

Frequency Change of Quartz Resonators Irradiated by 1 MeV Electrons

Takashi AOKI*, Keizo NORISAWA**, and Masakatsu SAKISAKA**

(Received September 10, 1975)

The resonant frequencies of natural- and synthetic-quartz AT-cut plates irradiated by 1 MeV electrons have been measured in the fluence range from 3×10^{10} to 2×10^{17} electrons/cm². The frequencies of purest synthetic quartz plates have increased rather monotonously against fluence, whereas those of impurity-abundant synthetic and natural quartz plates have shown different behaviors; once decreasing up to about 10^{15} electrons/cm² but increasing at higher fluence. This impurity dependence has been confirmed for sodium using a sodium-diffused crystal, of which the frequency has dropped drastically near 10^{17} electrons/cm² fluence.

1. Introduction

Quartz has been widely applied as a precision frequency generator because the oscillating frequency of its appropriately cut plate is definite and quite stable against temperature and ageing. In 1945, Frondel¹ reported a change of frequency for BT-cut natural quartz resonators exposed to X-rays. Since then, the effects of nuclear radiations on resonance frequency have been studied by many investigators²⁻⁸, but the mechanism has not been well understood.

We have made some experiments to acquire more informations about the radiation-induced frequency change, with the use of several natural and synthetic quartz together with a sodium-diffused crystal. The irradiations were carried out by using energetic electrons only, in order to avoid an implantation of bombarding ions. The fluence covered over seven decades, the range of which has never been reported in the literatures. A dependence of resonant frequency on impurities has been confirmed, and the representative example for sodium is presented.

2. Experimental Procedure

Six types of quartz, A, B, C, D, E, and F, were prepared, the characters of which are listed in the Table. All these are AT-cut resonator plates, operating at the fundamental vibration of 5 MHz in frequency, but 6 MHz for the sample E. The amounts of lattice defects and impurities in these crystals are different from one another according to their origins, but quantitative analysis has not been done. In

*Department of Engineering Physics

**Department of Nuclear Engineering, Kyoto University

Table. Quartz resonators used. In the Table, "purest" stands for low impurity levels among the crystals used. Other types of impurities such as Li and K, may possibly be incorporated in "purest" crystals, of which infrared absorption peak levels, however, have been found negligibly small. Kinsekisha, of course produce purest crystals, but we did not adopt such crystals in the present experiment.

Sample	Quartz	Origin	Shape (mm)	Coloration after exposure	Rich impurities
A	synthetic	Sloan*	square 19.0×19.0×0.332	(none)	purest
B	synthetic	Sawyer*	square 12.5×12.5×0.332	(none)	purest
C	synthetic	Kinsekisha*	square 12.5×12.5×0.332	brown	Al, Fe, Mg, Cu, Na
D	natural	Brazil	square 12.5×12.5×0.332	brown	Al, B, Fe, Mg, Na
E	natural	unknown	circular 17.35 in dia.	brown	Al, B, Fe, Mg, Na
F	synthetic NaOH-treated	Sawyer*	square 12.5×12.5×0.332	(none)	Na

* Name of manufacturer of quartz.

particular the sample F, of which the origin was quite the same as that of B, had been dipped in melted sodium-hydroxide at about 400°C and thus a sodium diffusion in quartz was performed.

After mirror-like polishing and HF-etching, gold films of about 700 Å in thickness were vapor-deposited on both surfaces of each plate. The patterns of gold films and the electrode configurations are shown in Fig. 1, where (a) and (b) were adopted for the square samples, while (c) and (d) for the circular ones.

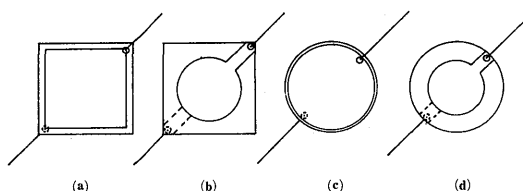


Fig. 1. Patterns of gold films and electrode configurations. Lead wires are bonded on the gold surfaces with a dotite-paint.

