

# Hot STM of nanostructure dynamics on SrTiO<sub>3</sub>(001)

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## Abstract

The dynamics of nanostructured surface phases on SrTiO<sub>3</sub>(001) have been analysed using *in situ* scanning tunnelling microscopy (STM) above 800 °C. During high-temperature annealing, the formation, growth and ordering of the nanostructures has been observed. Dilines, with a width of ~1 nm, are formed from a TiO<sub>2</sub>-rich intermediary at 800 °C. STM during annealing at 825 °C has enabled us to follow both the growth and dissolution of dilines. Following extended annealing, trilines with a width of ~2 nm and ordered two-dimensional (2D) nano-arrays form from the diline domains. Our observations of diline dissolution implies random nucleation and growth, followed by rearrangement at elevated temperature to form domains.

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## 1. Introduction

Self-assembled nanometre-sized structures are of particular interest due to their importance in the development of novel electronic devices such as single electron transistors and quantum dot lasers [1, 2]. Oxide crystal surfaces, such as SrTiO<sub>3</sub>, are good candidates for studying the growth of nanostructures as these are electrically insulating. Nanostructures grown on these materials may find application in the development of arrays of nanowires and quantum dots [3].

In general, nanostructures tend to form at elevated temperatures, but are often observed, using scanning tunnelling microscopy (STM), at room temperature [4–6]. This approach provides many insights into their properties, but does not show direct evidence of their nucleation and growth behaviour. Therefore, in order to study nucleation and growth directly, hot STM imaging is needed. However, obtaining STM images is more challenging at high temperatures due to sample, stage and tip drift arising from the temperature gradient. These experimental difficulties notwithstanding, Si(111) has been imaged at temperatures of up to 920 °C in order to study surface reconstructions [7]. Recently, there have been hot STM studies of GdSi<sub>2</sub> nanowire reactions on Si(100) which have helped to define the structure of a new type of nanowire [8]. Hot STM imaging has also been used to identify an intermediate, Bi-related, linear structure formed during Bi/Si(001) surface annealing [9].

STM of SrTiO<sub>3</sub>(001) has been carried out at temperatures of just under 800 °C and has been used to study the motion of step edges of the (2 × 2) surface reconstruction [10]. However, no study above the nanostructure formation temperature (800 °C) has been carried out, and hence no direct investigation of the nucleation and growth of nanostructures on SrTiO<sub>3</sub> has yet been undertaken.

Nanostructures on the c(4 × 2) reconstruction of SrTiO<sub>3</sub>(001) were first described by Castell and several different variants have since been reported [6, 11, 12]. These structures have all been shown to be TiO<sub>2</sub> rich using Auger electron spectroscopy [12].

The first nanostructures observed were dilines, which were initially referred to as nanolines [6] but, in order to distinguish them from the other types of structure, they have been renamed dilines [12]. Dilines, ~1 nm in width and 0.2 nm in height, consist of two rows of protruding atoms or atomic complexes which have a period of 0.8 nm. They form after an Ar<sup>+</sup> sputter and 30 min UHV anneal at 825 °C. After a 30 min anneal at 850 °C, large domains of dilines with a (6 × 2) surface pattern form.

Trilines, with a width of ~2 nm and consisting of three rows, form after Ar<sup>+</sup> sputtering and a 30 min anneal at higher temperature. The two outer rows are similar to those that make up a diline, however the central backbone has a shorter period of 0.4 nm. The apparent height of the backbone of a triline varies with changing imaging bias. This is an electronic structure effect due to the difference in the local density of

states between the backbone and the outer lines of the triline. Domains of trilines have a  $(9 \times 2)$  symmetry.

It is also possible to form nanostructures that consist of 2D rectangular arrays. One of these is the waffle structure which has a surface periodicity of  $(6 \times 8)$ . This forms after repeated annealing of dilines and consists of domains of ordered trenches with a depth of 0.2 nm interspersed with 0.1 nm high cross-like structures.

