

石英原料在太阳能产业及其他高科技 工业中的应用前景 ——以哈萨克斯坦和埃及为例

O B Beiseyev¹, 李有柱², A O Beiseyev¹, A M Zayed¹

(1. Kazakh National Technical University Named After K I Satpayev, Almaty 050013, Kazakhstan;

2. 长安大学, 地球科学与资源学院, 陕西 西安 710054)

摘要: 人类开发应用石英具有悠久的历史, 早在石器时代, 人类就曾将石英作为装饰品、工具、法器、武器、日用品等应用; 在工业时代, 石英主要作为玻璃原料及冶金熔剂使用; 当代, 石英广泛应用于许多工业和高科技领域。近年来, 石英作为可再生能源及其它高科技领域用的材料, 特别是以石英为原料制备多晶硅及单晶硅作为微电子学材料及太阳能利用材料方面展示了广阔的前景。但这个领域对石英纯度的要求很高, 通过传统的提纯和晶体生长技术将石英转化为硅很不经济, 因为传统方法大量使用氯、氯化氢及四氯化硅对环境有负面影响。而开发闭路循环技术系统或使用高纯度石英原料是解决这个问题的重要途径。前者取决于化学冶金技术水平, 而后者则取决于矿产地质。因此, 高纯度石英的找矿评价及工业硅的提纯是大力发展太阳能产业的重要途径。目前, 以石英为原料进行高纯半导体材料和微电子材料等的合成在有些国家已经大规模工业化, 并形成产业, 如太阳能产业和高科技工业。据预测, 在 2010 至 2012 年间, 高纯石英原料将会短缺且竞争激烈。根据发达国家的实践经验, 在哈萨克斯坦建立用于太阳能和其它高科技工业的高纯石英基地具有重要的理论和现实意义。哈萨克斯坦高纯石英资源丰富, 在哈萨克斯坦中部, 变质成因的石英脉及交代型的石英岩很普通, 在东部、中部、南部和西部, 石英结晶花岗岩则很多, 水晶矿床则主要集中在哈萨克斯坦的西南地区, 花岗岩侵入体的水晶矿以及粒状石英脉几乎在哈萨克斯坦到处都有分布, 结晶花岗岩则分布在哈萨克斯坦北部和南部地区, 但是该国针对高纯石英的工业化研究与应用则很少。埃及的石英原料也很丰富, 主要矿床位于该国中部和东南部地区, 工业化研究与应用也很少。建议这两个国家将高纯石英原料作为太阳能产业及其它高科技产业发展的重点研究领域。

关键词: 石英; 硅; 太阳能; 哈萨克斯坦; 埃及

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Past, Present and Future of Quartz-universal Material for Solar Energy and Other High-tech Industries in Kazakhstan and Egypt

O B Beiseyev¹, LI You-zhu², A O Beiseyev¹, A M Zayed¹

(1. Kazakh National Technical University Named After K I Satpayev, Almaty 050013, Kazakhstan;

2. School of Earth Sciences and Resources, Chang'an University, Xi'an 710054, Shaanxi, China)

Abstract This paper presents the results of theoretical generalization and analysis of materials in terms of occurrences and using of quartz raw materials and its varieties from prehistoric times to the present, and gives the scope of quartz exploitation in the manufacturing of jewelry, technical, medical, bio- and echo-defense destination. Particular attention of studying the problem of using quartz as a raw material base for the production of

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作者简介: O B Beiseyev(1935-), 男, 教授, 理学博士, 哈萨克斯坦科学院院士, 从事地质矿物学研究。E-mail: beiseyev@mail.ru

polycrystalline and monocrystalline silicon, and creating a cluster of solar energy and microelectronics in Kazakhstan and Egypt, which have huge reserves of high-purity quartz and favorable climatic conditions for the development of solar energy with presence of more than 300 sunny days in their territories. It was also noted that, in connection with the forthcoming depletion of traditional energy, mainly oil and gas, solar photovoltaic market will steadily grow and become a very promising not only technically but also in commercial terms. The quartz resources data of Kazakhstan and Egypt and the ways of their rational utilization are given.

