



Atomic layer deposition of high-mobility hydrogen-doped zinc oxide



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ABSTRACT

In this work, atomic layer deposition (ALD) has been employed to prepare high-mobility H-doped zinc oxide (ZnO:H) films. Hydrogen doping was achieved by interleaving the ZnO ALD cycles with H₂ plasma treatments. It has been shown that doping with H₂ plasma offers key advantages over traditional doping by Al and B, and enables a high mobility value up to 47 cm²/Vs and a resistivity of 1.8 mΩcm. By proper choice of a deposition regime where there is a strong competition between film growth and film etching by the H₂ plasma treatment, a strongly enhanced grain size and hence increased carrier mobility with respect to undoped ZnO can be obtained. The successful incorporation of a significant amount of H from the H₂ plasma has been demonstrated, and insights into the mobility-limiting scatter mechanisms have been obtained from temperature-dependent Hall measurements. A comparison with conventional TCOs has been made in terms of optoelectronic properties, and it has been shown that high-mobility ZnO:H has potential for use in various configurations of silicon heterojunction solar cells and silicon-perovskite tandem cells.

1. Introduction

Thin films of transparent conductive oxides (TCOs) are commonly used as transparent electrodes in a wide range of solar cell architectures, such as silicon heterojunction (SHJ), Copper indium gallium selenide (CIGS), and perovskite solar cells. Often-employed TCO materials are based on indium oxide (In₂O₃), zinc oxide (ZnO) and tin oxide (SnO₂). Ideally, such TCO layers are both highly conductive and optically transparent in order to minimize ohmic and optical losses, respectively. In order to achieve a sufficient level of conductivity, typically on the order of 1 mΩcm or lower, the carrier density in these materials is raised to the order of 10¹⁹–10²⁰ cm⁻³ by the introduction of n-type dopants, such as Sn in In₂O₃, Al or B in ZnO and F in SnO₂. However, increasing the conductivity by increasing the carrier density comes at the expense of reduced optical performance: At high carrier densities, the plasma frequency of the TCO enters the near infrared (NIR) range, and the free carriers start to affect the dielectric function in the NIR through the so-called Drude contribution. The extinction coefficient *k* is increased, leading to free-carrier absorption (FCA), whereas the refractive index *n* is decreased, leading to a non-ideally matched antireflection coating and thus free-carrier reflection (FCR). This is especially detrimental for solar cells for which the absorber layer has a band gap in the NIR, such as SHJ solar cells. For example, the

optical losses induced by free-carrier effects in conventional Sn-doped In₂O₃ (ITO) used as front electrode in SHJ solar cells in terms of photocurrent have been quantified by optical simulations to be around 2.4 mA/cm², compared to the 44 mA/cm² available in the AM1.5 g spectrum [1]. Because of these adverse effects induced by the free carriers, it is preferred to achieve a high level of conductivity through a high carrier mobility (i.e. low scattering of electrons) rather than through a high density of electrons.

In order to achieve a high mobility, the TCO material must be engineered such that electrons experience as little scattering as possible. In TCO materials there are various scattering mechanisms that play a role. Scattering from phonons and ionized dopants is in a sense unavoidable, and are therefore labelled as *intrinsic* scatter mechanisms. Other scatter mechanisms are related to material quality, and are called *extrinsic* scatter mechanisms. Examples of the latter mechanisms include scattering at grain boundaries, at impurities and at ineffective or clustered dopants. Therefore, the general aim is to mitigate the *extrinsic* scatter mechanisms such that the mobility limit set by the *intrinsic* scatter mechanisms is reached. For the carrier density range of interest of around 10²⁰ cm⁻³, the upper limit for the mobility set by the intrinsic scatter mechanisms is about ~55 cm²/Vs for ZnO-based and ~130 cm²/Vs for In₂O₃-based TCOs. [2,3].

