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Competition and Cooperation between Fluorine and Oxygen in SnO₂:F Films

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Abstract: The interaction of oxygen and fluorine (F&O) in an F-doped SnO₂ film, prepared by regulating oxygen partial pressure and the content of doped fluorine from 2.5 at% to 10 at%, was investigated in the large perspective through characterization methods including XRD, Raman spectroscopy, photoluminescence spectroscopy, wettability measurement and a Hall effect test system. The results show that F&O's competitive and cooperative relationship would be reflected in the structure and electrical characteristics of SnO₂ films. The oxygen action is overwhelming and restricts fluorine, so a growing number of F atoms occupy the position by the order of co-edge oxygen of tin-oxygen octahedron chains > oxygen vacancies > segregation, which leads to that carrier concentration modestly increasing from $\sim 10^{15}$ to $\sim 10^{17}$ /cm⁻³. As oxygen action is inadequate to restrain fluorine, more F atoms are likely to enter the SnO₂ lattice in a solid-solution way to replace the O atoms at the co-edge position of the octahedron chains, causing a dramatic increase in carrier concentration from $\sim 10^{16}$ to $\sim 10^{19}$ /cm⁻³. Furthermore, by continuing to weaken oxygen action, only 2.5 at% of fluorine content could bring about a carrier concentration augment from $\sim 10^{16}$ /cm⁻³ to $\sim 10^{18}$ /cm⁻³, then going up to $\sim 10^{21}$ /cm⁻³ by post-annealing. However, the impairment of oxygen action contributes to a more effective doping of fluorine on SnO₂ film. Such mutual action between fluorine and oxygen provides a direction for highly efficient production and tunable regulation of SnO₂ film on demand.

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1. Introduction

As a common wide-bandgap (~ 3.6 eV) N-type semiconductor oxide, tin dioxide (SnO₂) has been applied in a wide range of fields, including transparent conductive electrodes [1], solar cells [2], and gas sensors [3], owing to its excellent optical properties, electrical properties, thermal stability, gas sensitivity, and low-cost preparation. It is well-known that the crystalline structure and performance of SnO₂ could be markedly affected by oxygen vacancies (OVs). Maleki et al. [4] decreased OVs concentration in SnO₂ film by increasing oxygen flow rate during a CVD process to improve conductance and transmittance. Li et al. [5] prepared (110)-oriented SnO₂ films with low OVs concentration that showed a high H₂ gas sensitivity in air. Yang et al. [6] introduced OVs into the SnO₂ nanoparticles to narrow the band gap, which broadens its range of solar light utilization. Kamble et al. [7] also found OVs play a role in narrowing the optical band gap and masking the near band edge absorption.

However, OVs could not fully meet the demands for the effective tunability of the structure and properties of SnO₂. Excessive regulation for OVs would damage the order and perfection of the lattice. Hence, in order to further tune the structure and properties of

SnO₂, element doping was created. For example, doped cations like indium ion (In³⁺) [8], zinc ion (Zn²⁺) [9], and platinum ion (Pt²⁺) [10] occupy the position of tin ion (Sn⁴⁺) to improve its optical, electrical, and gas-sensitive properties, respectively. Likewise, doped anions like tellurium ion (Te^{2−}) [11], nitrogen ion (N^{3−}) [12], and fluorine ion (F[−]) [13] also substitute the site of oxygen ion (O^{2−}) to regulate various properties of SnO₂ materials. Among a multitude of doped elements, in SnO₂ lattices, fluorine has been a popular substitute for oxygen because they have a similar atomic radius, electro-negativity, and bond energy with Sn.

How oxygen regulation and fluorine incorporation work synergistically has not yet been uniformly concluded. The function of fluorine often shows a non-monotonous trend with the variable ratio between fluorine and oxygen concentration in crystals, which implies fluorine could be affected by oxygen. For instance, Xin [14] et al. found that resistivity of F-doped SnO₂ film firstly decreases and then increases with the introduction of oxygen fluxes. Yang [15] et al. prepared pure and F-doped SnO₂ films, in which the incorporation of F could better tune electrical properties with the help of oxygen. Benhaoua's study [16] shows that the conductivity of their F-SnO₂ film has not monotonically improved with the increase in the doped F levels.

