RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 40, NUMBER 3 15 JULY 1989-II

Kinetics of ordered growth of Si on Si(100) at low temperatures

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(Received 10 April 1989)

The temperature of the crystalline-disorder transition observed in temperature ramp silicon films grown on (100) Si by molecular-beam epitaxy is found to depend strongly on the deposition rate. This observation can be modeled if growth by random nucleation of dimer strings, as suggested by Tsao *et al.*, is assumed to be a thermally activated process which becomes frozen upon further deposition.

In the past years novel low-temperature techniques such as molecular-beam epitaxy (MBE) have been developed which now enable synthesis of semiconductor structures with tailored electronic properties.[1] Besides its practical importance the question of the lowest process temperature set by nature is also of fundamental interest. Elemental semiconductors are the most simple covalent solids to study this question since they have a reduced number of epitaxy parameters compared to the compound semiconductors. There is a further reason, however, to investigate the very low-temperature growth regime, particularly of silicon. A study on the doping kinetics of antimony has shown the existence of a transition temperature T^* separating regimes of high-surface segregation and kinetically limited segregation.[2] Thus, the very low-temperature range offers very promising feasibilities to construct atomic-scale Sb distributions in silicon MBE films.[3]

Since the early reports of vacuum evaporation silicon growth by Unvala[4] and Hale,[5] various attempts have been undertaken to clarify the question of the lowest temperature required for epitaxial growth. Using the low-energy electron diffraction (LEED), Jona[6] reported that a few monolayers deposited at room temperature on (100) Si exhibit the bulk structure. de Jong *et al.*,[7] however, who also used LEED, showed that the minimum temperature where the substrate LEED pattern is reproduced equals 470 K. A similar value of 440 K was suggested by Shiraki *et al.*[8] de Jong *et al.* found that room-temperature deposition results in ordered overlayers only below 10 nm layer thickness. Using Rutherford backscattering (RBS), Gossmann and Feldman[9] discussed in a recent study the initial stages of interface formation of Ge and Si on 2×1 reconstructed (100) Si and 7×7 reconstructed (111) Si and pointed out the role that the substrate reconstruction plays in epitaxial growth. Especially for Si on (100) Si they stated that deposition at room temperature relieves the 2×1 reconstruction of the substrate. To reach successful homoepitaxy on (100) Si, however, they suggested a temperature of 570 ± 30 K.

To determine the temperature of the crystalline-disorder (*C-D*) transition one of the authors[10] grew a homoepitaxial layer on Si(100) where the substrate temperature was lowered gradually from a temperature high enough to ensure epitaxial ordering to room temperature. The as-grown layer was evaluated by RBS. The depth of the *C-D* transition seen in channeling direction corresponded to a temperature of 510 K.

So far, experiments made on the conditions of ordered silicon growth were related to a fixed deposition rate. If ordered growth depends upon thermally activated processes at the growing surface the *C-D* transition is caused obviously by the kinetic limitation of these processes. Thus, we expect that the *C-D* transition shifts to lower temperatures when the deposition rate is reduced. To investigate this question we have performed a ramp experiment similar to the previous one[10] with the modification, however, that the temperature of the *C-D* transition could be determined at various deposition rates.

The layer was grown in an MBE equipment which was described already elsewhere.[11] The residual gas pressure during the process was in the 10^{-8} Pa range with hydrogen as the main component. High-purity silicon was evaporated by electron-beam heating. The substrate used was a 3-in.-diam (100) Si wafer which was wet chemically precleaned by an HF dip, and thermally annealed at 1170 K for 5 min. The substrate temperature was lowered from initially 870 to about 390 K at the end of deposition. The total time of deposition was 10^4 s.

Figure 1 shows a cross-section transmission electron micrograph (XTEM) from a sample with $R=0.1$ nm/s deposition rate. The interface between substrate and MBE film is marked by a broken dark line. It is probably due to a carbon contamination of the substrate surface-induced by the wet chemically precleaning step. The film grown in the temperature range from 870 to 590 K is single crystalline and shows no defects. A further lowering from 590 to 500 K results in the increasing generation of conelike defects. Finally, at temperatures below 500 K the film becomes amorphous.

In addition to the XTEM analysis we have used optical microscopy on a bevelled sample. Due to the higher refractive index in the amorphous part of the deposited film,[12] interference fringes are visible in the wedge-shaped *a*-Si film. The first maximum is visible at the thickness of the film given by $d=\lambda/4n$ where λ is the wavelength and n the refractive index of *a*-Si. Taking $\lambda\simeq550$ nm and $n\simeq5$ (Ref. 12) the temperature of the *C-D* transition was estimated to be 500 K, which agrees with the XTEM value.

