Effects of *in situ* doping from B_2H_6 and PH_3 on hydrogen desorption and the low-temperature growth mode of Si on Si(100) by remote plasma enhanced chemical vapor deposition

B. Doris
Microelectronics Research Center, and Department of Physics, University of Texas at Austin, Austin, Texas 78712

J. Fretwell
Microelectronics Research Center, University of Texas at Austin, Austin, Texas 78712

J. L. Erskine
Department of Physics, University of Texas at Austin, Austin, Texas 78712

S. K. Banerjee
Microelectronics Research Center, University of Texas at Austin, Austin, Texas 78712

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We demonstrate that di- and monohydride desorption peak temperatures are shifted lower for boron-doped films and higher for phosphorus-doped films compared to intrinsic Si(100). This observation is exploited to show that the shifts in di- and monohydride desorption peak temperatures with doping are accompanied by shifts in the growth mode transition temperatures, with one exception which is discussed. This work suggests that dihydrides lead to breakdown of epitaxial growth while monohydrides promote three-dimensional epitaxial growth. © *1997 American Institute of Physics.* [S0003-6951(97)03819-9]

The role of hydrogen in the low-temperature growth of Si is an important issue.[1–3] Recently, we have demonstrated that Si growth by remote plasma enhanced chemical vapor deposition (RPCVD) exhibits three distinct growth modes.[3] This work suggested that the onset of three- and two-dimensional epitaxial growth is governed by di- and monohydride desorption, respectively. In this letter, we report the observation that di- and monohydride desorption peak temperatures shift to lower temperatures for boron-doped films and to higher temperatures for phosphorus-doped films compared to intrinsic Si(100). Hydrogen desorption from intrinsic Si films dosed with near monolayer coverage of boron and phosphorus has been examined by others.[4,5] The results presented here differ in that we attribute shifts in hydrogen desorption energies to changes in the electrical character of the Si surface as determined by the low concentration of dopants. These effects are believed to be general for acceptor and donor impurities regardless of the dopant species in Si and Si/Ge systems. We use this phenomenon to show that shifts in hydrogen desorption temperatures are accompanied by shifts in the growth mode transition temperatures for the various film types, with one exception which we explain.

RPCVD was used to grow the Si films. Experimental procedures and growth conditions are described in detail elsewhere.[3,6] Resistivities of the wafers used in these experiments were 8–15 Ω cm. The Si(100) wafers were cleaned *ex situ* using a modified RCA process.[7] *In situ* doping was achieved by flowing 1 sccm of diborane (50 ppm in He) and 5 sccm of phosphine (5000 ppm in He) through the gas dispersal ring to produce dopant concentrations of about 2×10^{20} cm^{-3}, and 4×10^{19} cm^{-3} for boron and phosphorus, respectively. Ellipsometry and stylus profilometer measurements indicated that the growth rate for the various film types was constant to within 5%–10%, regardless of substrate temperature. All films were approximately 1000 Å. Temperature programmed desorption (TPD) studies were performed in another system described elsewhere.[8] Samples were transferred via a load lock and nitrogen purged glove box. Auger electron spectroscopy was used to monitor surface cleanliness and to verify that no dopant segregation occurred. Atomic hydrogen dosing at a sample temperature of 150 °C was performed by dissociating H_2 using a hot tungsten filament. Saturation coverage was later confirmed by desorption experiments. All TPD data were generated using a ramp rate of 5 °C/s.

Hydrogen TPD results for boron doped, phosphorus doped, and intrinsic Si(100) are shown in Fig. 1. These data clearly show that the di- and monohydride peaks shift to lower temperatures for boron doping, and to higher temperatures for phosphorus doping compared to intrinsic Si(100). Since dopant atoms constitute a small fraction of the total surface, and the peak intensity and total area under the TPD

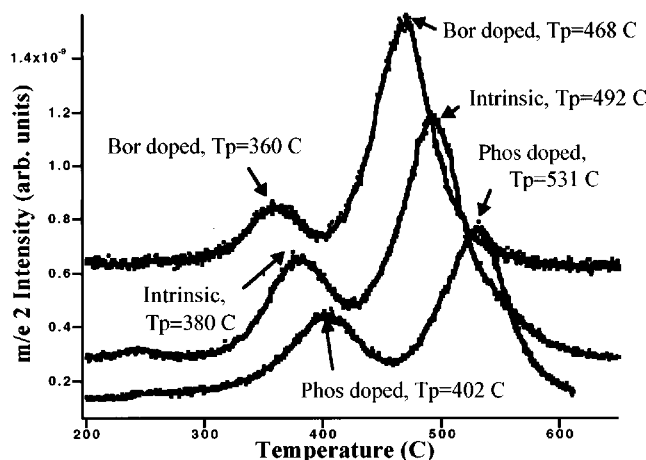

FIG. 1. TPD curves for hydrogen desorption from the boron-doped, phosphorus-doped, and intrinsic Si(100) surfaces.

