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Review on conductivity enhancement in n-ZnO/p-Si heterojunction diodes with the influence of Rare earth ions as donor impurities.

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ABSTRACT

Nanoelectronics is an emerging field of nanotechnology where innumerable nanomaterials are used to fabricate electronic devices like LEDs, Photodiodes, Transistors, FETs, UJTs, SCRs, Laser diodes, etc. The accomplishment of high-efficiency electronic devices at low cost tends to be the foremost challenging task in the field of nanoelectronics. The p-n heterojunction is a junction of two dissimilar p and n type crystalline materials with different bandgap, work functions and electron affinities.The n-ZnO/p-Si heterojunction device tends to be cost-effective and also potential candidates for integration with microelectronic based photonic and optoelectronic devices.The electricalproperties of n-ZnO/p-Si heterojunction diode can be fine-tuned by the addition of dopants at different concentrations.This article presents a brief overview on the influence of different rare earth dopants on chargecarrier enhancement and transport mechanism in n-ZnO/p-Si heterojunction diode. This review paper also presents an outline on heterojunction formation theories and applications of n-ZnO/p-Si heterojunction diode.

Indexing terms/Keywords

n-ZnO/p-Si, Nanostructure, Nano heterojunction diode, Current-voltage characteristics, Nanodevices

INTRODUCTION

A heterojunction is a junction of two, dissimilar, crystalline materials where the crystal structure is continuous across the interface. Fabrication of heterojunction devices is associated with few difficulties like lattice mismatch at the boundary, thermal expansion, change in crystal structure that cause strain in junction due to temperature and purity of materials used [1,2]. But the recent advances in technology have made the fabrication and experimental investigation easier. Different types of semiconductor materials are used to fabricate heterojunction devices, among which ZnO is the most extensively used material due to its excellent optical and electrical properties [3-7].ZnO is a wide-band-gap semiconductor material with 3.3 eV.The exciton binding energy of ZnO is 60 meV which is higher than other semiconductors. ZnO has a wurtzite structure (see Fig 1) with hexagonal closed packed oxygen ions with the tetrahedral interstices occupied by Zn ions.This crystal structure of ZnO also favors a major role for numerous application like piezoelectric, dielectric and optoelectronic devices [8-11].

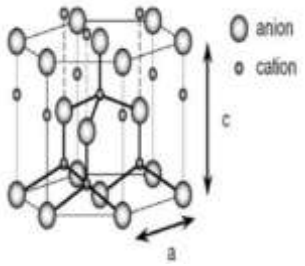

Fig 1: Wurtize Structure of ZnO (Source : Ahmed M. Nahhaset.al.,2013)

Heterojunction device based on p-ZnO semiconductor has limitations due to impurity substitution and donor defect sites. Therefore the realization of p-ZnO heterojunction device is difficult to achieve [12-14]. As a result an alternative approachof using n-ZnO on p-substrate is mostly preferred to fabricate efficient heterojunction devices. P-type substrates such as GaN, SiC and polymers are used in fabrication. However these substrates have its own merits and demerits. It is necessary to select p-substrate that should possess properties like band gap, lattice parameter and crystal structure similar to n-ZnO. Consequently n-ZnO grown on p-Si provides a good alternative to test the competences of ZnO overdefects and surface energy at the junction and enhances the charge carrier enhancement and transport behavior in

heterojunction devices. ZnO doping with Group III elements even though tune their properties still the 3d element orbitals are in delocalized state [15-17]. In this context the choice of doping with inner transistion lanthanide 3+ series [18-20] will be inevitable to modify the properties of n-ZnO/p-Si diodes by its unique characteristics. Herein we review the Rare Earth (RE3+ions) elements incorporation in n-ZnO/p-Si diodes for interrogating their efficient functionality of the diodes by structural, optical and electrical properties which mainly depends on the choice of dopant, percentage incorporation of the dopant impurity, synthesis methodology, temperature effects to meet the integration to semiconductor industry.

THEORIES BEHIND THE FORMATION OF HETEROJUNCTIONS

Numerous theories were formulated to study the electrical characteristics and charge transport mechanism of heterojunction devices. An outline of few heterojunction models put forward by researchers is discussed in this section.

