Nanoscale Self-patterning and Engineering of YSZ Surfaces

DISSERTATION

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By

Zhiyuan Niu, B.E.

Graduate Program in Materials Science and Engineering

The Ohio State University

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Dissertation Committee:

Sheikh Akbar, Advisor
Suliman Dregia, Co-advisor
Yunzhi Wang
Abstract

Strain energy induced self-assembly has recently been discovered in the rare earth oxides (REO)/ yttria-stabilized zirconia (YSZ) systems. This dissertation aims to deepen previous mechanistic understanding of this phenomenon and to develop a cost-efficient technique that can be used to pattern a large surface with nanoscale features. In this work, a new REO source dispersion strategy was used to address the dilemma of the process simplicity and the source controllability. With this method, we investigated the growth kinetics of the nanostructures in a quantitative manner. In contrast to previous hypothesis that both the nanoislands and the nanobars have parabolic growth kinetics, we observed a parabolic relation only for the nanobars on YSZ(110). It was further discovered that the growth is anisotropic on YSZ(110), which might explain the formation of bars instead of islands.

In efforts to improve the order of the nanoislands, we investigated the surface step morphology and the formation of self-assembled nanoislands on two different types of miscut yttria-stabilized zirconia (YSZ) substrates. It was found that ordered step arrays can be produced on both (001)-[110] and (001)-[100] miscut YSZ substrates via pre-annealing. These steps are subsequently used as templates for the self-assembly of the nanoislands, which results in significantly improved alignment of the islands along the step direction. Additionally, we observed a novel step faceting only on the (001)-[100] miscut YSZ substrates where the original [100]-steps decompose into <110> segments. Preliminary
investigation indicates that this faceting is induced by doping via surface diffusion, while the elastic interaction between the faceted steps also plays a significant role.

We further investigated the impact of annealing gas environment – an overlooked factor in previous studies - on the nanostructure morphology. It was found that 5% H\textsubscript{2}-95% N\textsubscript{2} forming gas environment can promote the reactions in Eu\textsubscript{2}O\textsubscript{3}/YSZ(001) systems, which results in an improvement in nanostructure coverage. It is believed that the existence of H\textsubscript{2} has dynamically changed the nanostructure formation. The role of H\textsubscript{2} and its effect on other REO/YSZ systems were also explored and discussed.
Dedicated to

My parents and my loving wife Catherine

For all your support and unconditional love
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Vita

June 2012 .................................................B.E., Materials Science and Engineering,
Tsinghua University, Beijing, China

August 2012 to present ...................................Graduate Research Associate, Materials
Science and Engineering, The Ohio State
University

Fields of Study

Major Field: Materials Science and Engineering
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Chapter 1: Literature Review

1.1 Introduction

The functionality of a solid material is closely related to its surface properties. In the past three decades, the development in science and nanotechnology has enabled us to design and fabricate nanoscale features on solid substrates, leading to paradigm shifts in the field of microelectronics, sensor technology, data storage, biotechnology and semiconductor industry. While conventional applications take advantage of the size, shape and the high specific area of the surface nanostructures, carefully designed periodic features are now being used to fabricate metamaterials with novel properties.\(^1\)\(^2\) Surface patterns can be created on solid substrates either by “top-down” approaches or by “bottom-up” methods. The top-down strategy generates patterns by imposing macroscopic controls such as masks or templates. It usually involves physical addition or removal of materials at selected regions on the substrate surface. On the other hand, one may take advantage of the intrinsic materials properties to grow micro/nanoscale surface structures and patterns – a process known as self-organization or self-assembly. In this chapter, we will briefly review several available top-down and bottom-up techniques for nanoscale surface patterning. Our main focus will be on the strain energy mediated self-assembly which has been reported in both semiconductor and ceramic systems.
1.2 Surface patterning via lithography

Lithography is the most common top-down method for surface patterning and has been extensively used in modern microelectronic device fabrication. Conventional lithography technique, also known as photolithography, uses light and a photomask to define geometric patterns on a layer of light-sensitive chemical (photoresist) coated on the substrate. It involves several successive processes, including substrate cleaning, photoresist coating and pre-baking, aligning and exposure (printing), developing and post-baking, etching (or post-deposition), and photoresist removal. Depending on the relative position between the substrate and the mask in the aligner, photolithography techniques can be further divided into contact printing, proximity printing and projection printing. Advanced photolithography now use extreme ultraviolet excimer laser and carefully designed projection systems to achieve nanoscale resolution (~32 nm), although the equipment is extremely expensive and complicated.

The resolution of photolithography is generally limited by diffraction effects between the light and the mask. Higher printing resolution (~10 nm) can be achieved by non-optical lithography techniques such as electron-beam lithography and nanoimprinting lithography. The electron-beam lithography is a maskless lithography technique where the patterns are directly drawn onto the photoresist by a focused beam of electrons. Despite its high resolution, this technique is not cost-efficient for large surface patterning due to the expensive equipment and its low throughput. Nanoimprinting lithography is a relatively low-cost and high throughput technology, where patterns are transferred onto the resist from nanostructured molds via imprinting. One major challenge of nanoimprinting
lithography is to fabricate durable molds with high-resolution and high-density nanostructures. The thermal expansion mismatch between the mold and resist is another concern since a temperature over 100 °C is typically needed for this process.

In general, lithography is a developed technology that has been commercialized for integrated circuit (IC) printing for years. As a typical top-down technique for surface patterning, it can be used to print designed patterns with superior resolution, great accuracy and high uniformity. However, demanding operating conditions such as clean room facilities, expensive equipment, experienced operators and high surface flatness are usually required for lithography. It is also not suitable for large surface patterning due to its process complexity and relatively low throughput. These drawbacks prompted research in alternative surface patterning techniques such as bottom-up strategies involving self-assembly.

1.3 Self-assembly in general

Unlike the “top-down” methods where surface patterns are artificially created, “bottom-up” approaches rely on the intrinsic chemical properties of the materials, where surface patterns usually form spontaneously under suitable conditions via self-organization or self-assembly process. The definitions of self-assembly and self-organization as well as the boundary between them are pretty vague, since both the terms have been widely used to describe the spontaneous ordering process in the fields of physics, chemistry, materials science and biology. Some researchers tend to differentiate them by whether external energy source is required⁷, while some others prefer defining them as “static self-assembly”
or “dynamic self-assembly”\textsuperscript{8}. Under the latter criteria, self-assembly processes can be found in a whole range of phenomena from crystallization (self-assembly of atoms), self-assembled monolayers (self-assembly of molecules) all the way up to the formation of schools (self-assembly of fish) and the galaxies (self-assembly of planets).\textsuperscript{8} Here we bypass the vigorous debate\textsuperscript{9} on the strict definitions of self-organization and self-assembly while focusing on the most important and appealing characteristics of these processes - spontaneous organization phenomena and the intrinsic interactions between the components. Self-assembled structures can either be directly grown on the substrates, or be used as templates for etching or deposition. The following section will give two examples of self-assembly which take place via different mechanisms but are both used for template fabrication. We will then review a specific type of self-assembly where the structure formation is driven by strain energy relaxation.

1.4 Self-assembled templates for surface patterning

Colloidal particles are widely used in industrial products and scientific research. During the past few decades, a variety of synthesis methods have been developed to produce monodispersed colloidal spheres with nearly identical size, shape and chemical composition.\textsuperscript{10} These particles can be further arranged into ordered 2D or 3D arrays by a number of methods.\textsuperscript{10} For example, 2D colloidal particle arrays can be obtained on solid substrates via solvent evaporation (Figure.1.1a), which is referred to as “two-dimensional crystallization” by Denkov et al.\textsuperscript{11} In their experiment, a water suspension of monodispersed colloidal particles was spread over a flat glass substrate for evaporation.
Due to the attractive capillary forces between particles, ordered particle arrays (nuclei) formed when the thickness of the water layer went below the diameter of the particles. The growth of these ordered regions was further enabled by the convective particle flux caused by solvent evaporation, eventually forming close-packed hexagonal 2D arrays on the substrate surface (Figure 1.1b). The idea of organizing colloidal particles by capillary forces can be combined with gravity sedimentation method to produce 3D photonic crystals (Figure 1.1c).\textsuperscript{12, 13} Self-assembled colloid monolayer can also be used as a mask for selective etching or deposition, which is sometimes referred to as “colloidal lithography” due to the process similarity.\textsuperscript{14} Patterns with tunable structure parameters can be prepared by adjusting the diameter of the colloidal spheres, which is typically between 50nm – 4.5\textmu m.

Self-assembly of block copolymers (BCPs) is another extensively studied phenomenon in which a variety of nanostructures can be produced for surface patterning. A block polymer consists of two or more chemically distinct polymeric chains (blocks), while the self-assembly phenomenon and the resulting features are closely related to the repulsive interaction between the chains.\textsuperscript{15} While the equilibrium structure of a bulk BCP is largely determined by the chain architecture and the volume fractions of blocks, boundary conditions such as surface energies, interfacial interactions and film thickness also play an important role when it comes to thin films.\textsuperscript{16} BCP thin films can be prepared on a solid substrate by dip-coating or film casting. Figure 1.2 shows the morphological evolution of a thin SBS (poly(styrene-b-butadiene-b-styrene)) film with increasing film thickness.\textsuperscript{17} While the result indicates the possibility of adjusting domain patterns, it also
suggests the importance of a well-controlled film casting process. Several different approaches such as solvent annealing and electric field inducing can then be applied to achieve oriented domain structures.\textsuperscript{16} By selectively removing one of the blocks, patterned BCP masks can be created for post-processing such as nanoparticle decoration or etching, which is referred to as “BCP lithography”.\textsuperscript{16} The feature size prepared by this method is between 5-50nm, which is difficult to achieve by colloidal lithography.

Both colloidal lithography and BCP lithography use self-assembled masks for surface patterning. Compared with conventional lithography techniques, these approaches provide a promising way to pattern a large surface with nanoscale features at relatively low costs. However, the limitations of bottom-up approaches are also evident. While patterns can be freely designed in the lithography techniques, self-assembled features are less adjustable since they are constrained by the intrinsic properties of the materials as well as the interactions between the components. Another major challenge is to fabricate highly periodic defect-free patterns. Although patterns with short-range order are usually obtained, long-range ordering or periodicity is rarely achieved. Defects are also common in the colloidal and BCP systems (Figure. 1.1b). To improve the order and eliminate the defects, lithographically defined patterns are sometimes used to guide the self-assembly.\textsuperscript{14, 16} Though a feasible strategy to balance pattern quality with economic and time efficiency, this methodology partly compromises the spontaneity of these processes.
1.5 Self-assembled nanoislands in semiconductor systems

1.5.1 General observations and mechanisms

A more straightforward method to pattern a solid substrate is to grow self-assembled structures directly on the substrate surface. Self-assembly of this type is usually associated with strain energy relaxation and the elastic interaction between the components and the matrix. The most widely studied examples of strain energy induced self-assembly are the nanoisland formation on heteroepitaxial semiconductor thin films. To produce islands in these systems, molecular beam epitaxy (MBE) is commonly used. It is believed that the film growth follows a two-stage process known as the Stranski-Krastanov (SK) growth mode.\textsuperscript{18, 19} Initially, the film grows in a layer-by-layer manner, forming a so-called “wetting layer” until the film thickness reaches a critical value. Beyond this critical thickness, 3D islands begin to form to relax the strain energy induced by lattice mismatch between the film and substrate. In low-misfit systems (e.g., Si\textsubscript{0.75}Ge\textsubscript{0.25} on Si(001), lattice mismatch strain <1\%), the islanding begins with a nucleationless process involving surface ripple formation\textsuperscript{20, 21}, which is essentially depicted by the Asaro-Tiller-Grinfeld (ATG) instability theory.\textsuperscript{22} In high-misfit systems (e.g., Ge on Si(001), lattice mismatch strain \sim 4\%), nucleation process is favored.\textsuperscript{21, 23} The islands are determined to be coherent and dislocation-free at the early stage.\textsuperscript{18} In this case, the strain energy is partially relaxed by introducing undulations to the substrate surface layers (Figure 1.3). With continued film growth, the increasing strain will eventually lead to misfit dislocation introduction, undermining the coherency of the islands.\textsuperscript{18} The formation of dislocations usually results in poor device performance, and is thus undesirable for practical applications.
SK islands have been observed in multiple heteroepitaxial semiconductor systems such as Si/Ge\textsuperscript{24}, InAs/GaAs\textsuperscript{25} and CdSe/ZnSe\textsuperscript{26}. These islands form by similar mechanisms, although the actual island shape, size and distribution depend on multiple factors such as film composition, structure of the substrate surface and growth conditions. Islands in Si/Ge systems are the most widely studied due to their compatibility with Si-based microelectronic technology. For Ge or SiGe on Si(001) surface, islands may have two characteristic morphologies as a result of surface energy anisotropy: hut clusters bound by \{105\} facets, or dome clusters with \{113\} facets.\textsuperscript{24,27} There exists a hut-to-dome shape transition when the film growth proceeds, which is investigated by Floro et al. on the MBE grown Si\textsubscript{0.8}Ge\textsubscript{0.2}/Si(001) heteroepitaxial thin films.\textsuperscript{27} They studied the morphological evolution as a function of Si\textsubscript{0.8}Ge\textsubscript{0.2} equivalent thicknesses, which is shown in Figure 1.4. They proposed that the hut-to-dome transition takes place when the islands exceed a critical volume, and the islands can interact through the mutual strain fields in substrate to reduce both the critical volume and the transition activation barrier originated from surface energy anisotropy. They further demonstrated that coarsened huts can be obtained by annealing low-equivalent-thickness film without transition to domes, which was explained by the weaker elastic interaction between neighboring islands due to the wider spacing at a lower equivalent thickness (Figure 1.4f).\textsuperscript{27}

This study provides an important guidance for island shape control, as the smaller hut morphology is typically favored for quantum dot applications. However, the size and shape distributions of these islands still need to be narrowed for any practical applications. Although the edges of the huts tend to align along the <100> directions on Si(001)\textsuperscript{24}, long-
range ordering is not observed due to the random nature of the nucleation process. Much effort has been taken to improve the uniformity and the lateral ordering of islands in heteroepitaxial semiconductor systems, while the strategies fall into two categories - by growing multilayer structures, or by applying pre-existing templates. These templates include lithographically defined patterns, dislocation networks and aligned surface steps. The following section overviews several techniques that can be used to improve the ordering of self-assembled nanostructures.

1.5.2 Strategies for order improvement

Lagally et al. studied the self-organization behavior of islands by growing Si$_{1-x}$Ge$_x$/Si multilayers on Si(001) surface. In their experiment, a 2.5nm-thick Si$_{0.25}$Ge$_{0.75}$ layer was firstly deposited on the Si(001) substrate, producing islands with typical hut morphology (Figure 1.5a). A 10nm-thick Si was then deposited as a spacer layer to compensate the strain in the first layer, followed by another layer of Si$_{0.25}$Ge$_{0.75}$. After depositing 20 bilayers, a significantly improved island size and shape uniformity was observed (Figure 1.5b).