In the case of In₂O₃-based TCOs, ITO has historically been the TCO

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material of choice. Nonetheless, its typical mobility value of 20–40 cm²/Vs [4] is well below the mobility limit set by the intrinsic scatter mechanisms. Therefore, in recent years there has been a strong interest in various *high-mobility* In₂O₃-based TCOs which employ novel dopants such as H, W and Mo. [5–8] Especially H-doped In₂O₃ (In₂O₃:H) has been shown to yield record high mobility values of 130 cm²/Vs, which is as high as the mobility limit [3]. This high-quality material has been prepared both by sputtering [5] and by atomic layer deposition (ALD) [6]. The enhanced mobility lowers the required carrier density to the low 10²⁰ cm⁻³ regime, thereby almost completely negating IR-losses and enhancing the *J*_{sc} of SHJ solar cells when applied as the front electrode [9,10]. The enhanced mobility enabled by the H dopant compared to the traditional Sn dopant is mainly ascribed to two key factors: Firstly, grain boundary scattering has been found to be negligible in H-doped In₂O₃. This has been attributed to the fact that H-doped In₂O₃ has very large grains of a few hundred nanometer. [3,5,6,11] In addition, the grain boundaries are well-passivated by the available H. Secondly, inactive H dopants have been shown to not contribute to electron scattering. [3].

Although such high-mobility In₂O₃-based TCOs yield excellent performance, concerns regarding the scarcity and price of indium are a strong driver to replace In₂O₃-based TCOs with doped ZnO-based TCOs. Despite many efforts, the level of performance in terms of optical transparency and electrical conductivity offered by Al- or B-doped ZnO TCOs is not on par with the In₂O₃-based TCOs. Experimentally-obtained mobility values are typically well below 30 cm²/Vs. Therefore, keeping the aforementioned mobility limit of ZnO films of ~55 cm²/Vs in mind, there is a lot of room for improvement of doped ZnO TCOs.

Similar as for In₂O₃, also in the case of ZnO hydrogen has emerged as a very promising alternative dopant. *Ab initio* calculations show that bond-centered (BC) H is the most stable configuration and acts as a shallow donor. [12,13] Experimentally, the beneficial effect of H on ZnO has been reported being either through H being embedded during deposition [14,15], by annealing in H₂ atmosphere [16], or through exposure to H₂ plasma [17,18]. For example, Ding *et al.* showed that mobility values as high as 58 and 46 cm²/Vs could be obtained for 2 μm and 350 nm thick films by exposing these films to H₂ plasma after deposition. [18] Gaspar *et al.* recently showed that high-mobility ZnO:H can be prepared by the addition of H₂ during rf reactive magnetron sputtering. [19] They achieved an optimized mobility value of 47.1 cm²/Vs and a carrier density of 4.4 × 10¹⁹ cm⁻³, resulting in a resistivity value of 2.8 mΩ cm. In addition, Thomas *et al.* have shown that ZnO:H can be prepared by ALD. [15] They interleaved standard ALD ZnO cycles comprised of diethylzinc (DEZ, Zn(C₂H₅)₂) and H₂O exposures with H₂ plasma exposures, and reached much higher carrier density values of up to 4.6 × 10²⁰ cm⁻³, respectable mobility values around 20 cm²/Vs and low resistivity values down to 0.7 mΩ cm.

In this work, we employ a process consisting of thermal ALD in conjunction with interleaved H₂ plasma treatments to prepare ZnO:H films, similar to the approach of Thomas *et al.* [15] It will be shown that the H₂ plasma treatment has an etching component that can be employed to strongly enhance the structural and optoelectronic properties of the ZnO:H films. More specifically, by growing ZnO:H films in a regime where film nucleation is in strong competition with etching from the H₂ plasma, a strong enhancement of the grain size and a preferential c-axis orientation can be obtained. Under such conditions, our process results in high-mobility (~47 cm²/Vs) and conductive (~1.8 mΩ cm) ZnO:H with excellent IR-transparency. Furthermore, insights into the doping by the H₂ plasma and into the electron scatter mechanisms in our high-mobility ZnO:H have been obtained from effusion and temperature-dependent Hall measurements, respectively. Finally, the material properties of ALD ZnO:H are compared to conventional TCO materials, and the potential of ALD ZnO:H for the application in various Si solar cell configurations is discussed.

