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Fabrication of Diisopropylammonium Bromide Aligned Microcrystals with In-Plane Uniaxial Polarization

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Abstract

Textured arrays of ferroelectric microcrystals of diisopropylammonium bromide were grown from solution at room temperature onto silicon substrates and studied by means of x-ray diffraction, atomic force microscopy, electron microscopy, and piezoresponse force microscopy. The needle-shaped crystals had dimensions of approximately $50\ \mu\text{m} \times 5\ \mu\text{m}$ in the plane and were approximately 200 nm thick, where the dimensions and arrangement were influenced by growth conditions. The observations suggest an Ostwald ripening mechanism of the microcrystal growth. The crystals had the structure of the ferroelectric phase, where the polarization axis was in-plane and parallel to the long axis of the crystals. The in-plane polarization could be switched at will with a scanning probe tip bias of 15 V and could be arranged in stable domain patterns with both charged and uncharged 180° domain walls.

Keywords: ferroelectricity, molecular electronics, self-assembly, crystalline film, piezo force microscopy

1. Introduction

Molecular crystals consist of low molecular weight chemical species that are related by a unique symmetry repeating itself periodically in 3D space. Molecular crystals have been widely studied due to their intrinsic scientific interest and for their practical use in a wide range of fields, such as non-linear optics [1], pigments and dyes [2], pharmaceutical drug delivery [3], liquid crystals [4], photovoltaics [5], and semiconductors [6]. Ferroelectric materials are a unique class of electroactive materials possessing spontaneous polarization that can be reversibly switched between two stable opposing polarization states by the application of an applied electric field [7] or external mechanical stimuli [8, 9]. Ferroelectricity is only possible in polar crystal structures, which account for 10 of the 32 crystallographic point groups [10], and therefore it can be challenging to engineer new ferroelectric materials with both the correct symmetry and useful properties [11]. Nevertheless, in recent years there has been an increased interest in developing organic alternatives to the inorganic ferroelectric systems [12–14]. Typical inorganic ferroelectrics are oxides [15, 16] belonging to the ABO_3 perovskite family, such as barium titanate (BTO), lead titanate and compound oxides such as lead zirconium titanate (PZT). The major drawbacks typically associated with inorganic ferroelectrics [17] are the use of toxic and heavy metals, costly high-vacuum fabrication methods, and high-temperature processing [18]. Another class of useful ferroelectrics is polymers [19], most notably those based on vinylidene fluoride (VDF) [20, 21]. Copolymers of VDF with trifluoroethylene (TrFE), P(VDF-TrFE), for example, have become the ferroelectric polymer of choice for applications, due in part to the variety of ways they can be prepared in bulk using inexpensive solution-processing methods [22] and can be formed into high-performance thin films and nanostructures [21, 23–27]. The ferroelectric polymers, however, have not proven particularly amenable to synthetic modification for optimizing ferroelectric properties in the way the ferroelectric oxides have [28]. Polymers are also limited to polymorphous sample structures, and are therefore limited in terms of performance, due to the difficulty in obtaining long-range crystalline order [29, 30]. Molecular ferroelectrics, on the other hand, readily grow into large single crystals and afford greater synthetic flexibility than polymers, while avoiding many of the difficulties presented by oxides. For these and other reasons, there has been renewed interest in the development of new high-performance molecular ferroelectrics [12–14, 31–35]. Some of the key properties of useful ferroelectrics are high spontaneous polarization, a transition temperature well above room temperature, and a low coercive field [7]. For example, while both BTO and P(VDF-TrFE) maintain stable ferroelectricity up to approximately 130°C, BTO has a higher spontaneous polarization, 26 $\mu\text{C cm}^{-2}$ versus 8 $\mu\text{C cm}^{-2}$, and a lower coercive field, 10 kV cm^{-1} versus 500 kV cm^{-1} [7, 21]. Recently, Fu *et al* reported the synthesis and ferroelectric properties of solution-processed organic ferroelectric crystals known as diisopropylammonium chloride (DIPAC) [33] and diisopropylammonium bromide (DIPAB) [34], with a remarkably lower coercive field and high polarization, comparable to that of conventional inorganic ferroelectrics such as BTO. In

