

# Chemical Vapor Deposition Epitaxy of Silicon and Silicon-Carbon Alloys at High Rates and Low Temperatures using Neopentasilane

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The silicon precursor neopentasilane is used to grow epitaxial silicon at high growth rates from 550 to 700 °C, with rates over 100 nm/min achieved at 600 °C. The layer quality as observed by TEM and the performance of FET's made in these films is high. Neopentasilane has also been used to grow dilute strained Si<sub>1-y</sub>C<sub>y</sub> alloys on silicon with very high growth rates. For carbon levels on the order of 2%, strained layers were grown at rates over 40 nm/min.

## Introduction

Source-drain engineering such as recessed epitaxial strained layers for high channel mobility [1] and raised source-drains for improved contacts are key enabling technologies for future FET scaling. These applications are different from typical blanket epitaxy on starting silicon wafers for CMOS in that the process temperature for future source-drain applications should be kept at 700 °C or below to prevent altering existing device profiles. At such low temperatures, however, it is difficult to achieve high growth rates. In high-volume applications, high growth rates are necessary for high throughput and a low process cost. High growth rates may also enable achieving high substitutional carbon levels in dilute silicon-carbon alloys. In this work, we present the use of a novel silicon precursor, neopentasilane, for achieving high epitaxial growth rates of both silicon and dilute Si<sub>1-y</sub>C<sub>y</sub> alloys on Si(100) surfaces at temperatures of 650 °C or less. For example, silicon growth rates well over 100 nm/min at 600 °C are achievable.

## Silicon Growth using Neopentasilane

The general trend of increased rates of epitaxial silicon growth with the chemical vapor deposition method by using higher order silanes is well known, even if the microscopic growth mechanisms are not well understood. Fig. 1 shows how the growth rates increase at low temperatures as one moves from dichlorosilane (slowest) to silane (SiH<sub>4</sub>) to disilane (Si<sub>2</sub>H<sub>6</sub>) (data from our lab) to trisilane (Si<sub>3</sub>H<sub>8</sub>) (Ref 2). Our interest is focused on the “low-temperature” regime, where growth rates are generally limited by a chemical reaction rate (often called a “surface reaction”), leading to an exponential dependence on inverse temperature. We will not focus on the “high temperature” regime where growth is limited by mass transport issues and has little temperature dependence.

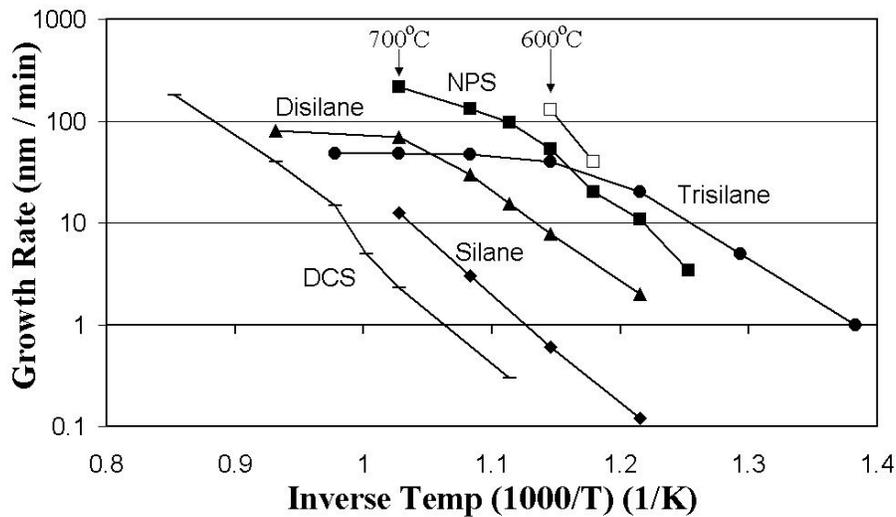


Figure 1. Comparison of low-pressure chemical vapor deposition (LPCVD) epitaxial silicon growth rates vs. inverse temperature for sources of dichlorosilane (DCS), silane, disilane, trisilane [2] and novel neopentasilane (NPS) precursor on (100) silicon substrates. For growth with NPS, the closed squares represent a 3 lpm hydrogen carrier flow and the open squares are a lower carrier flow, to increase the NPS partial pressure. All growth except trisilane was done at 6 torr in a hydrogen carrier.

