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Quartz Crystal Resonators with Electrodes of Conductive Polymers

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***Abstract*—Quartz crystal resonators are widely used in today's communication devices and systems as the essential enabler of signal processing with ubiquitous applications. The devices with metal electrodes are working well until recent years when the size of resonators is shrunk to such a degree that the metal density and consequently the gravimetric effect which causes frequency shift is considered to be avoided. With this objective, we began testing of conductive polymers as new materials for electrodes. With the conductive polymer PEDOT/PSS electrodes processed by a simple procedure, samples of quartz crystal resonator with polymer electrodes are made. Through a standard testing procedure, it is found that basically the resonator samples are usable with distinctive parameters. For instance, with the same crystal blank, the resonator by polymer electrodes has a resistance about 20 times of the one with metal electrodes, and the quality factor is also about 20th, as expected. Also the resonance frequency is higher due to less gravimetric effect. Clearly, the concept of polymer electrodes have been proven and future efforts will be on the improvement of the polymer materials and processing technique for acceptable properties and performances.**

Keywords—quartz, resonator, electrode, polymer, metal

I. INTRODUCTION

Quartz crystal resonators are popular frequency control unit for oscillators in communication devices and network products with extended applications as core sensor element in measurement technology also. In the nearly one hundred years of development, quartz crystal resonators have made tremendous advances, but the essential feather and materials remained the same-using quartz as the substrate and gold or silver or Aluminum as electrodes. Theoretical studies on electrodes [1] have been shown that the electrodes have important effects, sometimes adversary, on the performance of resonators [2-4]. From the viewpoint of product development, it is important to reduce the inertia and mass effects of electrodes through using metals with smaller density. Clearly, efforts should be made to reduce the mass of electrodes through possible approaches like reducing the thickness or using light-weighted metals for advantageous effect on resonator properties [5]. While there are improvements in the process of making thinner electrodes with metals, we want to take the advantage of using novel materials such as conductive polymers to make new products with new technology and process. Since the conductive polymers and novel materials with good conductivity are making rapid progresses to enter electronic products, innovative steps should be taken to change the technology for the manufacturing of quartz crystal resonators. With this objective in mind, we started to identify possible polymer materials for electrodes with the consideration of easy processing and good conductivity satisfying driving needs.

The conductive polymers for electronic devices are actually a hot research area for many reasons like the light weight and easy processing at much lower temperature in comparison with metals [6]. In addition, it is much lower in cost with a simple processing. We want the new materials to be tested with quartz crystal resonators, which have a much complicated electrode manufacturing process among electronic devices. We want to test relatively low cost materials with simpler process, and the finished products are tested as a validation of the idea and process. This paper summarized up all the inception and process along with a report on the quartz crystal resonators with polymer electrodes. It is concluded that the fully functioning resonators are fabricated with polymer electrodes with our experiment process, and the resonators are usable as designed with relatively larger resistance. The frequency change of the resonators from quartz crystal blanks are much smaller, as expected from light-weighted electrodes. The process of electrode manufacturing is relatively simple with much lower cost, and the resonator properties can be improved with better processing techniques. In addition, the resonator resistance can be reduced by adopting materials with much better conductivity also. With the combined efforts, we expect the properties can be improved dramatically from our research, and resonators with polymer or composite materials for electrodes can made with reasonably good performance for

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certain applications to enrich the product family and innovate the manufacturing process.

II. Suitable Conductive Polymers and Product Specifications

A. Suitable Conductive Polymers for Electrodes

There are extensive research activities on conductive polymers for various applications with electrode fabrication as an important one [7, 8]. The general requirement for conductive polymers for electrodes are that it must be good at conductivity, light-weight, eas-of-processing at low temperature, and good rigidity or hardness. With such considerations, conductive polymers available for industrial applications meeting these requirements are intrinsic conducting polymers family including typical material like polythiophene which is excellent in conductivity and good hardness. Other possible candidates for this purpose also include polypyrrole and polyaniline [9].

As typical polythiophene polymers of choice, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT/PSS) exhibits very good conductivity at room temperature and the density is also much smaller. It has good solubility in water, making it very easy to be added to the small surface area of quartz crystal resonator with simple experimental techniques. In this study, we employed a simple procedure to fabricate thin PEDOT/PSS layer on the surface area for electrodes. Wiring for current delivery is connected with polymer layers and sources.

B. Material Preparation and the Making of Electrodes

As we have described, PEDOT/PSS is selected as the polymer for electrode in our study. Commercial samples of PEDOT/PSS (CLEVIOS™ PH 1000) was purchased from HERAEUS Company (Hanau, German) for this experiment.