The above-mentioned self-organizing phenomenon suggests that there exists a vertical interaction between the layers which results in the improved lateral island alignment. It should be noted that the average size of the islands has greatly increased on the top layer, which indicates that the mechanism of this self-organization is more complicated than simply stacking new islands on top of the buried ones. Figure 1.5c shows a cross-section view of the multilayer structure that reveals the evolution and the possible
mechanism of this ordering process.\textsuperscript{28} In the first 10-15 layers, the size of the islands is preserved while their spacing becomes smaller. When a critical spacing is reached, only one larger island forms on top of each two neighboring islands. Continued growth will produce islands directly on top of these merged ones with a maintained size, as shown in Figure 1.5d.\textsuperscript{28} This evolution can then be explained qualitatively by the elastic interaction between the islands. According to the model proposed by Tersoff et al., an island forms at the local minimum of the strain field, while the diameter of the strain field around an existing island is independent of its size.\textsuperscript{23} For a small island, the strain field can be larger than the lateral size of the island. Neighboring islands can interact with each other through the overlapped strain fields, leading to a reduced island spacing in the subsequent layer. When the islands get close enough, the formation of one larger island over two smaller ones is energetically favored. After this transition, the islands exhibit direct vertical correlation since the increased island size and spacing are too large for the strain fields to overlap.\textsuperscript{28} According to this theory, the final island spacing can be directly controlled by the spacer layer thickness.\textsuperscript{23} It should be noted that an increased spacer layer thickness also weakens the elastic interaction in the vertical direction, which may result in an increased randomness in island distribution.\textsuperscript{29}

Vertical ordering in multilayers is not limited to the SiGe/Si system. Self-organization of islands has also been reported in other multilayer structures such as the InAs/GaAs\textsuperscript{25} and the PbSe/Pb\textsubscript{1-x}Eu\textsubscript{x}Te\textsuperscript{30} systems. Analogies can be drawn between SiGe/Si and these systems, although the specific phenomena may vary in different systems. For example, (100) faceted PbSe islands with pyramidal shape and triangular base can be
obtained on PbTe(111) surface.\textsuperscript{30} After growing multilayers by alternating PbSe layer with a PbSe/Pb\textsubscript{1-x}Eu\textsubscript{x}Te spacer layer for 60 periods, a nearly perfect hexagonal island arrangement was obtained. Unlike the direct vertical correlation exhibited in SiGe/Si, the islands stacked in an fcc-like A-B-C-A-B-C sequence, which was attributed to the large elastic anisotropy of the materials.\textsuperscript{30} In general, the pattern morphology depends on multiple factors such as lattice mismatch of the materials, crystal structures of the substrate surface, surface energy anisotropy and elastic modulus anisotropy of the materials. The islands interact with each other through the mutual strain fields, while the strain can be engineered by controlling the layer composition and thickness of the multilayer structure. By growing multilayer structures, misfit dislocation formation can be avoided. This approach significantly narrows the island size and shape distribution in heteroepitaxial thin films, while the long-range order can also be improved to some extent. However, it requires precise control of thin film growth and is very time consuming. The great thickness of the multilayer stacks also makes it difficult to integrate with other devices.\textsuperscript{31}

An alternative way to improve the order of the patterns is to guide the self-assembly by lithographically defined patterns. Zhong et al. studied Ge island growth on strip-patterned Si(001) substrate by controlling multiple parameters including pattern dimension, period, growth rate and temperature.\textsuperscript{32} They demonstrated that the islands can be preferentially grown at different positions under suitable conditions (Figure 1.6), while the growth kinetics, thermodynamics and the substrate strain field all contributed to the formation of favored nucleation sites.\textsuperscript{32, 33} Yang et al. patterned the Si substrate with square mesas and similar morphologies were observed after Ge layer growth.\textsuperscript{34} The major
advantage of this approach is the arbitrary in pattern design and the relatively low cost comparing to the high-resolution lithography. The long-range order is essentially determined by the lithographically defined patterns while the feature morphology and the short-range ordering is controlled by the self-assembly. It should be noted that this strategy is not limited to the semiconductor thin films, as previously mentioned in the block copolymer and colloidal systems. Disadvantages of this approach include the resolution limitation of lithography, defects or short-range disorder originated from self-assembly as well as the feature size and shape variation. It is also not suitable for large surface patterning due to the involvement of lithography.

Dislocation network can also be used to guide island nucleation. Teichert et al. investigated the Si\(_{0.7}\)Ge\(_{0.3}\) island formation on Si(001) by applying two-stage MBE growth.\(^{35}\) At the low-temperature stage, a 30nm thick Si\(_{0.7}\)Ge\(_{0.3}\) layer was grown under simultaneous Si\(^{+}\)-ion bombardment, creating a dense network of dislocations. A 50 nm Si\(_{0.7}\)Ge\(_{0.3}\) layer was then deposited at a higher temperature to produce the islands.\(^{35}\) These islands exhibited remarkable alignment along the dislocation lines, while highly-ordered island arrangement was achieved within a region of dense dislocations (Figure 1.7(a, b)). At the dislocation-free regions, the islands became disordered (Figure 1.7c). This study reveals a possible way to significantly improve the long-range order of the islands. However, producing large scale dense dislocation arrays seems quite challenging. The introduction of dislocations may also induce a negative impact on the performance of devices.\(^{33}\)
In practice, semiconductor devices are often fabricated on vicinal substrates that are a few tenths of a degree off the nominal surface orientation. This small misorientation will introduce a number of atomic steps onto the substrate surface, which may further self-organize into regular step bunches under suitable conditions. Several studies have suggested that step bunching is favored on vicinal Si substrates during heteroepitaxial growth, while the height and period of the step bunches depend on miscut angle and growth conditions. Research on miscut Si substrates has revealed the impact of step bunches on island nucleation and morphology, however, significantly improved long-range order has not yet been reported. This is partly due to the difficulty in producing highly-periodic step bunches, which is constrained by different kinetic limitations in semiconductor systems.

1.6 Self-assembled nanostructures in REO/YSZ systems

Nanoislands in semiconductor systems essentially form via a strain-relief mechanism. The strain originated from the lattice mismatch between the materials while the island morphology is dictated by multiple factors such as the elastic interactions, surface energy anisotropy and the structure of the substrate surface. It should be noted that these ingredients for self-assembly can also exist in other crystalline materials such as ceramics. The formation of self-assembled nanoislands in REO (rare earth oxides)/YSZ(Y_2O_3-stabilized ZrO_2) systems was first reported by Rauscher et al. during GDC (Gd_2O_3-doped CeO_2) thin film deposition on YSZ(001) single-crystal substrate. GDC and YSZ have a fluorite structure with a lattice mismatch of ~5.5%. Both of them
are commonly used materials in the solid oxide fuel cells. In Rauscher’s study, a planar film of GDC was deposited on the YSZ(001) substrate by radio-frequency magnetron sputtering.\textsuperscript{39} For thick GDC films (>200 nm), the large internal stress sometimes led to a film spallation which uncovers the underlying YSZ substrates. Rauscher annealed the film at 1150 °C in an attempt to relieve the internal stress, while the unexpected nanoisland formation was observed on the exposed YSZ surfaces (Figure 1.8(a, b)). These islands have a truncated pyramid shape with a size between 100-200 nm on an edge.\textsuperscript{39} Unlike the semiconductor systems where islands form almost randomly on the substrate surface, these islands tend to grow wall-to-wall, showing a certain degree of self-ordering (Figure 1.8c). They typically form within several microns around the GDC films, although isolated colonies or long strips of the islands are also observed occasionally (Figure 1.8(d, e)).\textsuperscript{40} A close look at Figure 1.8f reveals the formation of trenches at the island growth front. With the increasing distance between the islands and the remnant GDC films, the height of the islands gradually decreases.

Preliminary theories explaining the above-mentioned phenomena are proposed by Rauscher based on the widely accepted mechanisms for semiconductor nanoisland formation. He believes that the GDC thin film deposition essentially modifies the substrate surface composition with GDC, creating a stressed layer due to the lattice mismatch between the materials.\textsuperscript{40} On the other hand, the remnant GDC films on the substrate also yield stress fields around them, contributing to the stress accumulation at their vicinities.\textsuperscript{40} As a consequence, the stressed substrate surface breaks up into islands around the remnant GDC films to relax the strain energy, while the island morphology is dictated by the surface
energy anisotropy and the elastic interaction between them.\textsuperscript{40} Ansari cast doubt on the role of the GDC films and investigated the nanoisland formation by depositing lithographically defined square GDC patches on the YSZ(001) substrate.\textsuperscript{41, 42} After annealing the sample at 1150 °C, nanoislands formed in the vicinity of the GDC patches (Figure 1.9a).\textsuperscript{42} Based on this observation, Ansari proposed that the surface is not necessarily pre-modified during deposition while the modification can take place during annealing via surface diffusion.\textsuperscript{42} He further developed a powder suspension method which bypasses the thin film deposition as well as the lithography process.\textsuperscript{41} In this method, commercially available GDC powder is suspended in distilled water and applied to the YSZ substrates via a micropipette. The GDC powder is naturally distributed onto the surface when the water droplet evaporates, and the sample is annealed in a furnace after drying. The resulting morphology is essentially consistent with previous observations, where significant nanoisland formation is observed in the vicinity of the powder (Figure 1.9b). This result indicates that the impact of the stress induced by the GDC films is overemphasized by Rauscher, since the powder source is merely in contact with the substrate and is not likely to generate an extensive stress field due to the relative small size. Boyen et al. analyzed this phenomenon with a phase field model where the deposition stress is proven insufficient to drive sustainable island growth.\textsuperscript{43} Instead, it is demonstrated that localized stress from the lattice mismatch between modified surface layer and the bulk can induce surface instability and cause long-range island formation.\textsuperscript{43} This result supports Ansari’s theory that the major role of the GDC is dopant sources rather than stress centers, while the surface modification is completed via surface diffusion during annealing.\textsuperscript{42} This process essentially creates a
stressed solid solution layer on the substrate, which further breaks up into coherent islands to relax the strain energy. Both Rauscher and Ansari attribute the directional alignment of islands to the elastic modulus anisotropy of the substrate.\textsuperscript{39,41} It is believed that the islands tend to align along the most compliant principle directions on the substrate surface. For YSZ, the measured elastic modulus gives $E_{<111>} < E_{<110>} < E_{<100>}$,\textsuperscript{44} while this relationship is reversed for the Si.\textsuperscript{45} Since the most compliant $<111>$ directions are not available on YSZ(001) surface, the islands align along the second most compliant $<110>$ directions. For Si(001), the islands aligned along the most compliant $<100>$ directions which are available on the (001) surface.\textsuperscript{39} They also propose that the better island ordering on the YSZ substrates is due to the larger elastic modulus anisotropy.\textsuperscript{39,41}

Previous analysis on elastic anisotropy suggests that changing surface orientations may have an impact on the surface morphology. Ansari investigated the nanostructure formation on the YSZ(110) surface with both the lithographically defined GDC patches and the powders. Instead of forming nanoislands, the GDC/YSZ(110) system produces nanobars with their long axis aligning along the [-110] direction (Figure 1.10a).\textsuperscript{41} These bars are not perfectly straight and are sometimes “chopped” over several microns. A cross-section TEM image reveals that the bars are smoothly curved rather than sharply faceted (Figure 1.10b). The mechanism by which these bars form is considered similar to the one proposed for the nanoisland formation, although it fails to explain why the [-110] oriented bar morphology is preferred. Ansari’s theory about the elastic modulus anisotropy cannot explain the bar alignment since the most compliant $<111>$ directions are available on YSZ(110) surface. It also did not consider other anisotropic factors such as the surface
diffusivity and the surface energy. It should be noted that the bar morphology is not unique to the YSZ(110) surface. Both Rauscher and Ansari have reported that nanobars are sometimes observed at the growth front of nanoislands on the YSZ(001) substrates (Figure 1.8e).\textsuperscript{40, 41} Meanwhile, island morphology may also occur near the GDC sources on the YSZ(110) surface (Figure 1.10a). This is explained by the different doping level in these regions.\textsuperscript{41} Although the most stable morphology on YSZ(001) and YSZ(110) is island and bar, respectively, it is believed that the feature morphology can evolve from bar, island to a connected morphology when the dopant concentration increases.\textsuperscript{41} Since the dopant concentration is higher in the vicinity of the sources, connected morphologies are commonly observed in these regions. Moreover, a high annealing temperature can also result in an increase in the connected area, which is undesirable for nanostructure fabrication.\textsuperscript{41}

One major advantage of the powder suspension method is the process simplicity. It can be easily applied to many other systems simply by switching the powders. Ansari successfully produced nanostructures with this method by applying other rare earth oxide powders such as Gd\textsubscript{2}O\textsubscript{3}, Gd\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}, Eu\textsubscript{2}O\textsubscript{3}, Y\textsubscript{2}O\textsubscript{3} and Tb\textsubscript{2}O\textsubscript{3} onto the YSZ substrates, although the required annealing conditions and the resulting morphologies vary with the dopant species.\textsuperscript{41} It is experimentally determined that dopants with smaller ionic radius usually require higher temperature for nanostructure formation when the annealing time is fixed.\textsuperscript{41} This series of experiments demonstrated that nanostructure formation on YSZ substrates is a general phenomenon rather than a special case for the GDC. The possibility of producing nanostructures with the Y\textsubscript{2}O\textsubscript{3} source is also interesting, since Y\textsubscript{2}O\textsubscript{3} already
exists in the substrate and the nanostructures can be readily produced without introducing new dopant species.

The effects of experimental conditions such as annealing temperature, annealing time, heating rate and cooling rate have been qualitatively studied by Ansari in the GDC/YSZ systems. By performing heating and quenching experiments, he demonstrated that nanostructures form during the high temperature hold. He further proposes that different combinations of temperature and time can result in similar morphologies due to the diffusional nature of this process. By varying these parameters, the size, shape, spacing and coverage of the nanostructures can be adjusted within certain ranges. It is also observed that an excessively high temperature or long annealing time can reduce the yield of nanostructures. Ansari attributes this phenomenon to the merge of nanostructures at high doping level, while compositional homogenization via bulk diffusion is another possibility in this case. Both Rauscher and Ansari have made attempts to estimate the surface diffusivity of GDC on YSZ based on a parabolic surface diffusion model where 
\[ D = \frac{x^2}{t} \]. This assumption, however, was never quantitatively verified by the growth kinetic analysis in previous studies. For this purpose, GDC may not be the best dopant source because it contains both Gd\(^{3+}\) and Ce\(^{4+}\) as the diffusion species. A well-defined source is also needed to perform this type of analysis.

The first attempt of producing nanoislands on vicinal YSZ substrate was made by Ansari in efforts to improve the order of the islands. He used YSZ(001) substrate with 10° of misorientation towards the [010] direction and applied GDC with the powder suspension method. The sample was then annealed at 1125 °C for 25 hr to grow islands. SEM image
of a region with no GDC powder shows a zigzag surface step morphology with the step edges aligning along <110> directions (Figure 1.11a). Ansari believes that a bare miscut YSZ substrate without GDC powder would show the same morphology under the same annealing conditions, and the zigzag steps are intrinsically stable on this type of miscut YSZ surface. This argument, however, is demonstrated incorrect in our current study. Figure 1.11b shows a region near the GDC powder where the formation of islands on the step corners was observed. This is a direct evidence of surface steps guiding the self-assembly of islands, although the order is not significantly improved due to the poor arrangement of the template. Ansari believes miscutting YSZ(001) towards [110] will produce straight steps and a lower miscut angle can also be beneficial to order improvement. He also failed to explain why the steps exhibit such well-developed and organized morphology and how did the surface morphology change during the annealing. These issues will be addressed in Chapter 3 of this dissertation.

1.7 Motivations and organization for current work

Previous studies in the REO/YSZ have led to the following unanswered questions:

1. Why do the nanobars align along <110> instead of the most compliant <111> directions?
2. Can straight step arrays be produced on miscut YSZ substrates? Can we use these steps as template to improve the order of the nanostructures?
3. What are the growth kinetics of the nanostructures? Does the parabolic diffusion law apply to these systems? How much coverage of the nanostructures can we obtain within a reasonable amount of time?
4. Is there any other intrinsic or environmental factor affecting the formation of the nanostructures?

The motivation of this dissertation is to seek answers to the above-mentioned questions. The remaining chapters present our efforts on addressing these issues with different experimental designs. In Chapter 2, we present our standard procedures for nanostructure fabrication and introduce a new source dispersion strategy to fabricate controlled dopant source with reasonably good edge sharpness. Chapter 3 shows the successful development of surface step arrays on two different types of miscut YSZ substrates and their significant impact on the nanostructure morphologies. We also report a novel doping-induced step faceting phenomenon which has huge implication in template stability and the surface reactivity. Chapter 4 presents a qualitative investigation of the growth kinetics of the nanostructures which brings several new mechanistic understandings. Chapter 5 explores the impact of a new environmental factor, the annealing gas environment, to the nanostructure morphologies. We will end up with several directions of future works and a final conclusion in Chapter 6.
Figure 1.1: (a) Schematic presentation of solvent evaporation induced self-assembly;\textsuperscript{11} (b) SEM image of colloidal particle self-assembled into 2D arrays;\textsuperscript{46} (c) cross-section SEM image of colloidal particles self-assembled into 3D crystalline structures.\textsuperscript{13}

Figure 1.2: (a,b) Tapping-mode scanning force microscope phase images of thin SBS films on Si substrates; (c) schematic height profile of the phase images shown in (a,b); (d) Simulation of BCP thin film morphology with increasing film thickness.
Figure 1.3: (a) schematic plot showing strain relaxation of an isolated island by elastic deformation of the near-surface layers in the substrate. (b) Dark-field TEM image of a coherent SK island (right before dislocation introduction) showing strong strain contrast.

