Realization of *In Situ* Doped n-Type and p-Type Si-Microprobe Array by Selective Vapor-Liquid-Solid (VLS) Growth Method

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In this paper we report the development of n-type and p-type Si-microprobe arrays fabricated by using *in situ* doping in vapor-liquid-solid (VLS) growth employing a gas-source molecular beam epitaxy (GS-MBE) system as the growth environment. VLS growth using Si_2H_6 only gives intrinsic Si microprobes with the resistivity of $\sim 10^4$ Ω-cm, which decreases to $\sim 10^{-2}$ Ω-cm after phosphorous diffusion at 1100°C. However, by incorporating *in situ* doping into the VLS growth method, more conductive probes (resistivity $\sim 10^{-3}$ Ω-cm) can be realized at a temperature less than 700°C. The site and diameter of the VLS-grown probe can be controlled and the growth rate is higher than that of a poly-Si or epitaxial Si crystal grown by the vapor-solid (VS) method. Due to the low processing temperature, *in situ* doping is effective for realizing highly conductive probe arrays with smart sensor devices by a standard IC process followed by VLS growth. The wide range of doping leads to the possibility of using these probes for the fabrication of vertical active devices such as diodes and transistors.
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KEYWORDS: vapor-liquid-solid (VLS) growth, *in situ* doping, molecular beam epitaxy (MBE), Si-microprobe array, vertical active devices

1. Introduction

The growing interest in employing low-dimensional electronic structures in various applications has led researchers to realize probe-like Si crystals and to seek out their potential applications. In previous studies conducted by Wagner and Ellis[1] and other researchers,[2–4] it was found that probe-like Si crystals can be grown by vapor-liquid-solid (VLS) growth and that the grown probe is a single crystal. VLS is a method of growing a rod-like crystal from vapor, in which the process starts with the deposition of dots of catalysts (normally Au) on a Si substrate. When heated in a vacuum chamber, Au particles combine with Si atoms from the substrate to form Au-Si alloy droplets on the Si surface. Then, when a gas source of Si is introduced, the alloy droplets absorb Si atoms from the gas source. When the droplet becomes supersaturated with Si, Si atoms start to precipitate at the interface of the alloy droplet and the underlying Si surface, resulting in the growth of a probe-like Si crystal.

Some researchers have studied the properties of the VLS-grown probes[4–8] and some applications of these probes have already been proposed.[5,8] Asai *et al.*[8] developed a high-resolution probe card for integrated circuit (IC) testing, where VLS-grown Si probes are used as the pins of that card. Recently, Kawano and coworkers applied a Si-microprobe electrode array for recording neural activity,[5,6] and to facilitate the analysis of these recorded signals, they also developed Si-microprobe electrode arrays with on-chip metal-oxide-semiconductor field-effect-transistor (MOSFET) circuitry.[7]

Almost all of the previous researchers reported intrinsic Si probes grown by the VLS method using a gas source of pure Si.[1–5] The resistivity of the intrinsic Si probe grown by the VLS method using Si_2H_6 was found to be of the order of 10^4 Ω-cm.[5] However, this high resistivity presents a barrier to the use of these probes in some applications. For example, Si-microprobe electrode arrays developed by Kawano and coworkers require highly conductive probes in order to record the small signals from neurons. Consequently, phosphorous (P) diffusion was carried out to dope the grown probes and the resistivity was reduced to $\sim 10^{-2}$ Ω-cm with P diffusion at 1100°C.[5] Unfortunately, this high-temperature diffusion is detrimental to the devices when these probes are processed with on-chip signal-processing MOSFET circuitry. Here also, lower temperature diffusion does not sufficiently dope the probes; at 900°C, the depth of doping was found to be 0.5 μm from the surface of the probe sidewall.[7] Thus, this temperature issue limits the realization of highly conductive probes with on-chip circuitry by conventional doping via diffusion. Here, we introduced an alternate approach for realizing highly conductive VLS probes at low temperature, in which *in situ* doping is incorporated into the VLS growth method. In this work, we first demonstrate the growth of an intrinsic Si-microprobe array by the VLS method using Si_2H_6. Then, we present the doped probes realized by *in situ*-doping VLS and discuss their properties in comparison with those of intrinsic probes.

