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Development Trend of Inorganic Materials and Our Developments

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Inorganic materials such as single crystals, ceramics and glass have been used as key products and devices in semiconductor, automobile and life-science fields in recent years. Our GSO and LGSO single crystals are used as scintillators in PET medical imaging equipment, while our high-thermal conductive SiC ceramics and low thermal expansion ceramics are used as structural materials in lithography equipment. Our vanadium-based low melting glass paste is expected to have wide-ranging applications as a moisture-resistant sealing agent for electronic devices. Recent development trends in inorganic materials and our developments are described.

1 Introduction

Wide variation of characteristics of inorganic material can be attributed to the abundance of many types of constituent elements and the constitution of chemical bonds as mixed state of ionic and covalent bonds. Furthermore, inorganic materials can be classified into three categories, namely single crystal, ceramic and glass; based on the regularity of the 3D atomic alignment and crystalline state. In other words, a single crystal is a solid where the entire body comprises single crystals, whereas glass (amorphous material) is a solid, where atoms are randomly aligned. Conversely, ceramics is composed of multi-crystal with particle size of ranging from sub-micron scale to tens of microns. These inorganic materials have been used for key parts and devices in semiconductors, automobiles and life-science.

In our case example, GSO (Gd_2SiO_5: Ce) and LGSO ($Lu_{2-X}Gd_XSiO_5$: Ce) single crystals are used as scintillators in γ-ray detectors of PET (Positron Emission Tomography) medical imaging equipment, while high thermal conductive SiC and low thermal expansion ceramics are used as structural materials for semiconductor lithography equipment. Moreover, the use of vanadium-based low melting glass paste is expected to be used in wide-ranging applications as a moisture-resistant sealant for electronic devices. All these materials are melted or synthesized at high temperatures, hence we promote the development of inorganic products based on our upstream technologies, i.e. material and treatment technology at high temperatures. In this report, recent trends in single crystal, ceramic and glass materials are reviewed and our developments are noted.

2 Single Crystals

2.1 The Recent Trends in Single Crystal

The largest market for single crystal is semiconductor Si, the production of which exceeded 8,000 tons in 2010. Si is fabricated into a wafer, which is then used as a substrate for semiconductor devices. Si single crystals grown using the Czochralski (CZ) method are mainly shaped into wafers and used for semiconductor devices. The technical advancement of CZ-Si can be performed by enlargement of crystal diameter and currently 300 mm diameter single crystals are being mass produced. In future, the wafer size is going to be increased up to 450 mm in diameter in association with the trend of wafer-size enlargement for Si semiconductor fabrication process. Si, which is grown using the Floating Zone (FZ) method, is used in fields of power semiconductor devices where high purity and defect-free silicon is required, infrared optical devices, x-ray related parts and radiation detectors. The mainstream material, however, for rapidly expanding solar battery markets, is amorphous silicon.

The material second to Si in the single crystal market is quartz (SiO_2 single crystal). Due to its piezoelectric property, quartz is used in wide-ranging fields, such as frequency control devices, frequency-selective devices and various types of sensors. Recently quartz has been used for optical devices in cameras and pick up lenses in DVD due to its birefringence, polarization and optical rotation properties. Quartz is grown using a hydrothermal synthetic method. By future trend toward miniaturization and enhanced performance, high quality quartz is required continuously. $LiTaO_3$ (LT) and $LiNbO_3$ (LN) single crystals have a stable market also as piezoelectric crystals, which are used in SAW (Surface Acoustic Wave) devices for high-frequency filters in cellular phones.

The single crystal of next important market is compound semiconductors such as GaAs, GaP, etc. Traditionally, the horizontal BR (Bridgman) method and LEC (Liquid Encapsulated Czochralski) methods have been used to grow crystals for GaAs as optical devices and high frequency devices respectively. Recently, however, the VGF (Vertical Gradient Freeze) method has become mainstream. Recently, GaAs can expect significant market growth due to the expanding demand for high frequency devices used in smartphones and wireless networks, SiC single crystal, which is expected as a big market by replacing Si currently used in

power devices, are very active.