Figure 1.4: SEM images showing the evolution from (a) huts to (e) domes as a function of Si_{0.8}Ge_{0.2} equivalent thickness. (a) 10.4, (b) 13.0, (c) 17.0, (d) 24.0, (e) 27.5 nm, (f) static coarsening effect upon annealing a 10.4-nm film.
Figure 1.5: (a) 0.8μm x 0.8μm AFM image showing the morphology after deposition of the first Si$_{0.25}$Ge$_{0.75}$ layer$^{23}$; (b) 1.25μm x 1.25μm AFM image showing the morphology after deposition of 20 Si-Si$_{0.25}$Ge$_{0.75}$ bilayers$^{23}$; (c) Bright-field TEM image showing a cross-section view of the multilayer structure$^{28}$; (d) Schematic presentation of the island evolution in (c)$^{28}$

Figure 1.6: AFM images showing multiple morphologies of Ge islands on strip-patterned Si substrates. These islands were grown under different experimental conditions.$^{32}$
Figure 1.7: (a) AFM image showing island alignment along the dislocation network; (b) 3D image of the selected area in (a); (c) Morphology of the region with lower dislocation density. 

Figure 1.8: SEM images of nanoislands in GDC/YSZ(001) system. (a) Islands forming at the vicinal of remnant GDC films; (b) Spalled GDC films with a spontaneous curvature indicating the residual stress in the GDC film; (c) Short-range order and size uniformity within a few rows; (d) Isolated colonies of islands; (e) A strip of islands forming around a scratch on the surface; (f) Height variation of islands with the distance to the GDC films (A remnant GDC film is on the right side of this region).
Figure 1.9: SEM images of nanoislands produced by (a) lithographically defined GDC patches; (b) GDC powders via powder suspension method. 

Figure 1.10: (a) Nanobars produced by lithographically defined GDC patches on YSZ(110) surface; (b) Cross-section TEM image showing the shape and alignment direction of the bars.

Figure 1.11: (a) SEM image of the stepped YSZ substrate without islands; The nominal YSZ(001) substrate was miscut by 10 degrees towards [010] direction; (b) A trail of islands forming at the step corners.
Chapter 2: Powder Based Source Dispersion Techniques for Nanostructure Growth

2.1 Introduction

The role of the rare earth oxides (REO) in nanostructure formation has been extensively investigated in previous work on YSZ. It was concluded that the REO mainly act as dopant sources for diffusion rather than stress centers that induce surface instability. As long as the source is in good contact with the substrate, nanostructures can form around it upon annealing. Based on this understanding, a variety of source deposition techniques can be applied to this process for different purposes. For example, photolithography and magnetron sputtering can be used to achieve arrays of well-defined dopant source, as demonstrated in Rauscher’s and Ansari’s work. This type of source usually has sharp edge, regular shape and periodic arrangement, and is thus suitable for kinetic analysis, morphological evolution analysis or any other application that requires accurate position of the source. However, due to the involvement of lithography and sputtering, the entire process is quite complex, expensive and time-consuming. Apart from the scalability, the versatility of this method is also limited, as some ceramic materials (Such as Eu2O3) have poor adhesion in air and can hardly be made into a stable sputtering target. Ansari developed an alternative method where REO powders were randomly distributed onto the substrate surface via a water suspension. With this simple and cost-efficient process, it is possible to achieve wall-to-wall nanostructure growth on YSZ substrates of almost any size,
as long as the source distribution is proper. This strategy is particularly suitable for large surface patterning and qualitative sample analysis. However, due to the randomness in powder size, powder distribution and the degree of contact, variation in nanostructure morphologies is usually expected. It is also difficult to avoid the powders and perform tests purely on the nanostructures. Although most of the powders can be removed by ultrasonication after nanostructure growth, they leave large footprints behind which are essentially random defects within the nanoscale patterns.

In this chapter, two alternative source deposition techniques are explored in efforts to produce well-defined source in a relatively simple and scalable manner. These techniques involve delivering powders to a specific region on the substrate via a concentrated powder ink and can thus be described as controlled powder methods. To begin with, we first review the standard procedures for nanostructure fabrication using the powder suspension method, as many samples presented in Chapter 3 and Chapter 5 are prepared in this way. We then introduce the usage of a computer controlled inkjet printing system for source deposition. The use of the Picopump system will be discussed in the end.

2.2 Standard substrate cleaning procedures

Single crystal 8 mol% YSZ substrates, 10 mm x 10 mm x 0.5 mm in dimensions, were purchased from MTI Corporation (Richmond, CA) with one side mechanically and chemically polished to a roughness below 5 Å. The substrates are available in different surface orientations with a +/- 0.5° tolerance from the designated plane. To make full use of the substrates, each piece of the original substrates was cleaved into a few smaller pieces
(~2 mm x 2 mm x 0.5 mm) with a stainless steel razor blade. The substrates were then cleaned by bath sonication in acetone, ethanol and DI water, each for 5 min. They were usually dried by blowing air using a compressed air duster while holding them with the tweezers. This standard substrate cleaning procedure was applied to all the substrates prior to the experiments. Additional cleaning may be performed on processed substrates to remove any possible contamination from the environment.

2.3 Nanostructure fabrication via powder suspension method

Eu$_2$O$_3$ powder was acquired from Alfa Aesar (Ward Hill, MA). 0.1-0.2 g/L Eu$_2$O$_3$ powder suspension was made by adding the powder into DI water followed by 10-15 min bath sonication. This suspension concentration was proposed in Ansari’s work to achieve optimal source distribution, and should be adjusted accordingly when the powder size changes. Before the settling starts, 10 μL of the suspension were taken by a micropipette and applied onto the substrate in a plastic weighting tray, as shown in Figure 2.1a. The water suspension has a moderate contact angle on the weighting tray and a dome-shape suspension droplet will form. The amount of suspension was selected such that the sample-size substrate can be completely submerged in the droplet. The sample was then let dry in air for several hours before putting into a high temperature box or tube furnace. In a typical heat treatment, the sample was annealed in air at 1050-1125 °C for 12-25 hr with a 10 °C/min ramp up rate and 5 °C/min cooling rate. The surface morphologies of the samples were characterized on FEI Sirion FEG-SEM (Hillsboro OR, USA). The samples were
coated with a thin layer of Au before taking SEM images. SEM images showing the typical sample morphology from this fabrication process are presented in Figure 2.2.

2.4 Dopant source deposition via inkjet printing

2.4.1 Inkjet printing system

Inkjet printing is available as an advantageous deposition technique for achieving a porous layer of nanoparticles for sensing or electronic device applications. In particular, it is useful for mass production of controlled film arrays with a wide selection of the source particle materials. Figure 2.3 shows a picture of a MacroFab jetLab II inkjet printer which was used for our sample preparation. This instrument is equipped with a motorized piezoelectric printhead and a x-y stage for accurate film deposition. Multiple cameras were installed on the instrument to monitor the drop evolution as well as the stage location. The printhead contains a glass capillary orifice and was connected to the instrument via tubing and wires. The tubing was connected to the ink reservoir and the ink was pumped into the printhead by a controllable pressure. During deposition, a short pulse of voltage was applied to the printhead and a small amount of ink was ejected from the orifice to form a droplet. Details of the instrument operation and parameter optimization were thoroughly discussed in Beach’s work\textsuperscript{47} and should be referred to for inkjet printing procedures. The following sections mainly focus on the ink preparation and the observations during Eu$_2$O$_3$ source deposition.
2.4.2 Ink preparation

Before using the inkjet printers, a unique ink containing the source particle needs to be prepared and the quality of the ink has to meet several basic requirements. First of all, the ink should not contain any aggregates that may clog the orifice of the printhead, which is 50 μm in diameter. Second, the ink should be stable in air with time. An unstable ink may yield agglomerates during the deposition process, which can further clog the orifice or cause inconsistencies. Apart from these requirements, fluid properties such as the viscosity, surface tension and evaporation rates are all critical to the ink drop formation and the film quality. Much effort on ink formulation optimization has been taken by Beach and Andio in their previous work on SnO\textsubscript{2} and TiO\textsubscript{2}.\textsuperscript{47,48} Considering the similarities of metal oxide powders, we simply adapted their optimal recipes and used the following protocols for Eu\textsubscript{2}O\textsubscript{3} ink preparation:

Solvent was prepared by mixing 15 mL of 30:70 wt% water: ethylene glycol solution on a magnetic stirrer. 1 wt% Bicine (Sigma-Aldrich, St. Louis, MO) was added into the solvent as the surfactant and a clear solution was prepared by sonicating the mixture for 15 min at 150 W using a probe sonicator. The sonicator has a special container connected to a chiller to prevent the solvent from heating during the sonication. After complete mixing, 3 wt% Eu\textsubscript{2}O\textsubscript{3} nanopowder (~60 nm, Alfa Aesar, Ward Hill, MA) was added into the solution. The mixture was sonicated for another 15 min at 150 W to produce a homogeneous Eu\textsubscript{2}O\textsubscript{3} ink. This milky Eu\textsubscript{2}O\textsubscript{3} ink usually remains stable for days at room temperature and additional sonication was performed before using if any settling occurred.
The ink used for inkjet printing was passed through a 5 μm syringe filter to completely remove large agglomerates that may clog the orifice.

2.4.3 Morphology of inkjet printed Eu₂O₃ films

The printhead of the Inkjet printer is computer-controlled and a program was written to designate the locations for droplet deposition. Ideally, this would allow us to obtain periodic arrays of dopant source dots. It might also be possible to obtain line source or other shapes by adjusting the spacing between the dots and make them overlap. It is, however, much more challenging to achieve this level of precision and reproducibility in practice. Many factors may affect the quality of the film, such as the uniformity of the ink, the condition of the orifice, the magnitude and the duration of the voltage pulse and the number of droplets for each dot. Although the actual printing only takes a few seconds, finding the optimal parameters for the deposition is usually time-consuming and these values may vary from time to time. Defects in the pattern are also common, as shown in Figure 2.4a. At this magnification, it is apparent that the shape of each film is not uniform and the arrays are not perfectly aligned. More importantly, there are two sets of dots with different sizes printed on this sample, which is due to the formation of a satellite drop during the deposition. Several large contamination particles are also observed on this sample. Figure 2.4b shows an attempt of printing line source by adjusting the center-to-center spacing between the dots. Our ink usually produces dots with 80-120 μm in diameter, and the dots start to overlap when the spacing go below this value. It was found that upon overlapping, the droplets immediately merge with each other and the resulting shape is usually irregular. This observation suggests that producing complex patterns is not possible.
without further tuning of the ink formulation. These defects, however, have little impact on the current study as we mainly focus on the behavior of an individual source rather than the interactions between multiple ones. Our main concern here is the source edge sharpness because a broad or rough edge will introduce significant error to our measurement of nanostructure extension in Chapter 4. To evaluate this factor, we examined the source edge before and after heat treatment. Figure 2.5a shows arrays of Eu$_2$O$_3$ dots obtained from a successful inkjet printing process. In this case, the shape of the dots is more uniform and the satellite drop effect is absent. A closer examine of the source edge reveals reasonably good edge sharpness, as the boundary between the film and the bare substrate surface can be clearly identified (Figure 2.5b). Figure 2.5c shows the source edge of a similar sample after heat treatment where the formation of nanoislands is clearly observed. Although the original powder at the source edge has been partly consumed, we can still identify a boundary based on the onset of the connected morphology. This type of morphology represents the typical film edge of the inkjet printed samples after the heat treatment. Although the edge of the film is not as sharp as the lithographically defined patches, it still reveals the extension of the islands as well as their morphological transition.

As mentioned before, the pattern quality is affected by the ink properties, the condition of the orifice as well as the deposition parameters. Even with careful tuning, one may not be able to achieve sharply defined source every time. Figure 2.5d shows an example where the source edge is not well defined. In this case, the film edge is essentially a band of powders with relatively loose distribution and the boundaries of this band can be hardly identified. This type of morphology usually indicates poor ink quality or insufficient
sonication. If the nanopowder in the ink agglomerates heavily, most of the particles will be filtered out before the deposition and the film edge will look discontinuous. In fact, the size of the original powder may have a significant impact on ink quality and we did not attempt to optimize this factor in this study. The metal oxide powder used by Beach and Andio is usually below 20nm, while our Eu$_2$O$_3$ nanopowder has a nominal size of 60nm. If the powder size is reduced, we should be able to have more particles pass through the filter to form a denser film with finer and continuous edge. For more precise deposition, it might be worthwhile to ball mill the powders before ink preparation.

2.5 Dopant source deposition via Picopump deposition system

Dopant source deposition for most of the samples presented in Chapter 4 was completed using a PV830 Pneumatic Picopump (World Precision Instruments, Sarasota, FL) as shown in Figure 2.6. This instrument was attached to a compressed air cylinder and a small glass capillary with 200 μm inner diameter was used to deliver the ink. The Picopump essentially allows us to control the back pressure within the capillary tube and the ink can therefore be absorbed or ejected. The capillary holder can be directly used as a pen, or a joystick-controlled micromanipulator can be used for film positioning. Compared with the inkjet printer, this instrument has worse location accuracy and produces films with larger size. However, the deposition process becomes much simpler and the usage of a filter is unnecessary in this case because of the large capillary diameter. This allows more particles to be deposited onto the substrate, which is usually beneficial to the film edge quality.
During the film deposition, the back pressure of the capillary was carefully adjusted to a critical value where the ink completely wets the capillary tip. One way to complete the deposition is to further increase the pressure by a small amount so that the ink will be slowly ejected from the capillary. This requires some careful adjustments in practice because the pressure is controlled manually by a knob and our ink has a relatively low viscosity. If the pressure is too high, the ink may splash and the powder will be all over the substrate. Alternatively, we can deposit the film by touching the substrate rapidly with the capillary tip at the critical pressure. This procedure will transfer a small droplet of ink onto the substrate and the ink at the capillary tip is constantly supplied by the back pressure. Figure 2.7a shows the typical size and shape of the films deposited with this method. The sample was dried in a 60 °C oven for 15min after the deposition and no further heat treatment was performed. A closer examination of the film reveals three different morphological zones, as indicated in Figure 2.7b. The center of the dot (Zone I) is covered by a dense layer of powder which has relatively uniform distribution. When it gets closer to the edge (Zone II), the layer becomes thicker and the film starts to crack. Zone III is a thin band of fine Eu₂O₃ powders which constitutes the edge of the film. Due to the high powder content in the unfiltered ink, this band looks denser and more continuous than the edge of the inkjet printed dots, and the boundary between the film and the substrate can be clearly identified (Figure 2.7c). This type of edge morphology is desirable for kinetic analysis and most of the samples presented in Chapter 4 were prepared via the Picopump method.
2.6 Conclusions

In this Chapter, three different powder-based source deposition techniques were reviewed and introduced. The powder suspension method is useful for qualitative morphological study and wall-to-wall nanostructure fabrication, but is not suitable for quantitative analysis due to the randomness in powder distribution, powder shape and the degree of contact. Inkjet printing provides a viable approach to produce periodic arrays of source in a scalable manner, which is particularly useful when the source material is not available as a sputtering target. To achieve high edge sharpness and reproducibility, the powder size, the ink recipe as well as the deposition parameters need to be further optimized. Picopump is a relatively easy way to produce porous film source with sharp edges. It is suitable for different powders with relatively large size, but the film shape uniformity and the location accuracy is usually poor. In this manuscript, all these three techniques are used for sample preparation to meet different research purposes.
Figure 2.1: Dopant source deposition using powder suspension method. (a) Three samples completely submerged in the water suspension droplets. (b) A qualitative examination of the contact angle between the water suspension and the weighting tray.