2. VLS Growth of Si-Microprobe Array Using Si_2H_6

2.1 Experimental procedure

A Si (111) wafer (diameter: 2 inches) was used in the experiment, because the probes can be grown vertically in the ⟨111⟩ direction by VLS growth.[1] Figure 1(a) shows the steps required for wafer preparation. After the standard cleaning, the wafer was oxidized by wet oxidation at a temperature of 1000°C for 4.5 h in order to form a layer of SiO_2 with a thickness of about 850 nm, as shown in Fig. 1(a)(i). The wafer was then spin coated with positive photoresist (thickness: 2 μm). The wafer was exposed through a mask and developed to create arrays of circular holes through the resist. A window was created through the SiO_2 layer by etching out SiO_2 in the holes using buffered hydrofluoric acid (BHF), as shown in Fig. 1(a)(ii). Au

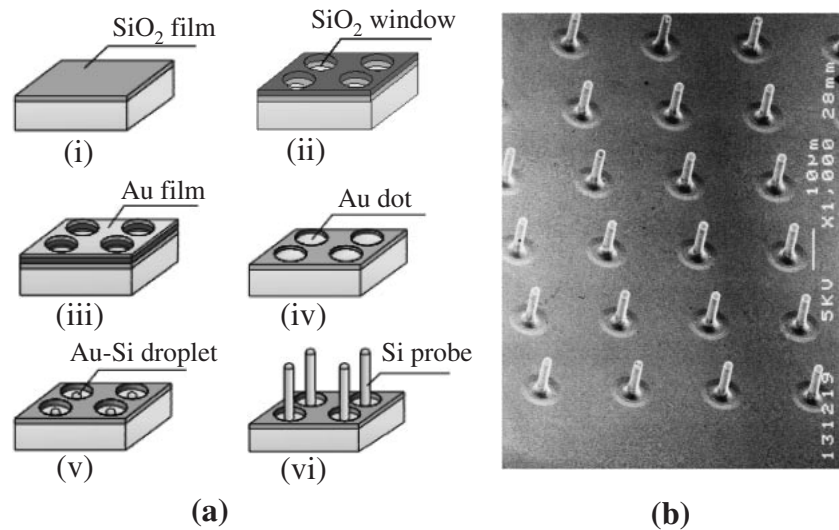*E-mail address: shofiq@dev.eee.tut.ac.jp

Fig. 1.   Schematic diagram of wafer preparation and SEM image of typical Si-probe array: (a)(i) SiO$_2$ layer formation by wet oxidation on Si(111) wafer; (a)(ii) photolithography to create circular window through SiO$_2$; (a)(iii) Au evaporation; (a)(iv) lift off of Au from resist site; (a)(v) annealing to form Au-Si alloy droplet; (a)(vi) introduction of source gas into the growth chamber to grow Si microprobes by VLS growth mechanism; (b) SEM image of Si-probe array formed by above-detailed VLS growth using gas source of Si$_2$H$_6$.

evaporation was carried out to deposit a thin film of Au with a thickness of about 120–160 nm, as shown in Fig. 1(a)(iii). Ultrasonic cleaning in acetone removed Au from the surface of the resist, leaving Au dots in the SiO$_2$ window, as shown in Fig. 1(a)(iv). The sample was then inserted into a high-vacuum gas-source molecular beam epitaxy (GS-MBE) chamber for annealing and probe growth. The chamber was equipped with the gas source of Si. The system includes a control gate valve (CGV) to control the opening of the exhaust path of the growth chamber, thereby controlling the growth condition, and a mass flowmeter for controlling the flow of the source gas. Annealing at a temperature of 700°C caused the formation of Au-Si alloy droplets inside the window, as shown in Fig. 1(a)(v). Then, the source gas, Si$_2$H$_6$, was introduced into the growth chamber via the mass flowmeter to carry out molecular beam epitaxy (MBE) to obtain a probe-like Si crystal by VLS growth, as shown in Fig. 1(a)(vi). The physical dimensions of the grown probes were estimated from scanning electron microscope (SEM) images.

