Decay of Two-Dimensional Holes on SrTiO$_3$(001)

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We have studied the decay kinetics of two-dimensional holes on SrTiO$_3$(001) surfaces using scanning tunneling microscopy (STM). We have created nanoscale unit-cell-deep holes on (001) terraces using a STM nanofabrication technique, and have performed real-time observation of the decay of the holes in a temperature range of 700 $\sim$ 800 $^\circ$C. From the observed time dependence of hole areas during decay, we have found that the rate limiting process of the decay is the surface diffusion. We have also investigated the effect of the existence of substrate steps and islands on the hole decay. [DOI: 10.1380/ejssnt.2006.307]

Keywords: Scanning Tunneling Microscopy; Surface diffusion; Surface structure, morphology, roughness, and topography; Single crystal surfaces;

I. INTRODUCTION

Knowledge about the mass transport mechanism is crucial for understanding of various surface dynamic phenomena, such as epitaxial growth. Real-time observation of the decay of individual two-dimensional islands and holes is a powerful method to study the mass transport mechanism, since comparison of experimental results with the prediction from analytically tractable models is feasible. To date, on surfaces of various crystals such as Si [1, 2], Au [3], Ag [4], and Cu [5], the decay kinetics of individual islands and holes has been studied.

In this paper, we have studied the decay kinetics of two-dimensional holes on SrTiO$_3$(001) surfaces using scanning tunneling microscopy (STM). SrTiO$_3$ has been widely used as a substrate for growth of thin films. However, our understanding of the surface mass transport on metal oxides such as SrTiO$_3$ is very poor, despite the technological importance. Previously, Lippmaa et al. [8] have performed real-time observation of morphological evolution of SrTiO$_3$(001) surfaces at high temperatures of 600 $\sim$ 800 $^\circ$C, using STM. However, the mechanism of surface morphological evolution on SrTiO$_3$(001) surfaces is still unclear. In this work, with the help of the STM nanofabrication technique, which enables us to control the size and position of holes, we examine the decay of individual holes under the well-defined environment suitable for analysis.

II. THEORY FOR DECAY OF ISOLATED HOLES

The driving force of the hole decay is the lower chemical potential at the curved edge of holes than a straight step in thermal equilibrium due to the Gibbs-Thomson effect. The chemical potential of a circular hole is given by $\mu = \mu_0 - \Omega \beta / r_h$, where $\mu_0$ is the chemical potential of a step in equilibrium, $r_h$ is the hole radius, $\beta$ is the step tension, and $\Omega$ is the area occupied by a surface atom. It is well known that the decay of two-dimensional islands and holes

![FIG. 1: STM images of a decaying unit-cell-high hole on SrTiO$_3$(001) at 760 $^\circ$C. The image size is 270 nm x 270 nm.](image)

![FIG. 2: Time dependence of the area of the isolated hole shown in Fig. 1. The solid line is the result of fitting the data to Eq. (1). The exponent $\alpha$ is estimated to be 0.72.](image)
follows the power law dependence as [1–6]

\[ A(t) \propto (t_c - t)^\alpha. \]  

(1)

The exponent \( \alpha \) is determined by the rate limiting process of the decay. Here, we consider the two different cases: one is attachment/detachment limited case and the other is diffusion limited case.

In the attachment/detachment limited case, the fast diffusion results in a spatially uniform concentration of adatoms on the terraces. The rate of change of hole area \( A \) is given by

\[ \frac{dA}{dt} = 2\pi r_h \Omega (\mu - \mu_{ad}). \]  

(2)

where \( \mu_{ad} \) is the chemical potential of adatoms and \( \kappa \) is the kinetic coefficient. In the condition where no sublimation and growth occur, \( \mu_{ad} \approx \mu_0 \), so Eq. (2) reduces to \( \frac{dA}{dt} = -2\pi \Omega^2 \beta \kappa \). Thus, we find that \( A \) decreases linearly in time, that is, \( \alpha = 1 \) [2].

In the diffusion limited case, the gradient of adatom concentration arises around the holes due to the slow diffusion. The adatom concentration around the circular hole obeys the diffusion equation in a polar coordinate system,

\[ \frac{\partial c(r)}{\partial t} = D \left( \frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right), \]  

(3)

where \( D \) is the diffusion constant of the adatoms. The steady state radial distribution of adatom concentration can be determined, applying a following generic boundary condition. Since the adatom concentration at the hole edge keeps to be the one at equilibrium through many times of attachment and detachment of adatoms, \( c(r_h) = c_{eq} \exp(\beta \Omega/kT r_h) \). Moreover, we assume that there is a region around the hole, \( r_h < r < r_h + w \), where concentration gradient exists, and that outside this region the concentration is homogeneous at \( c_{eq} \). Since the decay rate of the hole is given by \( \frac{\partial A}{\partial t} = -2\pi \Omega D r_h \partial c(r_h)/\partial r \), we obtain

\[ \frac{\partial A}{\partial t} = 2\pi \Omega D c(r_h) - c_{eq} \frac{\ln (R/r_h)}{\ln (R/r_h)}. \]  

(4)

where \( R = r_h + w \). When we assume that \( R \gg r_h \) and that \( R \) does not change during the decay, Eq. (4) reduces to \( \frac{\partial r_h}{\partial t} = -\Omega^2 D c_{eq}/(kT \ln R) \cdot \frac{r_h}{R^2} \). Thus, in the diffusion limited case, the area \( A \) decreases as \( A(t) = \pi(3\Omega^2 D c_{eq}/kT \ln R)^{2/3}(t_c - t)^{2/3} \), that is, \( \alpha = 2/3 \) [6, 7].

