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Optical and electrical properties of H₂ plasma-treated ZnO films prepared by atomic layer deposition using supercycles

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Abstract

High mobility H-doped ZnO (ZnO:H) thin films are prepared on thermal oxide coated silicon wafers by a novel supercycle approach of thermal atomic layer deposition (ALD) technique. The influence of H₂ plasma treatment and substrate composition on optical and electrical properties of ZnO films are studied using spectroscopic ellipsometry (SE) and direct electrical measurements. This work significantly expands the measured range of ZnO:H optical properties into the far infrared to obtain the complex dielectric function ($\epsilon = \epsilon_1 + i\epsilon_2$) spectra from 0.4 meV to 5.89 eV compared to what has been previously investigated by using SE. A blue shift in the optical band gap energy is observed with decreasing cycle ratio (n) or more frequent H₂ plasma treatments during deposition. The amplitude of phonon absorption is increased with decreasing n . Free carrier transport characteristics are determined by applying Drude model in modeling ϵ , and result indicates lower n improves material conductivity as confirmed by direct electrical measurements. Regarding the effect of substrate composition, the samples prepared using the same n but on bare thermal oxide, a 5 nm ZnO:H film, or a 5 nm intrinsic ZnO film each have differences in ϵ and free carrier transport characteristics resulting from substrate composition, demonstrating an additional method of tailoring material properties. Effective carrier mass (m^*) for the ZnO films are determined by combining results from Hall effect measurements with UV to THz spectra in ϵ . Thus, variation of n and substrate composition are demonstrated an effective mean of controlling the resultant opto-electronic film properties.

Keywords: ZnO; H₂ plasma treatment; Optical and electrical properties; Spectroscopic ellipsometry; Terahertz; Dielectric function

1. Introduction

Thin films of transparent conducting oxides (TCOs) are commonly used in a wide range of opto-electronic devices such as solar cells, light emitting diodes, flat panel displays, and touch-screen panels [1, 2]. These materials are wide band gap semiconductors exhibiting high conductivity and visible light transparency [3]. Commonly used TCOs are based on SnO₂, ZnO, and In₂O₃. For carrier density values $\sim 10^{20}$ cm⁻³, the upper limits of mobility resulting from intrinsic scattering are found to be ~ 130 and 55 cm²/Vs for In₂O₃ and ZnO based thin film TCOs, respectively [4, 5]. Currently, there is great interest in high mobility TCOs because of their utility in optimizing solar cell performance [4, 5]. Such TCOs help to minimize infrared (IR) losses and enhance short circuit current of single heterojunction solar cells when used as front electrodes [6, 7]. Though In₂O₃ based TCOs enable excellent device performance, the scarcity and cost of In has motivated alternative TCO development. Hydrogen doped ZnO (ZnO:H) is a promising alternative high mobility TCO candidate. Hydrogen is an appropriate alternative dopant in ZnO for several reasons. Similar to group III elements (Al, Ga, In), it also acts as a shallow donor in ZnO [8, 9]. A small amount of hydrogen doping has been shown to improve crystallinity, increase the band gap, and decrease electrical resistivity of ZnO films [4, 6, 8, 10].

Several techniques have been investigated for H-doping into ZnO thin films such as H being imbedded during deposition [8, 10], annealing in H₂ ambient [11], and exposure to H₂ plasma [12, 13]. Ding *et al.* reported that mobility (μ) of 46 cm²/Vs can be achieved with exposure of a 350 nm thick ZnO film into H₂ plasma after deposition

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[13]. ZnO:H film $\mu = 47.1 \text{ cm}^2/\text{Vs}$, carrier concentration (N) of $4.4 \times 10^{19} \text{ cm}^{-3}$, and resistivity (ρ) of $2.8 \text{ m}\Omega\cdot\text{cm}$ could be obtained with addition of H_2 during deposition by radio frequency magnetron sputtering [9]. Thomas *et al.* showed that ZnO:H films with $\mu = 20 \text{ cm}^2/\text{Vs}$, $N = 4.6 \times 10^{20} \text{ cm}^{-3}$, and ρ of $0.7 \text{ m}\Omega\cdot\text{cm}$ can be prepared using interleaved standard atomic layer deposition (ALD) ZnO cycles comprised of diethylzinc (DEZ, $\text{Zn}(\text{C}_2\text{H}_5)_2$) and H_2O with plasma exposures [10]. In this work, a novel supercycle approach of thermal ALD technique is used to prepare high-mobility ZnO:H films with $\mu \sim 47 \text{ cm}^2/\text{Vs}$ and ρ of $1.8 \text{ m}\Omega\cdot\text{cm}$ with excellent IR-transparency [14]. A schematic of supercycle approach of ALD process for ZnO:H is shown in Fig. 1. Here, we provide new insights into the ZnO:H optical response over the IR and terahertz (THz) spectral ranges for the samples studied previously by Macco *et al.* [14].

Fig. 1. Schematic of supercycle approach of the atomic layer deposition (ALD) process for high mobility ZnO:H. A supercycle constitutes n cycles of ALD ZnO followed by one cycle of H_2 plasma treatment.

In terms of optical response, the complex dielectric function ($\epsilon = \epsilon_1 + i\epsilon_2$) spectra from the near-IR to ultraviolet (UV) have been previously studied by spectroscopic ellipsometry (SE) [15]. Structural, optical, and electrical properties of ZnO:H have also been studied using other methods [14, 16-20]. The crystal structure of ZnO films have been extensively studied using x-ray diffraction (XRD), and increases in crystallite size and change in preferred crystal orientation from (100) to (002) with increased in doping concentration of hydrogen in the films have been reported [14, 16, 17]. Optical properties of ZnO has been investigated using unpolarized transmittance and reflectance spectroscopy, and found blue shifting in optical band gap with increased in hydrogen content in the films [16, 17, 19]. The electrical properties have been studied with Hall effect [14, 16-19] and alternating current impedance spectroscopy [20] which found a decrease in electrical resistivity and an increase in carrier concentration with increased hydrogen content. Additionally, IR extended measurements have also been carried out to study the vibrational modes of ZnO [21-24].