To determine the temperature of the *C-D* transition at

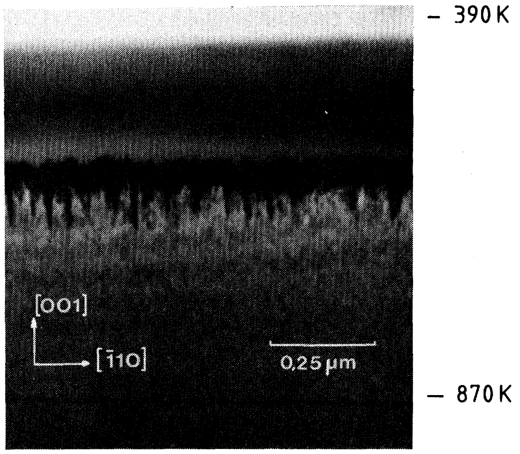

FIG. 1. Cross section TEM micrograph of a Si MBE film deposited on a (100) Si substrate at a temperature ramp ranging form 870 to about 390 K showing the transition from epitaxially ordered to disordered growth.

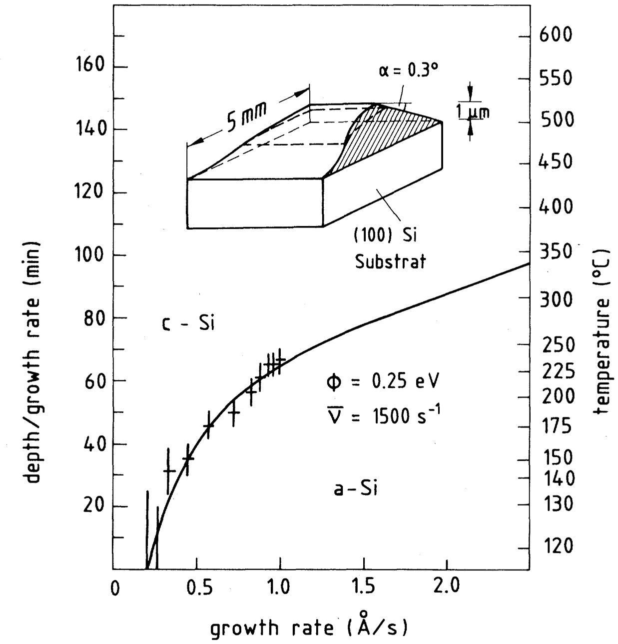

FIG. 2. The temperature of the crystalline-disorder transition visible in temperature ramp films vs deposition rate. The inset shows a segment of the shadow edge which has been bevelled to determine the position of the crystalline-disorder transition by optical microscopy. Taking into account thermal radiation from the electron gun the temperature inhomogeneity over a lateral width of 5 mm cross to the shadow edge can be estimated to be below 5 K.

deposition rates smaller than 0.1 nm/s we have partially shadowed the Si source by a beam shutter which was about 5 cm away from the wafer. By that means the layer thickness and, thus, the deposition rate decreases gradually over a range of a few mm on the wafer while the total time of deposition was maintained at 10^4 s. The misorientation at the growing surface in this range is not expected to be significantly different from the unintentional misorientation of commercially available substrates which was estimated to be about 0.25°.[13] The position of the *C-D* transition within this region, i.e., the *C-D* transition temperature at deposition rates below 0.1 nm/s was determined by optical microscopy as described above where the bevel was tilted normally to the shadow edge (see inset of Fig. 2). The result is shown in Fig. 2. The *C-D* transition temperature is lowered from about 500 K at 0.1 nm/s to below 390 K at deposition rates less than 0.025 nm/s.

In order to understand these results we want to outline some overall aspects of epitaxial growth. Generally, epitaxial growth of covalent solids is thought to proceed by transitions from a precursor state (which may be referred to the adsorbed state of the incoming atom) into a covalently bonded surface state. Following Gossman and Feldman, we may also speculate that this process is related to the reordering of the substrate surface.[9] Since the atom is either in the precursor (PC) or in the covalently bonded (CB) state the relation

$$P+P^*=1 \tag{1}$$

holds, where P and P^* are the probabilities of the PC and the CB state, respectively.