The samples were irradiated by 1 MeV electrons extracted from a 2 MV Van de Graaff accelerator of Kyoto University, after being settled in a vacuum chamber connected with the accelerating tube, as shown in Fig. 2. A thin aluminum foil was placed in front of the quartz plate to make the electron beam uniformly incident on it. The beam current, that is the fluence rate, was measured with the use of a beam current integrator. To generate oscillation of the quartz plate, a transistorized circuit was connected with it. But during the irradiation, the circuit was detached from the

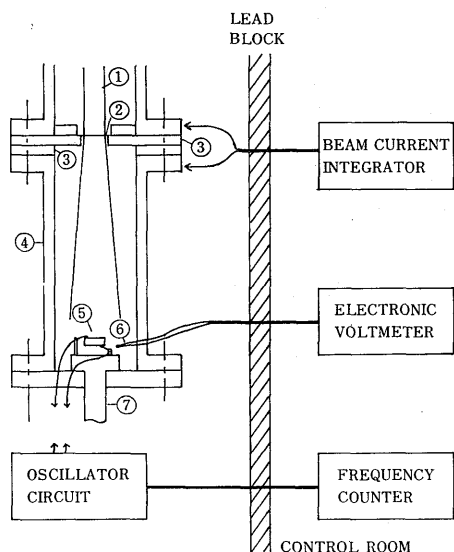


Fig. 2. Target assembly for electron irradiation and block diagram for measurement. ① incident electron beam, ② thin aluminum foil, ③ insulator, ④ sample chamber at the end of the accelerating tube, ⑤ quartz, ⑥ thermocouple, ⑦ copper base.

sample chamber and was kept outside the lead wall for the purpose of shielding bremsstrahlung X-rays.

The temperature at the target was kept monitoring by using a thermocouple, the indication of which was recorded on an electronic voltmeter. This precaution was needed to prevent an unexpected temperature-rise of the sample when irradiated by energetic electrons. Therefore a constant temperature of 19.5°C was maintained at the chamber and the associated instruments.

We have used three different oscillating circuits, designed as shown in Fig.3 (a), (b), (c), in order to make certain that the observed frequency is independent of the circuit design. Moreover, a transmission method^{9,10} was employed to confirm its validity. Each frequency measurement by using a precision frequency counter started immediately after the irradiation, and the frequency was determined thirty minutes after the irradiation. This time-lag was necessary to make the activated atoms in the irradiated sample

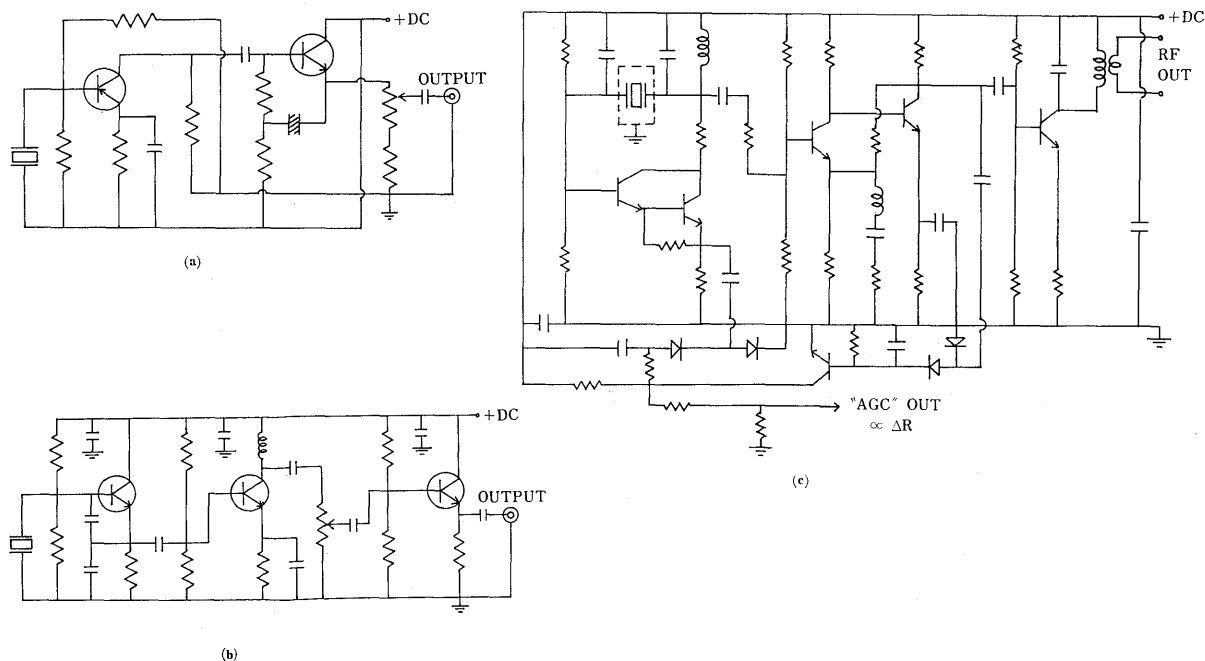


Fig.3. Oscillator circuits. The circuit (c) is after King et al. in Ref. 6.