Key words: quartz; silicon; solar energy; Kazakhstan; Egypt

0 Introduction

Quartz is one of the most common minerals and belongs to silicate varieties, which is the most widespread mineral group in the earth crust, occupying 75%. The volume content of quartz in silicate tetrahedron is about 12% of this percentage. Quartz is the main source of silicon and the second most common element in the crust of earth. According to the degree of crystallinity, quartz raw material is divided into holocrystalline, cryptocrystalline and amorphous^[1].

The first jewelry group includes the varieties of quartz, such as quartz crystal (colorless), amethyst (purple), citrine (yellow), rose quartz, aventurine (white with a strong green reflections), praseolith (onion green), morion (black), Perun (blue, no natural analogs^[1]), Rauchtopyaz (smoky quartz). In weathering zones, crocidolite deposits also occur hypergenetic-metasomatic variety of quartz, which is referred to "tiger's eye" (yellow lamellae and brown aggregates), finely germinated with ventilated crocidolite fibers (asbestos) and "a falcon eye" also lamellar, but germinated from intact aggregates of fibers crocidolite-asbestos. In addition, the Alpine-type veins are frequent so-called "hair-worm" (quartz crystals), fine-germinated with actinolite-asbestos fibers or bissoilite, and in metamorphites and metasomatites with acicular aggregates of rutile.

Chalcedony and their variety refer to the cryptocrystalline quartz raw materials, while opals and their variety refer to amorphous. The sources of silica materials include quartzite, jasper, organic and meta-biogenic siliceous raw material, such as diatomite, radiolar-

ite, rotten stone, flask (silica clay), novokulite, marshallite and slicified wood^[1-4].

1 Historical Aspects

Silica in its various forms is used by humans from ancient times. According to Melnikova^[2] from the early period, it could be as early as the Stone Age, jasper and rock crystals in the Urals in the era of the Middle Paleolithic. In the Neolithic flint, rock crystal, jasper and quartz were used as scraper, knives, needles, arrowheads, jewelry. This is proved by the archaeological discoveries during excavations saki burial grounds and parking lots in Pre-Urals 93 000 a BC.

The history of mining in the territory of Kazakhstan is also related to the ancient man of the Stone Age who used siliceous axes, knives, arrowheads. Belgian archaeologists have discovered the most ancient dilapidated flint mines around the world in Egypt about 50 km south of the city of Assuit. According to the isotope analysis, the age of these mines is 33 000 a old and the working out of the crystal veins is dated about 9 000 a BC in average, necklaces, cups, talismans and other subjects of everyday life, a cult and a toilet from agate, chalcedony, cornelian and other varieties of silica found in the tombs Mesopotomii (3 000 a BC), burials bikerov in England, the pharaohs in Egypt (2 000 a BC), early Nomads Lower Urals and Kazakhstan (1 000 a BC) and in other regions of Europe, Asia and North Africa.

2 Application in the Technical Purposes

The next period in the history of the use of silica is connected with the use of veined quartz as

a raw material in glass industry and as a flux in metallurgical manufacture. The discovery of the phenomenon of the piezoelectric effect of quartz crystals by the brothers Pierre and Jacques Curie in 1880 marks the beginning of the third operational stage of silica.

In the 20 century, the intensive use of silica in the form of quartz and agate, rock crystal is further enhanced its role as an important strategic raw materials. At present, quartz is widely used in many fields of technics and high technologies, for example, radio engineering, silica plates are used in the manufacture of resonators and filters of radio frequencies, telephony and telegraphs, microphones, in ultrasonic hydroacoustics, defectoscopy, frequency stabilizers in high-speed computing devices, and high-frequency devices for electrotechnical and electronic industry, in studying the properties of gases, liquids and solids, in piezometer for pressure measurement, definition of vibrations (including vibrations of bridges), for manufacturing of lenses and plates for the purpose of reception of ultrasonic waves, in sound receivers, loudspeakers, accelerographs, manometer, beam echo sounding and other devices. Optical quartz is used in the manufacture of spectrographical prisms, glasses and the lenses transmitting ultra-violet rays, plates and wedges for polarizing microscopes, Fresnel prisms, saccharimeter, polarimeter and other products and devices for semiconductor products and solar panels, plates for photo-electric stations. The detection of new properties and application of quartz and assortment of products continues to grow. Quartz is one of rare species of raw materials, from which jeweller are produced, constructional and decorative building materials (the quartz "carpets", self-leveled floors and walls, the ladder marches, illuminated traffic signs and other materials) working in high temperatures and pressures, in intensive radiation, in chemically active environments, without losing their bioprotective, extracorporal fertilization protection and medical properties^[5]. It is enough to tell that 90% of all

semi-conductors and other high-tech materials are produced from quartz now^[1-3, 6-8].

