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Role of steps in deposition rate in silane chemical vapor deposition on Si(111)

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Si(111) homoepitaxy using silane chemical vapor deposition was studied during growth with scanning tunneling microscopy at high temperature (730 K). The initial substrate corresponds to the 7×7 reconstruction while the layers grow in a 1×1 structure partially hydrogenated. The layer distribution is directly measured and shows a higher deposition rate on the 1×1 surface than on the 7×7 surface. We show that the regime of incorporation of silicon at step edges influences the reactivity of the surface.

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I. INTRODUCTION

Over the last few decades, numerous theoretical and experimental investigations have been performed to improve our knowledge on the phenomena of the early stages of growth. A thermodynamic and kinetic atomic scale description of the growth processes was given by Venables[1] within the framework of vapor deposition. This author gave an atomic view of the basic growth processes and introduced relevant corresponding energies such as adsorption, diffusion, and pairbinding. This atomic picture was successfully used to interpret some growth experiments, especially on unreconstructed surfaces. More recently, more complex phenomena involved in growth have been addressed. For instance, on reconstructed surface, the conversion of the surface reconstruction into an unreconstructed structure is a prerequisite to the nucleation and growth processes. Thus, in some cases, the destruction of the surface structure determines the behavior of the growth. As an example, Voigtländer and Weber have characterized, using a scanning tunneling microscope (STM), the atomic growth processes of Si islands on Si(111) during molecular-beam epitaxy (MBE) experiments in 500–900 K temperature range and have shown the influence of the 7×7 reconstruction on the growth processes.[2] However, despite the variety of phenomena that may be involved in the growth processes, the deposition rate in MBE is equal to the atom flux incoming on the surface as the sticking coefficient is close to 1, when no evaporation occurs. In other words, in MBE, the deposition rate does not depend on the surface features and is only driven by the vapor atom flux. On the contrary, in chemical vapor deposition (CVD), the deposition of matter results from the decomposition of molecules of the precursor gas on the reactive sites of the surface and so the deposition rate drastically depends on the density of these sites. In silane CVD on silicon surface, Si adatoms, silicon hydride species, and H atoms are released onto the surface under the dissociative adsorption of SiH_4. The presence of these species on the surface can modify the reactivity of the surface and so the steady-state density of these different species may affect the deposition rate. For example, hydrogen is well known to inhibit the reactive sites of the silicon surface leading to a lower deposition rate at higher H coverage. Because the hydrogen steady-state coverage is driven by H desorption, the deposition rate depends on the mechanism, and therefore on the surface structure, which can be involved in this process. In this paper, we show that, in addition to these chemical features of the surface, silicon incorporation into the crystal via mechanisms of attachment at step edges also affects the deposition rate. For this study, we have performed the growth of a silicon film during silane ultrahigh vacuum CVD (UHV-CVD) on 7×7 substrate at a fixed temperature (730 K). At this temperature, the surface of the grown film is covered by a disordered phase corresponding to SiH species diffusing on a partially hydrogenated 1×1 surface.[3] Thus, the first layer grows on the 7×7 structure while the upper layers grow on a unreconstructed surface.

II. EXPERIMENT

The experiments were performed in an ultrahigh vacuum system with a base pressure of 2×10^{-10} Torr, equipped with a commercial scanning tunneling microscope (VT STM Omicron) able to work at a fixed high temperature. Samples are As-doped (0.15–0.22 Ω cm) Si(111) oriented with a misorientation angle of less than 0.2°. The samples were heated by resistive heating on both the cleaning manipulator and the STM. The typical dimensions of samples were 9 mm × 1 mm × 0.5 mm in order to reduce the heating power during experiments. The Si(111) 7×7 substrates were prepared by *in situ* thermal treatment described elsewhere.[4] The cleanness of the initial substrate was systematically controlled before exposure. The growth experiments were performed as follows: after the surface cleaning, the sample was heated on the STM at a fixed high temperature. After 1 h, the thermal drift was sufficiently low to achieve atomic resolution with STM. Then, high-purity silane was introduced into the chamber through a leak valve. The ion pump was switched off allowing the experiment to proceed in the 10^{-4} Torr range. The surface was continuously imaged during the exposure to observe its evolution during growth. The sample temperature during STM experiments was determined by a calibrated heating-power-temperature relationship established with an ir pyrometer during sample cleaning on the manipulator. As mentioned in a previous paper,[3] the tip acts as a shield during the silane exposure increasing

