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LETTER TO THE EDITOR

Self-patterning of arrays of ferroelectric capacitors: description by theory of substrate mediated strain interactions

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Abstract

Self-patterning presents an appealing alternative to lithography for the production of arrays of nanoscale ferroelectric capacitors for use in high density non-volatile memory devices. However current levels of registration achieved experimentally are far from adequate for this application. To provide a guide for experiment we have applied the theories developed for self-patterning of semiconductor nanocrystals to two self-patterning systems of potential interest for ferroelectric memory applications, metallic bismuth oxide on bismuth titanate and ferroelectric lead zirconate titanate on strontium titanate.

Achieving higher density arrays of ferroelectric capacitors in a cost and time effective manner would be of great technological significance. One approach is to attempt to produce self-patterned arrays of nanocrystals, in which ordering is produced by interactions between islands through the substrate. This approach could be used to produce arrays of metallic nanoelectrodes on top of a ferroelectric film or alternatively arrays of crystals from the ferroelectric materials themselves. The first scheme was suggested by Alexe *et al* [1] who found that a bismuth oxide wetting layer on top of a bismuth titanate film formed an array of metallic bismuth oxide nanocrystals on top of the film, which were partially registered along the crystallographic directions of the underlying substrate. These nanocrystals were used successfully as electrodes to switch regions of the film [2]. In the second approach one might use a material such as PbTiO₃ on a SrTiO₃ substrate, which was first demonstrated to form islands when grown epitaxially at very thin film thicknesses by Seifert *et al* [3]. In the context of self-patterning of oxide materials a recent work by Vasco *et al* [4] studies the growth of self-organized SrRuO₃

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crystals on LaAlO_3 . In this letter we examine the structures formed in two of these cases, i.e. the self-assembly of top electrodes and the self-assembly of ferroelectric material, and show that the mechanism is the same as that evident in the formation of Ge islands on Si, for which a great deal of theoretical and experimental literature is available because they have been used to fabricate semiconductor quantum dots. A better understanding of the mechanism of formation of self-patterning ferroelectric nanocrystals should permit improved registration and regularity of crystal size by choice of materials and processing conditions.

When small amounts of materials are deposited on substrates where there is some degree of mismatch between the two materials, islands form and the repulsive interactions between them are mediated via strain fields in the substrate as first suggested by Andreev [5]. This idea has been developed into a detailed theory by Shchukin and Bimberg [6]; however, this theory is a zero-temperature theory, whereas a thermodynamic theory is required to describe the crystallization processes which occur at quite high temperatures. An extension of the theory to finite temperatures has been carried out by Williams and co-workers [7, 8]. The chief results of this theory are the prediction of three different kinds of structure (pyramids, domes and superdomes), a volume distribution for a particular species of structure and a shape map to describe relative populations of structures as a function of coverage and crystallization temperature. One interesting result from experiment is that similar shaped structures are observed in both the Volmer–Weber (VW) and Stranski–Krastanow (SK) growth modes, but on different size scales. In the work of Williams the thickness above which dome populations occur is of the order of 4–5 monolayers, corresponding to the critical thickness for misfit dislocations for Ge on Si(100). On the other hand, Capellini *et al* [9] studied via atomic force microscopy (AFM) the growth of Ge on Si(100) in the SK growth mode and found a much larger critical structure height of 50 nm at which dislocations were introduced and the structures changed from being pyramidal in geometry to domelike. The large increase in critical thickness is due to a substantial part of the misfit strain being taken up by the substrate in the SK growth mode, as described by Eaglesham and Cerrulo [10].

Initially we will discuss the application of the theory as applied to the sample first described by Alexe *et al* [1]. This sample consisted of bismuth oxide nanoelectrodes on a bismuth titanate film, where the bismuth oxide nanoelectrodes were partially registered along the directions of the underlying Si substrate. The details of the fabrication of this sample may be found in that publication. The structures defined for the growth of Ge on Si(100) have crystal facets with particular orientations. Pyramids have a square base and four facets which are either (105), (10 $\bar{5}$), (150) and (1 $\bar{5}$ 0) (Williams) or (113), (11 $\bar{3}$), (131) and (1 $\bar{3}$ 1) (Capellini). A useful definition of the transition to domes is the appearance of the top (100) facet, which has been identified with the appearance of misfit dislocations [11]; however, domes consist primarily of (113), (11 $\bar{3}$), (131) and (1 $\bar{3}$ 1) facets. The final largest structure, the superdome, is similar to the dome but is distinguished by the appearance of steep {111} facets at the boundary of the substrate. Figure 1 shows a profile of our sample displaying pyramids and domes and also a TEM cross-section of a bismuth oxide superdome; for comparison we refer the readers to the work of Kamins *et al* [18], where a similar cross-section of a Ge on Si superdome can be found, which contains the same facets, but in somewhat different proportions.