Sapphire (Al_2O_3 single crystal) is used as a substrate for GaN growth, which is necessary for blue LED and white LED and demand for sapphire is in rapid expansion in parallel with the market growing for LED. Methods used to grow sapphire crystals are Bernoulli, Kyropoulos, CZ and HEM (Heat Exchange Method). The plane direction and diameter of sapphire single-crystal wafer varies depending on its application; for example, 2- to 4-inch diameter, C-plane wafer is used for LEDs and 6-inch diameter, R-plane wafer is used for SOS (Silicon on Sapphire) devices. In the future, the trend toward enlarged wafer size will continue.

2.2 Single-Crystal Scintillator for Radiation Detectors

PET (Positron Emission Tomography) medical imaging diagnostic equipment has become popular rapidly, ever since it was approved for health insurance coverage in Japan and demand for the scintillator material used in PET is growing. Many years ago, we produced BGO ($Bi_4Ge_3O_{12}$) scintillation single crystals for PET on a commercial scale for the first time in Japan and newly proceed to develop GSO. GSO as a world first practically applied scintillator which has the luminescence center of Ce. The Ce luminescence center enables high-speed compared to conventional NaI:Tl, and BGO, and the realization of high performance PET.

LSO (Lu_2SiO_5: Ce), LGSO and LYSO ($Lu_{2-X}Y_XSiO_5$: Ce) are used in the latest TOF-PET (Time of Flight PET)[1]. By doping Ce as the luminescence center of the scintillator, an excellent timing resolution is realized. A photo of our ϕ90-LGSO single crystal is shown in **Figure 1**.

Triggered by market expansion of PET, new single-crystal scintillators are developed aggressively. We developed GPS (Ce-doped $Gd_2Si_2O_7$) single crystal scintillators jointly with Hokkaido University. GPS excels in energy resolution due to its high light output and short decay time with 50 to 100 ns. Since GPS contains no radioactive isotopes, it is expected to be used in a wide range of applications such as SPECT (Single Photon Emission Computed Tomography) medical image diagnostic equipment[2].

Other scintillator applications include various types of survey meters, radiation detectors for oil wll loggings and detectors for physics research. Regarding a recent topics linked to the discovery of the Higgs particle by CERN (The European Organization for Nuclear Research), contribution of around 80 thousand PWO($PdWO_4$) scintillators placed at the CMS detector facility in CERN must be pointed out[3].

Figure 1 ϕ90-LGSO Single Crystal

2.3 Future Evolution of Our Single Crystal Material

These days, the development of earth-conscious materials, such as SiC single crystal for power devices and sapphire single crystal for LEDs are attracting attention. We wish to contribute to society by developing new environmentally friendly single-crystal material. Also, to put single crystal to practical use, we will actively promote resource saving and resource circulation by conserving natural resources and recycling in the fabrication/manufacturing process.

3 Ceramics

3.1 Trend of Ceramic Material

Presently, ceramics can be deemed an essential industrial material, like metal materials such as iron and organic materials such as plastics. In general, ceramics based on polycrystalline, with strong chemical bonds formed by ionic or covalent bonds, can be characterized by its high melting point, high chemical resistance, high strength, high hardness and good stability. However, ceramics is generally brittle.

Main industrial ceramics include simple metal oxides such as SiO_2, MgO, Al_2O_3 and ZrO_2; complex oxides such as $BaTiO_3$ and PZT (PbO-ZrO_2-TiO_2 system); carbides such as B_4C and SiC and nitrides such as AlN, Si_3N_4 and BN. Many of these materials comprise elements with large Clark numbers, which are thus deemed environmentally friendly.

The performance and characteristics of ceramics composed of polycrystallines may vary depending on differences in microstructure, additives and sintering conditions. By exploiting such characteristics, special featured ceramics called fine ceramics are manufactured by well-controlled chemical composition, microstructure, shape and production, etc. The fine ceramics can be roughly classified into two groups, namely functional ceramics and structural ceramics. The fine ceramics has a wide variety of application as a most advanced parts and products in the field of IT, automobile, biotechnology, energy and so on.

As one example, our developed ZrO_2-toughened Al_2O_3 ceramics is a material with excellent fracture toughness better than conventional Al_2O_3 ceramics. Moreover, its superiority in both impact and wear resistance means it is employed in various types of consumable parts for grinder mill and wearing parts. Further, our SiC ceramics have high hardness, high thermal conductivity and are used as pump seals for cars. The unique combination of hard SiC and soft carbon forms liquid layer on sliding surface and enhances the lubricative property.

