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Boron-Silicon Thin Film Formation Using a Slim Vertical Chemical Vapor Deposition Reactor

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Abstract

A boron-silicon film was formed from boron trichloride gas and dichlorosilane gas at about 900˚C in ambient hydrogen at atmospheric pressure utilizing a slim vertical cold wall chemical vapor deposition reactor designed for the Minimal Fab system. The gas flow rates were 80, 20 and 0.1 - 20 sccm for the hydrogen, dichlorosilane and boron trichloride gases, respectively. The gas transport condition in the reactor was shown to quickly become stable when evaluated by quartz crystal microbalances at the inlet and outlet. The boron-silicon thin film was formed by achieving the various boron concentrations of 0.16% - 80%, the depth profile of which was flat. By observing the cross-sectional TEM image, the obtained film was dense. The boron trichloride gas is expected to be useful for the quick fabrication of various materials containing boron at significantly low and high concentrations.

Keywords

Chemical Vapor Deposition, Boron-Silicon Film, Boron Trichloride, Dichlorosilane

1. Introduction

A film formation technique of alloys and doped materials enables various applications for industrial materials production [1] [2] [3]. Films having various compositions and dopants are frequently formed by chemical vapor deposition (CVD) [1]-[7], because the CVD method can flexibly fabricate films having various compositions, even those in a non-equilibrium state [8] [9].

The boron-doped semiconductor silicon is an important application [1] [2]

[3]. In order to dope the boron into the silicon CVD film, diborane (B_2H_6) gas is currently used. However, the diborane gas must be carefully handled, because it is significantly flammable and toxic. The use of diborane gas is accepted but is strictly regulated by the rules and laws in many countries.

As an alternative dopant gas, boron trichloride (BCl_3) gas, is expected for use in the silicon CVD process, because it is moderately reactive, nonflammable and less toxic [10]. In order to avoid any unexpected accident, the use of a safe gas is the practical issue for a flexibly-designed manufacturing system, such as the Minimal Fab [11]-[17]. The Minimal Fab uses compactly-designed reactors and machines, which are flexibly arranged, day by day, depending on the various products and processes.

The boron trichloride gas has thus been studied for the formation of the boron-doped silicon film and the boron-silicon alloy film [6] [18]. While a previous study used the horizontal cold wall CVD reactor, the slim vertical cold wall reactor [15] [16] [17] [19] [20] was employed for the CVD of the Minimal Fab. The slim vertical reactor is expected to achieve the high-speed fabrication of electronic devices on the half-inch-diameter wafer based on its quick gas transport [20]. Because the gas flow in the slim vertical gas channel is influenced by the density and viscosity of the gas [20], the gas flow condition should be evaluated before employing a new precursor, such as the boron trichloride. For evaluating the gas flow condition, the in-situ real-time measurement by a quartz crystal microbalance (QCM) [20] [21] [22] provides the effective information in detail.

In this study, boron trichloride gas was utilized along with dichlorosilane (SiH_2Cl_2, DCS) gas to form the boron-silicon film in the slim vertical cold wall CVD reactor. The capability to obtain significantly wide boron concentrations in the formed film was studied taking into account the gas flow condition in the reactor.

2. Experimental Procedure

Figure 1 shows the CVD reactor for the boron-silicon film formation on the half-inch-diameter silicon wafer. The wafer was rotated at 10 rpm and heated by halogen lamps through the transparent quartz glass chamber. The wafer temperature was fixed at about 900˚C, at which temperature the boron trichlorosilane gas had the highest boron film formation rate [6].

The hydrogen, dichlorosilane and boron trichloride gases were introduced at atmospheric pressure from the inlet at the flow rates of 80, 20 and 0.1 - 20 sccm, respectively. When the net boron trichloride gas flow rate was adjusted to less than 1 sccm, argon gas was added for preparing the gas mixture containing the significantly dilute boron trichloride gas. The gas mixture of the boron trichloride and argon at 10 sccm was then introduced into the reactor. When the net boron trichloride gas flow rate was greater than 1 sccm, the argon gas was not added for the dilution.

