Effect of Ultra-Low Expansion Quartz Glass Layer on the Enhancement Performance of Quartz Optical Fiber

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Abstract: In this paper, the prefabricated rod of quartz fiber was prepared by MCVD method. A thickness of ultra-low expansion(ULE) quartz glass was deposited in the wall of quartz tube, and then quartz and its dopants were deposited. Finally, the prefabricated rod of quartz fiber preform containing doped TiO2 layer was successfully prepared by high temperature dehydroxylation treatment. The strength of quartz fiber obtained by wire drawing for the prefabricated rod is significantly improved. The experimental results showed that the quartz glass layer with TiO2 doped has a lower thermal expansion coefficient, the doped of TiO2 is amount 5wt%, and the doped layer thickness is 4%, the optical fiber has the best enhancement. The maximum tensile strength of the organic coating is up to 75.5N, which is higher (6.34%) than that of the commercial optical fiber (71N).

1. Introduction
Quartz fiber has a wide range of applications in the fields of national defense, military, civil communications, etc. In China, development technology of quartz fiber is relatively mature, however, the basic focus is on low-end products, low price, while high-end quartz fiber prices are still high, and rely on limited imports. Tensile strength is an important index to evaluate the performance of quartz fiber. The main component of optical fiber is quartz glass, which theoretically has a high tensile strength. However, in the actual process of drawing quartz optical fiber, microcracks will occur on the surface during the cooling process after forming. It is easy to lead to the microcracks diffusion on the condition of complex environment, such as air and water vapor, and then rapid reduction the strength of optical fiber[1-3]. This results in fibers that a tenth or less of their theoretical strength. In order to improve tensile strength of the silica fiber, we usually adopt the method of organic coating to enhance, although organic coating can effectively improve the tensile strength of quartz optical fiber. In fact, the tensile strength of organic coating itself is limited, and its bare fiber parts produced by the micro cracks has not eliminated. Therefore, restraining or avoiding the appearance and propagation of microcracks in bare fiber can further improve its tensile strength, which has important scientific significance for the enhancement of quartz fiber[4-6].

Currently, in order to reduce the generation and expansion of microcracks in the process of drawing quartz fiber, the generally techniques mainly include: strict optimized drawing time, cooling system, fire polishing, annealing optimization, atmosphere control, although such process have the effect of
reducing microcracks, but fiber still exists a certain number of microcracks, especially on the surface of fiber\cite{7-10}. Therefore, if we develop a coated layer with low expansion coefficient materials on the surface of optical fiber, a compressive stress will formed on the surface of the quartz layer by the outer layer with low expansion coefficient, which can inhibition of the generation and propagation of cracks, and is expected to significantly increase the tensile strength of the optical fiber. Recently, the ultra-low expansion(ULE) quartz glass with excellent low expansion characteristics was frequently reported\cite{11-15}. There main chemical components are TiO\textsubscript{2} and SiO\textsubscript{2}, and the melting point is close to quartz. Therefore, before the process of drawing, designs a layer of ULE quartz glass layer with TiO\textsubscript{2} in the outer surface of quartz optical fiber would restrain micro-crack extension. It’s due to the compressive stress caused by ULE characteristics when the micro-crack expansion near the ULE quartz glass layer, which is expected to significantly improve the tensile strength of the fiber.

The purpose of this study is to investigate the feasibility of ULE quartz glass layer with TiO\textsubscript{2} in the outer surface of quartz optical fiber to enhance optical fibers. The prefabricated rod of quartz fiber is prepared by MCVD method was adopted. The influences of TiO\textsubscript{2} concentration and temperature on the expansion coefficient properties of the Anti-pull force of quartz glass fiber were investigated. and accordingly the tensile strength proportions for quartz glass fiber were optimized. The properties of element distribution were characterized.

