

## Role of hydrogen desorption in the chemical-vapor deposition of Si(100) epitaxial films using disilane

John J. Boland

*IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, New York 10598*

(Received 1 February 1991)

A scanning tunneling microscopy and spectroscopy study of the role of hydrogen desorption in epitaxial film growth on the Si(100) surface is presented. Following disilane adsorption, epitaxial growth is shown to be driven by the rebonding of the disilane fragments induced by H<sub>2</sub> desorption. This requires the decomposition of only the higher surface hydrides and occurs between 640 and 670 K. The epitaxial layer formed in this manner has a 2×1 monohydride structure. Continuous exposure to disilane at 690 K resulted in multilayer epitaxial growth, the surface of which remains largely H passivated. This latter growth is in part due to a direct reaction between disilane and the monohydride surface.

An understanding of Si epitaxial film growth via chemical-vapor deposition (CVD) is both fundamentally important and essential to the control of numerous thin-film technologies. The reaction of film precursors with the vacant dangling-bond (DB) sites on the surface is believed to play an important role in the growth of such films.<sup>1,2</sup> These precursors are typically monosilane or disilane, although other gases have also been used.<sup>2</sup> The active DB sites are continuously regenerated by the removal of H<sub>2</sub> from the surface. In the absence of a plasma or some other means of excitation, this is accomplished by maintaining the substrate at a temperature where H<sub>2</sub> spontaneously desorbs from the surface. Under these conditions the growth rate is determined by the density of reactive DB sites on the surface, which in turn is controlled by the rate of H<sub>2</sub> desorption.

In this work we present a scanning tunneling microscopy (STM) and spectroscopy (STS) study of the role of H<sub>2</sub> desorption in the CVD of Si(100) epitaxial films. The disordered surface produced upon disilane adsorption is shown to undergo a structural rearrangement to form ordered 2×1 islands induced by the selective decomposition of the higher hydrides at 670 K. Epitaxial island growth is driven by the rebonding of the adsorbed disilane fragments following hydrogen desorption. These islands do not contain DB's and have structures similar to that observed in the Si(100)-2×1 monohydride phase. Exposure of the surface to disilane while the substrate was held at 690 K resulted in multilayer epitaxial growth. We show that the growth rate cannot be fully accounted for by the slow desorption of H<sub>2</sub> from the monohydride phase and thus under these low-temperature conditions free DB's are not a prerequisite for film growth.

The microscope used in this work is similar to that described by Demuth *et al.*<sup>3</sup> and was mounted in an ultra-high-vacuum chamber with a base pressure of  $8 \times 10^{-11}$  torr. The sample was a 1- $\Omega$  cm phosphorous-doped Si(100) wafer. The clean Si(100)-2×1 surface was prepared by heating the sample to 1350 K for about 30 s. Disilane adsorption was accomplished by dosing the sample via a leak valve at a pressure of  $4 \times 10^{-8}$  torr. The surface temperature was measured by both an ir pyrome-

ter and a thermocouple bonded to the back of the sample and is accurate to about  $\pm 20$  K. Unless otherwise indicated, the topographs shown in this work were recorded at a sample bias of  $-2$  V.

The clean Si(100) surface is shown in Fig. 1(a) and exhibits the 2×1 dimer row structure reported earlier.<sup>4</sup> STS spectrum *i* in Fig. 2(a) recorded over the dimer rows of this surface reveals the presence of a broad intense occupied state at about  $-0.9$  eV and a weak unoccupied state at  $+0.4$  eV which are the characteristic DB states of the clean 2×1 surface.<sup>5-7</sup> This spectrum also shows a peak at  $+1.5$  eV that is due to a surface backbond state,<sup>7</sup> which was not well resolved in an earlier work.<sup>6</sup> Figure 1(b) shows that the surface is disordered following a room-temperature saturation exposure to disilane. Disilane is known to dissociatively chemisorb on the Si(100) surface, and the SiH<sub>3</sub> fragments produced by this process react with the surface DB's or further decompose to yield

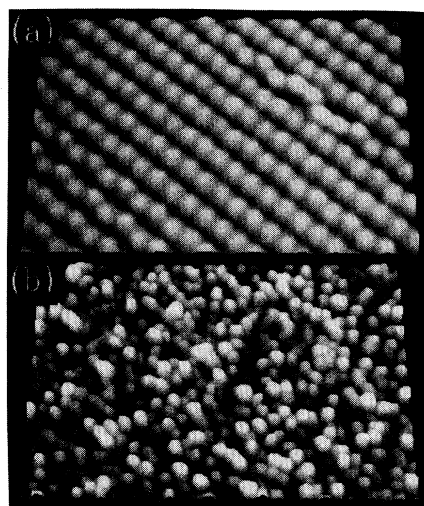


FIG. 1. (a) Clean Si(100)-2×1 surface imaged at a sample bias of  $-2$  V. The area shown is  $70 \times 90 \text{ \AA}^2$ . (b) A  $150 \times 195 \text{ \AA}^2$  STM topograph of the Si(100) surface following a saturation exposure to disilane.

