

“Liquinert” Process for High-Quality Bulk Single Crystal Growth

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Abstract: Bulk crystal growth technologies originate from the Czochralski (CZ) and Vertical Bridgman (VB) methods developed almost one century ago. Both methods were applied to prepare single crystals of many kind of inorganic materials, for example, semiconductors, halides and many oxides. In the VB process, molten raw materials are wetting the crucible wall easily. This phenomenon causes the sticking of grown crystals with crucibles and often leads to the cracking of the crystal and crucible. These issues prohibit us from obtaining high quality single crystals. Therefore, practical application of VB method is limited only on several materials such as CaF_2 and GaAs single crystals. The issue of crucible's wetting is present in the CZ method as well. For example, the purity of silicon single crystals is degraded from 11N raw material to 5~6N level by the oxygen and carbon contamination caused by the wetting between silicon melt and quartz crucible. These issues are yet to be solved in VB and CZ methods. Many molten materials reach the spherical shape driven by the surface tension when a residual moisture (H_2O) is completely removed from the raw material, the crucible, and atmosphere. We denote this condition as the “Liquinert” state meaning “liquid being in an inert state”, non-wetting and non-reactive with the crucible at high temperature. The author has prepared many high-quality bulk crystals of mainly metallic halides and semiconductors, except oxides, by VB method when applying the “Liquinert” process. This technology is applicable to high quality bulk crystal growth of silicon as well as other inorganic materials of huge industrial interest. In this review, the “Liquinert” process, its background, methodology, examples of applications in fundamental research, and practical development are exposed. In addition, we also discuss the future of this industrial process on bulk silicon crystals for semiconductors and solar cells.

Keywords: Liquinert, Single Crystal Growth, Bridgman Method, Silicon, Solar Cell

1. Introduction

Bulk crystal growth technologies originate from the Czochralski (CZ) and Vertical Bridgman (VB) methods developed in 1918 [1] and 1925 [2], respectively. Both methods were applied to prepare single crystals of many kinds of inorganic materials, for example silicon, sapphire, halides, and many kind of oxides. However, these methods were further modified into new methods, for examples MCZ method (Magnetic field-applied CZ) and VGF method (Vertical Gradient Freezing).

In CZ method, the raw material is molten in the crucible and a single crystal is grown by pulling the ingot upward from the melt after a seed touching the melt expands in diameter. The most successful example of CZ method is the preparation of dislocation free silicon single crystals for semiconductors.

Today, large size silicon single crystals with 300 mm diameter are produced routinely for semiconductor wafers and enormous size 450 mm diameter ingots are developed already for next generation electronic devices.

On the other hands in VB method, the crucible filled with molten raw material is pulled downward after melting a part of the seed crystal placed in the bottom part of crucible and the single crystal is grown with the diameter equal to the inner diameter of crucible. In the VB process, molten raw materials are wetting the crucible wall. This phenomenon causes the sticking of grown crystals with crucibles and often lead to the cracking of the crystal and crucible. These issues prohibit us from obtaining high quality single crystals. Therefore, practical application of VB method is limited only on several materials such as CaF_2 , CsI (TI) and GaAs single crystals. The issue of crucible's wetting is present in the CZ method as well.

For example, the purity of silicon single crystals is degraded from 11N raw material to 5~6N level by the oxygen and carbon contamination caused by the wetting between silicon melt and quartz crucible. These issues are yet to be solved in VB and CZ methods.

Generally, a great attention in crystal growth technology is paid to the crystallization process itself, which is thermal solidification of the molten raw material by setting suitable growth conditions in the electric furnaces. But the “Liquinert” pre-process is equally important to obtain high quality single crystals by VB and CZ methods. The “Liquinert” technology is based on the complete removal of moisture (H_2O) from the three process components: namely raw material, crucible, and atmosphere. At high temperature, H_2O is extremely chemically reactive with many metals (converting them into oxides), and with inorganic materials (where the reaction results in the formation of complicated compounds). These resulting materials cause the tough wetting with crucibles at high temperature and sticking of the grown crystals to crucibles after cooling at room temperature.

As a result, it is very important to keep the settings of the non-reactive and non-wetting “Liquinert” state of the three components in balance as shown in Figure 1. Further below, the details of the wetting mechanism of the melt and the crucible as well as the achievement of the “Liquinert” state is discussed on the example of the potassium chloride (KCl).

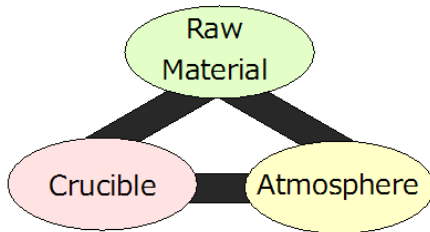


Figure 1. Three components of the “Liquinert” state.

2. Fundamentals of the “Liquinert” Process

In this section, fundamentals of the “Liquinert” process which are the difference between de-wetting and liquinert, drawbacks due to wetting, preparation of metallic halides single crystals and the principle of complete removal of H_2O are summarized.

