

1 Non-parabolicity and band gap re-normalisation in Si doped ZnO

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Abstract

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7 INTRODUCTION

8 EXPERIMENTAL METHODS

Films were deposited via RF magnetron sputtering using an AJA Phase II-J Orion system. The system was configured with a 'sputter-up' geometry with the substrate being suspended above two separate ceramic targets of ZnO and SiO₂ that were arranged off-centre and tilted at 5° towards the middle of the substrate. Soda-lime glass substrates (OptiWhiteTM, NSG) of size 100 × 100 × 4 mm³ were used throughout. They were cleaned by scrubbing with a nylon brush and a series of de-ionized water and isopropanol alcohol rinses followed by blow drying with a nitrogen gas jet. During deposition the ZnO and SiO₂ targets were sputtered from simultaneously using powers of 150 W and 50 W respectively. A growth pressure of 2mTorr Ar was used during deposition. The substrate temperature was maintained at 350 ± 5°C during growth and the substrate was kept static (i.e was not rotated). Deliberate gradients of both thickness and composition were subsequently achieved across the resultant film to generate a 'combinatorial' sample. A second film of pure SiO₂ was deposited under identical conditions (but without ZnO) to generate a reference film for calculating the % wt. profile of SiO₂ in the co-sputtered film.

A Shimadzu UV-Vis-IR 3700 spectrophotometer with mapping capability was used to measure the transmittance of the co-sputtered film over the range 250 - 2500 nm. 289 spectra were taken in total at 5 mm increments over the full sample surface. At each of these 289 points the sheet resistance was also measured using a CMT-SR2000 4-point probe mapping system. Following transmittance and sheet resistance measurements the sample was cut into one hundred 10 × 10 mm² pieces. A selection of these pieces, 10 in total, were further scribed into four 5 × 5 mm² sections and Hall measurement were performed on

each of these sections. The Hall measurement was performed with custom built equipment, provided by Semimetrics Ltd., using a field strength of 0.8 T. Ellipsometry was performed on the same sections using a Woollam M2000-UI system. Ellipsometry was also used to map the thickness profile of the pure SiO₂ reference film.

RESULTS

Fitting of optical spectra

Figure 1 shows a typical transmittance spectra taken from a single point on the combinatorial ZnO:Si sample. The full details of the model of the dielectric permittivity, $\varepsilon(\omega)$, used to fit the data are given in [?]. The key components of the model include: 1) a Lorentzian oscillator to account for the behaviour of the system's bound electrons and to provide a smoothly varying dielectric background over the range of interest (250 – 2500 nm), 2) an extended Drude model [?], to characterise the system's free electron response, and 3) an inter-band transition model to account for the steep increase in the material's absorption coefficient ($\alpha \propto (E - E_G)^{1/2}$) in the vicinity of its direct band gap (3.3 – 3.4 eV). The two key parameters extractable from the dielectric model are the film's thickness, d , and plasma frequency, ω_p , which is related directly to the carrier concentration according to

$$\omega_p = \sqrt{\frac{n_e e^2}{m_e \varepsilon_0}} \quad (1)$$

where m_e is the effective electrons (expressed in units of the free electron mass, m_0) and ε_0 is the permittivity of free space.

Fitting was achieved by using a Nelder-Mead downhill simplex algorithm [?], imple-

49 mented via python script, to minimize the quantity

$$\chi^2 = \sum_i^N \sqrt{\frac{y_i - O_i}{N^2}} \quad (2)$$

50 where N is the total number of data points in the spectra, O_i the observed transmittance at
51 each wavelength over the range of interest, and y_i the theoretical transmittance calculated
52 using the transfer matrix method [?] for a single thin-film on a finite, transparent substrate.
53 The fitting algorithm was iterated until the relative fractional change in consecutive χ^2
54 values was less than 1×10^{-6} . The fitting of all 289 transmittance spectra taken over the
55 combinatorial sample was fully automated, the only user input required being an initial
56 estimate of film thickness at the point of the first spectrum. This automation ensured that
57 the fitting of consecutive spectra was highly consistent. For all spectra, χ^2 values of < 1
58 were achieved indicating that all fits were as successful as that shown in figure 1.

