



Article Passivation Effect on ZnO Films by SF₆ Plasma Treatment

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Abstract: The passivation effects of SF₆ plasma on zinc oxide (ZnO) films prepared by magnetron sputtering were researched. After the SF₆ plasma passivation of ZnO films, the grain size increases, there is low surface roughness, and a small amount of Zn-F bonds are formed, resulting in the narrowing of band gap. The photoluminescence (PL) intensity of SF₆-passivated ZnO films has a 120% increase compared to the untreated samples, and the reduction in defects can increase the resistivity and stability of ZnO films. ZnO films are used in the preparation of ZnO/p-Si heterojunction diodes. The results of the measurement of current voltage (J–V) show that the reverse current is reduced after SF₆ plasma passivation, indicating an improvement in the electrical properties of ZnO films.

Keywords: ZnO; SF₆; passivation

1. Introduction

Zinc oxide (ZnO) semiconductor materials have the advantage of large band gap ($E_g = 3.36 \text{ eV}$), high electron mobility, high light transmittance, good chemical stability, and so on. The heterojunction structures based on ZnO films are widely used in solar cells [1–3], ultraviolet photodetectors [4,5], light emitting diodes [6], and field effect transistors [7,8]. Many methods are used for the preparation of ZnO films, but the magnetron sputtering method is the most commonly used. This method has the advantages of fast film deposition, good compactness, smooth surface, uniform film thickness distribution, and good controllability. However, since it has a high surface state density caused by the defects of oxygen vacancies (oxygen dangling bonds) and zinc vacancies (zinc dangling bonds) in ZnO films [9,10], the result is a strong Fermi level pinning and high surface recombination rate, which will seriously affect the properties of the related devices [11–13].

The passivation of ZnO films is generally realized by doping them with Group III elements (AI [14] and Ga [15]), transition metal elements (Mn [16] and Fe [17]), and rare earth elements (Eu [18] and Er [19]). Although the intrinsic luminescence of ZnO films can be improved by doping them with the above-mentioned metal elements, the self-defect still cannot be passivated effectively [16]. In addition, metal doping can also cause lattice distortion of ZnO films. At present, plasma treatment (oxygen ions, fluorine ions) is widely used because it can passivate the defects of ZnO films while improving the electrical conductivity. Although the oxygen plasma can fill the oxygen vacancies in ZnO films, a new non-radiative center can form due to excessive oxygen chemisorption on the surface of ZnO films, causing Fermi level pinning [20]. ZnO films can also be passivated by fluorine plasma. The gas source used for the generation of fluorine containing plasma is mainly CF_4 or SF_6 . CF_4 may generate carbon pollution on the surface of ZnO films, so SF_6 is preferred for plasma treatment experiments on ZnO films.

In this paper, we report fluorine incorporation in ZnO films by SF_6 plasma treatment. In principle, the oxygen or oxygen vacancies in ZnO films can be replaced by fluorine ions because of the similar ionic

radius of fluorine ions and oxygen ions. At the same time, fluorine ions with high electronegativity can attract hydrogen in the ambient, and the oxygen dangling bonds may be passivated by the formation of intermolecular hydrogen bonds F/OH. Thus, the density of states associated with oxygen vacancies will be effectively suppressed. Deep passivation may be possible because of the existence of voids in the ZnO films prepared by sputtering. The properties of SF₆-passivated ZnO films are characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), photoluminescence (PL), the Hall effect, and the current–voltage (J–V) measurement of the prepared ZnO/p-Si diodes.

2. Experiment

In the experiment, fluorine plasma was introduced by radio frequency (RF) glow discharge in SF₆ ambience. Si wafers, p-type doped with a resistivity of 5–15 Ω ·cm, were used as the substrate for depositing ZnO films by magnetron sputtering, and ZnO/p-Si diodes were prepared to characterize the electrical properties of the ZnO film. Before ZnO deposition, the substrate was ultrasonically cleaned with acetone and ethanol for 10 min, respectively, then rinsed with a large amount of deionized water and dried with nitrogen gas blow. ZnO sputtering was carried out when the chamber vacuum reachedd 5 × 10⁻⁴ Pa. According to a previous experiment, the optimized process condition by PL evaluation for 100 nm thick ZnO deposition was as follows: RF power of 160 W, chamber pressure of 1.2 Pa, and sputtering time of 23 min. It was then annealed in air at 400 °C for 3 h to relieve film stress. The optimized process condition by PL evaluation for SF₆ plasma-treated ZnO films was: RF power of 100 W, chamber pressure of 1.8 Pa, treatment time of 5 min, and SF₆ flow rate of 18 sccm. A square pattern of Ti/Au film with a thickness of 30/150 nm was prepared by magnetron sputtering, to be used as the top ohmic contact electrode to the ZnO surface and the back ohmic contact electrode to Si wafer bottom.

