Anisotropy in Thermal Properties of Single Crystal α Quartz Obtained by the Photoacoustic Method

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Anisotropy in the thermal properties in α SiO_2 single crystals SC cut mode 1 and mode 2 was investigated using the photoacosutic (PA) frequency transmission technique. The PA amplitude and phase diagrams were measured and numerically analyzed. The obtained results for the thermal diffusivity for SC mod1 was 0.34×10^{-5} m^2/s while it was 0.40×10^{-5} m^2/s for mode 2. The differences in PA spectra for both SC cuts were larger compared with much smaller differences which were observed using infrared reflectivity spectra.

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Quartz is the best known crystal with a piezoelectric effect and it is widely used in electronic devices and also in glass factories. Its physical properties have been studied a lot but mainly parallel and vertical to the z axis. At room temperature quartz α SiO_2 has a complicated structure – trigonal with 3 molecules per unit cell. Thus calculations of its electronic band structure are not easy. Infrared reflectivity spectra were properly analyzed by Gervais and Piriou[1)] where they showed that two type of vibrational modes A_2 (∥ z-axis) and E (⊥ to z-axis) exist. They observed 4 active IR A_2 modes and six E modes at room temperature for α - SiO_2, which change to two A_2 and only 3E modes for the β phase, existed at the higher temperature of 573.5 °C. More recently Bosio et al.[2)] studied VUV reflectivity of crystalline and amorphous SiO_2. They showed that polarization – dependent reflectivity data give new and more detailed information on the band structure of α SiO_2. Gan and Zhang[3)] studied the anisotropy of α SiO_2 using a photothermal method. They investigated thermal diffusivity for a quartz plate along directions perpendicular and parallel to the z-axis, using the "mirage" effect.

In this paper we have studied anisotropy of thermal properties of single crystal synthetic quartz samples. They were SC double rotated cut (mode 1 and mode 2) and were examined using the photoacoustic (PA) method with transmission detection configuration.

This SC double rotated cut is a modern version of SiO_2 crystal cut compared to various well-known high frequency (AT and BT) and low frequency (CT, DT, ET, FT) crystal cuts. The first SiO_2 crystal cut used in oscillators was a longitudinal vibration along the y or mechanical axis excited by a field applied along the electrical or x-axis. In order to improve the performance of the Y cut quartz crystal numerous investigations were conducted on how α - SiO_2 properties changed when the orientation angle of cutting was varied. In all cases there is a component of the electrical field along the y-axis, which produces a shearing motion until the angles of cut approach 90 degrees from the y-axis.

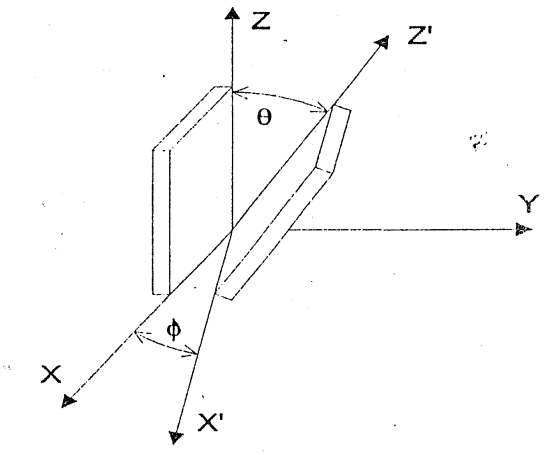

Fig.1. The crystallographic orientation of SC double rotated cut.

The orientation of the SC cut can be represented by two angles φ and θ as shown in Fig.1. Mode 1 has θ=34.07° and φ=23°, while mode 2 has the same θ, but φ=23°40′. The φ angle change is very important for the sharp change of the temperature frequency characteristic. This angle

accuracy must be kept in tolerance ± 5 minutes in the production of SC quartz resonators. The θ angle should be kept in tolerance better than ± 30 seconds or even ± 15 seconds[4].

Experimental Results

Single crystal quartz mode 1 and mode 2 with the thickness of the samples 270 μm were used. A thin Au film about 300 A thick was sputtered on one side of all samples. A He-Cd 25 mW laser was used as an optical source where the polarized laser beam was modulated with a mechanical chopper and the sample was irradiated by a relative large spot (about 3 mm in diameter). The samples had a disk shape with the diameter of 9 mm. In Fig.2 the amplitude (a) and phase (b) of the PA signals versus the modulation frequencies for SC mode 1 and mode 2 samples are given.