Zinc vacancy (V_{Zn}) and oxygen vacancy (V_{O}) native defects in ZnO have been thoroughly investigated [25-30]. Other native defects such as zinc interstitials (Zn_i), oxygen interstitials (O_i), Zn-on-O antisite defects (Zn_O) [31], small donor centers, oxygen vacancies with one electron called F^+ centers [32], and a center due to residual nitrogen called a N-center [33, 34] have also been reported in ZnO. The variation of V_{O} and V_{Zn} when ZnO interacts with an air+reducing mixture (air+ H_2 and air+CO) have been studied by Morazzoni *et al.* [28], which found significant variations in V_{O} only above 573 K. A strong correlation between 510 nm emission, free carrier concentration, and the density of singly ionized V_{O} in commercially prepared ZnO have been reported by Vanheusden *et al.* [29]. These defects were investigated using electron paramagnetic resonance (EPR) and photoluminescence (PL) spectroscopies. The presence of a F^+ -center in single crystal ZnO irradiated with 2 MeV electrons has also been reported by Smith *et al.* [35] utilizing electron spin resonance spectroscopy. To study defects in nanocrystalline ZnO, a core-shell model has been purposed by Kaftelen *et al.* [36] in which the core consists of negatively charged V_{Zn} and the shell is a medium containing a high concentration of positively charged V_{O} resulting in selective behavior of defect centers towards different excitation energies, as confirmed by EPR and PL spectroscopies. This indicates the possibility of p-type ZnO nanocrystals. Core defects were found to be more stable than the surface defects [37]. The defect evolution in nonstoichiometric ZnO quantum dots has been investigated by Repp *et al.* [38], and the EPR signal reported at $g = 1.959$ is related to core defects with a weak coupling to hydrogen atoms. The correlation between defects, synthesis route, and particle size of ZnO has been reported by Repp *et al.* [39]. The variation of native defect states, and their influence on structural, optical and electrical properties during annealing and quenching have been

studied by Dutta *et al.* [30, 40]. None of these native defects can provide a high concentration of shallow donors, but extrinsic intentional dopants like Al, Ga, In, and hydrogen act as shallow donors in ZnO [8, 9, 20, 41]. The theoretical evidence of hydrogen as a shallow donor in ZnO has been reported by Van de Walle [41], and then confirmed experimentally by Cox *et al.* [42] and Hofmann *et al.* [43]. Two types of shallow hydrogen donors have been assumed from first principle calculation—hydrogen atom incorporated on an interstitial bond-centered lattice site, H_{BC} , [41], and hydrogen atom occupied V_O , H_O [44]. These defects have been experimentally investigated by Lavrov *et al.* [45] using Raman scattering, IR absorption, PL, and photoconductivity, and found that H_{BC} is unstable to annealing above 190 °C. Though the exact microscopic structure of these defects is still not well understood, hydrogen is emerging as promising alternative dopant to manipulate desirable optoelectronic properties of ZnO [8, 9].

This work specifically varies substrate composition and the frequency of H_2 plasma treatments during deposition to study how such factors influence morphology, optical, and electrical properties of ALD ZnO thin films via scanning electron microscopy (SEM), SE, and direct electrical measurements. *Ex-situ* SE measurements collected span the THz range from 0.4 to 4.1 meV (3.1 to 0.3 mm) and the IR to UV spectral range from 0.035 to 5.89 eV (35.4 to 0.210 μm) to obtain sensitivity to layer thicknesses as well as optical properties in the form of ϵ through a continuous parametric model. In particular, this study investigates films deposited with various H_2 plasma treatment frequencies on both thermal oxide coated silicon wafers and on such wafers coated with an additional intrinsic ZnO (i-ZnO) “seed layer.” The degree of H_2 plasma exposure as well as underlying substrate composition are found to impact morphologies (i.e. grain size and surface roughness layer), the optical properties (i.e. band gap, free carrier absorption, phonon mode absorption), and transport properties (i.e. resistivity, scattering time, carrier mobility, carrier effective mass, carrier concentration) of ZnO:H films. Electrical transport properties derived from ϵ are also compared with direct electrical measurements obtained by four-point probe and Hall effect techniques. Increasingly frequent H_2 plasma exposure during deposition is ultimately found to result in ZnO:H films with increased crystalline grain size, higher optical band gap, increased free carrier absorption corresponding with increased N and μ leading to lower ρ . However, the systematic trends observed in film grain size, optical band gap, and electrical properties resulting from varying H_2 plasma exposure are found to be more substantial in the case of ZnO:H films grown on i-ZnO seed layers when compared to the films grown directly on thermal oxide coated silicon wafers. Additionally, ZnO:H films grown on i-ZnO seed layers also have decreased surface roughness layer thickness with lower free carrier absorption corresponding to higher ρ and lower μ when compared to otherwise identically prepared films without a seed layer. This study builds upon the previous work of Macco *et al.* [14] by extending optical characterization deeper into the IR and the THz spectral ranges and adding SEM to study the effect of substrate composition and number of H_2 plasma treatments on the optical and electrical properties of the ZnO:H thin films.

2. Experimental Details

The hydrogen doped ZnO films in this study are the same as previously studied by Macco *et al.* [14]. Hydrogen doped ZnO thin films have been deposited on commercial wet thermal oxide coated crystal silicon wafers (SIEGERT WAFER GmbH) at a substrate temperature of 200 °C using an ALD reactor (Oxford Instruments OpAL). DEZ and deionized water vapor are used as precursors for ZnO growth, and hydrogen doping is achieved by interleaving H_2 plasma treatments between specific numbers of ZnO layer growth cycles. In particular, the number of ZnO growth cycles between individual H_2 plasma treatments is defined as the cycle ratio, n , and a full set of n ZnO cycles combined with H_2 plasma treatment is defined as a supercycle. Thus, lower n corresponds to more frequent plasma treatment. For instance, cycle ratio $n = 3$ means there is one cycle of H_2 plasma treatment each three ZnO layer growth cycles, which together constitute one supercycle. The H_2 plasma treatments used a remote inductively coupled plasma with a power of 100 W, a H_2 flow of 50 sccm, and an exposure time of 4 s [14]. Four different kinds of films are prepared for this study: i) un-doped or non-intentionally doped ZnO (i-ZnO, no H_2 plasma treatments) (S1), ii) ZnO:H grown without a seed layer (S2, S3, and S4), iii) ZnO:H films on top of a 5 nm seed layer of i-ZnO (S5, S6, and S7), and iv) ZnO:H on top of a 5 nm $n = 3$ ZnO:H seed layer (S8). The fabrication details for the 8 different samples studied here are listed in Table 1.

