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Ultrahigh growth rate of epitaxial silicon by chemical vapor deposition at low temperature with neopentasilane

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A precursor, neopentasilane, is used to produce high-quality silicon epitaxy by chemical vapor deposition under 700 °C with very high growth rates. Low background dopant concentration and excellent crystal quality were determined from secondary-ion-mass spectroscopy and cross sectional transmission electron microscopy. Growth rates as high as 130 nm/min at 600 °C have been achieved. Growth rates in nitrogen and hydrogen ambients are about equal for neopentasilane, unlike those for growth with low-order silanes. A concerted reaction, where an open site is generated at the same time the adatom is adsorbed, is proposed as a possible mechanism for both the high growth rate with neopentasilane as well as the similar rate with hydrogen and nitrogen carriers.

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For silicon epitaxial growth, temperatures under 700 °C are required for the integration of front-end processes in very-large-scale integration structures, such as raised source/drains,¹ to avoid any dopant diffusion. In the commonly used chemical vapor deposition (CVD) approach, such low temperatures lead to a large reduction of epitaxial growth rate. This is significant because high growth rates are desired for throughput in modern single-wafer processing tools.

In this work, we report very high growth rates of high-quality epitaxial silicon grown by CVD from 600 to 700 °C. The work was enabled by a silicon precursor, neopentasilane (Si_5H_{12}). Growth was performed on (100) oriented silicon wafers. It has been observed that an increased number of silicon atoms in hydride precursors [i.e., switching from silane (SiH_4) to disilane (Si_2H_6), to trisilane, Si_3H_8]² leads to increased epitaxy growth rates at the same temperature and thus enables lower growth temperatures. For example, Fig. 1 compares growth rates using dichlorosilane (partial pressure=52 mtorr), silane (partial pressure=20 mtorr), disilane (partial pressure=10 mtorr), and neopentasilane (upper limit to partial pressure of 20 mtorr), with a 6 torr hydrogen carrier pressure observed in our laboratory. At 600 °C, dichlorosilane growth rates were negligible, the silane growth rate was 0.6 nm/min, and the disilane growth rate was 8 nm/min.

In this work, we explored the use of neopentasilane (Si_5H_{12}) in our homemade CVD reactor.³ Prior to loading into the reactor, the wafers were cleaned using a chemical mixture of sulfuric acid and hydrogen peroxide, followed by a 2 min, dilute HF dip.⁴ The chamber pressure for all experiments was set at 6 torr, with a hydrogen carrier flow of 3 SLPM (SLPM denotes standard liters per minute). Neopentasilane (NPS) is a liquid at room temperature: a bubbler

with a hydrogen carrier was used to introduce the NPS to the chamber.

The neopentasilane partial pressure is not known absolutely. Assuming the hydrogen leaving the bubbler is completely saturated with NPS (bubbler temperature is 35 °C, vapor pressure is 30 torr), then the estimated upper limit of the vapor pressure in the reactor of NPS is 20 mtorr (solid squares). We suspect that the actual partial pressure is up to a factor of 10 lower than this. The epitaxial growth rates were measured by step height measurements on patterned oxide samples. Epitaxial rates were 215, 130, and 54 nm/min at 700, 650, and 600 °C, respectively (solid squares, Fig. 1).

The growth rate increases linearly with partial pressure at 600 °C (Fig. 2). We have yet to observe any saturation of the growth rate with NPS partial pressures. Classically, the growth rate at high partial pressures saturates because growth becomes limited by desorption of hydrogen.⁵ At a high par-

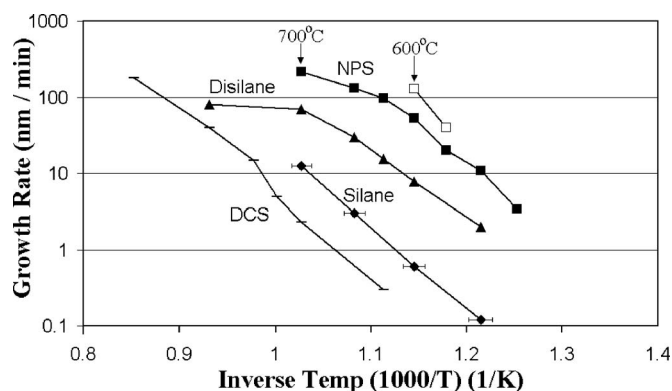


FIG. 1. Comparison of low-pressure CVD epitaxial growth rates vs inverse temperature for sources of dichlorosilane, silane, disilane, and neopentasilane (NPS) precursor on (100) silicon substrates. In all cases, the carrier was hydrogen at a pressure of 6 torr. The dichlorosilane, silane, disilane, and NPS partial pressures were 52, 20, 10, and 20 mtorr, respectively. The open squares are NPS with a partial pressure of 65 mtorr. Estimated temperature error is $\pm 1\%$ and growth rate error is $\pm 10\%$.