Anderson's Theory

Anderson suggested a model (see Figure 2) based on electron affinity differences of the two semiconductors and also discontinuities in the conduction and valence bands at the interface. The author stated that bandgap properties at the heterojunction were determined not only by the fermi levels in the two semiconductors but also by their relative electron affinities.

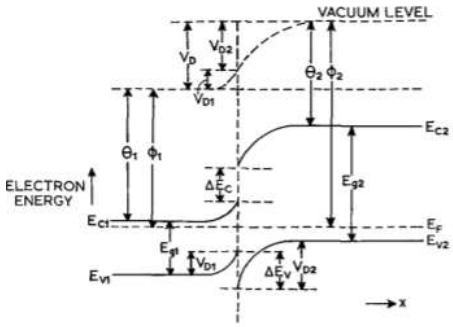

Fig 2: Energy band diagram at equilibrium (source: D. T. Calowet.al.,1967)

This theory can be further modified by considering the tunneling effects, image effects, and carrier generation and recombination [21].

Perlman and Feucht's Theory

Perlman model is formulated based on the effect of changes in electron affinity, electron effective mass, dielectric constant, and band gap at the junction. According to this theory, the p-n heterojunction has two operating modes [22]. One similar to a homojunction, where minority-carrier at the depletion region limits the current and another similar to a metal-semiconductor junction in which the current is limited by a potential barrier in the n-type semiconductor. By increasing the forward bias, the homojunction mode can be switched to the metal-semiconductor mode.

Oldham and Milne's Theory

Oldham et al studied the effect of interface states based on abrupt heterojunctions with edge dislocations at the interface [23]. It is concluded that the interface acts as a low-density free surface with edge dislocations that produces deep states in the bandgap which results in band bending and recombination of excess minority carriers

Van Ruyven, Papenhuijzen, and Verhoeven's Theory

Van Ruyvenet al,.stated that the heterojunction interface is similar to two semiconductors with a free surface that can store sufficient charge to make the surface behave like a thin, metal layer. Contact between these two different surfaces will lead to the formation of a dipole layer. Therefore the heterojunction consists of three separate junctions: a Schottky barrier between the first semiconductor and its own metal-like surface, a metal contact between two planes of surface states containing a dipole, and another Schottky barrier between the metal-like surface of the second semiconductor and the second semiconductor itself [24, 25].

SYNTHESIS TECHNIQUES TO OBTAIN RE^{3+} IONS DOPED n-ZnO/p-Si HETEROJUNCTION DIODES

Various synthesis techniques were used to obtain the RE^{3+}ions doped ZnO/p-Si heterojunction diodes. The colloidal dispersions of RE^{3+}ions doped ZnO nanostructures were collectively obtained [26-28] using sol-gel process, hydrothermal, solvothermal, co-precipitation, electrochemical method and pyrolysis. Collected powders/ dispersions are subjected to thermal treatments followed by deposition processes like spray pyrolysis, spin coating, dip coating and SILAR method to obtain the high quality thin film based heterojunction diodes [29-31]. Besides the heterojunction diodes are also fabricated by physical vapor deposition, chemical vapor deposition, metal organic chemical vapor deposition, pulsed laser deposition process, Atomic layer deposition and sputtering techniques etc., [32-35]. All the mentioned synthetic strategies convey its own merits and demerits.

Fig 3 : AFM,TEM images of ZnO and ZnGdO heterostructures with schematic of device (Source: Siva et.al.,2015)

Siva et.al., presented simple wet chemical route to obtain ZnGdO colloids (see Figure 3) followed by the process of spray pyrolysis coating technique to fabricate the ZnGdO/Si heterojunctions.This synthetic procedure and device fabrication is an easier, cost effective with good functionality [36]. Spin coating is a versatile method in the preparation of ZnO/Si heterojunctions(see Figure 4).

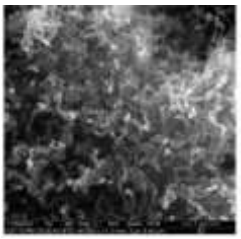

Fig 4: SEM images of devised junction (Source: Purnima Hazra et.al., 2014)

The starting materials were prepared in appropriate solution phases and directly coated over the Si substrates at 3000rpm for 60sec followed by thermal annealing at 4000^0C for 1 hour. The rectifying properties were improved by this synthetic methodology [37].R.S. Ajimsha et.al., fabricated the heterojunctions by pulsed laser deposition technique in which oxygen gas is employed with different pressures (see Figure 5).

