Materials Research Express

**PAPER**

Fluorination-enhanced photoconductive effect in a wide band gap Ca$_3$Ti$_2$O$_7$-xF$_x$ thin films

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**Keywords:** fluorination, photoconductive effect, Ca$_3$Ti$_2$O$_7$-xF$_x$ thin film

**Abstract**

In this work, Ca$_3$Ti$_2$O$_7$-xF$_x$ thin films on (110) SrTiO$_3$ substrates were prepared by two steps as deposited via pulsed laser deposition and fluorinated with polyvinylidene fluoride. Despite the unchanged crystal structure of the fluorinated films, the changed valence state can be used to confirm the incorporation of F$^-$ and the weakened chemical bond of Ca–O. Furthermore, we found that the photoelectric switch can be observed at a wide range of light wavelength from 405 nm to 808 nm. It is found that the photosensitivity of 4 × 10$^4$ (405 nm) in the fluorine has been increased by two orders of magnitude, which is most likely due to the deep energy levels in the reduced band gap of 2.3 eV. This work paves the way for the enhanced photoconductive devices via the anionic defect engineering.

1. Introduction

The 327 Ruddlesden-Popper (RP) layered A$_3$B$_2$O$_7$ compounds have been continuously investigated due to their special crystal structure and varying physical properties [1–4]. The inserted A-O layers in the 327 phase is different from the familiar perovskite ABO$_3$, which can bring in two different layers defined as rock-salt and perovskite layers [5]. In such orthorhombic oxides, two most studied systems are the Ca$_3$Ti$_2$O$_7$ (CTO$_7$) and Ca$_3$Mn$_2$O$_7$ compounds. The competition between interlayer rumpling and rotations occurred in this layer structure can lead to ferroelectricity or even multiferroicity [4, 6]. Although the ferroelectricity in RP material was derived from first principles calculations, the relevant switching of polarization still has been rarely observed in the pure 327 compounds. Therefore, the previous studies have come back to the traditional tuning method of cation substitution. To overcome the larger energy barrier for switchable polarization, the cation doping at the A-sites is a very efficient way for hybrid improper ferroelectricity in the CTO$_7$-based bulk [2, 7, 8]. Except for the above multiferroic behavior, the improved photocatalytic activity and photoluminescence has been formed via Rh and Eu substitution, respectively [9, 10]. Furthermore, to the pure CTO$_7$, it is worth pointing out that the stoichiometric bulk shows a direct gap of 3.94 eV while the Sr substitution for the reduced energy gap can be neglected [11]. Hence, we need to find out some else way to search the tuning effect on the electronic structure in the thin films with a wide band gap.

Despite the traditional cation doping, the anionic doping has been confirmed to be an effective alternative to enhance the physical properties of oxide films. The first one is oxygen vacancy, which is introduced during the deposition with high vacuum. A length of chemical bond and angle of the oxygen octahedron rotation can be changed by the oxygen vacancy effect [12]. However, the strain is often accompanied by this doping, causing that a competition mechanism can further result in an opposite tuning effect on the material character [13–16].
second one is fluorinated via the annealing after the deposition, from the thermal decomposition of polyvinylidene fluoride (PVDF) [17–19]. Monovalent F⁻ ions substituting for O²⁻ sites provide not only a certain concentration of electron donors but also a simulation as half oxygen vacancy [20]. Thus a wide range of varying in crystal lattice and resistance with the fluorine content can be realized in the fluorinated films [19, 21]. Additionally, the distortion of Mn octahedral can induce a local magnetic order in the electron doped SrMnO₃-based system [22, 23]. Here we report the effective way to prepare three groups of samples including CTOₓ₀.₆₂₅₄Fₐₓ, CTOₓ₂, and CTOₓ₂₋ₓFₓ films and compare the defect-induced photoconductive character of them. Our investigation begins with the definite crystal structure and verified fluorination in the CTOₓ₂₋ₓFₓ films. After the fluorinated treatment, the changed strain and chemical bonds can further lead to the subsequent photoelectric effect. Especially in fluorinated sample, there is a strong dependence between the photoelectric properties and the light of varied wavelength. Furthermore, we discuss that the origin of improved photoconductive behavior in the CTOₓ₂₋ₓFₓ film is the anionic doping and electronic reconstruction, via photosensitivity measurement and first-principles calculation.