Room temperature ellipsometric spectra (in $N = \cos 2\psi$, $C = \sin 2\psi \cos \Delta$, $S = \sin 2\psi \sin \Delta$) have been collected *ex-situ* at 50° angle of incidence over a spectrum from 0.4 to 4.1 meV using a millimeter wavelength range ellipsometer (J. A. Woollam Company THz-VASE) similar to that described by Hofmann *et al.* [46], from 0.035 to 0.75 eV using a Fourier transform IR (FTIR) range single rotating compensator ellipsometer (J. A. Woollam

Company IR-VASE) [47], and 0.75 to 5.89 eV using a single rotating compensator multichannel ellipsometer (J. A. Woollam M-2000FI) [47, 48]. It should be noted that the THz range ellipsometer used here differs from that described by Hofmann *et al.* [46] in the use of a rotating compensator followed by a fixed analyzer after beam interaction with the sample.

Table 1

Atomic layer deposition parameters for the films described by Macco *et al.* [14].

Test samples	Cycle Order	Seed Layer	Cycle Ratio (n)	Number of Supercycles	
S1	DEZ-H ₂ O	-	-	460	No H ₂ Plasma Treatment
S2	DEZ-H ₂ O-H ₂	-	3	167	Increased H ₂ Plasma
S3	DEZ-H ₂ O-H ₂	-	6	70	Frequency with Decreased n
S4	DEZ-H ₂ O-H ₂	-	10	50	
S5	DEZ-H ₂ O-H ₂	i-ZnO	1	360	Increased H ₂ Plasma
S6	DEZ-H ₂ O-H ₂	i-ZnO	2	200	Frequency with Decreased n
S7	DEZ-H ₂ O-H ₂	i-ZnO	3	135	+
S8	DEZ-H ₂ O-H ₂	$n = 3$	1	--	Influence of Seed Layers

The structural and optical properties of ZnO:H films are extracted in the form of layer thicknesses and spectra in ϵ , respectively, by fitting a single parametric model to the combined measured ellipsometric spectra collected by all three instruments. The fitting uses a least squares regression analysis that minimizes an unweighted error function [49] defined as

$$\sigma = \left\{ \frac{1}{3N - M} \sum_{j=1}^N \left[\left(\cos 2\psi_j^{mod} - \cos 2\psi_j^{exp} \right)^2 + \left(\sin 2\psi_j^{mod} \cos \Delta_j^{mod} - \sin 2\psi_j^{exp} \cos \Delta_j^{exp} \right)^2 + \left(\sin 2\psi_j^{mod} \sin \Delta_j^{mod} - \sin 2\psi_j^{exp} \sin \Delta_j^{exp} \right)^2 \right] \right\}^{1/2}, \quad (1)$$

where, N = the number of measured values, M = the number of fit parameters, and “exp” and “mod” denote experimental and model generated ellipsometric data, respectively.

The resistivity of ZnO:H films at room temperature has been measured by a 4-point electrical probe (Lucas Lab, Pro 4). The instrument measures the sheet resistance (R_s), which is then multiplied by the ellipsometry-determined thickness of the film to determine ρ [50]. Room temperature Hall effect measurements have also been performed to obtain resistivity, carrier concentration, and mobility for each sample as described in Ref. [14]. Scanning electron microscopy (SEM) is performed using a Hitachi S-4800 to study the surface morphology of the ZnO:H films on thermal oxide coated silicon substrates. The electron accelerating voltage is 30 keV with a beam current of 10 μ A. Grazing incidence XRD (GIXRD) patterns are collected using a Panalytical X'Pert PRO MRD employing Cu K α ($\lambda = 1.54$ Å) [14]. Transmission electron microscopy (TEM) (JEOL ARM 200 probe corrected TEM, operated at 200 kV) was used to study cross-sections of films using focused ion beam made lamellas [14].

3. Results and Discussion

Fig. 2 shows SEM results for the films listed in Table 1 to demonstrate that varying the H₂ plasma treatment sequences greatly influences the surface morphologies of resultant ZnO:H thin films. XRD reported by Macco *et al.*

[14] for the same samples shows crystallite size is enhanced with changes in orientation with decreasing n . Fig. 3(a) shows example XRD patterns of i-ZnO (S1) and doped ZnO $n = 3$ (S2). The crystallite size (d) is calculated using Lorentzian fitting of (002) peaks and the Scherrer equation [51]:

$$d = \frac{k\lambda}{\beta \cos \theta}, \quad (2)$$

where, $k = 0.9$ is the shape factor, $\lambda = 1.54 \text{ \AA}$ is the x-ray wavelength, β is the diffraction peak full width half maximum, and θ is the angle of diffraction. Fig. 3(b) shows the crystallite size as a function of n , plotted as $1/n$. The crystallite size of H-doped ZnO is found to be greater than that of i-ZnO and generally increases with decreasing n . Macco *et al.* reported that the i-ZnO sample has weak peaks originating from various orientations with a dominant (100) contribution. Upon decreasing n , the (002) peak becomes larger relative to other peak orientations with the lowest n film (S2) having the sharpest, most pronounced (002) peak. Thus, the H_2 plasma treatment is understood to increase the grain size and modify the dominant grain orientation. The SEM results in Fig. 2 show effects that are consistent with the XRD results. With more frequent plasma treatments (i.e. decreasing n ; $S4 \rightarrow S2$) for films grown without a seed layer, SEM shows increased size and more symmetric grains. Films grown on a seed layer ($S7 \rightarrow S5$) also exhibit the same trend, but relatively smaller grain sizes compared to the films prepared without a seed layer. The presence of an i-ZnO seed layer is observed to promote smaller grains, as is seen by comparing two samples both grown at $n = 3$ with one on an i-ZnO seed layer and the other on bare SiO_2 (i.e. $S7$ and $S2$). By contrast, ZnO:H samples $S5$ and $S8$ grown using $n = 1$ on top of 5 nm seed layers of i-ZnO and ZnO:H, respectively, have similar grain sizes but with qualitative differences in grain morphologies.

