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Orthogonal fractal growth of CsI domains forming a ladder-like structure

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ABSTRACT

A unique structure of a thin layer consisting of cesium iodine, manifested by a “ladder-like” fractal structure formed by spin-coating is reported herein. The ladder-like structure is made of mm-size domains, each comprising of a highly correlated, perpendicularly interconnected, network of CsI lines. Each line served as the growth origin of 2–3 levels of short, perpendicularly-oriented CsI crystals, yielding a fractal dimension of 1.53.

The observed structure differs from common Diffusion Limited Aggregation (DLA) shapes by the absence of any morphological indicators that may point on the origin of growth. Furthermore, the perfect orthogonal alignment of all junctions in the CsI structure is very rare in DLA type of growth.

A formation mechanism is presented, based on studying the evolution of this structure at different spinning rates and on a variety of substrates. It is proposed that this unique structure originates from a rare combination of conditions: strong anisotropy in surface energy between different facets arising from the primitive ionic crystal of CsI, the strong water-breaking property of cesium ions and an unusual effect of mesoporous substrates in preventing premature nucleation.

1. Introduction

Low cost renewable energy sources are needed to avert the risk of global climate changes [1]. There is no doubt that reliable and efficient Photovoltaic (PV) cells will be part of the solution. In recent years a new promising type of PV cell has emerged, with an active layer consisting of organo-metal trihalide perovskite. In particular, the methylammonium lead halide is being investigated intensely [2–4] achieving an efficiency as high as 20% [5].The pre-perovskite film can be deposited by a Chemical Solution Deposition reaction process; the product then undergoes a phase transformation to the cubic perovskite structure by a mild heat treatment (below 140 °C). Spin coating is a suitable deposition method, providing a high quality active layer. A major weakness of the methylammonium lead halide cells is their challenged stability, coupled with the toxicity of lead. Cesium- and bismuth-based perovskites, such as $Cs_3Bi_2I_9$, may serve as good candidates for replacing lead in this type of PV cells, [6] however their current performance status is far from being satisfactory [7].

One way to obtain cesium-based organo-halide perovskites involves the preparation of homogeneous thin film of cesium iodide serving as a precursor to be further doped, en route for perovskite PV cell preparation. During preparation of these films by spin coating, a unique structure of CsI was observed. While this structure shares some common features with previously reported dendritic structures grown by Diffusion Limited Aggregation (DLA), it is unique by the absence of a noticeable growth origin and by a stunning, perfectly orthogonal growth pattern.

Dendritic self-similar shapes are quite common in nature. From the technological point of view, their appearance may be advantageous in certain cases, or deleterious in others [8,9]. Whether advantageous or deleterious, these shapes easily attract the interest of the scientific and technological community. Indeed, the introduction of DLA models more than thirty years ago by Witten and Sander [10] has stimulated a large interest in the study of nucleation and growth processes on surfaces. In the “classical” DLA model clusters are grown from a seed particle (the origin). Individual particles are launched at some random distance from the origin and “walk” randomly until they stick to the growing cluster, forming a fractal structure, growing outward from an inner location of the origin and having a typical fractal dimension of 1.7 [11].

Thus far, scarce attention was given to the effect of the substrate on the DLA growth above it. One possible effect is the induction of epitaxial growth as observed in the two dimensional formation of cubic-structured silicon nanosheets growing along the ⟨110⟩ direction [12]. Another report describes the growth of silver islands on silica, where a 2D fractal structure was formed on thermal oxide, while on a native oxide substrate non-fractal, faceted, crystallites were formed under the same conditions [13]. Here, the effect of the substrate was explained in terms of the thinner oxide layer of the native oxide, which did not block

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the tunneling of electrons to the silver ions, thus facilitating its fast reduction and non-fractal deposition pattern.

One of the more relevant works to this report describes the growth of poly-ethylene oxide (PEO) on the surfaces of various alkyl halides [14]. There, Dendrites having right angle branches were formed along the ⟨100⟩ set of directions in NaCl. In contrast, the dendrites formed on KCl and KBr revealed the classical tree-like branching. A fractal dimension of 1.6 was found for PEO on NaCl, whereas the fractal dimension for PEO on KCl and KBr was 1.7 and 1.8, respectively.

2. Experimental

2.1. Materials and methods

Thin films of cesium iodide were grown on a thin layer (450 nm) of mesoporous titanium dioxide. The mesoporous TiO_2 layers were grown on 85 nm dense TiO_2 layers deposited on commercial 25 mm × 25 mm FTO-coated glass slides (Dysol, Australia). Prior to deposition of the dense TiO_2 layers, the FTO-coated glass electrodes were cleaned by sonication in de-ionized water, isopropanol (Gadot, Israel) and acetone (Gadot, Israel) for 30 min for each solvent. Then, 0.05 ml 0.15 M titanium diisopropoxide bis(acetylacetonate) in 1-butanol solution (75 wt % in isopropanol, Aldrich) were spread on the clean slides and spun (Polos, SPS ltd.) at 2000 RPM for 30 s. Subsequently, the samples were placed on a preheated hot plate to 125 °C for 5 min. and finally cooled to room temperature. This procedure was repeated twice, using a higher concentration (0.3 M) of titanium diisopropoxide bis(acetylacetonate). The samples were then heated in air at 2 °C/min to 450 °C and sintered for 30 min, yielding dense TiO_2 films of 85 nm in thickness on the FTO substrates.