Figure 2.2: SEM images of the nanoislands prepared with the powder suspension methods in Eu₂O₃/YSZ(001) system. (a) Island forming around the source powder; (b) Higher magnification of the islands shows size and shape similarity. The sample was annealed at 1100 °C for 12 hr.
Figure 2.2 continued

Figure 2.3: A picture showing the MacroFab jetLab II inkjet printer and the printhead.
Figure 2.4: (a) A low magnification SEM image of an inkjet printed sample showing satellite drops and film irregularities. (b) A low magnification SEM image showing an attempt of making line source by overlapping the ink drops. The circular object is an aperture of the SEM.
Figure 2.5: (a) A low magnification SEM image showing a successful production of Eu$_2$O$_3$ film arrays with the inkjet printing technique; (b) A high magnification SEM image of the source edge showing reasonably good edge sharpness before annealing; (c) Typical surface morphology around the source edge for YSZ(001) after annealing. The boundary between the source and the nanostructure is still identifiable in this case. (d) An SEM image of another sample prepared by inkjet printing showing poor edge quality.
Figure 2.5 continued

(c)

(d)
Figure 2.6: A picture showing the PV830 Pneumatic Picopump and the capillary tip.\textsuperscript{48}

Figure 2.7: (a) A low magnification SEM image of a Eu$_2$O$_3$ film deposited using the Picopump; (b) A higher magnification SEM image showing three morphological zones of the film upon drying; (c) A high magnification of the film edge showing fine powder and sharp edge.
Figure 2.7 continued
Chapter 3: Step Faceting and Nanostructure Formation on Miscut YSZ Surfaces

3.1 Introduction

In Chapter 1, we reviewed several techniques that can be used to improve the order of the self-assembled nanoislands in semiconductor systems. Compared with the semiconductor systems, REO/YSZ system seems to have a higher intrinsic capacity for ordering, as the nanostructures tend to show certain degree of self-alignment. It is therefore interesting to see whether the order of these nanostructures can be further improved using the previously mentioned techniques. The self-assembly of nanostructures in REO/YSZ system, however, differs from the semiconductor nanoisland fabrication as the process does not necessarily involve any thin film deposition. This rules out the option of growing multilayers under current experimental setup and directs us to the strategy of creating ordered templates. Compared with other templates, surface steps can be easily produced by off-axis polishing or miscutting crystalline substrates without compromising the spontaneity and scalability of self-assembly. The major challenge of this methodology lies in the template development, as the steps created by miscutting are usually in atomic scale. In order to show the ordering effect, it is believed that the period of the template must be comparable to the size of the nanostructures. Ansari made the first exploration in this strategy by spreading GDC powder onto the as-purchased YSZ(001)-[100]^{10^9}(Type II) substrate. His observation revealed the possibility of producing bunched step arrays on
YSZ(001) during heat treatment. Correlation between the islands and the steps were also observed, although the steps themselves are zigzag in his case. He concluded that <110> are the favored step orientations on miscut YSZ(001) and the occurrence of zigzag steps is due to the improper miscut orientation of the substrate.

In this Chapter, we present the successful production of straight step arrays in two different crystallographic orientations on miscut YSZ(001) surfaces. We further demonstrate that using self-organized step arrays as templates can significantly improve the alignment of the nanoislands on YSZ surfaces, and 2D ordered surface patterns can be produced by synergetic effects of island-step and island-island interactions. Moreover, we show that the zigzag steps reported in Ansari’s work are not intrinsically stable and are in fact introduced by doping. Observations on (110)-[11̅0] miscut YSZ substrate (Type III) will also be presented.

3.2 Experimental procedures

Single crystal 8 mol% YSZ substrates were purchased from MTI Corporation (Richmond, CA) with one side mechanically and chemically polished to achieve the following three different types of surface orientations: (a) (001) miscut about [110] rotation axis by 2° (defined as Type I miscut substrate); (b) (001) miscut about [100] rotation axis by 10° (defined as Type II miscut substrate). (c) (110) miscut about [11̅0] rotation axis by 2° (defined as Type III miscut substrate). The tolerance in the miscut angle is +/- 0.5°. The substrates were pre-annealed in a box or tube furnace in air after cleaning with the standard procedures described in Chapter 2. The pre-annealing conditions and its effect will be
discussed in the following section. Eu$_2$O$_3$ source was dispersed onto the pre-annealed substrates via the powder suspension method or the inkjet printing method. Before applying the source, the substrates were usually sonicated in DI water for 5 min to remove possible contamination from the pre-annealing or storage. Nanostructure was fabricated in a similar manner as described before. The annealing conditions for each sample will be specified in the context. The surface morphologies of the samples were characterized on FEI Sirion FEG-SEM (Hillsboro OR, USA) or under the tapping mode of the Bruker Atomic Force Microscope (Santa Barbara CA, USA). For the SEM characterization, the samples were coated with a thin layer of Au before taking SEM images.

3.3 Step bunching and nanostructure growth on Type I miscut YSZ surfaces

3.3.1 Surface morphology of as-purchased miscut YSZ substrates

Before any further processing, it is important to know the surface morphology of the substrates in the as-purchased form. Figure 3.1a shows an SEM micrograph of an as-purchased Type I miscut YSZ substrate. At this high magnification, the surface looks smooth and no other features were observed except for the cracks in the Au coating layer. In order to capture finer features which might be buried under the Au, a substrate of the same type was examined under the AFM (Figure 3.1b). Similarly, we observed a pretty smooth surface profile and no apparent surface steps were observed within the resolution limit. The variation in feature height is in the scale of angstrom, which is consistent with the manufacturer’s description that the surface roughness is below 5 Å. This type of surface morphology was representative for all as-purchased YSZ substrates regardless of the
surface orientation. We use this as a reference for the morphological studies on YSZ surfaces.

### 3.3.2 Step bunching on Type I miscut YSZ surfaces

The morphology of the as-purchased substrates suggest that the surface steps created by miscutting are in atomic scale. In order to develop the surface and to remove any possible inhomogeneity from the manufacturing, we pre-annealed the substrates in air without applying and REO source. Compared with our typical heat treatment for nanostructure growth, the pre-annealing was conducted at higher temperature for longer time so that the effect of the following heat treatment on substrate morphology becomes minor. In our early explorations, the pre-annealing time was fixed at 25 hr. It was found that a relatively low pre-annealing temperature (~1175 °C) will result in limited step bunching, while a high temperature (~1300 °C) can raise the discontinuity or the curviness of the steps. The optimal pre-annealing temperature was found to be 1250 °C for Type I miscut YSZ substrates, and this pre-annealing temperature was therefore used for all the subsequent samples. Figure 3.2a shows the surface morphology of a Type I miscut YSZ substrate pre-annealed at 1250 °C for 25 hr. Under these annealing conditions, the substrate produces arrays of sharp steps with an average period of 90 nm. The steps lie along [110] direction in plane, which is consistent with the miscut axis. The steps are not always perfectly straight and may occasionally have branches, as indicated by the arrow-marked regions in this picture.

Figure 3.2b shows the AFM image of another Type I miscut substrate pre-annealed under the same conditions. The step morphology is consistent with Figure 3.2a, but we do
observe some local variation in the step period. The average step period for this region is 100 nm, while the average step height is around 2 nm. Figure 3.2c shows a 3D AFM image of several well-formed steps as indicated by the marked region in Figure 3.2b. It can be seen that these steps are strongly faceted and the length of the slopes are not equal. It is believed that the longer slopes are essentially the (001) terraces while the short slopes are the step bunches. The ratio of their lengths is approximately 3:2 in this case. Based on this ratio and the average step height and spacing, we estimate an apparent miscut angle of 1.9°, which is within the ±0.5° tolerance of the manufacturer. These observations clearly show that the heat treatment does facilitate the bunching of the steps, and the in-plane orientations of the step arrays are dictated by the miscut orientation when dopant source is absent.

To explore whether the step period varies with the pre-annealing time, we produced five samples at 1250 °C for 16, 25, 36, 64 and 81 hr. It was found that the straight [110]-step morphology is stable up to 64 hr and the average step periods only change slightly within 80-110 nm, if any. The local step period, however, can have much larger variations, which makes the resulting average periods dependent on the selection of the area of interest. Due to the large error bar, we do not go further and perform the quantitative kinetic analysis in this work. It should be noted that the steps do show some morphological evolution during the annealing. The steps on the 16-hr sample seem to be less faceted than the 25-hr sample (Figure 3.3a), while the 81-hr sample shows a totally different surface morphology (Figure 3.3b). These observations suggest that the straight [110]-step
morphology is metastable and the template stability must be taken into consideration if the subsequent heat treatment becomes radical.

3.3.3 Nanostructure growth on pre-annealed Type I miscut YSZ surfaces

In this section, we demonstrate that the step bunches can be used as template to guide the formation of the nanostructures in REO/YSZ system. For this purpose, Type I miscut YSZ substrates were pre-annealed at 1250 °C for 25 hr before the Eu₂O₃ source dispersion via the powder suspension method. The samples were then annealed at 1050 °C for 12 hr to grow nanoislands, and the resulting island morphology was shown in Figure 3.4a. It can be seen that the island alignment along the steps direction, i.e., [110] in plane, is significantly improved. This improvement in order is also reflected in the Fast Fourier Transformation (FFT) of this image as shown in the inset of Figure 3.4a. Our observations on Type I miscut YSZ clearly shows that using aligned surface step arrays to guide the self-assembly is an effective strategy to improve the order of self-assembled nanostructures. Figure 3.4b shows the island morphology on this sample at a higher magnification. Apart from the remarkable alignment, we also observed other features such as the arrow-indicated short bars. The right part of this image shows an extra row of the islands. This defect corresponds to the step branching phenomenon in the template as indicated by Figure 3.2a. It can be inferred that the steps have pretty strong templating effect on the island formation, and the initial template quality is very important to the resulting island morphology.

Figure 3.4c shows an SEM image of the island growth front where both the initial islands and the surface steps can be seen. The initial islands here have a rectangular shape with the long axis along the steps. Careful examination of this region reveals that the islands
tend to form on the step edges rather than on the terraces between the steps, which sheds light on the origin of the alignment. We can also see in this picture that the [110]-steps remain straight beyond the growth front, indicating this type of template is stable with the presence of the dopant. Similar phenomenon is also captured in the AFM image as shown in Figure 3.4d. The arrow marked region clearly shows a row of initial islands forming on the outside step edges. These islands are smaller than the well-formed islands nearby and their height is below 10 nm. We can also see that the steps become indistinguishable near those well-formed islands and the surface beneath seems to be lower than other locations. This is consistent with previous theory that the islands form by mining materials from the surrounding areas.

Apart from the islands, we also observed the bar morphology in Figure 3.4c. This phenomenon is universal on Type I miscut YSZ surface and we have observed the bar morphology in multiple samples prepared under the same annealing conditions. Unlike the flat YSZ(001) surface where the bar morphology is only occasionally observed at the growth front, the bars on Type I miscut YSZ surface seem to be much more stable and they do not necessarily occur at the growth front. Even on the same sample, the bars can form at the growth front, between source and front or do not form at all (Figure 3.5a-c). The fact that the bar has a bone shape seems to indicate that the bar is breaking up to form individual islands. However, whether this bar will actually break up during longer heat treatment is debatable because the bone shape may only represent a transition in local morphological stability which could be time independent. It seems that miscutting the substrate has broken the four-fold symmetry of the YSZ(001) surface and the stability of the bar morphology
becomes comparable to the islands. With the formation of the step bunches, critical factors such as the elastic interaction, the surface diffusivity or the surface energy of the system may have been fundamentally changed.

3.4 Step bunching and nanostructure growth on Type II miscut YSZ surfaces

3.4.1 Step bunching on Type II miscut YSZ surfaces

We performed pre-annealing on Type II miscut YSZ surface in a similar manner. This type of miscut YSZ substrate has a different miscut orientation as well as a larger miscut angle, therefore a different step morphology is expected. Figure 3.6a-c shows the surface morphology of Type II miscut YSZ substrate after pre-annealing at 1250 °C for 16 hr, 25 hr and 49 hr, respectively. In all cases, straight steps along the miscut axis, i.e., [100] in plane, were observed. It can be seen that the steps on this type of miscut YSZ surface are less faceted than those on the Type I miscut YSZ substrate and one can hardly identify a sharp edge for each step. On the 16-hr sample, we see many branching events which resembles the behavior of the steps on Type I miscut YSZ surface (Figure 3.6a). With the increasing annealing time, the steps become straighter and more faceted (Figure 3.6b-c). This morphological evolution indicates that the surface has not reached thermodynamic equilibrium even with long time annealing, but the straight [100]-step morphology is favored on bare Type II miscut YSZ surface. The period of the steps, in general, does not show any significant change among these samples. It should be noted that the Type II miscut YSZ substrate is identical to what Ansari had used in his preliminary investigation on miscut YSZ, and our observations directly contradict with his argument that <110>
zigzag steps (Figure 1.11a) are intrinsically stable on this type of miscut YSZ surface. One possible explanation for this contradiction lies in the differences between our experimental procedures and Ansari’s. Our observations are based on the pre-annealing experiments performed on bare Type II miscut YSZ substrates while in his case, the substrate is not pre-annealed and the surface is covered by high areal density of GDC powders. Although islands are not present in Figure 1.11a, this region may still be within the diffusion zones of the nearby GDC sources. In order to show the intrinsic behaviors of the substrate, one has to find an unaffected region far away from the dopant source. We will further explore and discuss this step morphological transition in the following section.

3.4.2 Doping induced step faceting on Type II miscut YSZ surfaces

To examine the origin of the inconsistency in the step morphology, we produced a sample with the inkjet defined Eu$_2$O$_3$ source on as-purchased Type II miscut YSZ substrate. Here we arranged the source into arrays of sparse dots as shown in the inset of Figure 3.7a. The sample was then annealed at 1125 °C for 25 hr to grow islands. In this case, the spacing between these sources are so large that the diffusion zones around them essentially do not overlap. Figure 3.7a shows the surface morphology of a region far away from the source where [100]-oriented steps were present. It can be seen that the step morphology is quite similar to Figure 3.6b, even though the heat treatment temperature is 125 °C lower. It seems that the temperature requirement for step bunching on Type II miscut YSZ is lower than that for the Type I miscut YSZ, which is probably due to its large miscut angle. This observation further confirms that the stable step configuration on bare Type II miscut YSZ is [100]-straight step rather than <110>-zigzag step. Figure 3.7b shows the surface
morphology near the island growth front where we captured an interesting step morphological evolution. It can be seen that the initial [100]-steps start to facet when it gets closer to the source (on the left), and they eventually decompose into the zigzag step morphology at the very front of island growth. Similar morphological transitions are also captured by the AFM as shown in Figure 3.7c. The zigzag steps have their edges parallel to <110>, which is consistent with Ansari’s observation. The convex of these faceted steps always points toward the lower steps, which is dictated by the miscut direction. Since the zigzag steps are strongly correlated with the source, it can be inferred that the step faceting is induced by the doping process on YSZ surface. Figure 3.7d shows surface morphology at the island growth front. It can be seen that the initial islands tend to form at the outside step corners, which is consistent with Ansari’s observation in Figure 1.11b. The fact that the faceting occurs beyond the island growth front indicates that the actual diffusion zone could be much larger than the apparent reaction zone. The order of these islands, however, does not show much improvement in this case. This is because the template is not well-developed before the island growth while the zigzag steps themselves also have some variations in the degree of faceting. This irregularity can also be observed in the AFM image, as shown in Figure 3.7e.