Fig. 2. Scanning electron microscopy (SEM) of ZnO thin films grown on thermal oxide coated silicon wafers without H_2 plasma treatment (S1); using cycle ratios $n = 3$ (S2), 6 (S3), and 10 (S4); $n = 1$ (S5), 2 (S6), and 3 (S7) on a top of 5 nm i-ZnO seed layers; and $n = 1$ on a top of a 5 nm $n = 3$ ZnO:H seed layer (S8).

Fig. 3. (a) Grazing incidence x-ray diffraction (GIXRD) patterns of i-ZnO and doped ZnO $n = 3$ samples. (b) Crystallite size determined from XRD as a function of cycle ratio (n).

The full spectral range of ellipsometric measurements is analyzed to generate a single parametric ε describing the optical response of each film after that described previously for aluminum doped ZnO [52] and borosilicate glass [53]. In the IR to UV range (0.035 to 5.89), the structural model describing the film consists of semi-infinite silicon wafer substrate / thermal oxide / ZnO:H thin film layer / surface roughness / semi-infinite air ambient. A similar structure is used to model SE measurements in the THz range (0.4 to 4.1 meV), except that the silicon wafer substrate thickness is described as a finite-value fit parameter to account for the coherent multiple reflections that occur in this long wavelength range. A Bruggeman effective medium approximation consisting of 0.5 volume fraction ZnO:H and 0.5 fraction void describes ε of the surface roughness layer [54, 55]. The optical response of any seed layers is not separately accounted but included as part of the ZnO:H thin film layer. Although ZnO is uniaxially anisotropic in its single crystal form, the nanocrystalline or polycrystalline nature of the thin films here have a distribution of grain orientations. Therefore, an isotropic model is used to describe spectra in ε . The parametric model describing spectra in ε for ZnO:H consists of a constant additive term to ε_I (ε_∞), a Drude oscillator [56] describing free carrier absorption, a Gaussian oscillator [57, 58] related to IR phonon absorption, and two oscillators assuming critical point parabolic bands (CPPB) [59] to describe higher energy electronic transitions. Thus ε can be written:

$$\varepsilon = \varepsilon_\infty + \varepsilon_{Drude} + \varepsilon_{CPPB} + \varepsilon_{Gaussian}$$

$$\varepsilon = \varepsilon_\infty + \left[\frac{-\hbar^2}{\varepsilon_0 \rho (\tau E^2 + i\hbar E)} \right]_{Drude}$$

$$+ \left[\text{Re} \sum_{l=1}^2 A_l \exp(i\theta_l) \left(\frac{\Gamma_l}{(2E_l - 2E - i\Gamma_l)} \right)^\eta + i \left\{ \text{Im} \sum_{l=1}^2 A_l \exp(i\theta_l) \left(\frac{\Gamma_l}{(2E_l - 2E - i\Gamma_l)} \right)^\eta \right. \right. \left. \left. \begin{array}{ll} \varepsilon_{2,CPPB} \geq 0 \\ 0 & \varepsilon_{2,CPPB} < 0 \end{array} \right\} \right]_{CPPB}$$

$$+ \left[\frac{2}{\pi} P \int_0^\infty \frac{\xi \varepsilon_2(\xi)}{\xi^2 - E^2} d\xi + i A_m \left\{ \exp \left[- \left(\frac{E - E_m}{\left(\frac{\Gamma_m}{2\sqrt{\ln(2)}} \right)} \right)^2 \right] - \exp \left[- \left(\frac{E + E_m}{\left(\frac{\Gamma_m}{2\sqrt{\ln(2)}} \right)} \right)^2 \right] \right\} \right]_{Gaussian}$$

$$\text{Also, } \rho = \frac{m^*}{Nq^2\tau} = \frac{1}{q\mu N}$$

For the Drude oscillator, $\hbar$ ($h/2\pi$) is the reduced Planck's constant, ε_0 is the vacuum permittivity, τ is the scattering time, ρ is the resistivity, m^* is the carrier effective mass, N is the carrier concentration, q is the elementary charge, and μ is the mobility. The shape of each CPPB oscillator depends on four parameters: the amplitude A_l , phase projection factor θ_l , broadening parameter Γ_l , and threshold energy E_l . The exponent (η) in each ε_{CPPB} expression defines the dimensionality of the electronic transition. For ZnO:H thin films studied here, η is fixed to 1 which corresponds to excitonic critical points [60, 61]. Here the imaginary part of ε_{CPPB} is constrained to prevent an unphysical negative contribution to ε_2 . The amplitude A_m , broadening Γ_m , and resonance energy E_m define ε_2 for each Gaussian oscillator, and a Kramers-Kronig transformation of ε_2 generates the contribution to ε_1 .

