Annealing and surface conduction on hydrogen peroxide treated bulk melt grown, single crystal ZnO

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Abstract

We report on the studies carried out on hydrogen peroxide treated melt grown, bulk single crystal ZnO samples. Results show the existence of two shallow donors in the as-received ZnO samples with energy levels (37.8 ± 0.3) meV that has been suggested as Zn_i related and possibly H-complex related and (54.5 ± 0.9) meV which has been assigned to an Al-related donor. Annealing studies performed on the hydrogen peroxide treated samples reveal the existence of a conductive channel in the samples in which new energy levels have been observed, Zn vacancies, related to the Group I elements, X_{Zn}. The surface donor volume concentration of the conductive channel was calculated from theory developed by D. C. Look [1]. Results indicate an increase in surface volume concentration with increasing annealing temperature from 6.0×10^{17} cm^{-3} at 200°C to 4.37×10^{18} cm^{-3} at 800°C.

1. Introduction

Zinc Oxide (ZnO) has become the second widely studied material after Si. It is presently used in many diverse products, such as phosphors, paints, piezoelectric transducers, varistors and transparent conducting layers for the photovoltaic industry. Due to its superior electronic properties that include its high exciton binding energy of 60 meV, its wide, direct bandgap of 3.37 eV and excellent radiation hardness, it has attracted the attention of many researchers as

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it can be used considerably in electronic and optoelectronic devices that can operate in the blue and ultraviolet (UV) spectrum, though not very efficient as yet [2]. Other advantages of ZnO lie in the availability of fairly high quality bulk single crystals [3] and amenability to conventional wet chemistry etching, compatible with Si technology. The ease of etching ZnO with all acids and alkalis provides an opportunity for the fabrication of small-size devices [3].

Knowledge of the electrical properties of semiconductor material is of vital importance in device fabrication as it determines the use of the material in both electronic and optoelectronic applications. To date, several studies to find information about the electrical properties of ZnO have been performed using different techniques. Reports on the existence of native and unintentionally introduced defects have been published from photoluminescence (PL) measurements [3]. Hall Effect measurements have also been used to study the shallow defects in ZnO [4,5,6]. However, in all the studies of ZnO mentioned above, none of the researchers studied the effects of hydrogen peroxide on ZnO. Studies on the treatment of ZnO with hydrogen peroxide have been performed using the current voltage technique [7, 8] and deep level transient spectroscopy, DLTS [8]. Reports from these studies indicate the improvement of the quality of the Schottky behaviour of the samples after the peroxide treatment [9]. This clearly indicates that the hydrogen peroxide really affects or modifies the nature of ZnO on or closer to the surface, hence the need for a surface sensitive technique to study these effects. Other reports from DLTS indicate the introduction of defects within the material, helping the achievement of better devices after peroxide treatment [8]. Also, of most importance, is the annealing and existence of the conductive channel in ZnO as it affects device fabrication. Annealing of ZnO grown by different techniques have been studied by several researchers [5,3]. Look *et al* [1, 10] studied the effects of annealing hydrothermally grown ZnO samples in forming gas and nitrogen, while Kassier *et al* [4] also

studied the effects of annealing hydrothermal grown samples in argon ambient. Kassier *et al* [11] also studied the effects of annealing hydrogen implanted melt grown samples in an argon environment. The motivation is mainly to study the effects of high temperature annealing on surface conduction in ZnO as it helps get valuable and important information in device fabrication. Hall effect measurements have been performed on hydrogen peroxide treated melt grown ZnO samples annealed at different temperatures.

2. Experimental details

Undoped n-type ZnO square samples of orientation 0001 from Cermet Inc were degreased first in acetone and then methanol in the ultrasonic bath for five minutes. The samples were then boiled in hydrogen peroxide for 5 minutes at a temperature of 100°C and finally blown dry using nitrogen gas. Triangular indium ohmic contacts were then soldered onto the four corners of the samples. Two magnet poles were placed on either side of the sample to provide a probing magnetic field strength of 0.6 T. An HP 6030A system power supply was used as a current source to the magnet, supplying a current of approximately 7.29 A, as the voltage was controlled at about 70 V. An HP 3245A universal current source was used to supply current to the sample. Contact configuration together with voltage measurement across the sample was achieved by making use of the Agilent 34970A data acquisition unit. Temperature dependent Hall (TDH) measurements in the temperature range 30-330 K were then performed under vacuum provided by the Varian forepump. Annealing of the samples was done in an oven with a flowing argon atmosphere ambient at temperatures ranging from 200˚C- 800˚C for 30 minutes at every annealing temperature. After every anneal TDH measurements were carried out in the 30-330 K temperature range.