The observations on this sample provide a good explanation to the previous contradiction in the step morphology, as both the <110>-zigzag and the [100]-straight step morphology can occur on Type II miscut YSZ surface. What Ansari has observed is essentially the surface morphology not too far away from the source while the intrinsically stable step configuration on bare Type II miscut YSZ is the [100]-steps. Considering
previous results on Type I miscut YSZ, it can be concluded that the stable step orientation on bare miscut YSZ(001) surface is dictated by the miscut axis. On the doped miscut YSZ(001) surfaces, we observed a doping induced step faceting from [100]-steps to <110>-zigzag steps only on Type II miscut YSZ substrate. It can be inferred that the stability of the templates is dependent on the in-plane crystallographic orientation with <110>-steps being the most stable configuration on doped miscut YSZ(001) surface. The mechanism for this faceting has not yet been established at this stage. Our hypothesis is that the doping alters the step-energy anisotropy, and this in turn reverses the hierarchy of step energies for <100> vs. <110> inclinations, leading to the decomposition of straight <100> steps into zigzag <110> segments of lower energy/length to compensate for the increased step length upon faceting. However, the step decomposition itself may be an analogue to the island formation, as it involves rearranging/diffusing material from the inside (or re-entrant) corners to the outside (or convex) corners of the zigzag pattern. By analogy with the mounding up of doped islands, we might expect the outside corners to be built up of doped material. It should also be noted that the zigzag step arrays are not randomly arranged, and adjacent zigzags are typically “out-of-phase” (Figure 3.7f), which is an indication of elastic interactions between these steps. Indeed, the observed correlation of 3D islands with the outside corners of zigzag steps might be an indication that the same basic processes are responsible for both the island and the zigzag step formations. These hypotheses need to be examined by future studies, and a computational model involves both the elastic interactions and the composition dependent surface/step energy anisotropy is warranted.
3.4.3 *Nanostructure growth on pre-annealed Type II miscut YSZ surface*

Our previous observations suggest that the Type II miscut YSZ surface is undergoing several different morphological evolutions when annealed with the $\text{Eu}_2\text{O}_3$ source. First of all, the substrate itself is undergoing a step bunching process, which will result in straight steps along $[100]$. Meanwhile, the steps tend to facet and form $<110>$ zigzag steps when the diffusion front reaches. Finally, there is nanoisland growth taking place, which could be faster or slower than the step development. To simplify this scenario, we pre-annealed the substrate without $\text{Eu}_2\text{O}_3$ so that the step bunching becomes marginal during the subsequent heat treatment. This brought us to the following immediate questions: (1) Does the doping induced step faceting still occur when the steps have been well-developed? (2) Can we use the pre-annealed Type II as a template to improve the order of the islands? These questions will be addressed by our experiments presented in this section.

For all the samples, the substrates were pre-annealed in air at 1250 °C for 48 hr.

Figure 3.8a shows the surface morphological evolution of a sample annealed with inkjet defined $\text{Eu}_2\text{O}_3$ source at 1125 °C for 16 hr. In this case, the source is on the right side of this area of interest. It can be seen that the islands exhibit a general order improvement while the growth front also shows some step faceting. Figure 3.8b shows an SEM image of the same sample where the step faceting is clearly observed. The arrow marked region shows a row of initial islands forming on the outside corners of the zigzag steps, which is consistent with previous observation on as-purchased Type II miscut YSZ surface. Beyond the diffusion front, we see the straight $[100]$-steps formed during pre-annealing. This result indicates that the doping induced step faceting can also occur on well-formed steps. The
zigzag steps on this sample seem to show better alignment along [100] than those in Figure 3.7d. It can be inferred that the formation of the [100]-steps during pre-annealing improves the alignment of the zigzag steps, which further result in an improvement in island order.

Figure 3.9a-c show the island morphological evolution of a sample annealed with inkjet defined Eu₂O₃ source at 1125 °C for 1 hr. For these images, the source is on the left side and the distance from the center of each picture to the source edge is 1 μm, 3 μm and 5 μm, respectively. Combining these three images, we see a clear morphological evolution from connected islands to individual islands with decreasing structure height. In the center portion of the reaction zone (Figure 3.9b), we observed individual islands with remarkable alignment along [100]. This result confirms that Type II miscut YSZ substrate can also be used as a template to guide the island self-assembly. In fact, this type of substrate may be superior than Type I miscut YSZ in terms of order improvement as the islands tend to exhibit a pseudo-hexagonal 2D arrangement (Figure 3.9d). However, for this sample, we did not observe a clear step faceting phenomenon at the growth front (Figure 3.9c). This observation suggest that the zigzag steps are not a necessity for order improvement. It also does not contradict with our previous conclusion that the doping induced step faceting can take place on well-formed steps, as the steps next to the growth front in Figure 3.9c already show some morphological differences from those far away from the source. A possible explanation for the absence of the zigzag steps on this short-time-annealing sample is the competition between the step faceting kinetics and the island growth kinetics. We can assume these two processes take place independently, and the step faceting takes certain amount of time once the diffusion front reaches there. Initially, the island growth kinetics
is much faster than the step faceting and the islands already start to form before the zigzag steps occur. This will result in the absence of the zigzag steps as we observed in Figure 3.9c. For longer heat treatment, the island growth kinetics may slow down quickly while the step faceting kinetics do not change much. At some point, the step faceting start to occur before the island formation, which result in the observation in Figure 3.8b.

Based on the above-mentioned observations, we conclude that the improvement in pattern order on pre-annealed Type II miscut YSZ surface is achieved via two-dimensional confinement provided by the surface steps along [100] and the island self-alignment along <110>. In order to form this type of pattern, strong island-island elastic interaction between neighboring rows must present while proper step spacing also plays an important role by tuning the strength of such interaction. It should be noted that this improvement in order may also come with a side effect on the individual island shape, which is indicated by the islands with distorted square shape or rounded corners in Figure 3.9d. While the defects of the template are also reflected by the island arrangement, the short-bar morphology is not observed in this case. This may be considered as another advantage of using [100]-steps as the template.

3.5 Step bunching and nanostructure growth on Type III miscut YSZ surface

To explore whether the same technique can be used to improve the alignment of the nanobars, we used another type of miscut YSZ substrate for nanostructure growth. Ideally, this type of substrate will create straight step along the long axis of the nanobars, i.e., [1\(\overline{1}0\)] in plane upon pre-annealing. However, our preliminary investigation shows no
evidence of step bunching under multiple pre-annealing conditions from 1175 °C to 1450 °C. Nanobar growth on as-purchased Type III miscut YSZ surface also shows identical surface morphology as the non-miscut YSZ(110) samples. This result seems to suggest that either the substrates are not properly miscut, or the step bunching is intrinsically unfavored on miscut YSZ(110). Indeed, the mechanism for step bunching on ceramic surfaces has not been well-understood so far, and there is no reason to expect step bunching on arbitrary miscut ceramic surface.

3.6 Conclusions

In summary, we have successfully produced straight step arrays on two different types of miscut YSZ(001) surfaces. It was found that the stable step orientation on bare miscut YSZ(001) surface is dictated by the miscut axis. On the doped miscut YSZ(001) surfaces, we observed a doping induced step faceting from [100]-steps to <110>-zigzag steps only on Type II miscut YSZ substrate. We believe that the doping has altered the step-energy anisotropy, while the elastic interactions between the steps also played an important role. We further demonstrated that using self-organized step arrays as templates can significantly improve the alignment of the nanoislands on YSZ surfaces, and 2D ordered surface patterns can be produced by synergetic effects of island-step and island-island interactions. It would be interesting to see whether we can successfully apply the same strategy on YSZ(110) and YSZ(111) surfaces in the future. A deeper mechanistic understanding on the step bunching phenomena on ceramic surfaces will also greatly benefit our template development processes.
Figure 3.1: (a) SEM image of an as-purchased Type I miscut YSZ substrate showing cracks of the Au coating layer only. (b) AFM image of an as-purchased Type I miscut YSZ substrate showing a smooth surface profile.

Figure 3.2: (a) SEM image showing the surface morphology of a Type I miscut YSZ substrate pre-annealed at 1250 °C for 25 hr. (b) AFM image showing the morphology of another Type I miscut YSZ substrate prepared under the same conditions. (c) A 3D AFM image of the marked region in Figure 3.2b.
Figure 3.2 continued

(b)

[110]

2.0 nm

-1.9 nm

400.0 nm

(c)

59
Figure 3.3: (a) SEM image showing the surface morphology of a Type I miscut YSZ substrate pre-annealed at 1250 °C for 16 hr. (a) AFM image showing the surface morphology of a Type I miscut YSZ substrate pre-annealed at 1250 °C for 81 hr.
Figure 3.4: (a) Islands on pre-annealed Type I miscut YSZ substrate showing remarkable alignment along the step direction. The substrate was pre-annealed at 1250 °C for 25 hr without dopant source followed by annealing with Eu$_2$O$_3$ powder at 1050 °C for 12 hr. Inset shows a Fast Fourier Transformation pattern of this region. (b) A higher magnification SEM image showing the island morphology and the defects. (c) Islands and straight steps on Type I miscut YSZ substrate. Arrow-marked region shows a new generation of islands forming on the step edges. (d) An AFM image showing the step-island correlation and the surface morphology at the growth front.

Continued
Figure 3.4 continued
Figure 3.5: SEM images of three different regions on the same Type I miscut sample showing (a) bar morphology at the growth front; (b) bar morphology between the source and the growth front; (c) islands without bar morphology.
Figure 3.6: SEM images showing the surface morphology of Type II miscut YSZ substrate after pre-annealing at 1250 °C for (a) 16 hr; (b) 25 hr; (c) 49 hr. (d) 3D AFM image showing the step morphology on Type II miscut YSZ surface after pre-annealing at 1250 °C for 48 hr.

Continued
Figure 3.6 Continued
Figure 3.6 Continued

Figure 3.7: (a) Surface morphology of a region far away from any inkjet printed Eu$_2$O$_3$ source on a Type II miscut YSZ substrate. The sample was annealed at 1125 °C for 25hr. Inset shows arrays of inkjet defined source and the relative positions of the regions presented in (a) and (b); (b, c) SEM and AFM images showing the dopant induced step faceting at the island growth front. (d, e) SEM and AFM images showing the surface morphology at the island growth front. (f) A schematic plot showing the “out-of-phase” arrangement of the zigzag steps. The blue lines represent the original [100]-steps before faceting.
Figure 3.7 continued

(b)

[110]

[\bar{1}10]

2 \, \mu m

(c)

Continued
Figure 3.7 continued
Figure 3.8 (a, b) AFM and SEM images showing the surface morphological evolution of a pre-annealed Type II miscut sample. The substrate was pre-annealed without dopant source at 1250 °C for 48 hr followed by annealing with inkjet defined Eu$_2$O$_3$ source at 1125 °C for 16 hr.
Figure 3.9: (a-c) AFM images showing the surface morphological evolution of a pre-annealed Type II miscut sample. The substrate was pre-annealed without dopant source at 1250 °C for 48 hr followed by annealing with inkjet defined Eu₂O₃ source at 1125 °C for 1 hr. (d) A high magnification SEM image of the center portion showing a pseudo-hexagonal 2D arrangement of the islands.
Figure 3.9 continued
Chapter 4: Kinetic Analysis of Nanostructure Growth

4.1 Introduction

Surface diffusion is an important factor of the nanostructure formation in REO/YSZ systems. In Rauscher’s and Ansari’s work, the dependence of the nanostructure morphology on the annealing temperature and time was qualitatively studied with the lithographically defined source in the GDC/YSZ system. It was generally concluded that higher annealing temperature and longer annealing time will result in more coarsened structures and wider extension. It was also believed that the nanostructure growth is limited by the surface diffusion kinetics, which was often assumed to follow the simple parabolic diffusion law – $x \sim \sqrt{Dt}$. However, many of our previous experimental results show that the extension of the nanostructures does not increase rapidly, especially on YSZ(001). Under the typical annealing conditions, the extension of the nanostructure around an isolated source is always around 2-5 μm. In order to understand this phenomenon, the growth kinetics of the nanostructure must be studied systematically and quantitatively. In this chapter, we investigate the growth kinetics of the nanoislands and nanobars on non-miscut YSZ substrates by performing isothermal time evolution experiments with Picopump deposited Eu₂O₃ sources. The reason why GDC was not used is because it contains both Gd³⁺ and Ce⁴⁺, which may complicate the diffusion kinetics. The
morphological evolution of the nanostructures and the anisotropic behavior on YSZ(110) surface will also be discussed.

4.2 Experimental procedures

Eu$_2$O$_3$ was deposited onto the YSZ(001) or YSZ(110) substrate via the Picopump deposition system as described in Chapter 2. Samples were placed in an alumina combustion boat and an alumina covering piece was used to prevent possible contamination from the furnace chamber. Annealing was performed in a tube furnace with a 10 °C/min ramp up rate. Upon reaching the preset annealing time, the boat was immediately hooked away from the heating zone and the samples were let cool in air. For YSZ(001) and YSZ(110), the annealing temperature was set to 1125 °C and 1180 °C, respectively, and the annealing time was varied to investigate the growth kinetics of the nanostructures. The surface morphologies of the samples were characterized on FEI Sirion FEG-SEM (Hillsboro OR, USA). The samples were coated with a thin layer of Au before taking SEM images.

4.3 Growth kinetics on YSZ(001) at 1125 °C

This section presents the growth kinetics of nanoislands on YSZ(001) surface at 1125 °C. For this purpose, four samples were annealed for 1 hr, 4 hr, 16 hr and 49 hr and the extension of the reaction zones were measured from the SEM images. Figure 4.1-4.4 show the resulting island morphology of these samples. In all four samples, there is an island morphological evolution with the increasing distance from the source edge. By
morphology, we can empirically divide the reaction zone of each sample into three parts. Closest to the remnant powder is Zone 1, where we see a dense layer of film without powder or islands. This zone, however, can be part of the original Eu$_2$O$_3$ film which is partly consumed during the doping process. An observation supporting this argument is the absence of this zone in the powder suspension samples. From Figure 2.7 we also learned that the edge of the Eu$_2$O$_3$ film consists of very fine powder, which may sinter and partly dissolve to form this zone. The boundary between Zone 1 and Zone 2 is determined based on the onset of the pores. Zone 2 is essentially a layer of porous film formed by island coalescence. With the increasing distance from the source, the islands become less connected and more identifiable. The boundary between Zone 2 and Zone 3 is determined based on the onset of the individual islands. This boundary is sometimes difficult to identify and its determination is quite subjective. Zone 3 is basically the rest part of the reaction zone. Determining this zone sometimes can also be challenging due to the shallow features and local variations at the growth front. The actual zone division for these four samples are indicated in Figure 4.1-4.4.

We can qualitatively investigate the time evolution of the island morphology by making comparisons across the four samples. The square boxes in Figure 4.1-4.4 are 1 μm by 1 μm in size, and the distance between the center of each box to the corresponding Zone 1/Zone 2 boundary is fixed at 2.5 μm. For comparison, these regions were rescaled and combined into Figure 4.5. The images were also rotated so that the source is on the left side of these regions in all cases. Here we clearly see that the island is undergoing a growth and coalescence process with increasing annealing time. The initial islands are shallow,
rounded and have wider spacing. They grow bigger and more faceted during further annealing and it takes only several hours before they start to coalescence. The coalesced morphology is usually undesirable due to its irregularity. For practical island fabrication, it is probably better to use a lower annealing temperature in the future.

To understand the growth kinetics of the islands, we measured the extension of each zone, including Zone 1, for all four samples. The results for the measurement are presented in Table 4.1. We then plotted the extension of each zone (x) versus annealing time (t) in logarithm scale to determine the power of time dependence (n), as shown in Figure 4.6. Total extension of Zone 2 and Zone 3, as well as the total extension of all three zones, were also plotted for comparison. From the slope of the fitted lines, we learned that the power of time dependence for Zone 1, Zone 2 and Zone 3 are 0.50, 0.36 and 0.19, respectively. The power of time dependence for Zone 2+3 and Zone 1+2+3 are 0.28 and 0.31, respectively. In most cases, log x shows a strong linear dependence on log t, which means it is legitimate to depict the kinetics of the nanostructure growth with the $x \sim t^n$ model.

