Eng. &Tech.Journal, Vol. 32,Part (B), No.4, 2014

The 4th International scientific Conference on Nanotechnology& Advanced Materials &Their Applications (ICNAMA 2013)3-4 Nov, 2013

Thermal Stability of Sol-Gel Deposited Thin Film Zno-Based Schottky Ultraviolet Photodetectors

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ABSTRACT

The article reports fabrication, characterization and testing of the thermal stability of ZnO-based Schottky ultraviolet photodetectors. The ZnO thin film was grown on p-type Si ‹100 › substrate by sol-gel technique. The surface morphological and the structural properties of the thin film were studied by atomic force microscope (AFM) and scanning electron microscope (SEM). For the investigation of the surface chemical bonding, X-ray photoelectron spectroscopy (XPS) measurements were also performed. The I-V characteristics of the Schottky barrier photodetector were studied and the parameters such as ideality-factor, leakage-current, and barrier-height were extracted from the measured data at room temperature. With applied bias voltages in the range from -3V to 3V the contrast-ratio, responsivity, detectivity and quantum-efficiency of the photodetector were measured for an incident optical power of 0.1mW at 365nm wavelength. The electrical and optical study revealed that the performance of the device improves with increasing post metal deposition annealing temperature up to 100˚C. The device exhibited excellent thermally stability in the annealing temperature range of 100˚C to 200˚C. For annealing temperature beyond 200˚C the performance of the device degrades drastically. It was also found that under 200˚C there is a harmonious relation between the optical and electrical characteristics of the device. Above this annealing temperature there is no correlation between the variations of optical and electrical characteristics with increasing annealing temperature. The variation of the electrical and photoresponse properties of Schottky photodetector subjected to different post fabrication annealing can be attributed to combined effects of interfacial reaction and phase transition during the annealing process.

https://doi.org/10.30684/etj.32.4B.12
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الاستقرارية الحرارية لثنائي شوتكي ككاشف للاشعة فوق البنفسجية المعتمدة على الاغشية الرقيقة لاوكسيد الزنك

الخلاصة

بينت هذه الدراسة تصنيع وتوصيف واختبار الاستقرارية الحرارية لثنائي شوتكي ككاشف الاشعة فوق البنفسجية المعتمدة على الاغشية الرقيقة لاوكسيد الزنك. تمت تنمية غشاء اوكسيد الزنك بتقنية المحلول-الجيلاتين على اساس من رقاقة السليكون نوع موجب ‹ 100›. الخصائص الهيكلية لسطح الغشاء الرقيق تمت دراستها بواسطة ميكرسكوب القوة الذرية وميكرسكوب المسح الذري. ولتحري الروابط الكيميائية للسطح تم استخدام القياسات من المطياف الالكتروضوئي للاشعة السينية. دُرس منحني الخواص تيار– فولتية واستُخلصت المعاملات كعامل المثالية و تيار التسريب وارتفاع عتبة الجهد من البيانات المقاسة في درجة حرارة الغرفة. كذلك بتطبيق فرق الجهد من -3الى 3فولت تم حساب نسبة التباين, الاستجابة, الكاشفية والكفاءةتم قياسها بتسليط ضوئ بقدرة 0,1 ملي واط وطول موجي قدره 365 نانومتر. الدراسة كشفت ان الاداء الكهربائي والبصري للنبيطة يتحسن مع زيادة التسخين اللاحق حتى 100°م. وان النبيطة تبدي استقرارية ممتازة عندما يكون التسخين اللاحق مابين100°م -200 °م . اداء النبيطة يتراجع يصورة حادة عندما تزداد درجة التسخين اللاحق اعلى من 200°م. وجد ايضا بان هناك علاقة توافقية بين الاداء الكهربائي واليصري للنبيطة عندما يكون التسخين اللاحق اقل من 200°م. لكن مابعد درجة الجرارة هذه لايوجد ارتباط مابين الاداء الكهربائي واليصري للنبيطة. هذا الاختلاف في الخصائص الكهربائية والاستجابة الضوئية لثنائي شوتكي ككاشف الاشعة فوق البنفسجية عند تعريضه الى درجات حرارة مختلفة مابعد التصنيع يعزى الى اتحاد تأثير التفاعل مابين السطحين والتحول الطوري اثناء عملية التسخين.

