

# The tunability and dielectric properties of the compositionally graded $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ thin films

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**Abstract** The compositionally graded  $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  films with a compositional gradient from  $\text{BaTiO}_3$  to  $\text{BaZr}_{0.35}\text{Ti}_{0.65}\text{O}_3$  were fabricated on LNO-buffered Pt/Ti/SiO<sub>2</sub>/Si substrates by a sol-gel deposition method. In order to confirm the compositional gradient, a combination of X-ray Photoelectron Spectroscopy (XPS) and Ar ion etching was employed to produce the composition depth profile. Dielectric constant peaks, common to a ferroelectric transition, were not observed in the temperature range from –50 to 100 °C, within which the dielectric constant showed negligible temperature dependence. The compositionally graded  $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  thin films with weak temperature dependence of tunability could be attractive materials for situations in which precise control of temperature would be either impossible or too expensive.

**Keywords** Sol-gel · Gradient · Dielectric properties · Tunability

## 1 Introduction

Recent studies reveal that  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  (BST) and  $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  (BZT) thin films with concentration gradient and with improved dielectric and ferroelectric properties,

make a good choice to control the specific property of ferroelectric thin films [1–3].  $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  (BZT) ceramics and thin films have recently received renewal attention due to a high-strain level and high-piezoelectric effect in both single crystals and ceramics [4–7].  $\text{Ba}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$  materials have an orthorhombic or rhombohedral structure at room temperature [8, 9]. It is indicated that the system exhibits a pinched phase transition with increasing Zr concentration. It is obtained by substituting ions at the B site of the  $\text{BaTiO}_3$  with Zr in compounds of the perovskite structure  $\text{ABO}_3$ . It is reported that an increase in the Zr content induces a reduction in the average grain size, decreases the dielectric constant, and maintains a leakage current low and stable. This is possible because the  $\text{Zr}^{4+}$  ion has larger ionic size (0.087 nm) than  $\text{Ti}^{4+}$  (0.068 nm) [6, 7].

The Curie temperature of compositionally graded  $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  thin films can be tailored by the compositional gradients to meet the requirements of low temperature coefficient of dielectric constant and high dielectric constant. The improved temperature stability from the compositionally graded dielectric materials along with improved tunability, as recently reported for the BST system [2], are both beneficial to applications. For microwave devices, high tunability, low loss tangent and good temperature stability are required. Although much work has been devoted to developing tunable dielectric thin films having high tunability, low dielectric loss, there still exists a practical concern in tunable microwave resonators application where the resonant frequency depends strongly on the temperature change because the dielectric constant of a BZT film with a fixed composition is usually highly temperature dependent [10].

In this paper, thin films with a compositional gradient from  $\text{BaTiO}_3$  to  $\text{BaZr}_{0.35}\text{Ti}_{0.65}\text{O}_3$  were fabricated on LNO/Pt/Ti/SiO<sub>2</sub>/Si substrates. The dielectric behaviors of graded

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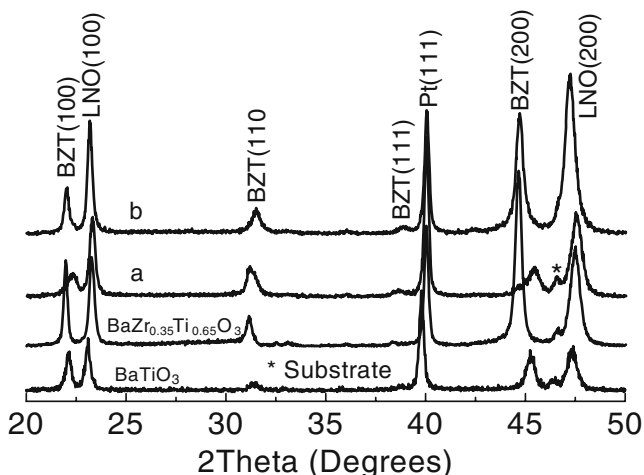
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films were analyzed. This study demonstrated how such factors as composition gradient, Curie temperature and applied voltage can be manipulated in a controlled manner to produce optimum effective dielectric properties.