To date, all STM observations of SrTiO<sub>3</sub> nanostructures have been carried out at room temperature after an anneal at high temperature. From these experiments, dilines are known to form at around 825 °C, but their nucleation has never been observed directly. In this paper we analyse the nucleation and growth of nanostructures on SrTiO<sub>3</sub> by observing their behaviour at temperatures up to 850 °C and accordingly investigate the mechanisms by which domain formation occurs.

## 2. Experimental methods

In bulk SrTiO<sub>3</sub> a cubic perovskite structure ( $a = 0.3905$  nm) forms, and along a  $\langle 001 \rangle$  direction the crystal is made up of alternating TiO<sub>2</sub> and SrO layers. Stoichiometric SrTiO<sub>3</sub> is an insulator with a band gap of 3.2 eV, which becomes n-type semiconducting on doping with substitutional Nb<sup>5+</sup> on the Ti sites. This increases the level of electrical conductivity, which enables analysis of the SrTiO<sub>3</sub>(001) surface using STM.

Single crystals of Nb (0.5 wt%) doped SrTiO<sub>3</sub> with epitaxially polished (001) surfaces were supplied by PI-KEM (UK). A low room-temperature resistivity of  $10^{-3}$  Ω m, which increased with increasing sample temperature, was measured as a result of the high level of niobium doping. For STM imaging, a JEOL JSTM 4500XT was used with an ultrahigh-vacuum (UHV) chamber pressure of  $10^{-8}$  Pa. Chemically etched tungsten tips were used to obtain constant current images with a bias voltage applied to the sample. The sample was resistively heated in the UHV chamber by passing a current through it. A disappearing filament optical pyrometer was used to measure temperatures above 750 °C. Initially, the samples were Ar<sup>+</sup> ion sputtered for 10 min with an ion energy of 0.5 keV and an ion current of 7 μA.

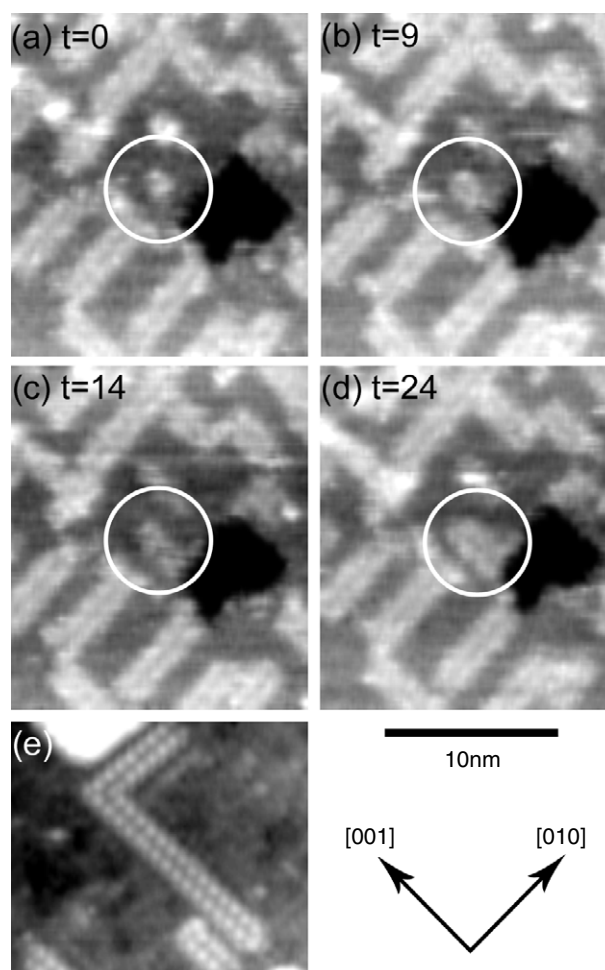
## 3. Results

### 3.1. Nucleation and growth of dilines

After Ar<sup>+</sup> sputtering and annealing at 800 °C for over 6 h, dilines are observed to nucleate on the underlying  $c(4 \times 2)$  surface reconstruction (figure 1).

Figures 1(a)–(d) were taken at 800 °C over a period of 24 min. In these images, the bright pairs of rows are dilines and the dark area is a section of lower terrace. The shape of this area changes during observation as the upper terrace grows over it. A room-temperature image of dilines at the same scale is shown in figure 1(e). Although the characteristic pairs of dots are clearly visible at room temperature, they are not resolved in the hot images. However, a dark streak along the centre of the dilines distinguishes them from the other small atomic protrusions present at 800 °C.