59 It was not possible to extract accurate values for the optical band-gap E_G from the inter-
60 band transition component of the model. All values were typically ~ 0.2 eV lower than
61 expected (even once non-parabolicity and re-normalisation effects had been accounted for,
62 see sections and). This is due to the presence of a population of impurity states located in
63 energy just below the bottom of the conduction band. The presence of these states generate
64 a broadening, commonly referred to as an ‘Urbach tail’ [?], in the onset of the absorption
65 coefficient. It is very difficult to determine the extent of this broadening by fitting the
66 dielectric model to a single transmittance spectra. The use of variable angle spectroscopic
67 ellipsometry (VASE) was therefore necessary to determine the true band gap of the material.

68 For each point over the combinatorial sample surface a set of three ellipsometric spectra,
69 taken at angles of 60, 65 and 70° with respect to a plane normal to the sample surface, was
70 measured and fitted using a parameterized semi-conductor (PSEMI-M0) model [?] over the
71 range 350 – 1000 nm. The use of multiple spectra allowed the effect of the tail states to be

extricated from the direct band to band transitions. Figure 2 shows the difference in the α^2 versus E behaviour extracted from transmittance and ellipsometry data respectively. This disparity between band gaps extracted from the two techniques has been reported previously by Srikant [?].

Conduction band non-parabolicity

For highly doped metal-oxides it has been shown that the conduction band, E_c , is ‘non-parabolic’ and that the origin of this non-parabolicity may be attributed to a carrier dependent effective mass, $m_e(n_e)$. The functional form of this dependence, first suggested by Pisarkiewicz *et. al* [?], is given by

$$m_e(n_e) = m_{e0} \sqrt{1 + \frac{2C\hbar^2 k}{m_{e0}}} \quad (3)$$

where m_{e0} is the value of the effective mass at the conduction band minimum and C is the non-parabolicity factor, expressed in eV^{-1} . The carrier wave-number can be expressed in terms of the carrier concentration according to $k = (3\pi^2 n_e)^{1/3}$. By re-examining equation 1 it is clear that the relationship between ω_p^2 and n_e is becomes non-linear if the effective mass is not a constant. Figure 3 shows a plot of ω_p , extracted from the spectrophotometry measurements, versus the carrier concentration, n_e^H , determined via Hall measurements, for the sample subset cut from the original combinatorial sample. A similar χ^2 minimization procedure to that described in section , in which the fitting parameters were m_{e0} and C , was applied to the data set using

$$\chi^2 = \sum_{i=1}^n \frac{(n_{e_i}^S - n_{e_i}^H)^2}{n^2} \quad (4)$$

where the superscript S corresponds to carrier concentrations calculated, using a carrier dependent effective mass $m_e(n_e)$ (equations (1) a 3), from the spectroscopically determined

92 plasma frequencies. The superscript H denotes values of n_e determined directly via Hall
 93 measurements. To determine the uncertainty associated with the fitted m_{e0} and C values a
 94 Monte-Carlo style error treatment [?] was implemented within which the χ^2 minimization
 95 procedure was performed 1000 times. The inset plot in figure 3 shows the mean $m_e(n_e)$
 96 relationship (solid line) and the corresponding spread (yellow line). An average extracted
 97 value of $m_{e0} = 0.35 \pm 0.02m_0$ is higher than previous published values of $0.24 - 0.28m_0$ for
 98 the effective mass in undoped ZnO. An average extracted value of $C = 0.30 \pm 0.01$ eV agrees
 99 very well with previously reported values of ~ 0.29 eV $^{-1}$ [?] for Al doped ZnO films.