2. Methods

The as-deposited CTOₓ₋ₓFₓ thin films on atomically flat SrTiO₃ (STO, 110) substrates were deposited via pulsed laser deposition (PLD, Lambda Physik, 248 nm, 3 Hz, 2 J cm⁻²). For the stoichiometric films, the fabrication process was maintained at the temperature of 850 °C and oxygen pressure of 0.1 mbar. Then the precursor films wrapped in Al foil were annealed with 0.1 g of PVDF, under a flowing gas of argon for 24 h to introduce fluorine. As shown in figure 1 (a), the PVDF pellets need to be placed on the foil rather than directly on the film sample, in order to fully fluorine dope rather than the charcoal-like adhere [21]. The thickness of three samples is kept at around 50 nm. The lattice constants and epitaxial characters of films were determined via an x-ray diffraction (XRD) 2θ-θ scan and reciprocal space mapping (RSM), using the Panalytical Empyrean concept, respectively. The presence and valence state of Ca, Ti, O, and F in the CTOₓ₋ₓFₓ film were confirmed by x-ray photoemission spectroscopy (XPS) at PH15000 VersaProbe. Three sets of films were chosen to measure for the photoconductive effect, including as-deposited CTOₓ₋ₓ, CTOₓ (annealed in an oxygen atmosphere of 500 mbar) and CTOₓ₋ₓFₓ films. Two point contacts are directly made on the surface of films by wire bonding. Electrical measurements were performed with a Keithley 6517B Source Meter at room temperature. The light illumination is supplied by the various semiconductor laser of 50 mW/cm², with various wavelength of, 405 nm, 532 nm, 655 nm, and 808 nm [24]. To investigate the underlying mechanism of fluorination-induced photoconductive effect, the generalized gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE) within the framework of density functional theory (DFT), as implemented in the Vienna ab initio simulation package (VASP) was carried out [25–28]. Monkhorst-Pack k-point meshes of 5 × 3 × 5 was used for 2 × 1 × 2 F-doped CTOₓ supercell [29]. A plane-wave cutoff energy of 450 eV was used for the self-consistent calculations. In order to obtain optimized geometries structures of fluorinated system, both lattice constants and atomic positions are fully optimized until the Hellmann–Feynman less than 0.02 eV Å⁻¹.

3. Results and discussion

Figure 1 (b) shows the XRD θ-2θ measurement, only the STO (110) and CTOF (010) reflections can be observed in spectrum. Without any additional peaks in the above spectrum, the influence on the epitaxial relationships and crystal structure of the films can be neglected after fluoride treatment. However, differ from the stoichiometric CTOₓ film fabricated on the STO substrate, the peaks of CTOF film appear at the higher 2θ angle, indicated a slightly decrement of the lattice constant along vertical alignment [3]. To estimate the three dimensional lattice constants, the symmetric and asymmetric RSM were performed and shown in figures 1 (c)–(e). The isolated CTOF (040) spot at a Qₓ of 0.7393 confirms the out-of-plane (020)CTOF//(110)STO which is consistent with the separated peaks in the θ-2θ scan. Meanwhile, a slight broadening along the Qₓ reveals that the lattice along b-axis is fully relaxed in the fluoride film (figure 1(c)). For the asymmetric CTOF (240) around the STO (310) reflection as shown in figure 1 (d), the lattice along a-axis is partially relaxed and stretched for a slight in-plane tension strain, same as that in the CTOₓ film [3]. Back to the lattice along vertical alignment, an out-of-plane contraction can be obtained from a higher Qₓ of CTOF (0 4 10) spots than that of STO (2 2 2) in figure 1(e). Hence, based on the above RSM images, we can obtain an orthorhombic CTOₓ₋ₓFₓ structure at room temperature with the lattice constants a = 5.469 Å, b = 5.411 Å, c = 19.257 Å. It is found that lattice misfit compared with the bulk is only 0.85% along the a-axis and −0.82% along the c-axis [30]. And the epitaxial relation between the film and substrate is [100]CTOF//(1–10)STO and [001]CTOF//(001)STO.

To further investigate the valence state and fluorination of CTOₓ₋ₓFₓ films, x-ray photoelectron spectroscopy (XPS) has been performed. After using Lorentzian–Gaussian fitting and Shirley background, the
Ca 2p and Ti 2p core level spectra both include one pair of spin–orbit doublets in figures 2(a) and (b). Similar with that in the CTO7 bulk, the peaks of Ti_{3p1/2} and Ti_{3p3/2} hold at 464.3 eV and 458.5 eV with no change on the binding energies, showing that the Ti-O bonds are stable after fluorination (discussed later) [31]. On the contrary, the binding energies of Ca_{2p1/2} and Ca_{2p3/2} peaks shifted to higher positions of 351.5 eV and 347.9 eV, both increased by 1.4 eV than that in the CTO7 bulk [31]. The peaks appears at higher binding energy due to the ionic character of the bonds and the weakened chemical bond of Ca-O, which is also responsible for the compensation of F inclusion [32]. Moreover, the asymmetric O1s spectra can be resolved into three peaks as shown in figure 2(c). Two higher peaks can be also observed in the CTO7_x_F_x film between that in darkness and under illumination, with the light of the constant intensity and various wavelengths. Whatever the wavelength, the sample resistance increases with the light on and decreases with the light off, presented good photoelectric responses at room temperature. In addition, it is found that the fluoride films take a more recovery time to dark resistance than to light resistance, attributed to the photogenerated charges trapped in the deep energy levels.
Figure 2. XPS spectra of (a) Ca 2p, (b) Ti 2p, (c) O 1s and (d) F 1s peaks for CTO$_{3-x}$F$_x$ film.

