Very high ($>10^{19}$ cm^{-3}) *in situ* *n*-type doping of silicon during molecular beam epitaxy using supersonic jets of phosphine

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(Received 7 October 1996; accepted for publication 20 December 1996)

The use of supersonically injected pulses of phosphine to achieve uniform and high levels of *n*-type doping in Si during gas-source molecular beam epitaxy is demonstrated. Uniform *n*-type doping up to levels of 5×10^{19} cm^{-3} is obtained. SiGe/Si junction diodes made with this doping technique show good doping profiles and rectifying characteristics. © *1997 American Institute of Physics.* [S0003-6951(97)02609-0]

Highly doped semiconductor regions and *p*-*n* junctions are required in a variety of applications. In the case of silicon, *p*-type doping at levels greater than 10^{20} cm^{-3} has been easily achieved using solid or gaseous precursors. However, obtaining *n*-type material at such high concentrations has proven to be very challenging. Solid phosphorus has a very high vapor pressure and hence is not generally used as a dopant source. Some dopants like antimony, which are conventionally employed as solid sources, have a strong tendency to segregate through the film to the surface of the growing layer, acting as surfactants. During molecular beam epitaxy (MBE), Sb doping also suffers from a small and temperature dependent sticking coefficient and strong surface segregation.[1,2] Hence, *n*-type doping, has been achieved up to 5×10^{18} cm^{-3} during MBE only from gaseous precursors like phosphine (PH_3).[3] Ultrahigh vacuum chemical vapor deposition (UHV-CVD) studies have reported higher levels of incorporation, but with associated changes in surface chemistry and reduced growth rates.[4–8] Also, very high levels of *n* doping ($>5\times10^{19}$ cm^{-3}) are presently achieved in the semiconductor industry using ion implantation followed by a high temperature anneal. Alternative techniques need development as device sizes shrink and low thermal budgets for processing become essential.

During conventional MBE, using thermal molecular or atomic beams with a broad (Gaussian) energy (velocity) distribution, a high substrate temperature is required to provide surface mobility of the arriving adatoms or dopant species. The high substrate temperature provides energy for Sb or P atoms to move from substitutional to interstitial sites and to promote surface segregation. If, on the other hand, a high (mono-) energetic beam is used instead, then very little surface migration is required for adatoms or dopant species and the substrate temperature can be reduced. We have recently shown[9,10] that low-temperature Si epitaxy is possible by using a disilane source with a supersonic jet. Growth was demonstrated at 450 °C, which is much lower than conventional temperatures of 550 °C and above normally used. In this letter we report on the use of supersonic jets of phosphine to achieve uniform and high levels of *n* doping during gas-source MBE (GSMBE) of Si.

The growth facility is described briefly. The experiments were conducted in a Riber-32 gas source MBE system modified to incorporate a pulsed supersonic valve (General Valve series 9, 0.7 mm nozzle) with an electronic controller. Silicon growth was conducted using disilane at a flow rate of 14 sccm resulting in a chamber pressure of about 3×10^{-6} Torr. The dopant is a 1% mixture of phosphine in hydrogen (Voltaix, Inc.) maintained at a source pressure of 1.1 atm and delivered through the supersonic nozzle at pulse widths (open time) varying from 5 to 60 ms. The ''off time'' was kept constant at 3 s. The substrate temperature was varied in the range of 550–650 °C. The substrates used were *p*-type Si(100) wafers (10–20 Ω cm), cleaned with an initial solvent, then degreasing followed by a 30 s HF (10%) etch, and drying in a N_2 jet before being loaded. Prior to growth, the sample was heated to about 800 °C to desorb the native oxide. A buffer silicon epitaxial layer was first grown at $T_s=650\,°\mathrm{C}$ to ensure a smooth starting surface as was observed by reflection high energy electron diffraction (RHEED). Samples were analyzed using secondary ion mass spectrometry (SIMS) to determine the atomic phosphorus concentrations and spreading resistance analysis (SRA) to obtain the active dopant levels. Hall measurements were performed using a van der Pauw geometry.