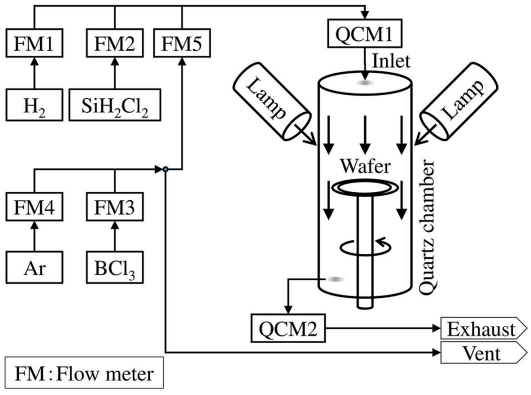

Figure 1. CVD reactor used in this study.

The quartz crystal microbalances (25 MHz), such as QCM1 and QCM2, were placed at the inlet and outlet, respectively, of the quartz chamber in order to evaluate the gas flow conditions [19] [20]. Because the QCM frequency is influenced by the density and viscosity of the gas mixture, in addition to the deposition on its surface [21] [22], the QCM frequency is expected to decrease and increase by the arrival of heavy and light gases, respectively.

Figure 2 shows the overall process and conditions used in this study. The wafer temperature was raised to that higher than 1000˚C for removing the silicon dioxide and organic contamination films on the wafer surface. After the surface cleaning, the wafer temperature was adjusted to about 900˚C. For the film formation, the boron trichloride and dichlorosilane gases were introduced into the quartz chamber. After the film formation, the boron trichloride and dichlorosilane gases were terminated; the wafer was cooled to room temperature in ambient hydrogen by terminating the electric power to the halogen lamps. The overall process was performed in ambient hydrogen at atmospheric pressure.

At the wafer surface, the boron trichloride and dichlorosilane gases were assumed to have the following overall chemical reactions [2] [6].

$$\text{Boron trichloride: } 2BCl_3 + 3H_2 \rightarrow 2B\downarrow + 6HCl\uparrow \quad (1)$$

$$\text{Dichlorosilane: } SiH_2Cl_2 \rightarrow Si\downarrow + 2HCl\uparrow \quad (2)$$

The expected elemental chemical processes at the surface are schematically shown in **Figure 3**. The boron trichloride and dichlorosilane are chemisorbed on the surface to produce the surface intermediate species of $^*BCl_x$ and $^*SiCl_2$, respectively. The symbol "*" indicates the intermediate species chemisorbed on the surface. The surface intermediate species are decomposed by the hydrogen to produce the boron and silicon on the surface while producing the hydrogen chloride gas.

The film formation rate was obtained by the difference in the weight and thickness before and after the film formation. The density of the boron-silicon film was assumed to be the same as that of the silicon. The composition and chemical condition of the obtained film was evaluated by X-ray photoelectron spectroscopy (XPS) (Quantera SXM, ULVAC-PHI Corp., Tokyo, Japan), after

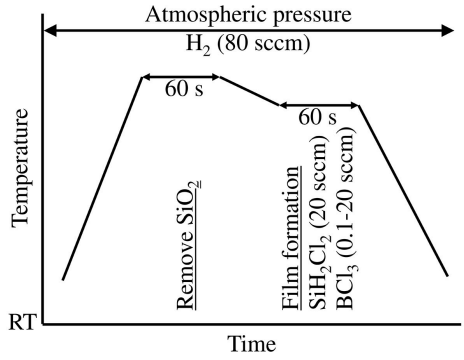

Figure 2. Film formation process in this study.