Having shown that the basic geometries of the structures are the same, we now fit the experimental volume distributions of the bismuth oxide crystals (as measured by analysis of AFM images) to the distribution function of Williams. The function is the following:

$$\ln[\omega_X(V)] = -\left(B_X V^{2/3} + A_X V^{1/3} + \frac{B_X^2}{4A_X} V\right). \quad (1)$$

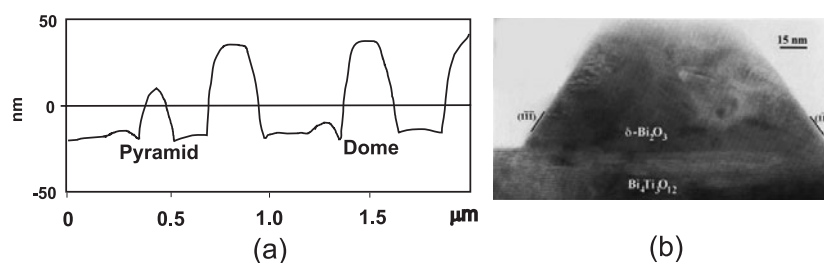


Figure 1. (a) AFM contours of bismuth oxide nanocrystals showing both pyramid and dome type structures, (b) TEM cross-section of bismuth oxide superdome with labelled $\{111\}$ facets. (This can be compared to the Ge on Si(100) superdomes of Kamins *et al* [18], noting the characteristic existence of $\{111\}$ facets at the boundary with the substrate in both cases.)

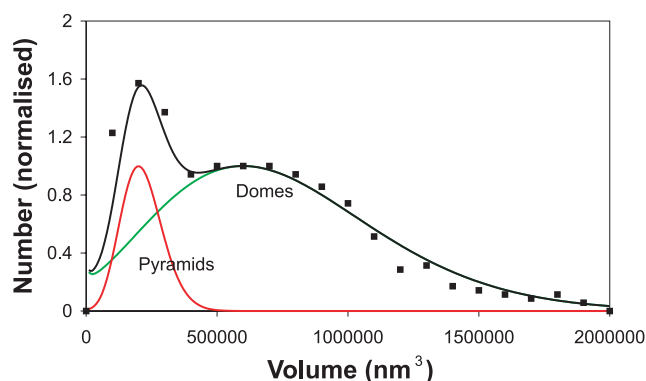


Figure 2. Bimodal volume distribution of bismuth oxide nanocrystals obtained by analysis of AFM images, showing the coexistence of pyramids and domes and the excellent fit to the distribution function of Williams *et al*.

(This figure is in colour only in the electronic version)

In the above ω_X is the frequency of a crystal of species X with a particular volume V , B_X is a facet energy parameter, while A_X is an edge energy parameter. These parameters are related to those of Shchukin *et al* [12] who first introduced a distribution function of this form. The fit of this distribution to the volumes of our bismuth oxide islands (figure 2) is excellent, distributions of both pyramids and domes are clearly visible and both are described well by the distribution function.

Because the bismuth oxide nanoelectrodes originated from an unintentional wetting layer there is little potential for fine control of thickness. In order to study the effect of thickness and temperature very thin films of sol-gel lead zirconate titanate (PZT) (composition 52/48) were deposited on SrTiO₃ substrates and crystallized at high temperatures to form ferroelectric nanocrystals. The dilution of the sol-gel solution was varied so that the equivalent thickness of the film could be controlled. The details of the fabrication of these samples, and AFM piezoresponse measurements demonstrating the ferroelectricity of the nanocrystals, can be found elsewhere [13]. From these experiments we were able to study the effect of temperature and thickness on the structures produced and compare this behaviour to that observed for Ge on Si(100). Creating a free standing array of ferroelectric nanocrystals may be of more technological utility than producing arrays of nanoelectrodes on a film, as there is less potential for cross-talk. Two groups have grown PbTiO₃ nanocrystals on (111) Pt/Si substrates to