2.1. De-wetting and “Liquinert”

Wetting of any liquid (including water) is defined as state when the interface of the liquid become flat on the solid surface at room temperature. On the contrary, the de-wetting is a state when liquid forms round or spherical shape on the solid surface. On the other hand, the “Liquinert” process [3, 4] allows to achieve the round or spherical state of inorganic molten materials at high temperature after their melting in the crucibles (Figure 2). The word “Liquinert” comes from the expression “liquid being in an inert state” as it was proposed

by the author in 1995 [3].

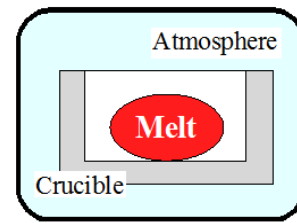


Figure 2. Spherical melt under the “Liquinert” state.

2.2. Drawbacks Due to Wetting

There are many drawbacks coming from the wetting of the melt and the crucible during CZ and VB growth processes. The first one is the sticking of crystals with crucibles which causes the cracking of both crystals and crucibles. In these situations, one can never obtain crack free high-quality crystals. The second one is the impurity contaminations in crystals from crucible materials during the crystal growth at high temperature. In this process, the purity of grown crystals is degraded from high purity raw materials. The third one is the polycrystalline growth that can easily occur due to the fact that the latent heat of crystallization does not flow through the crystallized ingot but flows through crucible walls.

All these drawbacks are serious prohibiting the mass production of high-quality single crystals by both CZ and VB. Moreover, in VB the cracking of the crucible and low material yield is highly limiting as well. In contrast, the attainment of the “Liquinert” state avoids these drawbacks entirely. Therefore, the “Liquinert” process is extremely advantageous for the preparation of high-quality single crystals by CZ and VB growth processes.

2.3. Preparation of Metallic Halides Single Crystals by the “Liquinert” Process

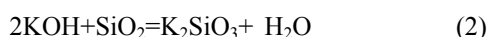
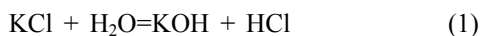
In this section, the details on the wetting of melt and sticking of crystals caused by H_2O presence will be mentioned for KCl and fundamental operation of “Liquinert” Process and the principle of complete removal of H_2O are summarized.

2.3.1. Wetting of Melt and Sticking of Crystals Caused by Presence of H_2O

Alkali halide single crystals have been extensively prepared worldwide for fundamental research in solid state physics for more than 50 years. Among them, German scientists have prepared high purity alkali halides single crystals for color center research by the RAP (Reactive Gas Atmosphere Processing) method [5, 6].

Wetting and sticking mechanism of halides with quartz crucible, originating in the content of the residual H_2O within the raw material, will be described below for the example of KCl. Many metallic halide materials are hygroscopic in nature and raw they contain residual amounts of H_2O . This residual H_2O needs to be removed to prevent the sticking of the crystal to the quartz crucible. If we cannot remove this low H_2O

amount from the KCl powder before its crystal growth in the quartz crucible, the wetting of the KCl melt and sticking of the crystal to the quartz crucible occur assuredly. Below the melting point of KCl (771°C), the H₂O reacts with KCl powder to form KOH, see equation (1). Further, the KOH reacts with the inner surface of the quartz crucible (SiO₂) at the temperature above the KCl melting point resulting in the formation of silicate compounds, for example K₂SiO₃, as shown in equation (2).



The resulting compound K₂SiO₃ becomes the wetting and sticking agent between the KCl crystal and the crucible.

We studied the composition of the interlayer between the KCl crystal and the crucible by X-ray micro-analysis.

Figure 3 shows the results of the analytical data^{(3) (4)}. In this figure, horizontal axis represents distance from inner surface of the quartz crucible into the crystal (logarithmic scale) and vertical axis shows normalized mass ratio of K, Cl, and Si elements. There is an intermingled region containing three elements of K, Cl and Si in range of 0.1 to 20 μm from inner surface of the quartz crucible into the KCl crystal. After 20 μm, the Si content drops to zero leading to a conclusion that the end of the intermingled region and start of the KCl crystal was reached. These data indicate that the intermingled region contains compound(s) with elemental composition similar to K₂SiO₃, as shown in (2), or even more complex ones, such as K₂SiCl₂O₂. This compound relaxes the surface tension of the KCl melt and enhances the wetting between the melt and the quartz surface.

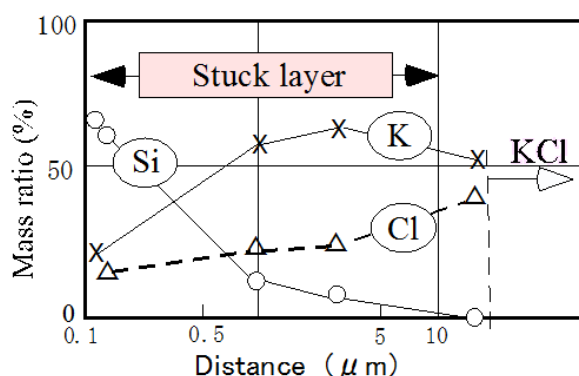


Figure 3. Mass ratio of stuck layer between KCl and quartz.

Conversely, the complete removal of H₂O from three components by the “Liquinert” process eliminates the content of silicate-based compounds in the KCl melt, increasing the surface tension of the melt and the formation of a round spherical shape of the melt.

