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Dynamics of Au-adsorption-induced step bunching on a Si(001) vicinal surface studied by reflection electron microscopy

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Dynamic processes of the step bunching on a Si(001) vicinal surface during Au deposition were studied by reflection electron microscopy. Due to formation of the Si(001)5×3.2-Au terraces and their growth the step bunching occurs and a hill and valley structure composed of (001) terraces and facets is formed. The time evolution of the (001) terrace width was analyzed for various substrate temperatures. The width develops in a form of t^{α} as a function of time t between 780 and 900 °C. The exponent α is $\frac{1}{4}$ at 820 °C and it increases gradually with increasing temperature and is $\frac{1}{2}$ above 870 °C. This means that the kinetics that governs the step bunching changes with increasing temperature. [S0163-1829(99)03827-8]

I. INTRODUCTION

Recently, adsorption-induced step bunching and faceting on metal or semiconductor surfaces have been studied.[1–11] Studies of the step bunching, especially, its dynamics are attractive for better understanding of the mechanism of adsorption-induced step bunching on a vicinal surface. On a Si surface, surface reconstruction plays a very important role in the step bunching.[4–6] The surface reconstruction changes upon adsorption of a foreign metal. Generally, the surface reconstruction on the Si surface induced by metal adsorption reduces the surface free energy because most of the metals grow in the Stranski-Krastanov mode. Thus, metal adsorption on a Si vicinal surface may induce surface reconstruction on low index surface and may cause a change of a regular array of steps to step bands and flat low index terraces. Formation of the Si(001)5×3.2 surface induces step bunching on the Si(001) vicinal surface and the step band areas transform mainly to (119) facets due to the formation of the Si(119)8×2-Au reconstruction.[11] In the present paper we investigate the dynamics of the Au-adsorption-induced step bunching on a Si(001) vicinal surface by reflection electron microscopy (REM).

II. EXPERIMENT

The experiments were performed in a ultrahigh vacuum electron microscope equipped with an Au evaporator and a thickness monitor. Si wafers were cut to a size of $7\times1\times0.3\,\mathrm{mm}^3$ from a wafer of the Si(001) vicinal surface 4° off towards the $[1\bar{1}0]$ direction. The miscut direction of the sample is parallel to the elongated side of the sample and incident electron beam is along the steps (the [110] direction). After chemical cleaning the sample crystals were mounted on a sample holder and transferred into the microscope. DC current heating at 1200 °C removed the native oxide on the sample surface. Au was deposited from a tungsten wire at substrate temperatures between 780 and 900 °C at various deposition rates for each substrate temperature. More than five deposition rates were used for each substrate temperature. For example, the deposition rates 1–3 ML/min at 900 °C and 0.2–0.5 ML/min at 780 °C. Maximum amount of deposited Au in all the experiments was about 15 ML. The saturation coverage of the 5×3.2 structure is about 0.6 ML (Ref. 12) so that the total amount of *adsorbed* Au in all experiments was about 0.6 ML. Au in excess of this amount forms droplet, desorbs or diffuses into the bulk, depending upon temperature and prehistory. The REM images are distorted by a foreshortening factor of about 1/40 along the electron beam direction.

III. RESULTS AND DISCUSSION

Figure 1 is a series of REM images that reproduces nucleation and growth processes of an (001) terrace and the accompanying step bunching process during adsorption of Au on a vicinal surface 4° off Si(001) at 870 °C. They are reproduced from a video tape. The time t shown in each image is an elapsed time after (a). Figure 1(a) was taken 170 s after the start of the deposition and no morphology change was observed until Fig. 1(a) was taken. The surface steps up to the downward direction in the image and an arrow in Fig. 1(a) indicates the direction of the electron beam. As shown in Fig. 1 all the images are distorted (see scale mark). Dark and bright lines running from upper right to lower left are seen in Fig. 1(a). This is due to the fact that the surface is wavy along the electron beam direction and the reflection condition is changed along the electron beam. (A REM image is very sensitive to small changes in surface morphology, especially along the electron beam.) The wavy surface is formed when steps are wandering and bright lines correspond to ridges of the surface with wandering steps and dark lines correspond to the areas in between.