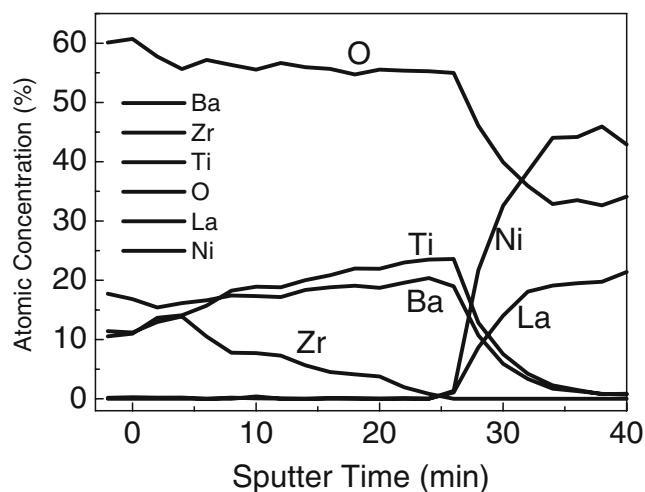
## 2 Experimental procedure

The barium acetate  $[\text{Ba}(\text{CH}_3\text{COO})_2]$ ,  $[\text{Zr}(\text{OC}_3\text{H}_7)_4]$ , and  $[\text{Ti}(\text{OC}_3\text{H}_7)_4]$  were used as starting materials. Acetic acid was used as solvent.  $\text{Ba}(\text{CH}_3\text{COO})_2$  was heated and dissolved in acetic acid. Zirconium isopropoxide and titanium isopropoxide were mixed in a ratio according to a predetermined number  $(\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3, x=0, 0.09, 0.18, \text{ and } 0.35)$ , and then dissolved into heated glacial acetic acid. After cooling to room temperature, ethylene glycol  $\text{CH}_2\text{OHCH}_2\text{OH}$  was added to control the viscosity and cracking of films. The details of the solution synthesis are as follows. Barium acetate was added in glacial acetic acid solution and heated to  $120^\circ\text{C}$  to reflux for 1 h. Ba:glacial acetic acid was in a ratio equal to 1:10 mol. After cooling to room temperature, the mixed solution of  $\text{Ti}(\text{OC}_3\text{H}_7)_4$ ,  $\text{Zr}(\text{OC}_3\text{H}_7)_4$ , and Acetylacetonate ( $\text{AcAc } \text{CH}_3\text{COCH}_2\text{COCH}_3$ ) was added slowly under continuous stirring in the solution ((Ti+Zr):AcAc=1:2 mol). Finally, 2-methoxyethanol and ethylene glycol were added to control the viscosity, cracking of films and the concentration of solution. The concentration of the final solution was adjusted to about 0.3 M.

Four solutions in the proportions of Zr:Ti=0:1, 0.09:0.91, 0.18:0.82, and 0.35:0.65 were synthesized. Compositionally graded BZT thin films were formed on the LNO/Pt/Ti/SiO<sub>2</sub>/Si substrate by sequentially depositing three layers of each composition onto the substrate. Pyrolysis and adequate heat treatment were carried out in an air muffle furnace at  $600^\circ\text{C}$  for 10 min for each spun-on coating. A final anneal in



**Fig. 1** XRD patterns of sol-gel deposited compositionally graded BZT thin films: (a) an up-graded, and (b) a down-graded sample



**Fig. 2** The composition depth profile of a typical up-graded BZT film, obtained from the XPS experiments

flowing  $\text{O}_2$  at high temperature of  $700^\circ\text{C}$  for 30 min. For convenience, the films with Zr/Ti ratio varying from  $\text{BaTiO}_3$  at the substrate to  $\text{BaZr}_{0.35}\text{Ti}_{0.65}\text{O}_3$  at the top surface are called “up-graded” films, whereas films with the opposite gradient are called “down-graded” films. Sol-gel deposition process was used to prepare thin films of approximately 680 nm in thickness.