100 **Band-gap renormalization**

101 The optical band gap of a degenerately doped metal-oxide system increases as a function
 102 of carrier concentration (Burstein-Moss shift [?]) according to

$$E_G = E_{G0} + \frac{\hbar^2(3\pi^2n_e)^{2/3}}{2m_{eff}} \quad (5)$$

103 where E_{G0} is the band-gap at the conduction band minimum and the joint density of states
 104 effective mass, m_{eff} is given as

$$\frac{1}{m_{eff}} = \frac{1}{m_h} + \frac{1}{m_e(n_e)} \quad (6)$$

105 A constant hole effective mass value of $m_h = 0.7m_0$ [?] is assumed throughout this work. Note
 106 that the non-parabolicity of the conduction band is accounted for when estimating the band
 107 gap by using the carrier dependent effective mass $m_e(n_e)$ determined in section . The data
 108 points in figure 4 show the band-gap values, determined via ellipsometry, plotted against the
 109 Hall carrier concentrations. The points lie some distance from the relationship predicted by
 110 equation 5. The apparent reduction in the real band-gap values is due the re-normalization

111 effects of many body electron-electron, electron-ion and hole-hole interactions. Lu *et. al*
 112 [?] have shown that the total energy shift due to re-normalization can be estimated by
 113 parameterising the detailed model described by Jain *et. al* according to

$$E_R = An_e^{1/3} + Bn_e^{1/4} + Cn_e^{1/2} \quad (7)$$

114 where E_R is negative with respect to E_G . The $n_e^{1/3}$, $n_e^{1/4}$ and $n_e^{1/2}$ dependencies correspond to
 115 the exchange energy of free electrons, their correlation energy and the electron-ion interaction
 116 energy respectively. The coefficients A , B , and C , quantify the strength of each of these three
 117 dependencies. The coefficient values for the data shown in figure 4, and a value for E_{G0} , was
 118 extracted using the established minimisation procedure. Table I show the extracted values
 119 and comparative values for n-type ZnO thin-films. The strength of the $n_e^{1/3}$ dependence is
 120 roughly three times than that reported for Al doped ZnO.

121 MAPPING OF COMPOSITIONAL DEPENDENCE

122 Film thickness profiles were determined for the combinatorial ZnO:Si and SiO₂ samples.
 123 The % wt. SiO₂ content at each point over the combinatorial sample was estimated according
 124 to

$$x = \frac{\Gamma_B d_B}{\Gamma_A d_A + \Gamma_B d_B} \times 100\% \quad (8)$$

125 where Γ_A and Γ_B are the bulk densities of ZnO and SiO₂ respectively and d_A and d_B are the
 126 corresponding thicknesses, d , of the ZnO and SiO₂ films. The carrier concentration profile
 127 for the combinatorial sample was calculated from extracted ω_p^S values according to equation
 128 1 and using the non-parabolic effective mass relationship, $m_e(n_e)$, determined in section .
 129 The corresponding mobility profile was calculated according to

$$\mu_e = \frac{1}{n_e^S R_S de} \quad (9)$$

130 where R_S are the sheet resistance values obtained directly from 4 point probe measurements.
 131 Figure 3 shows the three dimensional contour profiles of n_e and μ_e accross the surface of
 132 the combinatorial sample. In both cases, a maximal ridge, corresponding to $n_e \sim 4.5 \text{ cm}^{-3}$
 133 an $\mu_e \sim 16 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, runs diagonally across the sample. By superimposing the contour
 134 distribution of % wt. SiO_2 content (dotted black contour lines) a very strong correlation
 135 between carrier concentration and composition becomes apparent, the maximum n_e and μ_e
 136 values corresponding to a value of $x = 0.65\%$ wt. SiO_2 content.

137 By plotting the distributions of n_e and μ_e with respect to x the compositional dependence
 138 can be observed directly, see figure 4. Here the strength of the combinatorial analysis is
 139 fully appreciated by its ability to generate continuous, non-ambiguous distributions of the
 140 material's electrical behaviour and shows that it is highly sensitive to the composition -
 141 the resistivity spanning over three orders of magnitude within the compositional range $x =$
 142 $0 - 0.65\%$ wt. SiO_2 . Furthermore, the uncertainty in the optimum value of x , that minimises
 143 the resistivity, is significantly reduced when compared to the multi-sample analyses that are
 144 commonly reported.