2.2   Results and discussion

Figure 1(b) shows the SEM image of a typical Si-probe array formed by VLS growth using Si$_2$H$_6$ as the gas source of Si. The position and the size of these VLS-grown probes can be controlled by changing certain parameters. The experimental results showed that the diameter of a probe grown at 700°C with a Si$_2$H$_6$ pressure of 7×10^{-3} Pa using Au dots having the diameter of 4 μm and Au layer thickness of 160 nm was 2.3 μm. When the same size (4 μm) of the Au dot but a Au layer thickness of 50 nm was used, a probe with the diameter of 0.9 μm was obtained. The diameters of the probes grown using Au dots of different sizes (4–10 μm) increased linearly with increasing Au dot diameter, as shown in Fig. 2. Thus, by patterning the Au dots with different dot dimensions and layer thicknesses, the diameters of VLS-grown probes could be controlled. Again, the SiO$_2$ window
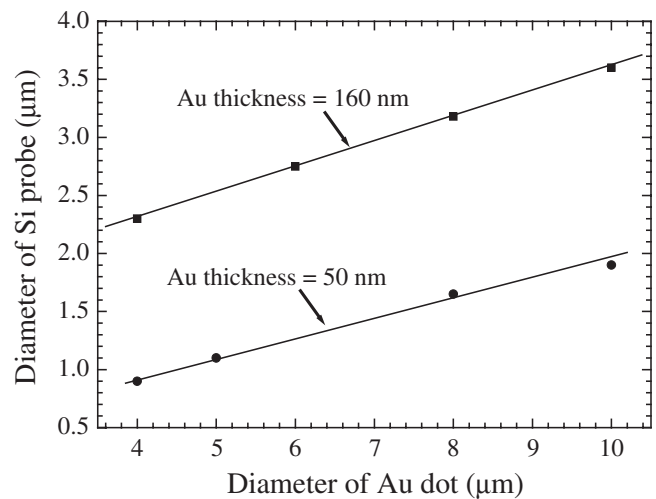

Fig. 2.   Dependence of diameter of Si probe on size of Au dot patterns with diameters ranging from 4 μm to 10 μm. Probes were grown at 700°C with Au layer thicknesses of 160 nm and 50 nm.

ensures the position of the Au-Si alloy droplet and hence the probe site. Therefore, by changing the spacing of the SiO$_2$ window, the position of the probes could also be controlled. By growing the probes at various Si$_2$H$_6$ pressures at 700°C, it was found that the diameters of the probes are almost independent of the growth pressure, as shown in Fig. 3, for a certain pattern of Au dots with a certain Au layer thickness. Therefore, by using the same Au dot patterns, probes with the same diameters could be grown at different growth pressures, whereas the lengths could be controlled by varying the growth conditions and time. Thus, probes with different dimensions could be grown repeatedly.