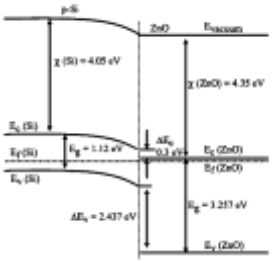

Fig 5: Band structure of ZnO/Si heterojunctions with varying partial pressure of PLD process (Source: R.S. Ajimsha et.al,2008)

The important parameters such as wavelength of laser, gas pressure, fluency of laser, repeation time are to be monitored to achieve high quality device junctions. The values of turn on voltage of the devices are greatly influenced by the variations of pressure of oxygen carrier gas. Atomic layer deposition (ALD) process is employed by Purnima Hazra et.al., using diethyl Zinc as source of zinc and oxygen as carrier gas. After 500 cycles of deposition the films are annealed and the thickness are measured followed by making contacts to the device(See figure 6). It is found that the annealing temperature, type of carrier gas and number of cycles of deposition influences the junction properties. The heterojunction diodes are also fabricated by thermal evaporation technique using the respective material targets. Purnima Hazra et.al., prepared the Si NW/ZnO heterojunctions via thermal evaporation method using ultra high vacuum. The fabricated thin films were annealed at 5500C to obtain the better crystallinity [38-40]. From the detailed literature review it is observed that the synthesis procedures and deposition parameters also influence the optical properties like band gap which in turn regulates the electrical properties of the RE^{3+} ions doped ZnO/ Si heterojunction devices.

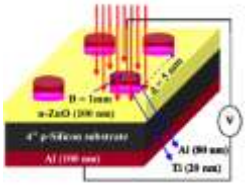

Fig 6: Schematic of diode structure (Source: Purnima Hazra et.al.,2014)

INFLUENCE OF RE DOPANT IMPURITIES IN BAND GAP ENGINEERING n-ZnO/p-Si HETEROJUNCTION DIODES

Band gap engineering is the key source for tuning the optical properties which in turn controls the electrical behavior and performance of the optoelectronic devices fabricated (n-RE3+ doped ZnO/p-Si) [31,33,36,]. Most of the RE^{3+}ions such as Ce, Sm, Er, Gd, Tb etc., have the impact in regulating the band gap energy when incorporated into the host crystal lattice of ZnO. M. Yousefi et al., studied the variation in band gap values of ZnO upon Ce doping. The band gap values are 3.349eV, 3.35eV, 3.37ev, 3.40eV, 3.42eV, 3.64eV corresponding to the 1%, 2%, 5%, 10%, 20% and 30% of Ce doping with ZnO in which they are derived from the first derivative of the transmittance spectrum [41].Alternatively Yimai Liang et.al., investigated the 3D nanostructured microflowers of Ce doped ZnO. It is found that the material exhibits strong absorption between 200 to 400nm due to the structural alignment. The light entrapment and transport property is greatly improved due to 3D morphology of ZnO. It was also found that there is a noticeable red shift towards 400 to 500nm which portrays the creation of new electronic energy levels in addition to ZnO energy states. The intensity of absorption is increased when ZnO is doped with 1% Ce. Whereas the intensity of absorption started to decrease when doping concentration increased with 3% and 5% of Ce. The author concluded that this decrease in absorption intensity may be attributed due to the fact that defect centres can act as recombination spots for the charge carriers. The band gap values drafted from the absorption spectrum seems to be get narrowed down upon Ce doping from 3.06 eV for ZnO to 2.93eV of 5% Ce doping [42]. Deepawali Arora et.al., studied the decrement in band gap values of ZnO from 3.201eV to 3.160, 3.154, 3.141, 3.135 and 3.126 eV with Sm doping is owing to the reason of formation of defect states present with crystal structure. Also presented the excitonic absorption of ZnO at 370nm (1Sh / 1Se transition) [43].Conversely no alteration in ZnO bandgap is noticed by the C. Peng et.al., by the doping of Sm_2O_3 since the rare earth oxide will not substitute the Zn ions in the crystal lattice rather than positioned as a separate phase by its larger ionic radius [44]. Due to Ce doping there is an increment in the atomic distance along with the formation of oxygen vacancies and defects. This shifts the absorption edge to longer wavelength regions and also reduces the value of band gap. Stronger absorption is elucidated by Xiying Ma et.al., upon Gd ions doping which anticipates the participation of Gd_2O_3 ions. Oxides of gadolinium also contribute to absorption and have a major role in shifting the absorption wavelength to lower energies. Gd ions undergo both substitutional replacement of Zn ions by Gd at low doping concentrations and occupy the interstitial sites in ZnO at higher percentage of doping[45]. A. Franco Jr and H.V.S. Pessoni stated that generation of new sub bands in addition to ZnO energy levels will tend to combine with the conduction band of ZnO leading to the creation of continuous energy band which in turn paves the way for reduction in the band gap values of ZnO upon Gd doping. The author also stated that red shift prevalence is ascertained due to the existence of defect states such as oxygen vacancies/ oxygen interstitials accounted by the synthetic procedures [46].R. Kumar et.al. also studied the effect of doping Ce. It is found that there is blue shift in the absorption spectrum which leads to the increased bandgap values. Furthermore a single absorption peak is observed which determines the precise incorporation of Ce ions in ZnO lattice [47]. Absorption of ZnO in the visible region influenced by the addition of Ce ions is investigated by V. Kuzhalosai et al. The author calculated the band gap value using KM theory. The band gap value of 2.5eV is achieved for Ce doped ZnO from KM theory [48] which is quite lesser than the undoped ZnO. Band gap engineering science relies on the crystal properties such as surface defects, addition of foreign elements in the host lattice, strain effects and amount of impurity ions addition (see figure 7). In this context RE^{3+}ions doped ZnO mainly improves the luminescence properties by the charge transfer mechanisms between ZnO and 4f electrons which are predominant in case of higher amount of RE ions incorporation. Further the creation of new energy levels will bring considerable changes in the fermi level of ZnO to facilitate the faster electron transfer in case of improving the mobility of charge carriers in the Heterojunction diodes.