The film quality of ZnO before and after SF₆ plasma treatment was analyzed by XRD (Bruker D8 Discover) with a 0.15406 nm wavelength Cu-K α radiation source. The surface morphology was measured by AFM (Agilent 5500), and the surface composition was analyzed by XPS (ESCALAB-MKII). The luminescence properties of ZnO films were measured by PL (Horiba Jobin-Yvon iHR320), and a He–Cd laser with 325nm wavelength was used as the excitation light source. The carrier mobility and concentration were measured at room temperature using a Hall effect (ECOPIA). The current–voltage (J–V) properties were obtained with semiconductor parameter analyzer (Keithley 4200A-SCS).

3. Measurement and Analysis

The X-ray diffraction curves of ZnO films with and without SF₆ plasma treatment are shown in Figure 1. It can be seen that there is a single diffraction peak at $2\theta = 34.4^{\circ}$, which represents the ZnO (002) diffraction peak according to the standard diffraction pattern (JCPDS 36-1451) [21,22]. This indicates that the deposited ZnO films are single phase films with hexagonal wurtzite structure, grown in a direction perpendicular to the c-axis of the substrate. The structural properties of ZnO films can be characterized by the peak shift and the peak width, i.e., the full width at half maximum (FWHM) of ZnO (002) peak. The ZnO (002) peak width is 0.46° and 0.44°, respectively for the original and the SF₆ plasma treated ZnO films.

The grain size can be expressed as [17,23]

$$D = \frac{0.89\lambda}{B\cos\theta},\tag{1}$$

where λ , θ , and B are the X-ray wavelength, the Bragg diffraction angle, and the FWHM of ZnO (002) diffraction peak, respectively. It shows that the grain size of ZnO films increased from 17.9 nm to 18.7 nm by SF₆ plasma treatment, which indicates that the defect of the ZnO films is reduced due to the fluorine ions replacing oxygen vacancies or passivating oxygen hanging bonds, and therefore the crystallinity of the films is improved. It indicates that the replacement of oxygen vacancies by fluorine

ions is not limited to a few nanometers on the surface of ZnO films due to the reduction of FWHM in XRD measurement. However, the ZnO XRD peak does not show an obvious shift after passivation treatment because the fluoride ions (1.34 Å) and oxygen ions (1.39 Å) have similar ionic radius, and the increase of grain size does not cause obvious lattice distortion of the films.



Figure 1. The X-ray diffraction (XRD) of ZnO films with and without SF_6 plasma treatment.

The surface morphology of ZnO films was compared by AFM measurement, as shown in Figure 2. It shows that the surface granule size increases by SF_6 plasma treatment. Passivation of defects in ZnO films, such as oxygen vacancies, zinc interstitials, and dangling bonds on the surface by SF_6 plasma may be the major reason for film quality improvement. The surface root mean square (RMS) roughness analysis of ZnO films was performed by AFM measurement and NanoScope analysis software. The RMS of ZnO films without and with SF_6 plasma treatment was 3.8 nm and 2.5 nm, respectively. A reduction of the surface roughness is achieved obviously, which means the SF_6 plasma treated ZnO films have a more uniform, dense grain structure.



Figure 2. The atomic force microscopy (AFM) of the surface of ZnO films with and without SF_6 plasma treatment, (**a**) without passivation, (**b**) with passivation.

The chemical state of the ZnO surface was analyzed by XPS. The XPS spectrums of Zn $2p_{3/2}$, F 1s, and O 1s of ZnO films treated by fluoride plasma are shown in Figure 3. The peak binding energy of non-passivated ZnO (Zn $2p_{3/2}$) films is 1021.49 eV [24], as shown in Figure 3a. The peak moves to 1022.00 eV by fluoride plasma treatment, and a 0.51 eV peak shift is found. The inner electron binding energy of zinc in Zn-F bonds is higher than that of zinc in Zn-O bonds, so the Zn $2p_{3/2}$ peak of ZnO films by SF₆ plasma passivation shifts to a higher energy position. Sulfur is not detected in the XPS measurement of S 2p by SF₆ plasma treatment, indicating that the passivation is achieved by fluorine ions. The XPS spectrum of F 1s is shown in Figure 3b; it is seen that the Zn-F bond (685.10 eV) is found after passivation [25]. The O 1s peak of ZnO films is shown in Figure 3c,d. The peaks with binding energy of 530.00 eV and 531.80 eV are Zn-O bonds and Zn-OH bonds, respectively [26,27]. The ratio

of the peak area of Zn-O bonds and Zn-OH bonds is calculated to be 2.21 and 1.16, respectively, for non-passivated and passivated samples. It is shown that the -OH bonds increase after the passivation of fluorine ions. Because fluorine ions with strong electronegativity can attract hydrogen in the air, fluorine/hydrogen can combine with the oxygen dangling bonds to form intermolecular hydrogen bonds F/HO.



