Chemical Vapor Deposition Epitaxy of Silicon-based Materials using Neopentasilane

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Neopentasilane (Si_5H_{12}) has been used as a precursor for the chemical vapor deposition epitaxy of silicon and $Si_{1-y}C_y$ alloys at temperatures from 550 to 700 ^oC. This paper summarizes the experimental findings of high growth rates of high quality epitaxy and planar films and then proposes mechanisms to support these observations. Concerted mechanisms, which can lead to growth without the usual requirement of open sites on an otherwise hydrogen covered surface are described as they relate to high – order silanes.

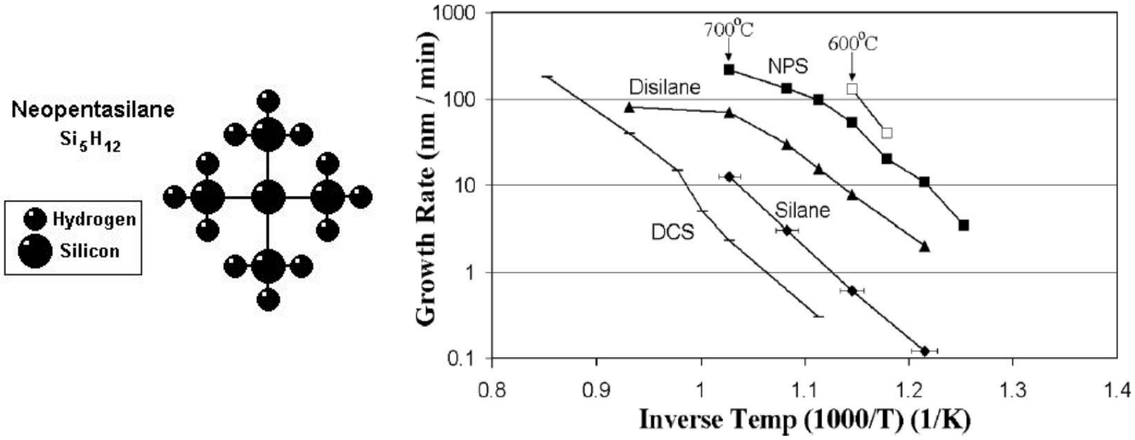
Introduction

The need for sharper doping interfaces and the more sophisticated integration of epitaxy into device structures (such as epitaxial source-drains for MOSFET stressors) is driving the growth temperature of epitaxial layers to the range of 700 ^oC or below. Traditionally, the rate of silicon chemical vapor deposition drops quickly below 700 ^oC, so that the cycle times for conventional single-wafer tools become high. Further, high rates at low temperatures are also of interest for metastable materials such as $Si_{1-y}C_y$ alloys with high substitutional carbon levels. Therefore, we have explored the use of neopentasilane (Si_5H_{12}, NPS) for the CVD epitaxial growth of silicon and related materials over the past few years. This paper will focus on the growth of silicon, its properties, and growth mechanisms.

Growth Rates and Material Properties

The chemical structure of neopentasilane is shown in Fig. 1 (a). It is a liquid at moderate pressures at room temperature. It was introduced into a quartz-walled lamp-heated single-wafer CVD reactor by bubbling hydrogen through the liquid in an apparatus heated to 35 ^oC, at which the vapor pressure is 30 torr. The partial pressures and flow rates for NPS stated in this paper assume the hydrogen became saturated with the NPS vapor, although we believe that the actual vapor pressure is up to a factor of ten lower than this amount [1].