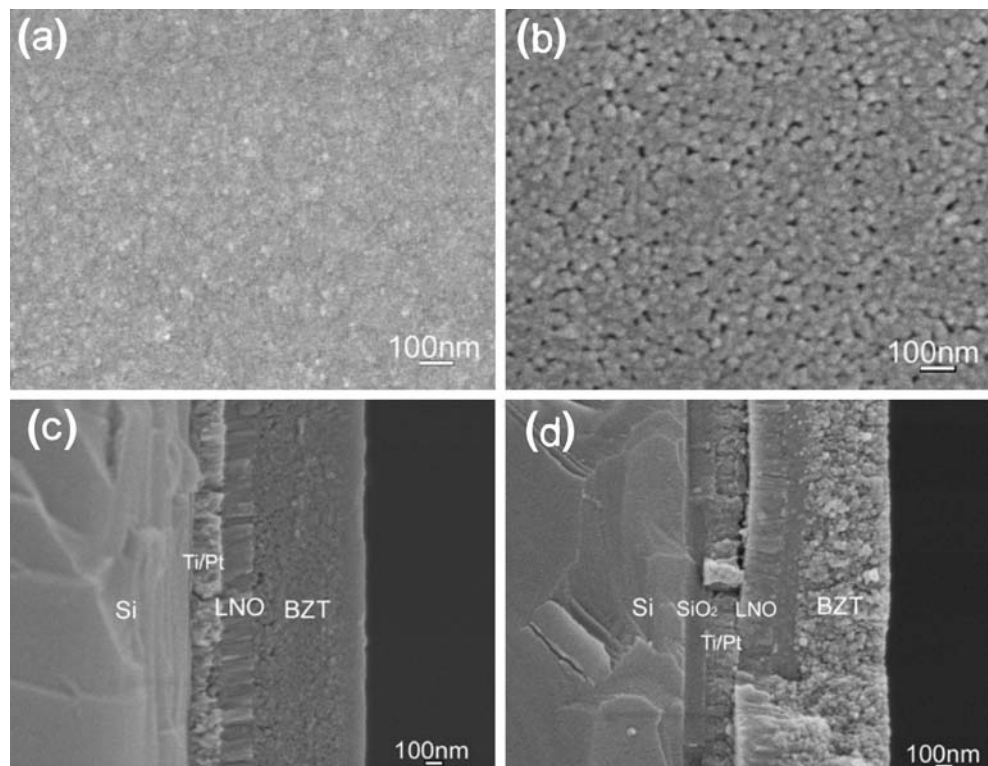
The crystalline phase of the thin films was identified by X-ray diffraction (BRUKER D8 Advance Diffractometer). The film thickness and the surface morphology were determined by FESEM. The distribution of compositional gradient in film was revealed by a combination of X-ray Photoelectron Spectroscopy (XPS) and Ar ion etching (PHI5802). For electrical measurements the top gold electrode of a  $200\ \mu\text{m}$  square was deposited by DC-sputtering. The capacitance-temperature (C-T) and capacitance-frequency (C-f) characteristics were measured using an Agilent 4284A LCR meter. The sample’s temperature was varied by using a Delta chamber.

## 3 Results and discussion

Figure 1 shows the XRD patterns of two compositionally graded BZT thin films: (a) an up-graded and (b) a down-graded films. It is evident that a single perovskite phase existed in both cases with up-graded and down-graded films. The XRD patterns also revealed that the up-graded film and the down-graded film were of polycrystalline structure. It was found that the up-graded and down-graded films have wider peak when compared with the films of  $\text{BaTiO}_3$  and  $\text{BaZr}_{0.35}\text{Ti}_{0.65}\text{O}_3$  films (as showed in Fig. 1). This result could be due to the presence of a distribution of compositional gradient in BZT films.

