

FAST TRACK COMMUNICATION

Nano-structured TiO₂ film fabricated at room temperature and its acoustic properties

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Abstract

Nano-structured TiO₂ thin film has been successfully fabricated at room temperature. Using a quarter wavelength characterization method, we have measured the acoustic impedance of this porous film, which can be adjusted from 5.3 to 7.19 Mrayl by curing it at different temperatures. The uniform microstructure and easy fabrication at room temperature make this material an excellent candidate for matching layers of ultra-high frequency ultrasonic imaging transducers.

(Some figures in this article are in colour only in the electronic version)

Matching layers are crucial components of ultrasonic probes for medical imaging. Without proper matching layers, large acoustic impedance mismatch between piezoelectric transducer and the imaging body will result in poor imaging quality due to reflection at the interface [1]. For single frequency transducers, such reflection greatly reduces the power efficiency and the sensitivity of the transducer. For a broadband transducer, such reflected signals could produce a long ringdown if the backing does not absorb the reflected energy so that the resolution will be greatly reduced. For a single frequency wave propagating in an infinite medium, a quarter wavelength matching layer in between the piezoelectric and imaging medium can resolve this problem. Theoretically, if the piezoelectric is also infinite or in the case when the finite transducer has a lossy backing, the acoustic impedance ($Z = v \times \rho$) of the matching layer is the geometric mean of the piezoelectric material (Z_c) and the imaging medium (Z_m), i.e. $Z = \sqrt{Z_c Z_m}$. For air backed transducers, the optimized acoustic impedance of the matching layer for a broadband transducer is $Z = Z_c^{1/3} Z_m^{2/3}$ [2, 3]. When two matching layers

are used, one of them needs to have a lower acoustic impedance than the geometric mean, while the other needs to have a higher acoustic impedance than the geometric mean. In general, the acoustic impedance of matching layers is in the range of 3–15 Mrayl. Unfortunately, there are no natural materials that can meet such requirements, therefore, solid particle/polymer composites are commonly used as matching layer materials in practice [4]. For ultra-high frequency transducers (centre frequency > 50 MHz), the thickness of the quarter wavelength matching layers is less than 10 μm . This demands that the particle size in the composite be much less than 0.5 μm in order for the composite to behave like a single phase material with minimal wave scattering. High acoustic impedance requires higher volume loading of solid particles, but it is impossible to load high volume ultra-fine powders into the polymer without introducing air bubbles. Therefore, all ultra-high frequency transducers currently used or under development use unfilled polymers as matching layer because of the lack of desired matching layer material [5]. This problem hinders the development of ultra-high frequency ultrasonic imaging

technology. In a previous work, we reported the development of SiO₂ nano-composite using the sol–gel technique [6], which can be made to have good uniformity and adjustable acoustic impedance between 2.2 and 5.7 Mrayl. Although a big step forward, the acoustic impedance of the SiO₂ nano-composite is still not high enough, particularly for broadband transducers for which the acoustic impedance of one of the matching layers is more than 8 Mrayl. In addition, the sol–gel film is difficult to lift off the substrate and the spin-coating method is not very convenient to use. It would be desirable to simplify the fabrication process and lower the processing temperature so that the matching layers can be directly coated onto the transducer without causing depoling of the piezoelectric piece.

Nano-size titanium dioxide (TiO₂) is one of the most important materials being studied in recent years by researchers for many practical applications [7, 8]. However, there were no reports on its elastic properties or acoustic properties to date. Compared with SiO₂, the acoustic impedance of TiO₂ is more than twice (~20 Mrayl); therefore, composites made of TiO₂ nano-particles should have a higher acoustic impedance than SiO₂ nano-composites.

From research on dye-sensitized solar cells [9], we found that TiO₂ nano-particles can be made into porous nanostructure by adding a small amount of Ti^{IV} tetraisopropoxide (TTIP) diluted with ethanol solution. The TiO₂ nano-particles were purchased from Degussa, Germany, which contains 30% rutile and 70% anatase. TiO₂ : TTIP : ethanol are mixed at the molar ratio of 1.0 : 0.05 : 6.0. The mixture paste was dispersed well using an ultrasonic horn (UPS400, Hielscher-Ultrasonic Technology) for 30 min. The mixture paste was coated onto a glass plate substrate by the doctor-blade technique. The thickness of the film is about 8 μm. The ethanol evaporated at room temperature and the TTIP formed amorphous TiO₂ to bond the TiO₂ nano-particles together. The amorphous TiO₂ bonds can crystallize if the sample is annealed at a temperature >400 °C. However, for matching layer applications, the acoustic impedance is the key parameter while crystallization is not necessary.

The fabricated films have a similar morphology to those fabricated by the traditional method at much higher temperatures [9]. From the micrographs of scanning electron microscopy (SEM) shown in figure 1, homogeneously distributed TiO₂ particles are well bonded together with the particle size distribution mainly in the range 25–40 nm. The porous structure is uniform in all the three dimensions.