The above results imply that there exists a competing relationship between fluorine and oxygen, which determines what way to incorporate fluorine, which position to be occupied by fluorine, and how to influence fluorine by oxygen. Generally, such issues have been understood by simulating calculations [17] and delicate characterization with high resolution, even to an atomic scale [18]. The former is not enough to mirror the comprehensive actual situation in crystals. The latter could still not completely reflect overall structural information of crystals with a certain degree of local occasionality, even though it follows the complicated operation on the complex platform. Therefore, in this work, we attempt to clarify the positional conflict of fluorine and oxygen (F&O) by suggesting a methodological analysis with a full-scale and statistical significance. This kind of approach would effectively determine fluorine substituting, filling, and precipitating in SnO₂ lattices, which would underlie a theoretical basis for a reasonable process design, and provide guidance for widely meeting the customized needs on all kinds of fields.

2. Materials and Methods

2.1. Preparation of F-SnO₂ Films

In this work, SnO₂:F films were prepared on a glass slide by a radio frequency (RF) magnetron sputtering of powder target (AE600X type radio frequency power supply, Advanced Energy Denver, CO, USA). SnF₂ and SnO₂ powders in 99.99% purity were mixed as targets by a molar ratio of 0:1, 0.025:1, 0.05:1, 0.075:1, and 0.1:1. In order to explore the relationship of competition of oxygen and fluorine in the film, sputtering atmospheres with different oxygen contents were created. After pumping a background vacuum, Ar with a purity of 99.99% was fully backfilled to create a less oxygen sputtering atmosphere. The sputtering pressure was regulated at 0.1 Pa under the power of 200 W (power density of 1.13 W/cm²), which could obtain the film with a relatively high quality and a greater depositing rate. For building a more oxygen sputtering atmosphere, as Ar with a purity of 99.99% had been backfilled under the background vacuum, O₂ with a purity of 99.99% was fully inserted the chamber in a certain flow to keep the sputtering pressure of 1.0×10^{-1} Pa under the power of 200 W. Based on the above experimental conclusion, we still prepared the SnO₂:F films with doped fluorine contents of 0% and 2.5% under a higher background vacuum to reach an oxygen-deficient atmosphere, with the same other process conditions. The detailed parameters are shown in Table 1.

Table 1. Preparing process parameter of F-doped SnO₂ film.

Preparing Process	Parameter
Sputtering pressure (Pa)	1.0×10^{-1}
Sputtering power (W)	200
Substrate-target separation (cm)	12
Substrate temperature	Room temperature

The 0% and 2.5% F-doped SnO₂ films prepared in the oxygen-deficient atmosphere were further annealed using rapid thermal processing equipment (RTP-500V, Beijing East Star Research Office of Applied Physics, Beijing, China) in ambient air with various vacuum degrees of 2.0×10^1 , 2.0×10^0 , 3.6×10^{-1} , 2.0×10^{-1} , 4.0×10^{-2} , and 4.0×10^{-3} Pa, respectively. The tiered-heating method was adopted in the annealing process to avoid over-rapid continuous temperature rising, which impairs the lattice structure of F-doped SnO₂ films, in which the temperature was maintained at 60, 100, and 200 °C for 5 min, and then was held at 400 °C for 60 min. The detailed parameters are shown in Table 2.

Table 2. Annealing process parameter of F-doped SnO₂ films.

Annealing Process	Parameter
Annealing Pressure (Pa)	2.0×10^1 , 2.0×10^0 , 3.6×10^{-1} , 2.0×10^{-1} , 4.0×10^{-2} , 4.0×10^{-3}
Heating rate (°C/s)	1
Passbying temperature (°C)	60/100/200
Passbying time (min)	5
Holding temperature (°C/s)	400
Holding time (min)	60

2.2. Characterization of F-SnO₂ Films

The preferred orientation and micro-structure of the F-doped SnO₂ films were characterized through X-Ray diffraction with a glancing angle of 0.3° (XRD, X'Pert Pro, Cu-Kα, Malvern Panalytical, Malvern, UK). The lattice structure and oxygen vacancies were detected by a Raman spectrometer at an excitation wavelength of 532 nm (Labram HR 800, Horiba, Kyoto, Japan). The wetting property of the films were studied by a contact angle measuring instrument (JC2000D1, Shanghai Zhongchen Digital Technology Apparatus Co. Ltd., Shanghai, China). The information of electron band structure was recorded by a steady-state photoluminescence spectrometer with 310 nm excitation light (PL, FLSP-920, Edinburgh instruments, Livingston, UK). Electrical characteristics including carrier concentration and mobility were analyzed by a Hall effect test system with a magnetic field strength of 5300 G (Hall 8800, Pusi Industries, Hongkong, China).