It is clearly seen that a dark area indicated by an arrow nucleates in Fig. 1(b) and grows larger in Figs. 1(c)–1(h). The dark area corresponds to a single (001) terrace with the 5×3.2 reconstruction[5] and it grows larger with increasing Au coverage on the surface. A growth speed of the (001) terrace is very anisotropic and much faster perpendicular to the miscut direction than along the miscut direction. When the (001) terraces expand along the miscut direction, mass transport of Si atoms across terraces is needed and the steps move to form step bands. On the other hand, there is no or

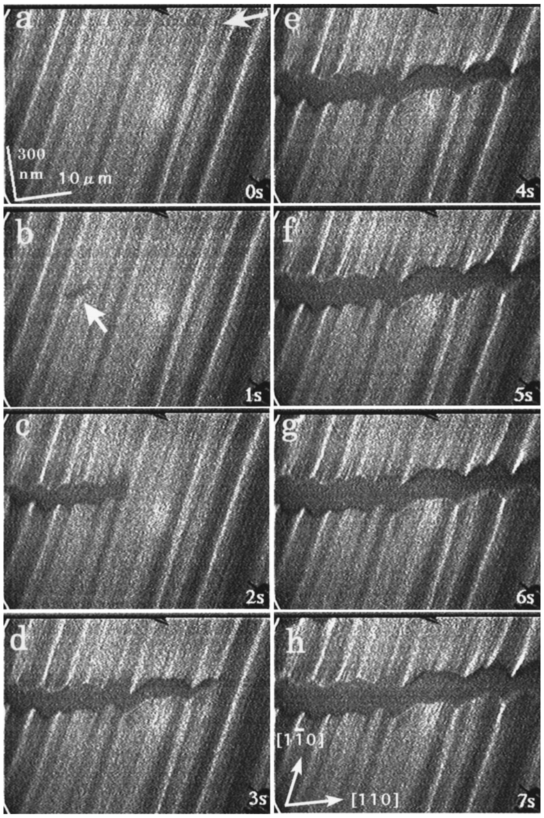

FIG. 1. A series of REM images showing nucleation and growth of (001) 5×3.2-Au terraces and consequent step bunching during the deposition of Au on a 4° off Si(001) vicinal surface at 860 °C.

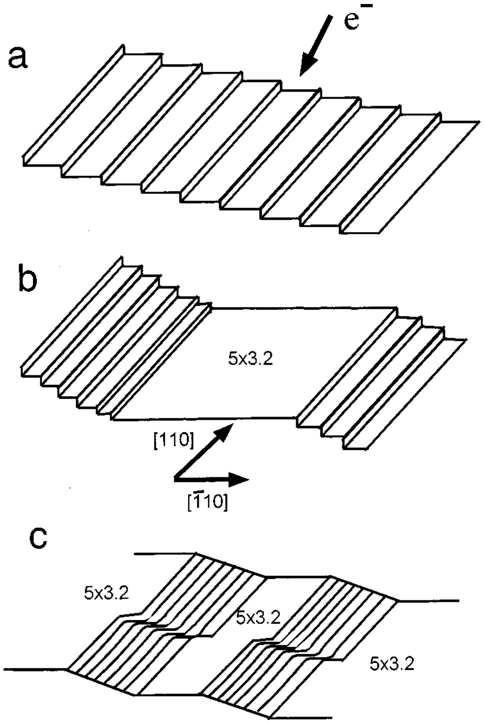

FIG. 2. A schematic diagram corresponds to (a) Fig. 1(a) and (b) Fig. 1(h). Figure 2(c) shows a hill and valley structure composed of the (001) terraces and facets. (001) terraces are zigzag shape due to a slight miscut toward the [110] direction.

very small mass transport when the (001) terraces expand perpendicular to the miscut direction. Thus, the growth speed of the (001) terrace should be very anisotropic as seen in Fig. 1. In our previous scanning tunneling microscopy (STM) study of Au adsorption on the Si(001) surface,[10] a drastic change of a step configuration even at 500 °C and anisotropic growth of the reconstructed structure at 700 °C were noted. This strongly suggests enhancement and anisotropic surface diffusion of Si adatoms on the Au-adsorbed Si(001) surface. The anisotropic growth feature should be partly related with the anisotropy of the surface diffusion of Si and Au atoms on the Si(001)-Au surface.[13] These anisotropic features cause formation of the (001) terrace with one-dimensional (1D) band shape in the early stages of the deposition as shown in Figs. 1(c)–1(e). After formation of the (001) terrace with 1D band shape it grows wider as in Figs. 1(i)–1(h). Figures 2(a) and 2(b) schematically show the surfaces before [Fig. 1(a)] and after [Fig. 1(b)] nucleation of a 5×3.2-Au terrace. Figure 2(c) schematically shows the way the dark (001) terrace is not seen as a straight band in Fig. 1. A small deviation of surface inclination from the $[1\bar{1}0]$ direction due to the wavy surface and unintentional miscut causes a shift of the step band as shown in Fig. 2(c). [See also Fig. 5(a) in the case of facet formation.] Within our all the experimental conditions no qualitative difference in the surface morphology change was observed and four stages of surface morphology change were observed.[11]

