

Development of single-crystalline diamond wafers

— Enlargement of crystal size by microwave plasma CVD and wafer fabrication technology —

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Industrial application of diamond has been limited to the use of its hardness, e.g., in machining tools, because large size crystals of diamond are difficult to synthesize and very expensive. If these problems are solved, it can be used for various purposes. Diamond is called 'an ultimate semiconductor' and is located after SiC or GaN in the semiconductor roadmap. If power electronic devices with diamond are realized which utilize its operability under high temperature and the highest thermal conductivity among all materials, the inverters for automobiles can be operated without cooling devices, which lead to energy saving through the reduction of power loss as well as the reduction of weight of the cooling system. The purpose of this paper is to report the process of enlarging the size of single-crystalline diamond using vapor phase epitaxy and the fabrication of diamond wafers.

Keywords : Single-crystalline diamond, microwave plasma CVD, crystal growth

1 Introduction

Until recently, the single-crystal diamonds were industrially manufactured using the high-temperature high-pressure method. The Ib type or the yellow crystals containing nitrogen are mass-produced for use in machine tools. Single crystals with high purity and low defect can be synthesized, and it is also possible to manufacture near-perfect single crystals to be used as dispersive crystals for radiated light^[1]. However, the size limit of the single crystal using the high-temperature high-pressure method is about 1 cm, and further increase in size is difficult because that will require large-scale pressure equipment. In contrast, the chemical vapor deposition (CVD) method used for the synthesis of polycrystalline diamond and homoepitaxial film has less size limit compared to the high-temperature high-pressure method. Therefore, there are several R&Ds for the single crystal synthesis using the CVD method to increase the size and to reduce the cost. Our R&D objective is to use the substrate in the next-generation power devices, and we aim to fabricate a 2-inch wafer needed for the manufacture line of the current prototype device. The single-crystal substrate with maximum 1 cm size that can be fabricated by ultrahigh-pressure synthesis is Ib type, and it is very expensive at 1 to 2 million yen. Cost reduction by one digit or more is expected by using the CVD method.

The reason that the CVD method has been used only for the synthesis of diamond film but not for the synthesis of bulk crystal until recently was because the growth speed was slow and the single-crystal growth could not be maintained over a long time due to the occurrence of abnormal grains. The solutions to these issues are the main topics in the research for the single-crystal CVD diamond synthesis.

In this paper, we shall explain the vapor deposition growth of diamonds, and then describe the increased high plasma density and nitrogen addition to solve the aforementioned issues in the single-crystal CVD diamond synthesis, particularly for the homoepitaxial growth. Then we shall address the development of the methods for shaping the diamond, an ultra-hard material, into the form of a wafer.

2 Development of the diamond synthesis by vapor deposition

The chemical vapor deposition (CVD) is a method where raw material gas (in the case of diamond, hydrocarbon gas such as methane and hydrogen) is broken down by heat or plasma under subatmospheric pressure, and the growth seeds produced undergo a chemical reaction on the substrate surface to grow into a diamond film^{[2]-[13]}.

The CVD synthesis of diamond based on thermal decomposition published in the 1950s had extremely slow growth rate, and was an unrealistic method due to the graphite inclusions. By the end of the 1960s, it was known that the graphite components could be selectively etched due to the presence of atomic hydrogen. However, the CVD diamond research rapidly lifted off in 1982~1983, after the National Institute for Research in Inorganic Materials (currently National Institute for Materials Science (NIMS)) published the production method of atomic hydrogen, and reported that it was possible to synthesize diamond at the growth rate of $\mu\text{m/h}$ level^{[14][15]}. These methods were called the hot filament CVD and microwave plasma CVD methods. In these methods, the methane gas diluted by hydrogen was decomposed by tungsten filament or microwave plasma heated to about 2200 °C, and the diamond grains were grown

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on the substrate of about 800 °C under decompression. Several CVD methods were developed since then, but these two methods were innovative, as they are still widely used in the CVD diamond manufacturing and R&Ds.

In the general CVD method, the raw material gas such as the hydrocarbon gases are decomposed under decompression, the non-diamond substrate is nucleated, and the polycrystalline diamond film is deposited. Such polycrystalline film has excellent properties for various uses such as coating tools. The production of atomic hydrogen and the decomposition of raw material gas can be accomplished by various methods. Depending on the method of the decomposition (activation), the methods can be roughly divided into thermal CVD and plasma CVD. While the decomposition of the raw material gas in the thermal CVD process is achieved by thermal activation, it occurs by electron-molecule reaction in the plasma CVD. Thermal CVD process includes the hot filament method and the combustion flame method such as the oxygen-acetylene torch. Plasma CVD method includes the microwave plasma, DC plasma, DC plasma jet, and RF plasma methods.