Since CLEVIOS™ PH 1000 has excellent conductivity, it has applications in some typical industrial products including new types of flexible displays, high performance electrolytic capacitors, OLED, OPV and printed electronics. CLEVIOS™ PH 1000 is a blue water solution, we transfer it on to the surface of crystal chips through spraying and brushing. After removing water at 120℃ for 1h, thin PEDOT/PSS coating was formed on the surface of crystal. The process is a manual operation on the polished and cleaned crystal chips with only areas for electrodes exposed by mask. The process has been simple and easy, and improvement on the processing can be made upon the completion of the initial tests and measurements. The testing samples are made in the Polymer Lab, Ningbo Institute of Materials Technology and Engineering (NIMTE). The quartz crystal blanks are provided by the TXC (Ningbo) Corporation from their existing products.

C. Quartz Crystal Blanks Specifications and Electrodes

The quartz crystal blanks are for the resonator of silver electrodes with a nominal vibration frequency of 4 MHz. The crystal blank has a size about 5.715×2.477 mm, and the thickness is about 420 μm. The quartz crystal blank has been grinded and polished to meet the requirements for affixing metal electrodes with a thickness about 400 Å with a nickel-chromium alloy layer and silver layer. With the polymer layer of electrodes even for much larger thickness, the gravimetric and stiffness effect are very limited, and the change of frequency is very small, as we shall observe and explain later.

III. Fabrication of Quartz Crystal Resonators with Polymer Electrodes

With essential elements of quartz crystal resonators available from the description in the previous section, we developed a simple process to make quartz crystal resonators with polymer electrodes for testing and proof of our approach. As in the early stage of this research, the main objective is the completion of quartz crystal resonators with polymer electrodes with a simple procedure. The quartz crystal blanks for the polymer electrodes are provided by the TXC and the polymer electrodes are processed by the Polymer Lab, NIMTE.

The main steps of the procedure for electrode processing are the follows:

A. Conductive Polymer Materials and Preparation

With conductive polymer PEDOT/PSS solution from HERAEUS Company, it can be easily sprayed to the quartz crystal blank surface area as electrodes. The part is done at the Polymer Lab of NIMTE. The quartz crystal blanks are fully polished and cleaned as required for metal electrodes production, and they satisfy the standard for high precision quartz crystal resonators.

B. Polymer Electrodes Processing and Trimming

After the polymer solution was sprayed on the designated area of quartz crystal blanks with electrode mask, then the mask is removed, and the electrodes are dried, cleaned, and trimmed with fluid and heat. Particularly, the edges of the electrodes are cleaned and trimmed to ensure the exact shape and clear from contaminations and residuals. The cleaned crystal blanks with coating are ready for next process such as wiring, sealing, and packaging.

C. Quartz Crystal Resonators with Polymer Electrodes

The quartz crystal blanks with polymer electrodes are processed as conventional ones for the mounting, sealing, wiring, and packaging. The completed quartz crystal resonators with polymer electrodes are finished and tested for key performance parameters. This part is completed in the production line of TXC to ensure the compatibility of the product and process.

D. Summary of the Processing and Results

With the completion of above procedure, it is clear that quartz crystal resonators with polymer electrodes are made with basic functions comparable with resonators of metal electrodes. The initial results show that the electric resistance is much bigger for polymer electrodes, but it is possible to find solutions and applications that the new product can be used as the alternatives of conventional product. The research work on polymers with good conductivity has been continued for decades with the key objective of utilizations in electronic devices including semiconductor. With recent advances of nanomaterials, there are some promising options to make highly conductive composites for our application target.

IV. Quartz Crystal Resonators with Polymer Electrodes

A. A General Description

We intended to fabricate a quartz crystal resonator sample with the following basic information: AT-cut quartz crystal with size 5.715 mm×2.477 mm×0.418 mm, and the nominal frequency of the fundamental thickness-shear mode is 4 MHz. With the PEDOT/PSS as the conductive polymer for electrodes, the vibration frequency will be a little higher due to less gravimetric effect of electrodes. It is expected that there will be changes of other performance parameters due to changes of electrode material, and the further improvement can be considered through future requirements and material selection. The fabrication of polymer electrodes is done with a manual process through prepare the quartz crystal blanks and polymer materials. The completed quartz crystal blanks are further processed to fully functioning resonators and tested for key performance parameters.