3. Results and discussions

3.1. Carrier concentration-temperature analysis.

Fig. 1 shows the variation of carrier concentration with temperature for the as-received melt grown samples obtained from Cermet as determined from TDH measurements between 30 – 330 K. It can be clearly observed that the variation of carrier concentration with temperature can be subdivided into three distinct regions, **a**, **b** and **c**. The region marked a is the high temperature region which shows a strong dependence of carrier concentration on temperature, b is the intermediate temperature region which also indicates the dependence of carrier concentration on temperature, while c gives the low temperature region, in which the carrier concentration is less dependent on temperature change (degenerate region). The dependence of carrier concentration on temperature in the three distinct regions can be attributed to the type of carriers, i.e. either bulk or surface that contribute to current flow within each particular region. The problem of the existence of more than one conducting channel in semiconductors has been reported by some researchers [12, 13]. In a case where two conducting channels exist in a semiconductor wafer, the total thickness of the semiconductor material will be given by the surface thickness, d_{surf} and bulk thickness d_{bulk} , $d = d_{bulk} + d_{surf}$, with the measured carrier concentrations denoted by n_{surf} and n_{bulk}.

At high temperatures, it is expected that all the donors will be ionized and current flow is due to bulk electrons, n_{bulk}, which is a volume concentration in cm^{-3}. However, there is a limitation in precisely obtaining the bulk thickness as Hall effect measurements are sensitive to surface concentrations and not volume concentrations [12]. We can assume that the surface thickness, d_{surf} is very small compared to the bulk thickness as was observed and modelled by Look *et al* [12], i.e. $d_{surf} << d_{bulk}$ and d_{bulk} will be approximately equal to the sample thickness, d. In this case, the bulk donor, $N_{D,bulk}$ and the acceptor $N_{A,bulk}$ volume

concentrations can be obtained accurately. Also the donor energy levels $E_{D,bulk}$ can be accurately determined.

In region **b**, conduction is mixed, i.e. both the surface and bulk electrons contribute to current flow. Minimum bulk carrier concentration is measured in this region.

In region **c**, conduction is dominated by the surface electrons. This is due to the fact that at low temperatures, the bulk electrons will be frozen out to their donor atoms since ionization will be less. This is also evidenced by an increase in bulk resistivity at low temperatures as in the insert of Fig. 1. The concentration obtained in this case is a sheet concentration in cm^{-2} as the thickness of the surface, d_{surf} is not known. This makes it difficult to obtain the surface donor and acceptor volume concentrations and the associated energy levels [10].

In this particular study, the experimental data was modelled for the carrier concentration obtained in regions (**a**) and (**b**) using a Matlab coded program. The modelling was performed by assuming that we have two *s*-like donors whose energy levels are temperature independent and one fully ionized acceptor. The position of the Fermi level relative to the valence band can be estimated by solving the charge balance equation,

$$n + N_A^- \quad \sum_{i=1}^{k} N_D^+ + p \tag{1.1}$$

where N_A^- is the ionized acceptor concentration, and N_D^+ the ionized donor concentration given by,

$$N_D^+ = \frac{N_{Di}}{\frac{g_{Di} n T^{-3/2}}{N_C} \exp\left(\frac{\Delta E_{Di}}{k_B T} \right) + 1} \tag{1.2}$$

where N_c is the effective density of states in the conduction band for ZnO at 0 K, n, is the concentration of electrons in the conduction band, p is the concentration of holes which is very negligible for n-type material and can be considered to be approximately equal to zero, ΔE_{Di} is the energy level of the donor within the energy gap or position of the donor relative to the conduction band (also called the activation energy of the donor), g_{Di} is the degeneracy factor equal to 2, k_B is the Boltzmann constant and T is the absolute temperature in Kelvin. It follows that,