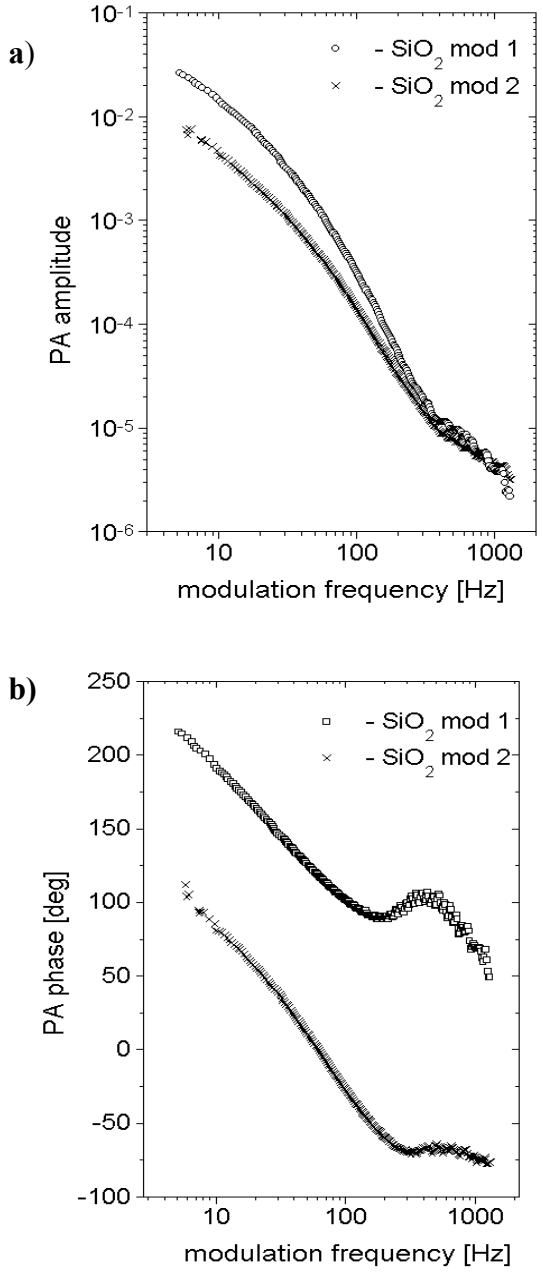

Fig. 2. The PA amplitude (a) and phase (b) diagrams versus modulation frequency for SC mode 1 and mode 2 quartz samples.

In Fig.2. one can notice differences in both amplitude and phase diagrams for modes 1 and 2. In Fig.2 one can notice differences in both amplitude and phase diagrams for modes 1 and 2, which is the consequence of their different thermal properties. These differences can be seen more easily if these two spectra are compared. So we calculated the ratio of their amplitude and differences between the phase data. These new diagrams, the amplitude ratio and the phase difference are given in Figs.3a and 3b, respectively.

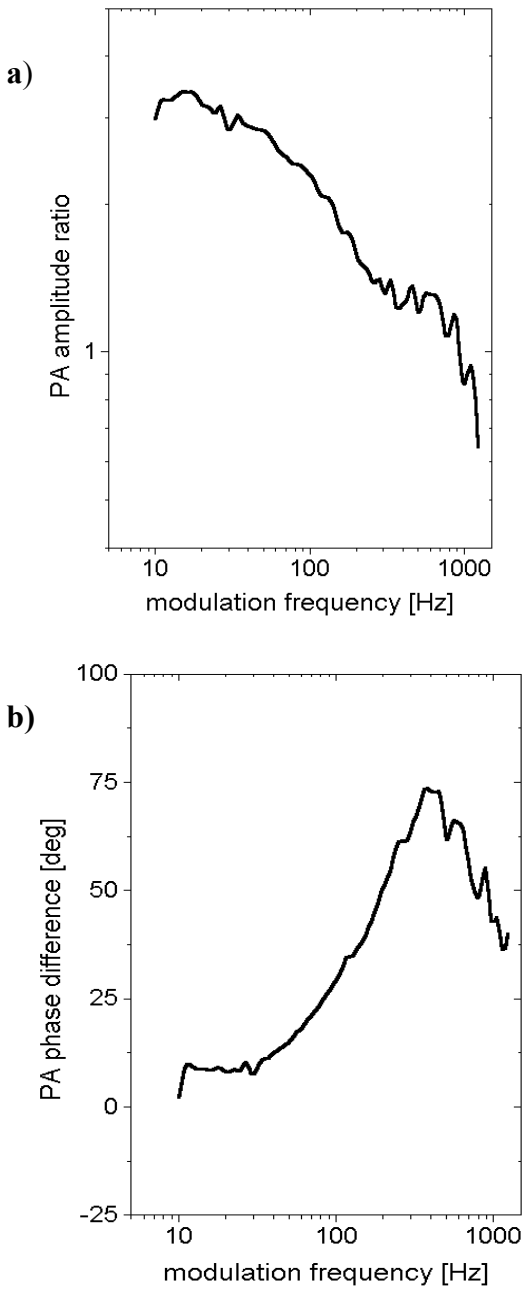

Fig. 3. The PA amplitude ratio (a) and phase difference (b) diagram for SC mode 1 and mode 2 quartz samples

Discussion

The PA amplitude and phase diagrams for mode 1 and mode 2 quartz samples, given in Fig.2, were numerically analyzed as explained elsewhere[5]. The obtained results for thermal diffusivity are given in Table 1.The dependence of the thermal diffusivity on the angle φ was measured by Gan and Zhang using the "mirage effect", and its D_T values for the cut parallel and perpendicular to the z - axis are given in Table 1, together with our results.