Neopentasilane ( $\text{Si}_5\text{H}_{12}$ ) is a liquid at room temperature, with a vapor pressure of  $\sim 12$  torr. In our work the neopentasilane supplied to the growth reactor by bubbling hydrogen at reduced pressure through the heated liquid. Because of hardware limitations, it is difficult to know exactly the amount of neopentasilane supplied by the bubbler, but it is estimated to be 0.1% of the hydrogen flow through the bubbler. The typical growth conditions used in this work are a reactor pressure of 6 torr and a hydrogen carrier of 3 lpm, independent of that used for the bubbler source. (Because the flow rate of the bubbler was limited, the highest growth rate (open squares in Fig. 1) was achieved with a lower carrier flow.) At 600 °C, epitaxial silicon growth rates in excess of 100 nm/min were achieved. In the range of 600 – 700 °C, a growth rate  $\sim 5\text{X}$  that achieved with trisilane,  $\sim 10\text{X}$  that with disilane, and  $\sim 100\text{X}$  that with silane are observed.

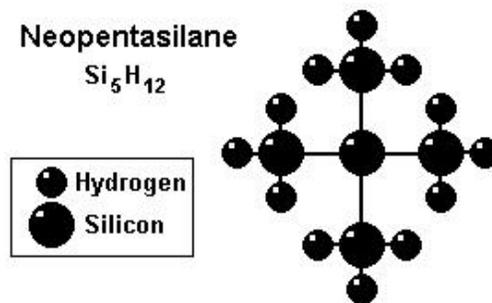


Figure 2. Schematic chemical configuration of neopentasilane (NPS).

Figure 3 shows the dependence of the growth rate on the neopentasilane partial pressure in an indirect way. Since we do not know the actual flow of the neopentasilane, we plot instead the partial pressure of the hydrogen which flowed through the bubbler (out of a total hydrogen pressure of 6 torr). The neopentasilane partial pressure entering the reactor is estimated at 0.1% of that of the partial pressure through the bubbler. The growth rates are approximately linear with neopentasilane flow, with only a hint of saturation.

The partial pressures of the dichlorosilane, silane, and disilane in Fig. 1 vary, but are on the order of 20-60 mtorr. This is over ten times higher than the estimated partial pressures of the neopentasilane, but the growth rates with neopentasilane are far higher, as noted earlier. Conventionally, the higher growth rates with higher-order silane precursors is partially attributed to the increased availability of  $\text{SiH}_3$  fragments. At present, the reason for the high growth rates with neopentasilane is not known. However, it is likely that some other mechanism beyond the availability of  $\text{SiH}_3$  fragments is probably important. This is currently under investigation.

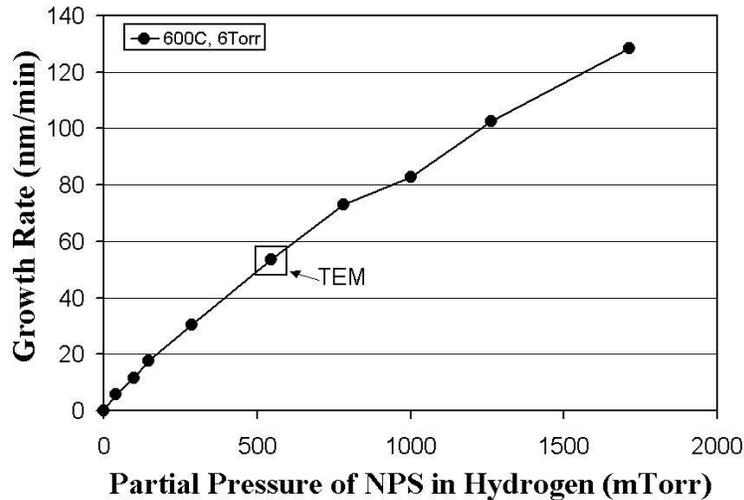


Figure 3. Growth rate vs. partial pressure of output flowing through the neopentasilane bubbler source, for a total reactor pressure of 6 torr hydrogen at 600 °C [3]. The sample used for the TEM analysis shown in the next figure is indicated.