The growth rate of Si probes as a function of temperature has been studied by growing the probes at three different temperatures, 700, 600 and 500°C, at a Si$_2$H$_6$ pressure of 7×10^{-3} Pa. The growth rate of the probe grown at 700°C
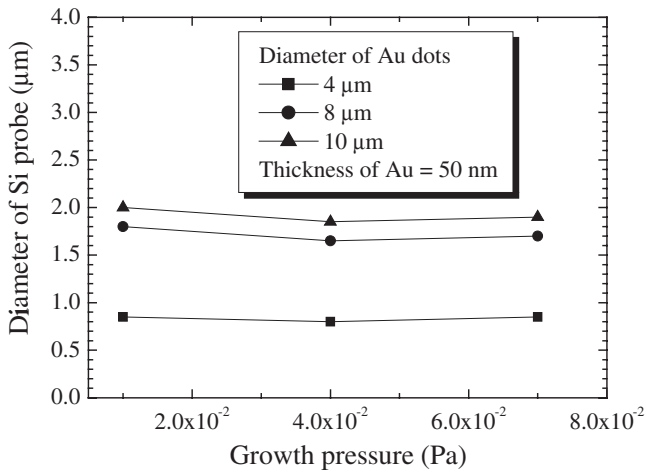
Fig. 3. Variation of diameter of Si probe as function of growth pressure for probes grown at 700°C using Au dots having diameters of 4, 8 and 10 μm all with Au layer thickness of 50 nm.
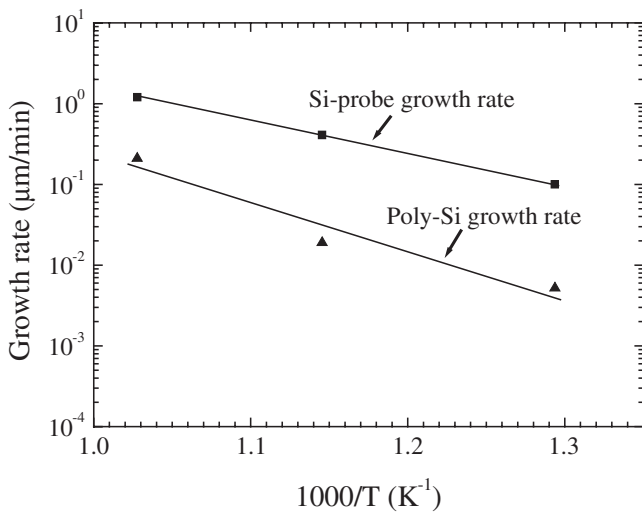

Fig. 4. Dependence of growth rate of Si probe and that of poly-Si on temperature. Both Si probe and poly-Si were grown at Si_2H_6 pressure of 7×10^{-3} Pa.

was about 1 μm/min and decreased with the increase in the reverse of absolute temperature (decrease in temperature), as shown in Fig. 4. The growth rate of poly-Si was also observed to vary as a function of temperature, and it also exhibited a similar declining nature to the decrease in temperature, as shown in Fig. 4. This illustrates how the temperature governed the growth of the Si probe and that of poly-Si.

3. Doped Si-Probe Array by in situ-Doping VLS

3.1 Experimental procedure

The wafer preparation is similar to that described in §2.1 for the intrinsic probe. In order to obtain doped probes, the growth chamber was equipped with the gas source of dopants (PH_3 and B_2H_6) in addition to the Si gas source (Si_2H_6) to facilitate the in situ doping of the probes formed by VLS growth. In our experiment, we used 0.1% PH_3 (diluted in 99.9%H_2) and 1% B_2H_6 (diluted in 99%H_2) with 100% Si_2H_6. The mixture of dopant gas and Si_2H_6, the flow
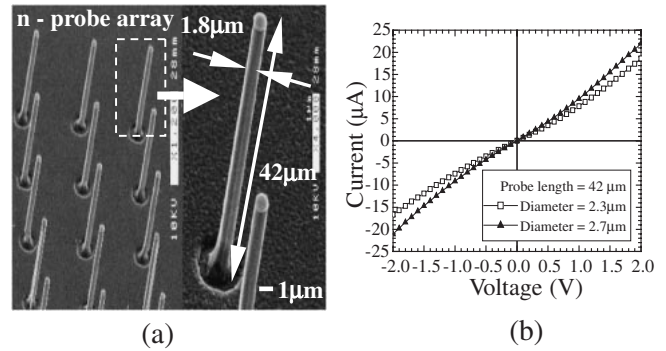

Fig. 5. SEM image and I–V characteristics of n-type probe array grown at 700°C by VLS growth with in situ doping with PH_3 to Si_2H_6 gas ratio of 180 ppm at growth pressure of 5×10^{-3} Pa. The probes exhibit electrical conduction in both directions with the resistivity of 1.8 Ω-cm.

rate of which was controlled with the mass flowmeter, was supplied to the growth chamber to maintain the desired gas ratio of dopants to Si and hence grow probes with the desired doping concentration. A micromanipulator system with tungsten (W) needles for achieving contact between the tip and base was used for measuring current–voltage (I–V) characteristics of these doped probes. The impurity concentration and resistivity of the probes were estimated from the measurement.