In the hot filament CVD method, the film can be formed on a large surface area, since large equipment can be manufactured at relatively low cost. It has already been realized as the polycrystalline diamond coating method for machine tools. However, the filament material (tungsten, tantalum, rhenium, etc.) heated to high temperature may become included in the film as impurities, and the growth rate is slow.

The microwave plasma CVD has few inclusions of impurities since the electrodeless discharge is used, and it is possible to form semiconductor-quality film. Although the growth rate was slow, the speed has been increased as explained later^[16], and the microwave plasma CVD is used in almost all cases of bulk single-crystal synthesis by CVD.

The characteristic common in the CVD diamond synthesis methods is the high-concentration hydrogen gas. Until recently, hydrogen concentration of 99 % or higher was necessary to obtain the diamond with small graphite component. In general, it is believed that the high-concentration hydrogen produces large amount of atomic hydrogen that plays an important role in the diamond CVD process. The diamond synthesis occurs as the radicals from the gas attach to the growth surface and then detach, that is, a surface reaction process takes place. When the diamond crystal grows, the nucleation of the diamond occurs first, and it is necessary to prevent the diamond growth surface to transform into a graphite phase. To do so, it is necessary for the high-concentration hydrogen atoms to bond with all the dangling bonds present on the diamond growth surface. It has been confirmed in the heating experiment that the diamond

structure is relatively stable in hydrogen. In ultrahigh vacuum, the diamond surface graphitizes at about 900 °C, but the diamond structure is maintained up to 2200 °C when heated in hydrogen^[17]. In oxygen, the mass decrease due to oxidation starts at about 585 °C^[18], and the diamond oxidation progresses along with the graphitization of the surface. The diamond growth is explained as follows. In the process of the formation of hydrogen molecules resulting from the reaction of bonding hydrogen that covers the growth surface with hydrogen atoms in the gas, holes (dangling bonds) are formed after the hydrogen is pulled from the growth surface. Next, methyl radical CH₃ produced by the decomposition of the raw material gas (the hydrogen atoms play a part in this reaction) bonds with the holes and growth occurs. Moreover, the atomic hydrogen selectively etches the graphite layer that deposits simultaneously with the diamond. This is useful in reducing the graphite component within the crystal grain boundary in the CVD polycrystalline diamond synthesis. The general procedure is to add oxygen to the raw material gas. In etching with oxygen, the selected ratio of graphite and diamond is not as high as with hydrogen, but since etching can be conducted effectively at low temperature, oxygen addition is useful in reducing the temperature of the diamond growth condition. Also, for the composition ratio of the carbon-hydrogen-oxygen in the raw material gas, the Bachman diagram^[19] that shows the range of composition ratio in which the diamond growth is possible is widely known.

In the diamond crystal growth technology, the formation of the diamond nucleus called the bias enhanced nucleation (BEN)^[20] is important. BEN is used as a nucleation technology for the heteroepitaxial growth on different substrates and for the growth of polycrystalline diamond and nano-diamond film. In the case where the polycrystalline diamond is grown without using the nucleation by BEN, the substrate must be pretreated by mechanical or ultrasound polishing in organic solvent using diamond abrasives before the growth process. This is called the “seeding” process where fine diamond grains are embedded into the substrate, and these become the seed crystals from which growth begins. BEN is a method to replace this. The substrate is charged with negative bias in the plasma with relatively high hydrocarbon concentration. Highly dense diamond nuclei are formed. To grow diamond on these nuclei, the normal growth without bias charge is conducted following the BEN process. Only the stable area formed during the BEN process survives to continue growth.

The film grown after the seeding process becomes polycrystalline where the crystal orientation is random in the growth face, while in BEN, the orientation of the seed crystals may align with the substrate, and the diamond film that grows upon this substrate will be oriented accordingly. This allows heteroepitaxial growth on single-crystal iridium

Ir, platinum Pt, and SiC. Since large diameter substrates such as the Si or SiC wafers have become available, the product realization of large single-crystal substrate using heteroepitaxial growth is being attempted, yet the improvement of crystal formation is an issue.