Figure 1(a) shows a plot of phosphorus atomic concentration versus depth for different pulse widths of the phosphine jet, as measured by SIMS. Concentrations of $\sim10^{19}$ cm^{-3}, not obtainable using thermal molecular beams, are easily achievable even at substrate temperatures as high as 620 °C. As the pulse width is increased, the thickness of film obtained (for a constant growth time) decreases, implying a reduction in growth rate. In fact the growth rate is reduced from 160 Å/min, under normal growth conditions to 65 Å/min with use of the phosphine supersonic injector. Other groups have reported reduced Si thin film growth rates with increased phosphine injection.[5–8] This reduction results from the adsorption of phosphorus atoms on the Si surface which, in turn, significantly reduces the dissociative chemisorption of Si_2H_4.[11] Two features are apparent in the data of Fig. 1(a). First, there is a slight amount of dopant surface

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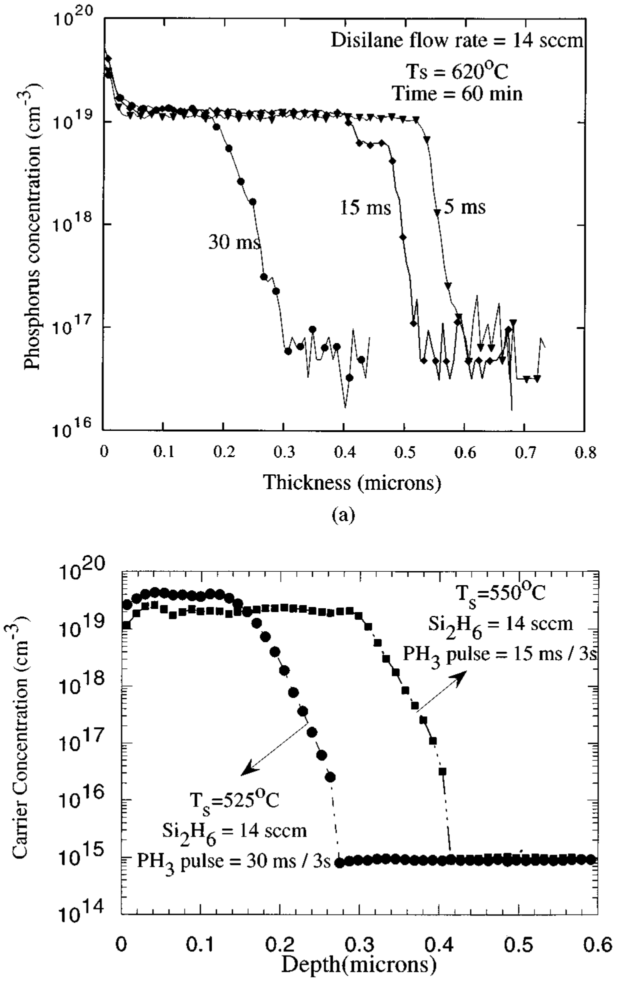

FIG. 1. (a) SIMS doping profiles in Si doped with phosphine from a supersonic injector at $T_s = 620$ °C for different injection pulse widths; (b) phosphorus doping profiles obtained from spreading resistance analysis with phosphine injection at lower growth temperatures.

segregation at a growth temperature of 620 °C. Second, the doping level seems to be independent of the supersonic pulse width. We believe that the two features are related, i.e., the high substrate temperature promotes segregation and less phosphorus incorporation. Under these conditions, there is little distinction between a supersonic beam and a thermal beam and there is no advantage in using a supersonic beam. The data of Fig. 1(b) which shows electrically active phosphorus doping profiles measured by SRA in samples grown at low temperatures proves the point. Here, we notice an increase of doping level with a decrease of substrate temperature and an absence of surface segregation indicating that, at the low growth temperatures, the supersonic flux pro-

TABLE I. Measured Hall electron concentrations and mobilities.

