Fig. 12, which shows there are a number of small crystals with an average dimension of 15 nm were formed. Some of them coalesced into large clusters of several crystallites, thus clearing the surrounding substrate area. Although LiF is insoluble in water in bulk quantity, thin evaporated film of alkali halides are porous and less dense as compared to the bulk. Since, LiF is not hygroscopic, it is unlikely that even a thin deposit of this material dissolves in normal atmospheric humidity, which is only 40% at room temperature. When thin deposit is exposed to water vapor, where the humidity and temperature are much higher, the small crystallites in the unexposed deposit dissolve and make droplets of solution and in the electron microscope water evaporates leaving behind small crystals or clusters of small crystallites.

The micrograph in Fig. 13 is from a 20 nm thick deposit of LiF after exposure to water vapor for 3 minutes. It shows a large number of cube shaped crystals. Nearly all crystals are linked to one another and most of them are electronically transparent. An other example of recrystallization of thin deposit of LiF is shown in Fig. 14, where a 5 nm thick deposit was exposed to water vapor for ½ minute immediately after evaporation. Since the deposit of such thickness does not form continuous film on carbon substrate, the isolate clusters in the unexposed deposit dissolve in water vapor and form droplets of solution, which resulted quite separated crystals. The selected area diffraction pattern of above is shown in Fig. 15, which indicates an orientation [001] normal to substrate surface and some extra spots represent some slightly disoriented superimposed crystals.

CONCLUSIONS

Most of the alkali halides are more or less hygroscopic. When thin deposits of these materials are exposed to the atmosphere they react with it and absorb water to make tiny droplets of there solutions. In the electron microscope the water evaporates leaving behind a number of oriented small crystals or a quite large crystal, depending on the thickness of the unexposed deposit and the time of exposure. Although the substrate carbon film is amorphous, a crystal said to be oriented means one of the plane of crystal is parallel to the surface of the substrate. The perfection and the shape of the crystals depend on the rate of crystallization. The mechanism of formation of these crystals is the same as growth from solution as given in comprehensive reviews by Mullin [1972, 1976], Brice [1973], Bennema and Gilmer [1973].

References

Bennema, P. and Gilmer, G.H. (**1973**) In: Hartman (Ed.) *Crystal Growth: An Introduction*, North-Holland Amsterdam, p. 263.

Bradley, D.E. (**1954**) *Brit. J. Appl. Phy*. 5, 65.

Brice, J.C. (**1973**) “The Growth of Crystals From Liquids”, North-Holland, Amsterdam.

Glang, R. (**1970**) In: Massel and Glang (Eds.) *Hand Book of Thin Film Technology*, Ch.1, McGraw-Hill Book Company, New York.

Muhammad, J. (**1984**) Ph. D. Thesis, University of London, p. 108.

Muhammad, J. (**2002**) *J. Research (Science)* B. Z. University, Multan, Pakistan, 14, 189.

Muhammad, J. (**2003**) *J. Pure and Appl. Sci.*, Islamia University, Bahawalpur, Pakistan, (In press).

Mullin, J.W. (**1972**) “Crystallization”, 2nd ed., Butterworths, London.

Mullin, J.W. (**1976**) “Industrial Crystallization”, Plenum Press, New York.

Raether, H. (**1976**) In: Dupuy and Cachard (Eds.) *Physics of Nonmetallic Thin Films*, Plenum Press, New York, p. 123.