the case of DIPAC, the spontaneous polarization is $8.9 \mu\text{C cm}^{-2}$ and the coercive field is 9 kV cm^{-1} , while for DIPAB the spontaneous polarization is $23 \mu\text{C cm}^{-2}$ with a coercive field of 5 kV cm^{-1} , approximately the same as BTO. In addition, the ferroelectric state of these new molecular ferroelectrics is highly stable at room temperature, because the ferroelectric to paraelectric (Curie) transition temperatures are even higher than BTO, 153°C and 163°C for DIPAB and DIPAC, respectively. Further synthetic modification may result in improved or tailored properties. Therefore, the DIPA-based molecular ferroelectrics are promising alternatives to oxide ferroelectrics for use in, e.g., organic electronics technologies.

Molecular ferroelectrics are generally grown in the bulk by hydrothermal crystallization, efficiently producing high-quality single crystals measuring many centimeters in size [34], which is useful for a number of key applications, such as nonlinear optics [36]. To play a role in organic electronics, however, it is necessary to fabricate high-quality crystals in thin film form or as readily integrated micro- and nanocrystals. Here we report successful fabrication of microcrystalline films of DIPAB by a solution-processing method, producing arrays of microcrystals that show some aspects of self-assembly. The films are highly textured, as determined by x-ray diffraction (XRD), with a uniform (0 0 1) orientation perpendicular to the substrate and the polar (0 1 0) axis lying in the plane of the substrate. The crystals have a strong inplane piezoelectric response and a weak or no out-of-plane response, and are amenable to domain manipulation, confirming the orientational scheme determined from XRD. The elemental analysis of select crystals using energy dispersive spectroscopy (EDAX) confirms the expected high bromine content.

2. Experimental methods

The substrates were prepared from highly doped *n*-type silicon (resistivity = $0.002 \Omega \text{ cm}$), with a (1 1 0) crystal cut purchased from University Wafer, and then coated with a 20 nm thick film of platinum by DC sputtering at an argon pressure of 2 mTorr and a deposition rate of $1 \text{ \AA s}^{-1}$. The DIPAB salt was formed in a 20 ml capacity test tube by the addition of hydrobromic acid added drop-wise at a rate of 2 drops/min to diisopropylamine in equimolar ratios at room temperature. All the chemicals were reagent grade, purchased from Sigma-Aldrich, and used as obtained. The exothermic chemical reaction produced a white salt of DIPAB.

Two methods were used to produce arrays of oriented microcrystals on the substrates. In the first method, similar to growth from solution [37], the DIPAB salt was dissolved in deionized water at 40°C for 30 min to form a supersaturated solution. The supersaturated solution and 1" by 1" platinum-coated silicon substrates were placed in a vertical-slot staining jar (Ted Pella, Inc.), cooled to 2°C and held at that temperature. The substrates were removed from the solution at increasing time intervals from 2 min to 6 h and allowed to dry in air room temperature. The size distribution, coverage, and thickness of the microcrystal array tended to increase with increased growth time. The substrate surface energies play a crucial role in the formation of these microcrystals by providing nucleation centers for the crystal growth.

In the second method, a spin coater was used to produce arrays of microcrystals on the substrate at room temperature. The salts of DIPAB were dissolved in methanol to a concentration of 10% by weight. Platinized silicon substrates measuring 1" by 1" were used for this process. The substrates were centered on the vacuum chuck of the spinner and approximately 50 μl of the solution was dripped onto the center by a digital micropipette. The substrate with solution was then spun at a constant speed of 2000 rotations per minute for 40 s to evenly disperse the solution. On evaporation the methanol solvent left behind many DIPAB crystals.

The optical images of the samples were captured using an Olympus microscope model BX51. The topographical images for individual microcrystals were recorded using a commercial atomic force microscope (AFM; Bruker Dimension Icon) equipped with ScanAsyst. The tips used for imaging were silicon tips on silicon nitride cantilevers with a spring constant of 0.4 N m⁻¹ and a resonant frequency of 70 kHz. The scanning electron microscope (SEM) images of individual microcrystals and the elemental analysis were performed using the Nova NanoSEM Model 450 (FEI Inc.) equipped with an Oxford AZtec Energy Microanalysis System with an X-Max 80 silicon drift detector. A PANalytical Empyrean Diffractometer with a source of copper K α radiation was used for the $\theta - 2\theta$ XRD measurement. The pole figure measurements were performed with a Rigaku SmartLab diffractometer.