$$n + N_A^- = \sum_{i=1}^{k} \left[\frac{N_{Di}}{\frac{g_{Di} n T^{-3/2}}{N_C} \exp\left(\frac{\Delta E_{Di}}{k_B T}\right) + 1} \right] \quad (1.3)$$

where n is the number of electrons in the conduction band, given by,

$$n(T) = \frac{1}{4}\left(\frac{2m^* k_B T}{\pi \hbar^2}\right)^{3/2} \exp\left[-\left(\frac{E_G(T) - E_F(T)}{k_B T}\right)\right] \quad (1.4)$$

where $E_G(T)$ is the band gap energy relative to the bottom of the valence band. Its temperature variation has been obtained from Jagadish *et al* [14], m^* is the electron effective mass of ZnO which is considered to be isotropic and is corrected for the polar coupling with the lattice. Once the value of $E_F(T)$ is known the conduction band carrier concentration deduced from equation (1.4) can be compared to the measured carrier concentration, n_H and the neutral donor and ionized donor concentrations can be deduced [15]. Fig. 2 shows the variation of carrier concentration with temperature for the modelled data. By assuming two *s*-like donors and one acceptor, the model fits well to the experimental data. Values of the donor and acceptor concentrations deduced from the fit to the data in Fig. 2 are shown in Table 1.

The two shallow donor energy levels in Table 1 are not far off from the reported levels of 33 - 35 and 49 – 53 meV ranges [14, 16] which have been attributed to native defects in ZnO, possibly Zn_i complexes and oxygen vacancies[17]. Comparing E_{D1} to these values, E_{D1} can be said to be H-related. The value of E_{D2} is also in close agreement to a level 60 – 63 meV that was also observed by Look *et al* [16] from photoluminescence measurements. We can also assign E_{D2} to aluminium, Al related defect. The acceptor concentration is very low compared to the total donor concentration, ($N_{D1} + N_{D2}$) and so the sample is not fully compensated.

3.2. Annealing studies of ZnO

Fig. 3 shows the variation of carrier concentration with the reciprocal temperature for the samples annealed in the 200˚C to 800˚C range in an argon atmosphere. The data as in Fig. 3 can be divided into three distinct regions where conduction can either be due to bulk electrons (**a**), a combination of bulk and surface electrons (**b**) and conduction due to surface electrons (**c**). Results obtained from the annealing studies of the hydrogen peroxide treated ZnO samples from Cermet indicate an increase in surface conduction with increasing temperature since the carrier concentration increases with decreasing temperature. At low temperatures, region (**c**), the shallow donors, $N_{D,surf}$, and acceptors, $N_{A,surf}$ can be deduced by first determining the value of the surface thickness, d_{surf}. An analysis in obtaining the surface donor and acceptor concentrations has been suggested and performed by Look *et al* [12] on hydrothermally grown ZnO samples. It should be noted that the data has been fitted to two donors and a single acceptor for all the annealing temperatures.

From Table 2, E_{D1} becomes shallower up to annealing temperatures of 400˚C. The 19.9 meV and 17.8 meV shallow levels could possibly be a Group I related element. This is in comparison with the 21 meV donor that was observed by Kassier *et al* [4] in hydrothermally

grown ZnO after annealing the samples at 930˚C. Since in melt grown samples there are low concentrations of Li, the two levels are Na or K related, occupying the Zn sites which exhibit an acceptor like behaviour. After annealing at 600˚C the observed donor with energy level, 31 – 33 meV can be said to be Zn_i related. The temperature dependent Hall-effect data for the annealed samples in Fig. 3 indicate the dominance of surface conduction in the 20 – 40 K temperature range (region c). The surface donor and acceptor concentrations can be approximately determined from the following equations [1]:

$$N_{D,surf} = \frac{1}{2}\left(\frac{7.647\times10^{17}T^{3/2}}{\mu_{H,meas}(T)\left\{\ln\left[1+y(d_{surf})\right]-\dfrac{y(d_{surf})}{1+y(d_{surf})}\right\}} + n_{meas}\frac{d_{total}}{d_{surf}} \right) \tag{1.5}$$

