Chapter

Production and Applications of Synthetic Quartz

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Abstract

Development of quartz industry in these 100 years, in the synthetic production and in application of quartz crystals, is surveyed briefly. Due to the discovery of piezoelectricity in 1880 by J. & P. Curie, the invention of a quartz resonator in 1921 by W. G. Cady, etc., it had been shown that quartz crystal can be used as a superior device material for electric wave telecommunication. After World War II ended, the civil use of quartz devices increased rapidly, in addition to the past military use. The study for large-scale industrial production of synthetic quartz was started first in the United States, and then spread out in other countries. In this development of synthetic quartz, the temperature-difference growth method that is used now was established. Large-sized quartz crystals of good quality (20–25 mm (*X*-direction) × 30–35 mm (*Z*-direction)) came to be obtained by around 1970, and now further large and good-quality crystals are produced. As another remarkable development in the quartz industry, the manufacture and spread of high precision quartz watch and clock should also be mentioned. Industry of synthetic quartz is progressing even now, and quartz devices are used in various places of our every-day life and of social activities.

Keywords: piezoelectric oscillation, telecommunication, quartz resonator, quartz crystal filter, synthetic quartz production, quartz watch, quartz clock

1. Introduction

For its good transparency and beautiful appearance, quartz has been used as a spiritual-powered stone in religious ceremonies and divination and has been valued as accessories and materials for accessories since the early days. It also has been used as an optical material for prisms. However, in the modern ages, the greatest application of quartz has been its use as an electric resonator owing to its highly precise and exact piezoelectric oscillation. Crystal material with such superior characteristics is not found besides quartz, although various crystalline materials have been developed for the electric resonator.

2. Invention of a quartz resonator and its subsequent developments

The quartz resonator stemmed from the discovery of piezoelectricity in a quartz crystal by Jacques and Pierre Curie (France) in 1880. Although the discovery had not been noticed directly, Paul Langevin (France) invented an ultrasonic-wave generator as an application of the piezoelectricity of quartz in 1917, finding that a strong inaudible sound wave is generated due to a responding piezoelectric flexural oscillation of a quartz plate when an alternating electric voltage is applied to it. The ultrasonic-wave generator was used for underwater communication and the search of submarines, etc., in World War I (1914–1918).

After that, in 1921, Walter G. Cady (USA) found that a quartz crystal shows a sharp resonance when changing the frequency of applied voltage to the natural frequency of it [1], and proposed to use such quartz resonators by incorporating them in an electric circuit of telegraphic communication (**Figure 1**), for the stabilization of the communication wave. The quartz oscillator was born thus. In 1923, George W. Pierce (USA) manufactured the so-called Pierce-type quartz resonator [2] by improving Cady's one [1], and this type of resonator came to be used widely in electric communication. The quartz resonator, which was invented by Cady, utilized the thickness longitudinal vibration of an X-cut plate (see **Figure 2(b)**). It was weak in the vibration intensity, and an oscillator that incorporated it had a fault that its operation often was not easy to start. The quartz resonator improved by Pierce utilized the thickness-shear vibration of a Y-cut plate and was large in vibration intensity and easy to start.

However, this Y-cut plate resonator also had a problem that the frequency temperature coefficient (hereafter, f-t coef.) was considerably large ($+100 \times 10^{-6}$/°C), so the resonant frequency shifted a little by a change in room temperature.

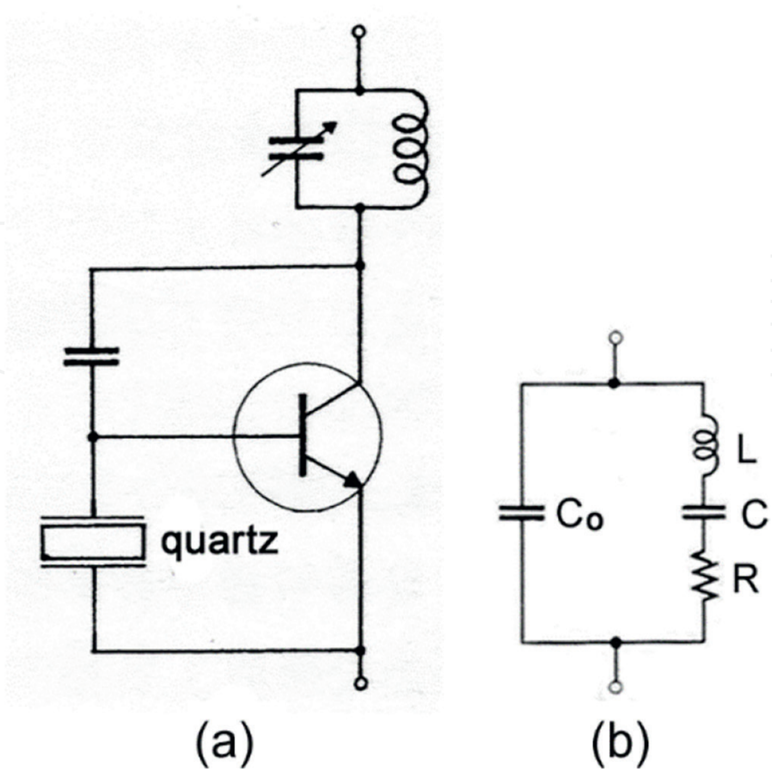

Figure 1.
(a) An example of the oscillating circuit where a quartz resonator is incorporated. (b) Equivalent electric circuit of the quartz resonator.