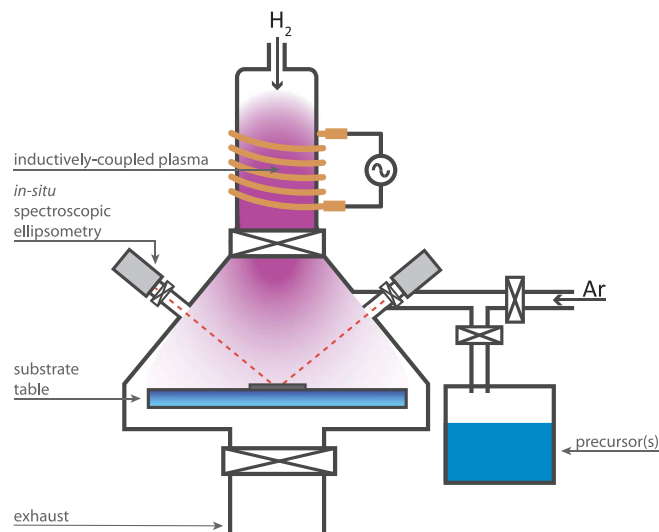


Fig. 1. Schematic of the Oxford Instruments OpAL ALD reactor used in this work. The spectroscopic ellipsometer used for in-situ film thickness determination is shown as well. Note that multiple precursor pots have been used in this work (for DEZ and H₂O), but that only one is shown.

2. Experimental section

Silicon wafers coated with ~430 nm of thermal oxide were used as substrates. ~75 nm thick H-doped ZnO films were deposited in an Oxford Instruments OpAL ALD reactor at a substrate temperature of 200 °C. DEZ and deionized water vapor were used as precursors for ZnO growth. A schematic of the setup is shown in Fig. 1.

H doping was achieved by interleaving H₂ plasma treatments every *n* ALD cycles, in a so-called supercycle fashion as shown in Fig. 2. The integer *n*, i.e. the number of ZnO cycles in between the H₂ plasma treatments, is called the cycle ratio. A remote inductively coupled plasma was used for the H₂ plasma treatment, with a plasma power of 100 W, a H₂ flow of 50 sccm and an exposure time of 4 s being the standard condition.

Film growth was monitored in-situ by spectroscopic ellipsometry (SE). The SE setup used for these measurements is a J. A. Woollam Co. Inc. M-2000D spectrometer with an XLS-100 light source (0.7–5.0 eV of photon energy). For analysis of the SE data, the dielectric function of the ALD ZnO:H films was modeled using a combination of a Tauc-Lorentz, Gaussian and Drude oscillator. [20] The electrical properties were determined from Hall measurements (Ecopia HMS-5300 Hall Effect Measurement System). In addition, temperature-dependent Hall measurements down to 80 K were performed using a stage cooled by liquid nitrogen. The surface morphology was evaluated by atomic force microscopy using a NT-MDT Solver P47 microscope in tapping mode

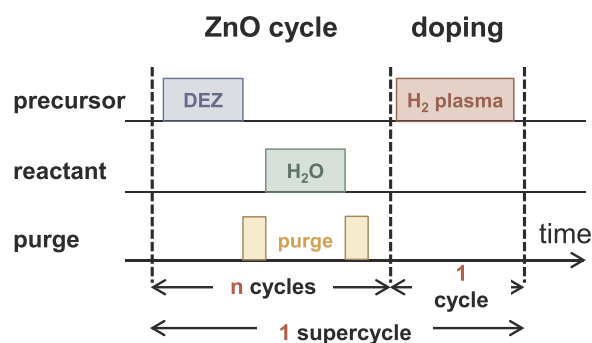


Fig. 2. Schematic of the so-called supercycle approach used to prepare ZnO:H. After *n* cycles of ALD ZnO, the film is exposed to a H₂ plasma treatment. Together, these *n* ZnO cycles and H₂ plasma treatment constitute a supercycle.

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