We aimed to fabricate a large diamond crystal using the homoepitaxial growth with excellent crystallization, by using the microwave plasma CVD method that has smaller surface area than the hot filament method but has relatively faster growth time that allows prolonged synthesis.

3 Diamond single-crystal synthesis by microwave plasma CVD method

The high-speed synthesis of diamond single crystal was conducted using the general-use ASTeX microwave plasma CVD device (2.45 GHz, 5 kW; Seki Technotron Corporation) shown in Fig. 1. Refer to Reference^[21] for the microwave plasma CVD device. Thinking that a high-density plasma production was needed for high-speed growth, the form of the Mo substrate holder to concentrate the plasma onto the substrate was modified^{[22]-[25]}.

The {100} face of the Ib type diamond synthesized by high-temperature high-pressure method was used as the seed crystal substrate. Methane and hydrogen were used as raw material gases, with flow rate of 60 and 500 sccm respectively, pressure of 21 kPa, and substrate temperature of about 1100~1200 °C. The substrate was heated by plasma. The luminescence from the plasma was collected by optical fibers and monitored by a spectroscope.

The synthesized growth layer was evaluated by the locking curve method using precise x-ray diffraction and Raman scattering spectroscopy. The half-value width of the (400) face locking curve that clearly showed the crystal quality of the synthesized single-crystal diamond was minimum 7.6 sec so far, and this was equivalent to the high quality Ib synthesized by the high-temperature high-pressure method.

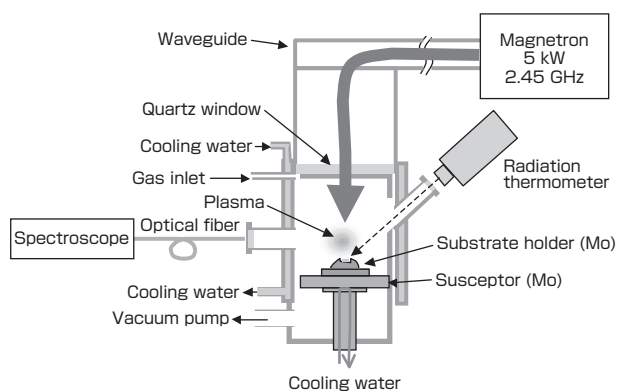


Fig. 1 ASTeX type microwave plasma CVD device

3.1 Growth rate

As mentioned earlier, one of the reasons the CVD method was used to synthesize the polycrystalline diamond film but not to synthesize the bulk crystal until recently, was because of the slow growth rate. For example, compared to the liquid phase growth of 1~2 mm/min in the Si ingot pull-up method and 0.2~1 mm/h of SiC by the sublimation method, diamond growth rate of a few $\mu\text{m/h}$ is too slow for the bulk crystal method. To increase the growth rate of diamond in the plasma CVD method, it was necessary to raise the raw material gas pressure and to increase the amount of activated seed supplied to the growth surface by increasing the density of the plasma by applying high power.

There are several reports of the increased growth rate by addition of nitrogen^{[22][26]}. Figure 2 shows the dependency of growth rate on nitrogen flow rate. The figure shows the two types of substrate holder used for the growth. The growth rate increased in both substrate holders as the nitrogen flow rate increased. While the growth rate in conventional microwave CVD was 10 $\mu\text{m/h}$ or less, it reached 50~100 $\mu\text{m/h}$ by the combined effect of increased plasma density and nitrogen addition. Although the growth temperature differed in the two substrate holders, it was known from experiments that the change in growth rate within this range of temperature difference was small. Therefore, Fig. 2 shows the effect of nitrogen addition as well as the large change in growth rate depending on the form of the substrate holders. The degree of concentration of the microwave field changes according to the form of the substrate holder, and more the concentration the faster it is due to the increased plasma density around the substrate.