2.3.2. Fundamental Operation of “Liquinert” Process and the Principle of Complete Removal of H₂O

In this section, the fundamental of “Liquinert” process and the operational principle of the complete removal of H₂O will be explained [7]. Figure 4 shows the experimental set up for

operation of the “Liquinert” process.

The system is composed of a vacuum pump, a liquid nitrogen cold trap A, a resistive furnace, a quartz tube and a reactive gas container. All are connected by glass tubes, vacuum valves and rubber tubes as shown in Figure 4. The quartz crucible is connected by a quartz pipe using a thin pipe located at the bottom end of the quartz tube. KCl powder is charged into the upper part of the quartz crucible and the residual H₂O in KCl is evacuated by the vacuum pump through the liquid nitrogen trap A. This cold trap prevents contamination of the pump oil with H₂O vapor and the reverse contamination of KCl powder by pump oil. KCl powder is dehydrated by heating up using the resistive furnace to about 100 degree below the melting temperature of KCl. This vacuum pumping process is the one way to partially remove residual H₂O. After this procedure, the reactive gas is introduced by vaporizing solid material in the cold trap B. The tiny amounts of residual H₂O react with the reactive gas and are converted to other materials. This two steps process of vacuum pumping and RAP reaction is the “Liquinert” process.

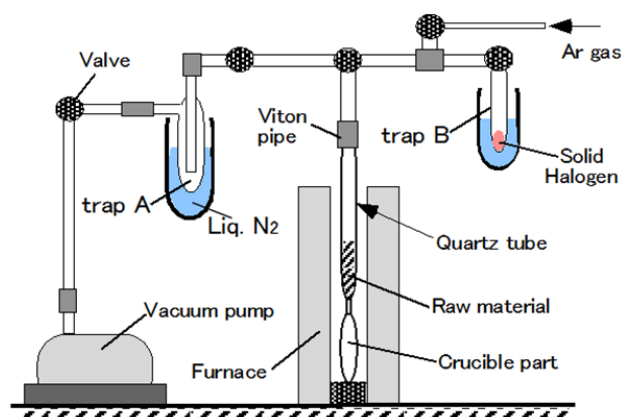
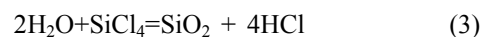


Figure 4. Experimental setting up for the “Liquinert” process.

The principle of perfect removal of H₂O by RAP method use halogen family or silane family compounds as reactive gas. They easily react with H₂O and produce other but inert, materials. The example of complete removal H₂O is shown in (3) using silicon tetrachloride (SiCl₄) as RAP gas.



The resulting SiO₂ and HCl are inert to KCl and to the crucible. There are many RAP gases in addition to SiCl₄, for example, CBr₄, HBr and SiBr₄ for metallic bromides. The know-how is to select the best RAP gas to optimize the “Liquinert” conditions, built through numerous experiments [7].

After this RAP treatment, the KCl powder is melt with a resistive furnace by raising the temperature up to around 800 degree. Molten KCl is pressurized with argon gas and dropped down gradually toward the crucible part through thin quartz tubes, thanks to setting different pressure between upper melt and the lower crucible region. When the whole melt has dropped down, the furnace temperature is lowered to room temperature and the KCl melt is solidified. The quartz crucible part is simply sealed off using a gas burner.

Figure 5 illustrates two quartz crucibles A and B containing molten KCl. In A, the melt surface of KCl is concave because of the wetting between melt and crucible. This concave melt surface results from residual H₂O in the raw material. On the other hand, in figure B, the surface of KCl is convex thanks to the non-wetting between melt and crucible thanks to the “Liquinert” state. In A, the crystal will inevitably have cracks. But in B, high quality single crystals will freely move in the quartz crucible after cooling. This illustrates briefly the efficiency and relevance of our “Liquinert” process.

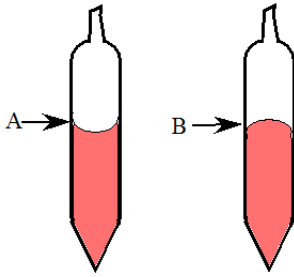


Figure 5. A, concave melt surface and B, convex melt surface.

The “Liquinert” process is usually performed in sealed quartz crucibles, in closed system. However, it can be applied in open systems as well. For instance, in arrangements where the crucible (of carbon or other materials) is placed in a large chamber with RAP atmosphere. In Figure 6(a) A, carbon plate with many dimples filled with raw materials is displayed. This plate is placed in a quartz or metal chamber which is connected to the same vacuum and gas system mentioned in 2.3.2. The chamber with raw material is evacuated to remove H₂O from raw materials under simultaneous heating and introduction of the RAP gas, as described before. Figure 6(a) B shows the molten material in the “Liquinert” state and its solidification into spherical-shaped crystals is depicted in Figure 6(a) C. Application of the “Liquinert” process allowed preparation of high-quality spherical crystals of KCl, Ge, and CaF₂, as shown in Figure 6(b). It is interesting that these crystals grew in nearly spherical shape with size below 3 mm in diameter and low nominal mass. This happens thanks to the surface tension becoming dominant even above the presence of gravity.

We can in fact prepare many kinds of spherical crystals under gravity using the “Liquinert” process instead of performing experiments under microgravity conditions in satellite missions.