$$N_{A,surf} = \frac{1}{2}\left(\frac{7.647\times10^{17}T^{3/2}}{\mu_{H,meas}(T)\left\{\ln\left[1+y(d_{surf})\right]-\dfrac{y(d_{surf})}{1+y(d_{surf})}\right\}} - n_{meas}\frac{d_{total}}{d_{surf}} \right) \tag{1.6}$$

where

$$y(d_{surf}) = 1.392\times10^{-6}\left(n_{meas}\frac{d_{total}}{d_{surf}} \right)^{1/3} \tag{1.7}$$

where $\mu_{H,meas}$ and n_{meas} are the TDH measured values of mobility and carrier concentration, respectively. d_{total} is the total layer thickness given by $d_{total} = d_{bulk} + d_{surf}$. Taking the value of d_{total} to be approximately equal to 540 nm [1] for melt grown samples, the minimum possible value of the surface thickness can be obtained by setting $N_{A,surf} = 0$ and using the measured values of the carrier concentration and mobility at the lowest temperature. The surface thicknesses and surface donor concentrations obtained from this method are shown in Table 3

for the annealing temperatures, 200 – 800˚C. As revealed by Table 3, the minimum surface donor concentration obtained from equation (1.5) increases with an increase in annealing temperature.

4. Conclusions

Temperature dependent Hall effect measurements performed on the as-received ZnO material have revealed the existence of two shallow defects. Fitting the experimental data to a model in Matlab by assuming two *s*-like donors has yielded donors with energy levels (37.8 ± 0.3) meV and (54.5 ± 0.9) meV and associated concentrations of (4.8 ± 0.3) x $10^{16}cm^{-3}$ and (5. 7 ± 0.3) x $10^{16}cm^{-3}$, respectively. The (37.8 ± 0.3) meV shallow donor has been explained as Zn_i related and possibly H-complex related, while the (54.5 ± 0.9) meV has been explained as an Al-related donor. The two shallow donor levels (19.9 meV and 17.8 meV) introduced after annealing the samples have been ascribed as being related to Group I elements occupying the Zn sites, X_{Zn}. An acceptor with concentration (1.3 ± 0.1) $10^{14}cm^{-3}$ has also been obtained from the fitting for the as received sample. The peak mobility for the as-received sample has been measured as 1250 cm^2/Vs. After treatment with H_2O_2, the mobility increased to a peak of approximately 1400 cm^2/Vs. The peak mobility of the samples decreases with increasing annealing temperature. This has been attributed to the increase in the number of the electrically active neutral donors possibly Group I element related that increase the probability of carrier scattering. Annealing studies performed on the hydrogen peroxide treated ZnO samples indicate an increase in surface conduction with increasing annealing temperature. Calculated surface donor volume concentrations for the annealed samples increases with increase in annealing temperature.

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Table 1: Values of the donor concentrations, activation energies and acceptor concentration for the as-received melt grown ZnO samples. Carrier concentrations are given in $10^{16}cm^{-3}$ and energy levels in meV.

$N_{D1}(10^{16}cm^{-3})$	E_{D1}(meV)	$N_{D2}(10^{16}cm^{-3})$	E_{D2}(meV)	$N_A(10^{16}cm^{-3})$
4.8 ± 0.3	37.8 ± 0.3	5. 7 ± 0.3	54.5 ± 0.9	0.013 ± 0.001

Table 2: Values of the bulk donor and bulk acceptor volume concentrations for the H_2O_2 treated annealed melt grown samples.

Annealing Temperature(^oC)	N_{D1} (x $10^{16}cm^{-3}$)	E_{D1} (meV)	N_{D2} (x $10^{16}cm^{-3}$)	E_{D2} (meV)	N_A (x $10^{14}cm^{-3}$)
Ref(No anneal)	5.3 ± 0.3	39.4 ± 0.3	3.7 ± 0.3	65.8 ± 0.9	1.2 ± 0.1
200°C	6.5 ± 0.3	19.9 ± 0.3	7.4 ± 0.3	50.6 ± 0.9	3.9 ± 0.1
400°C	5.2 ± 0.3	17.8 ± 0.3	8.6 ± 0.3	47.6 ± 0.9	3.9 ± 0.1
600°C	8.7 ± 0.3	50.4 ± 0.3	2.1 ± 0.3	33.5± 0.9	0.9 ± 0.1
800°C	9.7 ± 0.3	47.7 ± 0.3	6.5 ± 0.3	31.8 ± 0.9	2.0 ± 0.1

Table 3: Values of the surface donor volume concentrations for the H_2O_2 treated and annealed melt grown samples.