In order to confirm the compositional gradient, a combination of X-ray Photoelectron Spectroscopy (XPS)

**Fig. 3** FESEM micrographs of sol-gel deposited compositionally graded BZT thin films (a) Up graded (b) Down graded

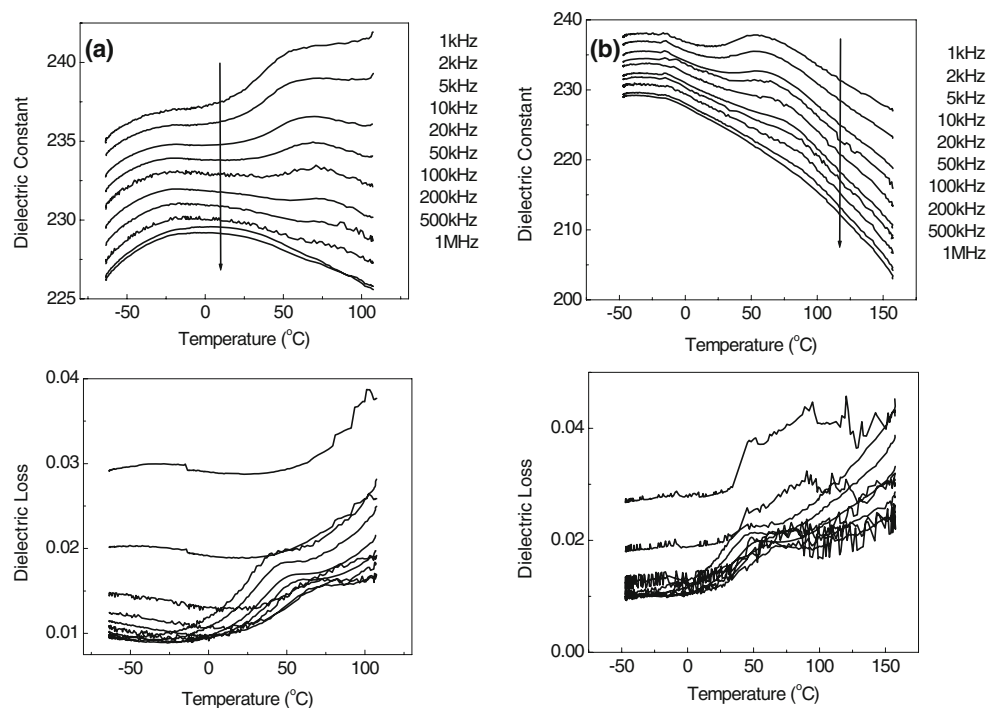


and Ar ion etching was employed to produce the composition depth profile as shown in Fig. 2 for an up-graded film. The compositional gradient of decreasing Zr and increasing Ti content from the surface of the film to the substrate was nicely demonstrated by the XPS data. The results confirm that the sol-gel processing method adopted

in this study produces uniformly graded composition variation.

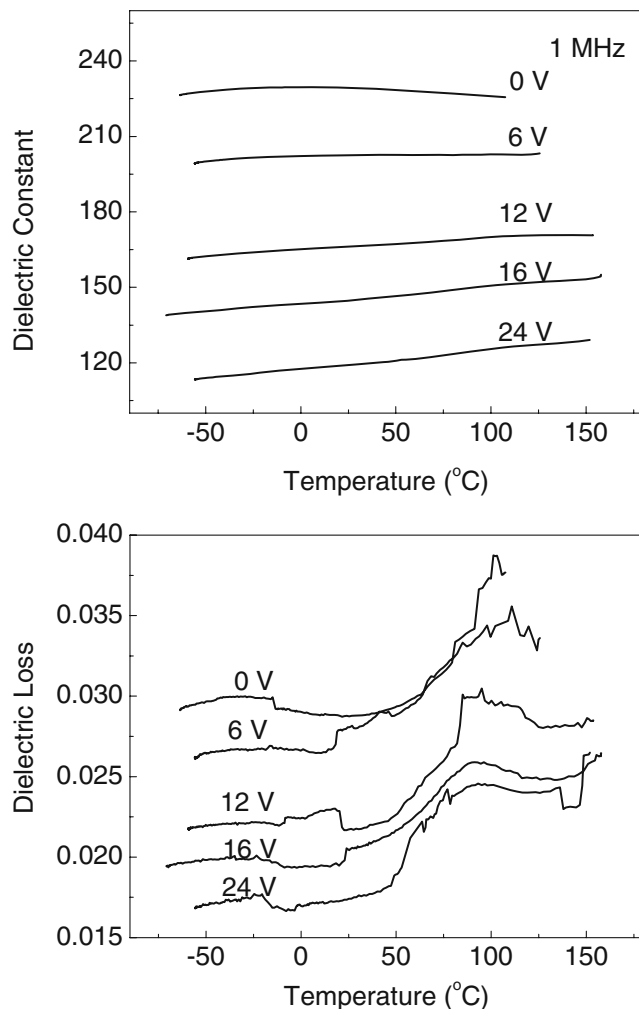
Figure 3 shows FESEM images of compositionally graded BZT thin films (a) an up-graded, (b) a down-graded. All films were subjected to a final annealing at 700 °C. The surface morphologies of the films appear to be related to the

