# Controlling film growth with selective excitation: Chemical vapor deposition growth of silicon

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We propose a method of controlling the growth mode in an epitaxial system. It takes advantage of differences in the vibrational frequencies of adatom–substrate bonds at terraces and steps. With a properly tuned infrared laser, one can selectively excite only the adatom–substrate bonds at steps and enhance the mobility of these adatoms, consequently promoting step-flow growth and reducing film roughness. The feasibility of this method is shown theoretically with respect to the prototype system of chemical vapor deposition growth of silicon. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1687452]

Thin film growth may occur by two-dimensional islanding, three-dimensional clustering, or by step-mediated growth, where deposited adatoms attach to a step.[1] The latter is often most desirable for smooth homoepitaxy, modulated growth, and other types of films. We discuss a growth-control method, called selectively enhanced adatom diffusion (SEAD), which can be used to promote the step-flow growth.

On an inhomogeneous surface, the same adatom–substrate bond can have different vibrational frequencies due to distinct local geometric structures, for example, terraces and steps shown in Fig. 1. One typical example is the silicon surface passivated by hydrogen adatoms.[2] At the Si(100) surface,[3] the terrace-bound hydrogen adatoms vibrates at $2087$ cm$^{-1}$ while the step-bound at $2150$ cm$^{-1}$; similarly at the Si(111) surface,[4] the vibrational frequencies of the Si–H bond are $2084.0$ cm$^{-1}$ at terrace sites and $2135.8$ cm$^{-1}$ at step sites. For easy reference, we call this frequency difference the geometric frequency difference.

In this SEAD method, we take advantage of the geometric frequency difference at a surface and use an infrared laser to selectively excite only blocking adatoms at steps. A blocking adatom, for example, is a hydrogen adatom bound to a step site, preventing Si attachment in the case of the chemical vapor deposition (CVD) of Si film. Once the adatoms are resonantly excited, the diffusion barrier $V$ is effectively reduced by one photon energy $\hbar\omega$ (see Fig. 2). As a result, these excited blocking adatoms at steps become more mobile and easier to detach from steps; the film is then favored to grow in the mode of step flow, reducing its roughness. The

mobility enhancement can be measured by a dimensionless parameter $\eta$ given by

$$\eta = \frac{\nu_e}{\nu} e^{\hbar\omega/kT}, \tag{1}$$

where $\nu_e/\nu$ describes the increase of the attempt frequency as a result of excitation.

The key to the method is to selectively excite blocking adatoms and enhance their mobility by properly tuning the laser frequency.

Selective excitation has seen tremendous success in chemistry.[5] In contrast, little success has been achieved when it comes to surface systems despite enormous efforts in the past.[6,7] It was noticed very early that one could utilize the selective excitation for efficient isotope separation at surfaces;[8] however, there were few successes.[9]

The reason for these unsuccessful attempts is that many other physical processes occur simultaneously as a result of
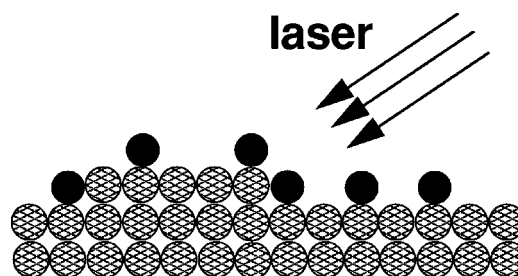


FIG. 1. Different local geometric structures for adatoms at a growth front. The same adatom at different binding sites (terraces or steps) can have different vibrational frequencies. An infrared laser can be tuned to resonantly excite only the adatoms at the steps, thereby selectively enhancing adatom diffusion (see Fig. 2).
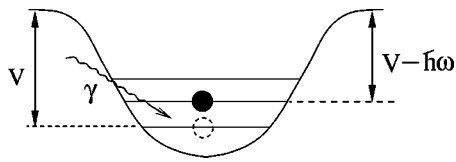
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FIG. 2. Enhanced diffusion of vibrationally excited adatoms. When the adatom is vibrationally excited to a higher level by absorbing a photon, its diffusion barrier $V$ is effectively lowered by $\hbar\omega$.
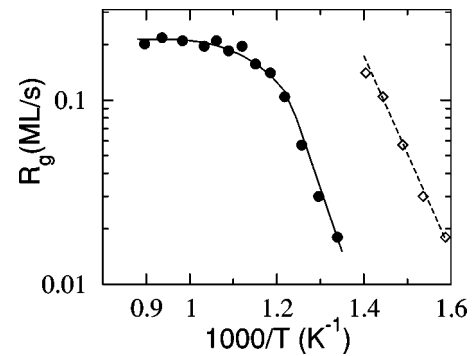