The time evolution of the terrace width (*W*) along the miscut direction in the series shown in Fig. 1 is plotted in Fig. 3 as a function of time *t* after nucleation. *W* increases with time and the lateral growth speed (slope of the plotted curve) slightly decreases with increasing *W*. This experimental data was fitted by using a function of $W\propto t^{\alpha}$ derived theoretically.[14,15] The fitting gives $\alpha=0.48$ in this case.

In the theory the kinetics of step bunching is classified into two types and the exponent α has different values in the two cases. When the mass transport is localized, in other words when mass exchange between neighboring steps is preserved; the (001) terrace grows as $t^{1/4}$ (the local mass exchange case). On the other hand, it grows as $t^{1/2}$ when the mass transport is nonlocalized and mass exchange between neighboring steps is not preserved (the nonlocal mass exchange case). Thus, the case in Fig. 3 corresponds to the case of the nonlocal mass exchange.

The factor α was measured under various deposition conditions and it was found that α does not depend on the depo-

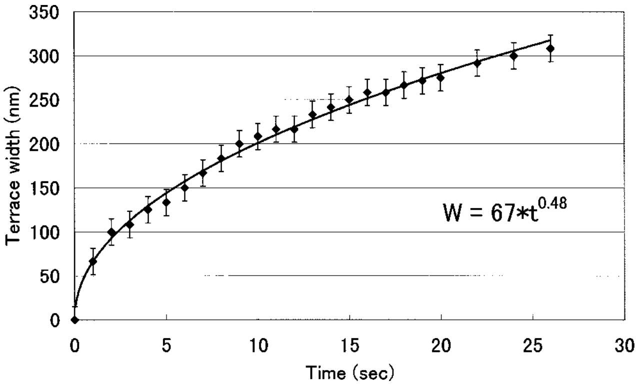

FIG. 3. A time evolution of the terrace width (*W*) along the miscut direction in Fig. 1.

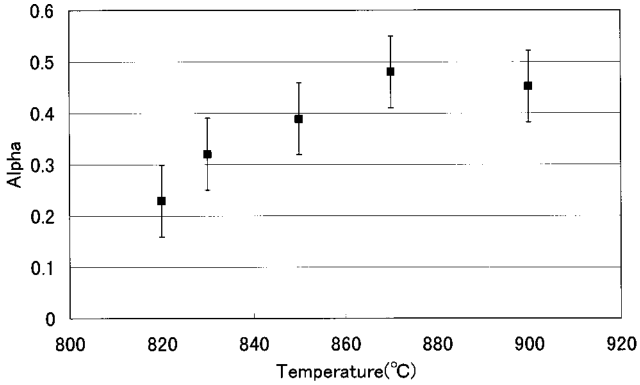

FIG. 4. The temperature dependence of the value α.

sition rate within our experimental conditions. On the other hand α seems to depend on the substrate temperature as shown in Fig. 4. Although the estimated values include relatively large errors probably due to kinetic effects, α is approximately $\frac{1}{4}$ in a low-temperature range at 820 °C and is approximately $\frac{1}{2}$ in the high-temperature range above 870 °C increases with increasing substrate temperature from $\frac{1}{4}$ to $\frac{1}{2}$ between these two temperature ranges. This indicates local mass exchange below 820 °C, nonlocal mass exchange above 870 °C and a gradual change of the two effects in between. The nonlocal mass exchange effect increases with increasing temperature.