In order to precisely measure the acoustic impedance of such thin films, the through-transmission ultrasonic spectroscopy technique based on the quarter wavelength matching principle has been used, which has a resolution of λ/4 [10]. One pair of 100 MHz immersion type ultrasonic transducers (Valpey–Fisher E9934) is carefully aligned by a customized 3-D automatic slider system in a water tank filled with deionized water. A Panametrics 5052PR 200 MHz pulser/receiver was used to drive the transducers and amplify the received signals. After averaging for 64 times, the received signals are acquired by a Tektronix TDS 430 digital oscilloscope with a sampling window set at 2500 points. The data are then downloaded to a personal computer via a GPIB

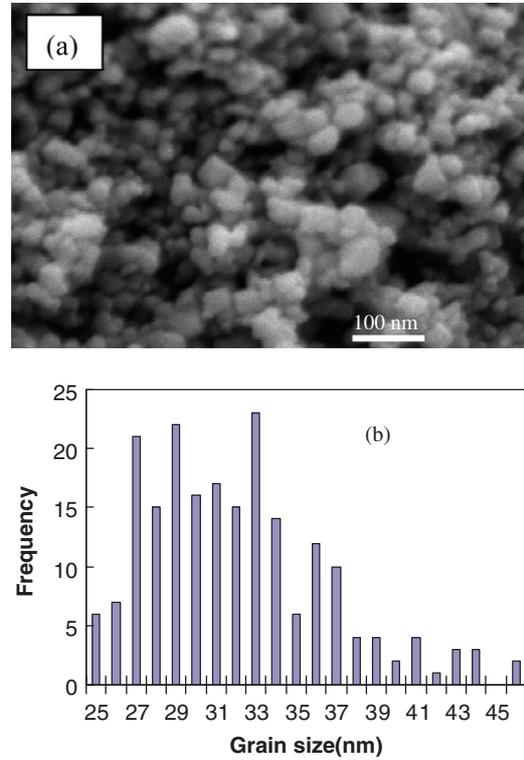


Figure 1. (a) SEM micrograph of the TiO₂ nano-structured film shows the size of TiO₂ particle around 25 nm. (b) The histogram showing the particle size distribution.

interface and then fast Fourier transform (FFT) was performed using MATLAB[®]. The frequency resolution in the measured data is 0.2 MHz.

As discussed in detail in [10], the amplitude spectra ratio is given by

$$\left| \frac{G(f)}{H(f)} \right| = \frac{T_{23}T_{31}}{T_{21}} \frac{e^{-(\alpha_3 - \alpha_1)d_3}}{|1 - R_{31}R_{32}e^{-2\alpha_3 d_3} e^{-i2\beta_3 d_3}|}, \quad (1)$$

where $G(f)$ and $H(f)$ are, respectively, the Fourier transforms of the signal through a thin film and substrate, and the signal from the substrate only. T_{ij} and R_{ij} denote the transmission and reflection coefficients from medium i to medium j . When the acoustic impedances satisfy the condition $Z_1 < Z_3 < Z_2$, the signal ratio $|G(f)/H(f)|$ maximizes at

$$\beta_3 d_3 = \left(n + \frac{1}{2}\right) \pi, \quad (n = 0, 1, \dots). \quad (2)$$

The corresponding peak frequencies and phase velocity are given by

$$f_n = \left(n + \frac{1}{2}\right) \frac{v_3}{2d_3}, \quad (n = 0, 1, \dots), \quad (3)$$

$$v_3 = 4f_0 d_3. \quad (4)$$

In order to further strengthen the bonding between particles and increase the density, the sample was annealed in an oven progressively at 20, 50, 80, 110 and 140 °C for 1 h at each temperature. Figure 2 presents the spectra ratio $|G(f)/H(f)|$ versus frequency after different temperature treatments. We can see that the peak frequency of the spectra

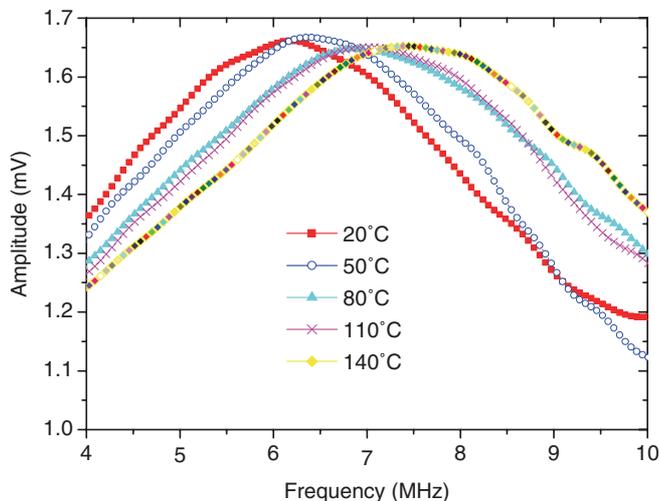


Figure 2. Received signal spectra ratios, $|G(f)/H(f)|$, for an $8 \mu\text{m}$ film on a 6 mm thick glass substrate. The peak shifts to higher frequencies after higher temperature annealing.