In figure 1(a), the indicated ring surrounds a small atomic protrusion which acts as a nucleation centre. After 9 min



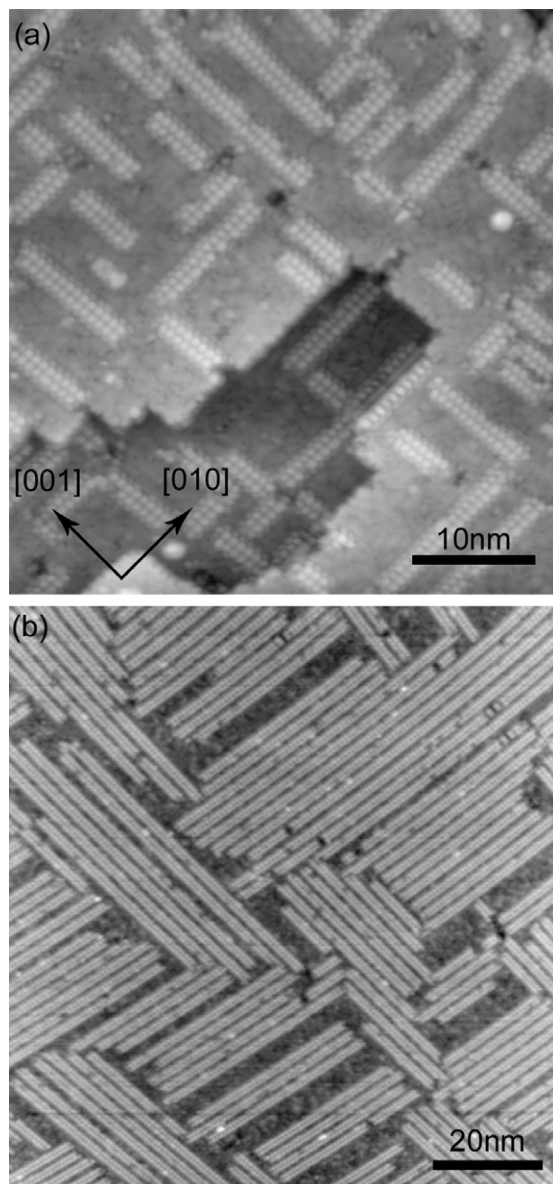
**Figure 1.** Formation of a diline from a nucleation centre at 800 °C (a)–(d). Time,  $t$ , is measured in minutes. (a) A nucleation centre is observed within the marked ring. (b) and (c) Growth of the nucleation centre is visible. (d) A fully formed nanoline is visible. (e) A room-temperature image of dilines. Sample voltages and tunnelling currents used: (a)–(d) 2.00 V, 0.10 nA; (e) 1.10 V and 0.10 nA.

(figure 1(b)), this has increased in size, but is less prominent than any diline. By figure 1(c), 5 min later, the structure is clearly elongated in one direction, but is still narrower and less bright than the established dilines. At 24 min (figure 1(d)), the nucleation centre is now of similar brightness to the surrounding dilines and has the distinct darker centre.

### 3.2. Formation of diline domains

After Ar<sup>+</sup> sputtering and annealing for 24 h at 825 °C, small domains of dilines begin to form. Large ordered domains are seen once the annealing temperature reaches 850 °C. Figure 2 shows room-temperature examples of randomly nucleated dilines (figure 2(a)) and larger domains of dilines (figure 2(b)). Hot STM experiments were therefore performed in order to elucidate the mechanisms by which the random isolated dilines rearrange into large ordered domains.