The results presented above clearly show that the general growth kinetics for the islands do not follow the parabolic law ($n=0.5$). The actual growth rate of the islands seems to be much lower than we expected, which explains the limited coverage of islands in our previous studies. The deviation of our measurements from the parabolic law is not hard to understand, as the parabolic relation is based on the assumption that the growth kinetics is limited by the longitudinal surface diffusion, which may follow the parabolic diffusion law under our current experimental setup. In fact, we have many previous observations indicating that the actual diffusion front may be far beyond the growth front of the
nanostructures. These observations include the doping induced step faceting on Type II miscut YSZ, and the occurrence of isolated nanostructures far away from the source as indicated by the arrow marked region in Figure 4.3. The fact that the diffusion front and the apparent growth front do not overlap indicates that the growth kinetics of the islands is probably not limited by the longitudinal diffusion kinetics. Since the nanostructures form by mining materials from the substrate, it is very likely that the rate limiting factor for the island formation is the local lateral surface diffusion. Moreover, the observation of multiple morphological zones on the surface indicates that even the longitudinal diffusion may not be as simple as the 1-D semi-infinite diffusion scenario. With all these structures forming on the surface, it is unlikely that the longitudinal surface diffusion can keep following the parabolic law without getting interfered by the local inhomogeneity. As a result, the diffusion coefficient may not be a constant along the longitudinal diffusion path. The arguments above only consider the diffusion on the surface. In reality, we still cannot completely rule out the effect of the bulk diffusion, which introduces even more complexity to this problem. Although the growth kinetics of the nanoislands cannot be described by a simple model, we can still use the empirical relation listed in Figure 4.6 to estimate the extension of the reaction zones under a given annealing time.

4.4 Growth kinetics on YSZ(110) at 1180 °C

4.4.1 In-plane anisotropic nanobar growth on YSZ(110)

The growth kinetics of the nanobars was expected to be different from that of the nanoislands due to the difference in substrate surface orientation. Before we discuss the
time evolution of the bar extension, we first present an interesting observation of anisotropic nanobar growth on YSZ(110) surface. Figure 4.7a shows the morphology of the nanobars prepared by the Picopump technique. In this case, the source edge can be easily identified by the onset of the porous morphology. This is consistent with our previous hypothesis that Zone I on YSZ(001) belongs to the source rather than the reaction zone. With the increasing distance from the source edge, the dopant concentration decreases and the nanobar morphology becomes visible. The initial bars are narrow, choppy and close-packed. Their period increases with the distance from the edge and the total number of bars decreases. They grow in [1\bar{1}0] direction, which almost coincides with the longitudinal diffusion direction (i.e., perpendicular to the source edge) in this case. The average extension of the bars is \( \sim 8 \ \mu\text{m} \) for this region. Figure 4.7b shows another region of the same sample where the diffusion direction does not align with [1\bar{1}0]. The fact that the extension of the bars, \( x \), becomes much smaller (\( \sim 4 \ \mu\text{m} \)) indicates that the nanobar growth is anisotropic in plane. When the angle between the longitudinal diffusion direction and [1\bar{1}0], \( \theta \), further increases, the bar extension becomes even smaller and it reaches minimum when \( \theta \) equals to 90°. (Figure 4.3c). To quantify this phenomenon, we measured the bar extension in multiple regions across the sample and the results are presented in Table 4.2. As a first approximation, we assumed that the nanobar growth follows the parabolic rate law:

\[
x^2(\theta, t) = K(\theta)t
\]
Where $K(\theta)$ is a rate constant which is anisotropic in plane. We further assume that the growth is diffusion limited and the rate constant is proportional to the diffusion coefficient in that direction. For a specific sample where $t$ is constant, we have

$$x^2(\theta) = K(\theta)t \propto D(\theta)$$

It is a well-known fact that the surface diffusion on (110) surface of a fcc crystal can exhibit directional anisotropy due to its two-fold crystallographic symmetry. In this case, the diffusion along the close-packed direction, $[1\overline{1}0]$, is expected to be faster than the diffusion along the transverse [001] direction. Let $\theta$ be the angle between the actual diffusion direction and $[1\overline{1}0]$, the diffusion coefficient in arbitrary direction in-plane can then be written as:

$$D(\theta) = D_{max} \cos^2 \theta + D_{min} \sin^2 \theta$$

which is equivalent to:

$$D(\theta) = \frac{D_{max}+D_{min}}{2} + \frac{D_{max}-D_{min}}{2} \cos 2\theta$$

where $D_{max}$ is the diffusion coefficient in $[1\overline{1}0]$ direction and $D_{min}$ is the diffusion coefficient in [001] direction. This result suggests that if our previous assumptions are all valid, the following relation must hold for arbitrary direction:

$$x^2(\theta) = \frac{x_{max}^2 + x_{min}^2}{2} + \frac{x_{max}^2 - x_{min}^2}{2} \cos 2\theta$$

Where $x_{max}$ is the bar extension in $[1\overline{1}0]$ direction, $x_{min}$ is the bar extension in [001] direction and $\theta$ is the angle between the longitudinal diffusion direction and $[1\overline{1}0]$. Figure 4.8a shows a plot of the bar extension $x^2$ versus $\cos 2\theta$ based on our experimental measurement where we observe strong linear correlation. This result strongly supports our
hypothesis that the nanobar growth follows the parabolic rate law and the bar extension is dictated by the anisotropic diffusion in plane. To confirm our findings, we analyzed multiple samples with different annealing time (1 hr, 4 hr, 16 hr and 25 hr) at 1180 °C and the results are presented in an $x^2 - \theta$ polar plot as shown in Figure 4.8b. It can be seen that the measured data points are in good agreement with the fitted lines which depict the in-plane anisotropic behavior of a symmetric second rank tensor such as the diffusion coefficient on fcc (110) surfaces. This result again supports our previous hypothesis and the anisotropy factor, $x_{max}^2/x_{min}^2$, was found to be ~7. It should be noted that this analysis is not sufficient to prove parabolic growth kinetics. Our observation only indicates that $x$ is proportional to some symmetric second rank tensor at a fixed time. To examine whether the nanobar growth kinetics obeys parabolic growth kinetics, the time dependence of the nanobar extension also needs to be examined.

4.4.2 Time dependence

This section presents the time dependence of nanobar growth on YSZ(001) surface at 1180 °C. For this purpose, five Eu$_2$O$_3$/YSZ(110) samples were annealed for 1 hr, 4 hr, 16 hr, 25 hr and 49 hr and the extension of the reaction zones were measured from the SEM images. As we mentioned before, nanobar growth on YSZ(110) is anisotropic. In order to make fair comparison, we repeated the above-mentioned angular dependence analysis and extracted $x_{max}$ at $\theta=0^\circ$ and $x_{min}$ at $\theta=90^\circ$ for each sample. The results of these analyses are presented in Table 4.3. Figure 4.9 is the $x^2$-t plot showing the growth kinetics of nanobars at 1180 °C. The strong proportional relation between $x^2$ and t suggest that the nanobar growth kinetics does follow the parabolic law. Here we exclude the last data point.
for the 49 hr sample because its poor $x^2 - \cos 2\theta$ linearity and the significant lower $x_{\text{max}}$ value. From the slope of the fittings, we can roughly estimate the diffusion coefficients of Eu$^{3+}$ on YSZ(110) surface as $K_{\text{max}} = K_{<110>} = (7.0 \pm 0.6) \times 10^{-12}$ cm$^2$/s and $K_{\text{min}} = K_{<100>} = (9.5 \pm 1.2) \times 10^{-13}$ cm$^2$/s. These values have the same order of magnitude as Ansari’s estimation of surface diffusion coefficient which are 6 orders of magnitude higher than the bulk diffusivity values.\textsuperscript{41}

4.4.3 Dependence of the nanobar period on the diffusion distance

Another observation we made on YSZ(001) surface is the increasing nanobar period with the increasing distance from the source. This phenomenon can be clearly seen in Figure 4.10 which is a higher magnification of Figure 4.7a. To quantitatively analysis this phenomenon, we measured the average period of the bars ($\lambda$) versus the distance from the source edge ($x$). We know from Table 4.2 that the distance from the growth front to the source is 8207 nm and the angle $\theta$ is 2.6°. We can then measure the spacing between the growth front and each horizontal line to extract the distance values. The periods of the bars are calculated from the following equation:

$$\lambda = \frac{l}{n} \times \cos 2.6^\circ$$

where $l$ is the length of each horizontal line and $n$ is the number of the nanobars covered by the line. All these measured values are listed in Table 4.4.

The increase in the nanobar period can be qualitatively explained by the ATG analysis.\textsuperscript{22} According to the ATG theory, the following equation must be satisfied for the initiation of surface breakup:
\[ \sigma_0 \geq \left( \frac{2\pi E \gamma}{\lambda} \right)^{1/2} \]

where \( \sigma_0 \) is the applied stress, \( E \) is the Young’s Modulus, \( \gamma \) is the surface free energy and \( \lambda \) is a characteristic wavelength of the surface profile. If we assume constant \( E \) and \( \gamma \) with \( \lambda \) being the nanobar period, we will have

\[ \lambda^{-1/2} \propto \sigma_0 \propto \varepsilon \propto c \propto F = erf\left(\frac{x}{2\sqrt{Dt}}\right) \]

The second, third and fourth proportional relations are based on the Hook’s law, the Vegard’s law and the 1D semi-infinite diffusion model. At a given temperature and time, \( F \) will decrease with increasing \( x \). Since all the scaling factors here are positive, a decrease in \( F \) will result in an increase in \( \lambda \), which explains the increasing nanobar period observed in Figure 4.10. We have also made an attempt to quantitatively analysis this phenomenon.

If all the above mentioned assumptions are valid, the \( F \sim \lambda^{-1/2} \) plot should be a straight line passing through the origin. Figure 4.11 shows the \( F \sim \lambda^{-1/2} \) plot based on the actual measurement presented in Table 4.4 and the estimated \( D \) from previous analysis. The deviations of the data from the linear fitting and the non-zero intercept indicate that the actual mechanism of this phenomenon may not be that simple. Indeed, our analysis is based on a series of assumptions whose validity is not carefully examined. The period of the nanobar itself may not be equivalent to the characteristic wavelength after all, and the Vegard’s law may also need some modification for this multi-component system.
4.5 Conclusions

In this chapter, we performed quantitative analyses on the growth kinetics of the nanoislands and the nanobars. It was found that the nanobar growth kinetics obeys the parabolic law at 1180 °C, while the nanoislands on YSZ(001) exhibit a non-parabolic growth kinetics with the power of time dependence being 0.28 at 1125 °C. These relations can be used to estimate the extension of the reaction zones under a given annealing time. We also found that the nanobar growth on YSZ(110) is anisotropic in plane with [110] and [001] being the maximal and minimal growth directions. This result is consistent with the anisotropic surface diffusion scenario on fcc (110) surfaces. We further investigate the dependence of the nanobar periods on the distance from the source and a hypothesis based on the ATG analysis was proposed.
Table 4.1  Extension of the morphological zones in four samples with different annealing time

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<th>x1 (nm)</th>
<th>x2 (nm)</th>
<th>x3 (nm)</th>
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Table 4.2  Angular dependence of the nanobar extension in a Eu$_2$O$_3$/YSZ(001) sample annealed at 1180 °C for 25 hr

<table>
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<tr>
<th>Figure 4.7</th>
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<th>b</th>
<th>c</th>
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Table 4.3  The maximal and minimal extension of the nanobars for five Eu$_2$O$_3$/YSZ(110) samples annealing at 1180 °C for different time.

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Table 4.4  x and λ values measured from Figure 4.10

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Figure 4.1: SEM image showing the surface morphology near the edge of the porous Eu$_2$O$_3$ film on YSZ(001) after annealing at 1125 °C for 1 hr.

Figure 4.2: SEM image showing the surface morphology near the edge of the porous Eu$_2$O$_3$ film on YSZ(001) after annealing at 1125 °C for 4 hr.
Figure 4.3: SEM image showing the surface morphology near the edge of the porous Eu$_2$O$_3$ film on YSZ(001) after annealing at 1125 °C for 16 hr.

Figure 4.4: SEM image showing the surface morphology near the edge of the porous Eu$_2$O$_3$ film on YSZ(001) after annealing at 1125 °C for 49 hr.
Figure 4.5: A side-by-side comparison of the island morphoogies of the marked regions in Figure 4.1-4.4. These regions are equally distanced from the source (on the left for all four images) and the field of view is 1μm x 1μm.

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</tr>
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Figure 4.6: log x-log t plot with linear fitting showing the growth kinetics of the nanoislands at 1125 °C. The table inset gives the parameters of the fitted lines.
Figure 4.7: SEM image of three different regions with (a) \( \theta = 2.6^\circ \); (b) \( \theta = 70.9^\circ \); (c) \( \theta = 82.3^\circ \) showing the angular dependence of the nanobar extension on YSZ(110) surface. The sample was annealed at 1180 °C for 25 hr.
Figure 4.7 continued

Figure 4.8: (a) $x^2 - \cos 2\theta$ plot of the sample presented in Figure 4.7 showing strong linear dependence. The table inset gives the parameters of the fitted line. (b) $x^2 - \theta$ polar plot showing the anisotropic nanobar growth on four samples annealed at 1180 °C for different times (1 hr, 4 hr, 16 hr and 25hr).
Figure 4.8 continued

(b)
Figure 4.9: $x^2 - t$ plot for $x_{\text{max}}$ and $x_{\text{min}}$ with linear fitting showing the parabolic growth kinetics of the nanoibars at 1180 °C. The table inset gives the parameters of the fitted lines. Data points at 49 hr are considered as outliers and excluded.

Figure 4.10: A high magnification of Figure 4.7a with equidistance lines (1-5) showing the increasing nanobar period with the increasing distance from the source.
Figure 4.11: $F - \lambda^{0.5}$ plot based on the actual measurement presented in Table 4.4 and the estimated D from previous analysis.
Chapter 5: Nanostructure Growth in Different Annealing Gas Environment

The morphology of the nanostructures can be affected by several different factors. On one hand, we can select different combinations of powder and substrate orientation to obtain different features. On the other hand, we can control the feature size and extension by adjusting the annealing time and temperature. These factors have been extensively studied in Rauscher’s and Ansari’s work as well as in previous chapters of this document. For all the previous experiments, the heat treatment was performed in air and the effect of gas environment to the nanostructure formation was not investigated. In practice, different gas environment may have a deep impact on the nanostructure morphology, as it can change the surface adsorption species, the oxidation states and the stability of the materials. It may also affect the materials transport by alternating dominant diffusion species as well as their concentration. Another motivation of this part of research is originated from Ansari’s work on different REO sources. While most REO produce similar nanostructures on YSZ, CeO$_2$ source produces a very different morphology, as shown in Figure 5.1. Under similar annealing conditions, the islands formed in CeO$_2$/YSZ(001) system does not exhibit any size similarity or self-alignment. The common morphological transition from connected morphology to isolated islands is also not observed. Ansari attributed this exception to the difference in dopant species, as all the other REO dopants have +3 oxidation state while Ce has +4 oxidation state in CeO$_2$. This is a reasonable explanation...
because higher oxidation state also leads to a smaller ionic radius, which further affects the lattice mismatch and the stress field. In this chapter, we experimentally examined this hypothesis by performing the heat treatment in reducing atmosphere for CeO$_2$/YSZ system. The effects of gas environment on other REO/YSZ systems were also systematically investigated.