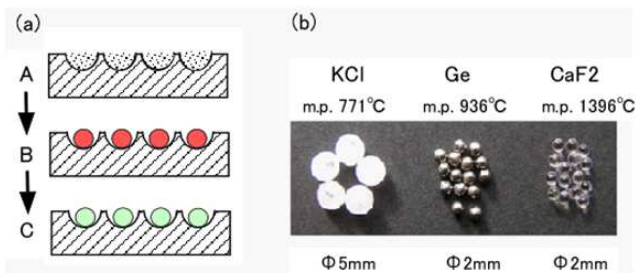


Figure 6. (a), The “Liquinert” process with carbon plate. (b), Pictures of spherical crystals of KCl, Ge and CaF₂.

3. Application of the “Liquinert” Process to Fundamental Research

When investigating the physical and chemical intrinsic properties of crystalline materials, lack of purity and defects are detrimental. Many inorganic crystals have high melting temperature from several hundreds to several thousand degrees. At these high temperatures, chemical reactions of the material and with H₂O and O₂ occur resulting in the degradation of the materials purity by the incorporation of oxygen. For example, alkali halide crystals grown in air atmosphere by CZ method are contaminated by O²⁻ and OH⁻ as mentioned above. Therefore, single crystals for fundamental research must be prepared by removing active materials, especially H₂O from raw material, crucible and atmosphere by the “Liquinert” process. The author has prepared many silver halides (AgCl, AgBr) single crystals by the “Liquinert” process for solid state physics from 1966 to 1978. Two experimental results of silver halide on photoluminescence (PL) and neutron inelastic diffraction studies are shown below.

3.1. Photoluminescence Study of AgBr-AgCl Mixed Crystals

AgBr and AgCl have been used as photosensitive materials for photographic films over one century. But today, they are replaced by semi-conductor photosensitive devices of CCD and C-MOS and only used a little for special fields. The PL study is a powerful experimental way to understanding of impurity and defects identification, exciton-phonon interaction and so on in the fundamental research of silver halides [8]. PL of AgBr originates from free exciton (F-PL) and PL of AgCl from Self-trapped exciton (S-PL) where one exciton is trapped in the phonon field due to the strong exciton-phonon interaction. We’ve prepared many compositions of AgBr_{1-x}Cl_x mixed crystals and measured their optical spectra at low temperature, $T=2\text{K}$ (Figure 7) [9]. The absorption spectrum (dotted line), which reflects unrelaxed exciton, of AgBr_{1-x}Cl_x changes continuously as the concentration x increases, whereas the PL spectrum (solid line), which reflects relaxed exciton, changes discontinuously from sharp F-PL to broad S-PL with large Stokes shift within narrow concentration region around $x=0.400\sim0.500$. In the concentration below $x=0.4$ the PL spectra is the F-PL type accompanied by phonon side bands. From $x=0.425$ to $x=0.500$ the spectrum rapidly changes: F-PL and S-PL coexists at $x=0.450\sim0.475$ and finally broad S-PL is the main component at $x=0.500$. These experimental results can be explained as follows.

According to the Toyozawa theory of exciton-phonon interaction of short-range type, [10, 11] an exciton is self-trapped if the exciton-phonon coupling strength g exceeds a critical strength g_c , while if $g < g_c$ an exciton is free. The effective coupling strength in mixed crystals can be considered as the concentration-averaged: $g_{(\text{AgBr}_{1-x}\text{Cl}_x)} = (1-x)g_{(\text{AgBr})} + x g_{(\text{AgCl})}$. Since $g_{(\text{AgBr})} < g_c$ and $g_{(\text{AgCl})} > g_c$, then

$g_{(\text{AgBr}_{1-x}\text{Cl}_x)}$ crosses g_c at around $x=0.450$, resulting abrupt change from free to self-trapped exciton.

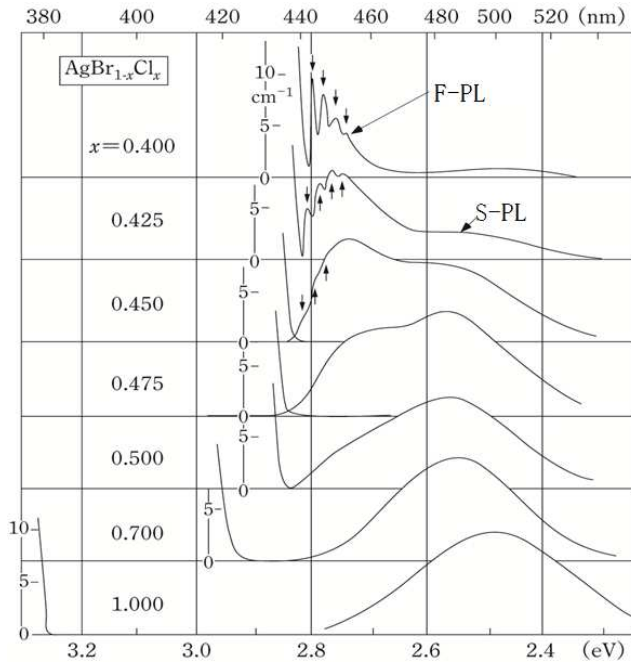


Figure 7. Optical spectra of $\text{AgBr}_{1-x}\text{Cl}_x$ mixed crystals at 2K.