Table 1. Thermal diffusivity (D_T) and thermal conductivity (K) for SC mode 1, SC mode 2 and literature values when E||z or E⊥z - axis

	K [W/mK]	D_T [m^2/s]
SC mode 1	7.5	0.34×10^{-5}
SC mode 2	8.0	0.40×10^{-5}
||z [lit.3]	14.0	0.66×10^{-5}
⊥z [lit.3]	7.0	0.33×10^{-5}

The differences for obtained D_T values for SC cut mode 1 and mode 2 are rather small but are clearly seen experimentally. This proves the sensitivity of the PA method used in this work. Our values for D_T are very similar to the literature data[3] when the laser beam was polarized ⊥z.

It is interesting to see if another method could also show obvious differences for our SC mode 1 and mode 2 crystals. We have measured mid and far infrared reflectivity diagrams versus the wave number for SC mode 1 and mod2 crystals.

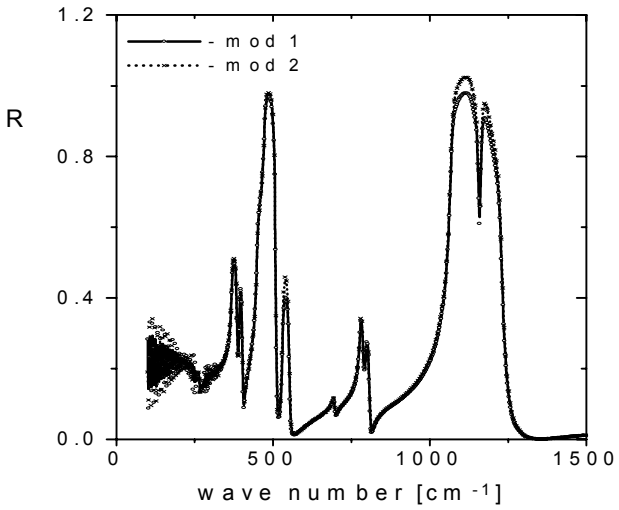

Fig.4. Far and mid infrared reflectivity versus wave number for α SiO_2 crystals SC mode 1 and mode 2.

In Fig.4. the reflectivity diagrams versus wave number are given for both samples. One can, first of all, see, that in the measured range nine of ten possible oscillators for both type of modes A_2 and E were observed. That means that both SC modes were oriented between either A_2 or E orientation. The differences between SC mode 1 and mode 2 in reflectivity diagrams were much smaller compared with the differences in their PA diagrams. Table 2 gives the positions of transversal (ω_{TO}) and longitudinal (ω_{LO}) modes for A_2 (|| z axis) and E(⊥ to z axis) modes from literature together with our values obtained for our SC modes using the Kramers-Krönig analysis.

Table 2. Positions of transversal and longitudinal modes for single crystal SiO_2: E||c (A_2) or E⊥c (E) and SC cut mode 1 and mode 2

SC cut Mode 1 Mode 2		A_2 (|| c) Lit. [1]		E (⊥ c) Lit.[1]	
ω_{TO} [cm^{-1}]	ω_{LO} [cm^{-1}]	ω_{TO} [cm^{-1}]	ω_{LO} [cm^{-1}]	ω_{TO} [cm^{-1}]	ω_{LO} [cm^{-1}]
372.0	386.6	363.5	386.7		
394.0	403.0			393.5	402.0
451.1	510.5			450.0	510.0
529.0	551.5	495.0	551.5		
693.7	697.1			695.0	697.6
777.6	790.0	777.0	790.0		
794.5	808.5			797.0	810.0
1053.0	1224.0			1065.0	1226.0
		1071.0	1229.0		
1159.0	1157.0			1158.0	1155.0

We did not observe the ninth oscillator with the transversal mode at 1071 cm^{-1}. All other oscillators were observed at similar wave numbers to data from literature.

Further improvement of both PA and IR investigations could be done, for the SC cut, using polarized light, but first one should orient the crystal to determine an orientation most similar to the ⊥z. Both SC cut modes will always have mixed A_2 and E modes, but the differences in oscillator values will be higher than those given for α - SiO_2[1]. This work on PA and IR methods is in

progress.

The anisotropy in thermal properties in α SiO_2 single crystals of SC double rotated cut (mode 1 and mode 2) has been for the first time clearly observed experimentally and numerically analyzed. Thermal diffusivity for these two modes was of the same order of magnitude, but similar to previous results[3] for E⊥z. The PA method was compared with the IR spectroscopy method and it can be concluded that the PA method being more sensitive give more information.

Acknowledgments

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