145 The solid straight line in the n_e vs x plot indicates the relationship predicted for a 100%
 146 doping efficiency, i.e. where every Si atom incorporated into film substitutionally replace a
 147 Zn atom and contributes two free electrons to the system. For low values of x , i.e. in the
 148 range $0 - 0.5\%$ wt. SiO_2 , this relationship is adhered to. However as x increases further the
 149 doping efficiency decreases rapidly and the carrier concentration is limited to $3 - 4 \times 10 \text{ cm}^{-3}$
 150 for compositions up to 10% wt. SiO_2 . After the optimum value of x is reached the mobility
 151 drops off steeply and approaches a value of zero for values of x beyond 6%. This suggests
 152 that as x is increased beyond the optimum composition, Si is no longer incorporated into
 153 the film as a substitutional dopant and instead acts to increase the scattering of the free

carriers, existing as an interstitial impurities or forming segregated Si-O phases at the grain boundaries.

Scattering

The behaviour of carrier mobility can be described further by considering its direct relationship with the carrier concentration. Figure 5 shows that by plotting μ_e versus n_e for all data points two distinct populations are revealed. The red data points correspond to compositions $x < 0.65\%$. Within this distribution, and for carrier concentrations below $2.5 \times 10^{16} \text{ cm}^{-3}$ the mobility of the free carriers can be described in terms of a grain barrier limited transport model proposed by Seto *et.al* [?]. The model assumes that at the grain boundaries a population of filled trap states exist within the band gap. This causes the conduction band to bend upwards at each grain boundary forming a barrier to charge transport. The inter-grain mobility, μ_B of free carriers is therefore limited by thermal processes according to

$$\mu_{ig} = \mu_0 \exp\left(-\frac{\Phi_B}{k_B T}\right) \quad (10)$$

where Φ_B is the barrier height at the grain boundary and is related directly to the carrier concentration according to

$$\Phi_B = \frac{e^2 n_t}{8 \varepsilon_\infty \varepsilon_0 n_e} \quad (11)$$

where n_t is the trap density and ε_∞ is the high frequency dielectric permittivity ($\varepsilon_\infty \sim 8.3$ for single crystal ZnO [?]). The pre-factor μ_0 is the internal mobility of the grain, expressed

as

$$\mu_0 = \frac{eL}{\sqrt{2\pi m_e k_B T}} \quad (12)$$

where L is the grain size. It is necessary to extend the Seto model in the case of degenerately doped ZnO to account for the tunnelling of carriers through the barrier Φ_B . As the carrier concentration increases the Fermi level rises towards the top of the barrier while the barrier height decreases proportionally to $1/n_e$. Following the onset of tunnelling the effective carrier mobility increases exponentially with respect to carrier concentration. The mobility and is eventually limited by other scattering processes, for example ionized-impurity scattering. A semi-empirical relationship the mobility due to the tunnelling of free carriers, μ_t can be expressed according to

$$\mu_t = \frac{\mu_{ii} - \mu_{ig}}{1 + \exp[-\frac{1}{\alpha}(\Delta_{BM} + E_R - \beta\Phi_B)]} \quad (13)$$

where the factor α accounts for the sharpness of the onset in tunnelling and is likely to be related to the depletion width of the grain boundary. A second empirical factor, β takes into account of any extra functional dependence of Φ_B on n_t which is likely vary with respect to n_e . The effective mobility may therefore be expressed as the sum of the inter-grain and tunnel mobilities according to

$$\mu_{eff} = \mu_{ig} + \mu_t \quad (14)$$

Figure 5 shows corresponding fit of this extended model to the data in the region of composition $x < 0.65\%$. An extracted value of $n_t = 1.79 \times 10^{14} \text{ cm}^{-3}$ is in excellent agreement with previously reported values for doped ZnO films [].

CONCLUSIONS

FIG. 1.

FIG. 2.