Figure 3 shows examples of the changes observed on the SrTiO<sub>3</sub>(001) surface after over 24 h of annealing at 825 °C. In figure 3, the darker areas are patches of lower terrace,



**Figure 2.** (a) Room-temperature image of randomly distributed dilines. (b) Larger domains of dilines at room temperature. Sample voltage and tunnelling current used: (a) and (b) 1.00 V, 0.07 nA.

and the growing nanolines are seen in the upper marked ring. Figure 3(a) shows the starting length of the nanolines and figures 3(b)–(d) show the growth of the upper terrace over the lower terrace. In figure 3(e), after 35 min the nanoline above the terrace has grown onto a new area of the terrace. During the course of the next three images (20 min) it is also observed to shrink and regrow.

In the lower marked ring, a nanoline disappears over the course of the scans. In figures 3(a)–(e), the nanoline shrinks progressively by one pair of atomic protrusions in each frame. In figure 3(f), a nanoline perpendicular to the original one can also be observed growing into the new gap. Seven minutes later (figure 3(g)) it has elongated, and after a further 11 min (figure 3(h)) it has extended to fill the space available.

In all our experiments, the nanolines were never observed to nucleate next to other nanolines. However, nanolines were

observed in pairs, and these pairs were more stable than the single nanolines.

### 3.3. Formation of trilines

Once dilines begin to form domains and collect together in groups of two or three, then trilines are also observed. These form at a temperature of at least 825 °C after annealing for over two days. The trilines were usually observed to form from a pair of dilines and were never seen to form from a single diline. They appear to be most stable, and grow to the greatest length when bounded on both sides, either by dilines or by the edge of a terrace or another domain.

The formation and growth of a triline at 850 °C is shown in figures 4(a)–(d) over a period of 4 min. Figure 4(e) shows a room-temperature image of trilines and dilines. The three rows of the triline are very clear at room temperature. At higher temperature, the triline is a wider and brighter line than the diline, but the individual rows are not visible. A small domain of trilines is present on the right-hand side of the image. In order to confirm that these structures were trilines, we measured the periodicity across the triline domains relative to that across the diline domains. The ratio of the periodicity across the rows of trilines to dilines at high temperature is 1.5. This is the same as the ratio measured at room temperature, thus verifying that the brighter nanolines are trilines.

In figure 4(a), two adjacent dilines are marked. In figure 4(b), recorded 1 min later, a short triline has nucleated from this diline. This triline grows (figure 4(c)) and then disappears again 2 min after it formed (figure 4(d)).