Piezoresponse force microscopy (PFM) imaging of the ferroelectric domain structures in the DIPAB microcrystals was carried out using a commercial AFM system (MFP-3D, Asylum Research). Conductive Pt-coated silicon probes (CSC37/Pt, Mikromasch) were used for domain imaging and polarization switching. The resonant-enhanced PFM mode [38, 39] was used to obtain the signal, with a typical AC voltage frequency of approximately 350 kHz and an AC amplitude of 0.5–1.0 V.

3. Results and discussion

3.1. Topographical characteristics

Optical images of the DIPAB microcrystals grown by self-assembly from the supersaturated solution for various durations and by the spin coating method are shown in figure 1. The representative morphology for samples grown for 2 min, 30 min, and 6 h are shown in figures 1(a)–(c), respectively, while figure 1(d) is a representative image for the spin-coated samples. The width and length distributions as well the surface overage of the microcrystals grown under different conditions were calculated with the public domain ImageJ software and are summarized in table 1.

Figure 1. Optical images of DIPAB microcrystals: fabricated by vertical deposition for (a) 2 min, (b) 30 min, and (c) 6 h; and (d) fabricated by spin coating. The scale bar is 20 μm in all panels.

Table 1. The mean effective length and width, and the thickness range of the microcrystals fabricated under different conditions calculated from a log normal distribution

Sample	Mean effective length (μm)	Mean effective width (μm)	Thickness (nm)	Surface coverage (%)
Spin-coating	22.72 ± 1.23	4.84 ± 0.15	30–200	42
Dip-coat 2 min	7.54 ± 0.23	4.17 ± 0.12	200–400	45
Dip-coat 30 min	25.54 ± 0.95	3.59 ± 0.11	400–700	32
Dip-coat 6 h	54.49 ± 5.04	4.6 ± 0.22	1000–1500	26

The typical morphology for all the growth conditions is that of needle-shaped elongated microcrystals arranged with a common orientation over large areas. It is evident that the growth conditions greatly influence the width and height distributions of the microcrystals. The crystallization starts with the formation of microcrystals within the first two minutes (figure 1(a)), followed by the growth of a dominating microcrystal with increased length along the “needle-direction” at the expense of smaller ones as the time of exposure to the supersaturated solution is increased (figures 1(b) and (c)). In the self-assembly from the supersaturated solution, the low temperature helps avoid free crystallization in the supersaturated aqueous solution of DIPAB and promotes crystal nucleation onto the sample substrate. The length and width of the microcrystals grown for various times are estimated by fitting with a normal distribution curve (see supplementary figure S1). Once the crystal nucleation starts, the duration for which the substrates stay in the solution controls

the effective length of the microcrystals, while the effective width does not significantly increase (see supplementary figure S2) [40]. This analysis is statistical in nature and we did find isolated microcrystals wider than the average fitted width, but these were fewer in number. These observations suggest that the Ostwald ripening mechanism may be responsible for the microcrystal growth [41, 42]. The arrows in figures 1(a)–(c) represent the direction in which the samples were suspended in the vertical slots, which also coincided with the direction of the gravitational force. Since the solution slowly evaporates from the surface, there is a natural concentration gradient; higher concentration near the surface opening and lower concentration near the base of the vertical slots. The Ostwald ripening coupled with the solution concentration gradient and the directional nature of the gravitational force may play a crucial role in the alignment of the microcrystals and subsequent growth along the “needle direction.” This, however, needs further detailed study.

The spin-coated samples involve the wetting of DIPAB in methanol solvent on the substrate when it is first dropped on the stationary substrate. Once the rotation begins, the solution is in a metastable state due to the volatile solvent undergoing spontaneous dewetting and subsequent crystallization, resulting in the formation of arrays of well-aligned microcrystals radiating out from the sample center. It is evident from the optical morphology that the process of crystal growth is similar in both approaches, resulting in large-area coverage of the substrate surface with DIPAB microcrystals aligned along the radial direction, as indicated by the arrow in figure 1(b).

