National Innovation Program titled "Manufacture of solar silicon from local quartz under mild energy usage"

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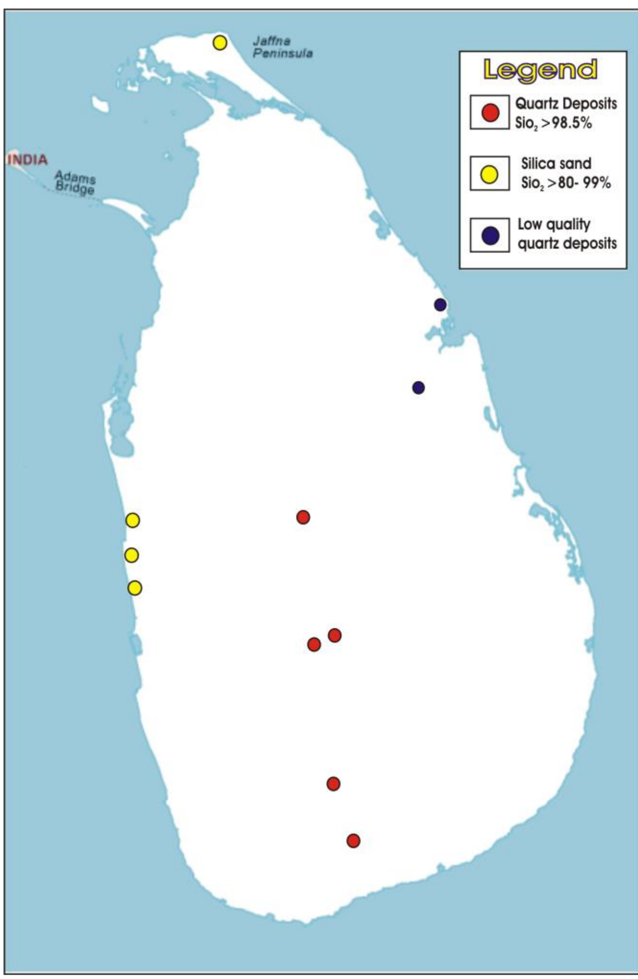
What are the attributes of National Innovation Programs (NIPs)? "These are actually ambitious large-scale, science driven, R&D initiatives providing a strong and broad basis for technological innovation and sustainable economic exploitation in a range of nationally significant areas, as well as novel benefits for the society. These are sometimes called next generation projects".

Back ground information of the primary ingredient, quartz:

Quartz is one of the most abundant minerals found on the earth's surface. It occurs in many different settings throughout the geological history. Silica, as the prime source of the mineral, has a variety of applications such as the manufacture of glass, ceramics, refractory materials and other traditional uses. However, only a very few deposits throughout the world are suitable for high purity applications. Accordingly, high purity quartz has become a key strategic mineral used in high-tech industries that include semiconductors, high temperature lamp tubing, telecommunications, optics, microelectronics and, especially, solar silicon applications.

As far as the high purity minerals are concerned, Mother Nature has been very kind to Sri Lanka because among the many varieties of natural resources it had gifted to Sri Lanka, high purity quartz holds the prime importance and it is found as economically viable deposits in many parts of the country. Geological Survey and Mines Bureau have mapped the country's quartz reserves, but so far ore reserve estimations were not carried out. According to them, vein quartz having purity greater than 98.5% of SiO_2 occurs in economic quantities at Pussella, Opanayake, Rattota, Naula, Galaha, Mahagama (Embilipitiya) and Wellawaya areas. Whereas silica sand of 80% to 99% SiO_2 occurs as economic deposits at Marawila, Nattandiya, Madampe, Sinnapadu and Vallipuram in Jaffna peninsula. In addition, some low quality quartz deposits too are found in areas along Giritale to Trincomalee.

