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Real time dynamics of Si magic clusters mediating phase transformation: Si(111)-(1×1) to (7×7) reconstruction revisited

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ABSTRACT

Using Scanning Tunneling Microscope (STM), we show that the surface undergoes phase transformation from disordered "1×1" to (7×7) reconstruction which is mediated by the formation of Si magic clusters. Mono-disperse Si magic clusters of size ~13.5±0.5 Å can be formed by heating the Si(111) surface to 1200 °C and quenching it to room temperature at cooling rates of at least 100 °C/min. The structure consists of 3 tetra-clusters of size ~4.5 similar to the Si magic clusters that were formed from Si adatoms deposited by Si solid source on Si(111)-(7×7) [1]. Using real time STM scanning to probe the surface at ~400 °C, we show that Si magic clusters pop up from the (1×1) surface and form spontaneously during the phase transformation. This is attributed to the difference in atomic density between "disordered 1×1" and (7×7) surface structures which lead to the release of excess Si atoms onto the surface as magic clusters.

1. Introduction

Small clusters with unique number and configuration of atoms (identified as magic clusters) have been found to exhibit unique stability and electronic properties distinct from the bulk [2]. This has in turn generated keen interest in the use of substrate supported magic clusters as building blocks to fabricate nano-structures from various material systems (i.e. Ag/Ag(100), Pt/Pt(110), In/Si(001) and Ga, Ag, Mn, Pb, Co/Si(111)) [3–19]. Understanding how Si magic clusters form and mediate Si surface ordering will aid the progress in areas of work driven by device miniaturization.

Si magic clusters on Si(111) have been previously observed by Tsong et al. [12–14], who found that these clusters were mobile at high temperatures. They studied the diffusion mechanism and determined the cluster diffusion barrier to be ~2.04 eV–2.55 eV [12–14]. They also demonstrated how the dissociation of Si magic clusters at the step edges contributed to the growth of step edges and propagation of (7×7) ordering, thus first identifying the critical role that Si magic clusters play in promoting Si(111) surface ordering and growth [29,30]. Recently, Ong et al. [1] demonstrated that Si magic clusters (size ~13.5±0.5 Å) exhibiting localized spatial ordering could be achieved directly from Si adatoms deposited on a Si(111)-(7×7) template using a molecular beam epitaxy solid source. The formation of the Si magic cluster was also shown to have occurred via a step-wise assembly of Si tetra-clusters. These tetra-clusters were formed from the deposited Si adatoms and a single Si magic cluster is found to consist of $n=12$ Si adatoms. The implication of the above observation was that Si adatoms on well ordered Si(111) surface can be assembled into magic clusters.

Although there is substantial work covering the surface transformation of Si(111)-"disordered 1×1" to (7×7), there are still information gaps with regards to this phase transition. During the phase transformation, the Si(111)-(7×7) reconstruction [24] is reported to disorder at temperatures above 900 °C into the (1×1) phase and reverts back into the (7×7) structure as the surface is cooled below this transition temperature [20–22]. The "disordered 1×1" unit cell has been shown to have a higher atomic density than the (7×7) unit cell structure, thus giving rise to formation of excess adatoms on the surface during the "disordered 1×1"→(7×7) transition [20]. It has also been assumed that these excess adatoms form DAS structures such as meta-stable (5×5), (9×9) and (11×11), and the stable (7×7) reconstruction. It was suggested that the phase transformation was mediated by Si adatoms. However with the observation of magic clusters forming from deposited Si adatoms on well ordered surfaces, it raises the possibility that excess Si adatoms could form Si magic clusters. Hence we re-visit this phase transformation and we will provide direct evidence that Si magic clusters are also formed during "disordered 1×1"→(7×7) transformation and that these mobile Si magic clusters mediate this process.

In addition we will show that heating the surface to 1200 °C and fast quenching generates mono-disperse Si magic clusters of size ~14.0±0.5 Å. These clusters are observed in addition to the (7×7) and DAS structures. The magic clusters can also be resolved

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into 3 blobs of ~4.5 `which are similar in shape and size to the clusters observed by *Tsong et al.* [12–14], thereby identifying them as Si magic clusters. By employing real time STM scanning techniques, we will show that the Si magic clusters pop out onto the "disordered 1×1" surface, thus propagating well ordered (7×7) domains.

2. Experimental

The experiments were carried *in-situ* out in an Ultra High Vacuum (UHV) system with an OMICRON Variable Temperature Scanning Tunneling Microscope (VT-STM), with an ambient pressure of 1.0×10^{-8} Pa. The samples were cut from P-doped *n*-type Si(111) single crystal wafers with dopant concentration of ~10^{18} cm^{-3} supplied by Virginia Semiconductors. The details of our sample preparation have been previously discussed [8,9]. These samples were first chemically etched *ex-situ* in 1:10 parts of 49% hydrofluoric acid (HF) acid to de-ionized water before outgassing for 8 hours at ~300 °C in the UHV chamber. The sample is subsequently flashed to 1200 °C to remove surface oxides and obtain clean Si(111)-(7×7) surface. The (7×7) surface typically consists of large terraces (~300 nm to 400 nm wide) with step edges running along the <110> direction. No surface features such as islands or clusters are observed on the terraces or at the step edges. We use this (7×7) reconstruction as the starting surface template to generate the "disordered 1×1" phase by heating it to 1200 °C before quenching to room temperature at various estimated cooling rates. By immediately cutting off the power supply, we can quench the temperature of the sample from 1200 °C down to 300 °C very quickly. This happens within seconds but the sample temperature cools down more slowly from 300 °C to room temperature. By taking the overall time it takes to cool the sample, we can determine the average cooling rate to be ~100 °C/min. In order to achieve a slower cooling rates of 50 °C/min or 1 °C/min, we do not cut off the power supply instantly. Instead we reduce the current supplied to the sample gradually while cooling the sample from 1200 °C to obtain the desired sample cooling rate. As STM observation of this process at such high temperatures is difficult due to a high thermal drift effect which renders inconsistency in scan frame capture. The imaging of the surface is thus best suited to room temperature scanning. However due to the high surface mobility associated with Si adatoms, where the activation energy for a single Si atom diffusion has been estimated to be ~1.14 eV [25,26], the adatoms are likely to diffuse very quickly to the step edges which they will attach and integrate into, thus making characterization of surface adatoms difficult. In order to overcome this problem, the surface to be would have cooled very quickly in order to trap the adatoms on the surface. This trapping process is only possible when the time required to quench to low temperatures is shorter than the time for the Si adatoms to diffuse across the terraces to the steps. The following cooling rates of ~1 °C/min, ~50 °C/min and 100 °C/min were studied.