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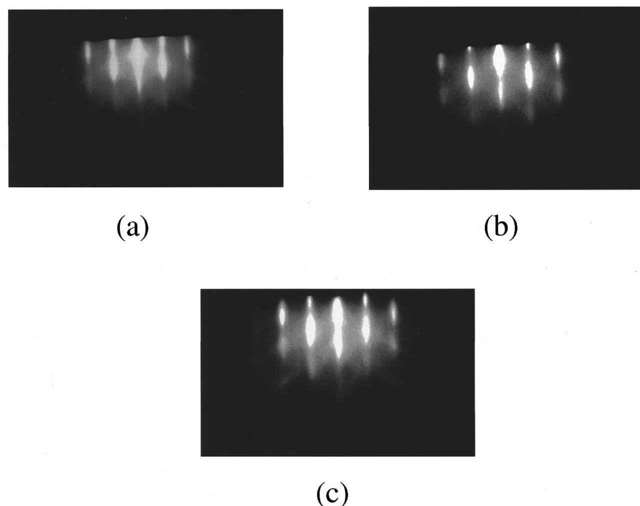

FIG. 2. RHEED patterns of the onset of three-dimensional epitaxial growth for (a) intrinsic Si at 350 °C, (b) boron-doped Si at 320 °C, and phosphorus-doped Si at 350 °C.

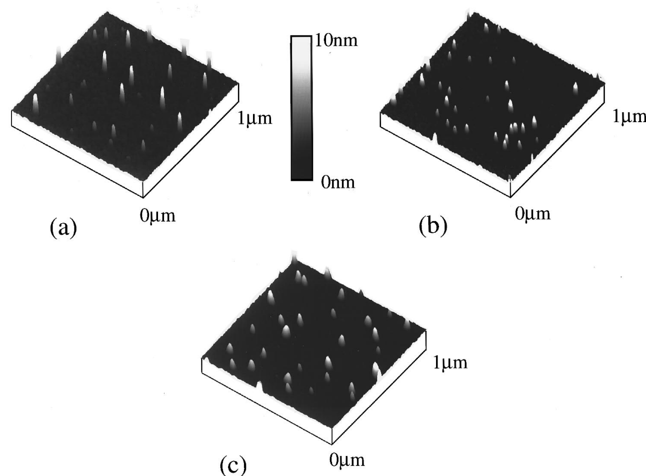

FIG. 4. AFM images of onset of two-dimensional epitaxial growth for (a) intrinsic Si at 470 °C, (b) boron-doped Si at 380 °C, and (c) phosphorus-doped Si at 530 °C.

curves are comparable for all three samples, the temperature shifts can be attributed to hydrogen desorption primarily from Si atoms and not from impurity atoms.

Reflection high-energy electron diffraction (RHEED) was used to determine the minimum temperature for epitaxial growth for the various film types. Although this technique cannot determine if amorphous nucleation initiated at the substrate, for the intrinsic Si film we have confirmed that the amorphous phase does initiate at the substrate by cross-section transmission electron microscopy.[3] Even without similar analysis for the doped Si films, the correlation between the shifts in the di- and monohydride desorption peak temperatures and the growth mode cannot be disputed. Figure 2 shows that the onset of epitaxial growth for intrinsic, boron- and phosphorus-doped Si occurs at 380, 320, and 350 °C, respectively. The diffraction streaks are lobed and slightly spotty, indicating rough but single-crystal films.

Figure 3 shows atomic force microscopy (AFM) images of three-dimensional film growth. The surfaces are composed of hemispherical bumps. Figure 3 shows three-dimensional epitaxial film growth at 440, 350, and 500 °C for intrinsic, boron-, and phosphorus-doped Si(100), respectively. These are the highest temperatures for which three-dimensional growth is observed for the various film types. We point out that the three-dimensional growth is observed for the various film types. We point out that the three-dimensional surface features shown in Fig. 3 are similar to those observed for the onset of epitaxial growth. The fact that these films are single crystal was verified by RHEED.

Figure 4 shows AFM images of the onset of two-dimensional film growth, characterized by a dramatic decrease in density of the three-dimensional surface features. The difference in heights of the three-dimensional bumps results from the inability of the AFM tip to probe between the three-dimensional features when they are closely packed together. Rms roughness is not a good parameter for characterizing this type of surface since it is composed of two distinctly different features. Figure 4 shows that the onset of two-dimensional epitaxial growth occurs at 470, 380, and 530 °C for intrinsic, boron-, and phosphorus-doped Si(100), respectively.