Growth rates of epitaxial silicon by sources of dichlorosilane, silane, disilane, and neopentasilane vs. inverse temperature observed in our lab on Si(100) surfaces are shown in Fig. 1(b). In all cases a hydrogen carrier of 3 lpm (6 torr) is used, with source partial pressures given in the range of 10’s of mtorr. At 600 ^oC, for example, the growth rate from dichlorosilane is not observable, and that for silane and disilane were 0.6 and 8



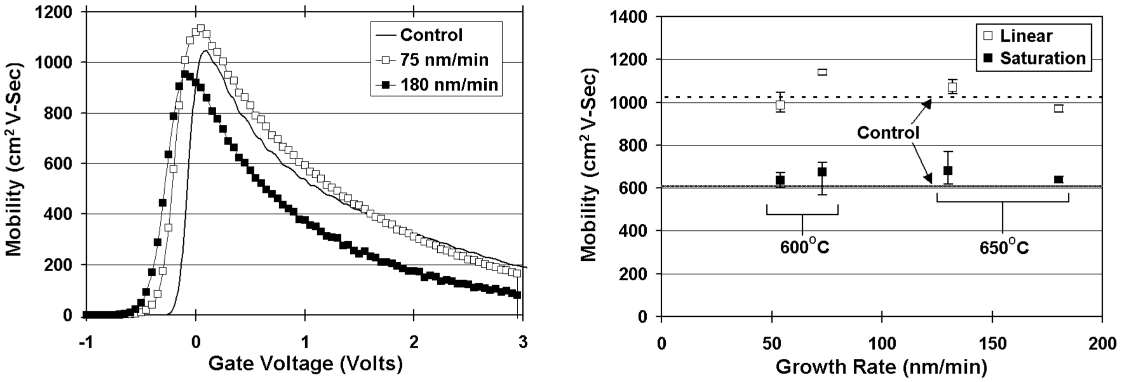
(a) (b)

Fig. 1. (a) Structure of neopentasilane and (b) epitaxial growth rates by CVD vs. inverse temperature for silicon sources of dichlorosilane (DCS), silane, disilane and neopentasilane (NPS) precursor on (100) silicon substrates. In all cases the carrier was hydrogen at pressure of 6 torr. The dichlorosilane, silane, disilane and NPS partial pressures were 52 mtorr, 20 mtorr, 10 mtorr and 20 mtorr respectively for the closed squares and 65 mtorr (NPS) for the open squares [1].

nm/min. At a vapor pressure of 20 mtorr, the rate at 600 ^{o}C for NPS was 54 nm/min, a factor of seven higher than that for the disilane. The growth rate in this range for a neopentasilane source was linear with the partial pressure with no little sign of saturation [2]. Raising the vapor pressure of the NPS by 65 mtorr at 600^{o}C raised the growth rate to 130 nm/min.

Secondary Ion Mass Spectroscopy (SIMS) showed the background levels of boron and phosphorus ~10^{16} cm^{-3} or lower (limited by background levels). There were significant levels of oxygen (~10^{18} cm^{-3}) and carbon (~10^{20} cm^{-3}). These are though to be the result of an impure NPS source. Transmission electron microscopy showed no extended defects such as stacking faults and excellent epitaxial quality on an atomic scale [1]. To evaluate electrical quality, FET's were fabricated with a self-aligned polysilicon gate process in nominally undoped epitaxial layers. A ring-type structure was used to eliminate field leakage with either boron or phosphorus source/drain implants. In both n-channel (p-type substrates) and p-channel (n-type substrates), the threshold voltages were ~0.2 V more negative control devices, and modeling showed that to be consistent with the epitaxy having an n-type background doping of 4 x 10^{15} cm^{-3}. Fig. 2 shows low field conductance as a function of gate voltage and both peak linear and saturation mobilities as a function of growth rate for n-channel devices. The growth rates were 55 and 75 nm/min at 600^{o}C and 130 and 180 nm/min at 650^{o}C.