B. Electrode Materials and Specifications

With the polymer material PEDOT/PSS for electrodes, it is treated with the sole objective of easy spraying on the designated surface of quartz crystal blanks we choose. Since there is no technology available to our project on the coating of polymer with better control and precision, it can only be done in a trial and error approach for a thinner layer with acceptable results. In the process to make a prototype of quartz crystal resonator with polymer electrodes, several methods of brush painting and spraying polymer liquid on the crystal surface have been tested, and eventually the end resonator products are tested for feasibility. Our measurement of the completed resonators are based on the electrode thickness of 10 μm and 20 μm. Further reduction of thickness of polymer electrode should be explored with the consideration of surface conditions and conductivity.

C. Experimental Results

After the prototypes of quartz crystal resonator with polymer electrodes are fabricated, a standard testing is performed on the new resonators. It is intended to make comparisons with conventional resonators of metal electrodes. For the tested samples of quartz crystal resonator with polymer electrodes, the basic properties of resonator are obtained. It is clear that we have a quartz crystal resonator with different performance properties in comparison with metal electrodes. For the same quartz crystal blanks, properties of resonators with metal electrodes are given in Table 1, while the results of polymer electrodes are in the Table 2. It is clear from a comparison to Table 2 that the vibration frequency and resistance are much smaller. With polymer electrodes, the static capacitance C0, dynamic capacitance C1, and inductance L are almost the same. However, the frequency Freq increased slightly due to smaller density of electrode material. The largest increase is seen on the resistance, which is about 20 times of metal electrodes. Of course, the quality factor Q also dropped proportionally, about 20th of the metal electrodes. A simple conclusion can be drawn from the tables are that the reduction of resistance will be important in the future work. It is possible that better conductive polymers with the addition of other materials will improve the conductivity and surface bonding to obtain improved electric resistance.

TABLE 1. The Key Performance Parameters of Quartz Crystal Resonators with Metal Electrodes

No.	Freq (MHz)	R (Ω)	C0 (pF)	C1 (fF)	L (mH)	TS (ppm/pF)	Q (k)
1	3.996	81.38	0.94	2.97	533.96	18.59	164.76
2	3.996	71.98	0.95	2.99	530.34	18.69	185.01
3	3.997	65.28	0.95	2.99	530.15	18.68	203.97
4	3.997	102.25	0.93	2.98	531.98	18.67	130.66
5	3.996	76.11	0.93	2.94	540.22	18.39	178.23
6	3.995	64.17	0.94	3.01	527.06	18.83	206.20
7	3.997	71.67	0.93	2.94	538.80	18.44	188.82
8	3.996	82.53	0.92	2.98	531.81	18.72	161.84
9	3.995	66.75	0.92	2.95	537.36	18.55	202.10
10	3.996	114.26	0.94	2.99	530.14	18.73	116.50

TABLE 2. The Key Performance Parameters of Quartz Crystal Resonators with Polymer Electrodes

No.	Freq (MHz)	R (Ω)	C0 (pF)	C1 (fF)	L (mH)	TS (ppm/pF)	Q (k)
1	4.009	1,782.55	0.70	3.04	517.67	20.10	7.32
2	4.018	3,599.45	0.32	3.04	515.68	21.95	3.62
3	4.009	1,773.08	0.70	3.07	512.36	20.33	7.28
4	4.007	1,859.65	0.74	3.13	503.64	20.52	6.82
5	4.003	1,473.75	0.89	3.16	499.68	20.02	8.53
6	4.006	1,561.50	0.76	3.07	513.19	20.01	8.27
7	4.003	1,437.79	0.83	3.10	509.51	19.87	8.91
8	4.007	2,169.21	0.74	3.15	501.19	20.60	5.82
9	4.007	1,635.22	0.78	3.08	511.37	20.01	7.87
10	4.009	3,877.34	0.29	3.07	513.66	22.31	3.34

V. Conclusions

We have successfully fabricated quartz crystal resonator samples with conductive polymer as electrodes and made comparisons with metal electrodes. It is clear that polymer electrodes can have advantages like ease-of-fabrication and low cost in the innovative manufacturing of quartz crystal resonators. The disadvantages shown from our experiment such as the larger resistance can be improved from better polymer materials and processing techniques. This research provides another direction for further exploration in novel quartz crystal resonator development. As the RF devices accelerate innovations in size, frequency, and performance through fast growing networking and interconnection technology, novel materials and processing are urgently needed to meet some of these challenges. By adopting some of the novel materials and processing technologies, the quartz crystal industry can be ahead of the tide of networking with reliable, precise, and superior resonators. Such new materials and process will definitely change the quartz crystal industry.

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