	Hall	SRA	Hall
T (°C)	Doping level ($\sim 10^{19} \mathrm{cm}^{-3}$)		mobility (cm^2/V s)
620	1.2	1.2	126
575	3.0	3.8	118
550	4.1	5.0	90

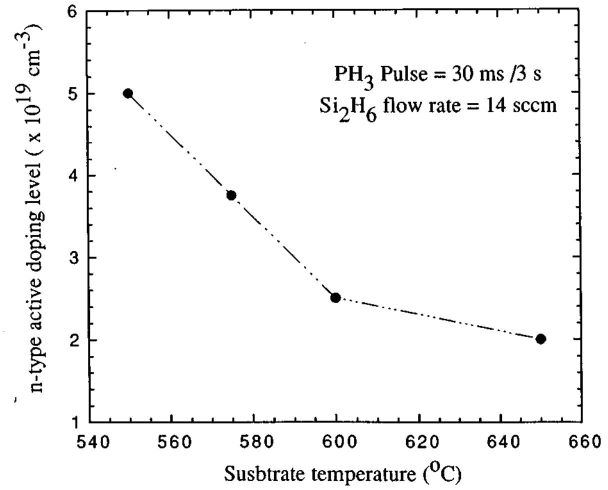

FIG. 2. Doping level as a function of the substrate temperature measured by SRA. The dotted line is a guide to the eye.

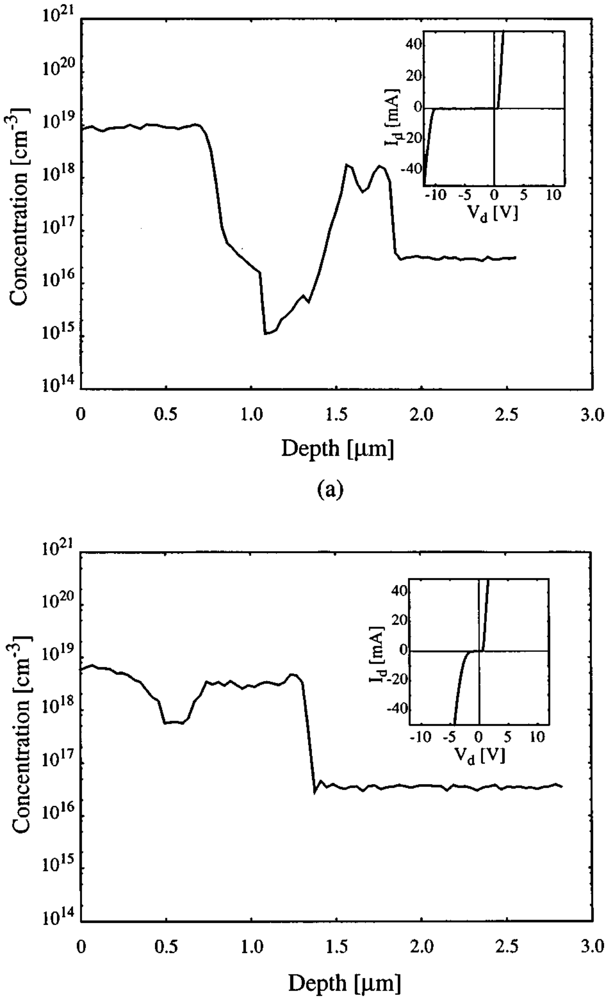

FIG. 3. Measured SRA doping profiles and current–voltage characteristics (inset) grown on $p^+(100)$ Si with the n^+ doping achieved by supersonic injection of PH_3.

vides the requisite energy for incorporation into the proper lattice sites.

Table I shows results of Hall measurements performed on representative samples using the van der Pauw technique. The thickness of the Hall samples varied from 0.3 to 0.6 μm. The Hall mobilities and carrier concentration values obtained are in good agreement with SRA results and with published values for electron mobilities in highly doped silicon.[12,13] This suggests that the films are of high electrical quality. Comparison of SIMS and SRA data indicates that the dopant activation is close to 100%.

As discussed earlier, the motivation for this work was to obtain uniform and high levels of dopant incorporation. Figure 2 presents data showing the variation of doping level, measured by SRA, with substrate temperature. Doping levels of 5×10^{19} cm^{-3} have been achieved at a growth temperature of 550 °C. This is the first report of such high active carrier concentrations at these temperatures. Other studies have utilized plasma and rf techniques to obtain such levels of doping.[14,15] The increase in doping level with the decrease of substrate temperature indicates that activation of the dopant species from substitutional to interstitial sites is suppressed with the lowering of substrate temperature.

