Contribution of Halides in CsX (X=Cl, Br and I) Thin Films on the formation of SPR peaks

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Abstract

This manuscript describes the evolution of grain structures in Cesium Halide films which results in appearance of Surface Plasmon Resonance (SPR) peaks in UV-visible absorption spectra. Thin films of Cesium Halide grown by thermal evaporation are polycrystalline in nature with large irregular tightly packed grains with sharp grain boundaries. With time these grain boundaries recede to become smaller and spherical in shape in order to minimize the free surface energy of the system. The process is also assisted by the presence of point defects/color centers in Cesium Halide films. These defects which appear due to the absence of massive halide atoms from the lattice results in residual tensile stress within the lattice which results in defect diffusion. The defects migrate outwards towards the grain surface giving rise to Cesium metal clusters. The lattice mismatch appearing between the lattices at the grain boundary and the bulk giving rise to Core-shell structure further contributes to grain division. Along with

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this volume diffusion, a surface diffusion of Cesium takes place towards sites of faceted grain boundaries resulting in a necking phenomenon, appearing like bridges between the daughter Cesium Halide grains (grains appearing due to division of a single grain). Breaking away of the daughter Cesium Halide grains results in nano-rods that contribute to the SPR peak seen.
Introduction

In our recent works we have reported about the optical properties of Cesium Halide thin films, namely, Cesium Chloride (CsCl), Cesium Bromide (CsBr) and Cesium Iodide (CsI). The optical properties stood out due to the singular appearance of Surface Plasmon Resonance (SPR) peaks in the visible region. While we confirmed that SPR peaks arise due to formation of Cesium metal clusters, two basic questions arise from these observations, “What mechanisms lead to the formation of cesium metal nano-clusters especially the observed nano-rods?” and “Why does CsI behave differently from CsCl and CsBr?” The direct experimental investigation into the formation of metal nano-clusters is not possible, however, we may logically speculate the sequence of events that led to the formation of metal nano-clusters.

Results and discussion

Thin films of cesium halide were fabricated by thermal evaporation in vacuums better than $10^{-5}$ Torr. The films were deposited on microscopy glass slides maintained at room temperature. All the films were fabricated in identical conditions. Looking at fig 1, an immediate observation is the striking similarity between morphology of CsCl, CsBr (not shown here) and CsI polycrystalline thin films. Large grains are tiled and tightly packed with sharp grain boundaries. The grains however do not have regular shapes. These SEM micrographs were taken within few hours of sample fabrication. The morphologies gradually change with time as neighbouring grains recede to become smaller and spherical in appearance (fig 2).

Grain Boundary Grooving: Surface Diffusion

Nature has a natural tendency to force grains to take up a spherical shape. This is nature’s way of minimizing the free energy of the system (G). The equation used to model this behavior of nature
Figure 1: SEM images show the surface morphology (polycrystalline nature) of thin films of Cesium Chloride and Cesium Iodide respectively.

Figure 2: SEM morphologies gradually change with time as neighbouring grains recede the become smaller and spherical in appearance (Images are of CsCl and CsI of samples shown in fig 1 after ageing.

is given as

\[ G = \gamma_s A_s + \gamma_b A_b \]  \hspace{1cm} (1)

where \( \gamma_s \) and \( \gamma_b \) are the surface energy per unit area and grain boundary energy per unit area respectively. \( A_s \) and \( A_b \) being the grain’s surface area and grain boundary area respectively. Grain boundary area is the area of contact between two grains. For a spherical grain of a given volume, the system’s free energy is the least due to a large decrease in grain boundary area, \( A_b \) at the cost
of a relatively small increase in surface area \( (A_s) \). The grain shaping or its change to spherical

\[
\text{Figure 3: Schematic representation of the triple junction, the point where grain boundary meets the surface.}
\]

shape is due to grain boundary grooving. “Grooving”,\(^1-3\) as the name suggests, is the phenomenon by which gaps appear between the grains of polycrystalline samples. The fissures develop from the film surface towards the substrate. Theoretical models show the grooving occurs due to atoms moving along the surface away from the “triple intersection point” by surface diffusion\(^4\) (fig 3). Fig 1, clearly shows due to the near hexagonal tiling of the grains, triple intersection points are formed even within the film. Fig 4 shows pictorial representation of fig 1 (initial situation is shown in inset) followed by how these triple intersection points evolve, pushing into the grain and thus giving a spherical shape.

In the above paragraph, we have assumed \( \gamma_b \) to be a constant. This is far from the truth since the grain boundary energy depends on the lattice defects caused by the mismatch between the lattice at the grain boundary and its bulk.\(^6-11\) This mismatch manifests as a shell region whose thickness is proportional to the grain size. Smaller grains have thinner shells with less lattice mismatch and hence smaller \( \gamma_b \). Thus nature breaks the grains into smaller spherical grains with time, thus reducing the system’s free energy by lowering \( \gamma_b \).\(^12\) Fig 5 highlights the formation of shell around the grain via volume diffusion of defect towards the surface. We shall be discussing
Figure 4: *Pictorial representation of how triple intersection points evolve, pushing grains to have spherical shapes. Arrows are for indication of the direction in which these triple points evolve.*

volume diffusion further, however at this point it is important to appreciate that if there is a lattice mismatch between the shell and core then $\gamma_b$ takes values to assist grooving of the grains.