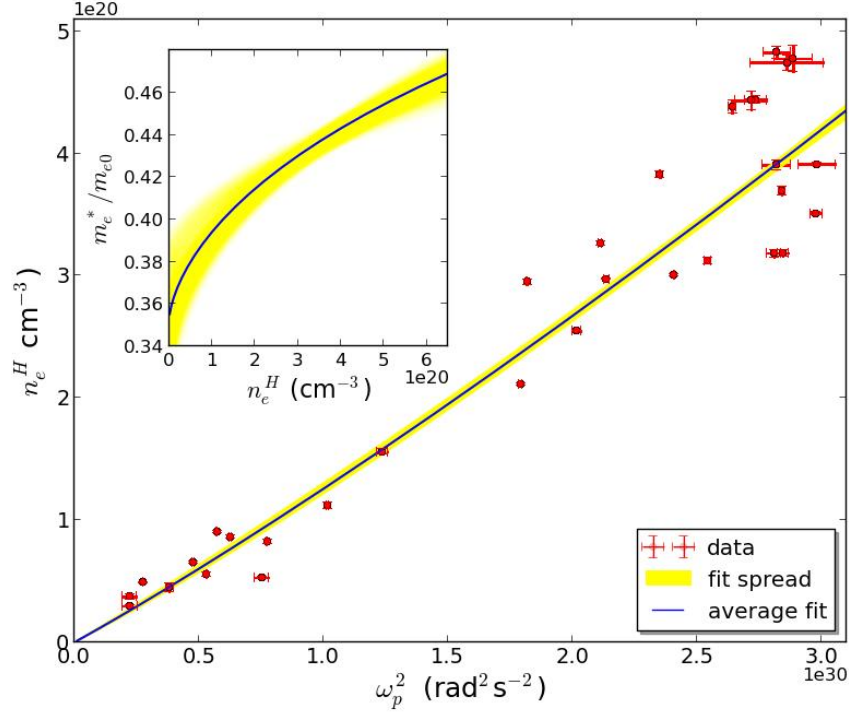


FIG. 3.

Parameter 1	Extracted Value	Copmparison [?]
$A (\times 10^{-8} \text{ eV.cm})$	2.1 ± 0.8	0.69
$B (\times 10^{-7} \text{ eV.cm}^{3/2})$	3.0 ± 2.6	1.6
$C (\times 10^{-7} \text{ eV.cm}^{3/4})$	8.7 ± 1.5	7.76
$E_{G0} (\text{eV})$	3.41 ± 0.01	-