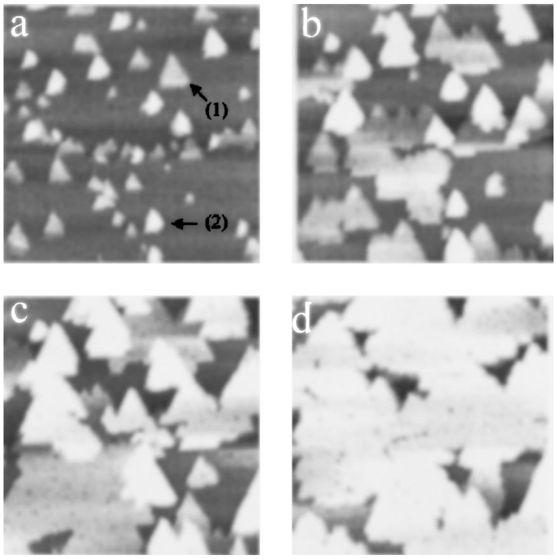

FIG. 1. STM images $[(256\ \mathrm{nm})^2]$ of the growth of Si on Si(111) by UHV-CVD at $T = 730$ K and $P_{\mathrm{silane}} = 4.5 \times 10^{-4}$ Torr. Images (a)–(d) were recorded at 0.25, 0.66, 1.16, and 1.77 ML grown on the initial 7×7 substrate, respectively. In (a), islands (1) and (2) are, respectively, single-layer and double-layer islands.

locally the surface temperature of about 50 K. As a consequence, the amount of deposited matter is slightly higher and the nucleation density is lower on areas under the tip. The effect is not awkward if the same area is imaged all along an experiment. The accuracy of the temperature measurement is ±25 K and its reproducibility is ±10 K. All STM images were obtained in the constant current mode with a 1 V negative sample bias voltage and a tunneling current of 100 pA.

III. RESULTS

To study the growth behavior of Si/Si(111) epitaxy by UHV-CVD, we have repeatedly imaged the same area by STM during growth at 730 K and $P_{\mathrm{silane}} = 4.5 \times 10^{-4}$ Torr. A movie of 50 STM images was recorded at a frequency of 1 image/87 s, showing the growth of a five-layer film. A series of selected images from the movie is shown in Figs. 1(a)–1(d). In Fig. 1(a), islands of triangular shape have nucleated on the bare 7×7 substrate and have started to grow. A preferred nucleation along lines that correspond to 7×7 domain boundaries is observed. Nucleation on top of several first-layer islands has also occurred, leading to the formation of double-layer islands. Figure 1(b) corresponds to the coalescence of most islands of the first layer. In Fig. 1(c), first layer islands almost completely coalesced while single steps of the second layer, generated upon coalescence of single-layer with double-layer islands, have started to move onto the first layer. We can notice that nucleation of second layer on top of first layer does not occur. In Fig. 1(d), the substrate is nearly completely covered. The coverage in the second layer has almost caught up with the coverage in the first layer. For higher coverage, the growth mode turns to a layer-by-layer growth.