3.2 Control of abnormal grain growth

The {100} face is often used as the crystal face orientation of the epitaxial growth substrate. The reasons are because the bicrystal is less likely to occur compared to other facial orientations, and because polishing of the {111} face is difficult for structural reasons. When the epitaxial growth is done on the {100} face, the abnormal growth of the abnormal

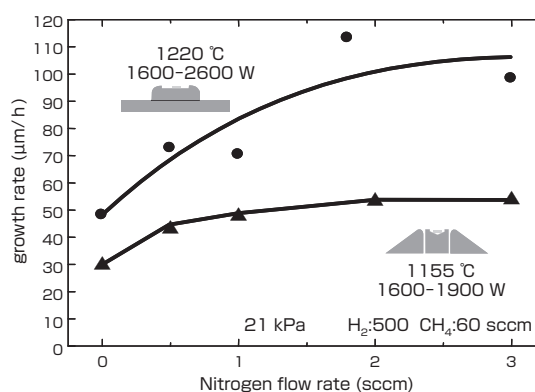


Fig. 2 Dependency of the growth rate on nitrogen flow rate

nucleus occurs in insufficient growth conditions. In many cases, this abnormal nucleus forms a pyramidal structure with grain of {111} orientation growing on top of the {100} face. This is thought to originate from the dislocation within the seed crystal, polishing flaw, etch pit, or fluctuation during growth. The methods to effectively control the occurrence and spread of such abnormal nuclei include the α parameter control, step flow growth using an off-substrate, and nitrogen addition. These are explained below.

1) α parameter control

In diamond crystal growth, the facets (automorphic face of crystal) that manifest are mostly {111} and {100} faces. Setting the growth rate perpendicular to those faces as V_{100} and V_{111} , the α parameter can be defined as follows^{[27][28]}.

$$\alpha = \sqrt{3} V_{100}/V_{111}$$

Since V_{100} and V_{111} have different dependencies for the growth conditions such as pressure, methane concentration, and temperature, α changes according to the growth conditions. In the case of polycrystal synthesis, the change of α is used for controlling the orientation. That is, the growth continues even if the growth is started from a nucleus with specific orientation, and as the film grows, the crystal orientation near the growth surface becomes oriented in the direction determined by α . Also, the form of the crystal grain is determined by α . At about $\alpha=3$, the polycrystal growth assumes the <100> orientation, and is effective in controlling the occurrence of abnormal nuclei in the growth on the {100} face used often as single-crystal growth surface. In this case, if the origins of the abnormal nuclei are present and the {111} oriented grains grow on top, the growth of {100} around it is fast, the abnormalities become buried, and they will not be able to grow into large abnormal grains. However, in this condition, the defects that occur during the dislocation and growth on the substrate are carried over to the growth direction, and may remain as perforating dislocations. Also, since the α differs by devices, the condition that yields a certain α is explored by mapping the α by changing the growth conditions.

2) Step flow on the off-substrate

It is known that the step flow growth occurs when the growth is done on a polished off-substrate that is inclined within a few degrees from the {100} face. When the step passes this part faster than the growth of the abnormal nucleus on the terrace, the abnormal nucleus cannot grow and flat growth can be expected. It is an effective method for forming a semiconductor grade film^[29].

In the case of the growth of a large crystal, even if the growth is started using the off-substrate as the seed crystal, the step growth occurs initially over the whole surface of the substrate as in the film growth, but the off is disengaged at the edge of the substrate, and finally the entire growth surface becomes the {100} face^[30]. Of course, the effect of

controlling the abnormal nuclei cannot be expected after that.

3) Nitrogen addition

During the epitaxial growth on the {100} face, the occurrence of the abnormal nucleus can be controlled by adding a small amount of nitrogen to the raw material gas. The α increases with ultralow volume addition of nitrogen. When the amount is increased, the {111} face can no longer grow normally and becomes polycrystalline. Either way, the growth of the {111} face is inhibited, and as a result, the abnormal nuclei are controlled. This method is used when synthesizing large single crystals by maintaining high-speed prolonged growth. However, when nitrogen is added, deep donor level and carrier trap are introduced and an insulating body is formed. Also, due to the defects accompanying nitrogen, absorption occurs in the visible light range. The control of the {111} face growth by nitrogen addition is thought to occur as the nitrogen atoms bond strongly to the {111} face at three coordinates, and the carbon atoms cannot bond to the {111} face covered with nitrogen^{[22][26]}.

Figure 3 shows the differential interference microscope image of the growth surface at various nitrogen flow rate. When nitrogen is not added, a pyramidal projection (growth hill) can be observed, and there is a typical surface form of the diamond synthesized by the CVD method on the {100} surface. This growth hill remains in the crystal as a large structural defect, and is a factor that inhibits the formation of a thick film by prolonged epitaxial growth. The growth hill is not seen at all when nitrogen is added, but rough surface caused by macro step bunching is observed. When more nitrogen is added, the steps become nonlinear and disturbed. When nitrogen is added, the surface roughens, but since there will be no growth hills, thick film and bulk formation by prolonged growth becomes possible. Conventionally, the single-crystal growth by CVD method was difficult due to the occurrence of abnormal nuclei, but as the result of control of abnormal grain growth by the addition of ultralow volume of nitrogen, the bulk single-crystal growth by CVD method became possible.