3. Results

3.1. Octahedral Structure in SnO₂

The Figure 1a,b presents an SnO₂ framework composed of SnO₆ regular octahedrons. The octahedrons are connected by the way of the coupled common-edge (co-edge) oxygen to form the straight octahedral chains, and then the chains are assembled by common-point (co-point) oxygen to build a three-dimensional SnO₂ structure. The Sn atoms in the center of such SnO₆ regular octahedrons form a typical tetragonal-rutile lattice structure of SnO₂ ($a = b = 0.4739$ nm, $c = 0.3187$ nm, $\alpha = \beta = \gamma = 90^\circ$), in which its c-axis is along the octahedral chains, and a-axis is perpendicular to the octahedral chains in Figure 1c. For the SnO₂ crystalline cell, the position of oxygen could be regarded as two kinds, O₁ (0.306a, 0.306a, 0) and O₂ (0.806a, 0.194a, 0.5c), just corresponding to the paired co-edge oxygen in octahedral chains and the single co-point oxygen among octahedral chains, respectively. It seems a common consensus that fluorine, as a typical incorporated element for SnO₂, would be a substitution for oxygen due to their similar geometric scale and physical characteristics.

However, whether a selective priority exists in the replacement of the fluorine atom for the co-edge or co-point oxygen atom remains to be answered. It would be meaningful for this issue to be clearly revealed.

Figure 1. Schematic diagram of SnO₂ structure: three-dimensional octahedral structure (a) and its top view (b); crystalline cell with (110) and (200) plane (c); co-edge O atoms substituted by F atoms in pairs (d); distortion of octahedral framework (e); crystalline cell with (101) and (200) plane (f); the lack of co-edge O atoms in pairs (g); co-point O atom substituted by F atom (h); schematic diagram of atom vibration in SnO₂ structure, including the shearing vibration (i), the stretching vibration (j) and the breathing vibration (k).

In Figure 1g, as some the co-edge oxygen atoms are losing, the lack of the constraint in octahedral chains cause them to produce a drastically stretching transformation, and even break in the c-axis direction. It destroys the crystalline structure, causing the whole SnO₂ system to be in a high-energy disordered state. In Figure 1d, as the position of the co-edge oxygen atoms are occupied by F atoms in pairs, due to the slight difference in the radius of fluorine and oxygen atoms, the octahedral chain would merely change in length along the c-axis direction. In this case, the neighboring octahedral chains could still keep some crystalline coherences. However, with the increasing substitution of co-edge O atoms by F atoms, the distortional energy caused by the forced coherences among octahedral chains would gradually accumulate. Then, at the position of co-point oxygen, the presence of oxy-

gen vacancies, caused by the originally connected octahedral chains mutually dislocating along the c-axial direction, is more effective to relieve the high distorting energy than the enforcing occupation by F or O atoms. If some positions of co-point oxygen are occupied by F atoms, there would appear severe asymmetric distortion including the twist and contortion in regular octahedrons. Meanwhile, these octahedral chains would drastically lean and skew in the c-axis and a-axis directions, and then the asymmetric connection would create a high-energy SnO_2 system, as shown in Figure 1h. Such competition and concession of fluorine and oxygen in the octahedral chains could not only be reflected on periodicity and perfection by XRD, but also be expressed on phonon vibration and electronic energy band structure by Raman and Photoluminescence, respectively, as analyzed below.