A natural question is if the high growth rate affects the quality of the epitaxial layer. For example, one might wonder if there is a limit to how fast silicon atoms can order themselves on the surface as the film grows. Fig. 4 shows high-resolution transmission electron microscopy (TEM) of a silicon layer grown on a silicon (100) substrate at 600 °C at a rate of ~ 55 nm/min. No defects in the layer or at the substrate interface were evident, and a selected area diffraction pattern from the epitaxial layer shows no evidence of rings or mis-oriented grains, etc, consistent with high quality single crystals. Further, photoluminescence of epitaxial layers of SiGe quantum wells grown on top of silicon layers grown with NPS show that the layers are of high quality [3].

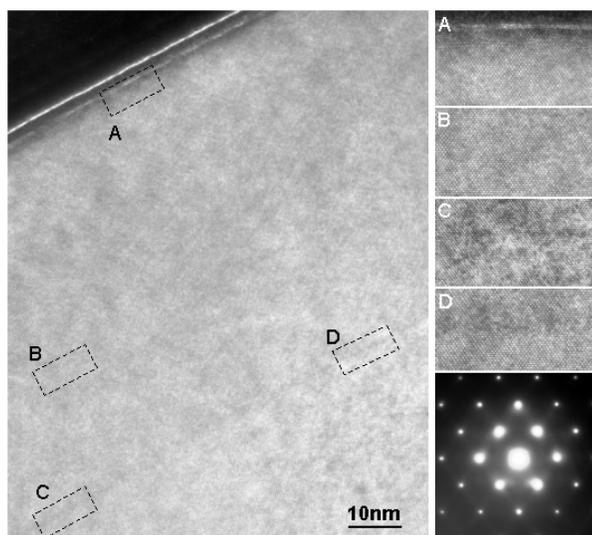


Figure 4. High-resolution cross section transmission electron microscopy and diffraction pattern of silicon epitaxial layer grown with neopentasilane source at 600 °C [3]. The growth rate was 55 nm/min. Images C and D were taken along the substrate/epitaxy interface.

To probe the electrical quality of the layers, both n-channel and p-channel metal oxide semiconductor field effect transistors (MOSFET's) were made in layers at 650 °C at a variety of growth rates. The 25-nm gate oxide was grown at 950 °C. The FET's were well behaved (Fig. 5). Over a range of growth rates from 55 to 180 nm/min, the n-channel (p-channel) mobilities averaged 850 (300)  $\text{cm}^2/\text{V}\cdot\text{s}$ , slightly higher than the mobilities observed in control devices made directly in substrates without epitaxy. There was little to no observable dependence on growth rate. That the mobilities were higher than those in the control devices without epitaxy is attributed to lower doping in the devices in the epitaxy compared to the substrates.) From the FET data, we conclude the epitaxial films grown with neopentasilane at high rates have excellent transport properties for majority carriers.

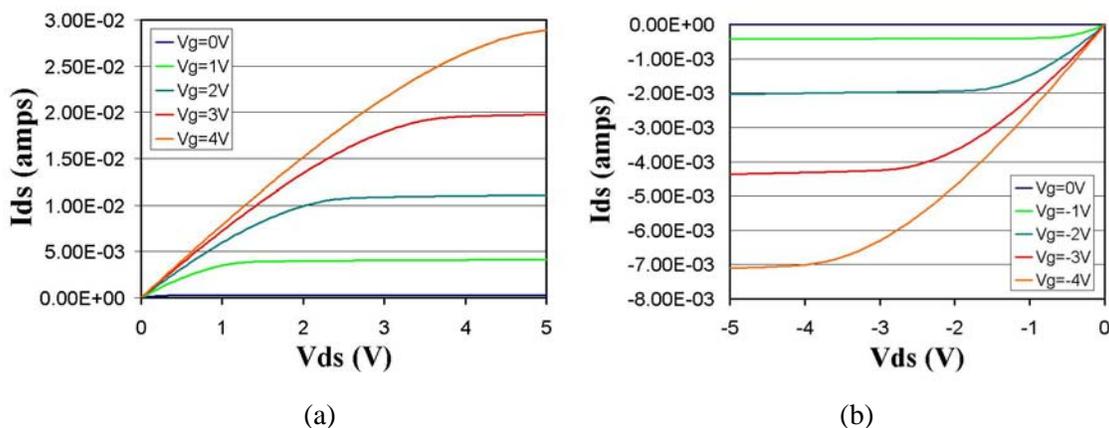


Figure 5. Drain current vs. drain-source voltage for (a) n-channel and (b) p-channel FET's made in epitaxial silicon layers grown with neopentasilane on separate substrates [4]. The growth temperature was 650 °C and the growth rate was 180 nm/min. The gate oxide thickness was 25 nm. The gate voltages are 0 – 5V in 1V increments (positive for n-channel, negative for p-channel).