Annealing Temperature (^oC)	Surface thickness d_{surf} (nm)	$N_{D,surf}$ (× 10^{18} cm^{-3})
200	32	0.63
400	48	1.15
600	45	2.67
800	72	4.37

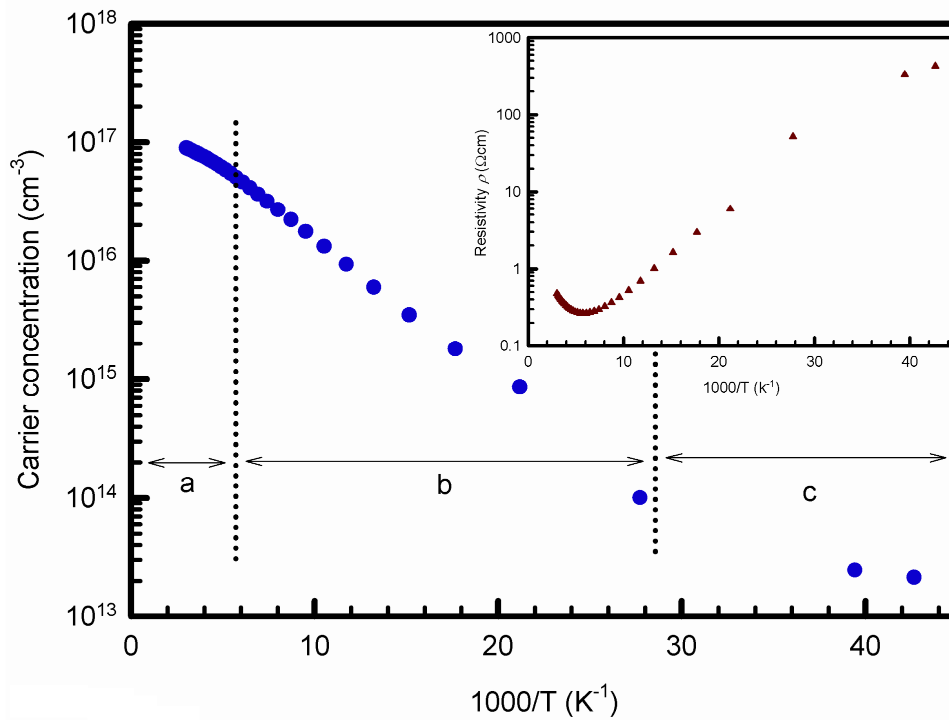

Fig. 1

Fig. Error! Main Document Only.: Semilogarithmic carrier concentration versus reciprocal temperature for the as-received ZnO sample in the 30 – 330 K temperature range. Insert shows the variation of bulk resistivity with temperature.