3.2. Expression of F&O Competition on Crystalline Plane

Figure 2a,b shows the XRD pattern of F-doped SnO_2 films prepared by the various doped F content, which reflects the destruction of periodicity and perfection that resulted from positional competition of fluorine with oxygen. As analyzed in Section 3.1, the substitution of co-edge O atoms with F atoms in pairs would deteriorate the order and periodicity of the lattice in the c-axis direction due to the stretching of octahedral chains. Meanwhile, owing to the lack of co-point oxygen atoms, the non-connection and unconstraint among octahedral chains would further impair the periodic arrangement of octahedrons in the c-axis direction, and the crystalline cell also loses the stable squareness structure to transform into a rhombus, as shown in Figure 1e. These two cases cause a relatively severe distortion of the lattice on c-axis than a-axis. In difference, the replacement of co-point O atoms by F atoms would lead to an almost identical distortion in the c-axis and a-axis. It means that periodic arrangements of the (110) and (101) crystalline planes were damaged to the same degree, as shown in Figure 1c,f. Regardless of oxygen action, with the increase in the doped F content, while whole peak profile become weak in Figure 2a,b, the (101) peak was more diffuse than the (110) peak, which illustrates that the periodic arrangement of c-axial direction in the SnO_2 lattice was more damaged. It corresponds to the fact that F atoms occupy the position of co-edge oxygen. In addition, the (101) peak of films prepared under the less oxygen atmosphere is more diffuse, further reflecting that after entering the lattice, F atoms prefer to substitute the co-edge oxygen to raise the disorder of (101) crystalline plane which is related to c-axis. Xu [19] et al. also reported that the energy in F-doped SnO_2 is the lowest, as fluorine replaces oxygen located at (0.306a, 0.306a, 0), which just corresponds to co-edge oxygen in octahedral chains. Therefore, F atoms would be more likely to firstly occupy the position of co-edge oxygen.

Compared with the films prepared under the less oxygen atmosphere in Figure 2a, all XRD peaks of the films deposited in the more oxygen atmosphere in Figure 2b present a narrower profile, in which there is a greater intensity ratio of (101) to (110) peak with the increase in the doped F content. It not only implies that there are fewer fluorine atoms and oxygen vacancies in the films prepared in the more oxygen condition, but also further reflects that F atoms prefer to substitute the co-edge O atoms to affect the periodic arrangement of the (101) crystalline plane. Under the supplemental oxygen, complete octahedrons and their orderly arrangement would be improved. The more co-point O atoms build bridges among the octahedral chains to stabilize their connection, which effectively limits the possibility that octahedral chains will mutually dislocate and block the incorporation of fluorine. On the contrary, under a less oxygen condition, the lack of co-point O atoms causes an unstable connection among octahedral chains, so that more F atoms could replace co-edge O atoms. Therefore, it could be seen that the effective incorporation of F atoms for SnO_2 film significantly depends on the power of the oxygen action.

Figure 2. XRD pattern of F-doped SnO₂ films grown under more (a) and less oxygen (b); Raman spectra of F-doped SnO₂ films grown under more (c) and less oxygen (d); the wetting angle (e) of F-doped SnO₂ films with the various doped F content; photoluminescence spectra of F-doped SnO₂ films grown under more (f) and less oxygen (g).

In Figure 2a, under the more oxygen condition, as the doped F content is 2.5 at%, the profiles of the (110) and (101) peaks are the most diffuse. It is caused by both the incorporation of F atoms in co-edge position and the increase in oxygen vacancies caused by mutual dislocation of octahedral chains. As F atoms are further incorporated into the SnO₂ lattice (5 at%), the diffracted peak profile is the sharpest. Under the condition that the action of oxygen is stronger than that of fluorine, the competitiveness of fluorine was restricted so that fluorine would be likely to be squeezed to oxygen vacancies to release distorting energy in the lattice. It makes F atoms become a bridging-point to connect octahedral chains, and then re-build the stacking of octahedrons in three dimensions. After that, with the continuous increase in doped F content, the peak profile becomes broader. This implies that excessive F atoms are excluded by oxygen to the crystal boundary. Fluorine segregated at the crystal boundary is likely to interact with the crystal boundary to negatively affect the growth of crystal grains.

In contrast, for the film sputtered under the less oxygen condition, there is a monotonically decreasing peak intensity and a constant peak width in the XRD pattern as the doped F content is elevating in Figure 2b. It demonstrates that the F atoms could be effectively incorporated into an SnO₂ lattice to occupy the position of the co-edge oxygen all the way because of the declining restriction of oxygen. The difference from fluorine competition between the two kinds of oxygen action demonstrates that oxygen could not only restrict fluorine from entering the film, but also determine the occupied order of the incorporated fluorine. It is worth noting that, under the two kinds of oxygen atmosphere in Figure 2a,b, the (200) peak became more and more sharp with the increase in the doped F content since the lack of squareness degree of rutile has less of an impact on the interplanar distance of the (200) plane.