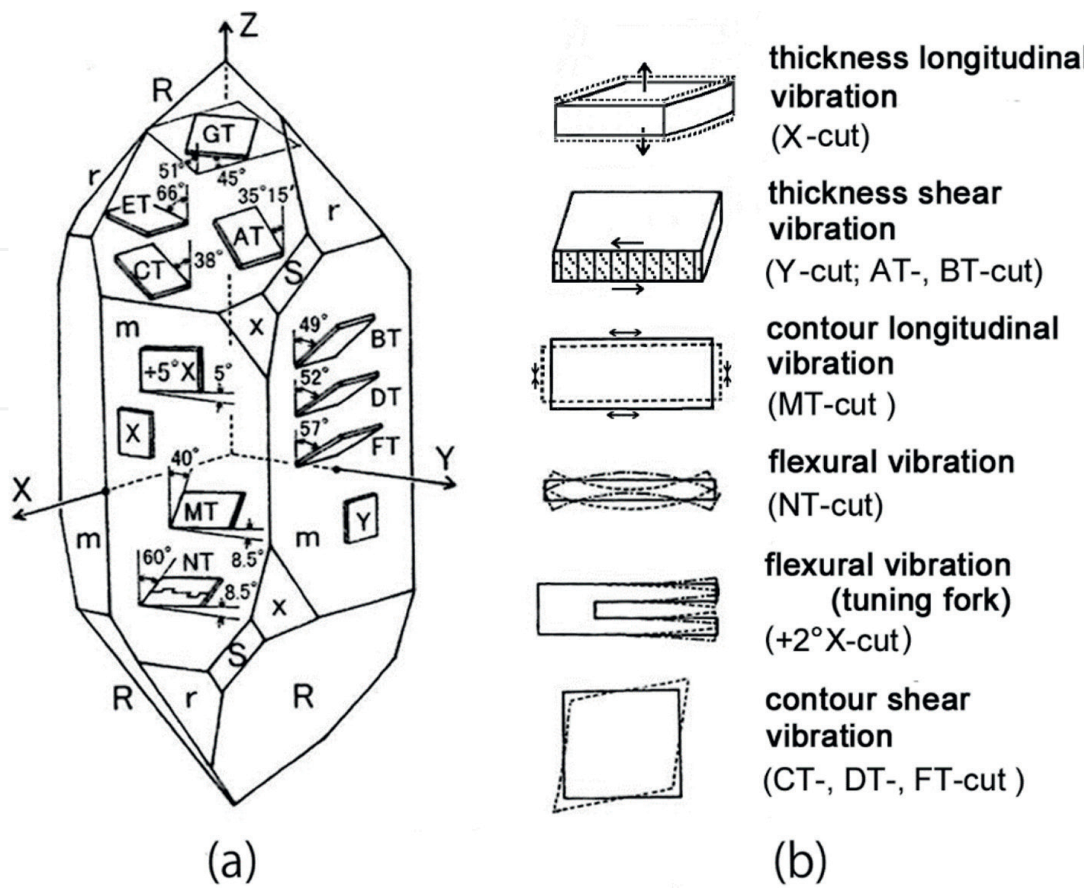

Figure 2.
(a) Cutting orientations of resonator plates of quartz crystal. X axis: [2-1-10], Y-axis [01-10], Z-axis: [0001] orientation. (b) Vibration modes of resonator plates.

Thus, search for the orientation of cut which has the zero f-t coef. characteristic began in the world. In this study, where many researchers joined, Issaku Koga (Japan) found in 1933 that the f-t coef. becomes zero in resonator plates cut out parallel to planes rotated around the *X* axis by 35° (more exactly, 35°15′) and − 49°, respectively, from the *Y* plane [3]. (Here, the zero f-t coef. means that the coefficient of the first-order term proportional to temperature is zero in the polynomial expression of the temperature dependence of the resonant frequency.) The two zero f-t coef. plates were named R_1 plate and R_2 plate, respectively, by Koga. Both of them are resonators of thickness-shear mode vibration. The f-t coef. of R_1 plate is less than 0.1×10^{-6}/°C at room temperature. One year later, in 1934, Bell Telephone Laboratories (USA) published the make of *AT*-cut and *BT*-cut plates as quartz resonators. However, they were the same as R_1 and R_2 plates, respectively, found by Koga. Nevertheless, the names of *AT*-cut and *BT*-cut are generally used in the world. Now, the *AT*-cut plate is representative of quartz resonator products.

3. Development of large-scale production of synthetic quartz resonator

3.1 Studies of synthetic quartz growth preceding large-scale development project

The zero f-t coef. quartz oscillator mentioned above was at once employed in World War II. The demand for quartz resonators for communication increased with the outbreak of the war, and the want for raw quartz for producing resonators came to be felt seriously in every country. Although natural quartz was produced in any region in the world, the source of good quality and large-sized raw quartz was limited to a few countries such as Brazil, etc. Thus, the dependence so far on natural quartz as the raw material for quartz products was reconsidered, and the production of synthetic quartz came to be demanded.