2. Experimental

2.1 Materials and methods

The MCVD in-tube deposition method was adopted, the doped titanium dioxide quartz glass layer was first deposited in the quartz tube. High purity SiCl\textsubscript{4}, TiCl\textsubscript{4} and O\textsubscript{2} were used as the gas source (purity > 99.999\%), and MCVD was deposited at 1200\textdegree C outside the tube. The reaction equations are shown in Equations (1) and (2).

\[
\text{SiCl}_4 + O_2 \xrightarrow{\text{High-temperature}} \text{SiO}_2 + 2\text{Cl}_2 \uparrow \quad (1)
\]

\[
\text{TiCl}_4 + O_2 \xrightarrow{\text{High-temperature}} \text{TiO}_2 + 2\text{Cl}_2 \uparrow \quad (2)
\]

After the deposition thickness is set, the gas source is changed to take high purity SiCl\textsubscript{4}, GeCl\textsubscript{4} and O\textsubscript{2} as the gas source (purity>99.999\%), and MCVD deposition is continued. The tail gas is discharged on the other side of the intake pipe. It is necessary to further vitrification this powder rod and place it in the high temperature sintering furnace for dehydroxy sintering to achieve transparent vitrification effect. MCVD powder deposition and vitrification of powder rod are shown in Schematic diagram 1.

![Figure 1. Schematic diagram of MCVD tube deposition process and powder rod vitrification](image)

The final transparent glass rod was machined and casing treated. Meanwhile, the surface of the glass rod was ground and polished. The outer quartz tube before deposition in the MCVD was ground.
The cleaning and assembly quality of the quartz bushing has a great impact on the performance of subsequent products (such as the broken fiber and core package in the prefab bar). The fiber prefab bar needs to be washed→pickled→washed→dried, and finally the fiber is drawn. The diameter of the drawn bare fiber is 125μm, coated with acrylic resin and curable. After the organic coating, the diameter of the wire is 250μm.

2.2 Characterization
According to GB/T 15972.31-2008 <Specification of optical fibre for test methods, Part-31: Measurement methods and test procedures for mechanical properties, tensile strength>, the tensile strength of the prepared optical fiber was tested. The test temperature of environment was 23℃±2℃, the relative humidity was 50%±5%, the loading rate was 5mm/min, the diameter of the winding wire diameter fixture was 60mm, and the standard distance of the test wire diameter was 500mm. Respectively, the optical fiber was organic coated at last, therefore, in the test results, the tensile strength is represented by the maximum tensile force, and the measured tensile force value is the arithmetic average of the results of 10 total numbers. The microstructure of the samples was observed by S-4800 scanning electron microscope, and the components were analyzed by EDS. Tube wall deviation, ovality tester is used to detect the geometric size of high purity quartz glass products. PK instrument is used to measuring the geometric size and refractive index profile of high purity quartz glass products. Fourier transform infrared spectrometer (FTIR) is used to test the hydroxyl content in quartz glass. ICP-MS is used to detect the content of each metal component to ensure the purity of raw materials.

3 results and discussion

3.1 Analysis of expansion coefficient curve of quartz glass with low expansion
The expansion coefficient of quartz glass is close to 5×10⁻⁷/℃, which is a material with low expansion coefficient. In order to verify whether the expansion coefficient will be lower after doping TiO₂, quartz glass samples with TiO₂ doping amount of 5wt% were prepared by MCVD vapor deposition technology. The thermal expansion analysis and comparison experiment with the undoped quartz glass sample were carried out, and the experimental results are shown in Figure 2.

![Figure 2 Curve of linear expansion coefficient versus temperature of quartz glass with and without TiO₂](image)

It was observed from Figure 2 that the curves of both quartz with and without TiO₂ firstly increase with the increase of temperature, then decrease, and finally remain unchanged. At the same time, it can be clearly found that the linear expansion rate of quartz glass doped with 5wt% TiO₂ is close to 1/10 of
that of undoped pure quartz, which indicates that the linear expansion rate of quartz glass doped with 5wt% TiO$_2$ is significantly lower than that of pure quartz. The expansion coefficient is closely related to the bond force between the anion and cation of the glass. The larger the bond force between the anion and cation results in the smaller expansion coefficient of the glass. The bond force $F$ between anion and cation can be expressed by formula (3) as below.

$$F = \frac{2z}{a^2}$$

(3)

Where $z$ is the valence of the cation and $a$ is the center distance between the anion and the cation.