3.3. Presentation of Atom Vibration on F&O Competition

The Raman spectra of F-doped SnO₂ films with the elevating F content are presented in Figure 2c,d. All spectra present the typical Raman vibration modes of pure phase SnO₂ with rutile structure. A_{2g} mode (~445 cm⁻¹) is attributed to the shearing vibration of O-Sn-O bond located at the diagonal plane in SnO₂ crystalline cell in Figure 1i. B_{2g} mode (~775 cm⁻¹) ascribes to a simultaneous breathing-vibration of six Sn-O bonds in a SnO₆ octahedron, and A_{1g} mode (~630 cm⁻¹) is closely related to the stretching vibration of six Sn-O bonds whose four co-edge Sn-O bonds shrink/expand and the two co-point Sn-O bonds expand/shrink simultaneously [20,21], as shown in Figure 1j,k. The strong peak near 568 cm⁻¹ is excited by oxygen vacancies with high concentration in SnO₂-based films [22].

Regardless of level of oxygen action in Figure 2c,d, during the preparation process of SnO₂ films, the shoulder peak at 630 cm⁻¹ to describe four/two stretching Sn-O bond vibration in Figure 1j gradually becomes weak with the increase in the doped F content. Meanwhile, peak intensity of B_{2g} mode remains still unchanged, which is used to depict a synchronous breathing-vibration of six Sn-O bonds, as seen in Figure 1k. The difference between A_{1g} and B_{2g} vibration mode caused by fluorine introduction indicates that the F atoms incorporated into the SnO₂ lattice either substitute co-edge or co-point oxygen. In combination with the above analysis of XRD from octahedral structure, F atoms would replace the co-edge oxygen instead of co-point oxygen.

In Figure 2c,d, with the increase in the doped F content, the peak at 445 cm⁻¹ moves towards large wavenumber under the more oxygen condition, while it has no change under the less oxygen condition. The peak represents the shearing vibration of O-Sn-O bond in the diagonal plane of the SnO₂ crystalline cell, in which O atoms just correspond to co-edge oxygen, as shown in Figure 1i. It illustrates that there are two kinds of different F&O competing process in the two kinds of oxygen condition, respectively. With the oppression of oxygen, it is difficult for fluorine to be incorporated into films to affect O-Sn-O bonds. Without restriction of oxygen, it is relatively easily entered into films to significantly impact O-Sn-O bonds, as analyzed in Section 3.2. In addition, compared with the weak splitting effect of 568/630 cm⁻¹ under the less oxygen condition, the splitting effect of 568/630 cm⁻¹ by bimodal peak is relatively obvious under the more oxygen condition. It further demonstrates that the lack of lattice oxygen would result in that the unstable connection among octahedral chains, so that more F atoms could easily invade the SnO₂ framework to occupy the position of oxygen, and then damage the vibration of Sn-O bonds in A_{1g} mode. On the contrary, supplemental oxygen not only provides more Sn-O bonds, but also builds the bridges that connect octahedral chains to establish a firm SnO₂ structure, and in turn, makes fluorine hard enter into films to substitute oxygen.

For the film prepared in the more oxygen condition, the intensity of peak at ~568 cm⁻¹ shows a trend of firstly rising and then falling as the doped F content elevates in Figure 2c, which presents the competing process of fluorine with oxygen, as analyzed from the XRD pattern. As the doped F content is lower at 2.5%, there exists the most amount of oxygen vacancies in the SnO₂ lattice, since the substitution of fluorine for the co-edge oxygen would match the presence of oxygen vacancies to release the distortion energy. It is not difficult to understand why this intensity of peak at 568 cm⁻¹ excited by oxygen vacancy is the strongest. After that, the continuously increasing level of fluorine is likely to be squeezed by oxygen to fill oxygen vacancies, and is even excluded to segregate at the boundary, thereby the intensity of peak at 568 cm⁻¹ gradually becomes weaker. It further reflects that, under the suppression of oxygen, fluorine is difficult to incorporate into film, even though the incorporated F atoms would also occupy lattice positions by the sequence of co-edge O > oxygen vacancy > segregation. In contrast, under the less oxygen condition in Figure 2d, every octahedral chain is relative free owing to the lack of lattice oxygen, so that F atoms are easily incorporated into the lattice and always occupy the position of co-edge oxygen in one octahedral chain instead of filling oxygen vacancies, which means the intensity of peak at 568 cm⁻¹ remains unchanged even though fluorine content is increasing.