### 3.4. Formation of waffle structures

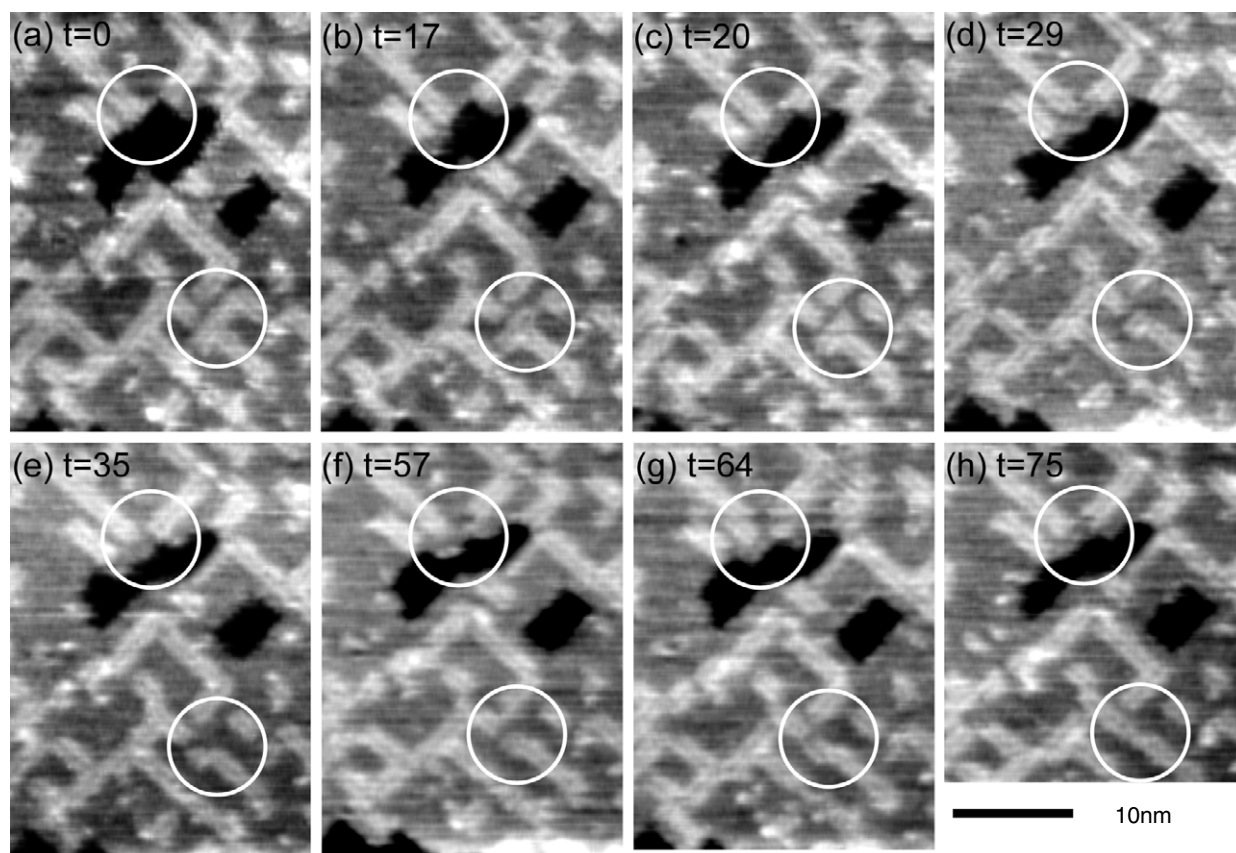
Waffle structures have also been observed at above 825 °C after annealing times in excess of four days. Figures 5(a)–(d) show waffle structures forming and growing from dilines at 850 °C, over 37 min. Figure 5(a) shows a small domain of dilines with a few elements of waffle structure visible within it. The number of waffle elements increases during the next 22 min (figure 5(b)) and, subsequently (figure 5(c)), the elements have joined together to form an extended section of waffle structure. After a further 12 min (figure 5(d)), a large area of the waffle structure is visible. This surface displays significant mobility, and the trenches and crosses that characterize it do not settle in any particular place.

Figure 5(e) is a room-temperature image with a large area of waffle structure in the bottom left, in which the characteristic dark trenches and lighter cross-like structures are visible. In the same image we also observe on the upper terrace a diline transforming into a waffle structure along its length.

## 4. Discussion

Dilines are observed to form via small nucleation centres. This nucleation structure is believed to be TiO<sub>2</sub>-rich as it produces the TiO<sub>2</sub>-rich dilines, as confirmed by previous Auger electron spectroscopy studies [12]. We also note that the dilines form with a specific length, of three or more pairs of atomic protrusions, within one STM scan, and then remain stable. In our high-temperature experiments, dilines are never observed





**Figure 3.** (a)–(h) Growth and dissolution of dilines at 825 °C. Time,  $t$ , is measured in minutes. The top ring shows the growth of a diline onto a new area of terrace over the course of images (a)–(e). In the lower ring, a nanoline disappears between images (a) and (e). A new nanoline grows perpendicularly in its place during (f)–(h). Sample voltages and tunnelling currents used: (a)–(h) 2.00 V, 0.08 nA. The supplementary data shows a movie sequence of this series of images (available at [stacks.iop.org/Nano/17/3543](https://stacks.iop.org/Nano/17/3543)).

to form with a length of either one or two pairs of atomic protrusions. At room temperature, single and double pairs of atomic protrusions are rarely seen [6].

Our most important observation is that dilines routinely shrink as well as grow, and on rare occasions dissolve entirely. A diline nucleating adjacent to another diline was not observed in the course of these experiments. This suggests that there is no preferential nucleation of dilines adjacent to other dilines. However, once a diline has formed next to another diline, this pair is more stable and grows longer than single dilines. This implies that the stability of domains is greater than that of randomly distributed lines. Taken together, these observations suggest that dilines nucleate randomly and subsequently reorder at elevated temperature to form large, more stable domains.