Step bunching occurs when a Au-adsorbed Si(001) 5×3.2 terrace is formed. Thus, the time evolution of W, in other words, the time evolution of the step bunching may be affected by the growth kinetics of the 5×3.2 areas. In the case that formation of the 5×3.2 structure is a rate-determining process of the step bunching, α is unity because the 5×3.2 areas increase linearly with increasing Au coverage on the sample surface at constant deposition rate. Within our experimental range, α is less than $\frac{1}{2}$ as in Fig. 3. This means that the formation of the 5×3.2 structure is not the rate-determining process of the step bunching. The fact that $t=0$ in Fig. 3 corresponds to 170 s after the start of Au deposition, which is much longer than a growth time of the terrace, also support this conclusion. Thus, our experiments indicate that mass transport of Si is the rate-determining process of the step bunching and the kinetics of step bunching, in other words, the kinetics of the mass transport changes with increasing temperature as described above. It should be noted that the temperature-dependent bunching kinetics has not been reported.

In the high-temperature range, mass exchange of Si between neighboring steps is not preserved. This means that the mass transport of Si occurs by sublimation into vacuum and surface diffusion across the steps. The average step-step distance on the 4° off vicinal surface is less than 4 nm and is much shorter than surface diffusion distance above 800 °C. If the nonlocal mass exchange were mainly governed by the surface diffusion across the steps, the bunching kinetics would not depend on the temperature contrary to the present case. Studies of step bunching due to surface electromigration have been reported and the importance of sublimation of Si been emphasized.[16] The sublimation of Si atoms becomes much faster and much effective in the step-bunching process at higher temperature. Thus, the step-bunching kinetics should be governed by the sublimation of Si atoms.

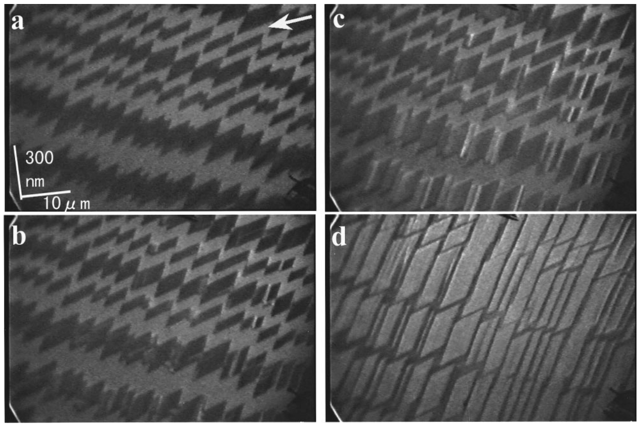

FIG. 5. A series of REM images showing step-bunching during debunching process at 900 °C.

However, it appears surprising that the effect of sublimation is so effective already at 870 °C because the sublimation of the clean Si surface may not be sufficiently fast so as to govern the bunching kinetics. Under the present Au deposition condition, desorption of the Au atoms and diffusion into the bulk crystal occur during Au deposition and place exchanges between Si and Au atoms will actively occur. In this case, sublimation of Si atoms should be enhanced during the site exchanges because the sublimation of atoms is enhanced during the site exchange process as in the case of low-temperature metal sublimation during surfactant mediated epitaxy.[17] Thus, the kinetics of step bunching can be said to be governed by the sublimation of Si atoms. The sublimation of Si atoms decreases with decreasing temperature and so does the step bunching kinetics so that the local mass exchange (surface diffusion of Si atoms) becomes more effective at lower temperatures.

When Au coverage decreases at high temperatures, debunching of the steps, hence, narrowing of the (001) terraces occurs. Figure 5 illustrates the debunching process during annealing at 900 °C. The direction of the electron beam is indicated by a white arrow in Fig. 5(a). In Fig. 5(a) bright and dark areas elongated in the direction normal to the miscut direction alternate. The bright and dark areas correspond to the (001) terraces and (119) facet areas, respectively. The (001) terraces have zigzag shapes due to slight unintentional miscut toward the [110] direction as was illustrated in Fig. 2(c). In Fig. 5(b) the image contrast of the dark areas changes slightly due to the transformation from the facet to step bands in Fig. 5(b), while there is no change in the bright areas [(001) terraces]. This suggests that desorption (or diffusion into the bulk) of Au atoms occurs preferentially at the facet or step-band areas. The width of the bright areas decreases in Fig. 5(c) due to further decrease of the Au coverage. In Fig. 5(d) the image contrast between the (001) terraces and step bands is reversed due to a slight change of the imaging condition so as to get a bright image in Fig. 5(d). Dark areas correspond now to the (001) terraces and the terrace width W of the (001) terraces is narrower in Fig. 5(d).