According to key force formula, the influence key force only cation valence and the size of the distance between the anion and cation, and a fixed groups valence is relatively fixed, affect the size of a key force mainly depends on the size of the ion center distance of cation and ion, cation and ion center distance, the greater the bond force is smaller, ion of cation and ion center distance, the smaller the key force, the greater the inversely proportional relationship. The main component of low expansion glass is SiO$_2$, so the most important bond in this low expansion glass is Si-O bond. Si-O bond has a relatively large bond force and a small expansion coefficient, which can reach the order of $10^{-7}$.

The structure of glass plays a decisive role in the expansion coefficient of glass. Oxides in low-expansion silicate glass have different effects on the structural strength of glass. Adding TiO$_2$ intermediate oxides can reconnect the broken silicon-oxygen network, strengthen the network structure and reduce the expansion coefficient of glass. There are also some cations in the network space gap, on the surrounding silicon oxygen tetrahedron polymerization, filling the gap while increasing the structure of the compact, but also can reduce the expansion coefficient of glass; The expansion coefficient of TiO$_2$ (-25×$10^{-7/\circ}$C) is negative, which can reduce the overall expansion coefficient of glass.

3.2 Influence of doped TiO$_2$ content on low expansion coefficient of quartz glass

As it can be seen from the part of 3.1, the uniform addition of TiO$_2$ to quartz glass can significantly reduce its thermal expansion coefficient. In order to explore the influence of TiO$_2$ doping concentration on the thermal expansion of quartz glass, MCVD vapor deposition technology was used in the experiment. Quartz samples with TiO$_2$ doping (of 0.5wt%, 2wt%, 5wt%, 10wt%, 15wt%, 25wt% and 38wt%) were prepared, and their thermal expansion rates were tested at different temperatures (50℃, 100℃, 150℃, 200℃, 250℃). The experimental results are shown in Figure 3.
It was observed from Figure 3 that, at different temperatures, the linear expansion coefficient of quartz glass decreases with the increase of TiO$_2$ doping amount. Meanwhile, it can also be seen from the figure that, at the same TiO$_2$ doping amount, the linear expansion coefficient of quartz glass increases with the increase of temperature. This indicates that the higher the TiO$_2$ doping concentration in quartz glass, the smaller the expansion coefficient.

In this paper, the main purpose of TiO$_2$-doped quartz layer is to form compressive stress on the surface of quartz to restrain the generation and expansion of cracks. Whether the difference of expansion coefficient between the two is greater is better remains to be further tested. Therefore, in order to explore and optimize the doping content of TiO$_2$, quartz with different doping content (0 wt%, 0.5 wt%, 2 wt%, 5 wt%, 10 wt%, 15 wt%) was designed respectively in the experiment, whose wall thickness was 1.6 mm, and the diameter of the undoped quartz in the optical fiber prebar was 40 mm. It is brushed and coated with acrylic resin for protection. The pulled quartz fiber was tested for tensile resistance, and the tensile test results are shown in Figure 4.

It was observed from Figure 4 that the tensile strength of quartz fiber increases first and then decreased with the increase of TiO$_2$ doping amount, reaching the maximum value of 75.5 N with the TiO$_2$ doping amount was 5 wt%. The expansion coefficient is closely related to TiO$_2$ concentration in quartz. The higher concentration of TiO$_2$ results in the lower expansion coefficient of the quartz, and can accordingly indicated that the higher the concentration of TiO$_2$, the greater the difference of expansion coefficient between the surface layer with TiO$_2$ doping and the quartz layer. It was also observed from Figure 4 that the difference of expansion coefficient is not the bigger the better. On the one hand, too much stress may lead to crack or doping layer produce microcracks when the concentration of TiO$_2$ was more over than 5 wt%; on the other hand, the softening point of quartz with higher TiO$_2$ concentration is lower than pure quartz, and the difference is larger, which leads to TiO$_2$ doping layer appears bubbles and too fast softening in the process of drawing, which is not conducive to improving the tensile resistance of optical fibers.