3.2 Results and discussions

We introduced pure Si_2H_6, as the source gas of Si and PH_3, diluted in H_2 as a doping gas into the growth chamber for growth of n-type probes by the VLS method. Figure 5 shows the SEM image and I–V characteristics of the n-type probe array grown at a temperature of 700°C by the VLS method using the gas ratio of PH_3 to Si_2H_6 of 180 ppm with a growth pressure of 5×10^{-3} Pa and a duration of 60 min. These probes were found to exhibit electrical conduction in both directions, as shown in Fig. 5(b). The resistivity and impurity concentration were 1.8 Ω-cm and 2.5×10^{15} cm^{-3}, respectively. Similarly, the mixed gas of Si_2H_6 and B_2H_6 was used to obtain a p-type Si-probe array, as shown in Fig. 6, which was grown at the same temperature of 700°C but with a B_2H_6 to Si_2H_6 gas ratio of 5000 ppm at a growth pressure of 3×10^{-3} Pa for 50 min. The resistivity of these p-type probes was found to be 0.81 Ω-cm and the impurity concentration was 2.0×10^{16} cm^{-3}. Thus, the probes could be grown using different doping gases for in situ VLS growth with the gas ratio varied from low to high. When using a high PH_3 to Si_2H_6 gas ratio of 10000 ppm, the grown probes shown in Fig. 7 were found to be highly conductive with the resistivity of 5.7×10^{-3} Ω-cm and impurity concentration of 1.8×10^{19} cm^{-3}. From the overall results, it was seen that the impurity concentration of n-type probes increases, and the resistivity decreases with increasing PH_3 to Si_2H_6 gas ratio, as shown in Fig. 8. The figure also indicates that arrays of doped probes having controlled resistivity and impurity concentration can be successfully realized by including in situ doping in the VLS growth method.

The growth rate of doped probes has been studied as a function of the ratio of dopant gases in Si_2H_6 compared with
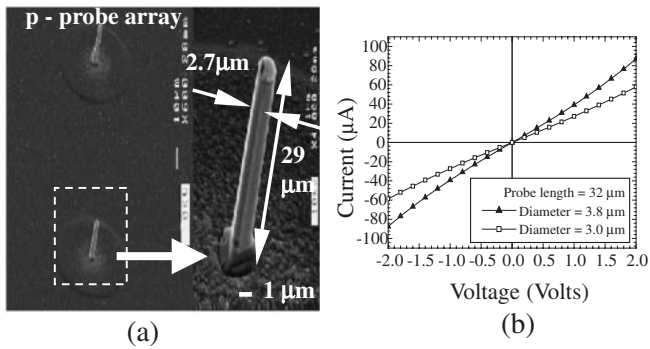
Fig. 6. SEM image and *I–V* characteristics of p-type probe array grown at 700°C by VLS growth with *in situ* doping with B_2H_6 to Si_2H_6 gas ratio of 5000 ppm at growth pressure of 3×10^{-3} Pa. The probes were conductive with a resistivity of 0.81 Ω-cm.
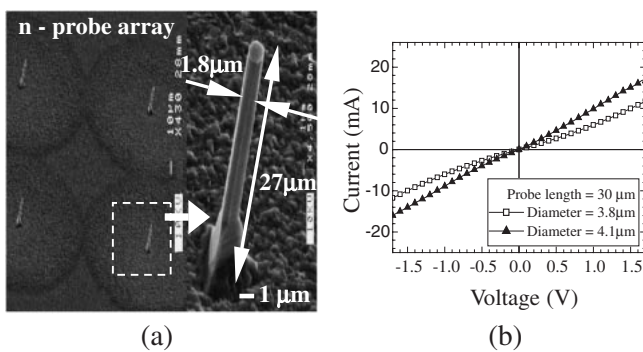