Figure 3. The X-ray photoelectron spectroscopy (XPS) measurement of the surface of ZnO films without and with SF₆ plasma treatment: (**a**) Zn 2p3/2, (**b**) F 1s, and (**c**) and (**d**) O 1s.

The PL spectrum and corresponding energy level diagram at room temperature are shown in Figure 4a,b. It can be seen from Figure 4a that the ultraviolet intrinsic luminescence peak at 380 nm (3.26 eV) and the defect peak are observed in the emission of ZnO films. The intrinsic luminescence peak corresponds to the emission at the near band edge (NBE), and the defect peak comes from the vacancy defects in ZnO films. In order to explain the emission mechanism of the defect peak, an energy level diagram is established, as shown in Figure 4b. It indicates that the difference of energy level between the V_{Zn} and the conduction band is 3.06 eV (405 nm), and the energy interval from valence band to the Zn_i (0.5 eV below the conduction band) is 2.9 eV (427 nm) [21]. The Zn_i is a shallow donor level by zinc interstitials. The oxygen vacancies (V_{O}) have two donor levels: one is the deep donor level at 1.3–1.65 eV below the conduction band, and the other is the shallow donor level at 0.3–0.5 eV below the conduction band [28,29]. The shallow acceptor levels at 0.25 eV and 0.2–0.5 eV above the valence band are formed by the zinc vacancies (V_{Zn}) and the oxygen interstitials (O_i) , respectively [28]. The blue light emission near 465 nm (2.66 eV) is due to the transition of electrons from the shallow donor level (Zn_i) to the valence band or the shallow acceptor level (V_{Zn}) . The green light emission occurs near 543 nm by the electron transition from the shallow donor level V_O to the shallow acceptor level VZn, or the transition of electrons from the deep donor level VO to the valence band. The transition from Zn_i to O_i is also consistent with the emission of green light. At the same time, the green light may also be due to the presence of oxygen antisite (O_{Zn}, 2.38 eV below the conduction band), which is formed by O_i and V_{Zn} [21,30]. The red light (630 nm) may be due to the presence of excess oxygen on the surface of ZnO film [31,32]. The V_O, V_{Zn}, and Zn_i of ZnO films are well confirmed by the presence of blue, green, and red light emission.



Figure 4. (a) The photoluminescence (PL) of ZnO films with and without SF_6 plasma treatment and (b) the energy level diagram of ZnO.

It has been found that after 5 min of SF₆ plasma treatment, the visible emission decreases, while the UV emission increases with a 3 nm red shift of the peak. The red shift of UV peak indicates that passivation by SF₆ plasma narrows the band gap of ZnO films. The fluorine can replace oxygen or passivate Vo defects due to the similar ionic radii of fluorine and oxygen. The Zn-F bonds can be formed by the replacement of oxygen by fluorine. The passivation of Vo defects by fluorine can reduce the concentration of oxygen vacancies and weaken the emission of green light. The V_{Zn} is filled by fluorine during the passivation process; therefore, the blue emission is weakened. The excess oxygen on ZnO surface also can be removed by fluorine plasma. Thus, as a result of the fluoride plasma passivation, a low trap density in the band gap is realized, which is beneficial to enhance the radiation recombination of NBE. Therefore, the UV peak intensity of ZnO films has a 120% increase by SF₆ plasma passivation process.

In order to further analyze the relationship between the defects and photoluminescence of fluoride ions passivated ZnO films, a low-temperature PL test was performed. The low temperature (86K) PL spectra of ZnO films is shown in Figure 5. The luminescence at 3.378 eV is the radiative recombination of free exciton A (FX_A); the luminescence at 3.360 eV is the transition of shallow donor-bound exciton (D^OX) to the valence band [33]. The D^OX intensity is dominant for the non-passivation samples, indicating that the ZnO donors are dominant and the conductive type is n-type. The luminescence peak at 3.318 eV is a complex composite peak with A-line luminescence [34]. This can be caused by some possible transitions, including the transition of excitons bound by neutral impurities, the transition of excitons bound by surface states or defect states, the two-electron transitions of excitons bound by neutral donors, and the donor-acceptor composite transitions [35,36]. The luminescence peak at 3.245 eV is the 1-LO phonon replicas of the A-line emission, and it is 70 meV lower than the A-line peak, which is consistent with the ZnO exciton binding energy.



Figure 5. The low temperature PL spectra of ZnO films with and without SF₆ plasma passivation.