3.2 Ceramics for Semiconductor Device Manufacturing Equipment

Semiconductor devices are used in electronic equipment such as PCs, cellular phones and gaming machines and their use is expanding in parallel with progress in IT technology in automobile and home appliance fields. Integration density of semiconductor devices increases annually according to design rules, and productivity enhancement also rises due to increasing silicon wafer size. A substantial quantity of ceramics is used in semiconductor manufacturing equipment by exploiting their high stiffness and thermal conductivity, low thermal expansion and superior chemical resistance.

For example, ceramics with high specific rigidity and low thermal expansion are required for semiconductor manufacturing equipment to enhance its positioning accuracy and improve throughput. To meet such requirements, we have optimized chemical composition, sintering aids and additives, and developed ceramics with a coefficient of thermal expansion (CTE) of which becomes zero at around room temperature. Our low-CTE ceramics and thermal expansion data are shown in **Figures 2** and **3** respectively. For practical application of the low CTE ceramics, it will be important to measure CTE with high precision and high reliability[4] to require the stability and reproducibility of CTE. Accordingly, AIST (National Institute of Advanced Industrial Science and Technology) and we have jointly developed a measuring method of CTE applicable to such low CTE ceramics with ease and #####. Consequently, we can constantly supply low-CTE ceramics with less than 20 ppb/K, thus enhancing the precision of semiconductor lithography.

Figure 2 Low CTE Ceramics

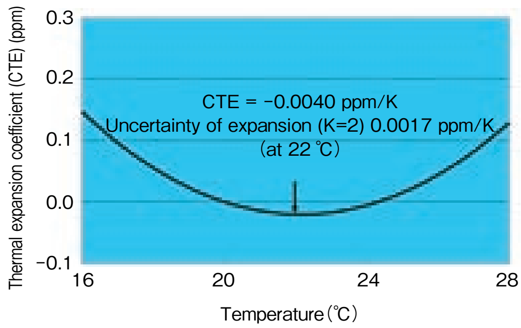

Figure 3 Thermal Expansion for Low CTE Ceramics

3.3 Evolution of Our Ceramic Material in Future

As mentioned above, we have been engaged in developing our ceramic materials; focusing on fabricated ceramics tailored for specific structural applications. Henceforth, we plan to fabricate the surface of ceramics chemically or to make hybrid of resins to add new function for the development of new applications. Further, we want to promote Global Environment Friendly Manufacturing by improving manufacturing technology, e.g. near-net shape technology, to reduce manufacturing waste and low-temperature sintering technology to reduce energy consumption.

4 Glass

4.1 Trend of Glass Material

Glass material shows glass-transition phenomena. In other words, glass has a unique feature to change itself from a solid state to a viscous fluid at glass-transition temperature or higher; allowing it to be shaped into various forms. Also in general, glass shows certain characteristics such as transparency and insulation, does not bend or rust, but is brittle. Such characteristics mean glass is used in everyday domestic items, such as windows, cups and bins, fluorescent bulbs, TV screens and automobile windshields. Recently glass has also been used in many industrial fields such as electronics, optics, display, storage and energy thanks to its freedom of composition, moldability, high strength and functional additionality as well as the aforementioned basic properties. These types of high-performance glass are called “new glass”.

Areas in which new glass can play active roles include optics, specifically transmission via optical fibers, optical amplifiers and non-linear optical glass in industrial fields. Synthetic quartz and fluoride glass varieties with distinguishable UV light transmission are used in IC photo masks and projector lens. The demand for glass in the display field is increasing alongside expanded liquid crystal applications. Thermal barrier super-insulated multi-layered glass, dimming glass and UV cut glass in automobile and construction areas, substrate glass in thin film solar batteries and glass film of fuel batteries in the energy field are already being practically applied.