Fig. 7. SEM image and *I–V* characteristics of n-type probe array grown at 700°C by VLS growth with *in situ* doping with high PH_3 to Si_2H_6 gas ratio of 10000 ppm at growth pressure of 3×10^{-3} Pa. The probes were highly conductive with the resistivity of 5.7×10^{-3} Ω-cm.
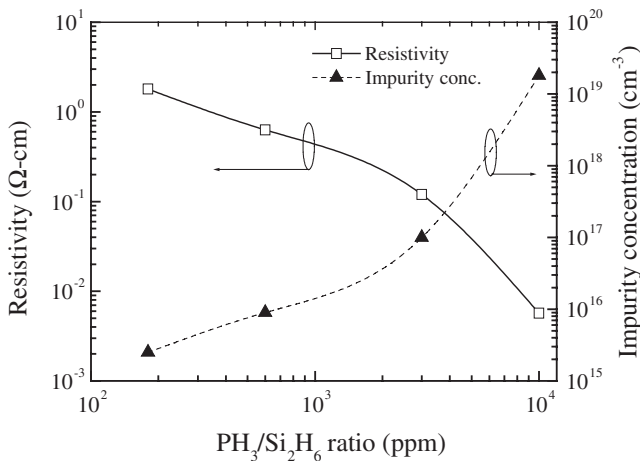

Fig. 8. Variations of resistivity and impurity concentration of n-type Si probes as functions of PH_3 to Si_2H_6 gas ratio. All the probes were grown at 700°C.
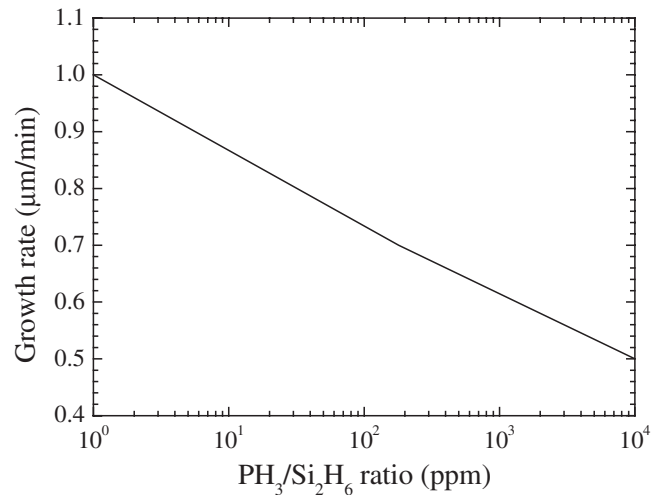

Fig. 9. Growth rate variation of n-type Si probes as function of PH_3 to Si_2H_6 gas ratio with growth carried out at temperature of 700°C.

grown at 700°C, decreased to 0.56 μm/min at the B_2H_6 to Si_2H_6 gas ratio of 5000 ppm.

The growth rate of Si crystal formed by VLS growth can now be discussed from the viewpoint of the activation energy compared with those in other methods. Using the curve of growth rate versus the inverse of absolute temperature shown in Fig. 4, the activation energy for Si probe growth was estimated to be 0.81 eV. Similarly, the activation energy of 1.20 eV was obtained for poly-Si growth, using the graph corresponding to poly-Si in Fig. 4. The previous study on crystal growth revealed that the epitaxial Si crystal grows by vapor-phase epitaxy with the activation energy of about 1.5 eV at a rate of less than 0.05 μm/min at temperatures of 700°C or less.[9] The VLS growth mechanism possesses a lower activation energy than that in the vapor-solid (VS) method. Consequently, the growth rate of a probe grown by the VLS method is much higher than that of poly-Si or an epitaxial Si layer grown by the VS method. Again we can see in some previous reports[10,11] that the introduction of PH_3 to Si_2H_6 during the epitaxial growth of Si by GS-MBE or ultrahigh-vacuum chemical vapor deposition (UHCVD), results in the reduction of the Si growth rate. P atoms bind H atoms on the growing surface and thus block the available reaction sites for the adsorption of further precursor Si_2H_6, thereby decreasing the growth rate.[11] Similar to the trend of Si growth in GS-MBE or UHCVD with respect to the effect of PH_3, the growth rate of the n-type probe grown by the VLS method also decreased with the increase in the PH_3 to Si_2H_6 ratio, as shown in Fig. 9.