3.2. Inelastic Neutron Diffraction Study of AgBr

AgBr has cubic structure and is NaCl type crystal. The Mohs hardness of AgBr is around 1~2 with no cleavage plane.

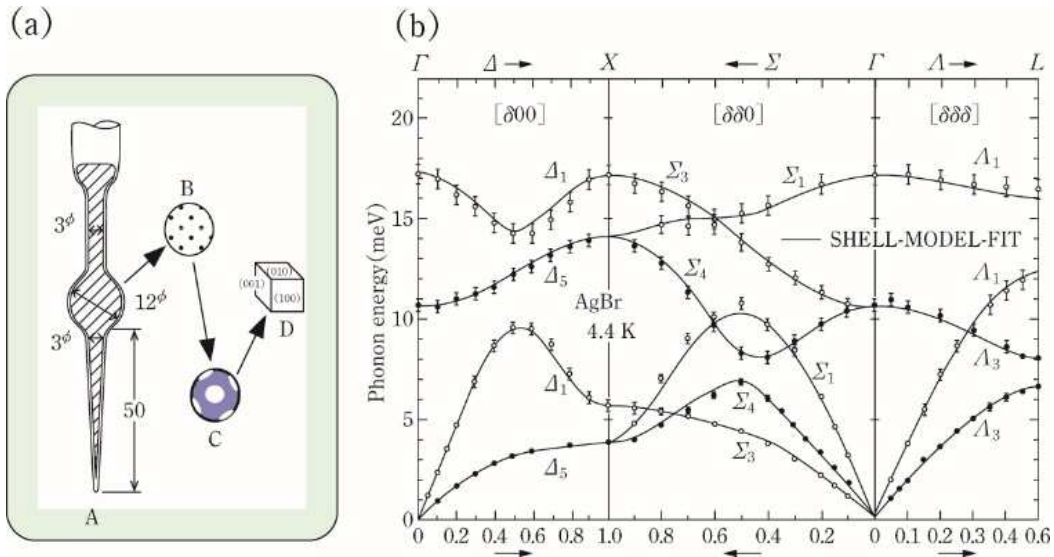


Figure 8. The sequential steps for making rectangular AgBr single crystal (a), Phonon dispersion data of AgBr (b), \circ : Experimental value, real curve: calculated data.

4. Application of the “Liquinert” Process to Practical Developments

For practical applications by VB method, it is important to keep the quality of raw materials and to obtain high production yields. The author has developed many kinds of

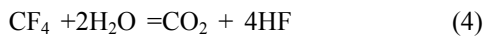
When studying the phonon dispersion data of AgBr by the inelastic neutron diffraction, it is necessary to use a single crystal of AgBr with a defined and accurate crystallographic plane. Generally, one uses X-ray for the definition of the crystallographic plane of a single crystal. But AgBr is photosensitive and Ag colloids are produced by photo-chemical reaction under X-ray irradiation. Then we used an optical patterning method by revealing facet planes on the AgBr sphere surface by selective chemical etching. Figure 8 (a) shows the sequential steps for making rectangular AgBr single crystal with (100) plane by preparing sphere AgBr single crystal. In Figure 8 (a), (A) is that “Liquinert” AgBr melt is filled in a sphere-shaped quartz crucible and grown by VB method. Grown crystal is taken out from quartz crucible without sticking and mechanically shaped into quasi-spheres. This is shiny polished by KCN-H₂O solution (B) and etched by selective etchant for AgBr of sodium thiosulfate (Na₂S₂O₃) (C). We can observe characteristic six-point spots of (100) plan on the sphere AgBr crystal and get cubic shape of AgBr with (100) plan (D) by planning away this with microtome. The phonon dispersion data for above AgBr crystal were obtained by measuring the inelastic neutron diffraction at Brookhaven National Laboratory (USA). In Figure 8 (b) shows phonon dispersion data of AgBr. The circle dots are experimental data and solid curves are theoretical curves obtained thanks to a shell model fitting: they are if fair coincidence [12].

high-quality inorganic crystals for practical applications by using the “Liquinert” process for 30 years. They are (1) KCl single crystals for 20KW CW CO₂ laser optics [13], (2) KRS-5 crystals for infrared fiber optics of CO₂ laser surgery [14], (3) CaF₂ single crystals for ArF and F₂ laser [15], (4) GaAs single crystals for semiconductors [16], (5) BiSbTe needle shaped crystals for thermos-electric devices, (6)

CsI(Tl) scintillation crystals for high energy physics at Cornell University (USA) and (7) $\text{SrI}_2(\text{Eu})$ scintillation crystals for radiation detectors [17]. Among these crystals, CaF_2 and $\text{SrI}_2(\text{Eu})$ are further shown below.

4.1. Development of CaF_2 Single Crystal for Vacuum Ultra-violet Region

CaF_2 single crystals are excellent optical material for near infra-red, visible to ultra-violet region and have been made by VB method by using vacuum electric furnace with carbon crucible for long. Light sources of photolithography of electronic devices (stepper) have shifted toward shorter ultra-violet wavelengths of ArF laser (193nm) and F_2 laser (157nm). CaF_2 single crystal is much more transparent than quartz (SiO_2) in this wavelength region down to 130nm. Therefore, CaF_2 optics for steppers must be the highest quality to minimize absorption. We have developed high quality CaF_2 single crystals for this purpose by 1) sufficient removal of H_2O from three elements of the “Liquinert”, 2) using highest purity of raw material and 3) adaption of a cryopump system for vacuum. The reactive gas for removal of H_2O was carbon tetrafluoride. The RAP reaction was down below 200 degree from melting temperature of CaF_2 (M.P. 1396 degree) as below.