INTRODUCTION

Thin film technology has drawn considerable attention of the researchers in many important electronic and optoelectronic applications such as solar cells, photodetectors, biomedical devices, transparent devices, flexible devices, memory disk, thin film integrated passive devices and other integrated circuits [1]. Thin film based UV photodetectors have been investigated by numerous researchers.[2-13] Some examples for UV photodetector based thin film include Si [5],Diamond [6], AlGaN [7], SiC [8], ZnS [9], ZnSSe [10], TiO_2 [11], GaN [12], ZnO [13]. However, these materials can divided to two categories e.g., narrow bandgap material and wide bandgap material. Narrow band gap materials are generaly suitable for devices operating in visible and infrared region. UV detectors made from these narrow-bandgap materials is is suffer from device aging, due to exposure to radiation of much higher energy than the semiconductor bandgap. These detectors also need additional filters to block out visible and infrared photons, resulting in a significant degradation in their efficiency.

The larger bandgap, higher electron mobility and higher breakdown field strength of the wide bandgap (WBG) semiconductors (e.g. diamond, SiC, GaN and ZnO) have been investigated extensivily therefore to develop some thin film devices for applications in the ultraviolet (UV) region. [2,4,6-14]. The zinc oxide (ZnO) is one of the potentially useful wide and direct bandgap semiconductors with many promising properties for developing UV photodetector. Some attractive features of the ZnO which make the material superior to the other WBG materials for optoelectronic applications include large bandgap energy of 3.4eV with high exciton binding energy (~60meV), high radiation resistance and low material cost. [14-16] The ZnO material offers the most diverse nanostructures than any material known today. These structures are ideal for detection application due to its large surface area to volume ratio. Further, the wet chemical etching method can be used in place of reactive ion etching employed in some WBG materials based thin film technology.

A number of thin film deposition techniques are currently used to grow good quality ZnO thin films. Some of the thin film deposition techniques include molecular beam epitaxy (MBE) [17], metal organic chemical vapor deposition (MOCVD) [18], sputtering [19], pulsed laser deposition (PLD) [20], hydrothermal method [21], thermal evaporation [22], sol-gel methods [23] , chemical growth method [24] etc.

ZnO material is inherently n-type because of the lack of stoichiometry by the presence of native donor defects, hydrogen defects, oxygen vacancies and/or zinc interstitials. However, it is difficult to obtain p-type ZnO [14]. As a result good quality ZnO based p-n junction devices are not very popular. On the other hand, the Schottky barrier diodes are relatively easy to fabricate. The ZnO thin film based Schottky barrier photodiodes could be a potential device for the detection of UV light. However, there a little progress so far in the area of ZnO thin film based Schottky photodiodes operating in the UV region [17, 19, 20].

In 1986, Fabricius et al. [19] fabricated an Au/ZnO/Mn structured Schottky barrier UV photodetector on a glass substrate where the ZnO thin film was deposited by the sputtering technique. They obtained a low quantum efficiency (1%), low photoresponsivity (3 mA/W), and long pulse response times (with 20 μs rise time and 30 μs fall time) of the detector. They attributed the poor performances of the detector to the recombination in the polycrystalline ZnO layers.

Using a ZnO:N capping layer, Oh et al. [17] have reported the photoresponse characteristics of a ZnO based Schottky barrier diode grown on GaN/Al_2O_3 substrates by plasma-assisted MBE. The ZnO Schottky barrier diode with Au/ZnO/In structure shows a reverse saturation current of $\sim 10^{-8}$ A in the dark. The diode has a time constant of 0.36 ms. Further, the diode shows stable characteristics with a large current buildup of $\sim 10^{-3}$ A under ultraviolet illumination.