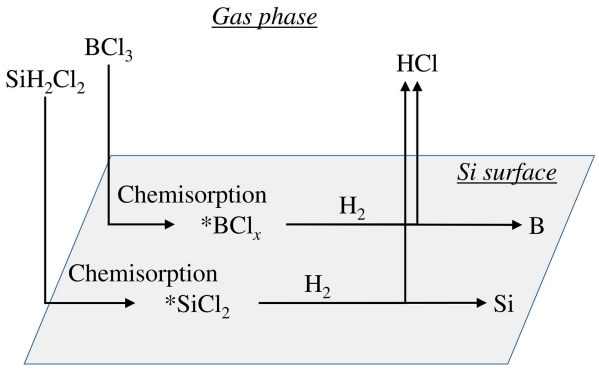

Figure 3. Surface chemical process of boron trichloride and dichlorosilane. *: chemisorbed at surface.

sputtering the 45-nm-thick surface layer. A cross section of the film was observed by a transmission electron microscope (TEM) (H-9500, Hitachi High Technologies, Tokyo). Secondary ion mass spectrometry (SIMS, CAMECA IMS-6f, France) evaluated the depth profile of the boron and silicon concentrations. The XPS, TEM and SIMS measurements were performed at the Foundation of Promotion of Material Science and Technology of Japan (Tokyo).

3. Results and Discussion

3.1. Gas Flow

The gas flow condition in the reactor was evaluated using the QCM at the boron trichloride gas flow rates of 0.1, 5 and 20 sccm, while the gas flow rates of hydrogen and dichlorosilane were fixed at 80 and 20 sccm, respectively. The QCM frequency was normalized so that the minimum frequency became −100 Hz.

Figure 4 shows the QCM frequency behavior at the boron trichloride gas flow rate of 20 sccm. In order to study the influence of the inlet gas condition on the outlet one, the gas flow rates of the boron trichloride and dichlorosilane were intentionally and irregularly changed. At time *a* in Figure 4, the boron trichloride gas was added to the ambient hydrogen without adding the dichlorosilane. The QCM1 frequency at the inlet immediately decreased at time *a* and quickly recovered, due to the sudden release of boron trichloride gas which was stored at

2 atm in the gas tube. The dichlorosilane gas was added from the inlet at time β. The QCM2 frequency continuously and moderately decreased after time γ. At times δ and ε, the boron trichloride and dichlorosilane gases were sequentially terminated. In contrast, the QCM2 frequency continued to monotonically decrease after times δ and ε. From the relationship of the behavior between the QCM1 and QCM2 frequencies shown in Figure 4, the sudden gas condition change at the inlet was moderated at the outlet. The gas condition change was expected to be similarly moderated around the wafer.

The QCM frequency behavior of the film formation is shown in Figure 5 and Figure 6 at the boron trichloride gas flow rates of 5 and 0.1 sccm, respectively. In these figures, the letters A and C are the time of QCM1 at the arrival of the precursors for the film formation and that at the arrival of hydrogen for the purging, respectively. Similarly, the letters B and D correspond to the time of QCM2 to the arrival of the precursors and hydrogen, respectively.

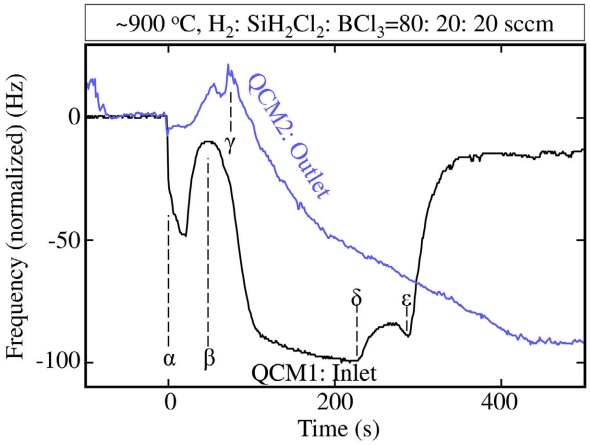

Figure 4. QCM frequency behavior measured at the inlet (QCM1) and exhaust (QCM2) at boron trichloride gas flow rate of 20 sccm in dichlorosilane-hydrogen system.