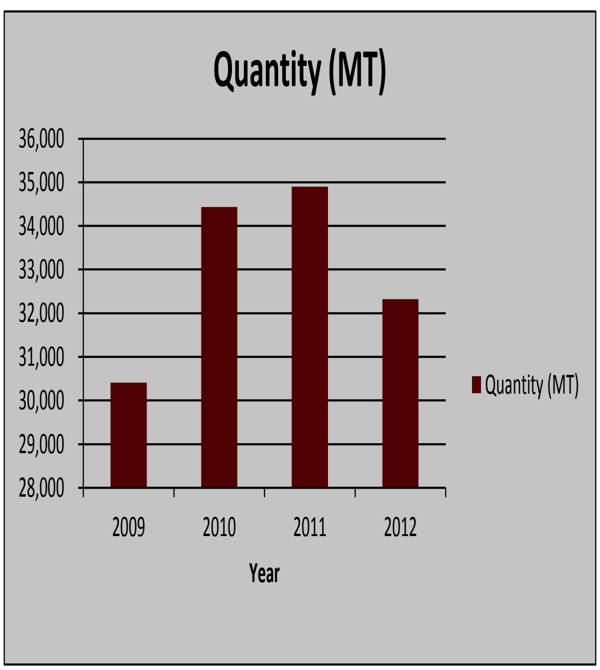


Sri Lankan map depicting quartz and silica sand deposits

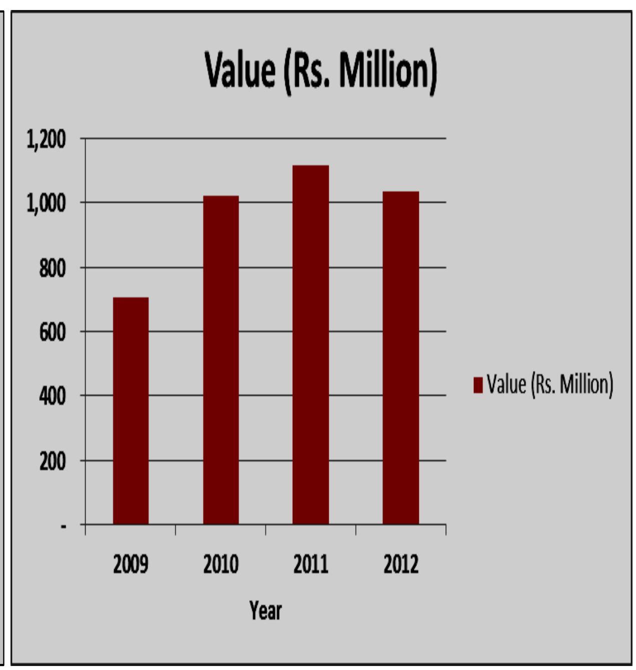
In relation to quartz exploration, licenses are issued only by the Geological Survey and Mines Bureau of Sri Lanka. Exploration license would be granted once the area falls within the limit of 1 km^2 to 100 km^2 and for a maximum exploration time limit of 10 years. In addition, Geological Survey and Mines Bureau also grants an industrial mining license allowing the applicant an exclusive right to explore, mine, transport, process and trade all the minerals mined within the specified areas. The applicant is expected to commence commercial production within two years of the receipt of the mining license in accordance with the Economic Viability Report (EVR). There are three categories of Industrial mining licenses (IMLs) such as IML - A, IML - B and IML – C, in terms of scale of operations; accordingly A is the biggest operation while C is limited to small scale operations. If the miner is intending to export the material mined, IML license should accompany a Mineral Investment Agreement (MIA) duly endorsed by the Secretary of the allied Ministry.

At present most vein quartz deposits were exploited by private companies and exported as raw material without much value addition. Since quartz lump exports were banned from 2010 onwards most companies export quartz in powder form merely removing the iron content (lump form around $100 per MT/ crushed form around $300 per MT). Compared to the lump exports of quartz, powder exports generate higher profits, but that is nowhere equivalent to the prices of value added quartz products ($20 to $ 100 per 1KG of Solar grade Silicon). Following graphs indicate an account of quartz exports from 2009 to 2012 in terms of volume and revenue.

Export of Quartz (Volume)



Export of Quartz (Value)



Export quantities of quartz, country wise (MT)					
	2008	2009	2010	2011	2012
Germany	407	281			40
Japan	21489	9056	13860	16669	12526
South Korea	5910	10838	7920	7111	7220
Malaysia	437	400	680	280	340
Singapore	5700	6140	9460	9184	10292
Taiwan	108		1		20
China		108		110	266
India		43			
	34,051	26,866	31,921	33,354	30,704

Most companies around the world employ simple technology to purify raw quartz such as hand picking, acid washing, etc., meanwhile, high-tech applications require tailor made processing techniques and specially designed equipment to achieve the highest standards sought after by high tech users. Conversion of raw-quartz into refined high-purity products, involves several stages of refinement in order to minimize the impurity level to comply with stringent end-use specifications. As a result, high purity quartz with a total impurity level of less than 20 ppm may be considered a highly valuable raw material. Such material is sought after by many reputed companies involved in high tech applications, especially, solar silicon production. Unfortunately, very few companies in Sri Lanka have this kind of capability. Following table gives some understanding about the purity levels expected by several high-tech applications.