If we ask for the time dependence of the probability $P(t)$ to find the atom in the PC state after deposition of a monolayer we need to distinguish different growth modes. Observations of the growing (100) Si surface using microprobe reflection high-energy electron diffraction (microprobe RHEED)[14] have shown that growth by atomic step propagation occurs at higher temperatures. The steps may be caused by an unintentional misorientation of commercially available substrates which was estimated to yield a distance of double steps of about 60 nm.[13] At lower temperatures, however, adatoms nucleate two dimensionally on the terraces between steps because of a decrease in adatom diffusivity[13,14] even with vicinal surfaces of 1° misorientation.[15] In this case an oscillatory behavior is observed in the RHEED pattern showing alternatively 1×2 and 2×1 reconstruction domains.[15-17] Recently, Tsao *et al.* have proposed a structural model of Si growth on (100) Si where they explained the observation of persistent RHEED oscillations, which are indicative of monolayer-by-monolayer growth, by random nucleation and anisotropic growth of dimer strings.[18]

In the following we adopt this picture of (100) Si homoepitaxial growth to construct a model of the *C-D* transition. If nucleation of a dimer string is a thermally activated process the probability to find a dimer nucleus in the topmost layer at the site j of a string of length N (equal to the number of dimers in a string) can be expressed as

$$P_j^*=1-\exp(-rt)\,, \tag{2a}$$

where the transition rate r into the dimer nucleus is written as

$$r=\nu\exp(-\Phi/kT)\,; \tag{2b}$$

t is the time after filling the monolayer with PC-state atoms, Φ and ν are the activation barrier and frequency factor, respectively. If the nucleation event has taken place at any site we assume that the residual dimers of the string are formed instantaneously. If, on the other hand, no such event has occurred for $j=1$ to N within the time t no dimer string can have been formed. The probability for the latter case is given by

$$P(t)=\prod_{j=1}^{N}(1-p_j^*)=\exp(-Nrt)\,. \qquad (3)$$

Subsequently, we set $\bar{r}=Nr=N\nu\exp(-\Phi/kT)$ with $\bar{\nu}=N\nu$ being an effective frequency factor. This result means that a fraction $P(t)$ of the topmost layer remains in a PC state at the time t after deposition.

Equation (3) is supported also by thermal annealing experiments of disordered Si adlayers of monolayer thickness deposited at room temperature.[19,20] These studies have revealed an activation barrier of 1.2 ± 0.2 eV for Si on Si(111). This value is significantly below that for solid-phase epitaxial (SPE) regrowth of thick amorphous films.[21] From this observation we conclude that at $t>t_m$ where $t_m=a_0/4R$ is the time needed for one monolayer deposition on (100) Si ($a_0/4=0.136$ nm, R denotes the deposition rate), the activation barrier increases strongly to a value which is more representative of SPE regrowth. Thereby, the current state at $t=t_m$ is virtually frozen at low temperatures. Thus, the substrate (which is now the first deposited layer) may contain PC-state defects when growth is continued with the second layer.

To reproduce the appearance of conelike defects observed in the XTEM micrograph (Fig. 1) we need to assume that atoms placed on PC-state defects cannot become regular CB-state (epitaxially ordered) atoms.[22] This condition yields the following iterative scheme for the probability to find an atom in the $(n+1)$th layer after completion of the $(n+2)$th layer in a regular CB-state

$$P_{n+1}^*=P_n^*[1-P(t_m)]\,, \qquad (4)$$

with $P_0^*=1$.

Using Eqs. (2)-(4), Fig. 3 shows a simulation of epitaxial growth under the conditions used in the ramp experiment, i.e., a total deposition time of 10^4 s and a continuous temperature decrease from 870 to about 390 K. The deposition rate was chosen to be $R=0.05$, 0.1, and 0.2 nm/s. The fraction of epitaxially ordered atoms P_n^* (solid lines) remains close to unity at higher temperatures. Depending on the deposition rate, however, P_n^* shows a sudden decrease to an almost vanishing small value in the lower-temperature range. The fraction of not epitaxially ordered (disordered) atoms $P_n=1-P_n^*$ increases correspondingly to a value of almost unity. In the following we denote the temperature where $P_n=P_n^*=0.5$ as the *C-D* transition temperature.

Figure 2 shows calculated values of the *C-D* transition temperature for running values of the deposition rate (solid curve). Good agreement is achieved to the experimental results when the effective frequency factor and the barrier energy are chosen to be $\bar{\nu}=1500\pm500$ s^{-1} and $\Phi=0.25\pm0.02$ eV.