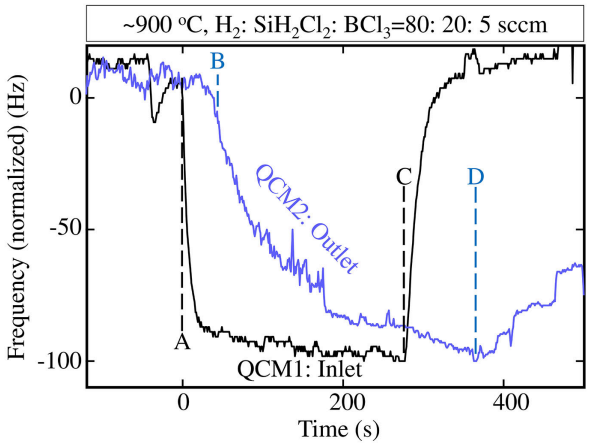

Figure 5. QCM frequency behavior measured at the inlet (QCM1) and exhaust (QCM2) at boron trichloride gas flow rate of 5 sccm in dichlorosilane-hydrogen system.

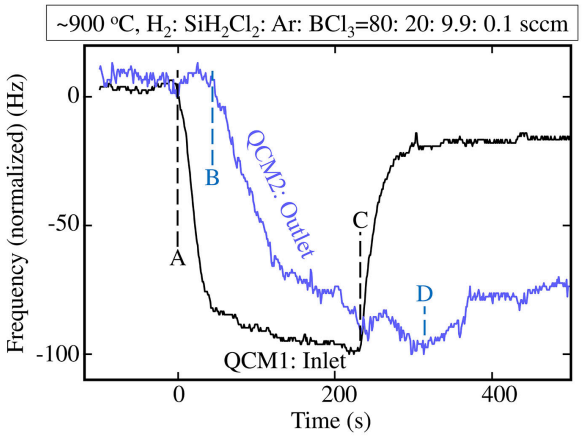

Figure 6. QCM frequency behavior measured at the inlet (QCM1) and exhaust (QCM2) at boron trichloride gas flow rate of 0.1 sccm in dichlorosilane-hydrogen system. Boron trichloride gas was diluted by argon gas at 9.9 sccm.

Figure 5 shows that the QCM1 frequency quickly drops at time A corresponding to the arrival of the heavy boron trichloride and dichlorosilane gases; it recovers at time C due to the termination of the heavy precursors. In contrast, the QCM2 frequency gradually decreases and increases after times B and D, respectively. The difference in the frequency behavior between the quick and moderate changes at QCM1 and QCM2, respectively, indicates the occurrence of gas recirculation and the non-existence of the plug flow in the quartz chamber, as reported in a previous study [11] [20].

Additionally, the QCM1 and QCM2 frequency behaviors, shown in **Figure 5**, indicate the small fluctuations from time A to C and from time B to D. Based on the overall frequency behaviors of QCM1 and QCM2, the gas flow in the reactor is considered to have a moderate and stable recirculation without any unstable and irregular gas motions.

Figure 6 shows the QCM frequency changes in the reactor when the boron trichloride gas flow rate was 0.1 sccm. As described in the Experimental procedure, the significantly small boron trichloride gas concentration was prepared by dilution utilizing the argon gas, as shown in **Figure 1**. The 0.1-sccm boron trichloride gas was introduced into the reactor with 9.9-sccm argon gas. The QCM1 and QCM2 frequencies along with time A to C and time B to D, respectively, showed overall moderate change with the time, similar to those in **Figure 5**. Thus, the gas flow condition in the quartz chamber was considered to have a stable gas recirculation.

3.2. Film Formation Rate

Figure 7 shows the film formation rate at about 900˚C and at various boron trichloride gas flow rates, when the hydrogen and dichlorosilane gas flow rates were fixed at 80 and 20 sccm, respectively. This figure shows that the film formation rate increases with the increasing boron trichloride gas flow rate. The

film formation rate increase with the increasing boron trichloride gas flow rate is considered to occur because of the high boron film formation rate at 900˚C, while the surface termination by the BCl_x occurred at 800˚C that decreased the film formation rate [6].

3.3. Film Quality

The chemical conditions of the obtained film were evaluated by the XPS. From the wide-scan XPS results, there were only silicon and boron in the film. **Figure 8** shows the chemical condition of boron in the film having the boron concentrations of 3%, 82% and 78%, which were obtained at the boron trichloride gas flow rates of 5, 10 and 20 sccm, respectively. As shown in **Figure 8(a)**, a clear boron peak was observed for the film obtained at 10 and 20 sccm. At the boron trichloride gas flow rate of 5 sccm, a weak boron peak was recognized, as shown in **Figure 8(b)**. **Figure 9** shows the condition of silicon, measured by the XPS. The silicon peak in the film formed at the boron trichloride gas flow rates of 5, 10 and 20 sccm was clearly observed.