The debunching process seems to be the reverse process of the bunching process. The time development of the terrace width during debunching was analyzed in the same way as the step bunching process. Figure 6 shows an example of the

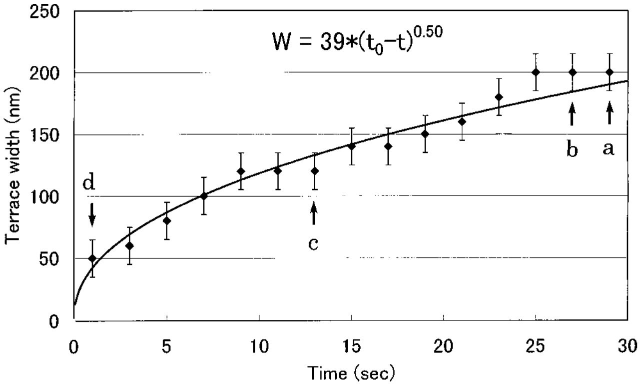

FIG. 6. A time evolution of the terrace width (W) along the miscut direction during debunching. $t=0$ is time when a 5×3.2 terrace disappears and a fitting curve and obtained parameter is shown in the figure. The corresponding stages of Figs. 5(a)–5(c) are indicated.

experimental results at 900 °C. Measurements were performed for each terrace. The time t is reversed and $t=0$ was chosen to the time when each (001) terrace disappeared. The width W was fitted by $W\propto(t_0-t)^{\alpha'}$, where t_0 is the time when each (001) terrace disappeared and W is shown in Fig. 6. Stages corresponding to Figs. 5(a)–5(d) are indicated in Fig. 6. In this case α' is $\frac{1}{2}$, which is the same value as that obtained during step bunching at the same temperature. Thus, the mass exchange kinetics is the same as that during step bunching in the high-temperature range and debunching should be governed by nonlocal mass exchange.

The temperature dependence of α' was also investigated as in Fig. 7 for comparison with the step bunching. To obtain one plot in Fig. 7, multiple observations were performed and time evolution of widths of several terraces in each observation were measured and evaluated values were averaged. A common feature in Figs. 3 and 6 is that both α and α' approach $\frac{1}{2}$ in the high-temperature range. This suggests that the mass transport kinetics during step bunching and debunching is the same and the nonlocal mass exchange process governs the step bunching and the debunching in this temperature range. Indeed, as described above, site exchanges between Si and Au atoms occur actively and the sublimation of Si atoms is enhanced during bunching and debunching in the high-temperature range.

On the other hand, it is noted that α' increases with decreasing temperature and is unity at 840 °C in the low-temperature range. In the low-temperature range the debunching process is not governed by neither the local nor the nonlocal mass transport of Si atoms because α' is unity. Thus, the kinetics that governs the debunching process is not the same as that which governs step bunching in the low-temperature range. The fact that the kinetics that governs step bunching and debunching are not the same in the low-temperature range seems to be strange because the debunching process is seen as the reverse process of the step-bunching process. The kinetics that governs step bunching and debunching are determined by the competition between the kinetics of mass transport of Si and that of Au atoms. It should be noted here, however, that in the step bunching process, mass transport of Au was excluded from the rate-determining process. This is because a growth time of a terrace is much shorter than the time of Au deposition before the start of nucleation of the (001) terrace and the Au coverage on the surface is high enough to form the 5×3.2 terraces after their nucleation. Since, the mass transport process of Si should not be the rate-determining process of the debunching, the annihilation of the 5×3.2 structure, in other words, mass transport of Au atoms is expected to be the rate-determining process of debunching. The decrease of the Au coverage of the surface is due to mass transport of Au from the 5×3.2 areas and occurs by diffusion into the bulk, sublimation into vacuum and surface diffusion from the 5×3.2 areas to the step band areas.

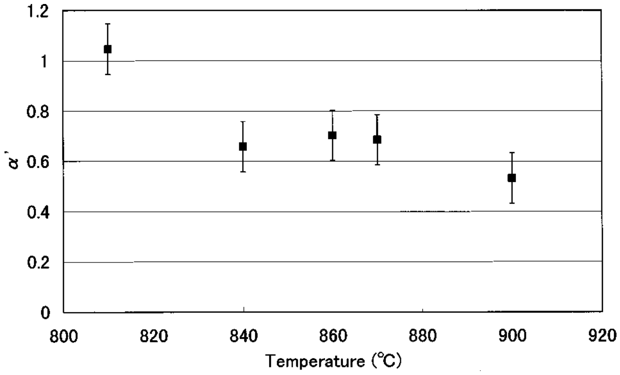

FIG. 7. The temperature dependence of the value α'.