From Eq. (4) we conclude that also with constant growth temperature there is a *C-D* transition since the fraction of epitaxially ordered atoms P_n^* decreases exponentially with increasing film thickness. Accordingly, the maximum epitaxy width (where $P_n^*=0.5$) reads

$$\Delta_E=(a_0/4)\ln2\exp[\bar{\nu}t_m\exp(-\Phi/kT)]\,. \qquad (5)$$

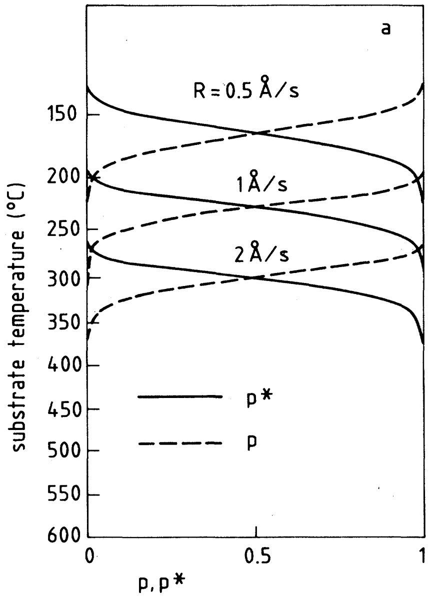

FIG. 3. The fraction of epitaxially ordered (P^*) and disordered (P) atoms as a function of temperature simulated under the conditions of the ramp experiment, using $\bar{\nu}=1500$ s^{-1} and $\Phi=0.25$ eV. The crystalline-disorder transition at $P=P^*=0.5$ shifts to lower temperatures when the deposition rate is lowered.

At modest growth rates ($R\simeq0.1$ nm/s) and high temperatures ($T>570$ K) Δ_E becomes virtually infinite. At lower temperatures, however, the *C-D* transition occurs within layers of accessible thickness. This is consistent with the early observations of Jona[6] and de Jong *et al.*[7] It agrees as well with a recent experimental result where at $T=470$ K and $R=0.1$ nm/s evidence was found to a finite epitaxy width of about 30 nm.[3] At high-deposition rates ($R>1$ nm/s), the model yields $\Delta_E<1$ μm even at higher temperatures ($T>870$ K). We believe this does not conform with the experiment. As mentioned before, surface diffusivity of adatoms becomes significant, and thus growth proceeds by step propagation rather than by two-dimensional nucleation.

A further limitation of the model is set by thermal annealing of PC-state defects which are no longer frozen at higher temperatures. This is supported by the large SPE regrowth rates in excess of $R=1$ nm/s at $T=870$ K.[21]

In conclusion, we report on a first study of the kinetics of the crystalline-disorder transition visible in temperature ramp Si MBE films grown on (100) Si. We found that the temperature of the *C-D* transition shifts to lower values when the deposition rate is lowered. At deposition rates below $R=0.025$ nm/s no *C-D* transition could be detected down to 390 K. At $R=0.1$ nm/s XTEM reveals the appearance of conelike defects prior to the *C-D* transition. These observations can be explained by a model which assumes that random nucleation and anisotropic growth of dimer strings is a thermally activated process which, in turn, becomes frozen upon further deposition. So, epitaxial growth can be kinetically limited either by high deposition rates or by low temperatures. The activation barrier is estimated to be $\Phi = 0.25 \pm 0.02$ eV, where the effective frequency factor amounts to $\bar{\nu} = 1500 \pm 500$ s^{-1}. Following this model the *C-D* transition temperature is correlated to the dimer string length and, thus, to the step distance on the vicinal substrate. As far as growth proceeds by two-dimensional nucleation large step distances are expected to reduce the *C-D* transition temperature. Questions concerning this dependency as well as the influence of the azimuth of the misorientation still need to be investigated.

Thanks are due to S. Lindenmaier for TEM analysis. Valuable discussions with Dr. E. Kasper are gratefully acknowledged. This work was partly supported by the German Ministry for Research and Technology.

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[1] *Molecular Beam Epitaxy 1988,* proceedings of the Fifth International Conference on Molecular Beam Epitaxy, Sappero, Japan, 1988, edited by Y. Shiraki and H. Sakaki (North-Holland, Amsterdam, to be published).

[2] H. Jorke, Surf. Sci. **193**, 569 (1988).