3.4. F&O Function on Plane Preferred-Growth

The above substitution of oxygen by fluorine would have an impact on the characteristic of crystalline planes, and then affect the growth of SnO_2 crystals which could be reflected on apparent performance of two-dimensional materials. As shown in Figure 2e, under both strong and weak oxygen action, the wetting angle gradually decreases with the increase in the doped F content, indicating an increasing surface energy of film. It could be seen from the XRD pattern in Figure 2a,b that SnO_2 crystals mainly grow along the (110), (101), and (200) crystalline planes. After F atoms replacing the co-edge O atoms, the presence of fluorine in the (110) plane in Figure 1c damages the coincidence of positive and negative charge center of the (110) plane, and then increases the plane energy. In the unsaturated polar (101) plane with an alternative layer of Sn atoms and oxygen atoms, the occupation of fluorine for oxygen gives rise to an increase in polarity of the (101) plane in Figure 1f. Meanwhile, by virtue of the increase in surface energy of the (110) and (101) planes, the SnO_2 crystal growth in the two orientations is restricted, so that the (200) plane in Figure 1c,f is unaffected by replacement of fluorine for co-edge oxygen, and could preferably evolve in the crystal growth. These processes are reflected in the XRD pattern in Figure 2a,b that with the increase in the doped F content, the (110) and (101) peaks are gradually diffuse, while the (200) peak shows a modest uptrend. In summary, the increase in (110) and (101) plane energy, together with the preferred evolvement of more high-energetic (200) plane [23], contributes to the increase in surface energy of films, and then brings about change in the wetting angle.

Certainly, the evolvement of different crystalline planes during the growth of SnO_2 crystals is dependent upon the competition of fluorine with oxygen. Under the weak oxygen action, more oxygen vacancies would be generated and more fluorine could be incorporated into the film, which both further enlarge the above-mentioned change in characteristics of the crystalline plane. Hence, the films grown in the less oxygen atmosphere had a higher surface energy, and present a smaller wetting angle.

3.5. F&O Regulation for Band Structure

The incorporation of fluorine has affected the electron energy band structure of films, and has an effect on the transition of electrons and holes among various energy levels, which would be reflected in photoluminescence spectra, as seen in Figure 2f,g. The ultraviolet emission peak at ~370 nm is attributed to electron transition between conduction band and valence band [24], the emission peak at ~540 nm is assigned to the electron transition mediated by energy level from oxygen vacancies [25], and emission peak at ~752 nm is related to energy levels of surface state in the band gap [26].

Whether the oxygen action is strong in Figure 2f or weak in Figure 2g, with the increase in the doped F content, the ultraviolet emission peak at ~370 nm firstly shifts towards long wavelength, and then shifts towards short wavelength. It depends on which one is dominant between up-shift of highest occupied molecular orbital (HOMO) in the valence band and up-shift of lowest unoccupied molecular orbital (LUMO) in the conduction band. As the less amount of fluorine enters the SnO_2 lattice to replace oxygen, free electrons provided by F atoms as the donor level would be not enough to fill the LUMO of the conduction band, while the HOMO in the valence band would move up due to the incorporation of fluorine [19]. It contributes to the emission peak at ~370 nm shift towards long wavelength. As an increasing number of fluorine atoms incorporate into the SnO_2 lattice, a large number of free electrons supplied by F atoms would increase the density of state in the conduction band, and then make the fermi level enter into the conduction band to bring about the Burstein–Moss effect [27], which broadens the optical band gap. In this case, the up-shift of LUMO in the conduction band begins to play a dominant role, making the emission peak at ~370 nm shift towards short wavelength.