Effect of annealing on the photoresponse properties of Schottky barrier UV detectors with Ag Schottky contacts made on ZnO thin films has been reported by Li et al. [20]. The ZnO thin films are deposited on Al/Si substrates by PLD. The ideality factor and barrier height has been reported to be 1.22 and 0.908eV, respectively. After annealing at 600˚C for two hours, the ideality factor was found to be reduced to 1.18 while the barrier height was increased to 0.988 eV. Under the illumination of 325 nm wavelength UV-light, the sensitivities of the detector measured before and after annealing are 140.4 and 138.4 at 5V bias voltage, respectively [20].

Very little work has been reported on the study of thermal stability of the UV detector-based on n-ZnO Schottky contacts [20]. The thermal instability of the Schottky diodes on n-ZnO turns out to be one of a major problems. Therefore, there is a need to study refractory metals with better thermal properties if these detectors are to be deployed in high temperature electronics or lasers operating at high current densities [14, 18, 24]. In the present study, we report fabrication, characterization, and testing the thermal stability of Au/Cr-ZnO Schottky barrier photodetector.

EXPERIMENT

In the present study we report fabrication, characterization and testing of thermal stability of Au/Cr/ ZnO/Al Schottky photodiode. The ZnO thin film was deposited by using sol-gel technique on p-Si <100> substrate (380 µm thick). Details of the cleaning substrate, synthesis and deposition of ZnO thin films by sol-gel method have been discussed elsewhere [23]. An array of eight Schottky electrodes (1×1 mm^2) was patterned and repeated throughout the wafer (size 2×2 cm^2) using a laser writer (model LW405 from MICROTECH, Italy). Cr (14 nm) and Au(100 nm) metallization were carried out by using Anelva rf Sputtering System (model SPF-332H). The thin layer of Cr is used to improve the adhesion of the Au-metal onto ZnO and lift-off technique was used in the fabrication. Al electrode was subsequently deposited at a distance of 1 mm from Schottky electrodes by using a vacuum coating unit (model 15F6 from HINDVAC, India), and the thickness monitor was set at 100 nm.

Surface morphology of the ZnO film was studied by an atomic force microscope (AFM) and a scanning electron microscope (SEM). The surface properties of the sample, such as the surface roughness and the grain size, were measured by using AFM of NT-MDT (Model: PRO 47, made in Russia) and by using e-line by Raith GmbH (made in Germany), operating at 10 kV. The crystal structure of the ZnO films were characterized by x-ray diffraction (XRD) analysis using CuKα radiation in the range 2θ = 20˚–80˚.The thickness of the ZnO film was estimated to be in the range of 125–150 nm, as measured by Dektak Surface Profiler (made in the United States). The absorbance spectra of the ZnO thin film were studied using a double beam spectrophotometer from Perkin-Elmer, Germany (model-Lambda 25), in the wavelength range from 200 to 1000 nm. The (I–V) characteristics were measured by using HP Semiconductor Parameter Analyzer (SPA) from Hewlett-Packard USA (Model No. 4145B) at room temperature (27 ˚C) for the applied voltage ranging between -3 V and 3 V under both dark and UV illuminated conditions. The devices were then isochronally annealed in an oven under air ambient in the temperature range 25˚C to 300 ˚C in steps of 25˚C for 5 min. The I–V characteristics under both dark and UV illumination measurements followed each annealing cycle. The optical characteristics were obtained by using a UV lamp from BENCHMARK (made in India) operating at 365 nm and Optical power meter Model No. FOMP-101 from BENCHMARK India.

RESULTS AND DISCUSSION

The scanning electron microscopy (SEM) images of ZnO film (not shown) confirm that the thin film is composed of closely packed hexagonal particles with a particle size of ~20 nm. The sizes of the crystals were not uniform throughout, a few clusters were also found to be formed in ZnO film. This nanocrystalline structure has a special significance in the context of UV detection. The nanostructured film makes the area-to-volume ratio large which, in turn, improves the detection capability of the photodetector.
The XRD spectrum for the ZnO thin film prepared by sol–gel on the Si substrate exhibited an intense peak of (002) *c*-axis orientation of the wurtzite structure as can be seen from Figure (1). The dominant peak in the XRD spectrum is at 34.4˚. The diffraction peaks in Figure (1) match the hexagonal ZnO structure with lattice constants of a = 0.325 nm and c = 0.521 nm [25, 26].

