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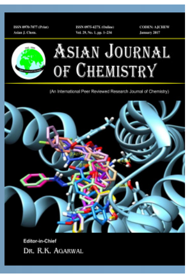

MINI REVIEW

Various Techniques to Optimize the Quality of Schottky Contacts on ZnO Thin Films: A Short Review

SUMIT VYAS

Department of Electronics and Communication Engineering, Thapar University, Patiala-147 001, India

Corresponding author: E-mail: sumit.vyas@thapar.edu; sumit.clooney@gmail.com

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Zinc oxide is a promising material for fabrication of electronic and optoelectronic devices. ZnO based Schottky diode is an important device that can be used for variety of applications. For a high quality Schottky contact on ZnO, it is essential that the quality of the ZnO film should be very good. In this paper, various techniques that can be used to improve the quality of ZnO thin film and hence the quality of Schottky contacts on ZnO have been reviewed. Techniques like surface treatments of ZnO, annealing of the film before and after deposition of the contacts, use of buffer layer and proper selection of deposition method greatly affects the quality of Schottky contact on ZnO. These methods are reported by various research groups that are discussed in this paper.

Keywords: Schottky diode, Annealing, Schottky barrier, Detector, Ohmic, UV rays.

INTRODUCTION

Zinc oxide based Schottky diode is used for fabricating many important electronic and optoelectronic devices like photo-detector, transistors, gas sensors, *etc*. Mead [1] in 1965 reported the first Schottky contact to ZnO. Till now a significant amount of work highlighting the important issues has been reported on Schottky contacts on ZnO. A good Schottky contact is charac-terized by very low series resistance with the semiconductor, a high rectification ratio, high thermal stability and a high barrier height. In general, the high work function metal such as Pd, Pt, Au, *etc.*, are used for Schottky contact on ZnO thin films. Ideally, the Schottky barrier height Φ_{SB} should be equal to ($\Phi_M - \chi_{ZnO}$), but in real the measured Φ_{SB} differs from ideal one. It is also found that barrier height is almost independent of the type of metal used for the contact. Most of the authors have reported the Schottky barrier heights in the range of 0.6-0.8 eV for the Schottky contacts fabricated on the *n*-type ZnO material [2]. The barrier height highly depends on the crystal quality, defects, surface treatments and deposition techniques. Also, the long-term stability of Schottky contacts to ZnO is one of the biggest challenges that are faced by the researchers. The poor performance of the contact is mainly due to the defects in the film that occurs due to the improper chemical bonding between Zn-O during the deposition. The surface defects are even induced by the deposition of metal contacts [3]. Therefore, the film should be appropriately treated before and after the deposition of metal with proper methods to lowers the defects levels and improve the performance of the film. Various tech-niques like surface treatments of ZnO, annealing of the film before and after deposition of the contacts, use of buffer layer, *etc.*, have been reported by many researchers to improve the stability and performance of the contact.