Fig. 4 shows a representative example experimental ellipsometric spectra and corresponding model fit for S2 ZnO:H film deposited on thermal oxide coated silicon wafers from 0.4 to 4.1 meV (left), 0.035 to 0.75 eV (middle), and 0.75 to 5.89 eV (right), which correspond to the spectra collected from the three instruments, respectively. Similar fits are obtained for other samples, as indicated by low fit errors for each parameter and overall low mean square error σ as listed in Tables 2-4. Table 2 lists the structural parameters in the form of ZnO:H bulk layer thickness, surface roughness layer thickness, thermal oxide layer thickness, and substrate wafer thickness for each sample as determined via SE model fitting. The silicon substrate thicknesses determined from sensitivity within the THz spectral range are listed in Table 2 and agree well with a direct measurement by a micrometer of nominally $520 \pm 10 \mu\text{m}$. Thermal oxide and ZnO:H bulk layer thickness are within expectations for these samples [14]. Given the

fact that larger crystalline grains will protrude upward from the film surface more than smaller grains, the surface roughness thickness can be interpreted as a proxy for grain size. Thus, the generally higher surface roughness of ZnO:H compared to S1 i-ZnO prepared without plasma treatment suggests that plasma treatments promote increased grain size by these accumulated film thicknesses. Additionally, the decreasing surface roughness thicknesses from samples S2 to S4 and from samples S5 to S7 indicate that decreased frequency of H₂ plasma treatments (i.e. larger n) results in reduced grain size in the films. Comparing samples S7 and S2 both prepared using $n = 3$, sample S2 which is prepared without a seed layer shows a higher surface roughness value. To determine seed layer influence on surface morphology of ZnO:H films deposition, the surface roughness of two films grown with the same n on two different seeds are compared. Sample S8 is grown on top of a 5 nm ZnO:H seed and shows higher surface roughness layer thickness than sample S5 prepared on top of a 5 nm i-ZnO seed layer using the same $n = 1$. These results are consistent with atomic force microscopy results reported by Macco *et al.* [14] and the SEM results in Fig. 2 here. Fig. 5 shows example cross-sectional TEMs of S1 and S2. These images also show that the hydrogen plasma treated ZnO:H sample has a rougher surface than that of un-doped i-ZnO [14].

Fig. 4. Example experimental ellipsometric spectra (open symbols) and model fit (solid lines) over the spectral ranges from 0.4 – 4.1 meV (left), 0.035 – 0.75 eV (middle), and 0.75 – 5.89 eV (right) for the S2 ZnO:H thin film deposited on thermal oxide coated silicon.

Fig. 6 shows spectra in ϵ describing all eight ZnO samples from 0.4 to 4.1 meV (left), 0.035 to 0.75 eV (middle), and 0.75 to 5.89 eV (right) respectively. The corresponding parameters that generate the spectra in ϵ shown in Fig. 6 and obtained from the fit of ellipsometric spectra (N , C , S) for each sample, are given in Table 3 and 4. Each oscillator used here to generate the parametric ϵ represents the effect of a different physical phenomenon. The Drude oscillator describes the free carrier absorption contribution to ϵ and dominates the spectra at lower photon energies. The Gaussian oscillator describes absorption due to IR phonon modes. The CPPB oscillators account for the contributions from interband electronic transitions at and above the band gap energy. The first allowed electronic transition defining the band gap is at the position of oscillator CPPB1, and an additional broader absorption above

the band gap is described by the CPPB oscillator labeled CPPB2. The sum of all oscillators results in a single, continuous ϵ that describes the optical response of the material over the full spectral range of 0.4 meV to 5.89 eV.

Fig. 5. Cross-sectional transmission electron microscopy (TEM) of ZnO thin films grown on thermal oxide coated silicon wafers without H₂ plasma treatment (S1) and using $n = 3$ cycle ratio (S2).

The spectra in ϵ from 0.75 to 5.89 eV obtained here for each sample from SE agrees well with previous reports [15, 22, 52]. From CPPB1, the band gaps obtained from the first critical point energy of the samples are found to be 3.42 – 3.52 eV, which agree well with literature reported values for similar materials [10]. The phonon absorption features are observed in the IR, shown in the middle panel of Fig. 6. Since free carrier absorption is strong in the IR, these measurements are only capable of resolving a single transverse phonon mode due to Zn-O bonding, modeled by one Gaussian oscillator with resonance energy near 0.042 – 0.049 eV (339 – 395 cm⁻¹) [22, 52]. Fig. 6 shows that there is no significant change in the near-IR to UV optical properties, except for slight blue shifting in the optical band edge for all the H₂ plasma treated ZnO samples relative to i-ZnO as listed in Table 3 as shown in inset graph of Fig. 6 (right). By decreasing n from 10 to 3 (S4 → S2) and 3 to 1 (S7 → S5), the band gaps increase. N increases with decreasing n for the films deposited on a seed layer but does not vary as much for those prepared without a seed layer. This increase in optical band gap with increase in frequency of H₂ plasma treatment (or decrease in n) during deposition of ZnO samples is due to Burstein-Moss effect [62, 63]. Sample S7 and S2 which are prepared using the same n with an i-ZnO seed layer and without a seed layer, respectively, show the same optical band gap value. However, sample S5 which is prepared on top of an i-ZnO seed layer has a higher value of optical band gap than the sample S8 prepared on top of ZnO:H seed layer using same $n = 1$. This indicates though the frequency of H₂ plasma treatment is the same, the optical band gap is influenced by the seed layer on which the films are grown.

Table 2

Structural parameters of each sample obtained from analysis of spectroscopic ellipsometry data.

Samples	Surface roughness layer thickness (Å)	ZnO:H bulk layer thickness (nm)	Thermal oxide thickness (nm)	Substrate thickness (μm)
S1	5.2 ± 0.2	69.2 ± 0.2	439.3 ± 0.1	534.0 ± 0.2
S2	8.6 ± 0.2	71.9 ± 0.2	438.2 ± 0.1	535.5 ± 0.3
S3	5.3 ± 0.2	71.3 ± 0.2	438.2 ± 0.3	534.3 ± 0.3
S4	4.5 ± 0.2	76.0 ± 0.1	437.3 ± 0.3	533.6 ± 0.3
S5	11.0 ± 0.2	68.2 ± 0.1	437.0 ± 0.1	534.7 ± 0.4
S6	8.7 ± 0.2	67.2 ± 0.1	439.0 ± 0.1	534.2 ± 0.3
S7	5.9 ± 0.2	68.4 ± 0.2	438.2 ± 0.1	534.6 ± 0.3
S8	16.9 ± 0.2	69.8 ± 0.2	436.5 ± 0.6	531.3 ± 0.4

Table 3

Parameters describing complex dielectric function, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, spectra for ZnO and ZnO:H samples. Root mean square error (σ) for the analysis of each sample yielding these results and those in Tables 2 and 4 are also listed.