3 Application for the Bioprotective and Medical Purposes

Silica glass is an irreplaceable material for the protective and security purposes: equipment of artificial satellites and piloted spaceships, the panoramic reactive glass for jet planes, for the manufacture of nasal fairing and monitored rockets, shells, night-vision equipment optical locator systems, systems of interception and fiber-optical communication, intensive and special light sources, in designs of nuclear, laser and radar systems, sensors for the prevention of fire conditions etc.

Particularly and intensive applications of quartz glass in medicine for the manufacture of quartz infrared lamp generators and quartz ultraviolet radiators, optical devices of different purpose, hydrogen, microbicides and actinic bulbs, have been developed. For pharmacological purposes, they are also used carnelian, amethyst, morion, citrine, prasiolite and other colored varieties, which contain radioactive substances in small and permissible doses^[1, 5, 9].

4 Application as a Raw-material Base for the Creation of a Renewable Energy Source and Other High-tech Materials

Now in the public consciousness growing belief, the future energy must be based, on large-scale, on the solar energy. The sun, which is a huge, inexhaustible, absolutely safe source of energy, equally owned by all and accessible to all. The focus on solar photo-energy should be considered as a safe and uncontested choice for mankind. According to Russian researchers' calculations, the power energy of sunlight beams falling on Earth is practically inexhaustible source of heat and light, where the quantity of a solar energy arriving to the

Earth^[3] essentially exceeds the energy received from all world's reserves of oil, gas, coal, uranium and other power resources (Tab. 1).

Tab. 1 World Energy Types and Quantity

Number	Types of energy sources	Quantity / 10 ¹²
1	Coal, oil, gas, thousands of standard fuel	11
2	Uranium, thousands of standard fuel	8
3	Solar energy, thousands of standard fuel/year	131
4	Wind energy, thousands of standard fuel/year	2
5	Hydropower, thousands of standard fuel/year	7
6	Biomass, thousands of standard fuel/year	0.1
7	The world energy consumption, thousands of standard fuel/year	0.01

One of the new directions for the use of quartz glass is the production of poly- and mono-crystal silicon for solar energy and micro-electronic. The basic requirement for all kinds of quartz raw materials is their high chemical purity, the maintenance of harmful impurity in quantity from 1 000 to 10⁻⁶ depending on the appointment of the synthesized products. Therefore, for manufacturing of such products there was a necessity directed by special experimental works on synthesis of monocrystals of the quartz raw materials, different from the natural analogues by high degree of chemical purity (natural quartz type of Melnikov^[2]).

The modern world photovoltaic market is quite complicated, fast-developing segment of the global economy with an increasing growth rate. The reason is firstly the practical orientation of national programs of the highly developed countries: 100 000 solar roofs in Germany, more than 200 000 solar roofs in Japan, 1 000 000 solar roofs in USA; it is allocated with 3 0 × 10⁹ euro for development of photopower till 2010 in EU. Polycrystalline silicon, which is a necessary resource for the manufacture, is not only solar batteries, but also the computer semiconductors. Cost of this kind of silicon in the world markets is currently 300 000 \$/t.

According to the forecasts in 2008 consumption of technical silicon will grow to 1.4 × 10⁶ t.

The main exporters of these raw materials are Brazil, China, USA and Norway; together they have more than 75% of the world market.

The increasing market of solar photo-energy, which is commercially very perspective market, characterized by the following factors: ① by the middle of 21 century, oil and gas reserves will be close to depletion and the solar electricity should compensate their decreasing extraction^[10]; ② increasing emission of carbon dioxide in atmosphere should lead to the accelerated development of ecologically pure solar photo-energy to reduce pollution of environment and global warming; ③ the solar electricity will be a dominating energy source with the ratio of approximately 60% by the end of the century due to practically not exhausted resource of energy (the sun). Beside these factors, concerning energy, there are also the social factors that stimulate the development of solar photo-energy.