The surface diffusion of Si governs the mass transport of Si during step bunching in the low-temperature range because α is $\frac{1}{4}$ as seen in Fig. 4. In the low-temperature range, site exchange between Si and Au atoms is not so active that sublimation of Si governs the step bunching. Thus, the mass transport of Au atoms is considered to occur by the surface diffusion in this temperature range, otherwise desorption or diffusion of Au atoms into the bulk should affect the mass transport of Si and the step-bunching kinetics should be governed by nonlocal mass exchange even in the low-temperature range. The decrease of the Au coverage on the surface may due to the direct desorption and diffusion of Au into the bulk but in these cases the time evolution of the Au coverage depends on area of the 5×3.2 terrace and it should be proportional to the terrace width because the debunching process can be regard as 1D process. In this case the decrease rate of the Au coverage, in other words, the decrease rate of terrace width W decrease with decreasing terrace width and this results in $\alpha'<1$. Thus, in the low-temperature range Au atoms diffuse on the surface as well as Si atoms and the decrease of the Au coverage of the surface occurs by surface diffusion from the 5×3.2 terraces and sublimation into vacuum (or diffusion into the bulk) in the step band areas where the density of Au on the surface is considered to be lower that that on the 5×3.2 terraces as follows. If the Au coverage on the step bands were higher than that on the (001) terrace, 5×3.2 structure should have been formed on the step-band areas even in the case the average step-step distance is not wide enough to form the 5×3.2 structure because step arrangement can be modified drastically during formation of the 5×3.2 terrace and this is nothing but nucleation of (001) terraces during deposition. The number of Au atoms that diffuse out from the 5×3.2 should be proportional to the total length of the boundaries between the 5

×3.2 areas and step-band areas and this does not change because the debunching process can be regarded as a 1D process. This results in $\alpha' = 1$.

The reason that the rate-determining processes of step bunching and debunching are not the same in low-temperature range is related to the different distribution of the Au atoms on the surface. During step bunching, the Au coverage on the stepped areas will be above a critical value because nucleation of the 5×3.2 terrace starts only after several minutes after the start of the Au deposition. On the other hand, during debunching, a very small number or almost no Au atoms exist on the step-band areas because Au atoms desorb into vacuum (or diffuse into bulk) preferentially form the step-band areas as described before. Thus, the distribution of Au atoms on the surface is quite different in the two processes. The difference in the distribution of Au atoms may change the competition between the kinetics of mass transport of Si and that of Au atoms, especially in the case that mass transport of Au and Si occurs by surface diffusion.

On clean Si(111) vicinal surfaces, surface reconstruction-induced step bunching occurs at the phase transition temperature on cooling from the 1×1 to the 7×7 structure (830 °C).[18] It was reported that α is neither $\frac{1}{4}$ nor $\frac{1}{2}$. This means that the step-bunching dynamics in this system is not described by the two cases and the authors discussed it in terms of the elastic relaxation by the facet edges. On the other hand, as seen in Fig. 4, step bunching on the Au-adsorbed Si(001) surface is governed by the two cases. Thus, the system of Au on the Si(001) vicinal surface is an ideal reconstruction-induced faceting system.

IV. SUMMARY

The dynamics of the step bunching on the Si(001) vicinal surface during Au deposition were studied by REM. Due to the reconstruction of the Si(001) surface step bunching takes place and a 1D hill and valley structure is formed. The change of the width (W) of the (001) terraces during step bunching and debunching were analyzed. $W(t)$ has the form t^{α} with α between $\frac{1}{2}$ and $\frac{1}{4}$ in the temperature range between 780 to 900 °C. α is $\frac{1}{4}$ below 820 °C and $\frac{1}{2}$ above 860 °C. During annealing W according to $(t_0 - t)^{\alpha'}$ with α' between 1 below 840 °C and $\frac{1}{2}$ at 900 °C. The point that we want to emphasize here is that in this system the kinetics that governs step bunching and debunching changes as a function of the substrate temperature. Local mass exchange governs step bunching in the low-temperature range, while nonlocal mass exchange governs step bunching and debunching in the high-temperature range. On the other hand, debunching is governed by the annihilation process of the 5×3.2 areas and that is related to the surface diffusion of Au atoms in the low-temperature range.

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