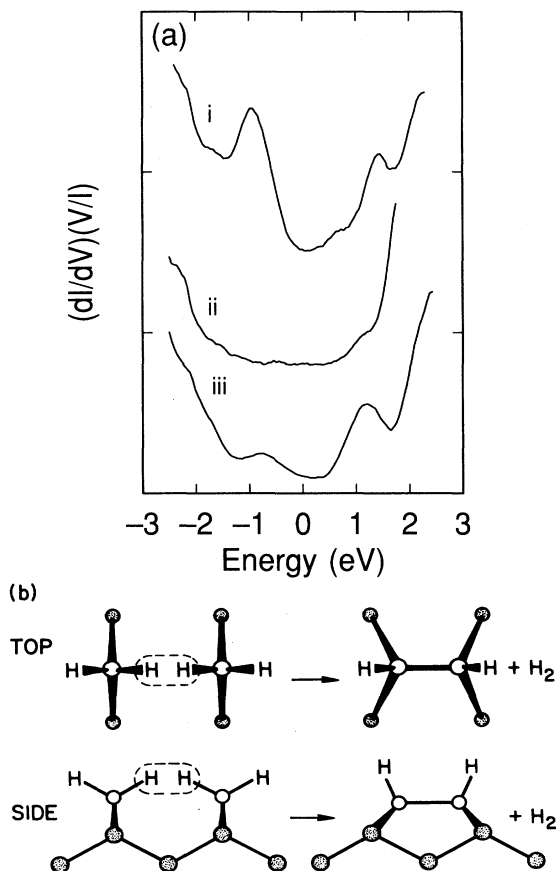


FIG. 2. (a) STS spectra of *i*, the clean Si(100) surface; *ii*, the saturated surface; and *iii*, the  $2\times 1$  islands in Fig. 3(a). These spectra were consistently observed on several samples using different tips. (b) Schematic of the decomposition of the  $\text{SiH}_2$  fragments to yield the epitaxial monohydride surface.

$\text{SiH}_2$  species.<sup>8-14</sup> Similar fragments are observed following exposure to monosilane.<sup>8</sup> The structure shown in Fig. 1(b) is due to the random distribution of these fragments on the surface. STS spectrum *ii* in Fig. 2(a) is typical of the spectra recorded over these fragments. The sharply increasing unoccupied state density is consistent with the presence of dihydride and trihydride surface species. The states associated with these species are broadened due to dispersion over the surface Brillouin zone, of which the lowest-lying unoccupied state is estimated to be at least 2.2 eV above the Fermi energy ( $E_F$ ).<sup>15</sup>

Annealing the surface in Fig. 1(b) to 670 K for 10 s produced the surface shown in Fig. 3(a). We note that the disilane fragments which are randomly dispersed in Fig. 1(b) have ordered to form  $2\times 1$  islands. This structural rearrangement was observed to occur over a temperature range from 640–670 K. The dimer rows, which comprise the islands in Fig. 3(a), are orthogonal to those of the substrate, consistent with the formation of a new Si(100) surface. The island growth is essentially one dimensional along the [011] direction. In some instances, the dimer rows of a given island are not in registry with those of neighboring islands, indicating the presence of

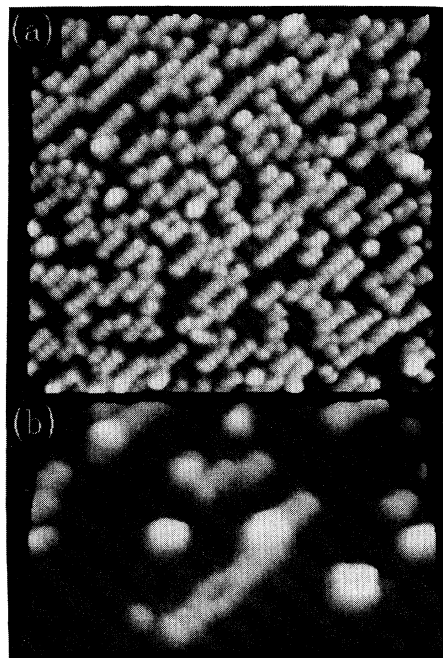


FIG. 3. (a) Surface in Fig. 1(b) following a 10-s anneal at 670 K. Area shown is  $250\times 250 \text{ \AA}^2$ . (b) A close-up following a brief 5-s anneal at 650 K. Note the presence of unformed dimers on this surface. The occasional bright features in these images are disilane fragments which are bonded to the new epitaxial layer.