At summit EU in Brussels on 9 March 2007, the leaders of European Union agreed about the substantial growth of the use of an alternative energy sources (such as sun and wind). By 2020 in the European Union, these alternative sources should make the fifth part (20%) all volume of the electric power. The decision is obligatory for each of 27 EU countries.

Leaders of EU have agreed about the measures of reduction of emissions of the gases creating the so-called "greenhouse effect". By 2020, emission is planned to be reduce to 20% in comparison with 1990. Kazakhstan could become the next country after Russia, which will be introduced legislation supporting the development of renewable energy sources (RES).

For Kazakhstan and Egypt with favorable weather conditions, which is the presence of more than 300 sunny days during the year, the wide use of photo-energy has great value because a lot of citizens of Kazakhstan, especially in Southern and other remote regions, live without the centralized electro-maintenance. Creation for these citizens the

necessary civilized conditions is the major government problem. One of the optimum decisions is the use of photo-energy.

The most important documents, in our opinion, which can serve for the revelation and development of the Socio-political aspects and legislative framework of the renewable energy sources and their raw materials base in Kazakhstan are the Decree of the President of the Republic of Kazakhstan “Concept of transition of the Republic of Kazakhstan to Sustainable Development for the period 2007-2024”, in which the RSE are considered as a means of improving the environment and reducing greenhouse gas emissions, the economic arguments in favor of renewable energy is also gaining momentum in the forthcoming exhaustion of fossil fuel reserves and the edition of the Law No. 144-IV of 26 March 2009, “On Ratification of the Kyoto protocol to the United Nations Framework Convention on Climate Change”, signed in New York on 12 March 1999.

The Law of the Republic of Kazakhstan “On the support of renewable energy”, No. 165-IV 3RK of 4 July 2009 and Law of the Republic of Kazakhstan “On introducing amendments and additions to some legislative acts of the Republic of Kazakhstan Support for renewable energy”, No. 166-IV 3RK of 4 July 2009.

All these documents support the production of more efficient and ecologically clean energy, including renewable energy. The adopted documents will create favorable conditions for conducting scientific research, R & D, skilled-experimental work on the search, evaluation of high-purity quartz, the development of ecologically clean technologies of enrichment and processing of quartz raw material, construction and operation of facilities for the production and use of silicon as a renewable energy sources, government support to entrepreneurs in the solar energy sector and protection of their rights. Renewable energy sources currently make about 0.1% of the reduction of traditional sources of electricity. It is expected that this figure in 2024

will rise to 5%.

Potential production of polycrystalline silicon in the Republic of Kazakhstan is very important because there are all necessary prerequisites and conditions for the production of polycrystalline silicon; the infrastructure and legislative bases, a source of raw materials of production of (Kazakhstan occupies the 3rd place in the world of stocks of raw materials of quartz for the production of silicon, after Madagascar and Brazil), relatively cheap energy, profitable geographer-economic conditions of the territory, the neighborhood countries, which are the world leader in the production of microelectronics and photo galvanizer and polycrystalline silicon donors, China, India, Russia, South Korea and etc., a sufficient reserve of qualified engineering personnel and labor.

Research of scientists of the Semiconductor Physics Institute of the Siberian Branch of the Russian Academy of Science concluded that low-cost technologies of photoconverters for solar batteries can be received from the amorphous, polycrystalline and multicrystal silicon, taken of high-purity quartz. As evidenced by scientists' researches of several countries to find deposits of high-purity quartz requires a very careful study of almost all genetic types of deposits and the development of a set of diagnostic criteria of selection. In particular the problem of availability of solar energy and microelectronics industry with high quality and relatively cheaper raw materials can be solved by the following way. First of all, it is necessary to pay more attention to high-quality raw materials than the quartzite contaminated by various impurity and, in the second turn, to try to adapt technology of clearing of technical silicon^[3, 6].