Representative crystals from each of the samples were imaged using a scanning probe microscope (SPM). The general morphology of the crystals grown by self-assembly from the supersaturated solution for different substrate exposure times are shown in figures 2(a)–(c). The thickness variations in the microcrystals grown from solution are 200 nm to 1000 nm, as shown in the line-section profile recorded along the red lines in the images. The longer growth time produces longer and thicker crystals. Figure 2(d) represents the SPM topography and a line-section profile of a spin-coated microcrystal with a thickness of approximately 30 nm. The typical thickness variation in the spin-coated samples is between 30 nm to 200 nm, with thicker crystals near the center and thinner ones at the edges along the radial direction of the spin-coating process. The dark regions in all the AFM images show the exposed Pt/Si substrate surface. The microcrystals grown by both these methods have a uniform thickness with sharply defined edges, as seen from both the optical and scanning probe microscopy.

Figure 2. AFM topography (left) and height profile (right) showing height variations in microcrystals grown from solution for (a) 2 min, (b) 30 min, and (c) 6 h. (d) AFM topography for a crystal from a spin-coated sample. (The red cross and line in each panel indicate the initial point and path of the height profile.)

3.2. Structure determination: XRD

The crystal structure of the ferroelectric form of DIPAB belongs to the monoclinic crystal system with a $P2_1$ space group having the following lattice constants: $a = 7.85 \text{ \AA}$, $b = 8.09 \text{ \AA}$, $c = 7.89 \text{ \AA}$, and an a - c angle of $\beta = 116.2^\circ$ [34]. The out-of-plane $\theta - 2\theta$ XRD measurements were carried out on microcrystal samples grown by supersaturated solution self-assembly as well as spin coating, as shown in figure 3(a). The XRD data show that the microcrystal growth favors the ferroelectric phase of DIPAB, being highly textured with the $\langle 001 \rangle$ reflections dominating the out-of-plane $\theta - 2\theta$ results, as shown in figure 3(a). The peak at $2\theta = 40^\circ$ corresponds to the Pt $\langle 111 \rangle$ diffraction peak. The microcrystals grown by both

methods yield similar diffraction patterns and thus the crystallographic c -axis is concluded to be in the out-of-plane direction. In the single crystal work by Fu *et al*, it was observed that the polar axis for DIPAB is along the crystallographic b -axis and therefore the polarization of the microcrystalline films grown by the two processes will presumably have polarization predominantly in the plane parallel to the substrate. This indicates that the microcrystal growth process is similar in both approaches, favoring alignment of the polar b -axis along the long morphological “needle” direction.

Figure 3. (a) $\theta - 2\theta$ XRD peaks for the microcrystal films for different growth conditions. Pole figure representation showing the distribution of crystal orientation (b) $\langle 001 \rangle$ and (c) orientation $\langle 010 \rangle$, which correspond to the directions of the c and b axes, respectively. The scale bar represents the intensity.

In order to obtain a complete picture of the orientation distribution of both crystallographic b - and c -axes, pole figure measurements on the spin-coated samples are carried out using a Rigaku SmartLab Diffractometer. The pole figure analysis is an important tool to determine the spatial arrangement of the crystallographic planes in textured samples.

Figure 3(b) depicts the distribution of the $\langle 001 \rangle$ crystallographic axes in a hemisphere. As was evident in the $\theta - 2\theta$ scan, the predominant distribution of the $\langle 001 \rangle$ pole is normal to the surface normal. The pole figure maps also show that the intensity is highest along the surface normal, spreading out from the surface normal, and is distributed mostly within 30° with respect to the surface normal. The continuous spread of intensity and the several sharp spots off the normal are an indication of several microcrystals in the film growing with their c -axis slightly off from the surface normal.

On the other hand, the $\langle 010 \rangle$ pole distribution shown in figure 3(c) clearly demonstrates that the b -axes of the crystals are distributed predominantly within the plane of the film. Interestingly, the distribution is discontinuous in the film plane and extends up to approximately 15° out of the film plane. In concurrence with the findings from figure 3(a), this pole plot also suggests that several microcrystals have grown with the b -axis approximately

randomly distributed in the plane. This observation is also supported by the optical microscopy images shown in figure 1, where few microcrystals seem randomly aligned and not along the general “needle” direction.

