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# Interaction of H and F atoms—Origin of the high conductive stability of hydrogen-incorporated F-doped ZnO thin films

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ABSTRACT

We intentionally incorporated H into fluorine-doped ZnO thin films (FZO) by plasma treatment. Upon treatment, both mobility and electron concentration have an observable increase, especially the mobility reaches up to 30.1 $cm^2V^{-1}s^{-1}$ (3 times higher than the untreated films). H distributes in the FZO thin films uniformly via plasma treatment. The treated FZO thin films showed good conductive stability at 500 °C and saved for 6 months, until now. Origin of high conductive stability was explained by first principle calculation. The results predicted that hydrogen atoms in interstitial sites next to $F_O$ are attracted by the incorporated fluorine atoms and this configuration has lower formation energy than the hydrogen in oxygen vacancy configuration. Thus, we owed the highly stable conductivity to the hydrogen as interstitial as well as hydrogen in oxygen vacancy.

## 1. Introduction

Doped ZnO thin films are attractive transparent conducting oxide (TCO) owing to their low cost, non-toxicity, and relatively low growth temperature, compared to ITO or $SnO_2$ [1–3]. ZnO thin films doped with cations such as Al or Ga are widely studied, due to their low electrical resistivity [4–9]. However, optical transparency, another fundamental property of these metal-doped ZnO thin films, is largely confined by their high carrier concentration and low mobility. In recent years, it is investigated that nonmetal dopants might get a better way to obtain transparent conductors. This is because nonmetal doping can induce fewer disturbances in the conduction band, and cause consequently less free carrier scattering and higher mobility and transparency. Among the nonmetal doping methods of ZnO, fluorine and hydrogen doping have attracted a lot of attention [10–24]. Unlike cation dopants which perturb conduction band, the fluorine dopant mainly perturbs the valence band when substituting oxygen, leading to high mobility as well as low absorption loss in fluorine-doped ZnO (FZO) thin films. Several groups have successfully prepared highly transparent and conducting FZO thin films up to now [10–16].

Hydrogen is a shallow donor in ZnO and the main source of its native *n*-type conductivity [17,18]. Many publications have demonstrated the beneficial impact on conductivity of integrating hydrogen during growth [19], post-deposition treatment annealing in hydrogen [20,21], or hydrogen plasma exposure [22,23]. However, the instability of hydrogen restricts the application of H-doped ZnO thin films [24].

Kim et al. prepared ZnO films co-doped with fluorine and hydrogen by radio frequency magnetron sputtering and reported the resistivity greatly reduced when a small addition of $H_2$ to the sputtering gas[25]. Here, we prepared HFZO thin films by treating FZO thin films with hydrogen plasma exposure. We investigated electricity property and thermal stability of the thin films. For the first time, we identified hydrogen position and relationship with F in the HFZO thin films to explore the origin of the high conductive stability.

## 2. Experimental details

FZO thin films were deposited onto glass using a RF magnetron sputtering system. The FZO target was fabricated by high-purity ZnO (99.99%) and $ZnF_2$ (99.99%) powders, and the atomic ratio of Zn/F was 97:3. Different substrate temperatures were adopted. The working pressure was maintained at 1 mTorr. By fixing the working power to 150 W and the deposition time to 45 min, a series of FZO thin films with a thickness of 100 nm were prepared. There is a post-annealing procedure (400 °C, 15 min) after the deposition. To introduce hydrogen, the FZO thin films were treated through H plasma process, during which the FZO thin films were placed upon a radio frequency power source, which was utilized to generate H plasma. The post-annealing procedure was conducted in a high vacuum environment. X-ray diffraction (XRD) using a XPERT-PRO system with a CuKα ($\lambda = 1.5406$ Å) source was used to characterize the crystal structure of the thin films. The surface morphology and the surface roughness (RMS) were studied using the

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atomic force microscopy (AFM; Dimension Edge). The depth profile of the thin films was investigated by secondary ion mass spectroscopy (SIMS; PHI6600). Electrical properties were examined by Hall measurements in the van der Pauw configuration (BIO-RAD HL5500PC) at room temperature.

## 3. Results and discussion

### 3.1. Electrical properties

Fig. 1 shows the change in electrical properties of FZO thin films with different substrate temperatures, as deposited, post-annealed and after H plasma. The resistivity of the as deposited FZO thin films has a variation in the range of 0.028–42,630 Ωcm depending on the substrate temperature (the black squares), as shown in Fig. 1a. Post-annealing decreased the resistivity of all the FZO thin films compared to their original ones (the red dots). It is interesting that the resistivity of all the H plasma treated FZO (HFZO) thin films significantly decreased to the order of $10^{-3}$ Ωcm, irrespective of their original values (the blue triangles). Fig. 1b shows the change of carrier concentration, from which we can see that H plasma treatment increases the carrier concentration substantially of all the thin films while post annealing did a little favor for this. The remarkable increase in carrier concentration indicates the formation of a shallow donor level as a result of hydrogen incorporated into the FZO thin films [23,26]. Furthermore, the higher carrier concentration usually leads to a strong carrier scattering and hence the mobility would be reduced. However, in our study, the mobility of H plasma treated films is almost 3 times higher than that of the untreated ones, which can be seen in Fig. 1c. If the incorporated hydrogen only introduced a shallow donor, this result would not be realized. The observed increase in both mobility and carrier concentration suggests that a substantial fraction of the incorporated hydrogen passivated defects at grain boundaries and/or acceptor impurities. Therefore, incorporated hydrogen not only introduces a shallow donor state, but also passivates most of the defects and/or acceptors.