stable enough. Such a procedure was repeated at every exposure of wanted fluence, piling up to 2×10^{17} electrons/cm². In this experiment, we do not refer to a dependence of radiation-induced frequency change upon fluence rate, because of the difficulty to irradiate the *same* resonator to the *same* fluence at different fluence rate.

3. Results and Discussion

The frequency deviation versus fluence (f - Φ) characteristics*** obtained is drawn in Fig.4 for each crystal, where an independence had been confirmed of the shape of

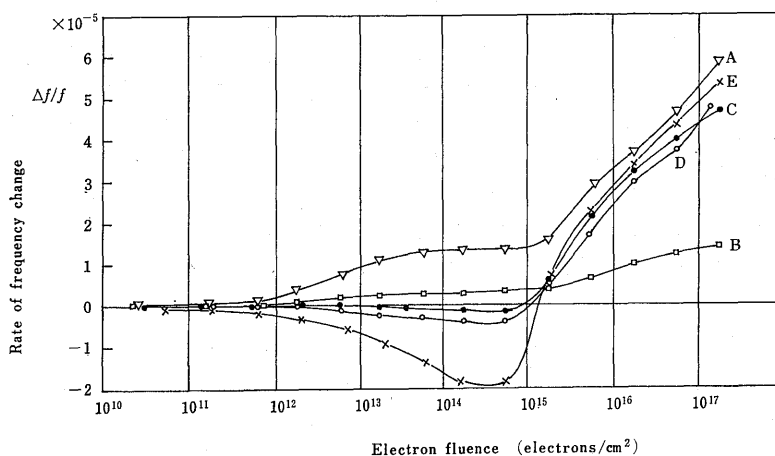


Fig. 4. Frequency versus fluence characteristics. The notations A~E represent the samples listed in the Table.

gold film as well as of the electrode configurations. The f - Φ relations were also independent of the oscillator circuit and were consistent with those measured with the transmission method^{9,10}.

In the case of semiconductor crystal of silicon, the lattice defects induced by irradiations have been studied and established fairly well.¹¹⁻¹⁷ It has been found that, the vacancies initially introduced are mobile and migrate within the crystal, and that they finally associate with the impurity centers such as oxygen atoms, phosphorus atoms, and vacancies themselves, resulting in forming complex centers.

In the case of quartz crystal, however, different types of complex centers involving various impurities are very likely produced by high energy electron irradiation. The reason is that any quartz is impure at present compared with a refined silicon or germanium. The complex centers and other lattice imperfections will modify the elastic constants of quartz. Then the resonant frequency should be changed, since it is related to the elastic constant as $f = (C'_{\phi\phi}/\rho)^{1/2}/2t$, where t is the thickness of quartz plate, ρ the density and $C'_{\phi\phi}$ the effective elastic constant dependent upon a cut angle of quartz. From Fig. 4, we can deduce three types of radiation-induced defects; (1) the defects that make the resonant frequency increase, (2) those give decreasing

***Exactly Speaking, the fraction of frequency deviation as a function of fluence ($\Delta f/f$ - Φ) is given.

characteristic of frequency, and (3) those with no effect on frequency.

Referring to Fig. 4 together with the Table, each sample shows a different f - Φ behavior according to its origin. Therefore it would be interesting to investigate which impurity is effective and how it affects the f - Φ relation.

The samples A and B, both synthetic quartz with best purity, show positive frequency change against fluence, and in particular, the crystal B has the most radiation-tolerant property. On the contrary, the specimens C, D, and E which have appreciable amounts of impurities express negative behaviors of frequency change until the fluence reaches about 10^{15} electrons/cm². These facts suggest that the decreasing behavior of frequency is attributable to some impurities as listed in the Table.