The experiment of the artificial synthesis of quartz was first made in 1845 by K. E. von Schanfhäutl (Germany). Gelatinous silica and water were sealed and heated up in an autoclave to obtain small quartz crystals of microscopic size. After that, several investigators made succeeding synthesis experiments. The experiment which directly led to the present growth technique of quartz was done by Giorgio Spezia (Italy) in 1905 [4, 5]. In his experiment, the growth was continued for 6 months in an autoclave under high temperature and high pressure, in which lasca quartz was charged as nutrient and a seed crystal was suspended in the Na_2SiO_3 solution. Through this experiment, he obtained a clear quartz crystal of 14 mm in length. In 1936, Richard Nacken (Germany) grew a quartz crystal of enough size to cut out a quartz resonator [6, 7], experimenting with a constant-temperature hydrothermal growth using amorphous silica, on the basis of Spezia's study.

3.2 Synthetic quartz production study in USA, starting after world war II

Although the necessity of raw quartz was understood, no project actually moved for the development of large-scale production of synthetic quartz, during World War II. After the war, demand for raw quartz was further increased with increasing civil use added to military use, so projects for large-scale production of synthetic quartz were planned. In the United States, a study for the industrial production of synthetic quartz was started in Brush Development Co., Ltd., Bell Telephone Laboratories, etc. [8], on the basis of Nacken's study. By these studies, synthetic quartz practically usable for telecommunication became producible in 1953, though at a research level.

As to the heating control of the autoclave, the constant-temperature method as used by Nacken and a temperature difference method were compared, and the latter method was concluded to be more suitable for mass production. In the latter temperature difference method, the autoclave is partitioned into two zones with a baffle between them, as known well (see **Figure 3(a)**); the one is the lower dissolving zone at a higher temperature (about 400°C) where nutrient lasca quartz is placed, and the other the upper growth zone at a lower temperature (about 350°C) where seed crystals are suspended. The temperature difference between the two zones was a few tens to several 10 degrees. As the working solution, a few to several weight % solutions of Na_2SiO_3, NaOH, etc., were used. As the seed crystal, a *Y*-directed slender bar-shaped crystal was concluded to be most suited, from various viewpoints; with this seed, quartz crystal grows fat in the perpendicular directions (*X*- and *Z*-directions) and not in the length direction (*Y*-direction) (see **Figure 3(b)**). This shape was favorable for producing many crystals in a tube-shaped autoclave. Furthermore, *Y*-bar quartz grown from *Y*-bar seeds was favorable for cutting out AT-cut plates efficiently without waste. Thus, the fundamentals of producing technology of synthetic quartz, which have succeeded to the present day, were established. The developing work for synthetic quartz production up to this time is well described in [8]. The developed manufacturing technology was then succeeded by Sawyer Research Products Co. Ltd. in USA. The company started as the first industrial maker of synthetic quartz crystal in the world, in 1956.