Samples	S1	S2	S3	S4	S5	S6	S7	S8
Root mean square error (σ)	1.9×10^{-2}	1.8×10^{-2}	2.0×10^{-2}	1.8×10^{-2}	2.0×10^{-2}	1.8×10^{-2}	1.8×10^{-2}	1.7×10^{-2}
ε_∞	3.16 ± 0.01	3.14 ± 0.07	3.17 ± 0.01	3.18 ± 0.01	3.13 ± 0.01	3.15 ± 0.01	3.16 ± 0.01	3.10 ± 0.01
CPPB1	Amplitude A_1 (Unitless)	2.14 ± 0.03	2.14 ± 0.01	2.13 ± 0.03	2.17 ± 0.03	2.05 ± 0.03	2.15 ± 0.03	2.20 ± 0.03
	Resonance Energy E_1 (eV)	3.42 ± 0.01	3.44 ± 0.01	3.44 ± 0.01	3.43 ± 0.01	3.52 ± 0.01	3.48 ± 0.01	3.44 ± 0.01
	Broadening Γ_1 (eV)	0.65 ± 0.01	0.59 ± 0.01	0.62 ± 0.01	0.61 ± 0.01	0.65 ± 0.01	0.62 ± 0.01	0.60 ± 0.01
	Phase θ_1 ($^\circ$)	-73 ± 1	-73 ± 1	-73 ± 1	-73 ± 1	-71 ± 1	-75 ± 1	-70 ± 1
CPPB2	Amplitude A_2 (Unitless)	1.66 ± 0.02	1.62 ± 0.02	1.62 ± 0.02	1.62 ± 0.01	1.71 ± 0.03	1.65 ± 0.02	1.66 ± 0.02
	Resonance Energy E_2 (eV)	6.17 ± 0.03	6.10 ± 0.03	6.10 ± 0.04	6.00 ± 0.03	6.17 ± 0.04	6.15 ± 0.03	6.14 ± 0.04
	Broadening Γ_2 (eV)	4.4 ± 0.1	4.1 ± 0.1	4.2 ± 0.1	4.1 ± 0.1	3.9 ± 0.1	4.2 ± 0.1	4.2 ± 0.1
	Phase θ_2 ($^\circ$)	0 (fixed)	0 (fixed)	0 (fixed)	0 (fixed)	0 (fixed)	0 (fixed)	0 (fixed)
Gaussian	Amplitude A_m (Unitless)	38 ± 2	52 ± 3	43 ± 2	41 ± 2	44 ± 2	44 ± 2	41 ± 2
	Resonance Energy E_m (eV)	0.045 ± 0.001	0.049 ± 0.001	0.042 ± 0.001	0.045 ± 0.001	0.045 ± 0.001	0.046 ± 0.001	0.046 ± 0.001
	Broadening Γ_m (eV)	0.016 ± 0.001	0.0065 ± 0.0004	0.021 ± 0.001	0.016 ± 0.001	0.017 ± 0.001	0.015 ± 0.001	0.015 ± 0.001

By contrast, in the IR range, the phonon and free carrier absorption, and in the THz range, the free carrier absorption, effects are seen to vary significantly with the varying H₂ plasma treatment routines. As shown in Fig. 6 (middle), the change in amplitude, position and broadening of Gaussian oscillator representing the phonon absorption feature may be correlated with changes in morphology (Fig. 2). The amplitudes of the phonon absorption peak in ε_2 as shown in Fig. 6 (middle) are found to be 38 – 52. The amplitude of the phonon peak in the film with no H₂ treatment is lower than others with H₂ plasma treated films. With decreasing n from 10 to 3 (S4 $\rightarrow$ S2) and from 3 to 1 (S7 $\rightarrow$ S5), the amplitude of phonon absorption is found to increase, along with the slight change in position and broadening. Sample S5 and S8 which are grown on two different seed layers using the same n have comparable phonon mode peak magnitudes. Though the cycle ratio n is same for samples S2 and S7, S2 prepared without a seed layer has a significantly higher and narrower phonon absorption peak compared to that of the S7 film prepared on top of the 5 nm i-ZnO seed layer. This more well-defined peak also supports the previous discussion from the SEM results that sample S2 without a seed layer has larger grains and better crystallinity relative to S7 with a seed layer. The i-ZnO film grown without plasma treatment (S1) and ZnO:H film grown with cycle ratio $n = 1$ on a top of 5 nm seed layer of ZnO:H with $n = 3$ (S8) have lowest and highest values of free carrier absorption, respectively, as seen in the low-energy amplitude of ε_2 . As can be seen for the sample sequences S4 $\rightarrow$ S2 (i.e. $n = 10$ to 3) and S7 $\rightarrow$ S5 (i.e. $n = 3$ to 1), decreasing n results in increased magnitude of free carrier optical absorption. Considering the two films grown with $n = 3$, the film grown without a seed layer (S2) has greater free carrier absorption than the film grown on the top of an i-ZnO seed layer (S7). Comparing the ZnO:H samples deposited on two different seed layers, sample S8 grown on the 5 nm seed layer of ZnO:H has significantly stronger free carrier absorption than sample S5

grown on the 5 nm i-ZnO seed layer though both are grown with same $n = 1$. These results reveal that not only n but also the seed layer on which the films grow greatly impacts the phonon and free carrier absorption features at low photon energies along with the surface morphologies.