3.3. SEM and element analysis

The microcrystals of DIPAB were coated with a 5 nm thick layer of conductive carbon to prevent charge build-up on the sample surface. The imaging and elemental analysis were carried out at an electron gun bias of 20 kV. Figure 4(a) shows an SEM image of the end of one representative microcrystal from the spin-coated sample. To the right of this image is a map of the bromine distribution, which was determined from the EDAX intensity distribution, for the area marked by the red box on the left. The bromine map has a bright region clearly corresponding to the location of the crystal as observed in the SEM image. A more quantitative picture of the bromine distribution was obtained by plotting the EDAX signal along a line across another microcrystal as shown in figure 4(b), where the x-ray fluorescence count rate for the bromine element along the dotted red line is plotted in the inset. The bromine count along the crystal cross-section is significantly greater than the background Pt/Si substrate.

Figure 4. EDAX fluorescence map of a DIPAB microcrystal fabricated by spin coating. (a) SEM image alongside its bromine EDAX map and (b) an SEM image with a red line indicating the path of the bromine EDAX profile shown in the inset.

Cross-sectional SEM imaging was also carried out on the spin-coated samples. The platinumized silicon wafer was pre-cleaved by scratching a line on the backside of the substrate. Once the microcrystals were spin-coated on the substrate, the substrate was broken along the pre-cleaved line by gently tapping it on the sides. The conductive carbon coating is not deposited for cross-sectional SEM as the imaging is performed at only 3 kV electron gun bias. The cross-sectional SEM image in figure 5 clearly shows the Si/Native SiO₂ layer, the platinum layer, and the microcrystal cross-section.

Figure 5. Cross-sectional SEM image of a spin-coated DIPAB microcrystal on a platinumized silicon wafer.

3.4. PFM analysis of as-grown domain structures

Three-dimensional PFM imaging [43, 44] of the DIPAB microcrystals fabricated from solution shows that the polarization axis is predominantly in the plane parallel to the substrate, which is consistent with the XRD results that show that the *b*-axis, which is also the polar axis, lies in the plane of the film. Figures 6(a)–(f) show a combination of the *y*-axis and *x*-axis lateral PFM (LPFM) (figures 6(a)–(d)), and vertical PFM (VPFM) (figures 6(e) and (f)) in the same area on a microcrystal. The results show that there is strong PFM signal only in the *y*-LPFM imaging (figure 7(a)) with polarization orientation in the *y*-axis relative to the image, and the as-grown polarization state develops into anti-parallel polarized strip domains along the needle long axis. There is only a very weak PFM signal in the *x*-LPFM (figure 7(c)) or VPFM imaging (figure 7(e)), which is likely due to topographical cross-talk [45]. Given that it is a uniaxial system, we conclude that the polarization axis is in the plane, parallel to the strip domains.

Figure 6. Three-dimensional PFM imaging on a DIPAB microcrystal grown from solution. y -axis LPFM amplitude (a) and phase (b) images of the as-grown strip domain structures. Areas corresponding to the dark color in the phase image polarize upward and light-colored areas polarize downward. x -axis LPFM amplitude (c) and phase (d) images in the same area. VPFM amplitude (e) and phase (f) images in the same area.

Figure 7. (a) The topography of a DIPAB microcrystal fabricated by spin-coating. The initial phase (b) shows stripe domains while the application of sequential ± 15 V biases creates charged domain walls (c).

The switchability of the stripe domains was checked by the application of external fields using the PFM tip. Figure 7(a) shows the topography of a representative microcrystal from the spin-coated samples with a thickness of approximately 200 nm. The initial PFM phase image for the as-grown DIPAB microcrystal shows striped domains (figure 7(b)) along the long axis of the crystal separated by uncharged 180° domain walls running parallel to the polarization axis. The PFM tip was then used to apply a $+15$ V DC bias along the green lines shown in figure 7(c) and a $+15$ V DC bias along the red lines on the same microcrystal. The application of the positive voltage created head-to-head 180° charged domain walls, while the negative voltage application creates tail-to-tail 180° charged domain walls, as

shown in figure 7(c). The stability of the charged and uncharged domain walls and the polarization switching dynamics of DIPAB microcrystals have been reported previously [46].