**Fig. 4** The dielectric constant and dielectric loss of compositionally graded BZT thin films as a function of temperature: (a) an up-graded and (b) a down-graded sample

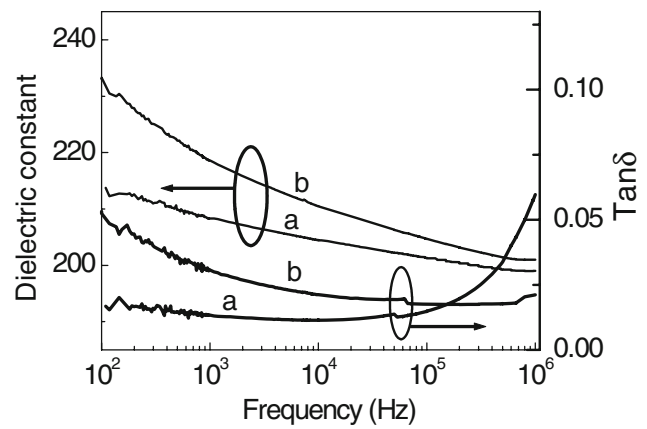


deposition sequence. Down-graded films have bigger grain sizes than up-graded films, and the up-graded film is more uniform and denser. The grain size decreased and the microstructure became dense with increasing of zirconium content. The addition of Zr to the BaTiO<sub>3</sub> lattice decreased the grain size of the crystallized films [11]. Figure 3(c) and (d) show the cross section of the up-graded and down-graded films, respectively, indicating a well-crystallized, dense, and void-free structure composed of granular grains randomly distributed throughout the film thickness.

The temperature dependence of the dielectric constant and the dielectric loss of the up-graded and the down-graded thin films are showed in Fig. 4. The data reveal a relatively flat profile with the up-graded and down-graded films. As expected there is no obviously steep change occurring in the range of temperature from -50 to 100 °C, to signify the ferroelectric transition. In BaZr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub>, the Curie temperature, *T*<sub>C</sub>, can be controlled by varying the mole fraction *x* of Zr [10]. Therefore, the composition-



**Fig. 5** The temperature dependence of dielectric constant and dielectric loss as a function of applied DC electric field for an up-graded film (Measurement frequency was 1 MHz)

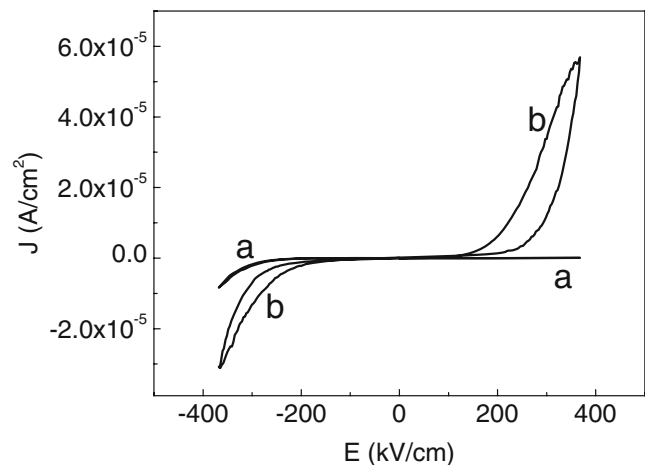


**Fig. 6** The dielectric constant and loss as a function of frequency for compositionally graded BZT thin films: (a) an up-graded, and (b) a down-graded sample (Measured at room temperature)

dependent Curie temperature should manifest itself in the graded BZT film to show a smeared or expanded diffuse transition, consistent with the results in Fig. 4.