FIG. 3. CVD growth rates of silicon. The circles are the growth rate data from Ref. 13 for Si(100) surface. The diamonds are projected growth rate when a properly tuned high-power cw infrared laser is applied.

laser illumination and they can obscure and overwhelm the selective excitation.[6,7] These processes include: (1) absorption of the laser power by the substrate; (2) energy redistribution among different adsorbates through collisions, dipole–dipole intermolecular interactions, or other means; (3) relaxation of the resonantly excited adsorbates via substrate phonons. All these physical processes can channel the laser energy to nontargeted adsorbates, thereby obscuring the desired selectivity.

For our proposed method to be successful, selective excitation must be dominant among all the physical processes induced by the laser. This depends on the specifics of a system. Therefore, we focus on a concrete system, instead of laying out the arguments in general.

We consider the CVD growth of silicon,[10] where one can use an infrared laser to resonantly excite the Si–H bond. We show convincingly that selectivity is feasible in this system and will not be obscured.

In the CVD growth of silicon,[10] a clean silicon surface is exposed to a silane ($SiH_4$) gas, which reacts with the dangling bonds on the surface, generating some intermediate products such as $SiH_3$ and $SiH_2$ before forming a Si film.[11] The film growth depends on the growth temperature,[10–13] as shown in Fig. 3. When the temperature is low ($\lesssim 700$ K), there is almost no growth as the Si surface is passivated by H atoms, leaving no Si dangling bonds for reaction with silane. As the temperature increases, growth becomes possible because the H adatoms are more mobile, can diffuse, and form $H_2$ molecules, which desorb from the surface and free dangling bonds for reaction.[14] When the temperature is above $\approx 830$ K, the system enters into a different regime, where the growth rate increases much slower.

We are interested in low growth temperatures ($\lesssim 830$ K), where the desorption of H adatoms and the growth of Si film are expected to be strongly influenced by an infrared laser properly tuned to the Si–H bonds. The effectiveness of the process lies in two aspects: (1) the strength of laser and Si–H bond interaction; (2) how much the infrared laser can enhance the mobility.

We examine first the coupling between the laser and Si–H bonds: if the coupling is too weak, it becomes meaningless to proceed further. According to experiments,[15] the cross section for photon absorption in amorphous Si is $\sigma \sim 7.4 \times 10^{-18}$ cm$^2$. The cross section for other Si–H configurations which correspond more closely to Si–H surface bonds is estimated to be $\sim 4.8 \times 10^{-17}$ cm$^2$.[16] In the discussion we use the more conservative value to estimate the efficiency of the process. Our following estimate shows that, indeed, close to 40% of targeted H adatoms can be excited by a laser readily available.

The estimate starts with a set of master equations,

$$dn_1/dt = (A+B)(n_0 - n_1) - \gamma n_1, \qquad (2)$$

$$dn_0/dt = (A+B)(n_1 - n_0) + \gamma n_1, \qquad (3)$$

Here $n_0$ and $n_1$ are the fractions of atoms in the ground state and the first excited state, respectively. The parameter $A$ is the transition rate induced by the laser, $B$ the transition rate due to the thermal environments (e.g., substrate phonons and black body radiation), and $\gamma$ is the rate of spontaneous decay. When the laser pulse is much longer than the inverse of the laser frequency $\omega$ and the lifetime of the excited adatoms, the adatom population probability in the excited state is

$$n_1 = \frac{(r-1)A + \gamma}{2(r-1)A + (r+1)\gamma}, \qquad (4)$$

where $r = e^{\hbar\omega/k_B T}$ with $\hbar\omega$ being the energy difference between the two states or the photon energy. This result is a steady state solution of Eqs. (2) and (3). Note also that $B$ is related to $\gamma$ since the steady state of Eqs. (2) and (3) should be a thermal equilibrium when $A=0$ (without laser). The experimental transition rate $A$ depends on the cross section for excitation of the adatom–substrate bond, the laser power $I$, and the spot size $S$ of the laser as $A = I\sigma/\hbar\omega S$.