Surface treatment of ZnO: The ZnO thin film consist of defects like oxygen vacancies (V_O) and zinc interstitials (Zn_i). These defects make ZnO electrically unstable and are responsible for the poor electrical characteristics of the device. These defects can be reduced by treating the surface of ZnO thin film by proper methods. Angadi *et al.* [4] studied the effect of oxygen (O_2) plasma treatment on epitaxial ZnO thin film. Au/ZnO/ITO structure was fabricated and the effect of O_2 treatment on the I-V characteristics was studied. Before the O_2 treatment, the sample exhibited ohmic behaviour but after the O_2 treatment, the sample started showing rectifying I-V characteristics. The structural and surface morphology of the film were not much affected by the O_2 treatment. The treatment resulted in the removal of conductive OH layer from ZnO surface that was confirmed by X-ray photoelectron spectroscopy (XPS). Oh *et al.* [5] used KrF laser to modify the Pt Schottky contact on *n*-type ZnO thin film. Before deposition of Pt contact, the ZnO film was treated with laser pulses in the presence of O_2 at the pressure of 0.1 M torr. The laser treated ZnO films were studied using Auger spectroscopy and cathode luminescence. The study revealed that the surface hydrogen and carbon compo-nents were removed after the treatment and also a reduction in sub-surface defects were observed. The Φ_{SB} obtained by I-V and C-V studies were 0.73 eV and 0.85 eV, respectively. Lee *et al.* [6] reported the conversion of ohmic ITO contact to Schottky contact on ZnO films by the hydrogen peroxide treatment of ZnO surface. The ZnO film was deposited on an ITO-coated glass substrate by the continuous wave (CW) CO_2 LASER evaporation method. The calculated Φ_{SB} was 1.16 eV, ideality factor was 2.31 and leakage current at -3 V was 3×10^{-7} A. The photoluminescence study showed the reduction in the surface defects of ZnO film after the H_2O_2 treatment. The reduction in surface defects improved the diode characteristics. Nakamura and Temmyo [7] reported the surface treatment of ZnO film by boiling the H_2O_2 solution. ZnO films were deposited by remote-plasma-enhanced metal-organic chemical vapour deposition (RPE-MOCVD) on a α-plane sapphire subs-trate. Platinum metal was used to make Schottky contact on ZnO thin film. Before the deposition of platinum metal, the ZnO films were cleaned with acetone and methanol followed by rising in deionized water and drying with a nitrogen stream. After cleaning, the circular platinum contacts were patterned by standard lift-off photolithography. The platinum Schottky contacts were treated with H_2O_2 solution for 1 min at 100 °C. The surface morphology of the film was studied using scanning electron microscope (SEM). The surface of the treated films was smoother as compared to the untreated films. By the transmission electron microscopy (TEM) analysis, it was observed that a very thin amorphous layer of ZnO_2 of thickness 20-30 nm was formed over ZnO due to the H_2O_2 treatment. The sheet resistivity was increased from 2 kΩ/square to 1 MΩ/square. The high conductive ZnO layer was removed by the H_2O_2 treatment and high resistive ZnO_2 layer was recovered. The non-treated sample was showing linear I-V whereas the treated sample exhibited excellent rectifying behaviour. Due to thin ZnO_2 layer the rectifying behaviour of the diode was significantly improved. The rectification ratio at ± 3 V was in the order of 10^6 and Φ_{SB} was 0.78 eV. Yao *et al.* [8] prepared a ZnO-based Schottky diode using Ni/Au metal. The ZnO film was deposited by RF magnetron sputtering method. The ZnO thin films surface was etched by the dilute HCl solution for 20 s and also for 40 s to remove the defects induced from the ion-bombardment damages during the film deposition. The pre-etched ZnO layer surface was then dipped in the dilute H_2O_2 solution at 100 °C and dilute ammonium sulfide ($(NH_4)_2S_x$) solutions at 60 °C, respectively. The Ni/Au (20/100 nm) metal was deposited on the modified ZnO film surface using electron-beam evaporation method. The current ratio (at ± 2 V), Φ_{SB} and ideality factor for non-etched film treated by H_2O_2 were 1035, 0.68 eV and 1.65, respectively. The current ratio (at ± 2 V), Φ_{SB} and ideality factor for films pre-etched and treated by H_2O_2 for 20 sec were 6923, 0.83 eV and 1.24, respectively. The current ratio (at ± 2 V), Φ_{SB} and ideality factor for films pre-etched and treated by H_2O_2 for 40 s were 3.3×10^7, 0.90 eV and 1.20, respectively. The current ratio (at ± 2 V), Φ_{SB} and ideality factor for films pre-etched and treated by $((NH_4)_2S_x$ solution were 3.10×10^7, 0.87eV and 1.3, respectively. The Schottky barrier height of H_2O_2 treated ZnO layer contact to Ni/Au was increased due to the compensation effect by the increase in ZnO and OH acceptors. The increase in the Schottky barrier height of $(NH_4)_2S_x$ treated ZnO thin film was due to the passivation of the $5I_O$ donors and Zn_i acceptors due to the formation of the Zn–S chemical bond. Tsiarapas *et al.* [9] studied the effect of hydrogen gas on the performance of Au/ZnO Schottky diode. The ZnO thin film was deposited using the DC-magnetron sputtering technique. Argon and hydrogen gases were used for the formation of the plasma. A significant improvement of the crystallinity of ZnO film was observed by varying the hydrogen concentration. At H_2 concentration of 33.3 %, the resistivity of the film was lowest and has a value of 2.22×10^{-4} Ω cm. The corresponding value of Hall mobility and carrier concentration were 68.6 $cm^2 (V s)^{-1}$ and 4.1×10^{18} cm^{-3}, respectively. The Φ_{SB} was in the range of 0.72 to 0.82 eV and the ideality factor was 1.42.