3.3 Size increase

The photograph of the sample synthesized over a long time on a 1 cm square substrate is shown in Fig. 4. In the {100} growth by nitrogen addition, the crystal diameter does not expand as shown in the photograph. To obtain the large diameter, the lateral face ({100} face) of the grown crystal is polished, and the growth is repeated on top of that face as shown in Fig. 5. Figure 6 shows an example of the crystals obtained by this method.

The similar lateral growth is seen in the method for reducing defects for the SiC single-crystal growth called the RAF method^[31]. The sublimation method is used for the single-crystal growth of silicon carbide SiC, which is expected to be

in practical use as power semiconductor in the near future. In conventional SiC sublimation method, the growth takes place along the *c* axis $\langle 0001 \rangle$, whereas in the RAF method, the dislocation structure change by the $\{1120\}$ and $\{1100\}$ faces called the *a*-face are used to reduce the dislocational defects. Since the growth is repeated toward the *a*-face direction, it is called the repeated *a*-face (RAF) growth method. From the ingot grown in the *c*-face direction, (1) the $\{1100\}$ face crystal is cut out and the growth is done on that face. Next, (2) $\{1120\}$ face crystal is cut out, and growth is done on that face. After repeating (1) and (2) several times, the seed crystal of the *c*-face is cut out from the ingot, and this is used for the *c*-face growth. The conventional *c*-face grown ingot has several dislocations, but the dislocation of the seed crystals is reduced by the *a*-face growth. Majority of the dislocations are present parallel to the seed crystal face, and it is thought that the defects parallel to the crystal face are not carried over during the *a*-face growth.

The motivation for developing the RAF growth method for the SiC single crystal was the reduction of crystal defects such as micropipes. In contrast, the $\{100\}$ face repeated growth method in the CVD diamond was primarily done to obtain a larger diameter. In the growth condition of ultralow volume nitrogen addition, the growth was only in the $\langle 100 \rangle$ direction, and an increase of the crystal diameter by growth could not be expected. There are dramatic differences in the diameter and quality of the SiC and diamond wafers. Although SiC is more

than 20 years ahead, it is interesting that the lateral repeated growth was proposed at almost the same time.

3.4 Wafer fabrication

Since diamond is the hardest material, it is not easy to process. Therefore, its formation into a wafer form necessary for the manufacture of semiconductor devices is very difficult. Laser cutting is used to process industrial diamonds, but the losses due to cutting reserve and processing time are issues. Also, flatness and low defects are required in the precision polishing technology. "Direct wafer technology" and mosaic method have been developed as methods for wafer fabrication.

In the direct wafer technology^[32], ion is implanted to the single-crystal diamond that will be used as a seed prior to the growth, and a defect layer is introduced immediately beneath the surface. After vapor deposition, the defect layer assumes a graphite structure, and can be removed by electrochemical etching. The seed crystal and the growth layer have diamond structures and are very stable chemically, and are not etched chemically. The seed crystal and the growth layer are separated to form a plate diamond (Figs. 7, 8). Some small parts of the seed crystal will be lost during the separation, but this thickness is only about 1 μm or the depth of the ion implantation. Therefore, the ordinary seed crystal can be used repeatedly, and the separated crystals can also be used as seed crystals.

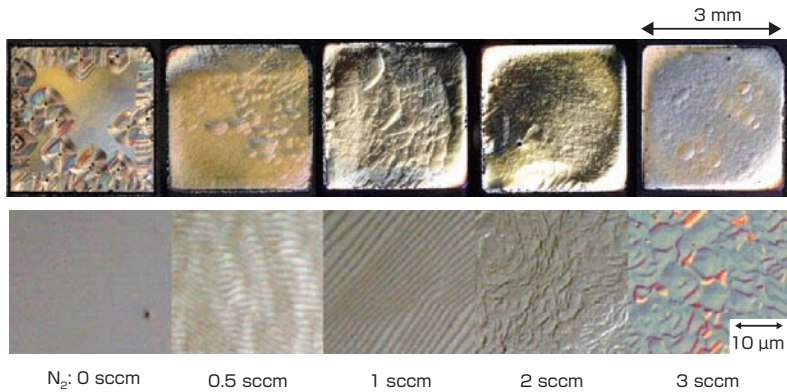


Fig. 3 Dependency of the surface form on nitrogen flow rate observed by a differential interference microscope

Top: Macro image (low magnification). Bottom: micro image (high magnification).