antiphase boundaries on the new surface. The presence of such boundaries is consistent with island formation at low temperature where diffusion is limited. We note that on the basis of Fig. 3(a), the saturation coverage of disilane on the Si(100) surface can be estimated to be about 0.5 monolayers.

The surface rearrangement following the anneal is due to the loss of  $\text{H}_2$  from the surface. It is well established that  $\text{H}_2$  desorption occurs in two stages, due to the separate decompositions of the dihydrides and trihydrides at or below 670 K (the so-called  $\beta_2$  state) and the monohydrides at about 810 K ( $\beta_1$  state).<sup>8,10,11,16,17</sup> Since the fragments produced by disilane adsorption are  $\text{SiH}_2$  and  $\text{SiH}_3$  species, these fragments selectively undergo loss of hydrogen during the 670-K anneal. To minimize the formation of DB's, this hydrogen loss necessitates the formation of additional bonds to the substrate or to a neighboring fragment. However, the structure of the Si(100) surface restricts the total number of bonds between each fragment and the surface to two, as is the case for  $\text{SiH}_2$  species. Further decomposition requires the positioning of two such  $\text{SiH}_2$  species so that they are in neighboring sites along the [011] direction, i.e., the dimerization direction [see Fig. 2(b)]. The two adjacent H atoms recombine to form  $\text{H}_2$  and a dimer bond is then formed between the fragments, giving rise to the  $2\times 1$  islands observed in Fig. 3(a).

The details of this rearrangement may be studied by imaging the surface over the temperature range (640–670 K) of the decomposition. Figure 3(b) shows the surface

following a brief 5-s anneal at 650 K. The islands contain unformed dimers, due to the presence of disilane fragments which have failed to eliminate hydrogen. Such unformed dimers have been observed on several occasions following a brief anneal and have never been observed on surfaces annealed above 670 K. These observations support the decomposition mechanism described in Fig. 2(b). We note that a similar reaction was proposed earlier to describe the decomposition of the Si(100) dihydride phase.<sup>18,19</sup>

An important aspect of this rearrangement, alluded to in Fig. 2(b), is that the islands formed in this way remain passivated, i.e., the new surface is a Si(100)-2×1:H monohydride phase.<sup>20</sup> This is readily seen from STS spectrum *iii* in Fig. 2(a) that was recorded over the islands shown in Fig. 3(a). These islands do not exhibit the DB's of the clean surface, rather a broad unoccupied state is observed at 1.2 eV above  $E_F$  which was shown earlier to be characteristic of the Si(100)-2×1 monohydride surface.<sup>6,7</sup> (Occasionally, spectra of this type are also observed on the unannealed surface [Fig. 1(b)] and are likely due to the original 2×1 surface which has reacted with the hydrogen released by the  $\text{SiH}_3 \rightarrow \text{SiH}_2$  decomposition.) Therefore, the structural rearrangement which results in the formation of the new epitaxial layer is driven by the decomposition of the higher surface hydrides derived from disilane adsorption. This desorption-induced rearrangement of the higher hydrides to yield a monohydride surface, explains why in contrast to atomic H, disilane adsorption results in parallel filling of the  $\beta_2$  and  $\beta_1$  states observed in thermal desorption.<sup>11</sup>

The observation of epitaxy following the decomposition of the higher hydrides suggests that continuous film growth may be possible under low-temperature conditions where the surface largely retains the 2×1 monohydride structure. To explore this possibility, a 2×1 monohydride surface (prepared by preadsorption of atomic hydrogen<sup>20</sup>) was exposed to  $8 \times 10^{-8}$  torr of disilane for 5 min while the sample was held at 690 K. (This slightly higher temperature was used to facilitate precursor diffusion on the surface). The result is shown in Fig. 4(a). The exposure resulted in the growth of 2×1 islands which occupy about 40% of the surface. These islands are larger than the simple 2×1 chains seen in Fig. 3(a), exhibiting in this case two-dimensional growth along both the [011] and [01 $\bar{1}$ ] directions. STS spectra of these islands are identical to those recorded over the 2×1 chains in Fig. 3(a) and indicate that the new surface retains the 2×1 monohydride structure. Further exposure to disilane resulted in multilayer epitaxial growth [see Fig. 4(b)], similar to that reported in Si molecular-beam epitaxy studies.<sup>21</sup>