The ability to write stable domain patterns in the DIPAB microcrystals (figure 7) can be exploited for multi-array individually addressable ferroelectric memory devices with novel device geometries [47, 48]. Such independent mesoscopic structures have been fabricated by nano-imprint lithography [25] or by high-temperature annealing of ultra-thin films of the VDF-based copolymer [49]. Most ferroelectric nanocapacitors or thin films have a strong out-of-plane polarization which requires cross-bar metal electrodes for electric field applications [50]. The ferroelectric domain manipulation in such devices is often compromised by electrostatic cross-talk between neighboring structures [51] and unavoidable stray electric fields created at the sharp electrode edges [52, 53]. For the case of the in-plane polarization geometry, memory devices can be constructed with just one or an array of electrodes, either at the top or bottom, for lateral electric field applications, and the memory states could be read by PFM, thus significantly reducing data loss due to electrical interference. Another important observation is that for thinner films with out-of-plane polarization the incomplete screening of charges on the surface leads to unstable ferroelectric domains [54]. In the case of in-plane uniaxially polarized systems, there is no restriction on the lateral dimensions and the device could have any length along the polar direction.

The ability to fabricate molecular ferroelectric films with in-plane polarization is a unique opportunity to study the nature of domain nucleation and growth in greater detail. The Kolmogorov-Avrami-Ishibashi [55–57] model predicts a two-fold way of polarization reversal—initial lateral domain wall motion followed by the forward growth of the domains. Only the lateral domain wall motion has been observed by conventional PFM [58] while transmission electron microscopy (TEM) has been used to observe both lateral and forward growth (cross-sectional TEM) in epitaxial ABO_3 type ferroelectrics [59]. TEM usually involves highly energetic electron beams, which organic samples cannot withstand. Thus, this geometry of DIPAB microcrystals can be employed to investigate the forward growth of domains in organic ferroelectrics using PFM. It should be noted that in epitaxial thin films of perovskite materials such as PZT [60], the spontaneous polarization can be tilted from out-of-plane to in-plane by changing the misfit strain between the material and the epitaxial interface, but this leads to a completely new crystal space group symmetry and in addition involves the tedious process of finding lattice matched substrates, a high vacuum for molecular beam epitaxial growth, and high temperatures.

4. Conclusions

In summary, fabrication methods for thin microcrystalline films of DIPAB have been developed based on an inexpensive solution-processing method yielding large area coverage of the substrates with highly unidirectional polarized domains in the plane of the film. It is also demonstrated that by employing different fabrication methods we can control the film thickness and make films tens of nanometers thick, which allows electrical characterization of these samples for low enough voltages. The polarization direction conforms to the crystal symmetry of the ferroelectric phase of the DIPAB system as supported by x-ray

characterization and PFM studies. The switchability of the lateral domains at low applied voltages in DIPAB can be exploited in hysteretic memory devices. Future work involves selective nucleation of the crystal growth on pre-patterned inter-digital electrodes for more control, which is independently addressable to be used in non-volatile memory read/write devices.

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Author contribution – The manuscript was written by SP and SD. The microcrystal growth, and optical and SPM characterization were performed by SP. X-ray characterization was carried out by SP, OG, and VS. PFM characterization was performed by HL and AG. SEM measurements were performed by SP and JS.

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Supporting Information

Fabrication of diisopropylammonium bromide aligned microcrystals with in-plane uniaxial polarization

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Size Distribution of microcrystals of DIPAB self-assembled on Pt/Si substrate by vertical deposition.

The Pt coated silicon substrates were immersed in the slotted jar containing supersaturated solution of DIPAB at a temperature of 2 °C. The method is described in details in the main article. The substrates are then removed from the solution at the following time intervals: 2 min, 10 min, 30 min, 90 min, and 360 min. The length and the width distribution for each of the deposition time interval are plotted in a histogram which when fitted with a normal distribution gives the effective length and width of the microcrystals for each of the cases. Fig. S1 shows the optical image of the area used for counting as well as the histogram of the length and the width counts.

Figure S1: The optical image of the area used for particle counting for different deposition times by vertical self-assembly. Scale bar shown at the bottom.

The mean effective length and width of the microcrystalline samples for various deposition times are plotted as shown in Fig. S2. It is evident that the microcrystals prefer to grow along the “needle direction” as the length increases asymptotically as a function of time whereas the width

seems to reach an optimal size with no significant change with deposition time. The Ostwald ripening may be responsible for the selective growth along the long axis. The detailed growth dynamics of the microcrystals on different metal substrates is the subject of a future study.

Figure 2: Variation of mean effective length and width as a function of growth time.