Another important phenomenon is that, each f - Φ curve has a turning point near the fluence described above, where every sample begins to show a rapidly increasing behavior in frequency. This is explained as follows: The impurity complex centers initially created have frequency-decreasing characters, but are saturated around the fluence of $\sim 10^{15}$ electrons/cm². Above it, other kinds of defects, which are commonly produced in any sample, become dominant and play an important role on frequency.

To establish the impurity effect, we applied the sample F, which had been artificially sodium-diffused into the crystal B, as described already. The results of f - Φ relation is presented in Fig. 5, where a drastic decrease of frequency is seen. The electrodiffusion

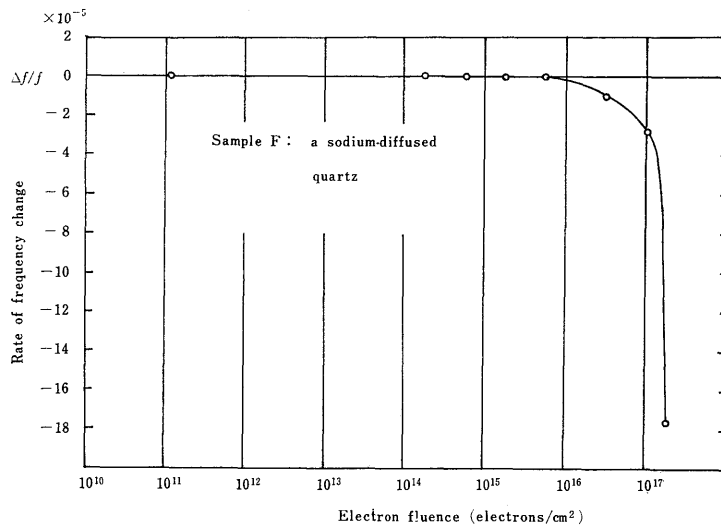


Fig. 5. Frequency versus fluence characteristic of a sodium-diffused quartz plate.

experiments done by several study groups²²⁻²⁶ have proved that alkali ions move in the crystal through the z-axis channel. Then the diffused sodium ions in our sample are expected to exist interstitially along the z-axis channel. By electron irradiation, these sodium impurities would easily turn to complex centers, resulting in a drop of resonant frequency.

There arises a question that, notwithstanding the drastic change as found in the

sample F, why the sodium-impure samples C, D, and E did not show the similar behaviors in frequency change. A possible explanation is that the sample F contained much more sodium atoms or sodium impurities existed not in the same way as those in other crystals.

Frondel¹ has found that the amount of frequency change for a BT-cut plate is closely related to the intensity of coloration. In our experiment, the coloration to be browned was also observed for the impurity-rich samples of C, D, and E, as shown in the Table. The intensity, however, was saturated near 10^{15} electrons/cm², the fluence of which was again nearly the same as the value at the turning point of f - Φ curve. Then a qualitative conclusion can be made that the defects above this value have no correlation with these color centers but continue the frequency increasing.

It has been shown by Griffith et al.¹⁸, O'Brien and Pryce¹⁹, O'Brien²⁰, and Mitchell and Paige²¹ that the coloration induced in most specimens by irradiation is due to substitutionally incorporated aluminum impurity. The frequencies of the discolored crystals have been found decreasing until coloration is saturated. Therefore it is also possible that the negative frequency change is attributed to the existence of substitutional aluminum. This explanation, of course, cannot be denied. Unfortunately, since no quantitative analysis has been done, aluminum is presently considered one of the possible elements to give a decreasing characteristic of frequency change.

Some defects make the resonant frequency decrease, while others increase. Therefore it would be possible to prepare such a crystal that is not affected by irradiation, by mixing frequency-lowering-impurities with frequency-raising-impurities, although the latter ones have not been established. An example is seen in Fig.5. The crystal B is of best purity and has a frequency-increasing property. However, its sodium-processed specimen, that is the sample F, shows a constant frequency up to nearly 10^{18} electrons/cm². Then sodium is concluded to have compensated an increase of frequency —sodium is frequency-lowering impurity.

Natural quartz contains usually several kinds of impurities with the order of 10^{-5} ~ 10^{-4} and also dozens of different impurities with the lower order. Even though the samples are cut from the same mother crystal, the impurity contents are slightly different. This makes the present study difficult enough. But if a precision impurity control is attained as in the cases of silicon and germanium, it would be able to get a crystal applicable to a dosimeter, of which the frequency change is a reliable measure of irradiated fluence.