To have concrete numbers on $A$ and $n_1$, we use the parameters of the free electron laser (FEL) at Vanderbilt University as an example. This FEL has a macropulse of 3–6 $\mu$s long; each macropulse consists of a series of 1 ps micropulses that are 0.35 ns apart. Since the lifetime of excited Si–H bonds is $\sim 0.8$ ns,[17] such a macropulse can be considered continuous and we can use Eq. (4) for the calculation. The power of the macropulse is $\sim 2.85$ kW; we choose $I = 1$ kW since one can always lower the power by certain means. As a result, for spot size $S \sim 10^{-4}$ cm$^2$ and photon energy $\hbar\omega \approx 0.25$ eV, we find the transition rate is $A \sim 2 \times 10^9$ s$^{-1}$. On the other hand, the decay rate is $\gamma \sim 1.2 \times 10^9$ s$^{-1}$ (the inverse of the lifetime). Since $r \gg 1$ for the temperature range of our interest ($\lesssim 830$ K), we have $n_1 \approx 0.38$, that is, close to 40% of the adatoms are excited. In addition, the long duration of the macropulse (3–6 $\mu$s) gives the excited H adatoms ample time to diffuse.

By selectively tuning the laser to excite only blocking H adatoms at the steps, one essentially creates two heat baths for the adatoms: H adatoms on the terraces feel the substrate temperature $T_0$ while the adatoms at the steps feel, equivalently in terms of mobility, an elevated temperature $T = T_0 V/(V - \hbar\omega)$ due to laser excitation.[18] For example, at

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$T_0 = 700$ K, where there is almost no growth on the terrace, the step H adatoms feel a heat bath of $\sim 800$ K, a temperature where the H adatoms love to diffuse and free Si dangling bonds for the growth. As a result, one achieves a control over the Si growth. In the calculation, we have used $V \approx 1.57$ eV, which is obtained by fitting the low-temperature data in Fig. 3. This number also agrees with both experimental and theoretical results in the literature.[14,19] As shown in Fig. 3 we have projected how the growth rate would be if one has a high power infrared laser operating in the mode of continuous wave (cw). A cw source is more efficient at removing H than pulsed FEL sources. Currently, off-the-shelf systems using only a 10 W source can produce about 0.1 W of cw intensity at the 5 $\mu$m (Si–H bond frequency). If improved to about 10 W or more of cw intensity, then more convenient laboratory based sources could be used.

In the following we argue that the resonant excitation of Si–H bonds in this silicon system by the infrared laser will not be overwhelmed by other physical processes. The absorption of laser power by the substrate is the most obvious physical process that can obscure the selective excitation. The absorbed laser energy will inevitably be transferred into heat and increase the substrate temperature, enhancing the mobility of all the adatoms without discrimination. In our system, the silicon substrate is transparent to infrared frequencies around 2000 cm$^{-1}$ (Si–H bond frequency). Therefore, little heat will be generated by the laser in the substrate.

Another unavoidable physical process is the relaxation of selectively excited adatoms, which occurs predominantly through the creation of substrate phonons. This also generates heat in the substrate, a phenomenon known as resonant heating. However, such heating in our case is negligible. Note the adatoms at the steps (one-dimensional objects) are a tiny fraction of all adatoms on the surface, and even a smaller fraction of the whole substrate. Therefore, the heat generated at the steps will not be sufficient to increase the substrate temperature significantly.

Furthermore, the adsorbates in this silicon system are simple H atoms, which are much simpler than the molecular adsorbates in many of the previously studied systems.[6,7] As a result, many complicated physical processes that are believed to have overshadowed the selectivity do not exist in this system, for example, the dipole–dipole molecular interaction.[6,7] Collisions can also occur between adsorbates, spreading energy from targeted species to nontargeted species. In our case the collision is, in contrast, welcomed since it is inelastic, producing H$_2$ molecules.

In summary, we have proposed a method of controlling film growth based on the geometric frequency difference of the same adatom–substrate bonds. With selective excitation, one can use an infrared laser to excite only blocking adatoms at the steps, promoting step-flow growth. We call it selectively enhanced atoms diffusion. We have argued its feasibility quantitatively for the CVD growth of silicon. This method of SEAD may find applications in other epitaxial systems, for example, the systems where different species of deposited adatoms have different mobilities.

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