Silicon $p^+-n^--n^+$ and SiGe $(p^+)-\mathrm{Si}$ (n^+) diodes were grown next using solid boron from an effusion cell and a $\mathrm{PH_3/H_2}$ supersonic jet as the dopant sources. Solid Ge from an effusion cell was used as the Ge source. The diodes were grown on (100) p^+Si substrates with resistivities of 0.004–0.02 Ω cm. The $p^+-n^--n^+$ Si diode consists of a 0.3-μm-thick p^+ $(1\times10^{18}$ $\mathrm{cm}^{-3})$ layer followed by a 0.7 μm n^- $(6\times10^{15}$ $\mathrm{cm}^{-3})$ layer and a 0.7 μm n^+ $(1\times10^{19}$ $\mathrm{cm}^{-3})$ layer grown at 570 °C. The phosphine flow rate was fixed at 1.1 atm and pulses of 3 ms separated by 3 s off times were used. The p^+-n^+ diode consists of a 0.5μm SiGe $p^+(3\times10^{18}$ $\mathrm{cm}^{-3})$ layer followed by a 0.7 μm n^+ $(6\times10^{18}$ $\mathrm{cm}^{-3})$ layer grown at 570 °C with the same injector parameters. Mesa diodes 84 μm in diameter were made by photolithography and metallization of the ohmic contacts. The measured doping profiles and the electrical rectifying characteristics of the two types of diodes are illustrated in Figs. 3(a) and 3(b); excellent rectifying characteristics are obtained. It may be noted that we have used a pulsed injector in this experiment. With a modified injector design whereby a continuous beam can be obtained, we hope to achieve higher n-doping levels.

In conclusion, we have been able to demonstrate very uniform and high levels of *in situ* n-type doping of silicon at low growth temperatures using supersonic jets of phosphine. Growth of uniformly doped thin films with electron mobilities close to bulk value was achieved. The p^+-n^+ and $p^+-n^--n^+$ diodes grown with this kind of doping of the n region show excellent electronic properties.

The authors thank Professor J. Singh for helpful discussions. This work was supported by the U.S. Air Force Office of Scientific Research under Grant Nos. F49620-95-1-0013 and F49620-94-0404 (AASERT Program) and by the University of Michigan Center for Display Technology and Manufacturing.

[1] R. A. Metzger and F. G. Allen, J. Appl. Phys. **55**, 931 (1984).
[2] J. C. Bean, Appl. Phys. Lett. **33**, 654 (1978).
[3] S. H. Li and P. K. Bhattacharya, J. Appl. Phys. **76**, 2213 (1994).
[4] B. S. Meyerson and M. L. Yu, J. Electrochem. Soc. **131**, 2366 (1984).
[5] M. Racanelli and D. W. Greve, J. Vac. Sci. Technol. B **9**, 2017 (1991).
[6] S. M. Jang, K. Liao, and R. Reif, Appl. Phys. Lett. **63**, 1675 (1993).
[7] D. W. Greve, Mater. Sci. Eng. B **18**, 22 (1993).
[8] L. P. Chen, G. W Huang, and C. Y. Chang, Appl. Phys. Lett. **68**, 1498 (1996).
[9] R. Malik, E. Gulari, S. H. Li, P. K. Bhattacharya, and J. Singh, J. Cryst. Growth **150**, 984 (1995).
[10] R. Malik and E. Gulari, Appl. Phys. Lett. **68**, 3156 (1996).
[11] N. Maity, L.-Q. Xia, and J. R. Engstrom, Appl. Phys. Lett. **66**, 1909 (1995).
[12] H. S. Bennett, Solid-State Electron. **26**, 1157 (1983).
[13] Landolt-Börnstein, *Numerical Data and Functional Relationships in Science and Technology,* New Series, Group III (Springer, Berlin, 1989), Vol. 22a.
[14] S. Thomas, J. Fretwell, D. Kinosky, R. Qian, A. Mahajan, P. Munguia, S. Banerjee, A. Tasch, and C. Magee, J. Electron. Mater. **24**, 183 (1995).
[15] A. S. Madhukar, H. A. Naseem, W. D. Brown, and S. S. Ang, J. Vac. Sci. Technol. A **11**, 1858 (1993).