The mesoporous TiO_2 layers were then grown on the dense TiO_2 layers. Here, 0.1 ml of a coating suspension made by diluting a commercially available paste (18NR-T, Dyesol, Australia) in ethanol (2:7 by weight) was spun for 30 s at 1500 PPM. The samples were calcined in air (450 °C for 30 min, ramp rate 2 °C/min), yielding a mesoporous layer, 450 nm in thickness, above the dense TiO_2 layer.

Deposition of the CsI layer was as follows: 0.256 g of CsI was dissolved in 1 ml of water. A volume of 0.1 ml of this solution was spread over the mesoporous TiO_2 substrates and spun under controlled humidity at various rates (375 RPM - 1500 RPM) for 90 s. The coated substrates were then dried for 5 min. in air on a hot plate held at 100 °C.

For comparison, CsI layers were grown also on three other types of substrates: (1) nonporous soda lime glass; (2) mesoporous Indium-doped zinc oxide (IZO), 450 nm in thickness, prepared as described elsewhere [15]; (3) mesoporous silica, obtained by spin coating (0.2 ml. 2000 RPM, 1 min) a commercial suspension of silica nanoparticles (Levasil, Akzonobel Ltd), following by sintering in air at 450 °C for 30 min.

2.2. Characterization

The morphology of the CsI-coated substrates was imaged using SEM (Zeiss Ultra-Plus FEG-SEM) with acceleration voltage of 4 kV. Film thickness was measured by profilometery (Dektak, Bruker). In-situ photography, taken during the formation of the CsI layers, was performed by a DSLR camera (D810, Nikon, Japan) at a shutter speed of 0.125–0.25 msec. The camera was mounted above the spin coater chuck.

Phase compositions of the CsI samples were investigated by XRD (MiniFlex X-Ray Diffractometer, Rikagu, USA). Measurements were performed at RT, in a 2Θ range of 20°-70° under scanning speed of 3°/min.

3. Results

Fig. 1 presents the SEM images of thin layers of CsI on mesoporous TiO_2, deposited by spin coating at various angular velocities (500, 750, 1250 RPM). An unusual structure is recognized: three scales of fractal-like oriented growth, characterized by the formation of long parallel lines of CsI on the mesoporous surface (termed hereby as level 1 lines), interconnected by perpendicular lines forming a ladder-like structure. Shorter lines of CsI (termed hereby as level 2 lines) emerge at right angles relative to the level 1 skeleton. The parallelism between the main needles is striking, so is the constant distance between the needles at all levels. In most cases, narrow "necks" are observed at the points

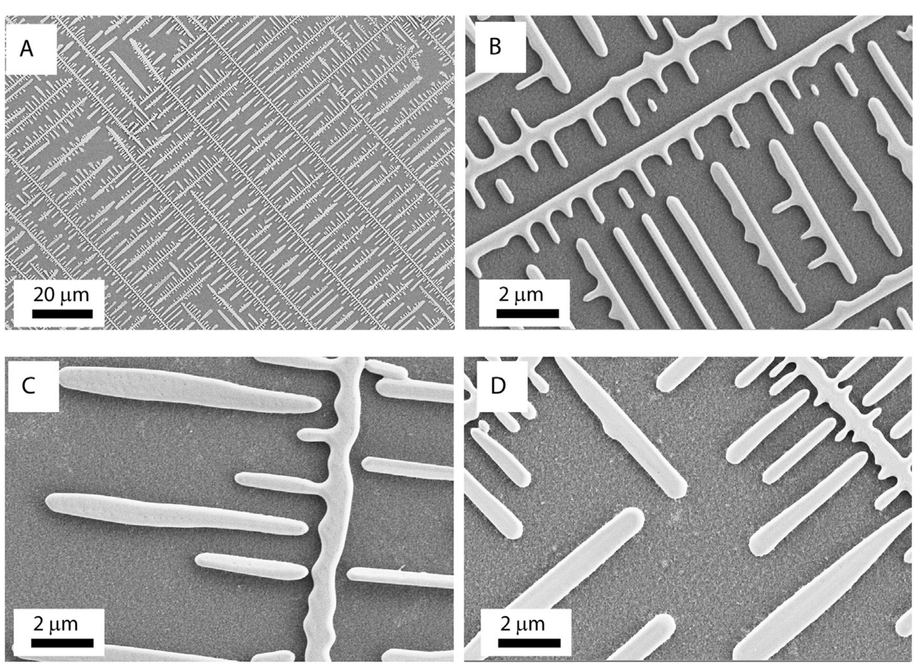

Fig. 1. SEM images of CsI ladder-like structure, deposited by spin coating. (A): low magnification (×500) grown at 1250 RPM. (B–D) high magnification images of structures grown at 500 RPM (B), 750 RPM (C) and 1250 RPM (D).