[3] H. Jorke, H. Kibbel, F. Schäffler, A. Casel, H.-J. Herzog, and E. Kasper, J. Cryst. Growth **95**, 484 (1989).

[4] B. A. Unvala, Nature (London) **194**, 966 (1962).

[5] A. P. Hale, Vacuum **13**, 93 (1963).

[6] F. Jona, Appl. Phys. Lett. **9**, 235 (1966).

[7] T. de Jong, W. A. S. Douma, L. Smit, V. V. Korablev, and F. W. Saris, J. Vac. Sci. Technol. B **1**, 808 (1983).

[8] Y. Shiraki, Y. Katayama, K. Kobayashi, and K. F. Komatsubara, J. Cryst. Growth **45**, 287 (1978).

[9] H. J. Gossmann and L. C. Feldman, Appl. Phys. A **38**, 171 (1985).

[10] H.-J. Herzog, E. Kasper, P. Eichinger, and H. Kibbel (unpublished); E. Kasper and H. Jorke, in *Chemistry and Physics of Solid Surfaces VII,* edited by R. Vanselow and R. F. Howe (Springer-Verlag, Berlin, 1988), p. 557.

[11] U. König, H.-J. Herzog, H. Jorke, E. Kasper, and H. Kibbel, in *Collected Papers of the Second International Symposia on Molecular-Beam Epitaxy and Related Clean Surface Techniques* (The Japanese Society of Applied Physics, Tokyo, 1982), p. 193.

[12] *Semiconductors: Special Systems and Topics, Comprehensive Index for III-17a–i,* Landolt-Börnstein, Group III, Vol. 171 (Springer-Verlag, Berlin, 1985), p. 43.

[13] E. Kasper, Appl. Phys. A **28**, 129 (1982).

[14] T. Doi and M. Ichikawa, J. Cryst. Growth **95**, 468 (1989).

[15] K. Sakamoto, T. Sakamoto, S. Nagao, G. Hashigushi, K. Kuniyoshi, and N. Takashi, in *Proceedings of the Second International Symposia on Si MBE,* edited by J. C. Bean and L. J. Schowalter (Electrochemical Society, Pennington, 1988), p. 307.

[16] T. Sakamoto, T. Kawamura, and G. Hashigushi, Appl. Phys. Lett. **48**, 1612 (1986).

[17] J. Aarts, W. M. Gerits, and P. K. Larsen, Appl. Phys. Lett. **48**, 931 (1986).

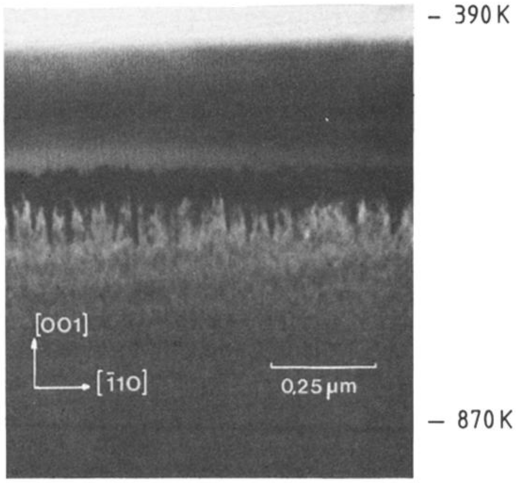
[18] J. Y. Tsao, E. Chason, U. Koehler, and R. Hamers, Phys. Rev. Lett. (to be published).

[19] T. F. Heinz, M. M. T. Loy, and S. S. Iyer, in *Photon, Beam, and Plasma Stimulated Chemical Processes at Surfaces,* edited by V. M. Donnelly, I. P. Herman, and M. Hirose, Materials Research Society Symposia Proceedings, Vol. 75 (Materials Research Society, Pittsburgh, 1987), p. 697.

[20] S. S. Iyer, T. F. Heinz, and M. M. T. Loy, J. Vac. Sci. Technol. B **5**, 709 (1987).

[21] L. Csepregi, E. F. Kennedy, J. W. Mayer, and T. W. Sigmon, J. Appl. Phys. **49**, 3906 (1978).

[22] This may also be tetrahedrally bonded atoms which are rotated by 180° around a $\langle 111 \rangle$ axis, thus forming a twin. On (100) Si twinning, i.e., rotation by 180° is possible when one of the normally two bonds to underlying layer atoms is absent. This structural condition may be fulfilled in the vicinity of PC-state defects [H.-J. Herzog and H. Jorke (unpublished)].



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