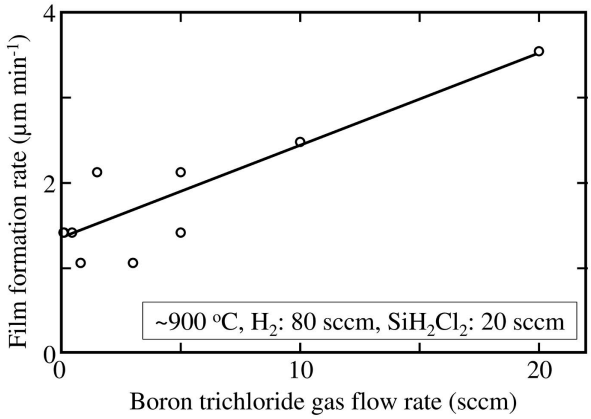

Figure 7. Film formation rate at various boron trichloride gas flow rates.

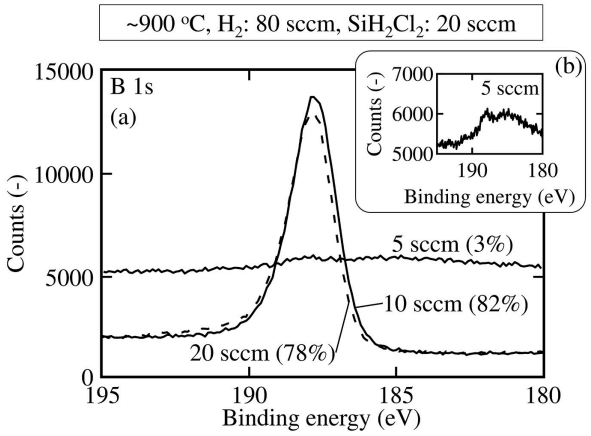

Figure 8. Chemical condition of boron in the obtained film (XPS B 1s).

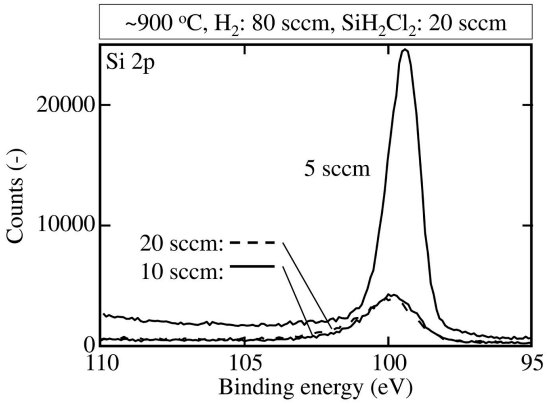

Figure 9. Chemical condition of silicon in the obtained film (XPS Si 2p).

Figure 10 and **Figure 11** show the TEM cross section of the film formed at the boron trichloride gas flow rate of 20 sccm. This film contained 74% boron measured by the XPS. **Figure 10** shows the TEM image of the film from the interface to the surface. The interface and the surface were flat without any voids; the main body of the film was dense.

Figure 11 shows a high resolution TEM image of the same film as that of **Figure 10**. The periodical arrangement of white dots in the lower region of this figure indicates the face-centered cubic crystal of silicon. The perfect amorphous arrangement of white dots is shown in the main body of the obtained film, as shown in the upper region of **Figure 11**. There is a 1.3-nm-thick transition layer showing a slightly different contrast from the substrate and the main body of the film, similar to a previous study [18]. **Figure 11** simultaneously shows that there are no voids in the obtained film. Additionally, the interface between the silicon substrate and the obtained film was significantly flat.