Effect of annealing: There are many reports on related to the improvement in structural, optical, surface and electrical properties of ZnO thin film and devices by annealing [10-12]. Many groups have studied the effect of annealing on the electrical properties of ZnO thin film Schottky diode. Li *et al.* [13] reported the ZnO-based UV detector with silver contact. The ZnO thin film and the Ag contact both were deposited by the pulse laser deposition method (PLD) using KrF excimer laser. The Ag/ZnO was annealed for 2 h at 600 °C. The ideality factor and barrier height of unannealed Ag/ZnO film was 1.22 and 0.908 eV, respectively. After annealing at 600, the ideality factor and the barrier height was 0.988 eV and is 1.18. The improvement in the electrical properties of Ag/ZnO was attributed to the annealing process. Mtangi *et al.* [14] investigated the effect annealing on the electrical properties of Pd/ZnO Schottky diode in the presence of argon, hydrogen and oxygen gases. The ideality factor, Φ_{SB} and series resistance for the unannealed sample were 1.43, 0.72 eV and 190 Ω, respectively. The ideality factor, Φ_{SB}, series resistance for samples annealed in H_2 were 1.64, 0.617 eV and 70 Ω, respectively. The ideality factor, Φ_{SB}, series resistance for samples annealed in O_2 were 1.57, 0.545 eV and 426 Ω, respectively. The ideality factor, Φ_{SB} and series resistance for samples annealed in Ar were 1.75, 0.571 eV and 79 Ω, respectively. The barrier height of the annealed samples decreased due to the increase in conductivity of the layer closer to the surface of ZnO that can be observed by the decrease in the series resistance. The deep level transient spectroscopy (DLTS) study revealed that the annealing process in the presence of Ar and H_2 decrease the concentration of defects whereas annealing in the presence of O_2 increases the surface defects. This can be attributed to V_O or Zn_i, which are the most common defects formed in ZnO under oxygen rich environment. Gu *et al.* [15] reported the transformation of Ti/Ni/Ti/Au Ohmic contact to Schottky contact on Al-doped ZnO thin films. The Al-doped ZnO thin films were deposited on a quartz substrate at 400 °C using PLD with a KrF excimer laser. Ti, Ni and Au contact metal layers of thickness 50 nm each was deposited sequentially using electron-beam evaporation method. The metal contacts were annealed at 200, 300, 400, 500, 600 and 700 °C, respectively for 60 s in the nitrogen environment. These metal contact on ZnO exhibited ohmic nature and the resistivity decreased as the annealing temperature increased to 500 °C. The resistivity of the as-deposited sample was 2.07×10^{-4} Ω cm^2 and decreased to 6.69×10^{-5} Ω cm^2 at an annealing temperature of 500 °C. The transformation from ohmic to rectifying started above 600 °C. At 600 °C, the calculated barrier height was 0.57 eV. At 700 °C, cracks were appeared in the sample due to the release of inherent stress. Saw *et al.* [16] investigated the effect of annealing on Ni contact on ZnO thin films. The Ni contact was deposited using evaporation method on the sputtered ZnO thin films. The sample was annealed at 800 °C. After annealing, the ohmic nature of Ni/ZnO sampled transformed to rectifying nature. They assumed that the change in the electrical behaviour of the sample was due to the oxidation of Ni into NiO due to the annealing. This was confirmed by X-ray diffraction (XRD) studies where the spectra showed the peak of NiO at 37.296 °C along with the peaks corresponding to ZnO.