As indicated in Fig. 4, the dielectric behavior of the up-graded film was different from the down-graded film. This dielectric behavior can be attributed to the grain size and grain morphologies due to the deposition sequence. With the addition of Zr, the grain sizes of films were found to decrease, whereas their microstructure became dense. The compositionally graded BaZr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> thin films prepared by sol-gel method, with the bottom layer of LaNiO<sub>3</sub>, serving as a seed layer to result in the different crystallinity for the up-graded and down-graded thin films [2].

Figure 5 showed the temperature dependence of dielectric constant and dielectric loss as a function of externally applied dc voltage for the up-graded film, all measured at 1 MHz frequency. The data reveal a relatively flat profile, especially in the temperature range between -50 and 120 °C.



**Fig. 7** J-E characteristics of compositionally graded BZT thin films: (a) an up-graded, and (b) a down-graded sample (Measured at room temperature)

The change of dielectric constant versus dc bias field is quite appreciable, indicating a high tunability over a wide temperature range. Generally, ferroelectric material is tunable in only a narrow temperature range near a phase transition. Ba(Zr<sub>x</sub>Ti<sub>1-x</sub>)O<sub>3</sub> compositionally graded films with weak temperature dependence of tunability in the temperature range between -50 and 120 °C could make attractive materials.

Figure 6 shows the frequency dependence of the dielectric constant and dielectric loss at room temperature for the up-graded and down-graded films. The dielectric constant shows dielectric dispersion typical of the thin films and low losses are obtained at frequencies less than 100 kHz. The dielectric constant showed a slight tendency, to decrease with higher frequencies, the increasing tendency of dielectric loss was obviously at higher frequency ranges, over 100 kHz, several possible causes exist for such dispersion, including the hypothesis of the influence of the contact resistance between the probe and the electrode. The difference of frequency dependence of dielectric constant and dielectric loss is attributed to the grain size and grain morphologies. This result was also agreement with that obtained from the  $\epsilon$ -T measurement.

The current-voltage (or current-field) characteristics have also been studied because the leakage current is one of the most important properties for applications. The difference in the leakage current characteristics of the up-graded and the down-graded thin films was shown in Fig. 7 that shows the change of current density  $J$  versus applied DC electric field  $E$  of the films measured at room temperature. It is indicated that the leakage current density of the up-graded thin films is lower than that of the down-graded thin film. The increasing of leakage current of down-graded film was due to the influence of the denser and grain sizes (as shown in Figure 3). The down-graded films with bigger grain sizes configurations have overall shorter conduction paths along the grain boundaries, which causes an increase in the leakage current.

#### 4 Conclusions

The compositionally graded BaZr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> films with compositional gradient from BaTiO<sub>3</sub> to Ba<sub>0.70</sub>Zr<sub>0.35</sub>Ti<sub>0.65</sub>O<sub>3</sub>

were fabricated on LNO-buffered Pt/Ti/SiO<sub>2</sub>/Si substrates by a sol-gel method. Compositionally graded thin-film structure was formed by sequentially depositing layers of increasing Zr (up-graded) or decreasing Zr (down-graded) composition onto the substrate. The XPS analysis reveals that the sol-gel processing method adopted in this study produces uniformly graded composition variation. The XRD patterns revealed that the up-graded film and the down-graded film were of polycrystalline structure. The dielectric behavior of the up-graded film was different from the down-graded film. This dielectric behavior can be attributed to the grain size and grain morphologies due to the deposition sequence. There is no steep change occurring in the range of temperature from -50 to 100 °C, to signify the ferroelectric transition. The change of dielectric constant versus dc bias field is quite appreciable, indicating a high tunability over a wide temperature range.

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