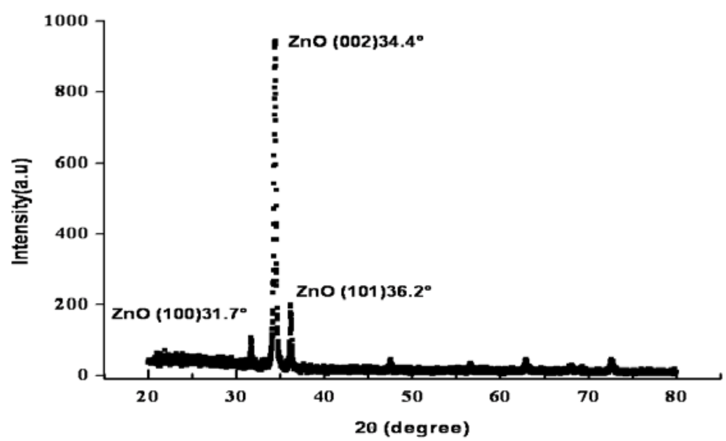

Figure (1) X-ray diffraction pattern for ZnO film.

The absorbance spectra of ZnO thin film were studied in the wavelength range from 200–1000 nm by using double beam spectrophotometer (model Lambda 25 from Perkin Elmer, Germany). The bandgap of ZnO is evaluated from the absorbance spectra of ZnO thin film using double beam spectrophotometer in the wavelength range from 200-1000nm. The optical bandgap of ZnO was estimated by using the fundamental relation given by [23]. The energy gap (E_g) was obtained by plotting $(\alpha h\nu)^2$ vs. hν where α is the absorbance, hν is the energy of absorbed light. The extrapolating the linear portion of $(\alpha h\nu)^2$ vs. hν so as to cut the hν axis as shown in Fig.2. The optical bandgap of ZnO was estimated to be 3.26 eV at 300K. Fig. 3 shows the I–V characteristics measured in the dark at room temperature for Schottky photodiode (Au-Cr/ZnO/Al). The device apparently shows rectifying behavior. The current across a Schottky diode is governed by thermionic emission theory given by [27]. The Schottky contact parameters such as ideality factor, Schottky barrier height and the reverse saturation current can be estimated as procedure explained in our previous work [23].

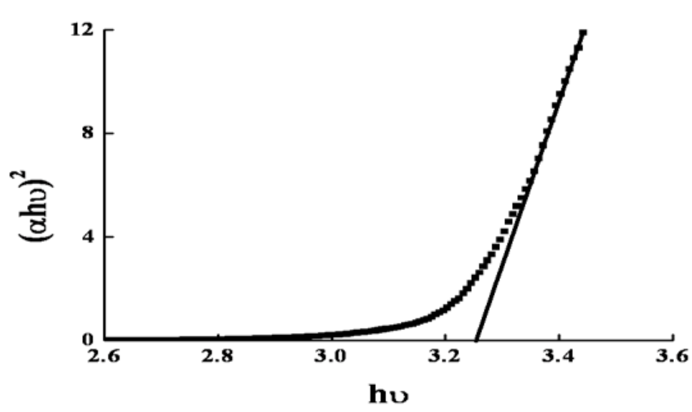

Figure (2) $(\alpha h\upsilon)^2$ vs. hυ plots for estimation of band gap of ZnO.