With the relations given in equation 3, Drude ρ and τ or alternately m^* and μ when N is fixed from direct electrical Hall effect measurements are extracted and reported in Table 4. The i-ZnO sample grown without H_2 plasma treatment has the highest ρ of $6.20 \times 10^{-3} \Omega \cdot \text{cm}$, whereas the ZnO:H film grown with cycle ratio $n = 1$ on top of a 5 nm ZnO:H seed layer with $n = 3$ has the lowest value of $2.06 \times 10^{-3} \Omega \cdot \text{cm}$. All other films have ρ intermediate to these extremes. In general, it is seen that ρ increases with increasing n . While comparing ZnO:H samples prepared with and without seed layer using same $n = 3$, the resistivity value is lower for the sample grown without a seed layer (S2) compared to that grown on i-ZnO seed (S7). Regarding $n = 1$ ZnO:H samples on two different seed layers, the resistivity of sample grown on the ZnO:H seed layer is lower than the sample grown on the i-ZnO seed layer. The good correspondence between ρ optically-extracted from the Drude model, ρ extracted from Hall effect measurements, and ρ obtained via four-point probe measurement is shown in Fig. 7. Hall effect ρ [14] are found to be slightly lower than optical ρ from the Drude model and direct electrical ρ from four-point probe. The source of the discrepancy between optical ρ and Hall ρ could potentially be the fact that the sample depositions and Hall effect measurements have been performed at Eindhoven University of Technology, The Netherlands, with SE and direct 4-point probe measurements performed later at the University of Toledo, USA. Regardless, the generally linear relationship between ρ obtained from the full spectral range SE analysis (THz + FTIR + UV) and direct electrical measurements like Hall effect and four-point probe measurements demonstrate the reliability of wide-spectral-range SE for electrical property characterization. These results corroborate previous findings demonstrating the importance of collecting low photon energy ellipsometric spectra (i.e. into the THz range) in order to achieve good agreement with direct electrical measurements [52, 64, 65].

Fig. 6. Complex dielectric function, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, spectra from 0.4 – 4.1 meV (left), 0.035 – 0.75 eV (middle), and 0.75 – 5.89 eV (right) for i-ZnO, and ZnO:H thin films deposited on thermal oxide coated silicon wafers. Regions of data collection are indicated by solid lines + symbols with extrapolation between measured regions by dotted grey lines.

The values of optical μ determined here from SE range from 29.5 to 41.5 cm^2/Vs . These values are relatively smaller than the values obtained from Hall measurements [14]; which may also be due to the measurements occurring at different times and possible sample aging. The H_2 plasma treatments improve the Hall mobility relative to the i-ZnO film with weaker difference seen in the optical mobility in some cases. The results show that optical μ generally decreases with increasing n , except the S6 has slightly higher μ than S5. While comparing optical μ for the ZnO:H films grown with the same cycle ratio $n = 3$, the ZnO:H film grown without a seed layer has higher μ than that of the ZnO:H film grown on the top of a 5 nm i-ZnO seed layer, likely here related to an expected decrease in μ with increasing N . To investigate the impact of seed layer on the mobility of ZnO:H films, the films prepared using same n on two different seed layers are compared. The mobility of ZnO:H grown on the $n = 1$ ZnO:H seed layer is

higher than the ZnO:H film grown on the i-ZnO seed layer. In terms of ρ and μ , the samples prepared without seed layer or with the ZnO:H seed layer are found to have increased electrical conductivity (i.e. lower ρ and higher μ) than the ZnO:H sample prepared on the i-ZnO seed layer for the same n . And for the same n , the N for the ZnO:H film grown on the same type of seed is slightly higher than the film grown on an i-ZnO seed. The range of 3.80 – 6.40 fs for τ determined here agrees reasonably well with other values reported in literature for ZnO films of comparable resistivity (i.e. in the $\sim 10^{-3} \Omega \cdot \text{cm}$ range) prepared by other methods [52, 66]. The values of m^* determined here from Drude equation are 0.22 – 0.29 m_e and agree well with the values reported for ZnO [67, 68]. The τ and m^* for H₂ treated samples are higher than i-ZnO, and their values decrease systematically with decreasing n (or increasing N) for the ZnO:H films on the 5 nm i-ZnO seed layer. Overall, varying the H₂ plasma treatment configurations have been demonstrated as a means of manipulating the electronic transport properties of ZnO films.

In a single crystal material, the transport properties such as μ and m^* always vary systematically in such a way that as N increases, μ decreases [69-71] and m^* increases [72-76]. However, in polycrystalline materials, the values of μ and m^* are influenced by film morphologies such as grains size and grain boundaries [75-79]. TCO films exhibit nanocrystalline, polycrystalline, or amorphous microstructures such that the grain size, grain boundaries, or ordered regions significantly impact transport properties, and therefore alter the general trend expected for single crystals. For instance, μ decreases and m^* increases as N increases from S3 to S4; and μ increases and m^* decreases as N increases from S3 to S2. Significantly higher μ of S2 is observed here compared to S3 and S4 with comparable N , which may be linked to the increased grain size and more symmetrical grains of S2 compared to others as is observed from XRD [14], SEM, and the IR phonon mode broadness. Similarly, μ increases and m^* decreases as N increases for the samples grown on 5 nm i-ZnO seed layers (S7 $\rightarrow$ S5). From SEM results, grain size increases from S7 to S5 which reduces contributions from grain boundaries and hence increases μ . Comparing samples S2 and S7 prepared with same $n = 3$ on two different substrate compositions, S2 has lower N and m^* , but significantly higher μ than that of S7 possibly due to increased grain size. To summarize, though there is no specific trend observed in the values of μ and m^* with increasing N , film morphologies are correlated to the transport properties.

Table 4

Drude parameters describing spectra in ε for i-ZnO and ZnO:H, and their comparison with transport properties from Hall effect and four-point probe direct electrical measurements.