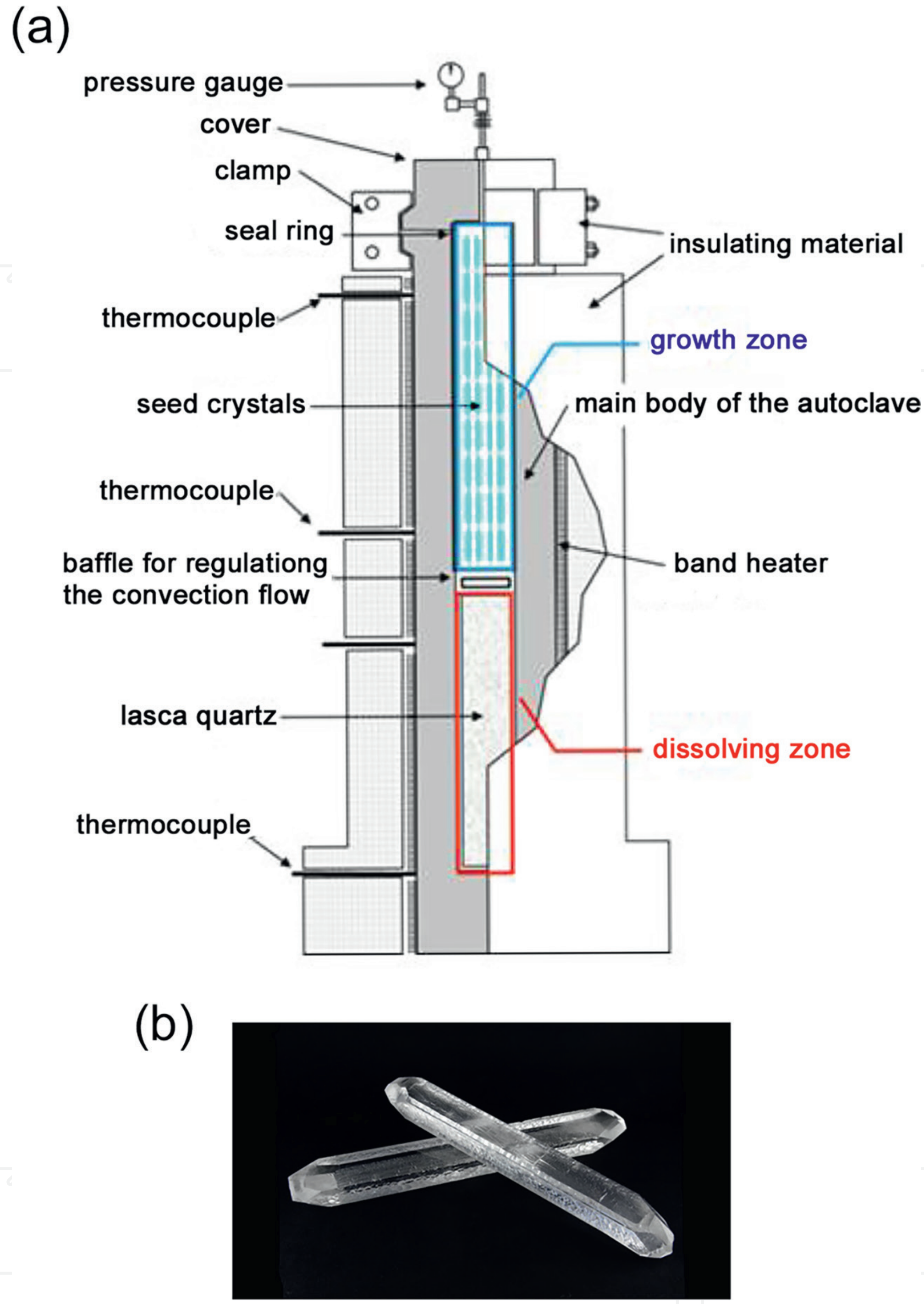

Figure 3.
(a) Autoclave for growing synthetic quartz crystals (of 650 mm in total inside diameter, and 14 m in total inside height). Figures cited from Reference [9]. (b) Grown Y-bar synthetic quartz crystals.

3.3 Synthetic quartz production in Japan

About the same time as above, the attempt to produce synthetic quartz also started in UK and France. In Japan, the research group of Minoru Kunitomi, Sadao Taki, and Junpei Asahara at Yamanashi University first succeeded in producing synthetic quartz in 1954 [10, 11]. The experiment was made by using an autoclave of 35 mm in inside diameter and 500 mm in inside depth. After that, Taki and Asahara transferred to Toyo Communication Equipment Co., Ltd. (hereafter, (Toyocom)) to participate in the technological development of industrial-scale production of synthetic quartz.

About the same time, several other companies such as Nihon Dempa Kogyo Co., Ltd. (hereafter, (NDK)), Kinsekisha Laboratory Corporation (hereafter, (Kinsekisha)), etc., also joined this business of industrial production of synthetic quartz. The technological development of quartz production by these Japanese companies reached an approximate completion in the early 1960s, but the effort to improve the technology for stably producing good quartz was further pursued.

In the hydrothermal growth of quartz a few to several weight % Na_2SiO_3 solution had mainly been used in a line from Spezia's experiment in 1905. However, in the development in (Toyocom) led by Taki, NaOH solution was employed. The gradient of the solubility curve to temperature is considerably lowered when the NaOH solution is used [12], compared with the case the Na_2SiO_3 solution is used. Accordingly, if the temperature difference set between the two zones in the autoclave is the same between the two cases above, the growth velocity with the NaOH solution is slower than that with the Na_2SiO_3 solution. However, in general consideration, better-quality crystals with the less defects can be obtained, corresponding to the slower growth. (Toyocom) chose to obtain better-quality quartz at the expense of some lowering of growth velocity. It is reported that obtained quartz quality was remarkably improved by this choice of growing solution in a report [10]. Another paper also reports that the clarity, or transparency, of NaOH-solution grown quartz was slightly higher than that of Na_2SiO_3 solution-grown quartz [13]. There would probably not yet be an exact comparative assessment of the qualities of the two kinds of quartz grown in NaOH and Na_2SiO_3 solutions. In Japan, while some makers other than (Toyocom) also employ NaOH solutions, other makers continue to use Na_2SiO_3 solutions.

3.4 Assessment of lattice defects of grown quartz crystals by X-ray topography, etc.

Around 1970, the development in Japan reached a goal line of producing apparently good quartz of enough size (20–25 mm (*X*-direction) × 30–35 mm (*Z*-direction)), and the concern of developers came to be also directed to the assessment of the quality of produced quartz. One of the to-be studied matters was the examination of lattice defects in the crystals, such as dislocations, and the related total assessment of the crystal quality. At that time, the assessment of lattice defects in silicon and other semiconductor crystals was still actively practiced using X-ray topography, etc. The study of lattice defects in quartz crystals entered such a current of study.

X-ray topographic studies disclosed that high-quality quartz crystals, which seemed to be usable as precision industrial materials, were grown in general [14–16] (**Figure 4**). Thin linear images in the X-ray topographs show dislocations. **Figure 4**(**a**) and (**b**), respectively, show an example of a crystal with very few dislocations and a crystal containing many dislocations. Dislocations contained in a synthetic quartz crystal generally were not more than a few thousand/cm^2, if the crystal was grown with enough care, and they were in the range of several to several hundred/cm^2. Many dislocations were continued from ones in the seed crystal. Besides, many dislocations were newly generated along the seed boundary (see **Figure 4**(**b**)) in case the lattice spacing of the seed crystal has a large difference from that of the newly grown region. Few dislocations were generated on the way of growth.

Although each crystal of the present study is a single crystal as a whole, growth sectors $\pm Z$, $\pm X$, s are formed in its inside. Strong black or white linear contrasts along sector boundaries are caused by strains induced by the difference in lattice spacing between growth sectors, which arise from different impurity contents between the growth sectors.

