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High-purity quartz. Application in high-tech industry, current quality's requirements

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Annotation

Purpose of the study. The article discusses the main areas of HPQ application, taking into account the newly emerging applications. The HPQ's main criteria and quality parameters are analyzed on the example of the world's leading manufacturers, including the Russian Quartz company.

Outcomes. The HPQ's main quality criteria in terms of chemical purity, gas-liquid and foreign inclusions have been determined. The HPQ's usage in different hi-tech application was indicated depending on the content of impurities.

Introduction

Quartz is one of the most widely distributed minerals on Earth. It is used in glass, construction, metallurgy and many other industries. Some quartz deposits have reserves estimated at tens of millions of tons of quartz ore.

At the same time, very few deposits are suitable in terms of volume, quality and suitability for the production of high-purity quartz (HPQ). This term (HPQ) refers only to quartz concentrates obtained from the direct beneficiation of natural quartz ore and does not refer to other kind of high-purity silicon dioxide, for example such as artificial quartz crystals (AQC) obtained by hydrothermal growth.

Despite the wide distribution of sources of quartz raw materials of various genesis (quartz sands, vein quartz, quartzites, pegmatites, alaskite, etc.), the requirements for the quality of quartz used for the HPQ production strongly limits the possible sources for raw materials. There are only two known deposits in the world which are fully certified by customers for usage in all HPQ applications, including the semiconductor industry. It is Spruce Pine deposit, USA (pegmatites and alaskite) [1] and Kyshtym deposit, Russia (vein quartz) [2].

Such a small number of certified deposits is due to the very high specific requirements of the modern hi-tech industry for the HPQ quality.

In addition being at the junction of traditional mining and processing industries with their tendency to mass production with capacity in the amount of millions of tons per year, on the one hand, and the high-tech industry with requirements for the purity of products, calculated in particles per billion, on the other hand, the HPQ is very specific, having few analogues in the world industry.

Outcomes

The unique properties of quartz glass and products made from HPQ (high chemical purity, light transmission in the ultraviolet part of the spectrum, thermal stability, etc.) make HPQ one of the so-called "basic" materials for a number of high-tech application - semiconductors, solar energy, special high-purity optics and lighting equipment, aerospace technologies and telecommunications. In particular 95% of the world's volume of monocrystals of silicon is grown using the Czochralski method [3], including semiconductor quality. At the same time the growth of monosilicon takes place in quartz crucibles which produced from HPQ. It means that HPQ is involved in the manufacture of almost every microelectronic device in the world from the simplest device to supercomputers.

For a long time the traditional areas of application of HPQ [4] are:

– in the semiconductor industry – outer (opaque) and middle (transparent) layers of three-layer quartz crucibles of semiconductor quality for growing monocrystals of silicon according to the Czochralski method; tooling used in the manufacturing and processing of semiconductor-quality silicon wafers (quartz reactors, cassettes, tubes, rods, wafers);

– in photovoltaics – outer (opaque) and inner (transparent) layers of two-layer quartz crucibles of "solar" quality for growing monocrystals of silicon according to the Czochralski method; tooling used in the process of manufacturing and processing silicon wafers of "solar" quality (quartz reactors, cassettes, pipes, rods, wafers);

– in lighting engineering – ultraviolet, halogen and high-temperature lamps;

– in the optical industry – emitters for microlithography, optics for excimer lasers, mirrors for optical telescopes and much more;

– in the fibre optic industry – the protective sheath of the optical fibre produced by the APVD process;

– in microelectronics – filler for EMC compounds.

Different areas of application determine a number of HPQ's grades produced by manufacturers depending on the required quality and price parameters (Table 1).

Table 1. HPQ's grades from world manufacturers used in the hi-tech application

Application	HPQ manufacturer		
	Sibelco	The Quartz Corp.	Russian Quartz
Semiconductor industry	IOTA STD-SV, IOTA 4, IOTA 6-SV, IOTA 8	NC4A, NC4X, NC4XF	RQ-2K, RQ-1K
Lighting & Optics	IOTA STD, IOTA 4, IOTA 6, IOTA CG	NC4A, NC4X, Q4DH	RQ-3K, RQ-2K, RQ-1K
Photovoltaics	IOTA 4, IOTA 6, IOTA CG	NC4A, NC4A-CG, NC4AF, Q4DH, NC4X	RQ-2K
Fiber Optic Industry	IOTA 6-SV, IOTA 8	NC4XF	RQ-1K
Microelectronics	–	NC1-LA5, NC1-LA12, NC1-LA20	–

A separate category includes the production of a new generation of high-purity materials using the high chemical purity of HPQ, for example for the production of semiconductor-grade silicon carbide used in power microelectronics and improved quality silicon carbide for various applications by carbothermal reduction [5].