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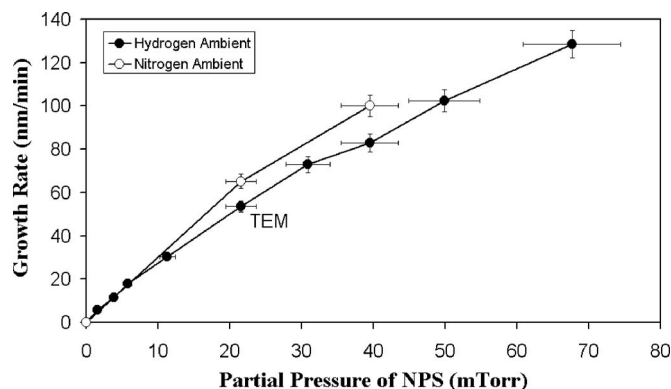


FIG. 2. Growth rate at 600 °C in 6 torr hydrogen ambient (solid circles) and in 6 torr nitrogen ambient (open circles) vs the partial pressure of NPS.

tial pressure of NPS (upper limit) of 65 mtorr, growth rates of 130 nm/min at 600 °C and 30 nm/min at 575 °C were observed (open squares in Fig. 1). Higher rates were experimentally limited by the maximum flow of NPS through the bubbler. Comparing our highest rate at 600 °C (130 nm/min) with that of the previously reported using trisilane,² our work represents a factor of 2.5 increased in growth rate at 600 °C. These growth rates are also significantly higher than the growth rates reported with ultrahigh vacuum CVD (6 and 1.2 nm/min at 650 and 600 °C).⁶

The quality of the silicon was analyzed using cross sectional transmission electron microscopy (x-TEM) from a sample grown at 600 °C at a rate of 54 nm/min (Fig. 3). Lattice images at point B inside the epitaxial layer shows an excellent crystalline quality. Also shown in the inset is an electron scattering pattern. The sharp pattern is also indicative of excellent crystal quality epitaxy. The background concentration of boron and phosphorus impurities were at the secondary-ion-mass spectroscopy resolution limit of 10^{16} cm^{-3} using a Cs primary beam. Oxygen levels were at 10^{18} cm^{-3} and carbon levels were 10^{20} cm^{-3} . The high carbon levels may be due to impurities in the NPS source. As a further check of crystalline quality, field-effect transistors (FETs) were fabricated from epitaxy layers grown with NPS at high growth rates (up to 180 nm/min at 650 °C and 80 nm/min at 600 °C) on both *n*-type and *p*-type silicon substrates. For *p*-channel and *n*-channel FETs, the electron and hole mobilities of the FETs were comparable to those of

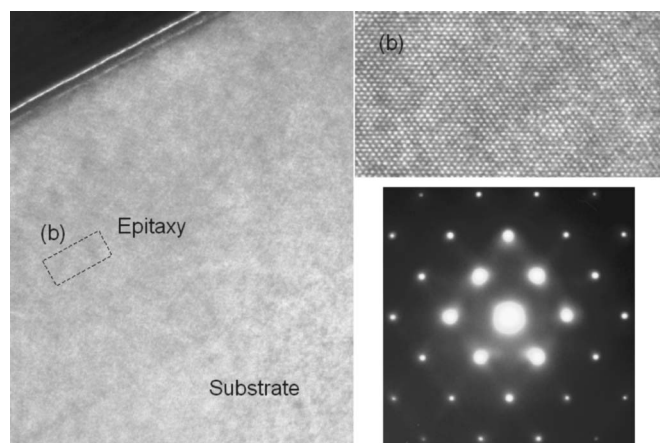


FIG. 3. Cross section transmission electron of a sample grown at 600 °C with growth rate of 54 nm/min growth time of the sample is 90 s.

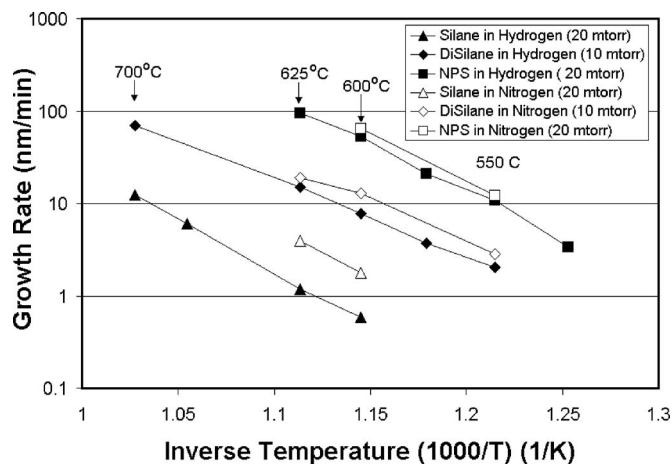


FIG. 4. Comparison of epitaxial growth rates vs inverse temperature for the precursors of silane, disilane, and NPS (squares) on (100) silicon substrates in hydrogen and nitrogen ambient. The partial pressures are 20 mtorr of silane, 10 mtorr of disilane, and 20 mtorr (estimated upper limit) of NPS.