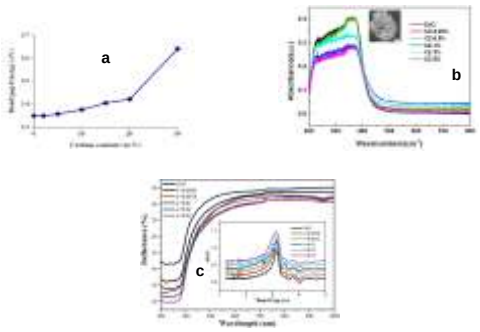

Fig 7: Band gap alterations of RE ions doped ZnO heterojunctions (Source: (a) M. Yousefi et al.,2011 (b) Yimai Liang et.al.,2012 (c) Deepawali Arora et.al.,2016)

IMPACT OF RE IONS IN THE ELECTRICAL CHARACTERISTICS n-ZnO/p-Si HETEROJUNCTION DIODES

To elucidate the enhancement in the electrical properties of ZnO based heterojunctions Shuai Liu et.al. fabricated Ce doped ZnO junctions by electrospinning (see Fig 8a). Well defined rectifying behavior was observed upto 19.5 at ± 10V. The device threshold voltage is about 7V far greater than ZnO. Conduction is dominated by holes as majority carriers.

Leakage currents also seemed to be very low at reverse bias conditions. The findings elaborate its function as p-type device [49]. Non-Ohmic performance of Ce doped ZnO heterojunction was studied (see fig 8b) by N. Sinha et al,. The decrease in the conductivity is ascertained by the fact of higher barrier height established between the schottky contacts [50]. The improved electrical conduction of ZnGdO/Si heterojunction by doping the Gd ions is studied by Siva et.al.,.This dominant current transport mechanism is due leakage current since the ideality factor of junction diodes in all the cases are found to be greater than 2. Upward shift in the Fermi level of ZnO is achieved by doping Gd. The author concluded that the conduction in the diode (see fig 8c) is due to electrons which act as a majority charge carriers [36].