To explore the mechanism by which this low-temperature growth occurs, it is necessary to consider the reaction of disilane with the DB sites produced by the slow decomposition of the monohydride surface. The extent of this reaction can be determined by directly measuring the rate of  $\text{H}_2$  desorption from this surface. A preliminary STM study indicates that about 0.1 monolayers of the monohydride surface desorbs during a 5-min anneal at 690 K, conditions identical to those in the growth experiment of Fig. 4(a). However, the analysis is complicated

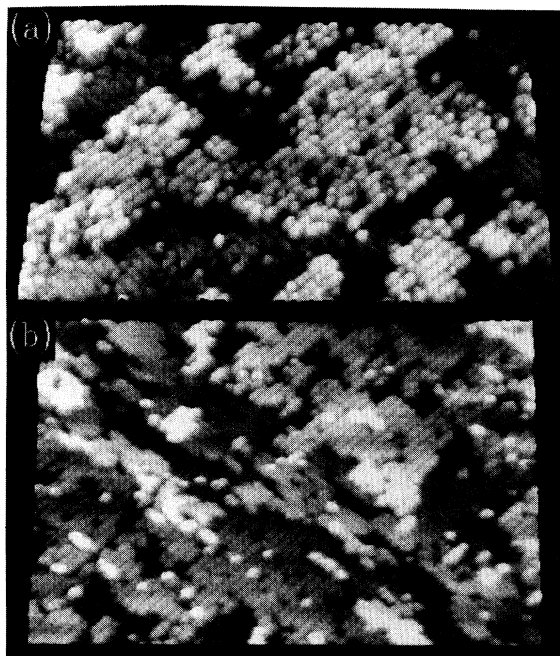


FIG. 4. (a) Epitaxial growth following a 5-min exposure of a 2×1 monohydride surface (prepared by atomic H adsorption) to  $8 \times 10^{-8}$ -torr disilane while the sample was held at 690 K. (b) Additional exposure to  $8 \times 10^{-8}$  torr for 10 min at 690 K followed by a 5-min postanneal at 650 K to promote ordering. Area shown is  $475 \times 335 \text{ \AA}^2$ .

by the observation of Si adatom diffusion on the surface at these temperatures.<sup>22</sup> This desorption rate is in good agreement with that predicted by Meyerson, Himpsel, and Uram<sup>17</sup> ( $2.7 \times 10^{-4}$  monolayers  $\text{s}^{-1}$ ) at 690 K, but is somewhat lower than that of Sinniah *et al.*<sup>16</sup> ( $9.3 \times 10^{-4}$  monolayers  $\text{s}^{-1}$ ). It is important to note that the desorption rate overestimates the contribution of the DB reaction since the sticking coefficient of disilane on a bare Si DB surface is known to be  $\sim 0.1$  at 690 K and drops off sharply with increasing coverage.<sup>9</sup> Clearly, this DB reaction cannot solely account for the epitaxial growth in Fig. 4(a).

The observed film growth is likely due in part to the direct reaction between disilane and the Si(100)-2×1 monohydride surface. Recently, Kulkarni and co-workers<sup>13,14</sup> measured the reactive scattering of disilane from a H-passivated Si(111) surface and observed reactivity at temperatures as low as 550 K. The reaction probability at 690 K was found to be about 0.05, although some flux dependence was noted. Assuming that this reaction is solely responsible for the epitaxial growth, a  $8 \times 10^{-8}$ -torr exposure of disilane for 5 min should result in a coverage of 0.65 monolayers of Si. This value is in reasonable agreement with the observed growth rate. Based on these results and the above discussion, we suggest that DB's are not a prerequisite for epitaxial film growth and in this low-temperature regime growth is possible via a reaction between disilane and the hydrogen terminated surface. This reaction probably involves the insertion of  $\text{SiH}_2$  from

the disilane into the Si-H surface bonds.<sup>13,14</sup> The SiH<sub>3</sub> species produced in this manner, decompose as described earlier, resulting in film growth. The impetus for such a reaction is the nature of the transition state which involves both Si-H bond breaking and Si-Si bond formation and hence avoids the high-energy intermediate state associated with a bare DB.