The requirements of today for the industry of high-purity quartz materials for semiconductor purposes (tubes, crucibles, reactors, equipment) result in another problem, identifying innovative sources of quartz. This is particularly the crust of weathering of granite massifs, quartz sand, some types of sandstone and quartzite. This area of re-

search requires new approaches; revolutionize our understanding of the traditional sources of raw materials for the quartz fusion, the involvement in the exploration of new regions. Special attention should be paid on silica (glass) sand and quartz kaolin crusts weathered from granitoids.

In this connection, based on the experience of the users of quartz for solar energy and microelectronics of the developed countries, performed effort to prognoses and establish of non-traditional and new fields of high-purity silica for solar energy and microelectronics in the territories of Kazakhstan has an important theoretical and practical significance.

The analysis of the developed situation in the polysilicon market shows that by 2010–2012, shortage of this kind of raw materials can be liquidated and there will be a sharp competition for quality and cost of silicon of “solar” quality as it is observed active development of cheap technologies of metallurgical refinement at laboratory-experimental level. In this concern, intensive development with participation of the countries with advanced technology, China and South Korea in the next years expect occurrence of a new source of manufacture of elite silicon, the refined metallurgical silicon of the “solar” quality, expected volumes of production are shown in table 2.

Tab. 2 Volume of Manufactured Metallurgical Silicon (Solar Silicon) by Different Companies Around the World

Type	Company	Silicon/ 10 ⁹ t	Year
	Trina Solar, China	10	2012
	Sichuan Yongxiang Polysilicon, China	10	
Siemens	LDK Solar Company, China	15	2009
Process	Dalu Polysilicon Company, China	18	
	Norsun As, Jubai Saudi Arabia	25	
	DC Chemical, South of Korea	10	2009
	Dow Corning, USA	10	2010
	EIKem, Norway	10	2008
Metallurgical Refining	Beancour, Canada	15	2009
	Solar Value, Canada	10	
	Jaca Solar Si, China	5	2010

5 Prospects of Kazakhstan and Egypt

As mentioned above, discovering the properties of semiconductor silicon and the extensive use of high-purity, un-defected thin plates of poly- and monocrystal silicon in the micro-electronic require not only revision of traditional technologies of reception and growing of crystals, but also make the choice of the raw materials in our first priority. At the first stage in connection with the requirements of the electrotechnical and microelectronic industry when silicon plates (wafers) of small diameter were made, and the total amount of produced crystals was insignificant, the requirement was completely meet with the continuously developed technology in the 60th year, multistage purification technology of silicon, and recovery (reduction) capro-thermal ways of receiving from a variety of genesis and cleaned quartzite.

In spite of the fact that silica is widely spread in the earth crust and is known in all genetic types of quartz raw materials from magmatogenic to metabiogenic^[1-2, 5, 9]: ①plutono-genic and metamopho-genic quartz veins; ②metamopho-genic-metasomatic quartzites; ③hypergenic-sedimentary sandstone arenite (quartzite-sand stone) and natural-dispersed quartz-glass sand; ④metabiogenic: diatomite, radiolarite, flask (silica clay), rotten stone novokulite, silicified wood; ⑤ nonconventional quartz from the zone of w reathing of the granitic crust, where only the high purity quartz varieties are the basic raw material of silicon reception. It is known that the use of piezoelectric properties of quartz in the defense and space industry was accompanied with the classification of plant production, results of geological estimation, geological prospecting and scientific research works. This led to significant reduction in turn in the number of publications concerning quartz.

The most complete genetic and geological-industrial classification of quartz is developed by Melnikova^[2], which agree with the elite production, ie. free of impurities, and silicon from the

most perspective quartz of hydrothermal origin, quartzites and quartz sand of hydrous sedimentary origin after additional enrichment and purification. As an additional or new nonconventional source of silica raw materials, kaolin core weathered from granitoids^[1].

6 Large Quartz Provinces in Kazakhstan

In the territory of the republic, there are large and widespread usable quartz raw material deposits of high geological and genetical type. Plutonogenic-metamorphogenic quartz veins and metasomatic types (quartzites) are most frequent in Central Kazakhstan. Quartz pegmatites are in East, Central, Southern and Western Kazakhstan^[1, 11-13].