There are three main criteria for the HPQ quality:

1. Chemical composition. Depending on the application, customers have different requirements for the chemical purity of HPQ but in general, current quality standards say that the total content of regulated impurities in HPQ should not exceed 20 ppm [6]. At the same time, some industries limit the content of certain elements in HPQ within very strong limits – for example, the iron content in HPQ used in photovoltaics should not exceed 0.5 ppm, and the content of boron and phosphorus should not exceed 0.1 ppm. For the semiconductor industry, the iron content should be no more than 0.1 ppm, and the copper, chromium and nickel content for the most critical applications in the semiconductor industry should be no more than 0.005 ppm for each of these elements, and the uranium and thorium content should not exceed the level of 0.5 ppb.

Historically the global quality standard has been IOTA grades produced by UNIMIN (now Sibelco), the chemical composition of which is determined by the chemical composition of quartz ore from the Spruce Pine deposit (USA) [7].

This situation makes it difficult to bring to market and certify HPQ from new sources, since natural quartz from various deposits has a unique chemical composition and distribution of impurity elements, which does not allow it to fall exactly within IOTA specifications.

However at this moment customers of high-purity quartz are more flexible in determining the chemical composition requirements for HPQ depending on the industry. For example titanium content is important for UV applications because titanium significantly reduces light transmission in the UV range. This factor is not critical for the photovoltaic and semiconductor industries. At the same time, the content of impurities such as sodium, potassium, boron, phosphorus (target content less than 0.1 ppm), copper, chromium and nickel (target content less than 0.005 ppm) are important for the semiconductor industry but not so strong for lighting technology.

Typical values of the content of impurities in the most commonly used HPQ grades supplied by the world's main producers (Sibelco (USA) [8], The Quartz Corp. (USA) [9], Russian Quartz (Russia) [10]) are given in Table 2.

Table 2. Typical Impurity Content in the Most Commonly Used HPQ Grades (in ppm)

Element	Producer					
	Sibelco		Russian Quartz		The Quartz Corp.	
	IOTA STD	IOTA 6-SV	RQ-2K	RQ-1K	NC4A	NC4X
Al	14	8	3,9	3,6	13	13
B	< 0,10	< 0,05	0,07	0,07	< 0,1	< 0,1
Ca	0,3	0,5	0,12	0,1	0,5	0,5
Cr	0,006	0,002	< 0,01	< 0,001	< 0,01	< 0,01
Cu	0,028	0,001	< 0,010	< 0,001	< 0,01	< 0,01
Fe	0,3	0,1	0,20	0,05	0,2	0,1
K	0,7	< 0,1	0,13	0,03	0,5	0,11
Li	0,5	0,2	0,3	0,29	0,4	0,4
Mg	0,04	0,02	0,05	0,07	< 0,1	< 0,1
Mn	0,039	0,004	0,004	< 0,001	< 0,1	< 0,05
Na	1,0	< 0,05	0,30	0,05	0,8	0,05
Ni	0,001	0,001	< 0,01	< 0,001	< 0,01	< 0,01
Ti	1,2	1,3	2,9	2,9	1,2	1,2

2. Gas and fluid inclusions (GFI). The presence of GFI in the grains of natural quartz determines the quality of quartz glass obtained from HPQ and is as important a parameter as the chemical purity of quartz. A number of technological properties of HPQ depend on GFI: losses during ignition, light transmission, and the rate of crystalbolitization [11]. Due to the high viscosity of quartz glass, GFI inherited from grains do not have the opportunity to escape from the molten glass mass and lead to the appearance of glass defects in the form of bubbles and capillaries, up to complete opacity of the melted glass. The content of such defects in glass is strictly regulated (See example in Table 3).

In Russian practice is used a very effective method of measuring of GFI content is the light transmission coefficient (T*, %) in an immersion liquid*. The light transmission coefficient of HPQ should be at least 80%. For example the light transmission coefficient of quartz from the Spruce Pine and Kyshtym deposits is in the range of 85–88% [13].