Samples	4-point probe	Hall parameters [14]			Drude parameters			
	$\rho (\Omega \cdot \text{cm})$	$\rho (\Omega \cdot \text{cm})$	$N (\text{cm}^{-3})$	$\mu (\text{cm}^2 \text{V}^{-1} \text{s}^{-1})$	$\rho (\Omega \cdot \text{cm})$	$\tau (\text{fs})$	$m^*(\times m_e)$	$\mu (\text{cm}^2 \text{V}^{-1} \text{s}^{-1})$
S1	6.80×10^{-3}	6.60×10^{-3}	3.37×10^{19}	27.1	$(6.2 \pm 0.1) \times 10^{-3}$	3.80 ± 0.06	0.228	29.6
S2	3.43×10^{-3}	2.81×10^{-3}	4.47×10^{19}	47.3	$(3.31 \pm 0.04) \times 10^{-3}$	6.21 ± 0.05	0.266	41.5
S3	4.45×10^{-3}	4.24×10^{-3}	4.41×10^{19}	36.4	$(4.30 \pm 0.07) \times 10^{-3}$	4.32 ± 0.08	0.237	32.5
S4	4.46×10^{-3}	4.08×10^{-3}	4.85×10^{19}	34.8	$(4.25 \pm 0.05) \times 10^{-3}$	4.47 ± 0.07	0.266	29.9
S5	2.68×10^{-3}	1.92×10^{-3}	7.23×10^{19}	40.3	$(2.65 \pm 0.03) \times 10^{-3}$	4.48 ± 0.05	0.248	32.2
S6	3.04×10^{-3}	2.41×10^{-3}	6.98×10^{19}	36.3	$(2.70 \pm 0.03) \times 10^{-3}$	4.67 ± 0.06	0.254	32.7
S7	3.98×10^{-3}	3.70×10^{-3}	5.25×10^{19}	32.1	$(3.98 \pm 0.07) \times 10^{-3}$	4.80 ± 0.07	0.289	29.5
S8	2.34×10^{-3}	1.78×10^{-3}	7.77×10^{19}	45.8	$(1.95 \pm 0.02) \times 10^{-3}$	6.40 ± 0.06	0.284	40.1

Fig. 7. Comparison of ρ determined from both the Drude model (optical resistivity) and Hall effect (Hall resistivity) with ρ determined from four-point probe measurement. Dotted line represents a 1:1 relationship.

Evaluating all the results, it is seen that there is a significant impact of H_2 plasma treatments and seed layers on the morphological, optical, and electrical properties of the ZnO films. The grain size of the films is bigger and more symmetrical with reduced n . The optical band gaps of ZnO:H samples also increase with decreasing n . Similar to the trend observed in morphologies, the amplitudes of Gaussian oscillator representing phonon absorption also clearly increases with reducing n . Again, the free carrier absorption of the films increases with the result of decreasing n . This trend observed in free carrier absorption due to plasma treatments causes the variation in the transport properties such as ρ , N and μ , in such a way that ρ decreases or N and μ increase with decreasing n . Regarding the impact of a seed layer, the ZnO:H samples prepared using the same n on a ZnO:H seed layer or without a seed layer have higher surface roughness layer thickness, higher free carrier absorption, lower ρ , and higher μ than those samples prepared on an i-ZnO seed layer. The electrical transport properties determined here from Drude model with the inclusion of THz range ellipsometry agree well with Hall effect and 4-point probe direct electrical measurements, although Hall effect resistivity is systemically lower than the other techniques possibly due to the different times at which the measurements had been collected. In addition to degree of H_2 plasma treatment and nature of the underlying surface, low energy native defects may also have some influence on the variation of these optoelectronic properties of ZnO films. The original defect states and their concentrations of ZnO may change after the plasma treatment. Also, the presence and influence of some defects may arise from the nature of the underlying substrate and its impact on the film growth evolution. Changes in the defect states may impact the optoelectronic properties of the films, which is not considered in this work, but would be interesting for further study.

4. Conclusions

A novel supercycle approach of ALD interleaved with H_2 -plasma treatments is used to prepare high mobility ZnO:H thin films. The surface morphology, optical response, and electrical properties of the films have been studied with SEM, SE, and direct electrical measurement techniques. Variation in how the H_2 plasma treatment is applied is found to influence resultant film properties. Application of H_2 plasmas enhances grain size and modifies dominant grain orientation. Additionally, increased H_2 plasma treatments result in larger N and μ , corresponding to a reduction in ρ . The optical properties in the form of ε are determined from 0.4 to 4.1 meV and 0.035 to 5.89 eV for all ZnO films. The H_2 plasma treatment is found to increase grain size in the films with decreasing n . Increases in the surface roughness with decreasing n determined from SE correspond to the known increases in crystallinity that accompany decreasing n . These variations in the surface morphologies with H_2 plasma treatment appear to be correlated with the optical and electrical properties of the films. Optical band gaps are found to be higher in films prepared with more

frequent H₂ plasma treatments. The amplitude of the Gaussian oscillator representing phonon absorption is found to increase with decreasing n . The magnitude of free carrier absorption shown in ε_2 at lower photon energy ranges is found to increase with H₂ plasma treatment, and the magnitude decreases with increasing n . These variations in free carrier absorption with n impact the transport properties in such a way that, ρ decreases or N and μ increase with more frequent H₂ plasma treatment during deposition of ZnO thin films. While considering the impact of the seed layer, the samples prepared using the same n with a ZnO:H seed or without any seed layers have higher values of ε_2 at lower photon energy ranges as well as lower ρ and higher μ than those prepared on i-ZnO seed layers. ρ and μ determined here from SE using THz range SE measurements are found to be in good agreement with direct electrical measurements. The analysis of wide spectral range SE provides access to phonon modes, the band gap, and electrical transport properties for these TCO thin films. When combined with N from Hall effect, m^* is deduced from spectra in ε obtained from SE. To summarize, these results illustrate the fabrication conditions such as substrate composition and how frequently H₂ plasma treatment occurred during deposition affect the degree of crystallinity as well as the optical and electrical properties of ZnO films. The ZnO:H samples fabricated with lower n show a great degree of crystallinity, higher optical band gap, more pronounced phonon mode absorption, and increased free carrier absorption accompanied by lower ρ with higher N and μ . These variations in morphological, optical, and electrical properties with n occur more systematically with the ZnO:H films grown on a 5 nm seed of i-ZnO.

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