After RAP reaction, melting and crystal growth were done under vacuum down to 10^{-3}Pa level. A grown crystal was machined in 20mm diameter (3mm and 30mm thickness) and polished for optical transmission measurement. The single beam vacuum ultra-violet spectrometer was used for transmission measurement between 220nm and 120nm. Bulk transmittance was obtained by subtracting of surface reflection loss from thickness of 30mm to of 3mm. By this operation, we obtained bulk transmission spectrum of the “Liquinert” CaF_2 crystal with 27mm thickness from 220nm to 120 nm shown in Figure 9. This spectrum shows the straight line along nearly 100% without any absorption band between 220nm and 130nm. We conducted long term degradation test under irradiation of 600mW ArF laser and did not observe dominant transmission reduction up to 9.9×10^8 pulse [15].

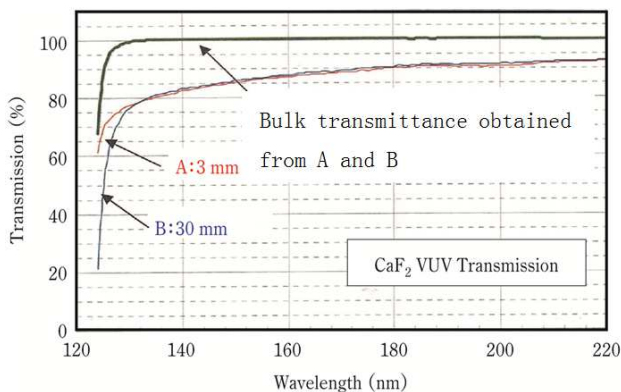


Figure 9. Bulk transmittance of the “Liquinert” CaF_2 crystal.

4.2. Development of $\text{SrI}_2(\text{Eu})$ Scintillation Crystal for Radiation Detector

$\text{SrI}_2(\text{Eu})$ scintillation crystals have better performance on energy resolution for many radiation sources than traditional crystal of NaI (Tl) and have received attention recently in the world [18]. We have succeeded to develop high quality $\text{SrI}_2(\text{Eu})$ scintillation crystals by the “Liquinert” process in 2014 [17]. We summarize the processes and results thereafter.

SrI_2 holds high water solubility of 176g/100cc (H_2O) and a strong hygroscopic nature similar with CeBr_3 . Today’s industrials prepare this crystal using expensive raw material dried to ppm level of H_2O content. The “Liquinert” process enabled us to prepare high quality $\text{SrI}_2(\text{Eu})$ crystals by using cheap raw material with 2~3% of H_2O content [19]. Among the many kinds of RAP gas of Cl_4 , CH_2I_2 , CHI_3 and HI for $\text{SrI}_2(\text{Eu})$, we selected HI . Although HI gas has weak reactivity with H_2O , we managed to optimize a “Liquinert” process by extensive experiments [20, 21].

Figure 10 shows the “Liquinert” melt of 1-inch $\text{SrI}_2(\text{Eu})$ (a), 1.5inch single crystal in (b) and encapsulated detector (c). (a), (b) are enclosed in quartz crucible with end-parts with convex shape which indicate the “Liquinert” state of crucibles. This shows the “Liquinert” process is effective for preparation of high quality single hygroscopic crystals. The 1.5inch crystal was finished for use in a detector by machining, polishing and mounting in an aluminum case. The energy resolution of this for 662 Kev ^{137}Cs gamma ray was 3.4%, a value comparable to a much larger, 1-inch size, regular detector. Generally, the energy resolution of the scintillation detector is dropping down along with the volume expansion due to the self-absorption and scattering of the scintillation light. But above result enables us to proceed commercial production of 1.5inch size of $\text{SrI}_2(\text{Eu})$ without degradation of scintillation performance against 1-inch size.

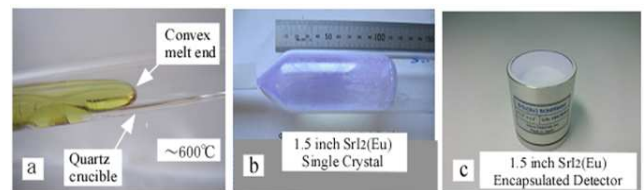


Figure 10. $\text{SrI}_2(\text{Eu})$ of the “Liquinert” melt (a), 1.5inch single crystal (b) and encapsulated detector (c).