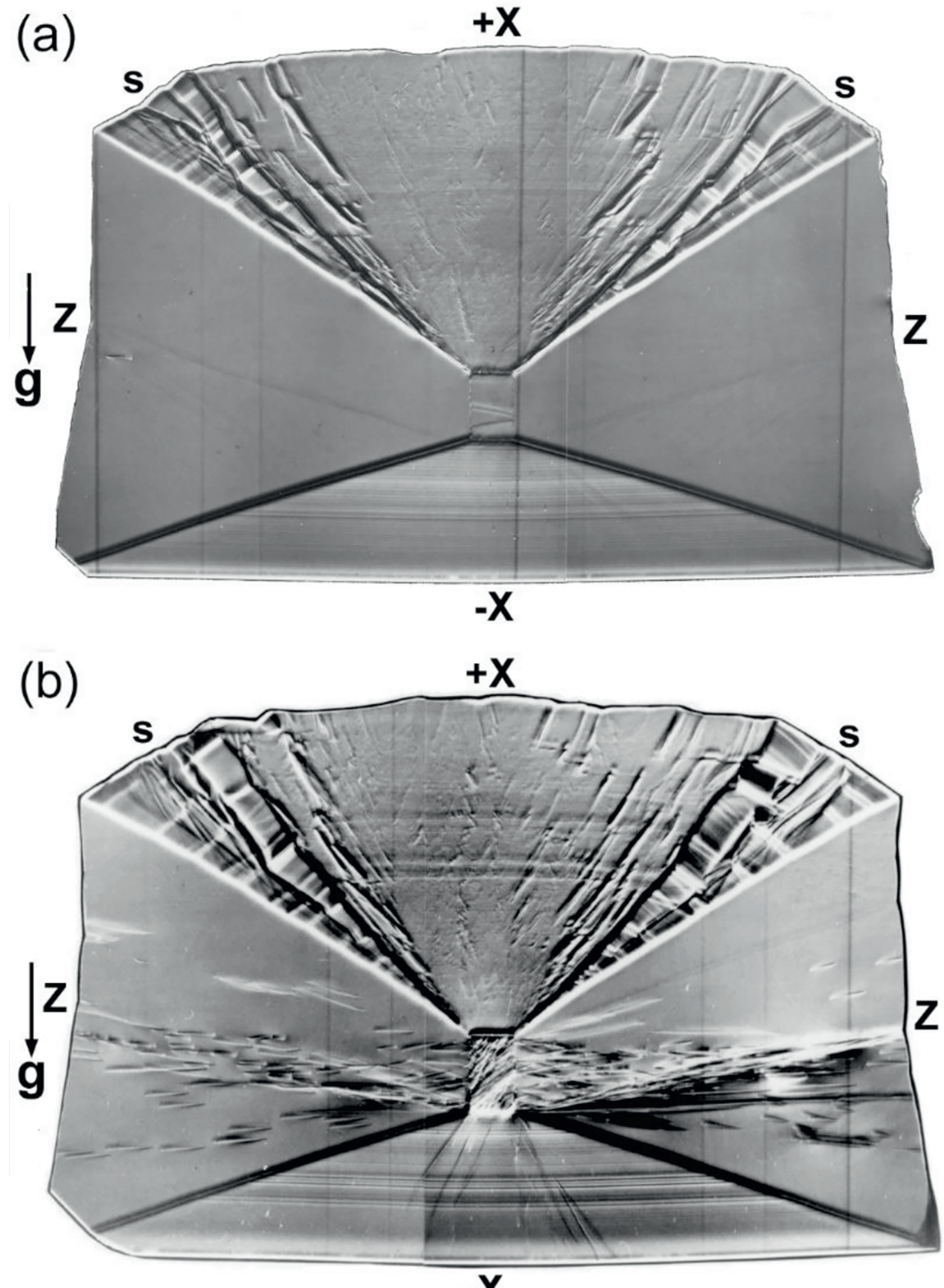

Figure 4.
X-ray diffraction topographs of Y-cut plates (0.3 mm thick) of Y-bar quartz crystals. Cu Kα radiation, -2020 reflection. g is the diffraction vector. The sizes of the crystals are 21-23 mm in the X-direction. Small rectangular regions at the centers of topographs respectively show the seed part of crystals.

Being different from the case of semiconductor crystals, the function of a quartz crystal as electrical device is not decisively influenced by one dislocation, but is influenced through a collective strain/stress effect from many dislocations. As the understanding at that time, dislocations as many as a tens/cm^2 were considered not to have a significant influence on the function of a quartz crystal. However, it was the knowledge up to 1990s. In the present day, after more than 30 years from that time, a study of the harmful influence of dislocations (screw type) is further progressed, and the influence is more seriously considered (see Section 4.3).

3.5 Progress in the crystal filter technology; the advent of MCF and SAW filters

Additionally, reference should be made to the progress in the technology of quartz crystal filters at that time. Now, a crystal filter and a quartz resonator are one of the major quartz products. Filters are used in electrical communication to take out or to cut only the selected bandwidth of frequencies from the received or transmitted electric waves. Initiatively used LC filters (inductor (L)-capacitor (C) electric circuit filters) were fabricated only from purely electric elements and were insufficient in the treatable frequency (10–40 kHz), frequency bandwidth, Q value characteristic, etc. For this condition of frequency filter, W.G. Cady suggested the use of quartz resonator as filter element in 1922 [17]. Quartz was expected to be used as superior filter material owing to its sharp resonance characteristic. In 1934 Walter P. Mason (USA) published his work on crystal filters [18], one of which (of "narrowband design") was widely used for the next 20 years. The one which is called the discrete type in literature is this type of filter (**Figure 5**(**a**)).