Table 1: Table for Lattice mismatch in core-shell structure

| Halides  | Core structure | Lattice constant | Shell structure | Lattice constants |
|----------|----------------|------------------|-----------------|------------------|
| Chlorine | Cubic          | 4.12             | Cubic           | 5.838            |
| Bromine  | Cubic          | 4.29             | Cubic           | 5.984            |
| Iodine   | Cubic          | 4.568            | Tetragonal      | 3.3645,3.4645,12.552 |

Figure 5: *Pictorial representation of shell formation.*

As described above, the lattice mismatch of the two regions contributes to $\gamma_b$. In our case, this lattice mismatch is due to a core-shell formation taking place with Cesium shell around a core of Cesium halide. The existence of free metallic Cesium were shown by the just resolvable XRD peaks.\(^{13,14}\) The XRD results also allowed us to determine the lattice structure and size for the two
regions. Table 1 lists the results for easy viewing. Larger mismatch in Cesium and Cesium Halide structures imply greater $\gamma_b$. Since, nature tries to bring down the system’s free energy by reducing $\gamma_b$ via grain division, the shells become thinner, thus reducing the region of lattice mismatch. Since the cesium shell in CsI takes a tetragonal structure, which is very different from the cubic structured core, it would necessarily indicate a faster grain division/breakage in CsI as compared to CsCl and CsBr.

**Core-Shell Formation: Volume Diffusion**

As stated above, a thin layer (shell) of Cesium is formed around the Cesium halide core in our samples. The question is, “how do the halide atoms disappear from the surface or possibly how does cesium reach the surface with no halide atom?” While iodine might have tendency to sublime, leaving behind free Cesium, the remaining halides do not sublime. Hence, the question of importance is “how does cesium clusters form at the grain surface?” Cesium Halides crystals/ films readily form color centers. These are point defects due to the absence of the massive halides atoms from the lattice which results in residual tensile stress within the lattice. The neighbouring lattices interturn experinces compressive stress. The resulting stresses graaidents in turn result in diffusion of defects.\(^{11}\)

Consider the diffusion process of a vacancy. From its intial position to final poistion, the vacancy moves through intermediate steps which is essentially marked by the vacancy choosing the highest free energy state and minimum energy diffusion path. The difference in the free energy between the intermediate steps is called migration energy ($E_{mig}$). The process of defect diffusion depends on (i) formation of defect ($E_{form}$) and (ii) its migration. Hence we can talk of an activation energy for defect diffusion which would be the sum of these energies, i.e.

$$A = E_{form} + E_{mig}$$
The diffusivity in terms of activation energy is given by

$$D = \frac{f \nu d^2}{6} \exp \left( -\frac{A}{KT} \right)$$

(2)

where, ‘f’ is a correlation factor (proportionality constant), $\nu$ the attempt frequency, ‘d’ the hop distance. The vacancies due to the stress gradient migrate outward towards the grain surface, leading to an accumulation of point defects at the surface. These point defect then would combine to give Cs metal clusters.

As a starting point of discussion, in eqn(2) let us assume the activation energy of all the three cesium halides to be comparable. We would find the diffusion coefficient to be proportional to

$$D_{\text{halide}} \propto \nu d^2$$

The hoping frequency, ‘$\nu$’, or the rate at which halide atoms would migrate to give vacancy’s diffusion, would depend on the halide atom’s inertia or mass. The heavier the atom would have lower frequency of hoping. Hence, ‘$\nu$’ would be inversely proportional to the halide atoms mass.

Also, ‘$d$’, the hoping distance would be directly proportional to the lattice constant. A plot between the lattice constant and halide atomic mass shows a linear relationship (fig 6). This is expected since, heavier atoms mean larger radius and in turn larger lattice dimensions. The atom’s migration for filling vacancy (hence give illusion of vacancy migration) would be discouraged with increasing distance. Hence, ‘$d$’ should show an inverse proportionality with mass, however, it should be noted here that the lattice size increases more rapidly than the radius of the halide atom as we move from CsCl to CsI. This would mean that it would be easier for the iodine atom to move from one unit cell to another as compared to chlorine atom in its lattice. Hence, taking these into account, ‘$d$’ is independent of halide atom’s mass ($d \propto \frac{1}{m} \times m = \text{constant}$). Hence, the diffusion coefficient (eqn 2) is inversely proportional to the concerned halide atom’s mass.
From the listings in Table 2 it is clear $D_{\text{Cl}} > D_{\text{Br}} > D_{\text{I}}$. This would imply that the cesium shell formation would be fastest in CsCl, followed by CsBr and finally CsI.