TABLE I. This is the caption

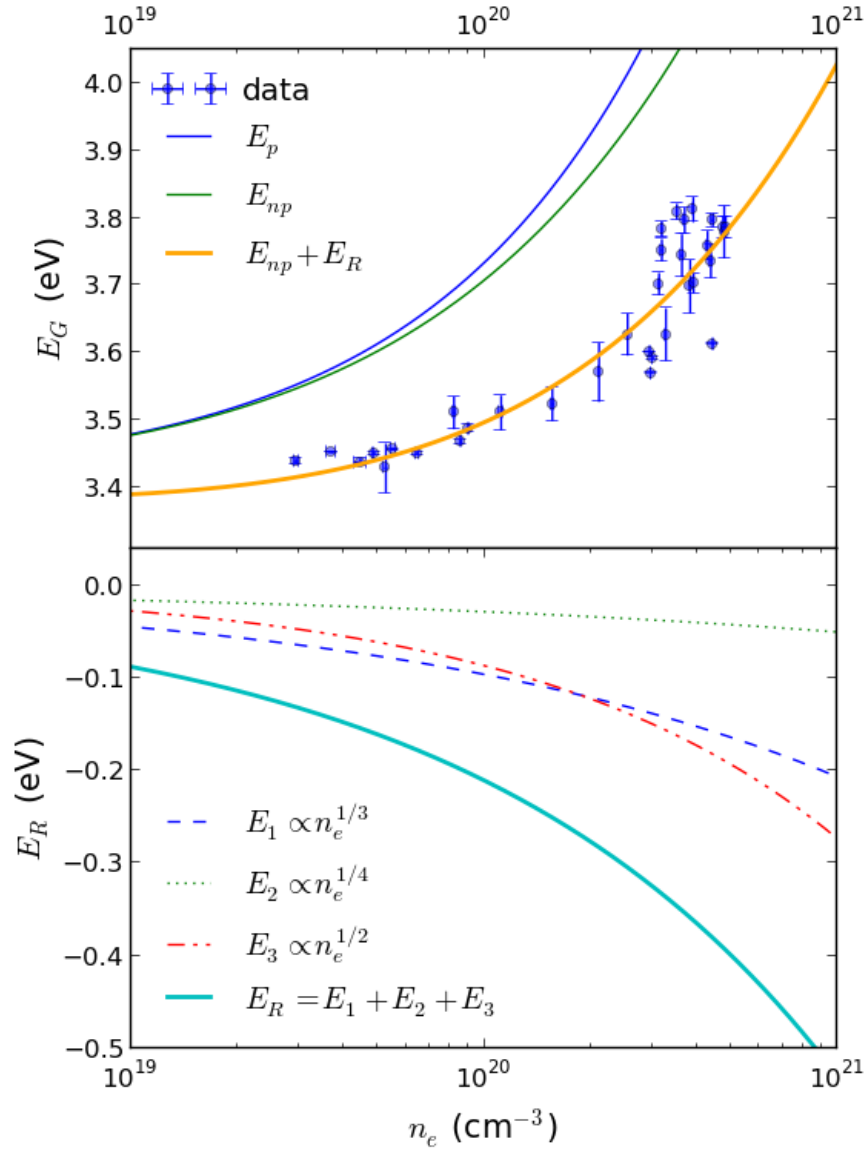


FIG. 4.