One exception to the notion that hydrogen termination governs the growth mode is the transition from amorphous to three-dimensional epitaxial growth for phosphorus-doped Si, which occurs at a lower temperature than expected. We believe that this discrepancy is due to the formation of PH_3. It is likely that the remote plasma source dissociates the PH_3 into PH_2 and PH before it reaches the surface. Other researchers have observed a large PH_3 peak at 370 °C in TPD curves for phosphorus-covered Si surfaces.[4] Thus, for the substrate temperature at which we expect the onset of amorphous growth for phosphorus-doped Si, formation and desorption of PH_3 occurs. One possibility is that this PH combines with dihydrides, thereby reducing the surface dihydride concentration, which would allow epitaxy to continue at temperatures below the dihydride desorption peak temperature as measured by TPD.

Shifts in the di- and monohydride desorption peak temperatures can be explained in terms of the electrical proper-

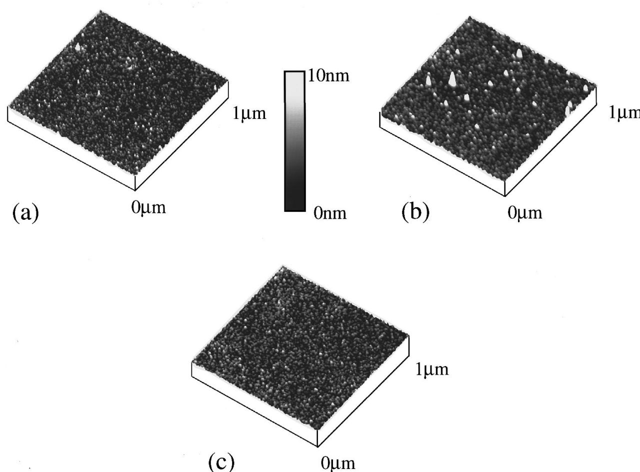

FIG. 3. AFM images of three-dimensional epitaxial growth for (a) intrinsic Si at 440 °C (rms=0.28 nm), (b) boron-doped Si at 350 °C (rms=0.37 nm), and (c) phosphorus-doped Si at 500 °C (rms=0.20 nm).

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ties of the various surfaces. The p-type material is electron deficient and, thus, the local electron density on Si surface atoms is lower compared to intrinsic and n-type material.[9] Electron orbitals of the surface Si atoms participate in adsorbate bonding. It seems reasonable, therefore, that the energy required to remove a hydrogen atom is less in the case of p-type doping. An opposite effect occurs in the case of n-type Si. These results demonstrate that a fundamental relationship exists between surface charge carrier density and hydrogen bonding strength.

The data presented here suggest that the presence of the various hydride species during low-temperature Si growth governs the growth mode. The bond angles of the dihydride may force Si adatoms into misregistry with respect to substrate atoms, thereby causing the breakdown of epitaxial growth. Monohydride bond angles, on the other hand, apparently allow adatoms to situate themselves in lattice sites leading to epitaxial growth. However, the density of the three-dimensional features decreases at higher temperatures. Thus, the number of three-dimensional features decreases with the number of monohydrides present on the surface. We, therefore, believe that adatoms tend to cluster around, and eventually grow over the monohydrides to create the three-dimensional surface features.

It is interesting that the grwoth mode transition from three-dimensional epitaxial grwoth to two-dimensional epitaxial growth is not abrupt. As evidenced by the AFM data, both modes of growth can exist on the same surface. The transition from amorphous to three-dimensional epitaxial growth is also believed to be somewhat gradual. Since the data show that the growth mode is related to the type of hydride present on the growing surface, it seems intuitive that the growth mode transition is governed by the rate of desorption of the various hydride species as well as the flux of hydrogen to the surface. The athermal rate of desorption component can be attributed to the plasma. Since there are well-defined, sharp peaks in these curves, one would expect the surface concentration of di- and monohydrides to decrease quickly with temperature. However, the tails of the di- and monohydride desorption peaks extend quite far, indicating that a small number of di- and monohydrides can exist at temperatures somewhat higher than the peak desorption temperature. From this discussion, it appears that the ratio of the hydrogen desorption rate, by whatever means, to the growth rate, which is proportional to the rate of flux of the various hydride species to the surface should be a universal constant that can be used to predict what the growth mode will be under various conditions.

In conclusion, we have shown how doping affects hydrogen desorption from Si(100), and the growth mode of Si on Si(100). This work supports the notion that the presence of dihydrides leads to the breakdown of epitaxial growth while monohydrides promote three-dimensional epitaxial growth.

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