Finally, we note that while the epitaxy in these experiments was done at “low-temperature,” before epitaxy the substrates were generally cleaned with a “high temperature” (~1000 °C) bake in hydrogen. Therefore the entire process was not a “low thermal budget” process. Separate work will be reported at this meeting on the use of chlorine to clean substrates before epitaxy at temperatures under 600 °C.

### Growth of Strained $\text{Si}_{1-y}\text{C}_y$ Alloys using Neopentasilane

Dilute  $\text{Si}_{1-y}\text{C}_y$  alloys in source drains are of interest for generating tensile strain in adjacent FET channels [1]. Achieving a high metastable substitutional carbon fraction is thought to be promoted by low growth temperatures and high growth rates [5-7], two criteria which traditionally are not mutually achievable in chemical vapor deposition (CVD). While there are several reports of achieving “high” (>1.5 %) carbon fractions by CVD in the literature, growth rates are very rarely reported. Thus we investigated the use of NPS as a silicon source and methylsilane as a carbon source to achieve high growth rates simultaneously with high substitutional carbon fractions, focusing initially on 575 °C. The growth conditions were similar to those used for silicon in the first part of this paper, except for the addition of the methylsilane.

Fig. 6 shows the high-resolution X-ray diffraction data and simulation from a 130-nm  $\text{Si}_{1-y}\text{C}_y$  layer with  $y = 1.8\%$  grown on a silicon substrate [8]. Several satellite peaks around the main peak from the  $\text{Si}_{1-y}\text{C}_y$  layer are evident, confirming the high quality of the layer and abruptness of interfaces. Fig. 7 shows the comparison of substitutional carbon levels from X-ray diffraction with the total carbon level as measured by Secondary Ion Mass Spectroscopy (SIMS) data [8]. Within experimental error, all of the carbon is fully substitutional up about 2% carbon levels. We have observed up to 2.5 % substitutional carbon levels (by XRD), but do not know the total carbon level in this sample.

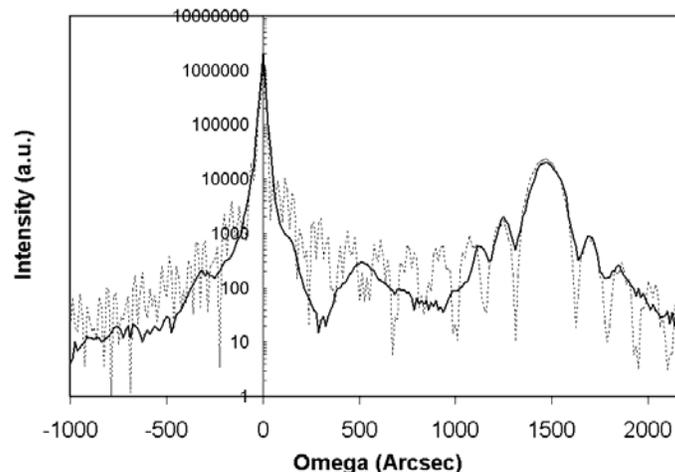


Figure 6. High-Resolution X-Ray Diffraction (HR-XRD) of a 130-nm  $\text{Si}_{1-y}\text{C}_y$  layer grown with neopentasilane and methylsilane on silicon substrate with a vertical lattice constant of 5.375 Å and  $y = 0.018$  [8]. The solid line represents the raw data while the dotted lines indicate simulation. The growth temperature was 575°C and the growth rate was 20 nm/min. The x-axis is defined with respect to the silicon substrate peak.