From the mid-1950s, demand arose for crystal filters usable for higher frequencies with a narrower bandwidth, and operating stably, from the extending use of filter elements in the military and civil-use apparatuses. Correspondingly, studies for the performance improvement of crystal filters came to be made actively. In such circumstances, in 1962, Yuzo Nakazawa (Japan) of (Toyocom) devised a new-type crystal filter, which is called afterward MCF (Monolithic Crystal Filter) [19, 20]. In this crystal filter, two sets of facing electrodes were installed on one quartz plate, and were acoustically connected to each other in the plate to realize the frequency filtering (**Figure 5(b)**).

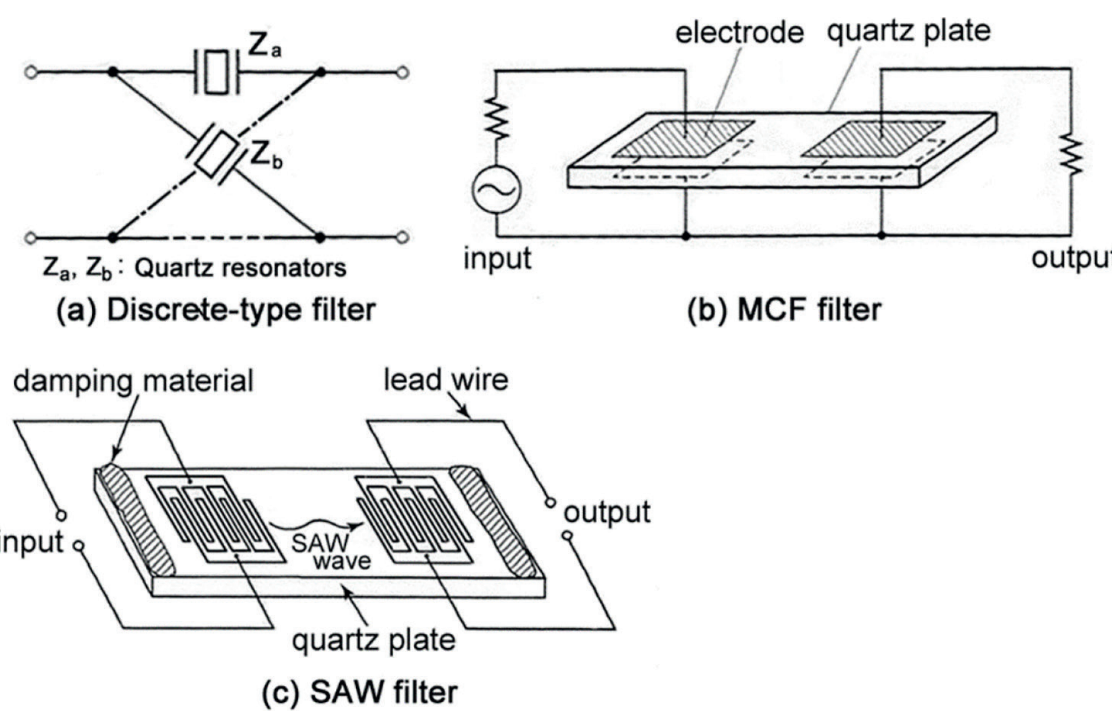

Figure 5.
Crystal filters as a quartz device.

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The advent of this small and light crystal filter with a superior filtering characteristics attracted a great deal of public attention, and its use spread quickly to the world.

(MCF) was first employed as filters in ultra-high frequency radio communication. With the succeeding advances in radio communication, the central frequency in crystal filters was demanded to become further higher, from 10.7 MHz at the beginning. For the treated frequency to be made higher, the quartz plate needs to be made thinner. However, thinning processing had a technological limit then, and 70 MHz was a limit of realizable high frequency. For this difficulty, a crystal filter utilizing SAW wave (surface acoustic wave) was considered as a new (MCF) which oversteps the frequency limit (**Figure 5(c)**); the (SAW) wave excited in the surface of the quartz plate was utilized instead of oscillation in the bulk of the quartz plate. Though the subsequent history of the development of such (SAW) filters cannot exactly be followed here, it was in 1984 that (Toyocom) put (SAW) filters on the market, according to a report published by (Toyocom) [20]. In the present day (SAW) filters are used in almost all cellular phones. The present treatable frequency limit reaches several GHz. Additionally, while quartz (SAW) filters are used for narrow-bandwidth communication and with good temperature stability, (SAW) filters made of $LiTaO_3$ and $LiNbO_3$ crystals are more preferably used with wider bandwidths.

4. The present state of production of synthetic quartz and quartz devices

4.1 The present state of synthetic quartz production industry

Compared with the state about 50 years ago (about 1970) when the technology of synthetic quartz production was established, the present state of the industry and technology of synthetic quartz had been changed not a little, although the fundamentals of the technology was unchanged. The present world production of synthetic quartz is reported to be about 3200 t/year, according to a report in 2021. Major producing countries are China, Russia, and Japan. As for producing companies, (Sawyer Research Products) Inc. (*now* (Sawyer Technical Materials) LLC.) in USA is still in a healthy condition and is doing good work. In Japan, (Toyocom) Co., Ltd. was affiliated with (Seiko Epson) Corp., but the production of quartz devices is still actively continued by subsidiary companies (Epson-Toyocom) Corp., etc. (Kinsekisha) Laboratory Corp. also was affiliated with (Kyocera) Corp., and the production of quartz devices is continued as a business of (Kyocera) Corp. (NDK) Co., Ltd. continues the production of synthetic quartz and quartz devices as before, without merging with other companies.