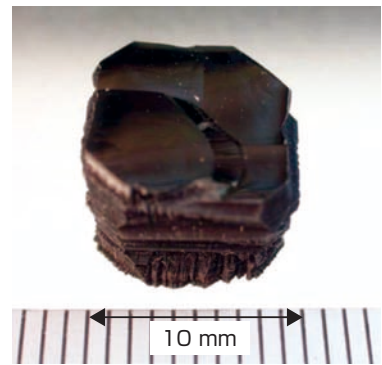


Fig. 4 CVD single-crystal diamond
Weight: 2 g (10 carat)

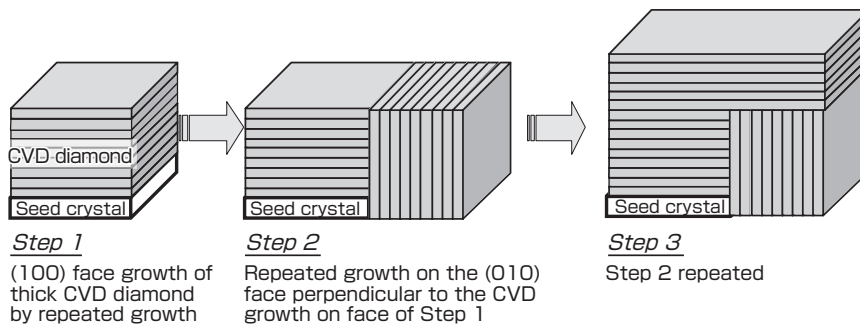


Fig. 5 Size increase of crystal by repeated lateral growth

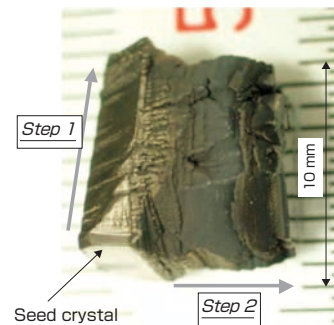


Fig. 6 Example of lateral growth

Although such separation method has been studied at several research institutes^{[33]-[46]}, they were limited to small size and the etching took a long time. The maximum size reported in the literature was about 3~4 mm square, and there was a barrier of conventional technology. The authors started to consider the etching method, and as a result, found a method to form dramatically large surface areas and at higher speed. Since, in principle, there are no problems in scaling up or mass processing, it is considered to have excellent prospects in the future diamond wafer manufacturing technology.

The mosaic method^{[47]-[54]} is a method where the small single-crystal diamond plates of a few millimeter square are closely packed, and the CVD growth is formed and bonded on top. Although the junctions cannot be used as a device, this method was developed to use the entire structure as a wafer and to apply it in the semiconductor process. The junctions produced abnormal grains, but it was found that the abnormal grains at the junction could be reduced dramatically when several crystal fragments fabricated from the same seed crystals using the direct wafer technique were bonded^[55]. It is thought to occur since the face orientation of the crystal fragments align automatically. We used this method to fabricate a mosaic wafer of about 1 inch, and we now have ideas for a mass production method by applying the direct wafer technology using the mosaic wafer as the seed crystal. The mosaic method can be used for size increase easily, and is a method that can fulfill the immediate demand for size increase.

3.5 Smart cut and direct wafer technique

As one of the manufacturing method for the silicon-on-insulator (SOI) wafer that can operate the device at high speed and at low power consumption, a cutting method using the hydrogen ion implantation is used^[56]. This cutting method that uses hydrogen embrittlement is called “smart cut” or “ion cut”, and is a process where the surface of the single-crystal wafer of the semiconductor such as that of silicon is peeled off at thickness of submicron to micron level (corresponding to the depth of ion implantation). The basic process for SOI wafer fabrication by the smart cut method is as follows. (1) SiO₂ insulating layer is formed on the silicon wafer surface by thermal oxidation. (2) Hydrogen

ion is implanted. (3) Hydrophilic treatment is done, layered with other silicon wafers, and bonded at room temperature. (4) Heat treatment is done at 400~600 °C, and the layers are separated at several micron thickness from the wafer surface that was implanted with hydrogen ion. This is possible due to the gaps formed by aggregated hydrogen. (5) Junction boundary is treated at 1000 °C or more. (6) Separated wafer surface is polished. The above process is called the direct bonding method. Other SOI wafer that uses ion implantation includes the “separation by implanted oxygen (SIMOX)” wafer. This is a method where an embedded oxidation film is formed from the silicon of the wafer and the implanted oxygen by high-temperature treatment after the implantation of oxygen ion to the silicon wafer, but no separation is done.