5. Application of the “Liquinert” Process to Silicon

Silicon (Si) is probably the most important materials supporting modern human advances today. Not only Si single crystal are key for semi-conductor wafers to support high tech and an information-oriented society but also Si poly- and single crystal wafer represent the 90% share for substrates of solar cell, also key towards clean energy. In practice, do we yet use the full physical and chemical potential of Si? The answer is no, and that is simply because

of H_2O and contamination! Molten Si has extremely high reactivity and makes many kinds of compounds by reacting almost all elements and materials except rare gases like He, Ne, Ar, Kr and Xe. For example, molten Si reacts instantly with the natural atmosphere components such as O_2 , N_2 , CO_2 and H_2O resulting in very stable ceramics such as SiO_2 , Si_3N_4 and SiC . At this moment, the practical production of Si crystals for semiconductor and for solar cell is hindered when they are grown using highest purity of 9N~11N level raw material and quartz crucible when the final purity of the grown Si crystals is degraded down to 5N~6N because of the contaminations from the crucible and atmosphere. Industry has using quartz crucible for over 50 years for Si crystal production. Molten Si wets and reacts with quartz (SiO_2) and incorporation of oxygen occurs into the melt. This is the main source of oxygen contamination and excess oxygen evaporates into Ar gas atmosphere as SiO gas. SiO gas reacts with carbon components in a furnace and results in CO gas. CO is in turn incorporated into the Si melt and becomes the origin of carbon (C) contamination. Si crystal growth technology has not yet to reach the “Liquinert” condition with quartz crucible and efficiently avoid contaminated Ar atmosphere. The author understood this problem from long and has performed R&D work to obtain “Liquinert” poly-Si ingots since 1988 [22, 23]. The results on these studies about fundamental experiment and recent application work are detailed below.

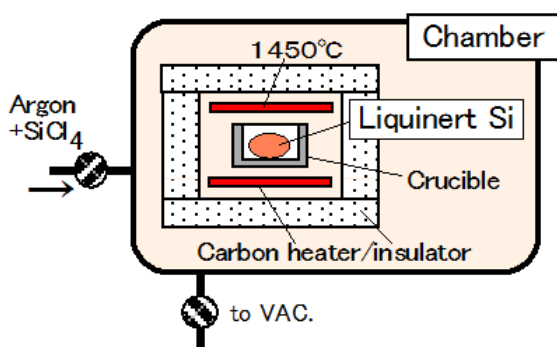


Figure 11. Setting up for fundamental experiment of the “Liquinert” polysilicon.

5.1. Fundamental Experiment of the “Liquinert” Polysilicon

Fundamental experiment for getting the “Liquinert” polysilicon was done by using a small size electric furnace presented in Figure 11. It includes a vacuum chamber, carbon heater and insulator elements, small crucible with Si raw material and Ar atmosphere. The crucible materials have been changed in many varieties like quartz, AlN , BN , SiC , sapphire and Si_3N_4 . Finally, we did experiments with Si_3N_4 powder coated porous SiC as crucible material and SiCl_4 added Ar gas as atmosphere. The SiCl_4 gas acts as H_2O killer during heating and melting processes and keeps the “Liquinert” condition in the chamber inner space. Figure 12 shows many kinds of shapes “Liquinert” poly-Si obtained in these conditions. All of these have shinny surfaces and convex growth ends. These

features show these crystals were grown under the “Liquinert” condition.



Figure 12. Many kinds of shapes “Liquinert” poly-Si.

5.2. Preparation and Evaluation of Big Size Poly- and Single Si by Using “Liquinert” Quartz Crucible

Recently, we are trying to prepare big size “Liquinert” Si using Ar gas only without SiCl_4 in atmosphere. This process should be a more practicable technology. The key is the development of BaO coated quartz crucible (BCC) which is “Liquinert” against molten Si. Fujiwara (Institute for Material Science, Tohoku University) and Horioka (FTB Research institute CO., LTD) have prepared poly- and single Si ingots for solar cell and evaluated them about carrier lifetime mainly. BCC has been developed by General Electric LTD, (USA) in 2000, but they did not come into wide use due to some issues about reliability. We have developed a stable BCC which withstands practical use [24]. These two published results on poly- Si [25] and single Si [26] are briefly shown below.

Table 1. Comparison between two kinds of wafers on resistivity and carrier lifetime.

Crucible	Liquinert crucible	Si_3N_4 coated crucible
Wafer Size (mm^3)	125x125x0.2	125x125x0.2
Ave. Resistivity (Ωcm)	2.42	1.21
Ave. Lifetime (μs)	67.7	20.3

Fujiwara prepared P-type/low resistivity $186 \times 186 \times 250 \text{ mm}^3$ poly-Si ingots using square quartz crucible coated with two “Liquinert” layers of BaO and Si_3N_4 . From these ingots, $125 \times 125 \times 0.2 \text{ mm}^3$ wafers were cut and measured for resistivity and carrier lifetime (CLT) and compared with two regular wafers. Data are shown in Table 1 [25].

The CLT of the wafer obtained from the ingot grown by BCC was 67.7 micro-second, that is three times higher than 20.3 micro-second obtained for the one grown by Si_3N_4 coated crucible (SCC). This shows the poly-Si ingot by BCC was improves the quality on purity or defects reduction: CLT became longer than for SCC. The poor CLT of the wafer obtained from SCC may come some contamination from the degraded Si_3N_4 coating layer during heating process before melting of Si. It is expected the poly-Si ingot grown by the BCC with the longer CLT may will yield to higher energy conversion efficiency.