In conclusion, in order to improve the tensile resistance of quartz fiber, with the optimal TiO$_2$ doping amount is 5 wt%, the enhancement effect is the most obvious.

### 3.3 Influence of film thickness on optical fiber strength

In order to improve the tensile resistance of the quartz fiber, we further optimized the thickness of the doping layer. The schematic diagram of the doping layer and quartz layer thickness is shown in Figure 5.
In the experiment, the diameters of the bare optical fibers before the organic coating were all 125μm after the fiber drawing of quartz fiber preforms with different diameters. Therefore, the film thickness $S$ was defined as shown in Equation (4).

$$ S = \frac{d}{D} \times 100\% $$

(4)

Where $d$ is the wall thickness of a single-layer doped quartz tube, $d$ is the diameter of the prefab rod of the quartz fiber. Experiments with different thickness ratios (1~10) were designed respectively, and the tensile strength of the quartz glass fiber changed with the thickness of the doped TiO$_2$ layer, as shown in Figure 6.

It was observed from Figure 6 that the tensile strength of quartz glass fiber increases first and then slowly decreases with the increase of the thickness of doped titanium dioxide layer. It is due to the low expansion quartz layer which is too thin, subsequently the compressive stress was not significant to suppress the generation of crack and extension. On the contrary, when the thickness is too thick, the low expansion quartz also can produce micro cracks itself, and the quartz by doping of TiO$_2$, bubbles may arise in the process of drawing, which will affect the tensile strength of the fiber. Therefore, when the thickness ratio $S$ is around 4%, the tensile strength of the prepared quartz fiber is the highest.

3.4 Microstructure and composition analysis

In order to further control the uniformity of titanium element distribution in the film layer, the ICP quantitative analysis of titanium in the implementation case 1 was carried out, as shown in Table 1.
Table 1 ICP analysis of outer element of wire diameter

| Element | Weight percentage (%) |
|---------|------------------------|
| O       | 52.76                  |
| Si      | 44.18                  |
| Ti      | 3.05                   |
| Total quantity | 100.00              |

It was observed from Table 1 that no element mismatch occurs after the doping layer is drawn at high temperature. Figure 7 shows the filament diameter morphology and surface sweep element distribution of quartz fiber.

Figure 7 Microstructure and surface element distribution of quartz fiber: (a) fiber diameter structure; (b) sweep area of element surface; (c) Element content distribution; (d) Surface sweep distribution of Ti elements

According to Figure 7(a), it was observed that the quartz fiber has uniform diameter, smooth surface and no obvious defects. According to Figure 7(b), a representative region was selected for EDS surface scanning test. It can be seen from Figure 7(c) that all elements have a certain intensity and the content was consistent with that in Table 1. According to Figure 7(d), surface scanning of Ti element showed that the Distribution of Ti element was uniform. Therefore, the prepared quartz fiber prerods containing TiO₂ doped layer with a certain concentration and thickness on the surface layer for drawn is feasible.

4. Conclusion

In this paper, an optical fiber preform with a quartz layer doped with TiO₂ was successfully prepared by MCVD method on the outer layer of the quartz fiber preform rod for the first time. The quartz fiber drawn by the quartz preform rod has a significant enhancement effect. The optimization experiment shows that the doped of TiO₂ is amount 5wt%, and the doped layer thickness is 4%, the optical fiber has the best enhancement. The maximum tensile strength of the organic coating is up to 75.5N, which is higher (6.34%) than that of the commercial optical fiber (71N). The scheme is feasible and the enhancement effect is significant, which lays a technical foundation for the field of optical fiber enhancement in future.
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