4.2 Technological changes in the production of synthetic quartz and quartz devices

In the technology of producing synthetic quartz, the autoclave for growing quartz had been increased in size year by year, in order to cut down production costs. For example, about 1960, its typical size was 2 m in depth and 120 mm in inside diameter, whereas about 25 years later, in 1984, its depth was increased to 14 m with the inside diameter of 650 mm [9, 10]. The size and shape of seed crystal, and accordingly those of grown crystal, were also changed considerably. The size of the conventional Y-bar seed (about 3 mm in the X-direction, and a little less than 2 mm in the Z-direction) was greatly extended in the X-direction to lengths from 70 mm to more than 100 mm, and such seeds are called Z-plate seed. Using seed crystals like this, quartz crystals are grown to much larger than before (see **Figure 6**), up to volumes from several times

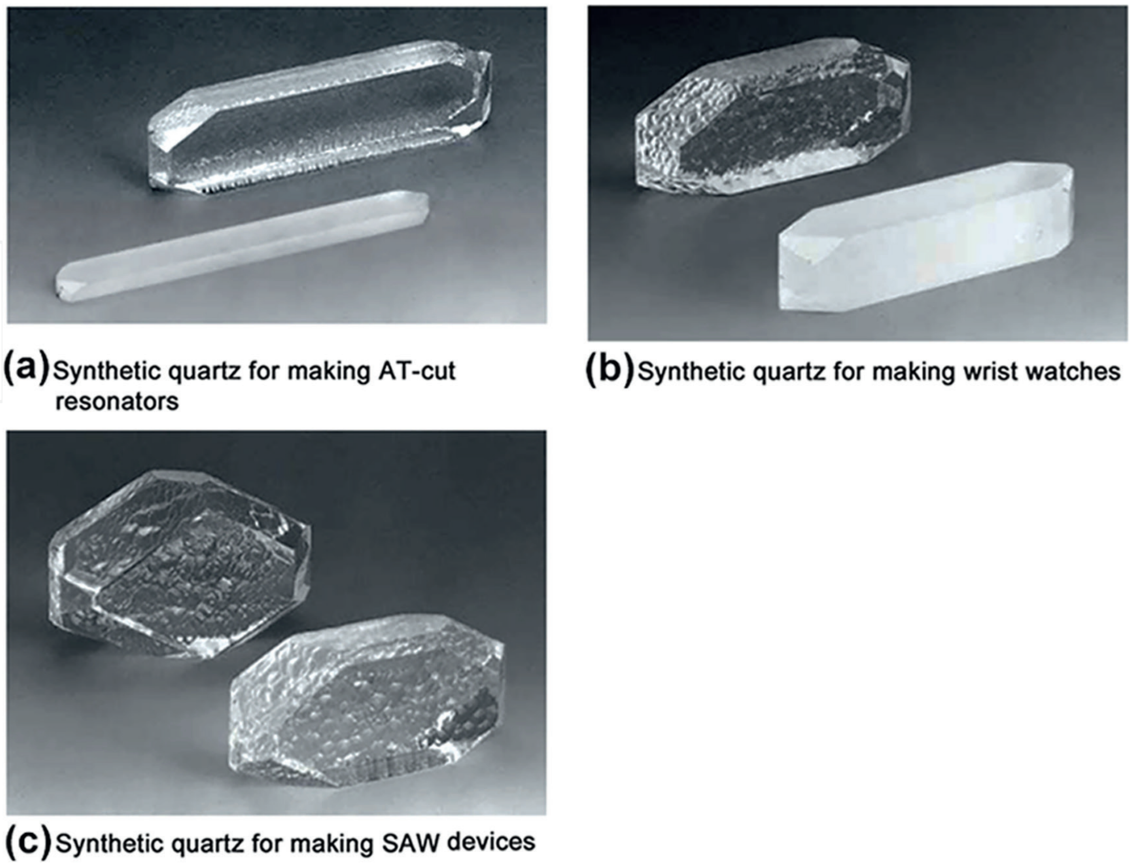

Figure 6.
Synthetic quartz crystals of various shapes and sizes, grown so as to match the purposes of use, in the present-day industrial production.

to dozens of times larger than that of former *Y*-bar crystals (**Figure 3(b)**); the weight of one crystal becomes 1–6 kg, while that of former *Y*-bar crystal is estimated to have been about 0.24 kg. One operating time of the autoclave is 2 to 6 months, while it was about 45 days (one and a half months) in the case of former *Y*-bar quartz. Though equally classified into the same category as *Z*-plate quartz, crystals are grown to separate sizes and shapes most suitable to the uses after the growth, for the manufacturing of *AT*-cut resonators, quartz watches, SAW devices, etc (see **Figure 6**).

As for manufactured quartz devices, the downsizing and thinning of quarts resonators is progressed, so that the devices of less than 1 mm in the substrate size are produced, and the thickness of the substrate is thinned down to 10 μm (the thinning is required for the use in high frequency). Many resonators and other devices of quartz are fabricated by lithographic processing.