Typical High Purity Quartz Applications

Element	Metallurgical grade silicon[18] (ppm)	Solar grade silicon[7,19] (ppm)	Polycrystalline solar grade silicon[21]	Electronic grade silicon[19] (ppm)
Si*	**99**	**99.9999**	**99.99999**	**99.999999999**
Fe	**2000-3000**	**<0.3**		**<0.01**
Al	**1500-4000**	**<0.1**		**<0.0008**
Ca	**500-600**	**<0.1**		**<0.003**
B	**40-80**	**<0.3**		**<0.0002**
P	**20-50**	**<0.1**		**<0.0008**
C	**600**	**<3**		**<0.5**
O	**3000**	**<10**		
Ti	**160-200**	**<0.01**		**<0.003**
Cr	**50-200**	**<0.1**		
*** Si content in mass%**				

Typical High Purity Quartz Applications

As shown in the table presented different high-tech applications seek different purity levels of quartz. Main applications are in the electronic grade that is semiconductors, high temperature lamp tubing, microelectronics, telecommunication and optics; most importantly, solar silicon industries. The semiconductor industry places the most stringent requirements on quartz purity; from single crystal silicon growth in quartz crucibles via the Czochralski process to the handling and processing of wafers in clean rooms. Fused quartz is the basic material for quartz wafers used in the semiconductor industry since it combines excellent high temperature properties (i.e. thermal shock resistance and thermal stability) and high purity in a unique manner. It withstands the high temperature gradients and high rates of heat transfer in rapid thermal processing, which are commonly applied to wafers in order to modify their properties. The high purity of the quartz prevents the contamination of wafers during different processing stages. The application of high purity quartz as a basic material in high temperature lamp tubing takes the advantage of its high transmission characteristic and its exceptional properties. Among the properties thermal shock resistance and thermal stability found on quartz are quite significant. It is used in the high performance, high temperature lamp manufacturing sectors for UV lamps, mercury, xenon and halogen bulbs; and high intensity discharge lamps. Silica glass is widely used as basic material for optical fibers and additional optoelectronic devices in the telecommunication industry. It is used in laser optics and other specialized applications of the optical industry. In the microelectronics industry, a major application is its use as a filler material in epoxy molding compounds (EMC) for electronic components. Silicon is the most common material for the production of solar cells in the photovoltaic industry either in mono- or polycrystalline form. Specific requirements as to tolerable limiting values differ from industry to industry. In the lamp tubing and optics industries aluminum content in the refined quartz matter should not exceed 20 ppm, other metals should be less than 1 ppm, and total impurities should be less than 30 ppm. For semiconductor base materials and crucibles aluminum content should be even lower, specified amount to be less than 10 ppm, other metals less than 0.1 ppm, and total impurities not to exceed 15 ppm. Feedstock for solar silicon used in the photovoltaic industry should generally have boron and phosphorus contents in the sub-ppm range, since these elements cannot be removed easily and they negatively affect the performance of the solar cells. For microelectronics applications, e.g. in epoxy molding compounds such as uranium and thorium that are responsible for soft errors by alpha radiation, should be less than 2 ppb, and in low alpha applications, even less than 0.5 ppb.

Solar silicon Industry

In solar industry all speculations indicate further growth in the coming years. Production of solar silicon in the 2007–2011 period showed 45% increase. In 2010 solar cell production compared to 2009 was up by 118%, thus, solar cells produced were more than the combined total of all the previous years. Grid parity has now been achieved in a number of countries. Based on the demand in high efficiency cells it is expected to keep on acquiring around 30% share at least for the next 3 years. However, new multi-pulling production techniques (recharging) and larger diameters of the monocrystals will demand more voluminous crucibles, i.e. less crucible silica glass per kg of monocrystals produced (volume to area ratio). The increase in high-purity quartz granule consumption will not equal the upcoming growth in c-Si monocrystal production, but it is still estimated to be above 5% p.a. Manufacturers of solar silicon are endeavoring to remain competitive by pushing production costs down. Prices, which are currently dominated by the demand, probably would diminish to balance the cost. This could attract new technologies which are based on high purity materials and less investment and operating costs to enter into solar silicon market. In addition, it will raise the demand in high quality quartz, especially, low in boron and phosphorus.