Figure 12 shows the depth profile of the secondary ion intensity of boron and silicon in the film obtained at the boron trichloride gas flow rate of 20 sccm. The secondary ion intensities of boron and silicon were 8000 - 20,000 counts·sec^{-1} and 30,000 - 70,000 counts·sec^{-1}, respectively. **Figure 13** shows the depth profile of the boron and silicon in the film obtained at the boron trichloride gas flow rate of 0.1 sccm. There is an interface between the obtained film and the substrate at about a 0.5 μm-depth. Because the boron trichloride gas was supplied earlier than the dichlorosilane, a clear boron peak was observed at the interface. Because the boron concentration peak quickly decreased with the advancing film formation, the peak width was narrower than 0.05 μm. The boron concentration between the depth of 0.05 - 0.45 μm was 2×10^{19} - 2×10^{20} atom·cm^{-3}. The average boron concentration in the obtained film was 8×10^{19} atom·cm^{-3} (0.16%). As shown in **Figure 12** and **Figure 13**, while the boron concentration showed some scattering, its profile was recognized to be flat without any local segregation.

In conclusion, the boron doping and boron-silicon alloy formation was possible at about 900˚C using the boron trichloride and dichlorosilane gases in the

slim vertical cold wall reactor. The boron trichloride gas is expected to industrially produce the doped and alloy films. In addition, the slim vertical CVD reactor is applicable to the CVD process utilizing various gases, such as boron trichloride, because it forms a regular and stable gas flow in the chamber.

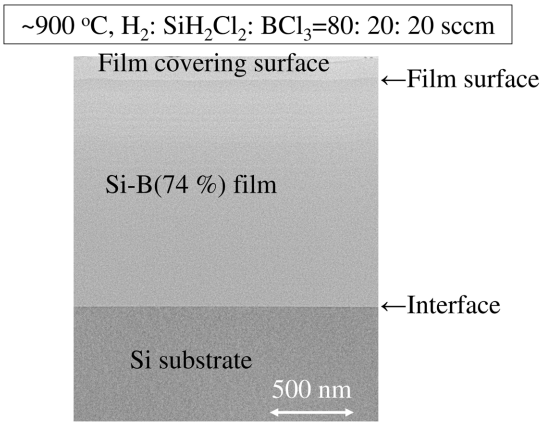

Figure 10. Cross section TEM image of the obtained film.

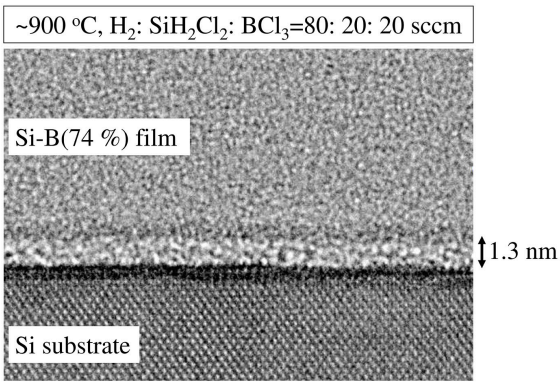

Figure 11. High-resolution cross section TEM image of the obtained film.

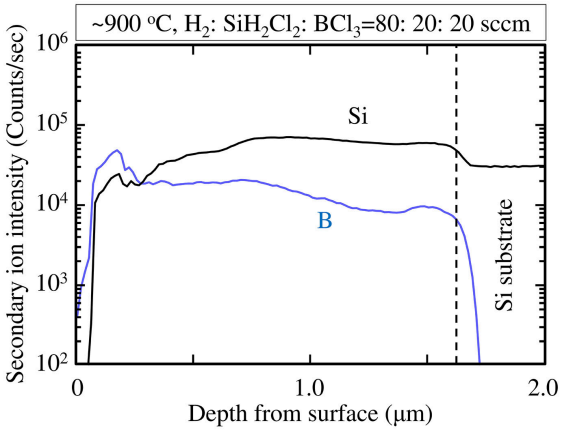

Figure 12. Depth profile of boron and silicon in the obtained film.