4. Applications

Some applications such as probe card pins for integrated circuit testing,[8] and insertion electrodes for recording neural signals,[6] require the realization of highly conductive Si probes with on-chip circuitry for processing the recorded information. The resistivity of VLS-grown intrinsic Si probes ($\sim 10^4$ Ω-cm) can be reduced to $\sim 10^{-2}$ Ω-cm by applying P diffusion at 1100°C.[7] However, *in situ* doping with the VLS growth system allowed us to realize more highly conductive probes ($\sim 10^{-3}$ Ω-cm) at a lower temper-

that of the intrinsic probe. The growth rate of the intrinsic probe grown at 700°C was about 1 μm/min but it was found to decrease with the increase in the gas ratio of dopants to Si_2H_6. Figure 9 shows the decreasing pattern of the growth rate of n-type probes grown at 700°C. It was reduced to 0.5 μm/min at the PH_3 to Si_2H_6 gas ratio of 10000 ppm. Similarly, the growth rate of p-type probes, which were

ature (700°C). Hence the *in situ* doping approach is applicable to processing highly conductive probes with on-chip circuitry and thus promotes the realization of smart chips for various applications. Again, the realization of doped probes reveals the possibility of fabricating probe-like p-n junctions via the growth of n-type probes followed by that of p-type probes or vice versa. The change in the reverse saturation current of a diode due to temperature may be exploited in the application of this probe-like p-n junction as insertion electrodes to elucidate the temperature distribution in living tissue, which may play a great role in medical science. These p-n junction probes may also be used as optical devices such as photodetectors and photosensitive emitter array devices. Similarly, by growing p-(n-)type layers sandwiched between repeated n-(p-)type layers, vertical npn or pnp transistors may be fabricated and configured for use in the amplification of signals collected from living tissue.

5.　Conclusions

The VLS method was proven to yield doped probes in addition to intrinsic ones. VLS-grown probes with diameters in the range of 2–4 μm could be grown using Au dots with diameters of 4–10 μm and a Au layer with a thickness of 160 nm, whereas using the same pattern of Au dots with a Au layer thickness of 50 nm resulted in probes with diameters of 1–2 μm. The activation energy for Si probe growth by the VLS method was found to be lower than that for poly-Si or epitaxial Si growth by the VS method. Consequently, the growth rate in the VLS method was much higher than that in the VS method. VLS growth using the gas source of Si_2H_6 yields intrinsic Si probes with a resistivity of $\sim 10^4$ Ω-cm. The conductivity of the probes could be improved by carrying out P diffusion after growth. An alternate approach to realizing highly conductive probes was introduced, in which *in situ* doping has been incorporated into the VLS growth method. The mixture of Si_2H_6 and PH_3 was used in VLS growth of n-type probes with impurity concentration varied from 10^{15} cm^{-3} to 10^{19} cm^{-3}. In a

similar manner, p-type probes were also realized by using a mixed gas of Si_2H_6 and B_2H_6. This approach allowed us to realize much more highly conductive n-(-p) probes at a temperature (700°C) less than that required for conventional impurity diffusion (1100°C). Due to this low processing temperature, the *in situ* doping approach is applicable to fabricating highly conductive probes with on-chip circuitry. The successful realization of both n-type and p-type probes also leads to the possibility of applying this technique to fabricate probe-like vertical devices and using them in various applications.

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