4.3 The frame seed method for inhibiting the harmful occurrence of etch channels

Regarding dislocations in quartz crystals, it came to be known that, in the etching process in the blank-crystal processing, dislocations cause etch channels and etch pits in crystals to have a bad influence on the characteristic of resonators. In Japan, according to the Japanese Industrial Standard (JIS), the quality of quartz crystals is graded into six ranks based on the number 2–300 of etch channels contained in an area of 1 cm^2 in AT-cut plates [9]. Such etch channels and etch pits are caused by only screw dislocation, and edge dislocations do not cause them. Most of those screw dislocations succeed from the ones in the seed crystal. Thus, the choice of seed crystals is important. However, obtaining good seed crystals from natural quartz has become difficult since the production of large, high-quality natural quartz has become scarce. Instead, seed crystals also must be prepared from synthetic crystals. One method was developed for this seed crystal preparation to grow preferentially only the +X growth region, where the generation of a screw dislocation is difficult, using seed crystals of a special shape. Such *+X* growth region is used to cut out seed crystals for growing quartz crystals of ultimate products. This way of growing quartz crystals containing no- or few dislocations is called the frame seed method [9, 21].

5. The present state of extending use of quartz crystals

5.1 General view

Finally, we briefly remark on the present state of the use of quartz crystals. Now the whole world enters into a highly information-oriented society, where radio waves carrying various information travel around us everywhere and every day. A telecast of a sporting event carried out in a spot site on the earth is delivered worldwide via satellite broadcast, so that several billions of people enjoy watching the sporting event in real-time. On the surface of the ground, radio waves of cellular phones, wireless LAN, SNS, car navigation, etc., travels *to and from* busily. On the sea ship, radio waves travel about, and in the sky plane, radio waves travel. In such all radio and wired communications, quartz devices work efficiently for the exact and stable transmission, reception, and processing of electric waves. According to a recent guidance article, several tens of quartz devices are installed in one car, and they become several hundred in a luxury-model car.

5.2 Use in other than the communication field; quartz watch and clock

We next mention the use of quartz other than in the communication field. The largest field of such use of quartz would certainly be the use for quartz watch and quartz clock. The quartz crystal oscillates very regularly at a constant frequency by its piezoelectricity, when an AC voltage is applied to it. The fabrication of quartz clocks had early been made utilizing this exact regular oscillation. It is reported that a quartz clock was first constructed using a quartz resonator by Warren Marrison and J.W. Horton of Bell Telephone Laboratories (USA) in 1927 [22]. However, the clock was as large as a wardrobe because of the many vacuum tubes installed in the clock body, and its use was limited to special institutions such as (NBS) (National Bureau of Standards). Also in Japan, a high-precision quartz clock of a large size had been constructed similarly and installed in a special institute; it was used for a special purpose, not like being used by general people.

(Suwa Seikosha) Co., Ltd. (*now* (Seiko Epson) Corp.) was challenged to produce such quartz clocks of the size of a wristwatch, and succeeded in producing them after the development effort for ten years since 1958 [23]. The products were put on sale as "quartz watch" from 1969. When the error of general high-precision mechanical watches was several tens s/day, the error of this quartz watch was ±0.2 s/day, and ± 5 s/month. A key to the successful development was the employment of a tuning-folk type resonator (of flexural-vibration mode) (see **Figure 2**(**b**)), with which the resonance frequency could be greatly decreased, compared with the case when AT-cut resonators were used. (Now the frequency of 32,768 vibrations/s becomes the standard.) (Although, in the firstly presented quartz watch in 1969, a *Y*-shaped resonator was used, it was soon after replaced by the tuning-folk type resonator.) Tuning-folk type resonators (about 100 μm thick) are produced by lithographic processing.

In the 1970s (Suwa Seikosha) released the process patent for quartz watch, so many makers entered the business of producing quartz watch. As a result of expanding production, the price down of quartz watches advanced. The price of a quartz watch was 450,000 Japanese yen in the opening sale in 1969, but it went down rapidly to nearly 1000 yen at the lowest price, in 10 years or so. Now, not only quartz watch, but wall clocks, table clocks, alarm clocks, etc., all are produced as a quartz clock. With this development of quartz watch/clock industry, the conventional industry of mechanical clock/watch, which had developed in Europe and other regions in the world since the 16th century, came to decline. Although it is never a desirable trend of the times, it would be an affirmable progress in society that everyone in the world can wear a high-precision wristwatch at a little expense. Recently, the value of classic-style wrist watches is reconsidered as an accessory, so the manufacture of such mechanical watches is reported to be revived in part.

5.3 Use in other than the communication field; quartz crystal microbalance (QCM)

Whereas quartz watches above utilized the accuracy of piezoelectric vibration of quartz crystal, an application of a small change in the piezoelectric vibration frequency is Quartz Crystal Microbalance (QCM). Even when a trace of material adheres or leaves from the electrode, the correspondingly occurring microgravity change can be detected through a frequency change in the resonator. The basic theory of this measurement method has been known since 1959 [24]. However, it was about 30 years ago (1990s) that the method began to attract attention as a high-sensitivity technique for microgravimetry [25]. According to the theory, if the resonant frequency of the quartz plate (AT-cut) is 10 MHz, an increase of 1 Hz in the resonant frequency corresponds to a decrease of about 4 ng/cm^2 in the mass. This sensitivity is evaluated to be higher than that of a conventional microbalance. Besides, the sensitive frequency change is also utilized in film-thickness meters, pressure sensors, etc.

6. Conclusion

As seen, quartz devices are used in various places of our everyday life and social activities now. Before, silicon semiconductor chips were compared to “rice of industry.” That simile lives even now. Following it, quartz crystals are now compared to “salt of industry.” The use of quartz crystals would extend further along with the development of a high information-oriented society.

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