Comparing Figure 2f with Figure 2g, the films grown in the less oxygen condition have an early blue-shift at ~370 nm as the doped F content is increasing. Without the restriction of oxygen, more F atoms incorporated into the film could always substitute co-edge O

atoms to provide more free electrons, which significantly increases the density of states of the conduction band, and then broaden the optical band gap to cause the blue-shift. The peak at ~550 nm excited by oxygen vacancies is relatively diffuse, so it is unreasonable to effectively analyze the corresponding physical mechanism. Nevertheless, the emission peak at ~752 nm related to energy levels of surface state presents respective features for different oxygen actions. Under the less oxygen condition, the emission peak occurs the obvious red-shift with the increase in the doped F content, since the effectively incorporated fluorine atoms cause the lattice disorder as seen in Figure 2b, and then bring about wide surface states above the valence band to accept more electrons. F atoms efficiently doped into films significantly prompt the up-shift of the valence band. Then, the gap between the HOMO in the valence band and the energy levels of surface state were shortened. For the films grown in the more oxygen condition that could restrict the function of fluorine, there is no obvious shift for the peak at ~752 nm due to the invariable energy level of surface states and valence band.

3.6. F&O Cooperation on Electrical Characteristics

The above regulation of electron energy band structure from the competition between fluorine and oxygen must be deeply reflected in the electrical characteristics in F-doped SnO₂ films. Figure 3a,b shows the trends in carrier concentration and mobility of films with the increase in the doped F content. Under the less oxygen atmosphere, as the doped F content increases, more F atoms could enter into the SnO₂ lattice to effectively substitute co-edge oxygen in pairs all the way, which provides a large number of free electrons to dramatically increase the carrier concentration of films from $\sim 10^{16}$ to $\sim 10^{19}$ cm⁻³, while the co-edge F atoms only cause the mobility decrease from 17 to 2 cm²/V·S, and then the resistivity of films drastically declined from 10^1 to 10^{-1} Ω·cm. In comparison to the monotonous change in electrical characteristics under the less oxygen condition, with the increase in the doped F content, the change in electrical characteristics under the more oxygen condition is divided into three stages which just correspond in competing process between fluorine and oxygen. In the first F-rising stage, F atoms replace co-edge oxygen in pairs and extra oxygen vacancies produce an overlapping effect to provide more free electrons, but form some barriers to hinder electron migration in SnO₂ films. In the second F-rising stage, additional F atoms are pushed to fill oxygen vacancies, which offsets the effect to provide free electrons between fluorine atoms and oxygen vacancies. Certainly, fluorine filling into oxygen vacancies could improve orderly arrangement in lattices to make carriers move more flexibly. In the third F-rising stage, the excessive F atoms form a segregation under the squeeze of oxygen to severely hamper electron mobilization, accompanying the modest increase in free electrons. In short, with the doped F content from 0 to 10 at%, carrier mobility sharply decreases from 70 to 0.2 cm²/V·S while carrier concentration merely increases from $\sim 10^{15}$ to $\sim 10^{17}$ /cm⁻³, and then the resistivity remains near $\sim 10^1$ Ω·cm in SnO₂ film, as shown in Figure 3c.

Based on the above discussion, the weak oxygen action seems to be beneficial to doping fluorine. Is this always the case? To clarify the issue, the SnO₂ films were obtained under an oxygen-deficient atmosphere with a higher vacuum degree. The result shows that only 2.5 at% of the doped F content could lead to a change in carrier concentration from $\sim 10^{16}$ to $\sim 10^{18}$ /cm⁻³, accompanying the decrease in mobility from 14 to 0.3 cm²/V·S, which totally decreases resistivity from 10^1 to 10^0 Ω·cm, as shown in Figure 3d. In addition, by comparing the average transmittance of the SnO₂ film prepared in different vacuum degree in Figure 3e,f, it could be seen that the weakened oxygen action in sputtering process not only prompts the effective F doping to increase carrier concentration, but also may maintain a higher average light transmittance. Therefore, in order to make the film meet a demand for excellent transparent and conductive performance, the suppression of oxygen during the growth of film should be one of the effective measures.

Figure 3. Electrical characteristics of F-doped SnO₂ films grown under more and less oxygen ambient, including carrier concentration (a), mobility (b) and resistivity (c); electrical characteristics (d) of F-doped SnO₂ films grown under oxygen-deficient ambient; transmittance curve (e) and average transmittance (f) of F-doped SnO₂ films grown under different oxygen ambient; the ratio of electrical characteristics of F-doped SnO₂ films, containing carrier concentration (g) and resistivity (h).