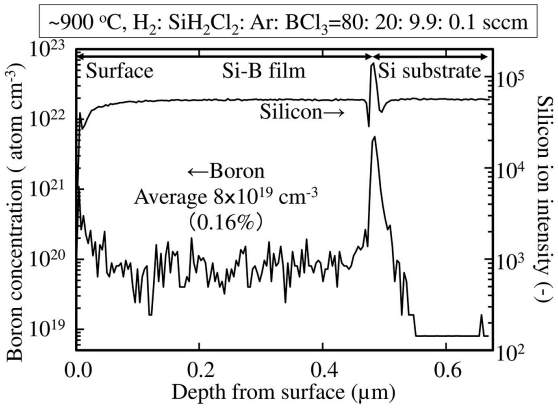

Figure 13. Depth profile of boron and silicon in the film obtained using boron trichloride gas at 0.1 sccm.

4. Conclusion

A boron-silicon film was formed from a boron trichloride gas and a dichlorosilane gas at about 900˚C in ambient hydrogen at atmospheric pressure utilizing a slim vertical cold wall chemical vapor deposition reactor designed for the Minimal Fab system. The gas flow rates were 80, 20 and 0.1 - 20 sccm for the hydrogen, dichlorosilane and boron trichloride gases, respectively. The gas flow in the reactor was shown to quickly become stable, based on measurements using a quartz crystal microbalance. A thin film was formed containing various boron concentrations of 0.16% - 80%, the depth profile of which was flat. By observing the cross-sectional TEM image, the obtained film was dense. The boron trichloride gas is expected to be useful for fabricating various materials containing significantly low to high boron concentrations. Additionally, the slim vertical cold wall CVD reactor is applicable to the film formation process utilizing various gases, such as boron trichloride.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Chang, C.Y. and Sze, S.M. (1996) ULSI Technology. McGraw Hill, New York.

[2] Shimura, F. (1989) Semiconductor Silicon Crystal Technology. Academic Press, San Diego.

[3] Ruzyllo, J. (2020) Guide to Semiconductor Engineering. World Scientific, Singapore. https://doi.org/10.1142/11706

[4] Zhang, Y., Zhang, L. and Zhou, C. (2013) Review of Chemical Vapor Deposition of

Graphene and Related Applications. *Accounts of Chemical Research*, **46**, 2329-2339. https://doi.org/10.1021/ar300203n

[5] Nakamura, S. (1991) *In Situ* Monitoring of GaN Growth Using Interference Effects. *Japanese Journal of Applied Physics*, **30**, 1620-1628. https://doi.org/10.1143/JJAP.30.1620

[6] Muroi, M., Yamada, A., Saito, A. and Habuka, H. (2020) Deposition and Etching Behaviour of Boron Trichloride Gas at Silicon Surface. *Journal of Crystal Growth*, **529**, Article ID: 125301. https://doi.org/10.1016/j.jcrysgro.2019.125301

[7] Habuka, H., Aoyama, Y., Akiyama, S., Otsuka, T., Qu, W.F., Shimada, M. and Okuyama, K. (1999) Chemical Process of Silicon Epitaxial Growth in a $SiHCl_3$-H_2 System. *Journal of Crystal Growth*, **207**, 77-86. https://doi.org/10.1016/S0022-0248(99)00360-7

[8] Kazuo Nakajima (2002) Epitakishaseichou no Mekanizumu. Kyoritsu, Tokyo.

[9] Demin, V., Borisov, V., Grachev, G., Smirnov, A., Khomyakov, M. and Bagayev, S. (2021) Laser-Plasma Deposition of Silicon Carbonitride Films by the HMDS Vapor Gas Flow Activation after a Laser Beam Focus. *Advances in Materials Physics and Chemistry*, **11**, 121-130. https://doi.org/10.4236/ampc.2021.117012

[10] Greenwood, N.N. and Earnshaw, A. (1997) Chemistry of the Elements. Butterworth-Heinemann, Oxford.