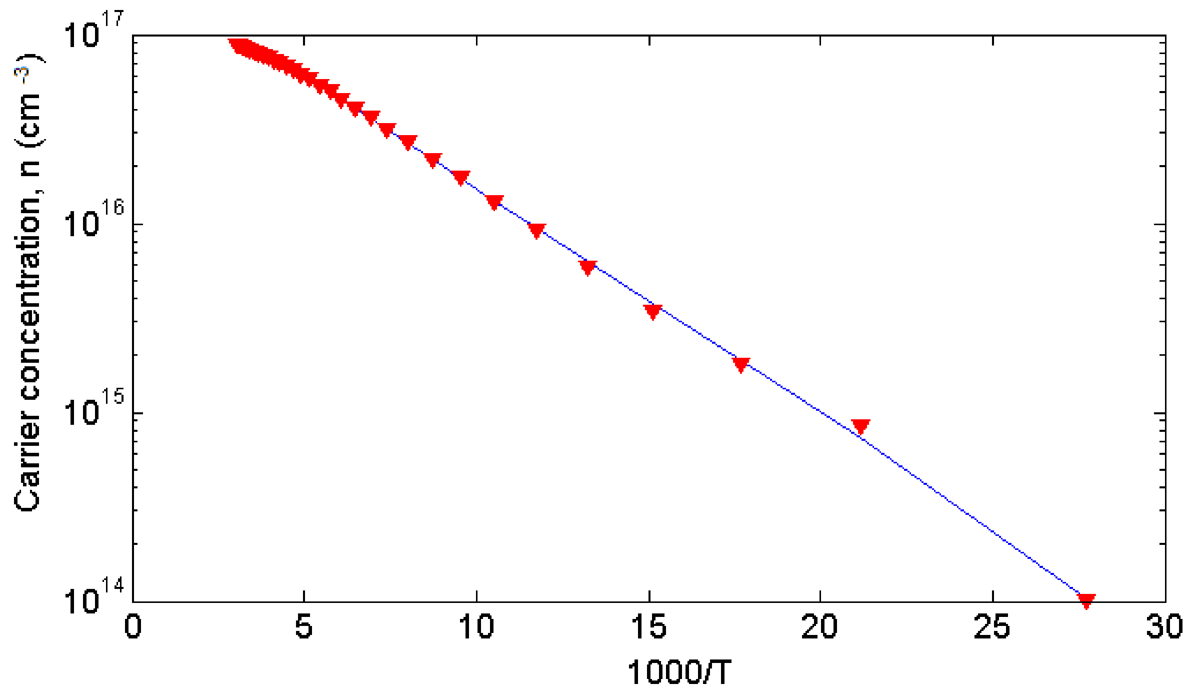

Fig. 2

Fig. 2: Carrier concentration versus reciprocal temperature. Triangles show the measured carrier concentration, $n_{H,meas}$ with the bold line showing the fit to the experimental data.

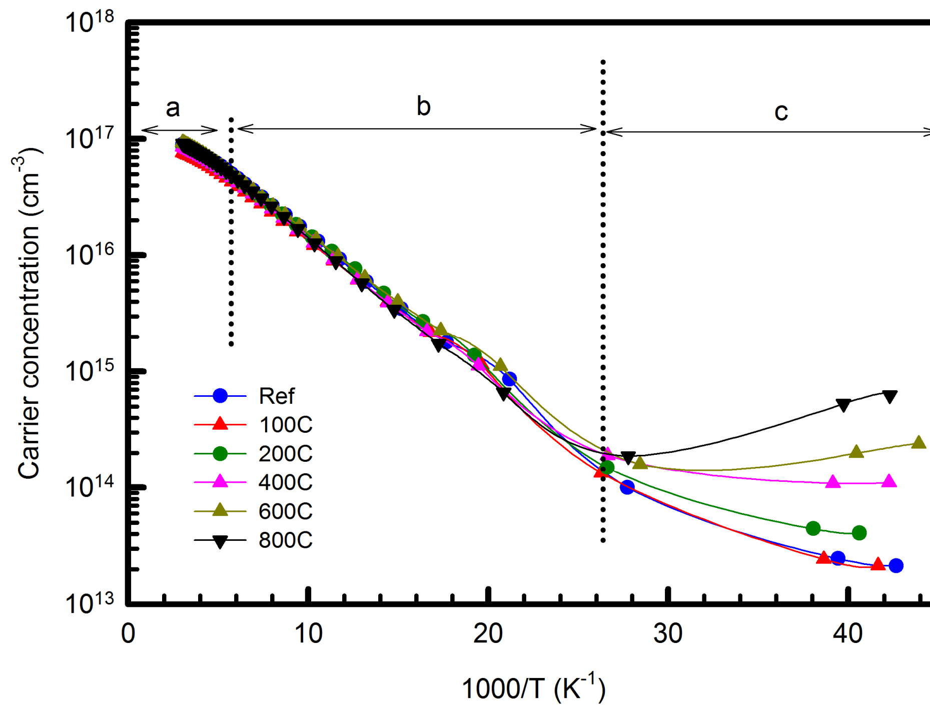

Fig. 3

Fig. 3: Carrier concentration versus the reciprocal temperature for the as received melt grown ZnO sample annealed in an Ar ambient at different temperatures.