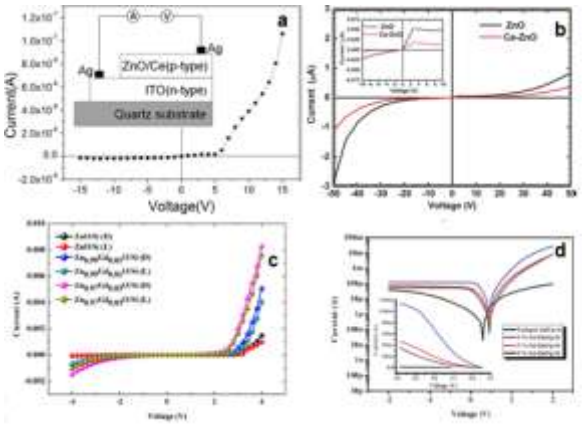

Fig 8: (a) : I-V Characteristics of Ce doped ZnO diode with its schematic diagram (source: Liu et al,2014) (b) I-V curves of Ce doped ZnO and ZnO (source: N. Sinha et al, 2014) (c) IV curves of ZnGdO/Si heterojunction diodes.(Source: Siva Chidambaram et.al., 2015) (d) lnI-V plots of the ZnO/p-Si and Gd:ZnO/p-Si heterojunctions under illumination with 100 mW/cm2 light (inset forward bias linear parts of I-V plots) (Source : Silan Baturay et.al.,2015)

The rectifying property of the ZnO:Gd/Si diodes with enhanced rectification ratios is explained by Silan Baturay et.al. The anisotype heterojunctions are obtained by the synthetic method. The current mechanism followed the thermionic emission under forward bias conditions. The current transport behavior of ZnO/Si heterojunction diode is altered by doping Gd ions into ZnO (see fig 8d). When Gd is doped into ZnO the recombination current is changed to diffusion current transport. The doping concentration of Gd ions greatly affects the width of the space charge region. The values are found to be greater than undoped ZnO, but when increasing the percentage of doping from 1% to 5% the values starts to decrease. It is also observed that the series resistance values are much lower than undoped ZnO. The light-behavior properties are also monitored for the diodes which is entirely different from the current-voltage curves obtained in dark conditions. Furthermore undoped and doped ZnO (3% and 5%) exhibits lower sensitivity to incident photons but when doped with 1%, ZnO/Si diodes shows high response to light sensitivity [51]. From the discussions, the electrical properties of the Heterojunction diodes are greatly influenced by the RE ions injection into ZnO crystal system. Interestingly the dark currents are significantly improved under forward bias conditions when comparing with the parent ZnO structures. The improvement is validated from number of factors like structural modifications leads to the quantum confinement by the adopted synthetic strategy paves the way to tailor the optical band gap values in which the new energy sub bands also contribute to enhance the conduction process by the respective shifts in the fermi levels. In this way the RE ions play an insignificant role in uplifting the conductivity of n-ZnO/p-Si heterojunction diodes.

CONCLUSION

From the discussions, the electrical properties of the Heterojunction diodes are greatly influenced by the RE ions injection into ZnO crystal system. Interestingly the dark currents are significantly improved under forward bias conditions when comparing with the parent ZnO structures. The improvement is validated from number of factors like structural modifications leads to the quantum confinement by the adopted synthetic strategy paves the way to tailor the optical band gap values in which the new energy sub bands also contribute to enhance the conduction process by the respective shifts in the fermi levels. In this way the RE ions play an insignificant role in uplifting the conductivity of n-ZnO/p-Si heterojunction diodes. This review briefs about the importance of heterojunctions in the semiconductor device technology. It entails the materials selection for forming the heterojunction to improve the functionality of the devices. ZnO is opted in this regard to fabricate the heterojunction diodes by their exceptional properties and to mold the characteristics behavior RE ions serve the best supporter material for doping with ZnO host atoms to obtain the efficient operation of n-RE doped ZnO/p-Si Heterojunction diodes. The transport mechanisms and theories in devising the heterojunctions are discussed. Upon doping the RE ions how the Fermi level shifting facilitates the faster transport is elaborately presented and the conductivity improvement also found to be astonished by the increase of the charge carriers. The n-type conductivity enrichment in ZnO is boosted up by the variety of factors such as Annealing temperature, RE 3+ ions addition, Structural

parameters modification, doping methodology, synthetic procedures, level of doping etc., are clearly envisaged in this review. These deep insights in n-RE doped ZnO/p-Si Heterojunction diodes will be readily fabricated and can be utilized in electronics field as optoelectronic devices, LEDs, Rectifiers, UV photodetectors and solar cells.

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