Table 3. Example of Bubble Requirements for Quartz Crucibles for Photovoltaics According to the Standard of the China Electronic Materials Industry Association [14]

Units. Measurements: mm

Name of the defect	Location		Requirements (pcs per 1 crucible), crucible size	
			D ≤ 22"	*D* > 22"
Bubbles	Inside the walls of the crucible		Ø > 2.5 are not allowed 2.0 < Ø ≤ 2.5 ≤ 2 pcs. 1.5 < Ø ≤ 2.0 ≤ 3 pcs. 1,0 < Ø ≤ 1,5 ≤ 5 pcs. 0.5 < Ø ≤ 1.0 ≤10 Pieces Ø ≤ 0.5, see p.5.2.2	Ø > 2.5 are not allowed 2,0 < Ø ≤ 2,5 ≤ 3 pcs. 1.5 < Ø ≤ 2.0 ≤5 Pieces 1.0 < Ø ≤ 1.5 ≤10 Pieces 0.5 < Ø ≤ 1.0 ≤12 Pieces Ø ≤ 0.5, see p.5.2.2
Bubble Clusters	Smooth inner surface of the crucible	Inside the walls of the crucible	Ø > 2.5 are not allowed 2,0 < Ø ≤ 2,5 ≤ 3 pcs. 1,0 < Ø ≤ 2,0 ≤ 5 pcs. Ø ≤ 1.0 ≤ 8 pcs.	Ø > 3.0 are not allowed 2,0 < Ø≤2,5 ≤ 5 pcs. 1,0 < Ø≤2,0 ≤ 8 pcs. Ø ≤ 1.0 ≤ 12 pcs.
	Area within 300 mm2	Inside the walls of the crucible	Should not exceed 2 pcs.	

3. Foreign inclusions. Foreign inclusions (commonly referred to as "black" and "white" dots) in the HPQ can be generally described as 2 types:

1) mineral impurities that have not been removed during the process of enrichment of quartz ore

2) technological contamination in the process of purification [15].

As a rule a very small amount of such impurities (for example, in the semiconductor industry in the manufacture of quartz glass blocks is allowed to be no more than one foreign particle with a size of more than 1 mm per 20 kg of glass) does not allow us to confidently determine them by chemical analysis. So the quality of HPQ in this case can be evaluated only after melting of quartz glass by the number and size of inclusions in product (See as example Table 4).

Table 4. Example of Requirements for the Content of Foreign Inclusions in Quartz Crucibles for Photovoltaics According to the Standard of the China Electronic Materials Industry Association [14]

Units. Measurements: mm

Name of the defect	Location	Requirements (pcs per 1 crucible), crucible size	
		D ≤ 22"	*D* > 22"
Inclusions/contaminants	Inner surface of the crucible	Ø >1.5 are not allowed 0.5 < Ø ≤ 1.5 ≤ 2 pcs. Ø ≤ 0.5 is not taken into account	Ø >2.5 are not allowed 1.5 < Ø ≤ 2.5 ≤ 2 pcs. 0.5 < Ø ≤ 1.5 ≤ 4 pcs. Ø ≤ 0.5 is not taken into account
	Inside the walls of the crucible	Ø > 2.5 are not allowed 2.0 < Ø ≤ 2.5 ≤ 2 pcs. 1.5 < Ø ≤ 2.0 ≤ 3 pcs. 0.5 < Ø ≤ 1.5 ≤ 5 pcs. Ø ≤ 0.5 is not taken into account	Ø > 3.0 are not allowed 2,0 < Ø ≤ 3,0 ≤ 3 pcs. 1.5 < Ø ≤ 2.0 ≤ 5 pcs. 0.5 < Ø ≤ 1.5 ≤ 8 pcs. Ø ≤ 0.5 is not taken into account
		No more than two long black dots with the following dimensions are allowed: Length ≤ 5 mm, ≤ 1.5 mm	

Depending on the application, the content of defects (number and size of bubbles, impurities etc.) in quartz glass is determined by both industry standards and the specific requirements of HPQ customers. As a rule, such requirements are a non-disclosed information.

Conclusion

It should be noted that at present, in connection with the development of the global high-tech industry, there are become more and more new HPQ application, which have their own requirements for the HPQ quality. This situation open up new opportunities for the involvement of new deposits and types of quartz raw materials in industrial usage.

On the other hand, the requirements for the HPQ quality from traditional customers are becoming more and more stronger due to the introduction of new technological processes, which forces manufacturers to improve their technologies for HPQ purification. Therefore the current HPQ's quality standards are not immutable and have a constant tendency to reduce the content of impurity elements, approaching to the limit of the beneficiation of the quartz ores.

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