In conclusion, we have shown that epitaxial growth is driven by the decomposition of the fragments produced by disilane adsorption on the clean Si(100) surface. Due to the structural and bonding constraints of this surface, epitaxial ordering of the disilane fragments requires the decomposition of only the higher surface hydrides. The surface produced in this manner has a 2×1 monohydride

structure. The growth of additional layers requires the interaction of disilane with this monohydride surface. At 690 K the growth is largely due to the direct reaction between disilane and the passivated surface. The reaction between disilane and the DB's generated by the slow decomposition of the monohydride surface cannot fully account for the observed growth. Epitaxial growth under these low-temperature and largely passivated conditions, offers a means to minimize potential contamination of the film during the growth process.

The author wishes to thank F. Bozso, S. M. Gates, and J. E. Greene for helpful discussions and J. M. Jasinski for the disilane used in these experiments.

- 
- <sup>1</sup>A. M. Beers and J. Bloem, *Appl. Phys. Lett.* **41**, 153 (1982).  
<sup>2</sup>J. M. Jasinski, B. S. Meyerson, and B. A. Scott, *Ann. Rev. Phys. Chem.* **38**, 109 (1987).  
<sup>3</sup>J. E. Demuth, R. J. Hamers, R. M. Tromp, and M. E. Welland, *J. Vac. Sci. Technol. A* **4**, 1320 (1986).  
<sup>4</sup>R. M. Tromp, R. J. Hamers, and J. E. Demuth, *Phys. Rev. Lett.* **55**, 1303 (1985).  
<sup>5</sup>F. J. Himpsel and Th. Fauster, *J. Vac. Sci. Technol. A* **2**, 815 (1984).  
<sup>6</sup>R. J. Hamers, Ph. Avouris, and F. Bozso, *Phys. Rev. Lett.* **59**, 2071 (1987).  
<sup>7</sup>S. Ciraci, R. Butz, E. M. Oellig, and H. Wagner, *Phys. Rev. B* **30**, 711 (1984).  
<sup>8</sup>S. M. Gates, C. M. Greenlief, and D. B. Beach, *J. Chem. Phys.* **93**, 7493 (1990).  
<sup>9</sup>S. M. Gates, *Surf. Sci.* **195**, 307 (1988).  
<sup>10</sup>F. Bozso and Ph. Avouris, *Phys. Rev. B* **38**, 3943 (1988).  
<sup>11</sup>R. Imbihl, J. E. Demuth, S. M. Gates, and B. A. Scott, *Phys. Rev. B* **39**, 5222 (1989).  
<sup>12</sup>Y. Suda, D. Lubben, T. Motooka, and J. E. Greene, *J. Vac. Sci. Technol. A* **8**, 61 (1990).  
<sup>13</sup>S. K. Kulkarni, S. M. Gates, B. A. Scott, and H. H. Sawin, *Surf. Sci.* **239**, 13 (1990).  
<sup>14</sup>S. K. Kulkarni, S. M. Gates, C. M. Greenlief, and H. H. Sawin, *Surf. Sci.* **239**, 26 (1990).  
<sup>15</sup>Photoemission (Ref. 19) shows the monohydride initial state is 2 eV below that of the dihydride while the EELS  $\sigma \rightarrow \sigma^*$  transition associated with the latter is 0.5–1 eV lower in energy (Ref. 12). Since the monohydride state is known to be 1.2 eV above  $E_F$  (Ref. 6) this places the dihydride at or above 2.2 eV.  
<sup>16</sup>K. Sinniah, M. G. Sherman, L. B. Lewis, W. H. Weinberg, J. T. Yates, and K. C. Janda, *Phys. Rev. Lett.* **62**, 567 (1989).  
<sup>17</sup>B. S. Meyerson, F. J. Himpsel, and K. J. Uram, *Appl. Phys. Lett.* **10**, 1034 (1990).  
<sup>18</sup>S. Ciraci and I. P. Batra, *Surf. Sci.* **178**, 80 (1986).  
<sup>19</sup>T. Sakurai and H. D. Hagstrom, *Phys. Rev. B* **14**, 1593 (1976).  
<sup>20</sup>J. J. Boland, *Phys. Rev. Lett.* **65**, 3325 (1990).  
<sup>21</sup>A. J. Hoeven, D. Dijkkamp, J. M. Lenssinck, and E. J. van Loenen, *J. Vac. Sci. Technol. A* **8**, 3657 (1990).  
<sup>22</sup>J. J. Boland (unpublished).