We have annealed some irradiated samples at various temperatures and measured the recoveries of frequencies. The results are very complicated and indefinite at present, which means that various types of defects appear and disappear as annealing proceeds.

When quartz is exposed to radiations, it accompanies also the changes of infrared absorption, electrical resistance R , quality factor Q as a resonator, etc. The measurements of these physical properties at the same time would be useful to understand

better the mechanism of frequency change. These new experiments are in progress.

Acknowledgements

We would like to express thanks to the members of the Department of Nuclear Engineering in Kyoto University for helpful suggestions.

Note added in proof —I. Koga kindly pointed out the influences of vacuum pressure and bombarding quartz electrodes on frequency change. But our experiment was done at the constant pressure of 5×10^{-7} Torr, and the electrodes were not bombarded by electrons. Substantially, no distinct differences were observed whether they were bombarded or not.

References

1. Frondel, C., *Amer.Min.* **30**, 432 (1945).
2. Poll, R.A. and Ridgeway, S.L., *IEEE Trans. Nuclear Sci.* **NS-13**, No. 6, 130 (1969).
3. Flanagan, T.M. and Wrobel, T.F., *IEEE Trans. Nuclear Sci.* **NS-16**, No. 6, 130 (1969).
4. Capone, B.R., Kahin, A., Brown, R. N., and Buckmelter, J.R., *IEEE Trans. Nuclear Sci.* **NS-17**, No. 6, 217 (1970).
5. Eernisse, E.P., *IEEE Trans. Nuclear Sci.*, **NS-18**, No. 2, 86 (1971).
6. King, J.C., and Sander, H.H., *IEEE Trans. Nuclear Sci.*, **NS-20**, No. 6, 117 (1973).
7. King, J.C., and Sander, H.H., *IEEE Trans. Nuclear Sci.*, **NS-19**, No. 4, 23 (1972).
8. Chi, A.R., *Phys. Rev.*, Vol. **107**, No. 6, 1524 (1957).
9. Gerbel, E.A. and Koerner, L. F., *Proc. IRE*, 1731 (1958).
10. IRE standards on Piezo-electric Crystals. *Proc. IRE*, 353 (1957).
11. Wertheim, G.K., *Phys. Rev.*, **111**, 1500 (1958).
12. Wertheim, G.K., *Phys. Rev.*, **105**, 1730 (1957); **110**, 1272 (1958).
13. Fan, H.Y. and Ramdas, A.K., *J. Appl. Phys.*, **30**, 1127 (1959).
14. Carter, J.R. Jr., *IEEE*, **NS-11**, No. 1, 290 (1964).
15. Aukerman, L.W., *IEEE, Trans. Nuclear Sci.*, **NS-17**, No. 6, 245 (1970).
16. Saito, H., and Hirata, M., *Japan. J. Appl. Phys.*, No. **11**, Vol. 2, 678 (1963).
17. Keery, S.L., *IEEE Trans. Nuclear Sci.*, **NS-19**, No. 3, 312 (1972).
18. Griffiths, J.H.E., Owen, J. and Ward, I. M., *Bristol Conference on Defects in Crystalline Solids*, 1954, pp 81-87. The Phys. Soc. London, 1955.
19. O'Brien, M. C. M. and Pryce, M. H. L., 1954, *Peport of Bristol Conference on Defects in Crystalline Solids*, Phys. Soc. London.
20. O'Brien, M.C. M., *Proc. Roy. Soc. A*, **231**, 404. (1955).
21. Mitchell, E.W.J. and Paige, E.G.S., *Phil. Mag.*, **46**, 1353 (1955).
22. Fraser, D.B., *J. Appl. Phys.* **35**, 2913 (1964).
23. Fraser, D.B., *Physical Acoustics*. Edited by Mason, Academic Press, Ch. 2, (1966).
24. Verhoogen, J., *Am. Mineralogist* **37**, 637 (1952).
25. Stuart, M.R., *J. Appl. Phys.*, Vol. **26**, No. 12, 1399 (1955).
26. Cook, R.K. and Wasilk, J.H., *J. Appl. Phys.*, 836 (1956).