Fig. 2 shows the results for n-channel devices, for both linear region mobility vs. gate voltage, and (peak) linear and saturation threshold voltage vs. growth rate. The horizontal lines in Fig. 2(b) show the results from control FET's simultaneously processed in lightly-doped substrates without any epitaxy. There was no significant



(a) (b)

Fig 2. (a) n-channel linear mobility as a function of gate voltage for control FET and FET's in epitaxial silicon by NPS. (b) linear and saturation mobilities as a function of growth rate. Growth rates were 55 and 75 nm/min (600 °C) and 130 and 180 nm/min (650 °C).

difference between the control FET and those in the epitaxial layers, even at the highest growth rates. Thus we conclude the high growth rates (and surprisingly the carbon levels) did not adversely affect the epitaxial quality. Similar results were obtained for p-channel devices.

Models and Mechanisms

For nearly all silicon-based CVD with more standard precursors (e.g. silane), the growth rate at low temperatures is usually limited by hydrogen desorption from the surface. The hydrogen on the surface can come from two sources: the adsorbing species themselves and from the interaction of the hydrogen ambient with the surface. This hydrogen coverage is a unique feature of CVD, vs. molecular beam epitaxy, for example. Hydrogen desorption is required for growth because an open site (or sites) are required for the adsorption of the growth species. This hypothesis is supported by the fact that when the partial pressure of the hydrogen carrier is reduced during the growth of silicon (reducing the equilibrium surface coverage of hydrogen), the growth rates rapidly increase [4,5].

Fig. 3. shows growth rates vs. inverse temperature from Fig. 1 (hydrogen carrier gas at 3 lpm and 6 torr) and for a nitrogen carrier gas (3 lpm and ~6 torr) for several silicon sources used in our lab. (In some cases, when a nitrogen carrier is used, there is still a small hydrogen vapor pressure since the silicon precursor gas was diluted in hydrogen, either from the bubbler or gas tank). Note that the silicon growth rate when using hydrogen increased sharply when a nitrogen carrier was observed (~ 3-4X), as expected. The effect with disilane was less (~1.5 - 2X), and that with NPS was almost negligible (~20 %, or 1.2X). Thus the hydrogen surface coverage normally present with a hydrogen carrier does not seem to depress the growth rate with neopentasilane, and has

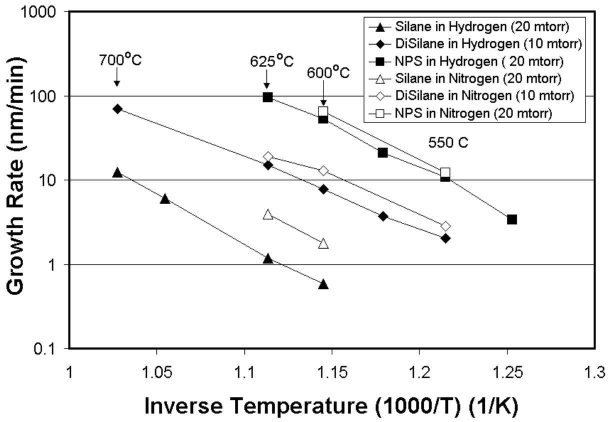


Fig. 3. Silicon growth rates vs. inverse temperature in both hydrogen and nitrogen carriers for various silicon precursors [1].

a smaller effect when using disilane that when using silane. This implies that neopentasilane can either grow without the open sites on the surface or can somehow create its own open sites.

We speculatively propose a "concerted" growth mechanism in higher-order silanes such as neopentasilane to explain such an effect [1]. 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 [6-8]. This thus promotes a "concerted" reaction of simultaneous bond breaking and bond forming. In this case, a carbon-carbon bond breaks and a hydrogen-metal surface bond breaks, and is replaced by a carbon hydrogen bond and a carbon-metal surface bond.