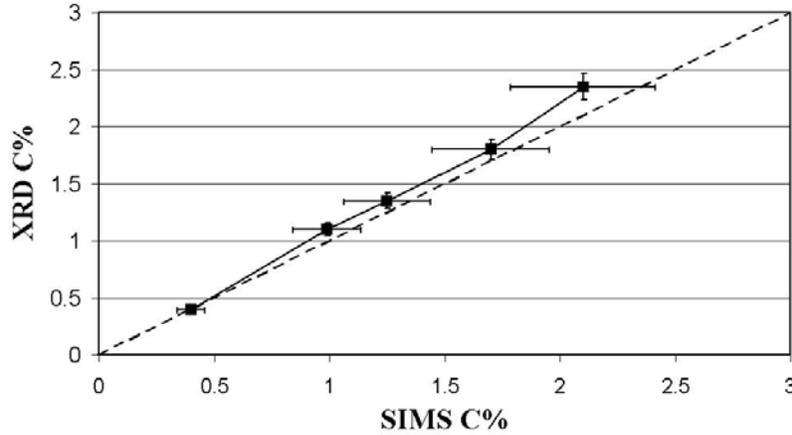


Figure 7. A comparison of substitutional carbon percentage measured from XRD vs. total carbon percentage determined by SIMS [8]. The dotted line is a slope of unity. Relative error bars of 5% and 15% were used for the XRD and SIMS measurements respectively.

Fig. 8 summarizes the progress we have made towards achieving high growth rates at high substitutional carbon levels for growth at 6 torr in hydrogen. Circles and squares represent total hydrogen flows of 600 sccm and 150 sccm, respectively, and closed vs. open circles and squares represent methylsilane flows of 1.0 and 2.5 sccm, respectively. With the neopentasilane data, within a given condition, higher carbon fractions were achieved by lowering the neopentasilane flow to achieve a higher methylsilane to neopentasilane ratio. This explains why the observed growth rate decreases as the carbon fraction of the grown layer increases – the reason is not because the methylsilane (or carbon) poisons the growth in any way (within the limits of our neopentasilane experiments). With higher methylsilane flows, higher neopentasilane flows and thus higher growth rates are achievable for similar carbon fractions. For substitutional carbon fractions of ~2%, growth rates up to 40 nm/min have been achieved to date.

For comparison, also shown in Fig. 8 are data for films grown with silane at 550 °C (Ref. 9) and for films grown with disilane at 625 °C in our lab. With silane, the growth rates are very low (only on the order of 1 nm/min). With disilane at 625 °C, high rates are possible (17 nm/min), but we have found the fraction of carbon which is fully substitutional to be limited below 1.5%. Higher substitutional carbon fractions have been reported with disilane [10], but due to the low temperature (525 °C), the growth rates (not reported) are probably very low. The data of growth rates achieved to date for carbon fraction and growth rates are summarized in Table 1.

Table 1. Comparison of fully substitutional carbon fractions and growth rates using different silicon sources. Silane data is from Ref's. 5 and 9 and disilane data from Ref. 10.

| Parameter\Silicon Source    | Silane<br>[5] | Silane<br>[9] | Disilane<br>[10] | NPS  | NPS  |
|-----------------------------|---------------|---------------|------------------|------|------|
| <b>Carbon Fraction (%)</b>  | 1.8           | 1.44          | 2.35             | 1.9  | 2.1  |
| <b>Growth Rate (nm/min)</b> | N/A           | 0.3           | N/A              | 40   | 13   |
| <b>Temperature (°C)</b>     | 550           | 550           | 525              | 575  | 575  |
| <b>Tensile Strain (%)</b>   | 1.05          | 0.85          | 1.35             | 1.05 | 1.23 |