From STM images of the movie, we have measured the deposited material in different layers. The coverage in each layer and the total coverage, expressed in monolayer ($1\ \mathrm{ML} = 1.56 \times 10^{15}\ \mathrm{atoms/cm^2}$), are plotted as a function of time in Fig. 2. Since the difference in atom density between the 7×7 surface and the grown surface (SiH species diffusing on a 1×1 surface partially hydrogenated) is 0.1 atoms per 1×1 unit cell,[3,5] 5% has been added to each measurement concerning the first layer growing on the 7×7 substrate. For coverage higher than two layers, the growth mode is very close to a layer-by-layer growth, when one layer is filled linearly up to one layer before the next layer starts to grow. For lower coverage, we clearly observe the double-layer growth mentioned above. The slopes in Fig. 2 correspond to the growth rate of the layers. The total coverage versus time can be fitted by a linear variation. Interestingly, we observe a jump in the total growth rate, denoted by deposition rate R hereafter, from 0.046 to 0.073 ML/min.

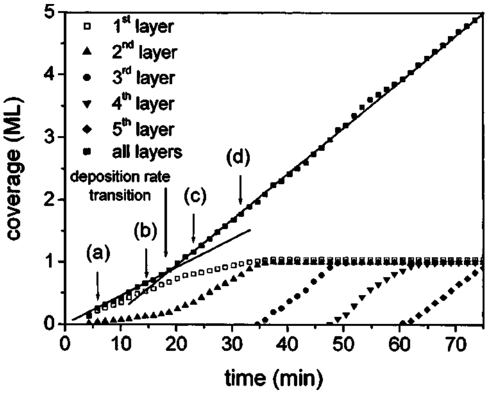

FIG. 2. The coverage in each layer and the total coverage is plotted versus time. The data points marked (a)–(d) correspond to the images in Figs. 1(a)–1(d). The dashed lines are an eye guide for the linear behavior of the total coverage. The slope is 0.046 ML/min at low coverage and 0.073 ML/min at higher coverage. The abrupt change in the deposition rate is also indicated.

IV. DISCUSSION

At low coverage, before coalescence of islands, single-layer and double-layer islands grow simultaneously. The processes of nucleation on the 7×7 substrate and on top of the first 1×1 layer occurred in the early stage of the exposure. From Fig. 1(a), we find that the probability of nucleation on top of the first layer is at least 2.5 higher than the probability of nucleation on the 7×7 initial substrate. We have also observed that the coverage of the second layer rapidly catches up with the coverage in the first layer and the density of single-layer islands step edges of the second layer is very low. This indicates that, as one can expect, the step edge advances faster on the unreconstructed grown surface than on the 7×7 structure. This behavior has already been observed on Si(111) with STM during MBE experiments.[6,7] In these experiments, the initial substrate and the growing layers corresponded to the 7×7 reconstruction. The authors correlated this behavior to the higher density of domain boundaries on the grown substrate than on the original one, which would enhance the nucleation and growth. These fea-

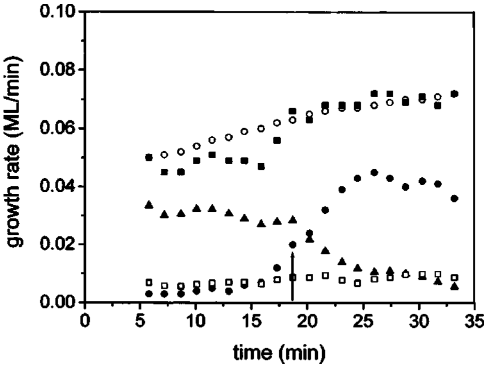

FIG. 3. Different growth rates are plotted versus time: the experimental deposition rate, i.e., the derivative of the total coverage versus time (■); the deposition rate given by Eq. (1) (○); R_{ss1} and R_{ss2}, the growth rates originating in the advancement of single-layer steps on, respectively, the 7×7 substrate (▲) and on the first grown layer (●); R_{ds}, the growth rate originating in double-layer steps advancement (□). The abrupt change in the experimental deposition rate is also indicated.

tures are associated with an upward mass transport, considering isotropic deposition. In our CVD experiments, we have also observed, as in MBE experiments, a transition from the initial multilayer growth (double layer in our case) to a layer-by-layer growth mode. This transition is caused by the different structure between the original substrate and the grown layers. Thus, a preferred nucleation and a higher deposition rate on partially hydrogenated 1×1 surface of the top layer explain the formation of double-layer islands. When the initial substrate is completely covered by the first two layers, the surface structure of the growing layer and the layer underneath are similar and a transition to a layer-by-layer growth occurs.