Somvanshi and Jit [17] reported Pd/ZnO thin film-based Schottky diodes with ideal Richardson constant and mean barrier height. The ZnO film was deposited on *n*-type Si substrate by vacuum thermal evaporation method. Before the deposition of metal, The ZnO film was treated with nitrogen gas for 30 min at 550 °C. The treatment with N_2 improves the crystalline quality of the film by minimizing the structural defects on ZnO thin film surface. The values of the effective Richardson constant and the zero-bias mean barrier height of the Pd/ZnO Schottky diode were and 19.54 A cm^{-2} K^{-2} and 1.41 eV.

Yadav *et al.* [18] reported the effect of annealing on the properties of ZnO thin film and Pd/ZnO Schottky diode. The ZnO film was grown by vacuum thermal evaporation process. The Pd/ZnO sample was annealed in the Ar atmosphere at 450, 550 and 650 °C temperatures, respectively for 20 min. The XRD study revealed that the structural quality of the ZnO film improved with the increase in the annealing temperature to 550 °C and then the quality of the film degrades at 650 °C. The barrier height, ideality factor and saturation current at 550 °C was 0.79 eV, 1.58 and 1.89×10^{-9} A and were better that that at 400 °C. By further rise in temperature, the electrical parameters were found to degrade. The electrical properties were in good agreement with the structural properties. Recently, Al-Salman and Abdullah [19] reported the annealing effect on undoped ZnO thin film. The film was deposited by RF sputtering method at room temperature and at 200, 300 and 400 °C, respectively. Palladium metal was used to form Schottky contact with the deposited ZnO film. The Pd/ZnO samples were annealed at 500 °C for 2 h in the presence of N_2 gas. The Pd/ZnO samples deposited at 400 °C showed excellent electrical properties after annealing as compared to the samples deposited at other temperature. The Φ_{SB}, ideality factor and leakage current of the unannealed sample deposited at 400 °C were 0.776 eV, 10.79 and 12.9 µA. After annealing at 500 °C, the Φ_{SB}, ideality factor and leakage current were 0.77 eV, 13.13 and 0.17 µA.

Effect of buffer layer: The lattice mismatch between the substrate and ZnO thin film can induce defects in ZnO thin films. These defects are responsible for the instability and poor performance of Schottky contacts on ZnO thin films. One of the easy methods to reduce the lattice mismatch is to deposit the film on the pre-deposited seed layer or buffer layer. There are few reports present in the literature on ZnO Schottky diode using buffer layers. Hwang *et al.* [20] reported the Au/ZnO Schottky diode using pre-annealed seed layer. The seed layer was deposited by two methods. First was the sol-gel method and the second was the hydrothermal method. The seed layer was annealed at 450 °C for 10 min in the presence of N_2 gas. The ZnO layer was deposited on the annealed seed layer by hydrothermal method. The Au contact was deposited by thermal evaporation method. The Au/ZnO grown on sol-gel deposited seed layer exhibited ohmic characteristics whereas the same exhibited excellent rectifying properties on the seed layer deposited by hydrothermal method. The rectification ratio of Au/ZnO Schottky diode at ± 2 V was 8000. The Φ_{SB} of Au/ZnO Schottky diode was 0.79 eV and a series resistance (R_s) of 13.88 kÙ. Somvanshi and Jit [21] reported the effects of Zn and Sn buffer layers on the rectifying behaviour of Pd/ZnO Schottky diodes. The ZnO thin film, buffer layers and the Pd contact both were grown by thermal evaporation method. The value of rectification ratio, Φ_{SB} and ideality factor for Pd/ZnO Schottky diode without buffer layer were 113, 0.67 eV and 2.36. The value of rectification ratio, Φ_{SB} and ideality factor for Pd/ZnO Schottky diode with Sn buffer layer were 885, 0.75 eV and 2.67. The value of rectification ratio, Φ_{SB} and ideality factor for Pd/ZnO Schottky diode with Zn buffer layer were 7561, 0.78 eV and 2.10. The series resistance of Pd/ZnO Schottky diode without buffer layer, with Sn seed layer and Zn seed layer was 4734 Ω, 4637 Ω and 1677.7 Ω, respectively. Clearly Pd/ZnO thin film Schottky diodes with Zn buffer layer exhibited excellent rectifying properties as compared to Pd/ZnO Schottky diode without seed layer and Sn seed layer.