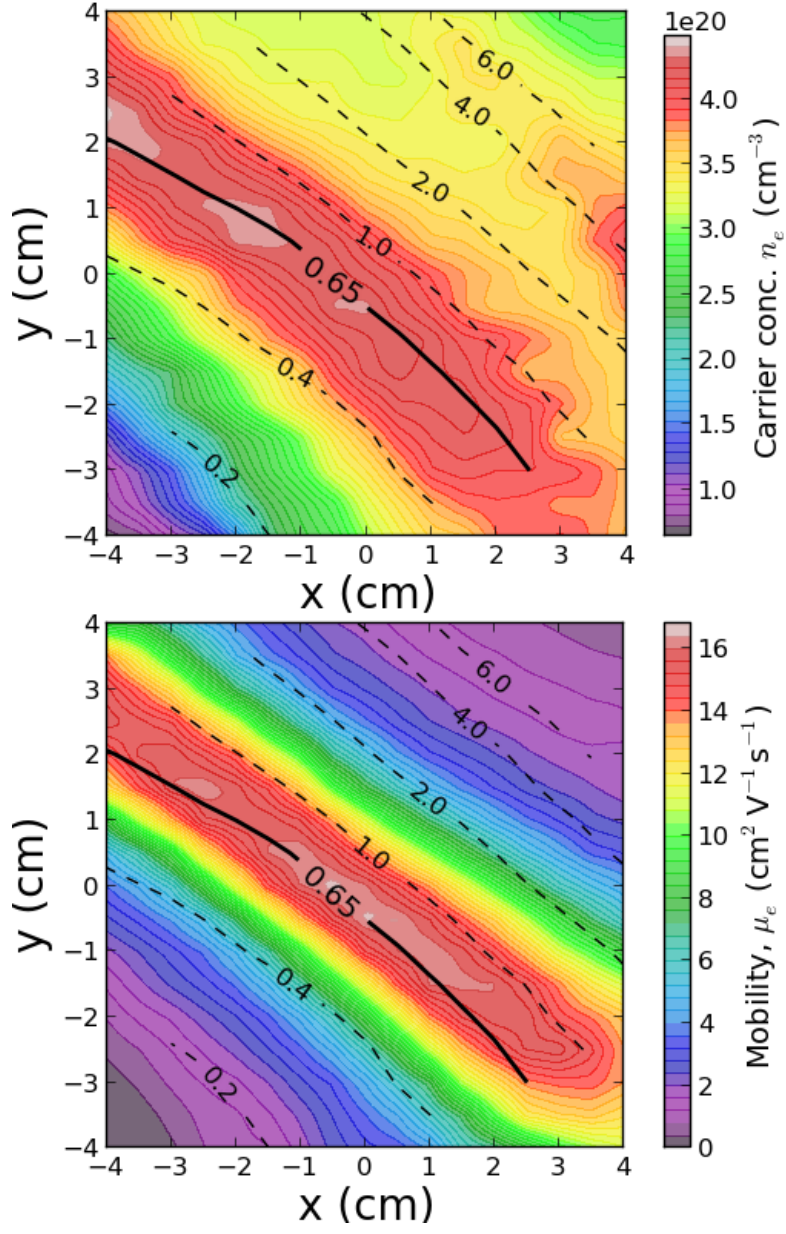


FIG. 5. Contour maps of carrier concentration and mobility over the combinatorial sample. The (—) contour lines show an overlay of the % wt. SiO_2 composition.

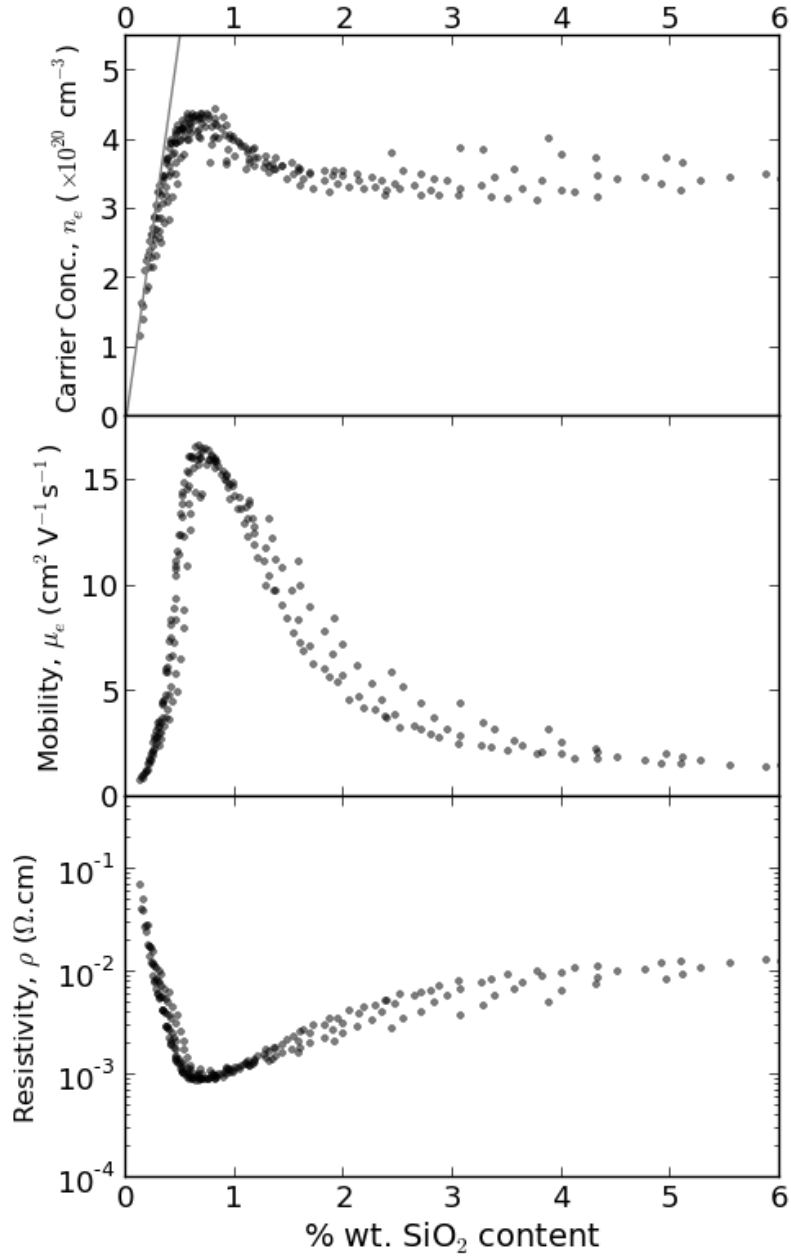


FIG. 6. Distributions of carrier concentration, mobility and resistivity with respect to % wt. SiO₂ content. The maximum values for n_e ($4.4 \times 10^{20} \text{ cm}^{-3}$) and μ_e ($16.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) coincide with a composition of 0.65% wt. SiO₂. The solid straight line in the top plot shows the maximum theoretical carrier concentration with respect to SiO₂ content should every incorporated Si atom be substituted at a Zinc site and donate 2 carriers.