It is worth noting that the competition between F and O not only occurred under the non-equilibrium sputtering condition, but also during the steady state annealing process. The pure and F-doped 2.5 at% SnO₂ films prepared under the oxygen-deficient atmosphere were annealed in the different oxygen partial pressures (OPP) at 400 °C. Figure 3g,h shows the ratio in carrier concentration and resistivity of the as-annealed films to the original as-prepared film under the various oxygen partial pressures, respectively. Under OPP between $\sim 10^{-2}$ and $\sim 10^{-3}$ Pa, there keeps the ratio of resistivity near a constant (≈ 1) since the entering and escaping of lattice oxygen in films is almost at a dynamic equilibrium, which could only bring about a slight change in oxygen vacancies. On the platform between $\sim 10^{-2}$ and $\sim 10^{-3}$ Pa, compared with pure SnO₂ film, F-doped SnO₂ films present a lower ratio of carrier concentration (< 1) and higher ratio of resistivity (> 1), as shown in Figure 3g,h. It illustrates that the presence of fluorine reduces the equilibrium OPP in the film and implies that there are more oxygen vacancies in F-doped film. Under the OPP $> \sim 10^{-1}$ Pa, there is a lower ratio of carrier concentration and a higher ratio of resistivity in F-doped films, which further demonstrates that the incorporation of fluorine is beneficial to the entrance of oxygen from ambient. Under the OPP $< \sim 10^{-4}$ Pa, the F-doped films show a sharper increasing ratio of carrier concentration as well as a ratio of resistivity. It manifests that the incorporated F could also prompt the escape of oxygen, since the substitution of fluorine for oxygen caused the octahedral chains to be in an unstable state, resulting in O atoms in chains that could more easily escape to release a large number of electrons from Sn. Hence, the incorporation of fluorine could effectively regulate the in and out of lattice oxygen in the post-annealing process. The basic scientific issue about competition of fluorine for oxygen in the post-annealing process, could broadly tailor the multi-element component, atom-scaled microstructure and comprehensive properties for oxide crystals. It would also be beneficial to the development of the scientific community of crystals.

4. Conclusions

In this work, F-doped SnO₂ films were obtained through magnetron sputtering under the atmosphere with different oxygen partial pressures, respectively, by which the incorporation behavior of fluorine was methodologically discussed in details. The results show that the doped effect of fluorine is dependent upon the restricting action of oxygen during the growth of crystals.

Under a more oxygen sputtering atmosphere, the prevailing oxygen vigorously suppresses the function of fluorine, so that a smaller amount of F atoms can be embedded in SnO₂ film, by which F atoms are gradually squeezed from occupying the position of co-edge oxygen on octahedral chains to filling oxygen vacancies, and finally segregating at grain boundaries with the increase in doped F contents. Such evolution leads to that carrier concentration modestly increasing from $\sim 10^{15}$ to $\sim 10^{17}$ /cm⁻³ as well as a resistivity near $\sim 10^1$ Ω·cm in SnO₂ film.

Under a less oxygen sputtering atmosphere, the dominant fluorine without restraint of oxygen more easily enters into SnO₂ film. F atoms can always take place of co-edge O atoms on the octahedral chains, regardless of doped F contents, as the amount of OVs is hardly affected. Such occupation causes that carrier concentration to drastically increase from $\sim 10^{16}$ to $\sim 10^{19}$ /cm⁻³ in combination with a decreasing resistivity from $\sim 10^1$ to $\sim 10^{-1}$ Ω·cm in SnO₂ film.

Under an oxygen-deficient sputtering atmosphere, competition and cooperation between fluorine and oxygen still keep the above-mentioned trend. Considering further decreased oxygen partial pressure, merely 2.5 at% of fluorine could make carrier concentration of SnO₂ films an augment from $\sim 10^{16}$ to $\sim 10^{18}$ /cm⁻³. Moreover, the incorporated fluorine excessively boosts the in and out of lattice O atoms in SnO₂ film during the post-annealing process, which results in the film having a carrier concentration of $\sim 10^{21}$ /cm⁻³ and a resistivity of $\sim 10^{-2}$ Ω·cm.

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