[11] Muroi, M., Matsuo, M., Habuka, H., Ishida, Y., Ikeda, S. and Hara, S. (2018) Real Time Evaluation of Silicon Epitaxial Growth Process by Exhaust Gas Measurement Using Quartz Crystal Microbalance. *Materials Science in Semiconductor Processing*, **88**, 192-197. https://doi.org/10.1016/j.mssp.2018.08.014

[12] Irikura, K., Muroi, M., Yamada, A., Matsuo, M., Habuka, H., Ishida, Y., Ikeda, S. and Hara, S. (2018) Advantages of a Slim Vertical Gas Channel at High $SiHCl_3$ Concentrations for Atmospheric Pressure Silicon Epitaxial Growth. *Materials Science in Semiconductor Processing*, **87**, 13-18. https://doi.org/10.1016/j.mssp.2018.07.006

[13] Khumpuang, S., Maekawa, S. and Hara, S. (2013) Photolithography for Minimal Fab System. *IEEJ Transactions on Sensors and Micromachines*, **133**, 272-277. https://doi.org/10.1541/ieejsmas.133.272

[14] Khumpuang, S., Imura, F. and Hara, S. (2015) Analyses on Cleanroom-Free Performance and Transistor Manufacturing Cycle Time of Minimal Fab. *IEEE Transactions on Semiconductor Manufacturing*, **28**, 551-556. https://doi.org/10.1109/TSM.2015.2487324

[15] Li, N., Habuka, H., Ikeda, S. and Hara, S. (2013) Silicon Chemical Vapor Deposition Process Using a Half-Inch Silicon Wafer for Minimal Manufacturing System. *Physics Procedia*, **46**, 230-238. https://doi.org/10.1016/j.phpro.2013.07.059

[16] Li, N., Habuka, H., Ishida, Y., Ikeda, S. and Hara, S. (2016) Reflector Influence on Rapid Heating of Minimal Manufacturing Chemical Vapor Deposition Reactor. *ECS Journal of Solid State Science and Technology*, **5**, 280-284. https://doi.org/10.1149/2.0251605jss

[17] Yamada, A., Li, N., Matsuo, M., Muroi, M., Habuka, H., Ishida, Y., Ikeda, S. and Hara, S. (2017) Transport Phenomena in a Slim Vertical Atmospheric Pressure Chemical Vapor Deposition Reactor Utilizing Natural Convection. *Materials Science in Semiconductor Processing*, **71**, 348-351. https://doi.org/10.1016/j.mssp.2017.08.024

[18] Muroi, M., Otani, M. and Habuka, H. (2021) Boron-Silicon Film Chemical Vapor Deposition Using Boron Trichloride, Dichlorosilane and Monomethylsilane Gases. *ECS Journal of Solid State Science and Technology*, **10**, Article ID: 064006. https://doi.org/10.1149/2162-8777/ac08d6

[19] Takahashi, T., Otani, M., Muroi M., Irikura, K., Matsuo, M., Yamada A., Habuka, H., Ishida, Y., Ikeda, S. and Hara, S. (2020) Quartz Crystal Microbalance for Real-Time Monitoring Chlorosilane Gas Transport in Slim Vertical Cold Wall Chemical Vapor Deposition Reactor. *Materials Science in Semiconductor Processing*, **106**, Article ID: 104759. https://doi.org/10.1016/j.mssp.2019.104759

[20] Otani, M., Takahashi, T., Habuka, H., Ishida, Y., Ikeda, S. and Hara, S. (2020) Quartz Crystal Microbalances for Evaluating Gas Motion Differences between Dichlorosilane and Trichlorosilane in Ambient Hydrogen in a Slim Vertical Cold Wall Chemical Vapor Deposition Reactor. *Advance in Chemical Engineering and Science*, **10**, 190-200. https://doi.org/10.4236/aces.2020.103014

[21] Habuka, H. and Matsui, M. (2013) Langasite Crystal Microbalance Frequency Behavior over Wide Gas Phase Conditions for Chemical Vapor Deposition. *Surface and Coatings Technology*, **230**, 312-315. https://doi.org/10.1016/j.surfcoat.2013.06.052

[22] Habuka, H., Sakurai, A. and Saito, A. (2015) By-Product Formation in a Trichlorosilane-Hydrogen System for Silicon Film Deposition. *ECS Journal of Solid State Science and Technology*, **4**, 16-19. http://jss.ecsdl.org/cgi/content/abstract/4/3/P86 https://doi.org/10.1149/2.0031502jss