The value of ideality factor was estimated to be about 6.7. The barrier height evaluation at room temperature (300 K) was found to be φ_B=0.73 eV which was in good agreement with the theoretically predicated value. The turn-on voltage was found to be 0.5 V and the saturation current equal to 2.26×10^{-8}A. It is imperative to note that the ideality factor estimated on the basis pure thermionic emission theory is significantly large and is in agreement with those reported by others [25]. This fact strongly suggests that the transport of charge carriers across a ZnO film-based Schottky contact cannot be explained purely by thermionic emission theory, as speculated by previous researchers [24]. The estimated BH for ZnO/Cr-Au Schottky contact is larger than reported for ZnO/Au Schottky contact by others [28]. The turn-on voltage and reverse saturation currents are also on par with those reported by others for different ZnO-based Schottky contacts [28].

In the present study, the contrast ratio (sensitivity) of the Schottky photodiode measured at room temperature was found to be 8 for an applied bias of -3 V. The physical mechanism responsible for the photoresponse in ZnO thin-film based photodetectors has been explained by Sharma et al. [26]. The photodetector parameters such as contrast ratio (sensitivity), quantum efficiency (η), responsivity (R) the resistance-area-product (RA) and the voltage dependent detectivity can be estimated as procedure explained in our previous work [22, 23]. The R_0A product is found to attend a value 0.4 $\Omega.m^2$ at zero bias. The high value of R_0A product would provide a large value of detectivity for photodetector. The estimated detectivity hasa value of 1.45×10^9 $mHz^{½}W^{-1}$ zero bias. The O/E conversion efficiency is measured by the quantum efficiency. It is observed that the photodetector has quantum efficiency 72% for a bias voltage of -3 V under UV illumination. The current responsivity of the photodetector at -3 V bias voltages for UV illumination (365 nm) is measured to be 0.21 A/W.The device

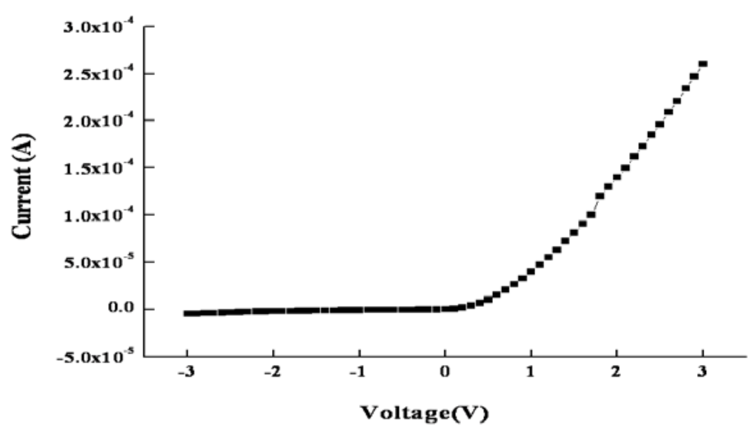

Figure (3) I-V Characteristics of Au/Cr/ZnO/Al Schottky contact.

Figure (4) shows the variations of ideality factor and contrast ratio (senstivity) as a function of postmetal deposition annealing temperature. The values of the ideality factor and contrast ratio have been found from the characteristics after different annealing treatments, and are plotted in Figure (4). The ideality factor its magnitude in the range of 2.7 to 3.9 in the annealing temperature range of 50 to 200 °C. The ideality factor reaches a minimum value after annealing at the optimal temperature of 100 ˚C and it was approximately a constant (3.3 ±0.06) within the limits of experimental errors in the annealing temperature range of 50 °C to 200 °C. Han et al. [29] have confirmed that the annealing process reduces the number of -OH bonds and increases the grain size. Based on these results, it may be concluded that the improvement in the ideality factor is caused by the removal of undesirable surface states and the enhancement of mobility at an optimum post metal deposition annealing temperature. It is further observed that the structure becomes leaky after the annealing temperature increases beyond 200 °C. It is found to increase from 3 to 7 when the annealing temperature is increased from 200 to 225 °C. The ideality factor becomes as high as 17 when the temperature is nearly 250 ˚C. The large value of ideality factor indicates that the current transtransport cannot be described by thermionic emission theory alone and that other transport mechanisms must be dominant.