FETs fabricated from bare silicon substrates as controls, a further evidence of the high crystal quality.

To understand the reason for the fast growth rate, growth was done in a nitrogen ambient as well as on a hydrogen ambient for silane, disilane, and NPS sources (Fig. 4). Silicon epitaxy growth rates with silane typically see a significant enhancement in a nitrogen ambient versus a hydrogen ambient.⁷ In our experiments, the growth rate using silane (partial pressure=20 mtorr) at 600 °C increased five times in nitrogen versus hydrogen, and the growth rate using disilane (partial pressure=10 mtorr) increased two times in nitrogen versus hydrogen. In contrast, the increase in growth rate using neopentasilane was only 20% higher in nitrogen versus hydrogen. The growth in all of these experiments was still increasing linearly with the partial pressure of the source. Because of the equilibrium between the hydrogen on the silicon surface and that in an ambient (hydrogen desorbs and adsorbs), the switch from a hydrogen ambient to a nitrogen ambient is thought to reduce the hydrogen coverage on the surface. This increases the number of open sites on the silicon surface for chemical adsorption of the growth species and increases the growth rate in the case of silane.⁷

All of these observations were made not in the range when growth is mass transport-limited (little dependence on temperature) but in the low temperature range where surface reactions control the growth rate.⁷ Within this region, the lack of increase in rate from hydrogen to nitrogen ambient suggests that open sites from the hydrogen ambient-surface equilibrium play a small role in determining the growth rate with NPS and play a smaller role with disilane than with silane. With NPS, it appears that the adatom can adsorb either without open sites, or that the growth cycle can create its own open sites, without relying on conventional hydrogen desorption to create them. We speculatively propose the latter as a possible mechanism. As a model, consider the well-studied cracking of linear and branched hydrocarbons on catalytic hydrogen covered metal surfaces. As the branching of the hydrocarbon increases, the carbon-carbon bond weakens and cracks more readily.⁸⁻¹⁰ This thus promotes a “concerted” reaction of simultaneous bond breaking and bond forming. In this case, a carbon-carbon bonds break and a hydrogen-metal surface bond breaks and is replaced by a

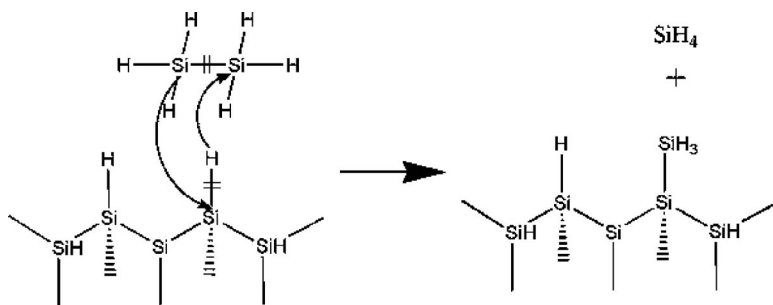


FIG. 5. Schematic for a concerted reaction for disilane. The Si-Si bond of disilane cracks and SiH₃ is inserted onto the surface, while the surface hydrogen is inserted onto the other side of the disilane forming SiH₄. The double slashes indicate bonds broken by the concerted reaction and the arrows represent the bonds formed. The dashed triangle represents the reconstruction of the surface silicon atoms in/out of the plane of the figure.

carbon-hydrogen bond and a carbon-metal surface bond.^{8–10} Hydrocarbon fragments formed by C-C bond scission are more stable. The greater the degree of branching, the more facile cracking occurs. By analogy, the Si-Si bonds are weaker than the Si-H bonds,¹¹ which would preferentially lead to a concerted reaction on the Si surface, as shown in Fig. 5: as the Si-Si bond breaks, a hydrogen-surface bond would also be broken, along with the insertion of the previously surface-bonded hydrogen into one side of the silicon-silicon bond, while the other side of the silicon-silicon bond is adsorbed onto the freed surface site as an adatom. These reactions may take place without the need for a prior open site, explaining the independence of open site coverage for higher order silanes. Note that this mechanism would also explain the main technological point of this paper; i.e., the higher growth rates with high order silanes (such as disilane, trisilane and NPS) in hydrogen ambients.

In summary, in this work, we have demonstrated high-quality, silicon epitaxy with high growth rates at low temperature using CVD and neopentasilane in a hydrogen ambient. Growth rates as high as 130 nm/min at 600 °C have been achieved. The reason for the high growth rates of sili-

con using neopentasilane may be due to concerted surface reactions, which allow growth faster than the conventional number of open sites would imply.

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