All the STM images were taken using constant current mode, with tunneling currents of 0.10–1.00 nA and biases of $-2.0\ V \le V \le +2.0$ V applied to the sample. The dimension and periodicity analysis were performed with the use of the WSxM software [23].

3. Results and discussion

3.1. Different rates of quenching

The clean Si(111) surface was flashed to temperatures of 1200 °C and subsequently cooled to room temperature at different cooling rates of ~1 °C/min, ~50 °C/min and 100 °C/min, before being scanned using STM. The respective STM images at different scan sizes of 1000 nm×1000 nm (Fig. 1a), 100 nm×100 nm (Fig. 1b) and 30 nm×30 nm (Fig. 1c) are shown in Fig. 1a(i–iii), b(i–iii) and c(i–iii).

The surface topography as shown in Fig. 1a(i) and Fig. 1b(i) appears to be similar and is dominated by flat terraces which are about ~300–400 nm wide, with step edges running in the <110> direction. In contrast, Fig. 1c(i) shows large triangular domains with trails leading from the domain apexes to the step edges on the terrace surface. Zoom-in 100 nm×100 nm observations of these respective surfaces are shown in Fig. 1a(ii), Fig. 1b(ii) and Fig. 1c(ii). There is little difference between the two surface morphologies in Fig. 1a(ii) and Fig. 1b(ii), which generally show large terraces and step edges. We also observe trails of cluster-like particles on the wide terraces leading to step edges (Fig. 1b(ii)). Fig. 1c(ii) shows large triangular (7×7) domains co-existing with bright regions of "disordered 1×1" phase on wide terraces. A closer examination of this surface reveals well resolved cluster-like particles which appear bright and round in shape residing in the "disordered 1×1" regions while the (7×7) domains are characterized by large and well ordered triangular domains comprising of well defined (7×7) unit cells.

Zoom-in 30 nm×30 nm images of the surface microstructure are shown in Fig. 1a(iii), Fig. 1b(iii) and Fig. 1c(iii). Well ordered (7×7) reconstruction are observed to dominate the terrace surfaces with no other features present as shown in Fig. 1a(iii). This could be attributed to the slow cooling rate of ~1 °C/min, for which there is sufficient time for Si adatoms to diffuse to and assimilate into the step edges. Similarly, Fig. 1b(iii) shows long range (7×7) ordering, however Si cluster-like particles are now observed on the surface. These particles typically decorate the step edges and this observation may be attributed to the faster cooling rate of ~50 °C/min. This suggests that this cooling rate is still sufficiently slow enough for Si diffusion to the step edges, but still quick enough for us to observe that these particles are trapped at the steps. Fig. 1c(iii) shows a considerable number of these same cluster-like particles existing on the "disordered 1×1" phase, indicating that the cooling rate of ~100 °C/min is quick enough to capture sufficient particle populations on the terrace surface. Further inspection of the surface shows initial ordering among the "disordered 1×1" phase with the presence of metastable DAS phases such as (5×5), (7×7) and (9×9) as well as non-DAS phases such as (2×2). It is interesting to note from the STM data, that in addition to the meta-stable structures, the feature with the largest occurrence existing on top of the "disordered 1×1" phase appears to be the cluster-like particles.

3.2. Characterization of Si magic clusters

We obtain the dimensions of each cluster-like particle by taking the average of STM line profile measurements to represent the estimated size and height of each particle. The size of each magic cluster was determined from the separation between opposite fringes of the bright cluster protrusions. An example of the cluster size measurement is shown in Fig. 2(a). The separation across the area occupied by the bright maxima of the cluster is measured by line profile in 3 directions along the <110> direction. This is shown to be (A) 13.5 Å, (B) 13.5 Å and (C) 13.7 Å respectively. The average of these 3 readings is estimated to be ~13.5 Å, and consequently assumed to be the representative size of each cluster. These measurements were also taken when the same cluster is scanned under different tunneling biases (ranging from −2.0 V to +2.0 V) and the changes in size associated with the different biases is reflected in the error bar. This is to reduce any electronic effects associated with changes with the electron density distribution.

The average cluster sizes are counted as shown in Fig. 2(b) and tabulated into a histogram showing the cluster size distribution for each scan (about ~100±5 clusters per scan). The statistical data collected from 5 scans shows a narrow cluster size distribution with the largest occurrence of the estimated average cluster size to be 13.5±0.5 Å. This information coupled with the STM observation of the same clusters consistently possessing a uniformly round shape suggests that each of these particles are magic clusters. This identification of the Si magic clusters is significant, as these clusters are consistently present during the surface evolution during (7×7) reconstruction