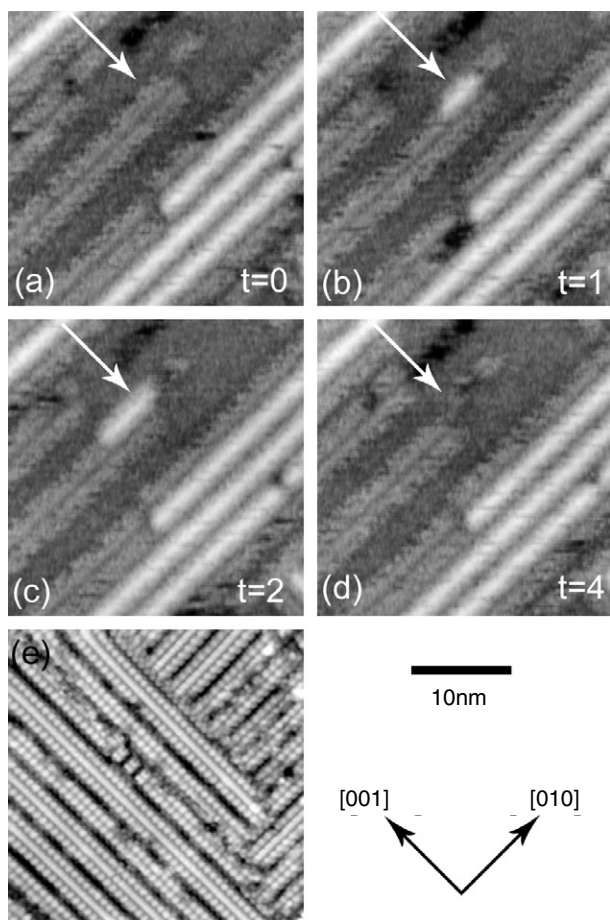
The thermodynamic evolution of the dilines progresses from the isolated lines to the equilibrium state of ordered domains. However, during the series of images taken in these experiments, the main observations are due to statistical fluctuations. This is because of the short periods of observation relative to the timescale of the evolution of the domains at 825 °C. Thus the movements that we see do not, on the whole, represent a progression towards equilibrium. Using an Arrhenius relationship, we have calculated a value of  $1.2 \pm 0.1$  eV for the activation energy of diffusion of the  $\text{TiO}_x$  diline

units. This value is likely to be a high estimate, as some of the diffusion activity is not observed due to the relatively slow STM scan speed and low resolution of the images.

Trilines and waffles structures have been observed to grow from diline domains. The trilines showed stability when bounded on both sides by dilines, other domains or terrace edges. The waffle structure that we have observed on the  $\text{SrTiO}_3(001)$  surface is similar to the cross-linked  $(1 \times 2)$  surface that forms on the  $\text{TiO}_2$  surface [13–15]. The theoretical models that have been suggested for the cross-linked  $\text{TiO}_2$  structure could present a very good starting point for the development of a structural model of the  $\text{SrTiO}_3$  nanostructures.

The mobility of terrace edges of the  $c(4 \times 2)$  reconstruction at over 800 °C is also observed, and terraces frequently grow and retreat during the course of imaging. Following annealing for four or five days, however, the terraces become more stable, and fewer changes occur. This mobility of the terrace edges is similar to that of terrace edges on the  $\text{SrTiO}_3(001)$   $(2 \times 2)$  reconstruction previously observed [10].

These vacuum anneals do not conserve material on the  $\text{SrTiO}_3$  surface. From Auger studies, there is evidence of O depletion in  $\text{SrTiO}_3$  samples annealed at these temperatures in UHV and also an enrichment of  $\text{TiO}_x$  at the surface. However, one monolayer of  $\text{TiO}_2$  added to the surface only causes a