From the experience of the embedded SiC layer formation using the high-temperature carbon ion implantation to the silicon wafer^{[57][58]}, we obtained the knowledge to apply the aforementioned ion implantation technique, and we considered the use of ion implantation as the method for creating the wafer from diamond, a material difficult to process. A thin film such as SOI is not necessarily needed, but to manufacture a wafer with thickness of 0.3 mm or more, epitaxial growth is necessary after ion implantation. In the smart cut, the separation may occur during the growth by heat treatment at around growth temperature of 1150 °C. To prevent this, in the direct wafer method, the amount implanted is the amount where the implanted layer transforms into graphite, and the growth layer is separated by removing the graphite layer by etching after growth. There is a pioneering study by Marchywka *et al.* for the etching of the graphite layer^[59].

4 Conclusion

We demonstrated that it was possible to synthesize a 12 mm single-crystal and 25 mm mosaic crystal using the plasma CVD method, surpassing the maximum size of 1 cm square using the high-temperature high-pressure method. Also, it was shown that a 2-inch size was possible using polycrystals in the direct wafer technology. In the next 1~2 years we plan to fabricate a 2-inch mosaic crystal. The verification for the usability as a wafer is in progress right now, but at

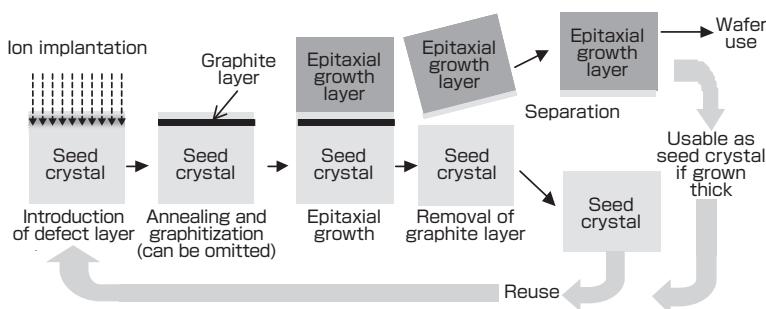


Fig. 7 Direct wafer technology

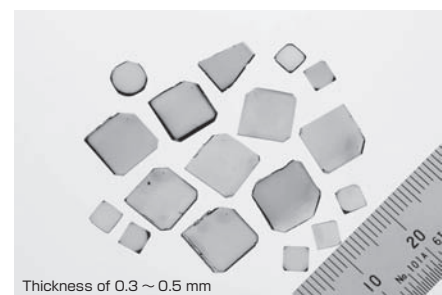


Fig. 8 Single-crystal diamond plate fabricated using the direct wafer technology

the least, it has been shown that it can be used in place of the ultrahigh-pressure substrate^[60]. To obtain higher quality, the reduction of dislocation density is necessary, and we are aware that the pretreatment of the epitaxial growth is important. In the case where there is nitrogen related absorption in the visible range and this is a problem for optical use, it is possible to create a transparent product if it is grown without nitrogen addition. However, at this state, the growth rate will be 10 $\mu\text{m}/\text{h}$ or less. As it can be seen from the fact the CVD polycrystalline diamond coating is widely used for machine tools, the cost of the CVD process itself is not particularly expensive. If the mass production of CVD diamond is realized in the future, the several millimeter single crystals will become readily available, and 1 cm or over will be possible. As a rough estimate, for high-temperature high-pressure synthesis, when the price of a Ib type 1 cm square single-crystal diamond plate is about 1~2 million yen, it will be a digit lower with CVD. This is dependent on the scale of mass production and the corporate strategy, and it is also necessary to consider costs other than synthesis such as shaping. In the case of diamond, since there are demands besides the semiconductor, we can expect the shift to the CVD synthesized product with excellent cost efficiency even with current manufacturing technology. An AIST venture^[61] based on the single-crystal diamond manufacturing technology described in this paper was established, and is supplying samples. If the diamond semiconductor manufacturing is realized, there will be great demands, and as a result, we may see new uses for the single-crystal diamond that will become more readily available.