4.2 Low-melting-point Glass

Electronic parts such as crystal oscillators, IC ceramic packages, MEMS (Micro Electro Mechanism Systems) and semiconductor sensors often employ hermetic sealing at 400 ˚C or less, using glass melting at low temperatures and containing significant poisonous lead or expensive Au/Sn solder. Lead-based low-melting-point glass contains fluorides to lower the melting point and cannot be used for vacuum sealing, given the tendency of fluoride to vaporize. In general, lowering the melting point of glass tends to reduce its reliability, due to moisture resistance and other factors. Conversely, Au/Sn solder is a highly reliable material, with the impact on environmental load in mind. Also, since it can be hermetically sealed, it has been employed as a low-

temperature sealing material for electronics parts requiring enhanced performance and reliability. With this background in mind, new high-performance and reliable sealing material allowing low temperature sealing at 400 ˚C or less, further miniaturization with environmental impact and cost in mind was needed. With that, we developed vanadium-based low-melting-point glass that can be sealed at 350 to 400 ˚C and contains no poisonous lead nor any other controlled substance jointly with Hitachi Research Laboratory, Hitachi, Ltd.

Conventional glass containing significant V_2O_5 has layer structures resembling V_2O_5 crystal and there were problems of structural disorder, whereby the grinding atmosphere or water molecules contained in the solvent was prone to penetrate between the layers to weaken the adhesion between them and leading to structural disorders. Accordingly, in this development work, we changed its structure to one of a 3D network, which was effective against water molecules penetration by controlling the ionic valency of vanadium. Further we could also successfully lower the melting point, preventing crystallization and significantly enhancing reliability, e.g. in terms of moisture resistance, by incorporating many elements with a large ionic radius and low-melting-point into the intermediate spaces of the network structure. The exterior appearance of our developed glass is shown in **Figure 4**, and the relations between sealing temperatures of various glasses and CTE are shown in **Figure 5**. Conventional lead-, bismuth- and tin-based glasses tend to increase CTE alongside decreasing sealing temperature. Moreover to date, bismuth- and tin-based glass have not been sealable at 400 ˚C or less.

Samples of the environmentally friendly vanadium-based low-melting-point glass we developed are shipped as pastes or powders and the property of the developed product is shown in **Table 1**. Because the CTE of the developed glass can be controlled over a wide range and is compatible with ceramics, glass, metal and semiconductors, we anticipate applications to various electronics parts in future.

Figure 4 Samples of V-based Glasses

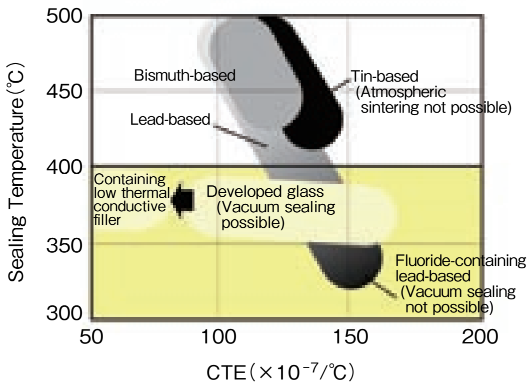

Figure 5 Relationship between CTE and Seal Temperature for Low Melting Glasses

Table 1 Properties of V-based Low Melting Glasses

Glass product number	VP−1175	VP−1176	VP−1177	VP−1179
Standard sintering condition	370 ℃−10 min	380 ℃−10 min	390 ℃−10 min	400 ℃−10 min
Color	Black	←	←	←
Specific gravity	4.0	3.7	3.8	3.7
CTE*1 ($\times 10^{-7}$/℃)	160	105	75	60
Standard average particle size (μm)	3	←	←	←
Moisture proof resistance: PCT*2	Good	←	←	←
Acid resistance*3 (%)	<1	←	←	←

*1 : 25–250℃
*2 : Saturation-Type Pressure Cooker Test (PCT : 120 ℃−100%Rh−202 kPa)
*3 : Dissolution in dilute nitric acid

4.3 Evolution of Our Glass Material in Future

The vanadium-based low-melting-point glass we developed not only features a reduced environmental load but can also be heated by light sources such as various lasers. This means the glass area alone can be heated and glued without heating the whole body, including the elements with low heat resistance and substrate. Henceforth, by exploiting these featured characteristics, we plan to use our glass for partial heating, sealing and adhesion of elements and metals, while preventing thermal degradation.

5 Summary

The development trends of inorganic materials, including single crystals, ceramics and glasses as well as our products, are reviewed. In recent years, these inorganic materials have been considered indispensable for key parts and devices in semiconductors, automobiles and life science equipments. We continue these developments, in the hope that our inorganic materials may benefit humankind and preserve the earth environment.

【References】

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