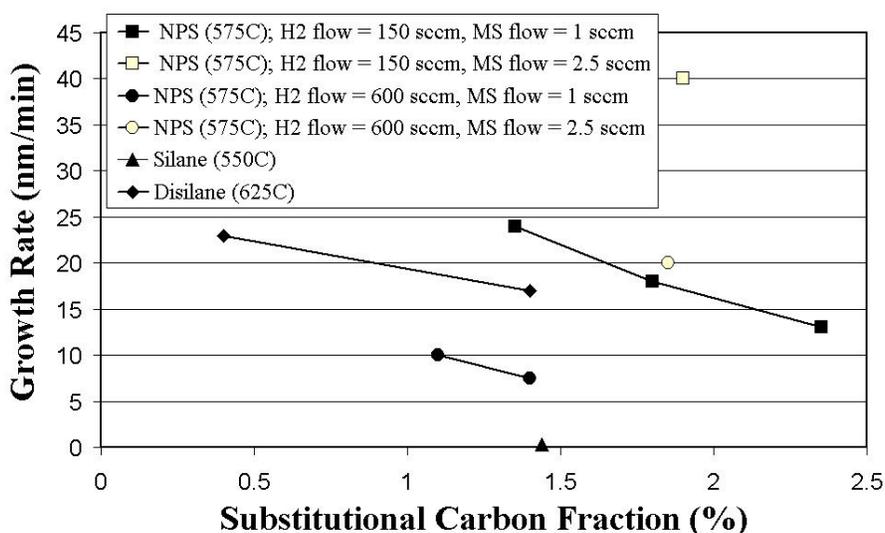


Figure 8. Plot of growth rate vs. substitutional carbon fraction for  $\text{Si}_{1-y}\text{C}_y$  samples grown with different silicon source gases. The samples grown with neopentasilane (NPS) were grown at 575 °C using methylsilane (MS) as a carbon source and a hydrogen ( $\text{H}_2$ ) background, with a total pressure of 6 torr. The squares represent a hydrogen flow of 150sccm, and the circles represent a hydrogen flow of 600sccm. Open (closed) circles and squares represent a methylsilane flow of 2.5 (1.0) sccm. To achieve higher carbon fractions the neopentasilane flow was reduced. Data for silane as a silicon source (grown at 550 °C) is from Ref. 9 and data with disilane as a silicon source (625 °C) is from our lab.

### Summary

Neopentasilane is presented as a silicon precursor for the high growth rate of silicon and dilute silicon-carbon alloy films by chemical vapor deposition in the temperature range of 550 – 700 °C. The high growth rates, up to ~ 100 nm/min at 600 °C, do not appear to adversely affect the quality of the films as reflected through TEM, photoluminescence, and MOSFET mobility measurements. For dilute silicon-carbon alloys, neopentasilane offers the possibility of achieving high growth rates at low temperatures. This is of interest for achieving technologically useful growth rates at high carbon fractions.

### Acknowledgments

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### References

1. Kah Wee Ang, King Jien Chui, V. Bliznetsov, Anyan Du, N. Balasubramanian, Ming Fu Li, Ganesh Samudra, Yee-Chia Yeo, Tech. Digest International Electron Devices Meeting, pp. 1069-1071 (2004).
2. M.A. Todd and K.D. Weeks, Appl. Surf. Sci. **224**, p. 41-45 (2004).

3. Keith H Chung, Nan Yao, James C Sturm, Kaushal K Singh, David Carlson and Satheesh Kuppurao, presented at Symp. Materials Research Soc., San Francisco, CA, USA (April, 2006).
4. K. Chung, J.C. Sturm, K.K. Singh, D. Carlson, and S. Kuppurao, presented at the Elec. Mat. Conf, State College, PA, USA (June, 2006).
5. T. O. Mitchell, J.L. Hoyt, and J.F. Gibbons, Appl. Phys. Lett. **71**, p. 1688 (1997).
6. H.J. Osten, K. Myeongcheol, K. Pressel, and P. Zaumseil, J. Appl. Phys. **80**, p. 6711 (1996).
7. J. L. Hoyt, T.O. Mitchell, K. Rim, D.V. Singh, and J.F. Gibbons, Thin Solid Films **321**, p. 41-46 (1998).
8. K. Chung, J.C. Sturm, E. Sanchez,, K.K. Singh, and S. Kuppurao, Semiconductor Sci. and Tech. **22**, pp. S158-S160 (2007).
9. J.M. Hartmann, T. Ernst, F. Ducroquet, G. Rolland, D. Lafond, A-M. Papon, R. Truche, P. Holliger, F. Laugier, M.N. Séméria, and S. Deleonibus, Semiconductor Science and Technology **19**, pp. 593-601 (2004).
10. J. L. Hoyt, in *Silicon Germanium Carbon Alloys*, edited by S. T. Pantelides and S. Zollner (Taylor & Francis, New York, 2002), pp. 59-89.