Although it is feasible to produce a variety of value added products out of our vein quartz, so far no one had come forward to venture into this type of value added quartz industry. Currently, the most discouraging disclosure is that Sri Lanka still imports end products derived from vein quartz from elsewhere at an exorbitant price such as solar cells, computer chips and silicon carbide, compared to the price of quartz exports. One may ask why Sri Lanka is not adapting the value addition process for quartz and silica sand. Ostensibly, the inference would be that Sri Lanka lacks the necessary technology or the expertise to do so and also the very high prices associated with electricity. Actually the methodology no longer remains a secret. One of the arguments brought forward is that Malaysia's medium voltage industry variable charge is equivalent to SL Rs. 8.62. Although, in Sri Lanka level 2 industries pay Rs. 13.00 for a unit and Rs. 24.15 for a unit during peak hours, it pays only Rs. 8.05 for a unit during off peak hours. As such, the off peak charges are even less than the Malaysia's charges.

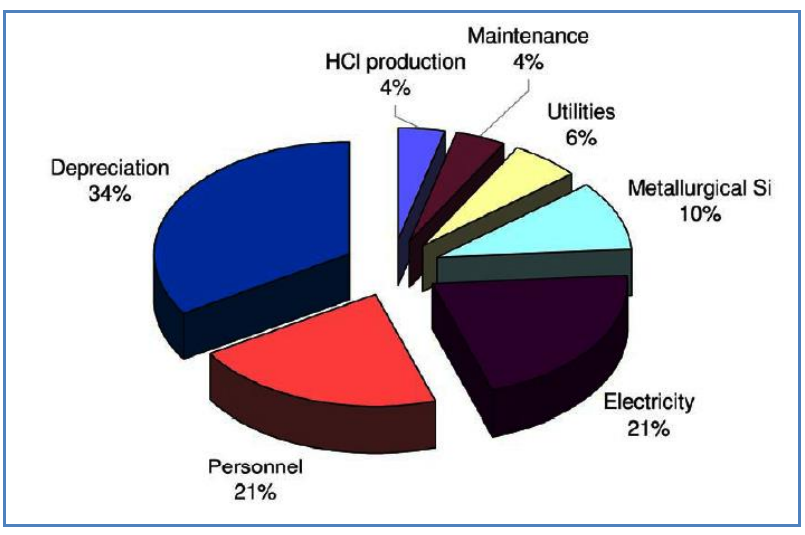
In order to enter into value addition process Sri Lanka has a number of options, such as manufacturing metallurgical grade silica, production of silicon carbide, production of higher grades, manufacture of electronics, semiconductors, solar cells, optical fiber, etc.

When considering the purification levels expected for different applications it must be noted that for solar cells silica must be 99.9999 percent pure (often referred to as "six nines" or 6N pure). The silicon purity grade used in electronics is even more, typically 9N to 11N. In order to reach semiconductor grade, whether for solar cells or integrated circuits, silicon must be processed extensively. The least purification expected is the Metallurgical Grade Silicon (MG-Si).

When quartz obtained from a silica mine is put into a furnace with a carbon source such as coal, coke, woodchips, or charcoal, the mixture gets heated and the silicon is chemically reduced to form liquid silicon, carbon dioxide, and silica fumes. The liquid silicon is poured out of the furnace and further purified. The resulting silicon material is referred to as metallurgical grade silicon (MG-Si).