Deposits of rock crystal (source of piez-raw materials) raw materials for optical glass fusion, and reception of elite silicon are basically in the southwestern part of the central-Kazakhstan region, Ulytauskoy zone^[1, 12, 14-15]. In this zone, extends in the meridional direction for 400 km and a width of 70 to 100 km recorded more than 1.6×10^4 crystalline quartz veins emerging at the surface, most of which are concentrated in 12 deposits of rock crystal, these transparent and translucent, precrystalline, milky white quartz veins. On separate deposits, large crystalline pockets and sockets are present (West Aschilysay, Kotra, Serek), but in the majority of deposits stocks of rock crystal which can be selected for extraction of milky-white quartz veins are preserved^[12].

Rock crystal is also found as lenses and sockets in granite intrusions almost in all regions of Kazakhstan. Large crystalline pegmatites are found in North and South Kazakhstan regions. The greatest quantity of pegmatite bodies are found in Zerendinsky, Balkashinsky and Borovsk granite massif (Northern), in granite massif of Kent, Bektauata (Central), in the granite intrusions of Kaib, Maykol, Geltau, Hantau, etc. (Southern) and in the Akzhajljasuky granite massive in the East of

Kazakhstan^[1].

In Kazakhstan, the resources of highly siliceous quartz and quartzitic raw materials are huge (one of the first places in the world). However, Kazakhstan quartz veins and pegmatitic kernels bodies of quartz that are suitable for industry are not studied yet. None of the known quartz vein-field regions, with the exception of some quartz veins of the Ulytauskoy zone, have no data on the chemical composition of their quartz^[1, 11-13].

Major accumulations of granular quartz are concentrated in the quartz-pegmatites^[13], which are formed from substantially silica residual melt in magmatic stage of pegmatization process. Monomineral hydrothermal quartz veins form a group of high-concentration field's vein or located as isolated vein area with large stocks of metamorphogenic quartz^[14-15]. Within the medium massive of Kokshetau and Ulytau, quartz-vein granulation in the field is associated with the shear zones with saturation in separate sites from 10 to 50 of the vein body. Up to date, in the republic territories there are more than 500 deposits and manifestations of quartz raw material of various genetic types, but not all of them are evaluated and explored. The general reserves of prospected object in detail are: plutonogenic-metamorphogenic veins (6.5×10^9 t), metasomatic (quartzites, 7 massifs) about 2.65×10^8 t, sediments (quartzite sandstone natural, dispersed quartz sand) more than 1.0×10^7 t^[1].

Resources of quartz and siliceous raw materials of Egypt are also enormous. But they still have not received proper industrial evaluation, although preliminary data are well suited for use as a source of metallurgical and solar silicon^[8]. The main quartz deposit located in the western regions of the Arabian platform in the central and southern Eastern Desert^[4, 8, 16] in the area of Wadi Fanat-Wadi warabeit, Marwit Alimikan, Marwit Rod El Leqah, etc.

Geochemical studies revealed that the studied quartz deposits have high degree of purity ranging

from 98.0%~99.9%, mechanical resistance ($1.399 \sim 2.232 \text{ kg/cm}^3$), and low water absorption weight percent values (0.02%~0.06%). These characteristics are desirable for the silicon solar cell production after minor upgrading, as well as in other sectors of high technology, including ferrosilicon. Currently, in accordance with modern requirements of quartz raw material for solar energy Iota standard^[3,17], sorting (clustering) of the Kazakh and Egyptian deposits of quartz raw materials and the degree of their suitability for high-tech industries will be carried out.

7 Conclusion

Quartz is one of the most common minerals in the crust. Its Clarke content in the lithosphere is 27%. It has unique physical and technical properties, through which it was exploited in many high-tech industries and the national economy. Quartz, mainly its high-pure varieties, as sources of the elite silicon for solar energy, is becoming a commercial product. In this regard, from year to year, the price of the high-purity quartz and its retrieved silicon are steadily increasing. Among the concentrators and converters of sunlight into electricity, silicon alternatives are not found yet. Therefore, the search, evaluation, exploration and development of quartz raw materials are of great scientific, practical and economic importance.

Kazakhstan and Egypt are leading countries in the world in the resources of quartz raw materials. But their use for the development of solar photovoltaic, is still weak, but has good prospects. It is important to put special thematic and experimental work to assess their suitability as raw materials for production of solar silicon and other high-tech materials.

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