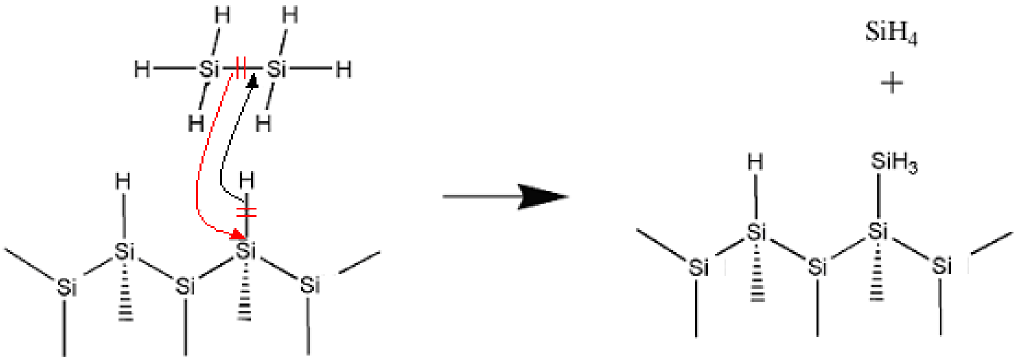


Fig. 4. Schematic example of adsorption of SiH3 from disilane vs. onto a hydrogen covered surface via a concerted surface reaction. Note no prior open sites are required.

With a high-order silane, we can postulate a similar concerted process on the hydrogen covered silicon surface. Fig.4 shows the process as it might occur with disilane (chosen for simplicity of illustration). The Si-Si bond of the disilane and the surface Si-H bond are broken (indicated by the two marks across their bonds) as the SiH_3 fragment bonds to the surface site vacated by the H, and the H bonds to the remaining SiH_3 fragment (indicated by the arrows). These reactions may take place without the need for a prior open site, explaining the independence of open site coverage for higher order silanes. This mechanism is different than those often used for higher growth rates from disilane, which usually focus on the properties of disilane alone, ignoring the lower sensitivity to hydrogen pressure and hydrogen surface coverage. Note this mechanism would 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.

The thermodynamic driving force for such reactions can be inferred from Table I, which shows the bond enthalpies for linear silanes and alkanes of different order for the average Si-H (or C-H) bond, and for the bond energy to split off the end –SiH_3 (-CH_3) groups. Note for SiH_4 and CH_4 these two energies are the same as they represent the same bond, but for higher order silanes (alkanes) the first bond energy column represents a Si-H (C-H) bond and the second a Si-Si (C-C) bond. Significantly as one goes from silane to disilane, there is a very sharp drop in the enthalpy of the bond for the end SiH_3 group, much larger than the drop of an average Si–H bond. This favors the formation splitting of the Si-Si bond in disilane and other high order silanes (leading to the formation of a silane by-product) as indicated in Fig. 4.

Table I. Bond enthalpies of average –H and endgroup –SiH_3 (or –CH_3) bonds in linear silanes and alkanes in kcal/mol (Ref. 8 for silanes and 9 for alkanes)

Silanes	**-H**	**-SiH_3**	**Alkanes**	**-H**	**-CH_3**
SiH_4	383.4	383.4	CH_4	436.3	436.3
Si_2H_6	371.6	317.6	C_2H_6	422.5	370.9
Si_3H_8	369.3	313.4	C_3H_8	425.8	368.5
Si_4H_{10}	368.9	312.7	C_4H_{10}	425.2	372.3
Si_5H_{12}	368.6	312.5	C_5H_{12}	425.2	371.6

The bond enthalpy data of Table I. is given for linear molecules, not neopentasilane, which has a different structure (Fig. 1). However the basic bond energies trend of lower bond energies for neopentasilane compared to silane is expected to be similar. We also point out that while the mechanism of Fig. 4 is shown with disilane for simplicity, a similar mechanism can occur with higher order silanes. The byproduct for trisilane would be disilane (vs. silane for the dislane case), and this disilane could then again react as shown in Fig. 4.

Finally, we bring up the issue of surface planarity. Silicon films grown with silane at low temperature can be rough [5]. Smooth films result when the adsorbing growth species can migrate to step edges; rough films result when diffusion is so slow (compared to the rate of adsorbing species) so that such migration does not have enough time to occur. Nucleation on previously flat terraces occurs, leading to roughening. Thus high growth rates can give rise to rough surfaces since the time allowed for migration is reduced.

