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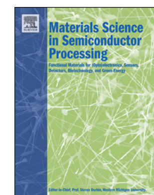

Optical and electrical properties of H_2 plasma-treated ZnO films prepared by atomic layer deposition using supercycles

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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 H_2 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 ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) 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 H_2 plasma treatments during deposition. The amplitude of phonon absorption is increased with decreasing n. Free carrier transport characteristics are determined by applying the Drude model in modeling ε, and the 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 as an effective mean of controlling the resultant opto-electronic film properties.

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 SnO_2, ZnO, and In_2O_3. For carrier density values $\sim 10^{20}$ cm^{-3}, the upper limits of mobility resulting from intrinsic scattering are found to be $\sim$130 and 55 cm^2/Vs for In_2O_3 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 In_2O_3 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 H_2 ambient [11], and exposure to H_2 plasma [12,13]. Ding et al. reported that mobility (μ) of 46 cm^2/Vs can be achieved with exposure of a 350 nm thick ZnO film into H_2 plasma after deposition [13]. ZnO:H film $\mu = 47.1$ cm^2/Vs, carrier concentration (N) of 4.4×10^{19} cm^{-3}, and resistivity (ρ) of 2.8 mΩ 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 $\mu = 20$ cm^2/Vs, $N = 4.6 \times 10^{20}$ cm^{-3}, and ρ of 0.7 mΩ cm can be prepared using interleaved standard atomic layer deposition (ALD) ZnO

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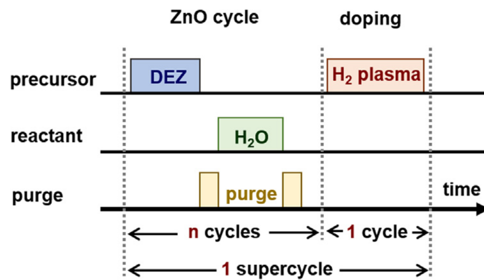

Fig. 1. Schematic of supercycle approach of the atomic layer deposition (ALD) process for high mobility ZnO:H. A supercycle constitutes *n* cycles of ALD ZnO followed by one cycle of H_2 plasma treatment.

cycles comprised of diethylzinc (DEZ, $Zn(C_2H_5)_2$) 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 $\mu \sim 47\ cm^2/Vs$ and ρ of 1.8 mΩ 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].

In terms of optical response, the complex dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) 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 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 spectroscopies, and found blue shifting in optical band gap with increased 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 (3.1–0.3 mm) and the IR to UV spectral range from 0.035 to 5.89 eV (35.4–0.210 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

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