5.1 Experimental procedures

REO was deposited onto the YSZ(001) substrate using the powder suspension method as described in Chapter 2. The sample was then placed in an alumina combustion boat and an alumina covering piece was used to prevent possible contamination from the furnace chamber. The boat was placed in our specially designed 1500 °C tube furnace with two aluminum end caps to improve air tightness. The furnace chamber was connected to a mechanical pump and an Ar flush procedure was performed before annealing to remove the remnant air. 5%H$_2$-N$_2$ forming gas was used to create reducing gas environment. The gas flow rate was controlled by a digital flow meter with an instrumental control and data acquisition LabView program written in-house. The samples were typically annealed at 1000 °C for 16 hr with 10 °C/min ramp up rate and 5 °C/min cooling rate. Any deviation from this annealing condition will be specified in the context. The gas flow rate was set at 500sccm in all cases.
5.2 CeO$_2$/YSZ(001) in reducing atmosphere

Ce has two available oxidation states in compounds: +3 and +4. We have previously suspected that the abnormality in CeO$_2$/YSZ(001) is due to the difference in the oxidation states between CeO$_2$ and other REO. If this argument is true, we should expect nanoislands with similar morphology when using Ce$^{3+}$ as the dopant. Ce$_2$O$_3$ powder is very difficult to handle and preserve due to its high oxidizability and instability. However, it is reported in the literature that CeO$_2$ can be partly reduced in H$_2$ at a temperature above 800 °C, which is lower than our typical processing temperature. We can therefore verify our hypothesis by annealing the CeO$_2$/YSZ system in H$_2$ atmosphere. Figure 5.2a shows the morphology obtained by annealing CeO$_2$/YSZ(001) at 1000 °C for 16 hr. At lower magnification, the nanostructures look dense and are strongly correlated to the powder. The extension is not wide, which is probably due to the low annealing temperature. Compared to the Eu$_2$O$_3$ powder, the CeO$_2$ powder we used seems to be much finer. Figure 5.2b shows the higher magnification of the marked region in Figure 5.2a. A close examination of this region reveals a morphological evolution of the nanostructures, as the regions close to the source usually have denser and more connected structures than the region apart. This observation was consistent with other REO source and it is believed that the morphological evolution corresponds to the variation in dopant concentration. There is a distinct bimodal island morphology forming between different sources, where the large islands are typically 2-3 times bigger than the small ones. The small islands have a size of only 20 nm, which is much smaller than what we usually see in the GDC/YSZ(001) and Eu$_2$O$_3$/YSZ(001) systems. The edges of these islands are always aligned in the <110> directions. The fact
that some large islands have irregular polygonal shapes indicated that they form by small island connecting. While this morphology is quite different from the previous CeO$_2$/YSZ(001) sample annealed in air, it strongly resembles the low temperature La$_2$O$_3$/YSZ(001) morphology reported in Ansari’s work (Figure 5.3).

The above-mentioned similarity in the nanostructure morphology can be understood by comparing the ionic radii of the dopants, as shown in Table 5.1. It can be seen that Ce$^{4+}$ has significant smaller ionic radius than other lanthanide ions, while the ionic radius of Ce$^{3+}$ is very close to that of La$^{3+}$. The ionic radii of the dopants essentially dictate the lattice mismatch and therefore the strain energy which drives the island formation. It can be reasonably inferred that dopants with similar ionic radii will show similar behavior on YSZ, just like the Gd$^{3+}$ and the Eu$^{3+}$ which have been extensively used in previous studies. We therefore conclude that the forming gas environment can effectively reduce Ce$^{4+}$ to Ce$^{3+}$ and the latter dominates the nanostructure formation under this condition. The change in oxidation state from +4 to +3 may also have played an important role by affecting the charge and coordination characteristics of the dopant or the surface energy of the system.

5.3 Eu$_2$O$_3$/YSZ in different gas environment

5.3.1 Eu$_2$O$_3$/YSZ(001) at 1125 °C

As mentioned before, performing annealing in different gas environment may profoundly affect materials transport, materials stability and their surface properties. To further explore its impact on the nanostructure morphology, we applied the reducing
atmosphere to the Eu$_2$O$_3$/YSZ(001) system. In our first attempt, the dopant source was
deposited by the Picopump system and the annealing was performed at 1125 °C for 16 hr.
This annealing temperature and time combination is typical for our YSZ(001) samples
prepared in air, and the morphology of a sample prepared under these conditions has been
presented in Figure 4.2. Figure 5.4 shows the surface morphology of the source edge after
annealing the sample in the forming gas. Compared with Figure 4.2, the surface structures
look totally different and our typical island morphology is not observed. The most distinct
features on this sample are the particles and short bars which lay above the connected
morphological zone. At the first glance, one may suspect these are simply loose Eu$_2$O$_3$
powders which is similar to the case in Figure 2.5d. However, careful examination of these
features reveals that the particles are evenly distributed and strongly faceted, while the bars
seem to exhibit preferential alignment in <110> directions. These morphologies are quite
different from the typical morphology of sintered powders. The connected features beneath
show a morphological transition with the increasing distance from the source, but exhibit
no correlation with the particles. These observations suggest that the particles are more
likely single crystal new phase rather than sintered Eu$_2$O$_3$ powders. However, if the
formation of these structures only involves the substrate and the gas, we should be seeing
faceted particles all over the substrate surface. The fact that these particles only occur near
the source edge indicate that Eu$_2$O$_3$ must have been involved in this process. Based on
these observations, we come to the conclusion that the particles are likely to be a new Eu
containing phase which is stabilized by the reducing environment.
Once we rule out the possibility that the faceted particles are Eu$_2$O$_3$, we can approximately identify a source edge as indicated in Figure 5.4. By qualitatively comparing Figure 5.4 with Figure 4.2, we found that the apparent reaction zone in forming gas is larger than in air. There are several other features worth noting in Figure 5.4, which include the weird Eu$_2$O$_3$ powder morphology, the plate morphology at the film edge and the increasing porosity of the connected layer from the source to the growth front. In order to confirm that these structures are not originated from undetected contaminations or the ingredient of the ink, we reproduced a sample with the powder suspension method with other experimental conditions kept the same. Figure 5.5a shows a low magnification SEM image of this sample. Along with many other features, we see some long bars forming around the powders. The bars are 10-20 μm in length and most of them seem to have preferential alignment along certain crystallographic orientations. Figure 5.5b shows a high magnification of the region indicated by the smaller black rectangle. It can be seen that the bars are faceted and the surface is porous rather than smooth. Judging from the edge of the pores, we can empirically conclude that the bars align along <110> in this case. This is similar to the short bar morphology observed in the Picopump sample. Figure 5.5c shows the surface morphology of another region (indicated by the larger rectangle in Figure 5.5a) where the faceted particles and the plate morphology are observed. All these features form on top of a porous layer of connected structures and bare substrate surface can hardly be found on this sample. The fact that similar features occurred on both the Picopump and the powder samples confirms that the unique substances in the ink are not the cause of these distinct features. All these observations on the two samples indicate that the forming gas
environment does play a role in the nanostructure formation, and the reactions in forming
gas seem to be more drastic than in the air. Considering the inert nature of \( \text{N}_2 \) and its
existence in both air and forming gas, it is highly likely that the \( \text{H}_2 \) changed the
thermodynamics and kinetics of reactions on YSZ(001) surface. Instead of forming
nanoislands, new phases start to form under the given experimental conditions, which
results in the occurrence of totally different features. The extensive coverage of the
connected layer also indicates that the annealing temperature may be too high and milder
experimental conditions must be applied to produce isolated nanoislands.

5.3.2.1 Annealing in air

In order to produce islands rather than connected morphology in forming gas, we
reduced the annealing temperature to 1000 °C while keeping other experimental conditions
the same. Before discussing the experimental results in other gas environment, we present
the low-temperature nanoisland morphology of a \( \text{Eu}_2\text{O}_3/\text{YSZ}(001) \) sample prepared in air
(Figure 5.6a) This sample was annealed at 1000 °C for 16 hr, which is milder than our
typical processing conditions. It is evident that nanoislands do form at this lower
temperature, although their extension (≈2 μm) is not as large as the high temperature
samples. Figure 5.6b shows a higher magnification of a region between several powders.
The major characteristics of the islands are similar to other samples prepared in air except
for the smaller size (≈50 nm). We use this sample as a reference to investigate the effect of
the gas environment.
5.3.2.2 Annealing in forming gas

Figure 5.7a shows a low magnification SEM image of a sample annealed in forming gas at 1000 °C for 16 hr. The contrast of the image was adjusted to show the extensive coverage of the nanostructures. It can be seen that almost the entire substrate surface is covered by nanostructures, although the areal density of the islands varies from one region to another. There was a long straight line observed on the right side of the image, which corresponds to a scratch on the surface and will be discussed in Chapter 6. Figure 5.7b shows the typical surface morphology of the regions in bright grey color in Figure 5.7a. In this case, the nanostructures are pure islands and those faceted high-temperature morphologies are not observed. This image has the same magnification as Figure 5.6a and the improvement in nanostructure coverage can be clearly observed. Figure 5.7c shows a higher magnification of the islands. It can be seen that the islands are not always in square shape but can still grow wall-to-wall near the source. The islands are small in size and the degree of self-alignment is weak compared to the islands grown in air. Figure 5.7d shows the surface morphology of the regions far away from the source, which are essentially the relatively dark areas Figure 5.7a. Instead of seeing bare YSZ substrate, we observed islands which are sparsely distributed on the surface. The characteristics of these islands are similar to the ones in Figure 5.7c, however, they form randomly on the surface and do not grow wall-to-wall. This is an interesting observation as the dopant concentration is assumed to be monotonically decreasing when the distance from the source increases. If the rate limiting factor of nanoisland formation is surface diffusion, we should expect continuous nanoisland formation from the source to a growth front, as we see in most of the samples.
prepared in air. However, in this case, we see large empty space between these islands without any structure forming, while the diffusion must have reached there to feed these islands. It seems that the sparsely distributed islands are simply nucleating on random sites, while the diffusion front has already passed these regions. This is another observation indicating that surface diffusion is not the only deterministic factor in nanostructure formation.

Nanoislands produced in forming gas sometimes have minor variations in the morphology. Figure 5.8a shows the island morphology of another sample annealed under the same experimental conditions. Along with the extensive coverage and wall-to-wall growth, the islands exhibit a bimodal distribution in size. This phenomenon can happen via two mechanisms. On one hand, the difference in island size can be caused by the difference in island age. It is possible that the bigger islands formed first and have undergone some coarsening when the small ones start to form. On the other hand, it is possible that the islands are of similar size when they initially form, but some of them start to coalesce locally to form the bigger ones during the later growth. Figure 5.8b shows a higher magnification of the islands. It is observed that the bigger islands are usually twice as wide as the small ones, and they sometimes show shape irregularity. These observations lead us to believe that the bigger islands are more likely a result of the small island coalescence. The reason why these islands tend to coalesce locally remains unclear to date. The coalescence of islands is commonly observed at the vicinity of the dopant source where the dopant concentration is high. In this case, however, the dopant concentration is expected to be moderate and more or less uniform within this region, as the islands cover the entire
region and there is no Eu₂O₃ powder nearby. It seems that some areas within this region are locally activated, which is similar to the nucleation phenomenon we observed in Figure 5.7d. Figure 5.8c shows another region on this sample where the islands have size and shape similarities. A distinct feature of this region is the absence of nanostructures at the vicinity of the powder where the dopant concentration is supposed to be the highest. It is unclear to us what have caused the passivation of these regions. Understanding this phenomenon may require additional compositional and structural characterizations via TEM.

5.3.2.3 Annealing in argon

To further explore the role of the gas environment in nanostructure formation, we prepared one Eu₂O₃/YSZ(001) sample in Ar at 1000 °C for 16hr. Figure 5.9a shows a low magnification SEM image of this sample with the contrast adjusted to show the reaction zones. Compared with Figure 5.7a, the coverage of the nanostructures is much lower when the sample was annealed in Ar. Figure 5.9b shows the island morphology on this sample. In general, islands prepared in Ar have similar characteristics with the islands prepared in air as they both show size and shape similarity, wall-to-wall growth and certain degree of self-alignment. The extension of the reaction zone is usually 1-2 μm under the given temperature and time, which is much smaller than the forming gas samples.

The formation of nanoislands in Ar have several implications in the role of the gas environment. First of all, it confirms that N₂ does not play any significant role in the nanostructure formation, as both the air and the forming gas contain a significant amount of N2. Second, it shows that the growth of nanoislands is not sensitive to the oxygen partial
pressure. Previously we have suspected that oxygen may be a necessary ingredient in nanostructure formation, as the doping process must involve the transportation of both Eu and O. If the oxygen in the air is involved in this transportation, there might be a correlation between the island morphology and the oxygen partial pressure. The Ar we used in the experiments has an impurity level of 0.002%, which means the oxygen content in the gas is up to 20 ppm. Our experimental observations show that the morphology of the nanoislands prepared under this oxygen content is not that different from what we obtained in air, while the oxygen partial pressure has 4 orders of magnitude difference. However, we cannot completely rule out the effect of oxygen, as 20 ppm of oxygen may still be excessive for the nanostructure growth. The forming gas, on the other hand, has a much lower Po$_2$ and we do observe some variations in the nanostructure morphology. In this work we did not make any attempt to anneal the samples in pure oxygen. However, based on our observations in air and in Ar, we can reasonably expect that the island morphology obtained in O$_2$ will be similar to the air and Ar samples.

5.3.3 Nanoisland growth via different annealing route

Previously we have shown that using forming gas environment for heat treatment can improve the coverage of the islands. We also found the islands may exhibit size and shape irregularity, which is usually undesirable for practical applications. It then becomes interesting to see if we can improve the island coverage while maintaining the size and shape similarity by combining the air and the forming gas treatment during the annealing.
This usually involves multiple segments of heat treatment. For convenience, we use the following short expression to describe the experimental conditions for each segment:

Source/Substrate/Temperature (°C)/Time (hr)/Gas

For example, Eu$_2$O$_3$/YSZ(001)/1000/16/Forming gas simply means the sample is annealed the sample at 1000 °C for 16 hr in forming gas with the Eu$_2$O$_3$ source on YSZ(001) substrate. The so-called “pre-annealing” process for the Type I miscut substrate can then be described as Blank/Type I miscut/1250/25/Air. All the other procedures, such as the substrate cleaning, the heating and cooling rate and the gas flow rate remain the same.

5.3.3.1 Blank/YSZ(001)/1000/16/forming gas + Eu$_2$O$_3$/YSZ(001)/1000/16/Air

In our first attempt, we pre-annealed the YSZ(001) substrate in forming gas and then grew nanoislands in air at 1000 °C. The purpose of this experiment is to further examine if the H$_2$ is simply reacting with the YSZ substrate or helping the substrate surface development. Figure 5.10 shows the resulting island morphology of this sample, which is quite similar to what we have observed from the air or Ar treatment. This observation confirmed that H$_2$ was not irreversibly modifying the substrate surface during the pre-annealing. It is also consistent with our previous hypothesis that the interaction between the gas and the powder played a key role in the morphological variation.

5.3.3.2 Eu$_2$O$_3$/YSZ(001)/1000/16/forming gas + Eu$_2$O$_3$/YSZ(001)/1125/2/Air

In this part of work, we applied an additional heat treatment in air after the forming gas environment nanoisland growth. The purpose of this design is to use the forming gas to facilitate the nucleation first, and then develop the islands in air to achieve size and shape similarity. Figure 5.11a is a low magnification SEM image of this sample showing the high
coverage of the nanostructures. This observation, again, confirms that the forming gas environment can promote the nanostructure formation. Figure 5.11b shows a higher magnification of this sample. It can be seen that the surface is dominated by the connected morphology and some ring-shape structures rather than isolated islands. It seems that the second segment of heat treatment only facilitated the coarsening and connecting of the nanostructures rather than reshaping or rearranging. Once the islands nucleate, their locations are relatively fixed and the coalescence takes place by filling the gaps between the islands. The ring shape structures can be considered as direct evidence showing four neighboring islands coalescing in this way. Apparently, this annealing route increases the variations in island size and shape and is not suitable for producing uniform structures.

5.3.3 $Eu_2O_3/YSZ(001)/1125/2/Air + Eu_2O_3/YSZ(001)/1000/16/forming\ gas$

In this attempt, we swapped the sequence of the two heat treatment in the previous section. Based on our current mechanistic understanding, the uniformity and self-alignment of the nanoislands produced in air are associated with the “row-by-row” growth mode. This means the nucleation sites and the characteristics of the new islands are constrained by the stress field of the existing islands, which essentially shows an effect of self-templating. If we produce some islands in air first, their stress field may act as a template and the islands produced next in the forming gas may show similar characteristics as well as high coverage. Figure 5.12a is a low magnification SEM image of this sample showing the high coverage of the nanostructures. Apart from those densely covered areas, there are also regions with sparsely distributed islands due to the forming gas treatment. Figure 5.12b shows the morphology of the islands on this sample. It can be seen that the islands are quite uniform.
in size and shape, which is similar to the typical air-annealing sample. Figure 5.12c presents another region on this sample where we observe sparsely distributed islands. A distinct feature of this region is the formation of satellite islands around the individual islands, as indicated by the red circles. The size difference between the center islands and the satellite islands gives away their relative age, while the locations of these satellite islands clearly show the effect of self-templating. This observation confirms our theory about the self-alignment, and the two-step heat treatment successfully improved the uniformity and the coverage of the islands. However, due to the short-range nature of this effect, the long-range order of the islands is still poor.