Open sites (free of hydrogen) are thought to be required for surface diffusion [5]. We (Table II) and other groups (e.g. Ref. 5) have observed that silane-based growth is smoother when a nitrogen carrier is used vs. a hydrogen carrier in the range of 575-600 ^{o}C, (3.5 vs. 4.1 nm) despite the much higher growth rates with nitrogen (4.5 vs. 1.2 nm/min). Table II also shows roughnesses for growth in hydrogen ambient for silane and neopentasilane sources. With disilane, growth rates are faster than with silane (with hydrogen or nitrogen carriers) and the surfaces are smoother. With NPS in hydrogen, the growth rates are 40X higher than those with a silane source, but the films are again smoother. This is attractive from a technology point of view, but surprising considering the reduced times for migration at high growth rates.

Table II. Growth rates and surface roughness for different source gases and carriers at 600 °C. (Roughness is not absolutely calibrated, but relative values are correct).

Gas Source	**Temp**	**Carrier**	**Growth Rate**	**Thickness**	**Relative rms roughness**
Silane	600°C	H_2	1.2 nm/min	35 nm	4.1 nm
Silane	600°C	N_2	4.5 nm/min	90 nm	3.5 nm
Disilane	600°C	H_2	7.8 nm/min	95 nm	2.7 nm
Disilane	600°C	N_2	13 nm/min	65 nm	2.7 nm
Neopentasilane	600°C	H_2	55 nm/min	80 nm	2.6 nm

We are currently investigating several concerted surface mechanisms similar to those in Fig. 4 which do produce open sites. The driving force is the production of SiH_4 due to its large Si-H bond strength compared to the Si-Si bond strengths in higher order silanes. The open sites would then enable surface diffusion to promote planarity (and themselves would contribute to high growth rates).

Summary

Neopentasilane can be used to achieve high silicon and dilute silicon-carbon alloy growth rates at temperatures below 700 °C. Silicon growth rates up to130 nm/min at 600 °C have been obtained. High quality as evidenced by TEM and MOSFET mobility has been observed. The layers also remain relatively smooth even at high growth rates. The growth mechanism appears not to be dependent on the open surface sites created by normal hydrogen desorption. Therefore surface concerted reactions have been proposed as a growth mechanism, in which bond-breaking and bond-formation occur in a single step. These mechanisms are consistent with high growth rates at low temperatures, and possibly can explain surface migration to enable very smooth films as well.

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References

1. K. H. Chung , N. Yao,J. Benziger, J. C. Sturm, K. K. Singh, D. Carlson, S. Kuppurao, *Appl. Phys. Lett*. **92**, 113506 (2008)
2. J. C. Sturm, K. H. Chung, N. Yao, E. Sanchez, K. K. Singh, D. Carlson, and S. Kuppurao, 211th Meeting of the Electrochemical Society, Chicago, IL (May, 2007)
3. K. Chung, J.C. Sturm, E. Sanchez,, K.K. Singh, and S. Kuppurao, *Semiconductor Sci. and Tech*. **22**, pp. S158-S160 (2007)

4. W.A.P. Claassen, *Philips J. Res* **36**, pp. 122-137 (1981)
5. P. Meunier-Beillard, M. Caymax, K. Van Nieuwenhuysen,, G. Doumen,
B. Brijs, M. Hopstaken, L. Geenen, W. Vandervorst, Appl. Surf. Sci. 224, 31-35 (2004).
6. T. F. Narbeshuber, H. Vinek, and J. A. Lercher, *J. Catal*. **157**, 388 (1995)
7. Y. V. Kissin, Catal. *Rev. - Sci. Eng*. **43**, 85 (2001)
8. A. Farkas and K. Bonhoeffer, *Z. Phys. Chem*. **231**, 638 (1931)
9. . I. Alkorta, *Chemical Physics Letters*, **426** 58-61 (2006)
10. I. Alkorta, *Chemical Physics Letters*, **425** 221-224 (2006)