Figure 3. Time dependent resistance of CTO$_{3-x}$F$_x$ film with the light wavelength of (a) 405 nm, (b) 532 nm, (c) 655 nm and (d) 808 nm at room temperature. The vertical filling rectangular with various color represents the light with the different wavelength is on. (e) A comparison of the resistance under the various light, for the CTO$_{3-x}$F$_x$ film. (f) A comparison of the resistance between CTO$_7$, CTO$_{7-x}$ and CTO$_{3-x}$F$_x$ films with a light of 405 nm.
However, the other photoelectric characters of CTO7-F film are dependent on the wavelength, such as stability and photosensitivity. Especially, the both resistance with an 808 nm laser start to fluctuate after four cycles, which illustrate that the photoelectric effect is gradually eliminated. The most stable photoelectric behavior appears from 532 nm to 655 nm. For the photosensitivity with the different light, we selected a continuous period of on-off-on, from the whole resistance switch curves. For comparison, the photosensitivity is defined as $P_s = \frac{R_{\text{dark}}}{R_{\text{light}}}$, where $R_{\text{dark}}$ and $R_{\text{light}}$ is the resistance with the light off and on respectively. In figure 3(e), the photosensitivity increases with the decrement in wavelength from $10^8$ (808 nm) to $4 \times 10^5$ (405 nm). This is because the more photogenerated charges can be produced with the increasing in the photon energy, leading to the reduced resistance under the illumination. As shown in figure 3(f), the photosensitivity of CTO$_7$, CTO$_7\delta$ and CTO$_7\times$F$_x$ films were compared to show that the fluorination can enhance the photoelectric behavior at room temperature. Based on the photosensitivity of CTO$_7$F$_x$ film as the reference, it is estimated to be $2 \times 10^3$ and $4 \times 10^2$ in CTO$_7\delta$ and CTO$_7$, respectively. The best photoconductive property can still be presented in the CTO$_7$F$_x$ film with a 405 nm light. In addition, it should be notice that a recovery time in the CTO$_7$ film differs from another two films. It recovers directly to dark resistance after the light remove, like as that to light resistance. By contrast, the slower recovery of resistance both can be observed in the CTO$_7\delta$ and CTO$_7\times$F$_x$ films, owing to the trapped centers caused by oxygen vacancy and fluorinated defect.

Back to the fluoride films, the first principles calculations were performed to uncover the underlying mechanism of enhanced photoelectric character. According to the above physical properties, two different positions of doped F ion (F1 and F2) were marked as black and red in the inset of figure 1(b). Specifically, the F1 position locates at the rock-salt layer while the F2 position locates at the perovskite layer. As shown in figure 4(a), the target system doped at F1 represents two distinct changes in the total density of states (TDOS). The first one is the decreasing in the band gap, from 2.45 eV (pure CTO$_7$) to 2.3 eV (fluorine) [8]. Both calculated band gap are lower than the bulk value of $\sim$3.94eV [11], because the GGA method were confirmed to underestimate the value of band gap [1]. Secondly, the distribution of TDOS appear at the Femi level ($E_F$, marked as magenta dashes), showing that this doping system possesses a certain conductivity induced by electron filling. Deep into the partial DOS in figure 4(b), the contribution near $E_F$ is mainly from Ti $d$-bands, not from the incorporation of F. The additional electron donors created by monovalent F cause that the $E_F$ moves up to the occupied conduction band, which is the origin of a certain conductivity. Besides, the hybridization between O 2p and Ti 3d explain that the fluorination can weak the chemical bond of Ca–O rather than that of Ti-O. The similar changes can be observed in the second system with the doped position of F2 (figures 4(c) and (d)). Hence, with the
incorporation of doping fluorion, the multiple effect of the reduced band gap and deep energy levels have an influence on the above photoelectric character.

4. Conclusion

In sum, we fabricated the CTO\(_{2.8}\) thin films on the STO (110) substrates via PLD, then post-annealed in the oxygen and argon atmosphere for CTO\(_2\) and CTO\(_{2.8}\)–F\(_x\) films, respectively. For the crystal structure, the CTO\(_{2.8}\)–F\(_x\) film owns an orthorhombic structure with a slight tension along a-axis and compression along c-axis. From the changed valence states, we found that the F-doping can replace the lattice oxygen led to not only the decreased O\(^{2-}\) ions but also the weakened Ca–O bonds. Meanwhile, the photosensitivity of fluorinated film shows a dependent relation with the wavelength, and has a better photoelectric behavior than that in another two films. The first principles calculations suggest that the induced fluoride can induce the equivalent oxygen vacancy, resulted in the upper Femi level and reduced bang gap.

Acknowledgments

We acknowledge the support of the National Natural Science Foundation of China (NSFC) under Grant No. 51802210, 11974304, 11704272, 12074282, 62004136, 22008164. This work also supported by the Natural Science Foundation of Jiangsu Province (Grants No. BK20180970, BK20190939), Jiangsu Undergraduate Training Program for Innovation and Entrepreneurship (No. 201910332020Z) and the Natural Science Foundation of the Jiangsu Higher Education Institutions of China (Grants No. 19KJB150018).

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