The CR increases with increase in annealing temperature, attains a maximum value of 442 at 200 °C. There exists a fair amount of correlation between the variations of ideality factor and CR with annealing temperature up to 200 ˚C. This enhancement in contrast ratio is due to the reduction in reverse saturation current with an increase in annealing temperature, as reported by others [24]. Above 200 ˚C, there is little correlation between the variations of contrast ratio and ideality factor with annealing temperature.

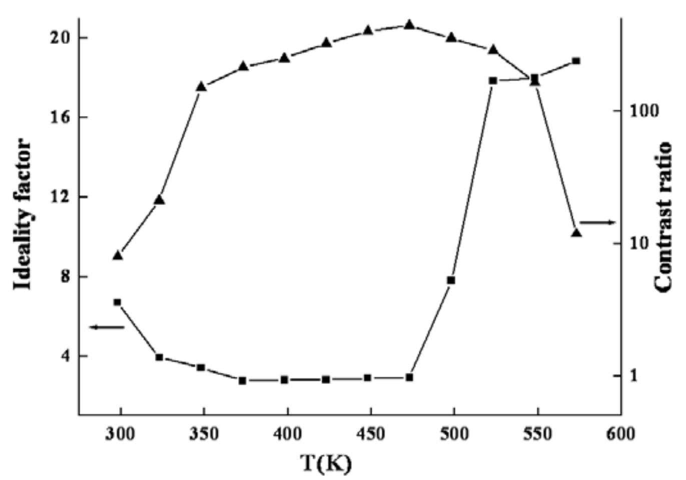

Figure (4) Variation of contrast Schottky barrier height and ideality factor as a function of annealing temperature.

The strong dependence of ideality factor on the annealing temperature may be accounted for the formation of interface phases at the contact with different work functions leading to a different barrier potential. It may be noted that enthalpy of chromium oxides (i.e., Chromium(IV) oxide -598.0 kJ/mol, Cr2O3 Chromium(III) oxide-1128 kJ/mol, Cr3O4 Chromium(II,III) oxide-1531.0 kJ/mol) is much lower than the enthalpy of ZnO (-348.0 kJ/mol) [30], [31]. Therefore, Cr can easily react with O in ZnO at high temperature. The chemical reaction of Cr with O in ZnO also results in more vacancies of O which act as donor in ZnO and increases the carrier concentration further. At the same time, the work function also increases because of the formation of chromium oxide at the interface. Further, leaky I-V characteristics of the device beyond 250 °C suggest that current transport via tunneling cannot be ruled out. The rise in the ideality factor at higher annealing temperature (beyond 200 °C) is accounted for the increase in carrier concentration in ZnO film caused by interfacial reaction. The increased carrier concentration also lowers the Schottky BH and the contact tends to behave more like an Ohmic one and thereby lowering the contact resistance [23].

A comparison of the results of our study with those reported for the Au/ZnO Schottky diode by others reveals that the Au Schottky contacts result in poor current-voltage characteristics and degrade easily with thermal cycling of the samples [24, 25, 28] even at an annealing temperature as low as 365 K due to the reaction with the ZnO surface [28]. The present study shows that the thermal stability of Au/Cr is better than that of the Au Schottky contact on ZnO since the degradation starts in the former case only after 473 K. Therefore, addition of Cr as an adhesion layer improves the thermal stability of the device.

CONCLUSIONS

In conclusion ZnO thin film based Schottky photodiodes subjected to an optimum postmetal deposition annealing temperature can be used as a sensitive UV photodetector with high contrast ratio. The study also reveals that the electrical and optical performance of the device, in general improves when the postmetal deposition annealing temperature is restricted up to 200 °C approximately. The device performance degrades dramatically when the annealing temperature is increased beyond 200 °C. The variation in performance with thermal treatment may be attributed to interfacial reactions of metals (Cr) with ZnO and the phase transitions of the chromium oxide during annealing. The outcome of the study will be useful for the design of ZnO based UV detectors for deployment in high temperature electronics.

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