**Formation of Nano-rods: Surface Diffusion/ Necking**

As the grooving is taking place and the large grains are separating into two daughter grains, surface diffusion of cesium metal also takes place with the volume diffusion of defects. This surface diffusion takes place towards sites of faceteds on the grain boundary. This assists in accumulation of Cesium that pushes the daughter grains apart and formation of a bridge of Cesium between the two grains (see fig 7). As the distances between the two grains increases this bridge is elongated.

Transmission Electron micrograph of fig 8, shows the bridges/ nano-rod formations between two evolving “daughter grains” of Cesium Bromide. These bridges are called “necks”, marking the region of constricted areas joining two grains. As stated, necking is usually formed at sites of faceted grain boundaries. With a core-shell structure in all three halides, formation in necking
is expected. The necks are marked by difference in curvature. While the grain surfaces are convex in nature, necks have concave surface. Matter flows from the grain surface to region of maximum variation of curvature, i.e. towards the neck. That is, the neck growth and elongation results due to surface diffusion. Surface diffusion is different from volume diffusion (defects migrating towards the surface). Since our grains have Cesium shells, surface diffusion essentially ends up carrying Cesium towards the neck. Hence, the bridges formed are made up of Cesium which on breaking free from the daughter-grains gives the nano-rods which contribute to the Surface Plasmon Resonance seen in the UV-visible absorption pattern.

Another important observation we reported was the ageing of our samples. That is, the optical properties of the films were found to change with time. The absorption peaks not only red-shifted but also their intensities diminished with time. Also, we observed that the rate of ageing was sensitive to the ambient atmosphere in which the samples were maintained, with ageing being more rapid in samples kept out of the dessicator. Our Gan’s model calculations explained the red-shift due to the nanorods going smaller with lower aspect ratio. We believe the Cesium nanorods and free Cesium on the grain surfaces are eroded by the reaction

\[ 2Cs + 2H_2O = 2CsOH + H_2 \]

K. Arima et. al. have observed that this reaction proceeds slowly for atmospheric relative humidity (RH) less than 30% and increases with RH. Also, there is a near exponential increase
in the rate of reaction for RH above 80%. K. Arima et. al.\textsuperscript{20} works would explain difference in ageing observed by us in the samples maintained in the dessicator and those left in open. Also, Antonelli et. al.\textsuperscript{21} have shown that vacancy generation increases under the high hydrostatic pressure (compressive). Hence, metal Cs formation is encouraged in dessicator with slower $\text{Cs} + \text{H}_2\text{O}$ reaction rate. While this reaction involves only Cesium, we do observe a difference in ageing rate depending on which halide is in bonding with Cesium. This is due to fact that ageing depends on (i) what rate Cesium clusters are formed at the surface (volume diffusion which is inversely dependent on halide mass) and (ii) thicker shell leading to faster grooving (surface diffusion due to lattice mismatch).

Comparing the ageing rate of 600 nm thin films of CsCl, CsBr and CsI, we found the rate of
ageing in the following order, $\text{CsCl} > \text{CsBr}$ and no ageing in CsI. The fastest ageing was seen in CsCl since color centers moved towards the surface faster with volume diffusion rate being inversely proportional to the halide atom’s mass. With lattice mismatch being low, grooving was slower and formation of nano-rods retarded. While in the case of CsI, formation of Cesium shell would be slower, but grooving faster. The thinner Cesium shells would not enable formation of large nanorods, giving impression of no ageing in CsI.

**Conclusion**

To summerize, thermal evaporated films of the three halides result in polycrystalline films with large grains and sharp grain boundaries. The grain boundaries become sites of grooving with mass of material being pulled away from the grain boundary to give spherical grains. Along with this, vacancies in the form of color centers in the cesium halide lattices move towards the grain surface. The rate at which this volume diffusion occurs depends on halide atom’s mass (its faster in CsCl than CsBr or CsI). At the surface, these color centers accumulate, forming metal clusters and giving rise to a core-shell structure. Depending on the type of lattice mismatch in the core-shell structure two alternative paths of sequencing occurs. While the screw dislocation leads to necking, the mismatch in lattice size leads to an accelerated grooving. Grooving is faster in CsI than CsCl and CsBr. Accelerated grooving leads to smaller grains. Smaller grains encourage reaction with water vapor, thus reducing the shell size. Making it difficult to sustain the necking. The necks break off faster. Ageing observed in our samples is essentially due to the nanorods of Cesium and in decreasing aspect ratio. The decreasing aspect ratio, with time and inturn successive grain division would be due to the smaller grain size. Smaller grain size would inturn imply thinner shells and lesser amount of Cesium. This in turn would not allow for growth of longer nanorods. Since CsI have a large mismatch in their core-shell lattices, grooving is faster and shell is thinner compared to CsCl and CsBr. Hence the nano-rods formed are of smaller length. This makes it difficult to obtain SPR peaks shifting throughout the full visible range with ageing in CsI.
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