5.3.4 Other substrates in forming gas

Previous experimental results suggest that the forming gas environment can promote the reactions on YSZ(001) surface. To examine whether this is true for all YSZ surfaces, we applied the forming gas heat treatment to some other types of YSZ substrates. For comparison, all the samples in this section were annealed at 1000 °C for 16 hr in forming gas with Eu$_2$O$_3$ powder.

Figure 5.13a shows the resulting surface morphology on Type I miscut YSZ surface. In this case, the shape of the islands becomes even more connected and irregular while the coverage of the structures is low. Although the morphology is quite different from the non-miscut sample, these islands still show some correlation with the steps. This again indicates that the templating effect of the steps is much stronger than the self-alignment. YSZ(110) surface also shows a totally different morphology, as shown in Figure 5.13b. Instead of
producing uniform nanobars, it yields small islands and large irregular particles. The structures around the powder seem to show a tendency to form bars, but the uniformity of these structures are not comparable with the nanobar morphology in air. We also explored the YSZ(111) surface with the forming gas environment. It turns out that the surface remains passive and no nanostructure formed around the powder, as shown in Figure 5.13c. It seems that the YSZ(111) surface is intrinsically stable and surface breakup is unfavored. This surface orientation dependence of nanostructure formation cannot be explained by the ATG theory alone, and the variation in surface energy must also be taken into consideration.

5.3.5 Discussion

The very different behaviors of these systems, again, suggest that the forming gas is not simply affecting the diffusion kinetics of the dopants. In fact, we have always ignored the variability of an important parameter in the ATG theory, which is the surface energy term. While the surface breakup reduces the elastic strain energy, it must overcome the increase in the total surface energy due to the generation of new surfaces. It seems that the H₂ in the forming gas has reduced the magnitude of the surface energy term probably by adsorption. This will change the thermodynamics of the island formation and therefore the behavior of the entire system. On the other hand, the H₂ may also affect the oxidation state of the dopant, as demonstrated in the CeO₂/YSZ(001) system. It is reported in the literature that Eu does have a +2 oxidation state and EuO is a ferromagnetic semiconductor with high spin-polarization. However, the growth of EuO thin film is demanding and the processing temperature is usually lower (~400-800 °C). Due to the lack of thermodynamic
data, we cannot confirm the stability of EuO at our processing temperature at the Po2 provided by the forming gas. Although Eu2O3 is considered as the stable phase at higher temperature, there is still a possibility of partial reduction due to the low Po2. If the dopant species changed, the diffusion kinetics and the phase stability will also change.

5.4 Conclusions

In this chapter, we investigated the effect of annealing gas environment on nanostructure formation in several different ways. Our observations from these experiments have led us to the following conclusions:

(1) The forming gas environment can partly reduce CeO2 and produce Ce3+ dopant. This is supported by the similarity of the resulting island morphology and the ionic radius between Ce3+ and La3+.

(2) The forming gas environment can dynamically promoted the reactions in the Eu2O3/YSZ(001) system. This conclusion is supported by several observations such as the occurrence of connected morphology and new phases (faceted structures) at 1125 °C, the improved coverage at both 1125 °C and 1000 °C, and the extensively observed nucleation events at 1000 °C. The fact that the faceted particles only exist near the source and the forming gas pre-annealing experiment suggest that the effects of the forming gas are associated with the dopant source. The totally different behaviors of other types of YSZ substrate also indicate that the gas is not simply affecting the diffusion kinetics. Our hypothesis is that the gas changed the total surface energy of the system which has a deep impact on the reaction dynamics. The reduction of Eu2O3 under the given experimental
conditions may also played a role. These phenomena were only observed under very low Po$_2$ provided by the forming gas, while the Ar annealing only shows limited effect on the island morphology.

(3) The uniformity of the islands produced in forming gas can be improved by adding a short time air environment growth beforehand. This is due to the self-templating effect of the existing islands which is directly observed in Figure 5.12c. Once the islands nucleate, they coarsen and coalescence by filling the gaps between them.

Our discoveries in different gas environment for heat treatment have both scientific and engineering significance, as we now have an additional degree of freedom for pattern engineering. The kinetic analysis in Chapter 4 shows that the extension of nanostructures we can obtain within a reasonable period of time is limited. From a manufacturing point of view, we can now break through this limitation and achieve higher nanostructure coverage at even lower temperature. Towards the mechanistic understanding, our observations demonstrated that surface diffusion is not the only factor that dictates the nanostructure formation. Beyond that, we also investigated the role of the H$_2$, the evolution of the nanostructures and the effect of self-templating in nanostructure formation. The annealing conditions we used for the gas environment heat treatment are not optimized in the current work. In the future, it might be worth exploring different combinations of annealing temperature, annealing time and H$_2$ concentration to see if we can further enhance the coverage, reduce the processing temperature or improve the structure uniformity and alignment. It might also be worth exploring the effect of forming gas with other REO such
as Gd$_2$Zr$_2$O$_7$ and Y$_2$O$_3$. This will give us more insights to the role of the H$_2$ as Gd and Y have no stable intermediate oxidation state between 0 and +3.
Table 5.1 Ionic radii of lanthanide ions. The ionic radii of yttrium (Y\(^{3+}\)) and zirconium (Zr\(^{4+}\)) ions are also listed due to their presence in the YSZ substrate.

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<tr>
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Figure 5.1: (a) Islands produced by pure CeO\(_2\) powder source in air; (b) a higher magnification image of the area indicated by the rectangular box in (a).
Figure 5.2: (a) Islands produced by CeO$_2$ powder source in 5%H$_2$-95%N$_2$ forming gas; The sample was annealed at 1000 °C for 16 hr. (b) a higher magnification image of the area indicated by the rectangular box in (a).
Figure 5.3: Islands produced by La$_2$O$_3$ powder source in air; The sample was annealed at 1050 °C for 5 hr.

Figure 5.4: SEM image of a Eu$_2$O$_3$/YSZ(001) sample prepared via Picopump in forming gas; The sample was annealed at 1125 °C for 16 hr.
Figure 5.5: (a) SEM image of a Eu$_2$O$_3$/YSZ(001) sample prepared via powder suspension in forming gas; The sample was annealed at 1125 °C for 16 hr. (b) A higher magnification of the center region in (a) showing the bar features; (c) A higher magnification of the region indicated by the larger rectangle in (a) showing various features.
Figure 5.5 continued

Figure 5.6: (a) SEM image of a Eu$_2$O$_3$/YSZ(001) sample prepared via powder suspension in air; The sample was annealed at 1000 °C for 16 hr. (b) A higher magnification of a region between the source.
Figure 5.7: (a) SEM image of a Eu$_2$O$_3$/YSZ(001) sample prepared via powder suspension in forming gas showing extensive coverage of the nanoislands; The sample was annealed at 1000 °C for 16 hr. (b) A higher magnification shows the variation in island areal density; (c) A high magnification SEM image of the islands showing their variations in shape; (d) A region far away from the source shows the formation of sparsely distributed islands.
Figure 5.7 continued
Figure 5.8: (a) SEM image of another Eu₂O₃/YSZ(001) sample prepared in forming gas at 1000 °C. In this case, the islands show wide coverage with bimodal distribution in size; (b) A higher magnification shows the morphology of the islands; (c) Another region on this sample showing passivation around the powder.
Figure 5.9: (a) A low magnification SEM image of a Eu₂O₃/YSZ(001) sample prepared via powder suspension in Ar showing limited coverage of the islands; The sample was annealed at 1000 °C for 16 hr. (b) A higher magnification showing similar island morphology to the air-annealing samples.
Figure 5.10: SEM image of a Eu$_2$O$_3$/YSZ(001) sample prepared via two-step annealing; The sample was first annealed without Eu$_2$O$_3$ in forming gas at 1000 °C for 16 hr, and then annealed with Eu$_2$O$_3$ in air at 1000 °C for 16 hr.

Figure 5.11: (a) SEM image of a Eu$_2$O$_3$/YSZ(001) sample prepared via two-step annealing showing extensive coverage of nanostructures; The sample was annealed with Eu$_2$O$_3$ in forming gas at 1000 °C for 16 hr, and then annealed in air at 1125 °C for 2 hr. (b) A higher magnification showing the variations in nanostructure morphology.
Figure 5.11 continued

Figure 5.12: (a) SEM image of a Eu$_2$O$_3$/YSZ(001) sample prepared via two-step annealing showing extensive coverage of nanostructures; The sample was annealed with Eu$_2$O$_3$ in air at 1125 °C for 2 hr, and then annealed in forming gas at 1000 °C for 16 hr. (b) A higher magnification showing improved size and shape uniformity of the islands; (c) Another region on this sample showing sparsely distributed islands and their self-templating effects.
Figure 5.12 continued
Figure 5.13: (a) SEM image of a Eu$_2$O$_3$/Type I miscut YSZ sample prepared in forming gas; (b) SEM image of a Eu$_2$O$_3$/YSZ(110) sample prepared in forming gas showing totally different morphologies compared to the bar morphology obtained in air (inset); (c) SEM image of a Eu$_2$O$_3$/YSZ(111) sample prepared in forming gas showing no nanostructure formation. The samples were annealed at 1000 °C for 16 hr.
Figure 5.13 continued
Chapter 6: Suggestions for Future Work

6.1 Artificial scratches on YSZ surfaces

Previous studies in REO/YSZ systems suggest that the formation of nanostructures is a complex process involving surface diffusion, elastic interactions and surface energy anisotropy. With all the efforts towards a comprehensive mechanistic understanding, there are still several phenomena which are not well-understood and warrant further investigations. One of such phenomena is the occasional occurrence of long scratches with nanostructure forming around them, as shown in Figure 6.1a. These scratches usually have random orientations on the surface while their lengths can reach tens to hundreds of microns. They are likely to come from the polishing process during manufacturing and while the reactivity along them is exotic. We have observed on multiple samples that nanoislands can form around these scratches even if the nearest dopant source is tens of microns away. The alignment of these island typically has a strong dependence on the scratch orientation (Figure 6.2b). The fact that the islands become smaller with the increasing distance from the scratch center indicates that the scratches are acting as diffusion or stress centers. A possible future work based on these observations is to see whether we can artificially create this type of scratches on YSZ surfaces to achieve significant improvement in nanostructure coverage and alignment. This work may require some fine control in practice, as the observed scratches are very shallow and severe damage
on the surface is usually undesirable. Apart from the traditional polishing or machining route, we may also utilize high energy laser beams to create these scratches. The laser will allow us to draw different scratch patterns and the damage level can be controlled by adjusting the laser intensity. It would be very interesting to see if the nanostructure formation will be guided by these artificial scratches.

6.2 Strain characterization

The current mechanistic understanding for REO/YSZ systems is based on a strain energy induced surface stability. However, the actual strain in these systems, if any, has not been experimentally measured in previous works. Nanoscale strain measurement can be done by several TEM based techniques, such as the convergent beam electron diffraction (CBED), nano-beam electron diffraction (NBED), high resolution imaging (HRTEM or HRSTEM) and dark field electron holography (DFEH). Beche et al. have made a comprehensive comparison between these techniques which can be used to guide this part of work in the future.\(^{51}\) Considering the limited doping level and small possible strain in the REO/YSZ systems, the best available technique for this work might be CBED. A quantitative strain measurement will certainly deepen our mechanistic understanding to the nanostructure formation and help us resolve the unanswered questions.
6.3 Nanostructure formation on miscut YSZ substrates

In the current study, we investigate the step bunching phenomenon and the nanoisland formation on three types of miscut YSZ substrate. We observed step bunching only on Type I and Type II miscut YSZ surfaces, which are both miscut YSZ(001). The major difference between these two types of substrates is the miscut orientation which dictates the stable step configuration without doping. However, the difference in miscut angle can also affect the easiness of step bunching and the resulting step period. It might be interesting to investigate the effect of miscut angle with a fixed miscut orientation, say, (001)-[110], in the future. On miscut YSZ(110), we can look into other miscut orientations such as (110)-[001] and (110)-[111], probably with a higher miscut angle. In particular, it is interesting to see whether we can have step bunching or nanostructure formation on miscut YSZ(111) surface, as the elastic isotropic non-miscut YSZ(111) does not produce any nanostructures. By breaking the crystallographic symmetry via miscutting, we might be able to grow nanostructures with unique morphology on YSZ(111).

6.4 Towards functionality and applications

YSZ substrates are widely used for thin film depositions. There has been report showing that atomic steps on vicinal YSZ(001) can stabilize the cubic phase against the hexagonal phase upon MBE growth of InN films. It would be interesting to see whether this effect can be enhanced by using pre-annealed miscut YSZ substrates with step bunches. This phase stabilization effect on miscut YSZ can also be explored in other processes such as the deposition of YBCO.
YSZ(110) produces the unique nanobar morphology along [1\bar{1}0]. A possible future work for this part is to explore whether this topology has induced in-plane anisotropy to surface related properties such as the surface conductivity. We can also use patterned YSZ(110) surface as a template to guide the phase separation of the block copolymers, which may induce directional alignment to the resulting polymer morphology.

Surface structural related effects such as superwettability\textsuperscript{53} and field enhancement\textsuperscript{54} can also be explored on YSZ surfaces. Combining the miscut strategy and the reducing annealing gas environment, we should be able to achieve ordered nanostructure with decent coverage for these studies. Alternatively, we can take advantage of the doping induced step faceting on Type II miscut YSZ and fabricate zigzag steps with sharp corners for field enhancement studies. If we deposit a thin layer of GDC on pre-annealed Type II miscut YSZ and anneal the sample for sufficient long time, we might have the entire surface covered with the zigzag step without island formation or morphological transition.

6.5 Final conclusions

Controlled powder-based source dispersion techniques were developed and used for nanostructure growth kinetic analysis. It was found that the nanobar growth kinetics obeys the parabolic law at 1180 °C, while the nanoislands on YSZ(001) exhibit a non-parabolic growth kinetics with the power of time dependence being 0.28 at 1125 °C. We also found that the nanobar growth on YSZ(110) is anisotropic in plane with [1\bar{1}0] and [001] being the maximal and minimal growth directions. This result is consistent with the anisotropic surface diffusion scenario on fcc (110) surfaces. We further investigate the
dependence of the nanobar periods on the distance from the source and a hypothesis based on the ATG analysis was proposed.

We have successfully produced straight step arrays on two different types of miscut YSZ(001) surfaces. It was found that the stable step orientation on bare miscut YSZ(001) surface is dictated by the miscut axis. On the doped miscut YSZ(001) surfaces, we observed a doping induced step faceting from [100]-steps to <110>-zigzag steps only on Type II miscut YSZ substrate. We believe that the doping has altered the step-energy anisotropy, while the elastic interactions between the steps also played an important role. We further demonstrated that using self-organized step arrays as templates can significantly improve the alignment of the nanoislands on YSZ surfaces, and 2D ordered surface patterns can be produced by synergetic effects of island-step and island-island interactions.

The effect of annealing gas environment on nanostructure formation was systematically investigated in this work. It was found that the forming gas environment can partly reduce CeO$_2$ and make it behave like La$_2$O$_3$ on YSZ(001) surface. The forming gas environment can also dynamically promoted the reactions in the Eu$_2$O$_3$/YSZ(001) system. It seems that the gas has changed the total surface energy of the system which has a deep impact on the reaction dynamics. On the other hand, the reduction of Eu$_2$O$_3$ under the given experimental conditions may also played a role. These phenomena were only observed under very low Po$_2$ provided by the forming gas, while the Ar annealing only shows limited effect on the island morphology. It was also found that the uniformity of the islands produced in forming gas can be improved via self-templating by adding a short time air
environment growth beforehand. Combining the miscut strategy and the reducing annealing gas environment, we might be able to achieve ordered nanostructure with decent coverage. Future studies in the REO/YSZ systems should focus on surface functionalization, while acquiring a deeper mechanistic understanding through phase field modeling and strain characterization can also greatly benefit the development of this technique.
Figure 6.1: (a) SEM image showing long scratches on YSZ (001) with nanostructure forming around them. (b) SEM image showing strong correlation between the islands and the scratches.
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