It is already known that it is easy and economical to produce solar silicon from refining Metallurgical Grade Silicon (MG-Si) instead of direct production of solar silicon from expensive methods such as single crystal silicon growth in quartz crucibles via the Czochralski process. On the other hand, when producing Metallurgical Grade Silicon most of the time silicon carbide too forms as a byproduct, which is also a substance exported to Sri Lanka in very high volumes for a

very high price tag. As such, it is possible to introduce it as an import substitute and stop the huge expenditure for silicon carbide imports. This will create the needed marketing avenue for this product.
When producing solar silicon by refining the Metallurgical Grade Silicon the energy usage can be controlled to a minimum level, thereby, earning the maximum profit. Right now Sri Lanka does not consume much solar silicon, but countries like Germany heavily invest on solar energy and they are on the look out for more and more solar silicon. Therefore, if Sri Lanka produces solar silicon in future it can very easily find the market for its products because silicon is still the dominant material for the fabrication of solar cells, low-cost solar-grade silicon (SoG-Si) feedstock is demanded. World's energy needs are growing at the moment; hence energy production must include renewable energy to assist in decreasing global warming. Using energy more efficiently and reducing carbon dioxide emissions are the two key issues to be addressed in formulating the energy policy for the 21st century. In this connection solar panels made from silicon play an important role in expertly transforming solar rays into energy for people all over the world. In fact, harnessing even 0.3% of the solar energy falling in the Sahara and Middle Eastern deserts is enough to meet the energy needs of the continents of Europe, North Africa and Middle East. The notion among the people that solar power is a more competitive energy source is an important trend towards promoting its growth. A simple formula indicates that 6,000 tons of solar-grade silicon is able to produce 650 MW of energy (solar cells), or an electricity supply for a town of 55,000 for a year. The most critical component in a solar cell is its good quality silicon. Considering Sri Lanka's very high purity vein quartz deposits it is an ideal prospect to venture into the manufacture of Metallurgical Grade Silicon; thereafter, convert it into solar silicon.



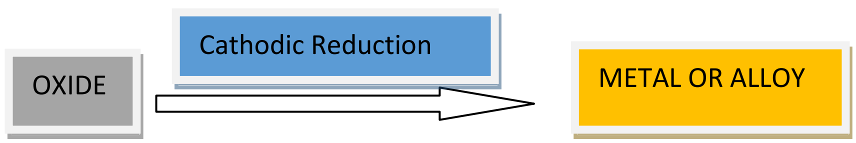
Break down of the cost involved in the manufacture of solar silicon through metallurgical silicon

Right now Sri Lanka exports quartz in lump form for a price of around $100 per MT (although this is banned from 2010 onwards exports are still carried out under different labels) and in crushed form around $300 per MT.; whereas it is possible to earn about $20 to $ 100 per 1KG of solar grade silicon. This is actually an increase of export earnings from 66% to 333%. Because of the global demand for this material; if one invests in this type of venture it is possible to recover the capital within a short period, while maintaining a good profit in the meantime.

Methodology by Professor R.M.G. Rajapakse

Conversion of silica into solar silicon

There are several methods available for the conversion of silica into solar silicon. Out of these methods the one based on electro-reduction of silica into solar silicon is supposed to be the most attractive approach since it is the lowest cost method. This method is generally known as the "FFC CAMBRIDGE METHOD" which is a general method that is applicable for the reduction of many oxides into their metals. In general, the process takes the form



This process is typically carried out at 900 ˚C to 1100 ˚C where the anode material used is typically carbon and the cathode material being the oxide to be reduced. The electrolyte is typically molten calcium chloride.

At the cathodic potential imposed silica generates oxide ions which react with $CaCl_2$ generating CaO. The required cathodic potential depends on the nature of the oxide and also the CaO content present. The normal melting point of $CaCl_2$ is 772 ˚C though that of CaO is 2572 ˚C. The mixture can have a melting point between these two temperatures.

At the anode CO or CO_2 is evolved if carbon is used as the anode material. However, if an inert anode material is used oxygen gas is evolved instead of CO or CO_2.

At the cathode, $MO_x + xCa \longrightarrow M + xCaO$

The CaO produced is then electrolyzed according to the following equations.

$$xCaO \longrightarrow xCa^{2+} + xO^{2-}$$
$$xCa^{2+} + 2xe^{-} \longrightarrow xCa$$
$$xO^{2-} \longrightarrow (x/2)O_2 + 2xe^{-}$$

The net reaction being: $MO_x \longrightarrow M + (x/2)O_2$

LOW-COST OPTIONS

The major cost components involved are the electricity used to melt $CaCl_2$ and to reduce silica. We proposed to bring down the costs involved in both these processes by utilizing our knowledge in nanotechnology. We hope to modify these processes by incorporating nanotechnological modifications to the FFC Cambridge Process.