III. EXPERIMENT

Samples were cut from Nb-doped SrTiO\(_3\)(001) wafers. The experiments were conducted in an ultra high vacuum (UHV) chamber with a base pressure of 1.0 \times 10^{-8} \text{ Pa}. Sample heating was achieved by a resistive heater, and the sample temperature was monitored by an optical pyrometer. The samples were installed into the UHV chamber without any chemical treatment and then degassed at 500 °C for 4 h. In order to form a flat surface composed of flat terraces and unit-cell-high steps, samples were heated at 800 °C for 5 hours [9].

Two-dimensional holes were created by approximating the STM tip to the surface further than the imaging position with the sample bias of 2.0 ∼ 2.3 V while heating the sample at 700 ∼ 800 °C. We consider that the mechanism of the nanofabrication is identical with that performed on Si surfaces [10, 11]. After fabricating the two-dimensional hole, subsequently we monitored the decay of the hole by STM.

IV. RESULTS AND DISCUSSIONS

Figure 1 shows a series of STM images showing the decay of a unit-cell-deep hole situated in the middle of a wide terrace, which is about 230 nm in width, during annealing at 760 °C. This hole disappeared completely.
within 26 min. The area of the hole is plotted as a function of time in Fig. 2. This result is obviously inconsistent with the linear dependence expected in the attachment/detachment limited case. By fitting the data to the form of Eq. (1), the exponent $\alpha$ is estimated to be 0.72. Though this value is slightly larger than 2/3, this result indicates that the decay is limited by the diffusion on the terrace rather than the attachment/detachment at the hole edge. By estimating the proportional constant in Eq. (1), we find that $\pi(3\Omega^2D_{eq}3/kT \ln R^2/3) \approx 1.9 \text{ nm}^2/\text{s}^{2/3}$.

In the diffusion limited case, the decay of individual holes is affected by the environmental surface structures, such as substrate steps, because they change the boundary condition for the diffusion field. Here, we see the effect of substrate steps on the decay of a hole. Figure 3 compares the decay feature at 715 °C between a hole near the step and that situated far from the step. Figs. 3(a)∼(d) show the decay of a hole (hole $A$) created far from the step. After hole $A$ disappeared, in the same surface region, we created a new hole (hole $B$) near the step edge at a distance of about 7 nm and the feature of the decay is shown in Figs. 3(e)∼(f). The size and position of the small particle seen in the lower right images did not change during observation, and thus we consider that the decay of the holes is not affected by this particle. Figure 4 shows the time dependence of the hole areas for these two holes. The solid curves show the fits to the form of Eq. (1), and for holes $A$ and $B$, the exponents $\alpha$ are estimated to be 0.78 and 0.69, respectively. The average decay rates of holes $A$ and $B$ are 0.054 and 0.11 nm$^2$/s, respectively, and thus, the hole near the step decays faster than the isolated hole. In the diffusion limited case, the adatom concentration at the step edge is $c_{eq}$. If the distance between the hole edge and the step is shorter than $\omega$, the diffusion field around the hole is modified by the step. The resultant diffusive current from the step to the hole accelerates the decay of the hole. Previously, the decay rates of holes and islands located at a straight step are calculated in the diffusion limited case by Natori et al. The behavior of the decay of hole $A$ is obviously inconsistent with the $t^{2/3}$ dependence, which is due to the effect of the island. In Fig. 6(b), the time dependence of hole $B$ is extracted. We find that the decay of hole $B$ is decelerated by the disappearance of the island at 95 min. The solid curve shows the fit to the form of Eq. (1) for the data since 95 min, and the estimated $\alpha$ is 0.73. After vanishing the island, the behavior of hole $B$ agrees with the $t^{2/3}$ dependence as expected in the diffusion limited case. Moreover, in Fig. 6(a) we notice that the decay of the hole is slower than that of the island. Previously, Natori et al. [12] have shown similar results by Monte Carlo simulation and analytic calculation. As found from Eq. (4), the rate of decay is proportional to $\Delta r = |c(r) - c_{eq}|$. Since the equilibrium adatom concen-
trations, \(c(r)\), at the edges of an island and hole of radius \(r\) are \(c_{eq}\exp[\gamma \Omega/kT r]\) and \(c_{eq}\exp[-\gamma \Omega/kT r]\), respectively, \(\Delta_r\) for islands is larger than that for holes. Thus, we find that generally islands decay faster than holes. This tendency becomes more considerable with decreasing temperatures and island/hole sizes. Using \(\gamma \approx 0.93\ \text{eV/nm}\), which is previously estimated for SrTiO\(_3\)(001) [9], we obtain \(\gamma \Omega/kT = 1.6\ \text{nm}\) at 1000 K. In this estimation, we use \(\Omega = a^2\), where \(a = 0.39\ \text{nm}\), the lattice constant of SrTiO\(_3\). Thus, we expect that at radii below \(\sim 10\ \text{nm}\) the difference of \(\Delta_r\) between holes and islands becomes measurable. Moreover, this asymmetry between islands and holes is enhanced if a step edge barrier against downward diffusion of adatoms across the step exists [4]. At present, it is not clear whether such step edge barrier exists or not on SrTiO\(_3\)(001). Work to address this problem is in progress.

V. SUMMARY

We have studied the decay of two-dimensional holes on SrTiO\(_3\)(001) surfaces by STM. The time evolution of the area of an isolated hole is consistent with the \(t^{2/3}\) dependence expected for the diffusion limited case. We have also studied the decay of the holes located near a substrate step and island. Our overall observations can be understood based on the diffusion limited kinetics.

Acknowledgments

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