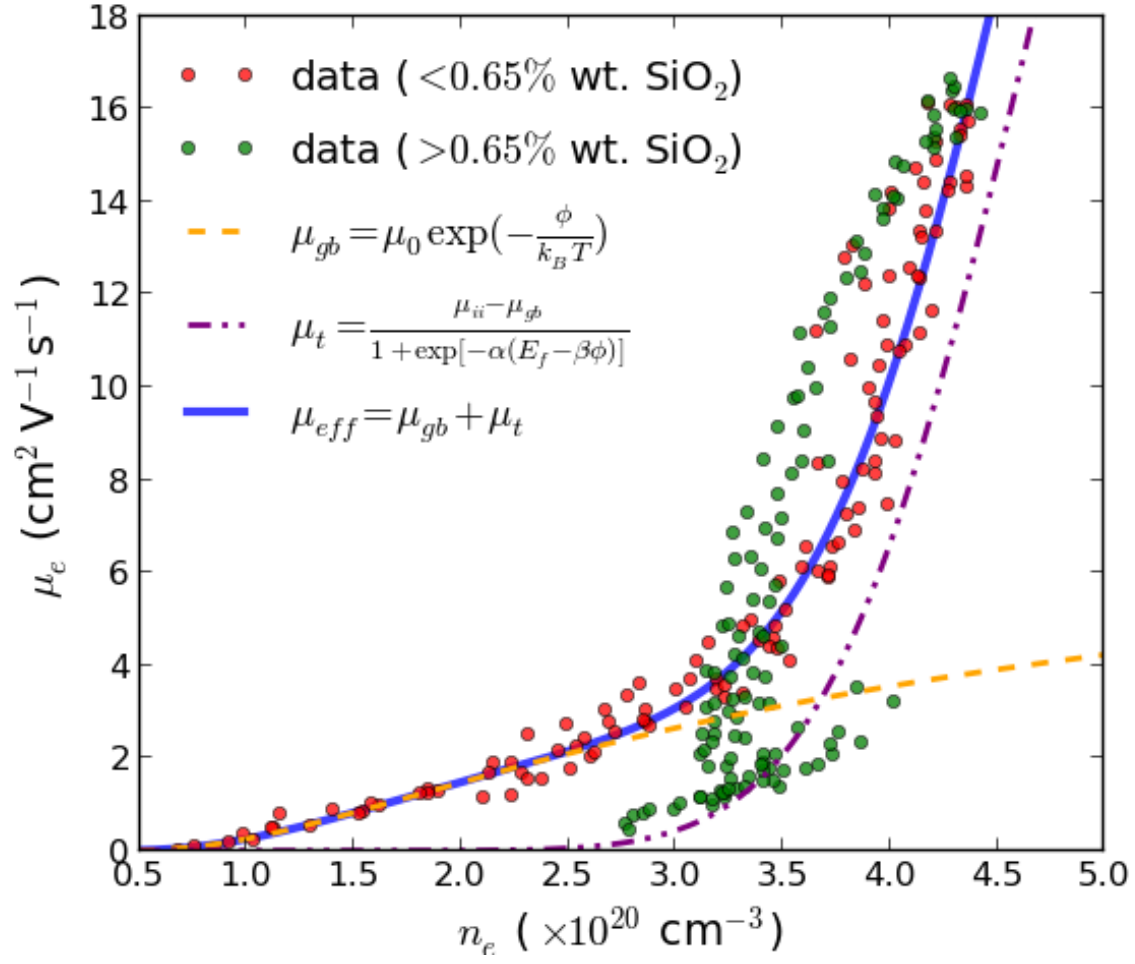


FIG. 7.