The main difference between MBE experiments and our CVD experiments concerns the deposition rate. We would like to emphasize that the higher growth rate of the second layer reported in Ref. 7 does not lead to an increase of the deposition rate, which remains constant in MBE, as mentioned by the authors. We emphasize that the increase in the deposition rate in our CVD experiments, i.e., an increase of the rate of material deposited on the surface, implies an increase in the reactivity of the surface.

One interpretation of the deposition rate R behavior could be a variation of the reactive sticking coefficient between the 1×1 disordered phase and the 7×7 structure. In this case, the deposition rate could be written as follows:

$$R = R_{7\times 7}(1.05 - \theta_1) + R_{1\times 1}\ \theta_1, \qquad (1)$$

where θ_1 is the coverage of the first layer, $R_{7\times 7}$ and $R_{1\times 1}$ are rate constants of the 7×7 substrate and 1×1 grown surface, respectively. $R_{7\times 7}=0.042$ ML/min and $R_{1\times 1}=0.07$ ML/min are given by boundary conditions. The experimental deposition rate R is inferred from the derivative of the total coverage versus time. The calculated and experimental deposition rates, plotted versus time, are shown in Fig. 3. We clearly see the jump of the experimental deposition rate between two values. The deposition rate given by Eq. (1) does not fit the experimental data. In particular, the calculated deposition rate increases gently and does not exhibit the observed jump. Thus, we conclude that this jump cannot be solely due to a variation of surface two-dimensional (2D) properties between the 1×1 disordered phase and the 7×7 structure.

To explain the experimentally observed behavior of the deposition rate, we have been interested in the movement of the different kinds of steps on the surface. Using the coverage of the first and second layer as a function of time shown in Fig. 2, we have studied the deposition rate at the different kinds of step edges of the first two layers. Let us call R_{ss1} and R_{ss2} the growth rates originating in the advancement of single-layer steps on the 7×7 substrate and on the first grown layer, respectively, and R_{ds} the growth rate originating in double-layer step advancement. Usually, the advancement of steps is extracted from the difference images, where each image of the movie is subtracted from the previous one. Because the information concerning the layer numbering is lost on difference images, this method is not easy to use in our case, when we study the growth of numerous islands of different height at different levels. Moreover, the enhanced noise and the drift on difference images prevent accurate measurements. Indeed, to determine R_{ss1}, R_{ss2}, and R_{ds}, we have evaluated the growth rate of the first and second layer, R_1 and R_2. The latter growth rates are determined from the derivative of the first- and second-layer coverage versus time respectively, coverages directly measured on each STM image of the movie and shown in Fig. 2. R_1 and R_2 can be written as follows:

$$R_1 = R_{ss1} + R_{ds}, \qquad (2)$$

$$R_2 = R_{ss2} + R_{ds}. \qquad (3)$$

Introducing the velocity of advance of different kinds of steps, the growth rates can be written as follows:

$$R_{ss1} = v_{ss1}d_{ss1}, \quad R_{ds} = v_{ds}d_{ds}, \quad R_{ss2} = v_{ss2}d_{ss2}, \qquad (4)$$

where v_{ss1} and v_{ss2} are the velocities of the step advance of, respectively, single-layer islands of the first and second layer, and v_{ds} is the velocity of the step advance of double-layer islands. d_{ss1} and d_{ss2} are, respectively, the densities of the single-layer islands step edges of the first and second layer, and d_{ds} is the density of the double-layer island step edges. These densities have been directly measured on STM images. For the same reasons mentioned above, the different velocities cannot be easily measured from STM images. However, from the first five STM images of the movie, the velocities v_{ds} and v_{ss1} can be evaluated. To determine these quantities, we have measured the growth rate and the step density of single-layer and double-layer islands that have not coalesced. These islands are present in the early stages of growth [see, for instance, numbered islands in Fig. 1(a)]. From theses measurements, we find that the ratio v_{ss1}/v_{ds} is nearly constant on the first five STM images:

$$v_{ss1} = 1.7v_{ds}. \qquad (5)$$

If the incorporation of adatoms was only limited by the transport of matter, we should have $v_{ss1}=2v_{ds}$. This result confirms that the destruction of the 7×7 structure is a ratedetermining process in material incorporation into substrate.[2,7–9]