### 3.2. Structural properties

Fig. 2 shows the XRD patterns of FZO thin films deposited at 250 °C, the as deposited, post-annealed and after H plasma. Only the peaks indexed to (002) and (004) appear in thin films, indicating that these thin films are preferred c-axis orientation with hexagonal wurtzite structure, which means post-annealed and H plasma treated has no effect on crystal orientation. According to Scherer formula, the values of the full-width at half-maximum (FWHM) of the (002) peaks are used to estimate the crystallite size [27]. The FWHM decreases from 0.36° to 0.28° and the grain size increases from 23.9 Å to 32.0 Å after annealing, indicating that the crystalline quality of the FZO thin films is greatly improved after annealing treatment. However, the FWHM gets larger and the grain size becomes smaller after H plasma treatment, revealing poor crystallinity due to that the hydrogen atoms might insert into the ZnO lattice and extract oxygen from the thin films. All in all, the crystallinity of the treated FZO thin films is better than the as-deposited one.

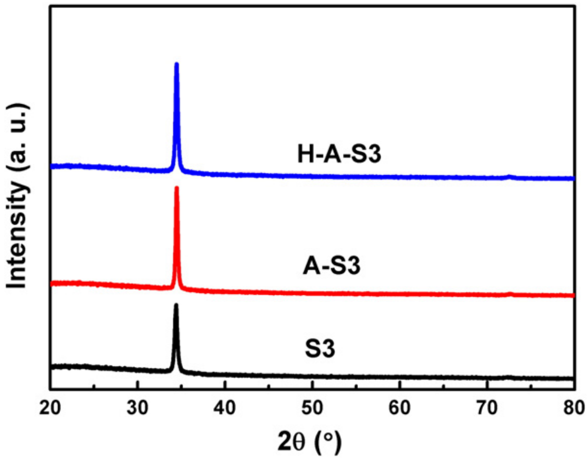

**Fig. 2.** XRD patterns of FZO thin films grown at 250 °C, the as deposited, post-annealed and after H plasma.

Fig. 3 displaces the AFM images of FZO thin films deposited at 250 °C, the as deposited, post-annealed and after H plasma. As can be seen, the grains grow up uniformly after annealing, and the RMS decreases from 3.74 nm to 2.36 nm. But, the H plasma treatment deteriorates the surface through bombarding it with charged particles, resulting in the RMS increases to 2.70 nm.

The depth profile of O, Zn, F and H in the plasma treated FZO thin films was carried out by SIMS measurements, as shown in Fig. 4. It can be seen that the H has been clearly detected, and uniformly distributed in the thin films, indicating H atoms incorporated via plasma treatment.

### 3.3. Thermal stability of hydrogen

The thermal stability of hydrogen in ZnO transparent conductive thin films cannot be ignored for the future applications of HFZO thin films. Here, we presented a preliminary result about the thermal stability of hydrogen in H plasma treated FZO thin films deposited at 250 °C. The HFZO thin films were annealed at 500 °C in vacuum for 5, 15, 30, and 60 min, respectively, and the corresponding electrical properties are shown in Fig. 5a. The resistivity of the thin films reaches saturated

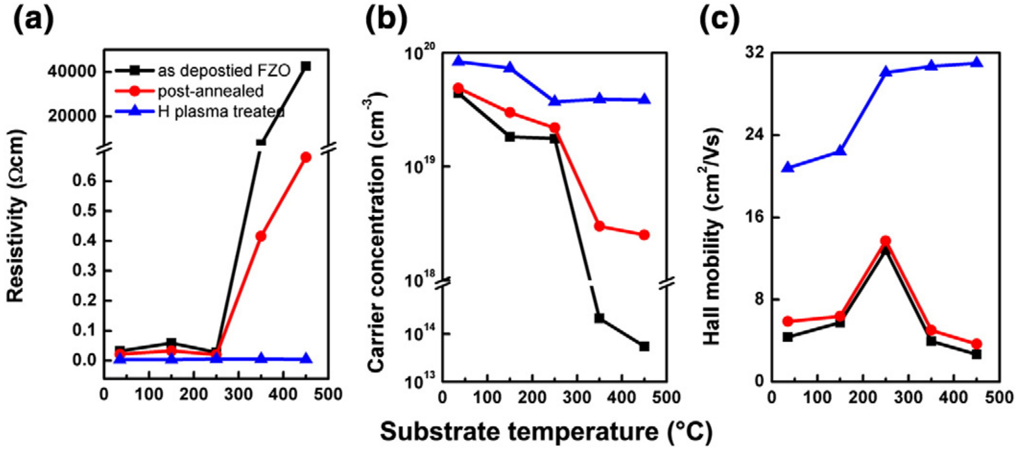

**Fig. 1.** Electrical properties of FZO thin films with different substrate temperatures, the as deposited, post-annealed and after H plasma.