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Discussions with Reviewers

1 Clarification of the development goal and comparison of the existing technologies

Comment (Kazuo Igarashi, Institute of National Colleges of Technology, Japan and Hisao Ichijo, Tsukuba Center, Inc.)

In this paper, the ways of using the single-crystal diamond wafer is not stated clearly. For example, if the target is for use in the power device substrates, I think you will have a paper with better scenario scheme by stating the size you set as the target for size increase as indicated in the subtitle, where you stand now in achieving the target, and the superiority of the direct wafer fabrication technology and its applicability to size increase.

Also, there are technological developments to address the topics of high-speed growth, low defect crystal, and size increase. I think people can better understand the result of this research if you provide numerical comparison (such as how much faster it is) with the existing or other technologies.

Answer (Akiyoshi Chayahara)

The objective of this development is the utilization in the substrate of next-generation power devices. We aim to create the 2-inch wafer needed for the manufacturing line of the prototype device. Currently, we can fabricate a maximum 1 cm single-crystal substrate by ultrahigh-pressure synthesis, and this is called the Ib type that costs 1 to 2 million yen. The size and cost make it use difficult. The direct wafer technology can be applied to a substrate with 2-inch diameter for polycrystal. We believe it is possible to attain the target size, and a one-digit decrease in price can be expected.

For the numerical comparisons with existing or current technologies, other than the crystallization property, I added

sentences that contain the numerical values in the appropriate places in the text to make the comparisons easier.

2 Quality of the wafer

Question (Kazuo Igarashi)

While it depends for what the single-crystal diamond wafer is used, I think the quality (transparency, impurity concentration, concentration of crystallizations/defects, etc.) must be guaranteed. What is the level of the current wafer fabricated by the microwave plasma CVD method in terms of quality? If further improvement of the quality is needed, what key technologies are required?

Answer (Akiyoshi Chayahara)

When synthesizing the single-crystal using the microwave plasma CVD method, we add ultralow volume of nitrogen to control the macro defect called the abnormal nucleus. The crystallization to the same degree as in the ultrahigh-pressure synthesis Ib type has been obtained from the half-value width of the x-ray locking curve. For semiconductor use, this level is sufficient as the replacement for use in the R&D of the devices that conventionally used the Ib type substrate. To further develop the research, the reduction of the dislocation density is necessary, and we are aware that the pretreatment of the epitaxial growth is important. Currently, the disadvantage of the direct wafer technology using the electrolysis etching is that the conductive substrate cannot be separated. Therefore, a technology that enables this is awaited. For optical use, there is a problem since nitrogen-related absorption occurs in the visible range. When growth is done without nitrogen addition, transparency can be obtained, but currently the growth rate is 10 $\mu\text{m}/\text{h}$ or less. Or, the transparency can be obtained by treating the nitrogen added diamond with ultrahigh-pressure. In either case, cost will be an issue.

3 Selection and integration in the wafer technology

Comment (Hisao Ichijo)

Since you explain the reasons for employing the microwave plasma CVD, if you briefly explain the selection and integration of the various technologies for wafer creation, I think the importance as a *Synthesiology* paper will become clearer.

Answer (Akiyoshi Chayahara)

In the wafer fabrication, unless there is some innovation in the cutting technology, there is no room for selection other than laser cutting and "direct wafer" technologies. In the case of laser cutting, about 1 mm width disappears as the reserve portion to cut diamond to 1 cm size. Even if we achieve high speed, the cost will be a problem at the current growth rate of 50 $\mu\text{m}/\text{h}$, and when over 1 inch is cut, reserve portion cannot be tolerated. Therefore, at this point, we believe the "direct wafer technology" is the most realistic and optimal manufacturing method. We hope the people of the processing fields will become aware that such issues are present, and propose an applicable cutting technology.

For mosaic wafer, we plan to continue the size increase of the single crystal by the repeated growth method, but at this point we do not have any ideas for further accelerating the size increase. In contrast, bonding is done in the lateral direction in the mosaic method, and is a method that matches well with the CVD that enables deposition on large surface area, and immediate size increase is possible. Also, if the defects are reduced in the crystal fragments, these can be "copied" and bonded, and the mosaic wafer, in principle, can be increased in terms of quality instantly. Therefore, we shall work on the mosaic technique as our immediate topic.