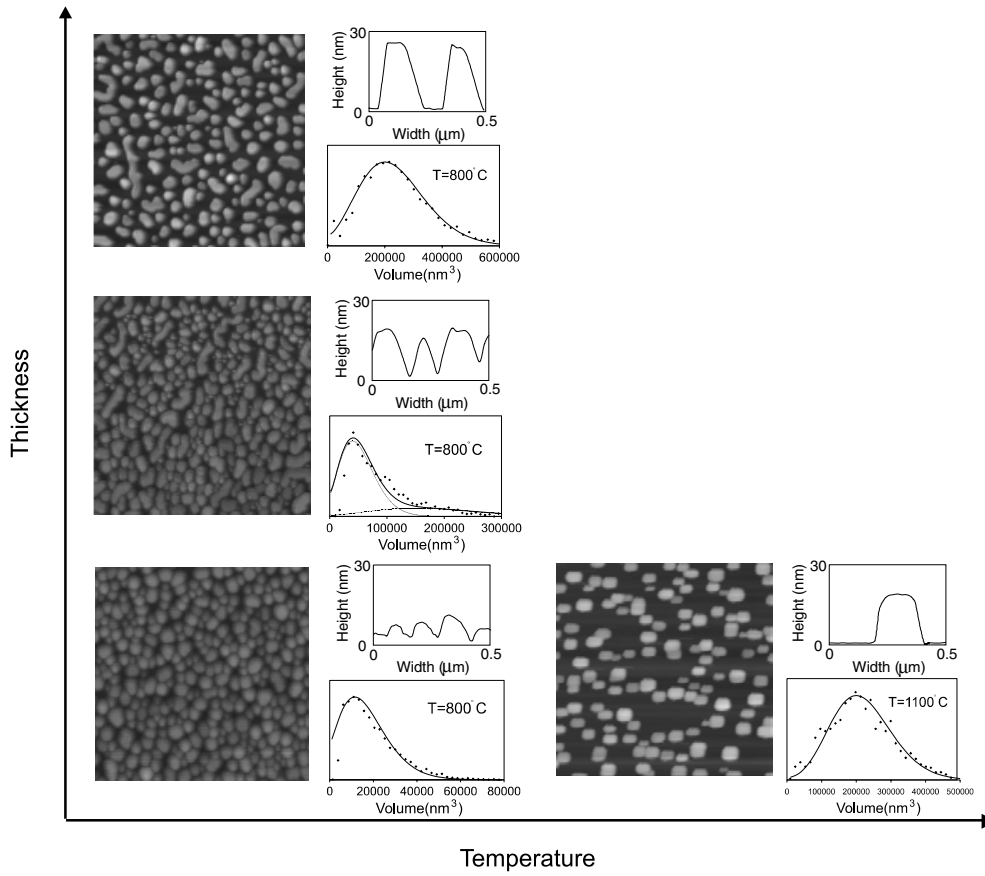


Figure 3. AFM images (size: $2.5 \times 2.5 \mu\text{m}$), profiles and volume distributions of PZT nanocrystals on SrTiO_3 for different dilution levels and temperatures. At 800°C there is a transition from superdomes to domes as the dilution is increased (decreasing PZT thickness). Surprisingly at higher temperatures the most dilute film forms superdomes contrary to our expectation based on the results for Ge on Si(100).

measure size effects in ferroelectricity [14, 15]. Interestingly, because of the (111) orientation of their substrates and the epitaxial relationship between the substrate and the islands, instead of square-based pyramids they obtain triangular based structures that display hexagonal rather than cubic registration (an analogous result is observed when Ge is grown on Si(111) [16]). At this point we also refer readers to the detailed works on the effects of lattice mismatch strain for epitaxial PbTiO_3 on various substrates by Speck and Pompe [17].

In our study we have compared distributions for different dilution levels for PZT on SrTiO_3 where crystallization has been carried out at 800°C (figure 3). It can be seen that in general the structures are not as strongly faceted as the bismuth oxide structures. For large thicknesses superdomes are dominant and as the thickness is decreased we move from coexistence of domes and superdomes to dominance of domes. The domes and superdomes can be distinguished both on the basis of size (superdomes are significantly larger than domes) and the kind of facet present (superdomes have steeper side facets and a larger flat top facet than domes). However, if one processes the most dilute deposition at a much higher temperature (1100°C) then superdomes become dominant again. This result is quite different to Ge on

Si(111) where for higher temperatures superdomes become increasingly unfavourable. The processing temperatures are much higher in our experiments than those of Williams, so perhaps the much easier generation of dislocations at these temperatures favours the superdomes which contain multiple dislocations.

In any case our experimental results show that processing at higher temperatures means that superdomes become dominant at higher temperatures for smaller thicknesses. This may be advantageous as one can then obtain an array of superdomes which are further spaced from each other and thus avoid the structures formed by merged domes which drastically reduce the degree of registration in an array of nanocrystals.

As in the case of the bismuth oxide nanocrystals the volume distributions are well described by equation (1). It was found that the edge energy A_X was constant for a given processing temperature, independent of the nanocrystal species or the dilution level, but increased with increasing temperature. For both species the surface energy B_X was seen to increase as the quantity of deposited material was increased, resulting in larger nanocrystals. Like the edge energy the surface energy also seems to increase with increasing temperature.

In conclusion, we have analysed two systems of self-patterned nanocrystals successfully using the theories developed for analogous semiconductor systems. It is hoped that these theories can be used to guide experimental efforts to produce self-patterned arrays with greater registration. Our general conclusion, however is that highly registered memory arrays will not occur spontaneously in the absence of a pre-patterned field.

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