Horioka and Fukuda (Renewable Energy Research Center,

National Institute of Advanced Industrial Science and Technology (AIST)) have pulled two kinds of P-type single Si by CZ method using BCC and conventional quartz crucible (CQC) with the size of 200mm diameter and about 1000mm in length [26]. They picked up small chips of a quartz crucible after experiment and observed the contact region between melt Si and crucible by optical micro-scope. Figure 13 shows these pictures of A from CQC and of B from LQC. They observed dissolved part of about 1mm hollow on the inner surface of CQC—contacting region between melt Si and crucible. On the other hand, they observed no dissolved part on the same region with BCC and the existence of the “Liquinert” layer clearly. The dissolved silica-glass region in A is the direct evidence of SiO_2 reduction from CQC in conventional CZ silicon process. They have evaluated CLT and analyzed oxygen (O) and carbon (C) by SIMS [26].

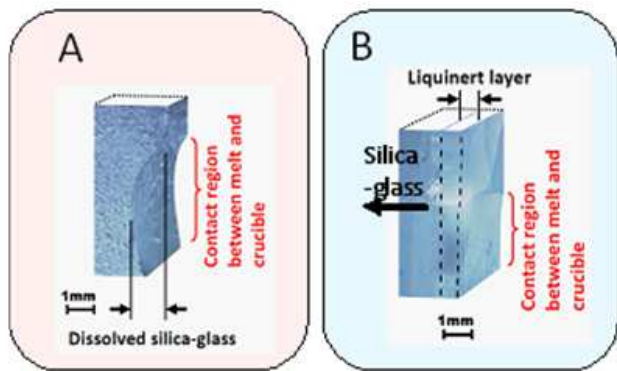


Figure 13. Contact region between melt Si and crucible---A: CQC, --- B: BCC.

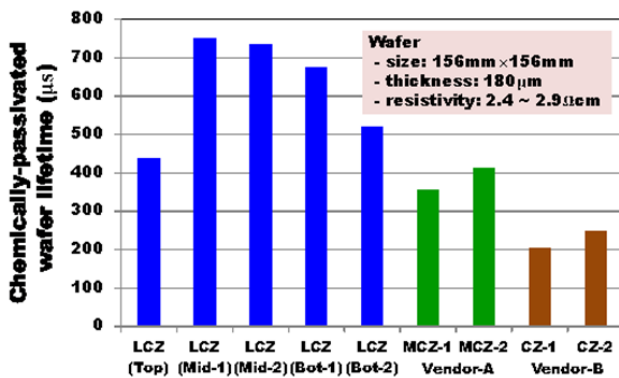


Figure 14. Three kinds of CLT data of CZ, MCZ and LCZ wafers.

CLT measurements were done on three kinds of wafers from CZ method from vendor A, MCZ method from vendor B and LCZ (Liquinert crucible applied CZ) method which is noted the BCC applied CZ by Fukuda [27]. These data are summarized in Figure 14. The two brown bars are CLT for CZ wafers with the average value is 220 micro-second, the green bars are for MCZ wafers with the average value is 380 micro-second and the blue bars are for LCZ wafers with the average value is 624 micro-second.

From CLT data, there is remarkable improvement of CLT on the LCZ wafers about three times than CZ wafers and 1.6

time more than MCZ wafers. The effectiveness of BCC was proved by these CLT data not only for poly-Si ingot but also for CZ single Si ingot.

Analytical data by SIMS showed that O concentration of BCC wafers was reduced 30% compared to CQC wafers. The O reduction does not so much value which was expected and there may exist some oxidization of Si raw material from atmospheric contamination before melting. But C concentration of BCC wafers reduced to background level of 5×10^{14} (atoms/cm³) which is nearly one order reduction compared to that of CQC wafers. This C reduction should contribute to the long CLT and lead to higher conversion efficiency of single-Si solar cell.

6. Conclusion

The “Liquinert” Process was born through half a century of countless experiments of the author from 1966 to 2016. The author mentioned here the backgrounds of this technology and summarized the basic process, application examples in several fields and potentialities for application to Si crystals. Nevertheless, practical application examples are yet to be seen widely, the “Liquinert” process should spread to a basic crystal growing technology for obtaining high quality single crystals by VB, CZ and other methods.

Today, advanced technologies and sciences have been concentrating to the extremely radical and fine stages. In general, people involved in the advanced application fields exemplified above believe the crystal growing technology is an old and past craftsmanship unfortunately. Nevertheless, basic technologies and scientific studies have been left behind although progress can still be expected. One example is the wetting and de-wetting problems of molten materials at high temperature. Almost all studies on experiments and theories for these problems are about water and some organic materials at around room temperature. The author has proposed the word of “Liquinert” for this high temperature phenomena of molten materials.

Another hindrance to energy conversion of our societies is the purity degradation of Si from 11N raw material to 6N crystals. Although it is the common sense that many metals are oxidized under heating up in contaminated atmosphere by oxygen and H₂O, this issue has been left behind in the material processing industries, not only for silicon but also on many inorganic materials. The experimental facts and experienced ideas of the “Liquinert” process by the author open a clear pathway to more efficient and productive crystal growth with social impact.

Finally, renewable energy is indispensable for humankind and Si solar cell remains a key for using this energy source. But the quality of polysilicon (for solar cell) and single Si (for solar cell and semiconductor) crystals are not good enough due to O and C contaminations during preparation processes. The “Liquinert” process can contribute drastically to increase conversion efficiency of solar cell [25] and to improve the quality of wafers for semiconductor. This left problem should be solved towards clean energy society as soon as possible.

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