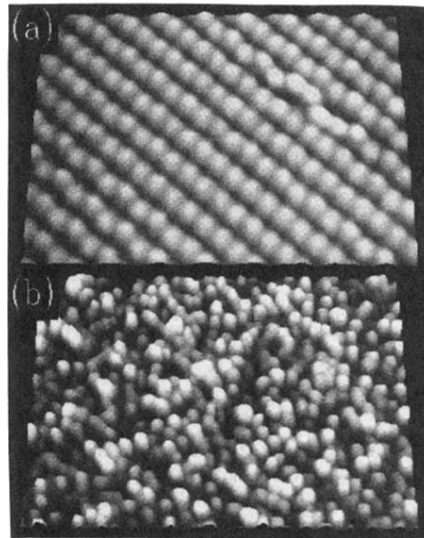


FIG. 1. (a) Clean Si(100)- $2\times 1$  surface imaged at a sample bias of  $-2$  V. The area shown is  $70\times 90$   $\text{\AA}^2$ . (b) A  $150\times 195$   $\text{\AA}^2$  STM topograph of the Si(100) surface following a saturation exposure to disilane.

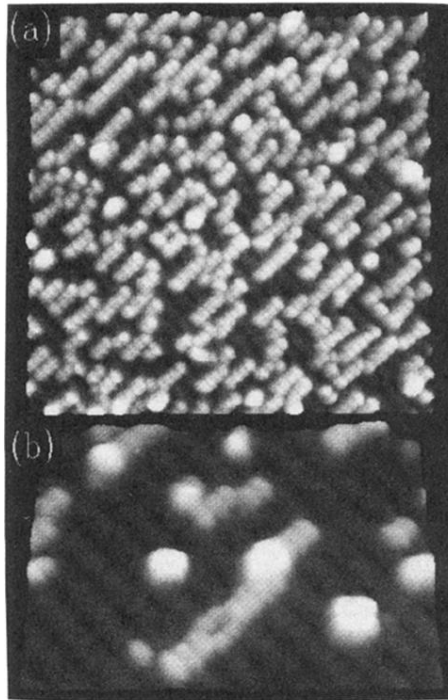


FIG. 3. (a) Surface in Fig. 1(b) following a 10-s anneal at 670 K. Area shown is  $250 \times 250 \text{ \AA}^2$ . (b) A close-up following a brief 5-s anneal at 650 K. Note the presence of unformed dimers on this surface. The occasional bright features in these images are disilane fragments which are bonded to the new epitaxial layer.

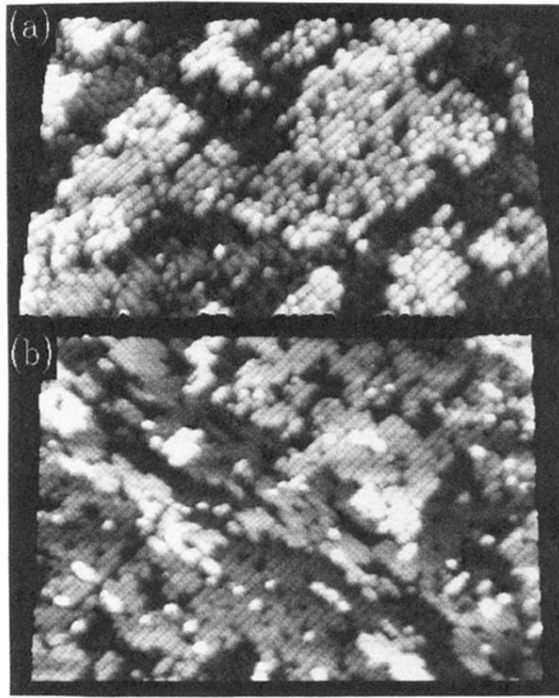


FIG. 4. (a) Epitaxial growth following a 5-min exposure of a  $2 \times 1$  monohydride surface (prepared by atomic H adsorption) to  $8 \times 10^{-8}$ -torr disilane while the sample was held at 690 K. (b) Additional exposure to  $8 \times 10^{-8}$  torr for 10 min at 690 K followed by a 5-min postanneal at 650 K to promote ordering. Area shown is  $475 \times 335 \text{ \AA}^2$ .