In the following, we assume that this relation remains during the overall growth. The growth rates R_{ss1}, R_{ss2}, and R_{ds} can then be inferred from Eqs. (2)–(5) and are plotted versus time in Fig. 3. We see that R_{ds} remains roughly constant during the growth. We clearly observe that the jump is correlated to a rapid increase of the growth rate R_{ss2} originating in the advancement of single-layer steps on the first grown layer. This occurs when a large part of islands of the first layer coalesce, which allows the expansion of the second layer of double-layer islands on the first grown layer. These features are clearly correlated to the switch from a growth mode resulting mostly from incorporation of material at 7 ×7 step edges via deconstruction to a growth mode where incorporation at 1×1 step edges is preponderant. Nevertheless, the jump in the deposition rate is necessarily correlated to a jump in the reactivity of the surface. Thus, the question we have to address is how the properties of the steps can affect the reactivity of the surface. The reactivity of the surface is driven by the density of free reactive sites where silane molecules can adsorb and decompose. This density depends on the reactive site density and on the presence of different species released by decomposition of silane on the surface, which can inhibit these reactive sites. As we have shown above, the jump of the reactivity is not correlated to a difference in 2D properties between 7×7 and 1×1 surfaces such as the density of reactive sites. Then, this jump must be correlated to a variation of the steady-state densities of different species on the surface. These steady states are controlled by the kinetics of adsorption and decomposition of silane on one hand and the void kinetics of each species on the other hand. Concerning the void of hydrogen, we do not expect that H desorption can be drastically influenced by the step properties. On the contrary, we expect that the void of silicon species, i.e., the incorporation of silicon species into the crystal, is driven by properties of incorporation at steps. As mentioned above, due to the mechanism of deconstruction, the rate of adatom incorporation at 1×1 step edges is higher compared to 7×7 step edges. This higher rate of incorporation leads to an increase of the free reactive site density on the surface and then can lead to an increase of the reactivity of the surface. Thus, the regime of incorporation of matter into the crystal influences the reactivity of the surface, leading to a higher deposition rate on the unreconstructed 1×1 surface than on the 7×7 surface. Another mechanism could be responsible for different kinetics of Si incorporation into the two types of steps. The species released on the surface under the dissociative adsorption of silane molecules, such as hydrogen, could induce such difference. Even if we cannot exclude such a mechanism, we rather expect that hydrogen does not play a crucial role concerning this point. Previous publications concerning the MBE growth of silicon on Si(111) 7×7 show that the growth occurs at a higher rate on 7×7 surfaces with a high density of defects. Thus, hydrogen is not necessary to observe different kinetics of Si incorporation at step edges. Moreover, as H atoms can easily be inserted into silicon bonds,[10] we showed in a previous publication[11] that hydrogen enhances 7×7 deconstruction. We could then expect that hydrogen rather reduces the difference in the kinetics of Si incorporation into the two types of steps.

V. CONCLUSION

In conclusion, we have provided experimental evidence demonstrating that in UHV-CVD, the rate of deposition of matter depends on the step edges. The rate of adatom incorporation at steps drives the steady-state density of silicon species released by silane decomposition. Because these silicon species inhibit reactive sites, the properties of the steps involved in the growth influences the reactivity of the surface. As a result, independently of considerations concerning the 2D chemical properties of the surfaces, the growth kinetics using silane CVD is lower on the 7×7 surface than on the unreconstructed 1×1 surface.

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