Effect of deposition method: The properties of ZnO thin film is highly affected by the deposition technique used. There are very less reports present in the literature that compares the effect of deposition techniques on the properties of ZnO thin film. Aal *et al.* [22] used sol-gel and thermal evaporation method for depositing ZnO thin films. They observed that ZnO thin films deposited by the sol-gel method have more surface roughness and larger grain size as compared to thermally evaporated ZnO films calcined at same conditions. XRD analysis revealed that the ZnO film deposited by the sol-gel method has preferred orientation along 002 plane whereas ZnO film deposited by thermal evaporation method was polycrystalline in nature with orientation along 100, 002 and 101 planes, respectively. Singh and Chakrabarti [23] deposited ZnO thin films by three different techniques *e.g.*, sol-gel derived, thermal oxidation of pre-deposited metallic zinc (Zn) and RF sputtering method. The optical, structural and electrical properties of the ZnO films by different deposition techniques were studied by using various characterization techniques and were systematically compared. They observed significant differences in optical, structural and electrical properties of the ZnO films by three deposition techniques. The structural properties of ZnO films obtained by oxidation of pre-deposited zinc were much better than those obtained by RF-sputtering and sol-gel. The electrical and optical properties of thermally oxidized ZnO film was found to be good enough as compared to ZnO films by sol-gel and RF sputtering for fabrication of electronic and optoelectronic devices. Similarly, Vyas *et al.* [24] compared the properties of ZnO thin films that were deposited on p-type Si <100> substrate and glass substrate using thermal evaporation, PLD and RF sputtering method. Their XRD result revealed that the as-deposited ZnO thin films by thermal evaporation and PLD method were polycrystalline in nature. The ZnO film by thermal evaporation method had major orientation in (101) plane and the ZnO film deposited by PLD process has major orientation in (002) plane. The films deposited by RF sputtering method had orientation along a single plane (002). The AFM studies revealed that the ZnO film by RF sputtering method had larger grain size with smoother surface as compared to the ZnO film by thermal evaporation and PLD method. The band gap was found to be around 3.2 eV. The transparency in the visible region for films obtained by PLD and RF sputtering method was better than that of the film obtained by thermal evaporation method. The electrical properties of Pd:Au/ZnO (RF sputtered) was better as compared to electrical properties of Pd:Au/ZnO (PLD and thermally evaporated). The better quality of RF sputtered ZnO thin film was attributed to the fact that RF sput-tering method results in a uniform deposition over a large area whereas by thermal evaporation and PLD method it is not possible.

Conclusion

Zinc oxide thin films are polycrystalline in nature and various factors like grain boundary, crystal defects in ZnO thin film and instability of electrical properties of ZnO thin films in ambient oxygen affects the performance of ZnO Schottky diode. The performance can be enhanced by treating ZnO thin film with various methods like surface treatment, annealing, insertion of buffer layer, *etc*. All these methods improve the crystal quality and reduce the defects in ZnO thin film. By choosing proper deposition methods, it is also possible to achieve a single crystalline ZnO thin film. A high quality ZnO thin film is required for fabricating high performance ZnO Schottky diode. The performance of ZnO based Schottky diode can be further improved by post metallic deposition treatment like annealing and surface treatment in presence of various gasses.

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