Table 1. Measured acoustic characteristic of TiO_2 nano-structured film after annealing 1 h at different temperatures.

Annealing temperature	20 °C	50 °C	80 °C	110 °C	140 °C
Velocity (m s^{-1})	1953	2031	2207	2221	2344
Density (kg m^{-3})	2715	2892	2965	3032	3068
Acoustic impedance (Mrayl)	5.30	5.87	6.54	6.73	7.19

ratio increases with the annealing temperature, which means that the heat treatment leads to an increase in the ultrasonic velocity.

The measured acoustic properties are listed in table 1. At room temperature, the sound velocity in the film is 1953 m s^{-1} . It increases almost linearly with each higher temperature annealing and goes up nearly 20% to 2344 m s^{-1} after the annealing at 140°C . Density measurement is obtained by the Archimedes principle using xylene liquid. Compared with the theoretical density of 3.95 g cm^{-3} , the density of the porous structure is about 67.4% after the 20°C annealing and 77.3% after the final annealing at 140°C .

In order to demonstrate the effectiveness of the matching layer made of TiO_2 nanoparticle porous film, we have simulated the performance of a lithium niobate 100 MHz ultrasonic transducer using PiezoCAD and the results are shown in figure 3. Compared with Parylene matching, the power transmit efficiency (output acoustic power/electrical input power) can increase by more than 100%. There is more than a 10% increase compared with SiO_2 nano-composite matching layer design. The 3 dB bandwidth is almost the same for all cases. Therefore, for a single matching layer design with lossy backing, a better matching layer mainly increases the sensitivity.

In summary, a TiO_2 nano-structured material has been successfully fabricated at room temperature, whose acoustic impedance can be further increased by low temperature annealing. The porous nano-structured film

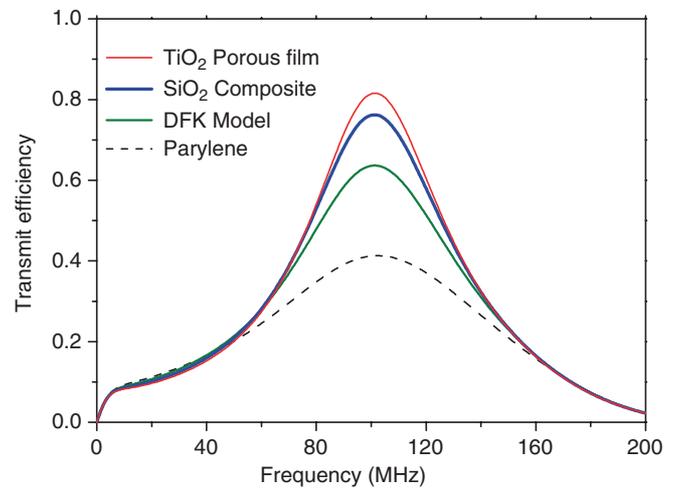


Figure 3. Power transmission efficiency spectra of a 100 MHz transducer with single matching layer using different materials. The DFK model curve was generated using the acoustic impedance of $Z = Z_c^{1/3} Z_m^{2/3}$ [3].

has been characterized by the quarter wavelength ultrasonic spectroscopy, which shows that the acoustic impedance can be made from 5.3 to 7.19 Mrayl. The high acoustic impedance achieved is irreversible and permanent and is thermally stable within the operating temperature range of medical imaging transducers. More importantly, the simple room temperature fabrication process makes this material easy to apply onto any transducer surface without causing any damage to the device assembly. From the measured results we can conclude that this material is an excellent candidate for the matching layers of ultra-high frequency medical imaging transducers.

Acknowledgments

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References

- [1] Xiang S H and Zhang Y T 1995 *Proc. IEEE 17th EMBS (Montreal, Canada)* vol 1 p 623
- [2] Goll J H and Auld B A 1975 *IEEE Trans. Son. Ultrason.* **SU-22** 52
- [3] DeSilets C S, Fraser J and Kino G S 1978 *IEEE Trans. Son. Ultrason.* **SU-25** 115
- [4] Zhou Q F, Cha J H, Huang Y, Zhang R, Cao W, Cannata J M and Shung K K 2006 *Proc. IEEE Ultrasonics Symp. (Vancouver, Canada)* p 2365
- [5] Lockwood G R, Turnbull D H, Christopher A and Foster F S 1996 *IEEE Eng. Med. Biol. Mag.* **15** 60
- [6] Wang H, Cao W, Zhou Q, Shung K K and Huang H 2004 *Appl. Phys. Lett.* **85** 5998
- [7] Carotta M C, Ferroni M, Guidi V and Martinelli G 1999 *Adv. Mater.* **11** 943
- [8] Grätzel M 2001 *Nature* **414** 338
- [9] Zhang D, Yoshida T, Oekermann T, Furuta K and Minoura H 2006 *Adv. Funct. Mater.* **16** 1228
- [10] Wang H and Cao W 2004 *IEEE Trans. Ultrason., Ferroelectr., Freq. Control* **51** 211