It is shown that the peak intensity of $D^O X$ is reduced for the passivated ZnO films. The peak at 3.354 eV comes from the radiation recombination of neutral-acceptor-bound exciton ($A^O X$), and the $D^O X$ peak is still the dominant peak, indicating that the passivation by fluorine ions do not change the conductivity type of ZnO; the several defects in ZnO films caused by the sputtering method may be the major reason for this. However, the PL intensity of $D^O X$ peak decreases by 19.5% through the fluorine ions passivation of the V_O donor level, while the peak intensity at 3.318 eV and 3.245 eV is also reduced by 27.5% and 26.9% respectively, which may be caused by the fill of V_{Zn} and V_O by fluorine ions, simultaneously. The above results are consistent with current voltage (J–V) measurement of ZnO films, and an increase in bulk resistivity is found by fluorine ions passivation.

The PL stability of ZnO films were tested for a period of 30 days in air, as shown in Figure 6. It has been found that the PL intensity of ZnO films without passivation has a slight decrease, while a nearly unchanged PL intensity is measured for ZnO films by fluoride plasma passivation.



Figure 6. The PL intensity stability of ZnO films with and without SF₆ plasma treatment.

The electrical parameters of ZnO films passivated by SF₆ plasma were also characterized by Hall measurement. Table 1 lists the electrical parameters of ZnO films. It can be seen that the ZnO films with and without passivation are both n-type conductive, which is consistent with the PL measurement at low temperature. It can be seen from Table 1 that the resistivity increases to $1.11 \times 10^{-1} \Omega \cdot cm$, the mobility to $15.2 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, and the carrier density decreases to $1.44 \times 10^{17} \text{ cm}^{-3}$, after the passivation of ZnO films by fluoride ions. It is believed that the high carrier density in ZnO by sputtering method is mainly caused by structural defects; the fill of V_O by fluoride ions will result in a physical reduction of Hall carrier density. The increase of Hall mobility is realized by the reduction of the scattering center related to the Vo defects, in the passivated ZnO films. A small increase of measured resistivity is primarily caused by the obvious reduction of Hall carrier density.

Table 1. The electrical properties of SF₆ plasma passivated ZnO films.

Sample	Resistivity (Ω·cm)	Mobility (cm ² ·V ⁻¹ ·s ⁻¹)	Carrier Density (cm ^{−3})
ZnO	2.92×10^{-2}	8.34	2.47×10^{19}
F-ZnO	1.11×10^{-1}	15.2	1.44×10^{17}

The electrical properties of ZnO films were analyzed by the current–voltage measurement of the ZnO/p-Si heterojunction diodes. The schematic device structure is shown in Figure 7a, and current density (J) voltage (V) curve is shown in Figure 7b. It can be seen from Figure 7b that the non-passivated device shows high current density, which may be caused by interface trap-assisted tunneling [37] of carriers, and the interface state. Furthermore, the defects in ZnO films can also diminish the conduction band offset between ZnO and p-Si substrates and cause an increase in current density in advance. By SF₆ plasma passivation, the reverse current density decreases from

 1.07×10^{-4} A/cm² to 1.77×10^{-5} A/cm² at -1V bias, indicating that the heterojunction diode after passivation has a high-quality interface and a low defect density in ZnO, the trap assisting the tunneling of carriers [37,38] can be effectively restrained.



Figure 7. (a) ZnO/p-Si heterojunction diode and (b) the J–V curve of ZnO/p-Si heterojunction diode with and without SF₆ plasma treatment.

4. Conclusions

The properties of ZnO films by SF₆ plasma treatment are analyzed in this paper. Using XRD and AFM measurements, it can be confirmed that the ZnO films prepared by magnetron sputtering are high-quality and have a single-phase hexagonal wurtzite structure growth in the direction perpendicular to the c-axis of the substrate. The ZnO films after SF₆ plasma treatment have an increased grain size and a dense bulk structure; therefore, surface roughness is reduced. The XPS measurement shows that the SF₆-treated ZnO films are passivated by fluoride ions, and a small amount of Zn-F bonds are formed on the surface. The PL measurements show that the impurity peak luminescence of ZnO films after SF₆ plasma passivation is effectively suppressed and the UV emission increases by 120% with a good PL stability. The low-temperature PL and Hall measurements show that the defect level of ZnO films after SF₆ plasma treatment is reduced and the resistivity is increased. The J–V measurement of the prepared ZnO/p-Si heterojunction diodes shows that the reverse current density decreases from 1.07×10^{-4} A/cm² to 1.77×10^{-5} A/cm² at -1V bias. From these experimental results, it can be concluded that the SF₆ plasma treatment of ZnO films can effectively passivate the oxygen vacancies, zinc interstitials, and surface dangling bonds in ZnO films prepared by RF magnetron sputtering.

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