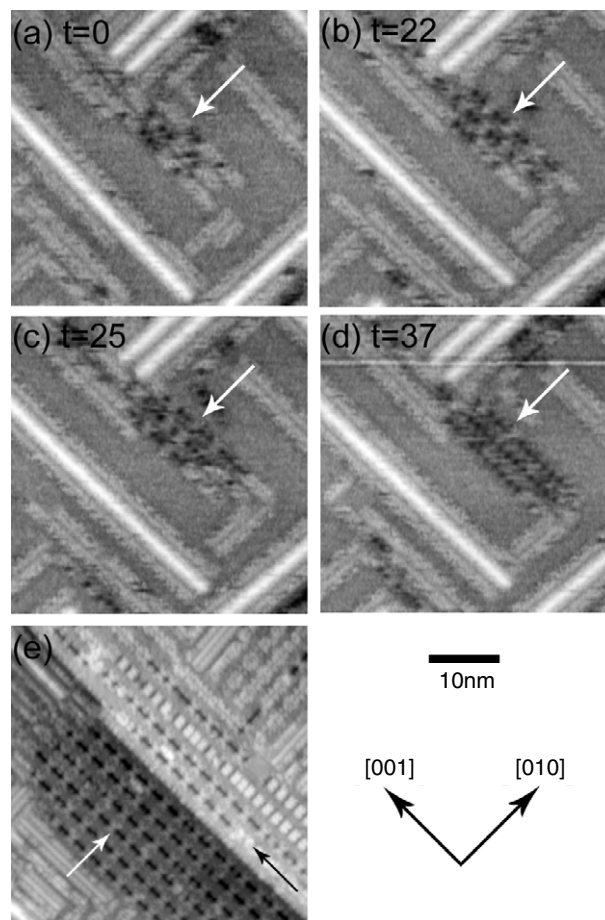


**Figure 4.** (a)–(d) Formation of a triline from a diline at 850 °C. Time,  $t$ , is measured in minutes. A pair of dilines are marked in (a). In (b), a triline has nucleated on part of the left-hand diline (arrowed). This triline is observed to grow (c) and then disappear (d). (e) A room-temperature image of dilines and trilines. Sample voltages and tunnelling currents used: (a)–(d) 2.00 V, 0.20 nA; (e) 0.80 V, 0.30 nA.

0.0001% increase in the number of titanium vacancies in the bulk. Therefore the bulk of the sample is not measurably strontium enriched. Oxygen vacancies within the bulk of the crystal do not significantly influence the electrical conductivity, since the sample is already n-doped with 0.5 wt% Nb.

It is important to be able to discount the effect of tip–surface interaction from our observations. In order to do this, a smaller area of surface is scanned several times and then compared to the surrounding area. No changes due to the scanning, and thus the tip–surface interaction, are seen. The formation of nanolines and domains whilst annealing at these temperatures without scanning is another indication that the images are not affected by the tip [6, 12].

An interesting effect of the high-temperature imaging reported here is the lower annealing temperature required to produce certain nanostructures. This is believed to be due to the length of the anneals performed in these experiments; typically several days, rather than times of up to an hour, as used in previous experiments [6, 12]. In practice, these timescales are necessary in order to allow the surface to



**Figure 5.** (a)–(d) Formation of a waffle structure from a domain of dilines at 850 °C. Time,  $t$ , is measured in minutes. In (a), the arrow marks a small domain of dilines, with a few elements of the waffle structure visible within it. In (b) and (c), the amount of waffle structure present increases and, in (d), a large area of waffle structure can be seen. (e) shows a room-temperature image of a large area of waffle structure (white arrow) and a diline which becomes a waffle structure along its length (black arrow). Sample voltages and tunnelling currents used: (a)–(d) 2.00 V, 0.20 nA; (e) 0.80 V, 0.30 nA.

equilibrate at the high temperatures used, such that the system is stable enough to image successfully.

## 5. Conclusions

The dynamics of several nanostructures have been observed using hot STM at over 800 °C for periods of up to 80 min. Observations of the growth of dilines suggests that these randomly nucleate and then reorder into domains at higher temperature. It has also been observed that nanolines are more stable in pairs than when isolated, hence suggesting the stability of domains over randomly distributed lines. The nucleation and growth of both trilines and waffle structures from small diline domains has also been reported.

Overall, this study shows that at high temperatures nanostructures are mobile on the  $c(4 \times 2)$  surface of SrTiO<sub>3</sub>(001). It has also demonstrated that the diline domains form by high-temperature reordering of randomly nucleated dilines.

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