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Epitaxial Sb-doped SnO_2 and Sn-doped In_2O_3 transparent conducting oxide contacts on GaN-based light emitting diodes

Min-Ying Tsai [a], Oliver Bierwagen [b,c,*], James S. Speck [b]

[a] Department of Electrical and Computer Engineering, University of California, Santa Barbara, CA 93106, USA
[b] Materials Department, University of California, Santa Barbara, CA 93106, USA
[c] Paul-Drude-Insitut für Festkörperelektronik, Hausvogteiplatz 5-7, 10117 Berlin, Germany

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ABSTRACT

We demonstrate the growth of epitaxial (100)-oriented, rutile Sb-doped SnO_2 (ATO) and (111)-oriented, cubic Sn-doped In_2O_3 (ITO) transparent conducting oxide (TCO) contacts on top of an InGaN/GaN(0001) light emitting diode (LED) by plasma-assisted molecular beam epitaxy (PAMBE). Both oxides form rotational domains. The in-plane epitaxial alignment of the two ITO(111) rotational domains to the GaN(0001) was: GaN [21-10]||-$ITO_{Domain1}$[-211]|| $ITO_{Domain2}$[-1-12]. A growth temperature as low as 600 °C was necessary to realize a low contact resistance between ATO and the top p-GaN layer of the LED but resulted in non-optimal resistivity (3.4×10^{-3} Ω cm) of the ATO. The current–voltage characteristics of a processed LED, however, were comparable to that of a reference LED with a standard electron-beam evaporated ITO top contact. At short wavelengths, the optical absorption of ATO was lower than that of ITO, which is beneficial even for blue LEDs. Higher PAMBE growth temperatures resulted in lower resistive ATO but higher contact resistance to the GaN, likely by the formation of an insulating Ga_2O_3 interface layer. The ITO contact grown by PAMBE at 600 °C showed extremely low resistivity (10^{-4} Ω cm) and high crystalline and morphological quality. These proof-of-principle results may lead to the development of epitaxial TCO contacts with low resistivity, well-defined interfaces to the p-GaN to help minimize contact losses, and enable further epitaxy on top of the TCO.

1. Introduction

Recent developments in GaN-based optoelectronic devices including light emitting diodes (LEDs), laser diodes, and solar cells have drawn much attention to the problem of attaining low resistance ohmic contacts to both n- and p-type GaN for the improvement of the device performance. In general, a low Schottky barrier or heavily doped GaN is needed for the formation of high-quality ohmic contacts. For n-type GaN, ohmic contacts can be easily formed by using metals with a work function smaller than that of n-type GaN. Low contact resistances ranging from 10^{-5} to 10^{-8} Ω cm^2 have been reported for state-of-the-art devices. On the other hand, metals with large work functions are necessary to produce ohmic contacts to p-type GaN. However, due to the difficulty in growing highly doped p-type GaN, appropriate metals to form specific contact resistances lower than 10^{-4} Ω cm^2 are absent. Furthermore, the high resistivity of p-type GaN leads to current crowding under the p-type electrode, which limits the efficiency of the devices.

Therefore, a contact layer with high electrical performance not only can avoid a large voltage drop across the GaN/contact interface, but also provide uniform current spreading to maximize the efficiency of light generation. The thin metal-based (e.g., Ni/Au) contacts annealed under an oxygen environment were first used as a semitransparent conducting layer. However, due to the poor transparency (around 70%) and significant absorption in the visible blue-green spectral regime of 450 to 550 nm [1], it has mostly been replaced by indium tin oxide (highly Sn-doped In_2O_3) as transparent electrode today. Indium tin oxide (ITO) contacts have a transparency up to 90% and resistivity down to 10^{-4} Ω cm [2,3]. Recently, the potentially advantageous use of ITO even as cladding layer in GaN-based laser diodes has been demonstrated [4].

Due to the scarcity of indium resulting in increased fabrication costs, other transparent conducting oxides (TCOs) such as binary and ternary compounds consisting of SnO_2 and ZnO are being studied as alternatives to ITO [2,5–7]. Doped ZnO, in particular, has been intensively explored as it shares the wurtzite crystal structure with GaN [2,8–10]. With high thermal and chemical stability, highly transparent and conductive doped SnO_2 is also used as transparent electrodes for LEDs and photovoltaic technologies [11–13]. Sb_{sn}, F_o and Ta_{sn} are common n-type donors in SnO_2. The n-type conductivity of SnO_2:F thin film with low resistivity of 3.9×10^{-4} Ω cm and carrier concentration of 4.7×10^{20} cm^{-3} was reported by Yadav et al. by spraying solution [14]. Kim et al. also demonstrated a comparable resistivity of

* Corresponding author at: Paul-Drude-Insitut für Festkörperelektronik, Hausvogteiplatz 5-7, 10117 Berlin, Germany
E-mail address: bierwagen@pdi-berlin.de (O. Bierwagen).

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5×10^{-4} Ω cm for SnO_2:F thin film by pulse laser deposition [15]. A Ta-doped SnO_2 grown on the TiO_2 substrate shown by Toyosaki et al. revealed a resistivity as low as 1.1×10^{-4} Ω cm which is similar to the lowest value of epitaxial ITO [16]. A detailed study of electrical properties on Sb-doped SnO_2 (ATO) oriented along [200] by spray pyrolysis technique were reported by Goyal et al. showing lowest electrical resistivity of 5.4×10^{-4} Ω cm [17]. More recently, White et al. showed a systematic study of single crystalline Sb-doped SnO_2(101) on r-plane sapphire substrates grown by plasma-assisted molecular beam epitaxy (PAMBE) [18]. With a doping concentration of 2.6×10^{20} cm^{-3}, a low resistivity of 6.7×10^{-4} Ω cm was achieved. Based on these promising transport properties, ATO was also proposed as a potential transparent electrode for InGaN/GaN LEDs.

While most optoelectronic device research and applications rely on polycrystalline TCOs, the possibility to realize epitaxial TCOs has been widely neglected. Potential advantages of epitaxial TCOs on optoelectronic devices are improved TCO transport properties due to higher crystalline quality, better defined interfaces to the device for potentially lower contact resistance, and the possibility to add further epitaxial layers on top of the TCO contact (e.g. utilizing the TCO as current-spreading layer only). The epitaxial combination of TCOs and III-nitrides has already been demonstrated by PAMBE of InN(0001) films on ZnO(0001) [19] or on In_2O_3(111) [20] (isostructural to ITO) with improved lattice match compared to GaN or Al_2O_3(0001) substrates, as well as GaN(0001) on ZnO(0001) [21] or on Sn-doped β-Ga_2O_3(100) [22] simultaneously using the oxide as substrate and TCO contact for GaN-based LEDs. Apart from lattice mismatch dislocations, potential issues for the interface formation are the formation of secondary oxide phases (e.g. In_2O_3 [19], $ZnGa_2O_4$ [21]) from the nitride's metal ions and the oxide's oxygen ions, or the in-diffusion of oxygen from the oxide into the nitride where it acts as unintentional donor [20]. The epitaxial growth of TCOs on GaN(0001) have been demonstrated with the examples of ZnO(0001) [23] by metalorganic chemical vapor epitaxy and ITO(111) [24] by solid-source electron cyclotron resonance plasma deposition. Challenges for the epitaxy of TCOs on GaN(0001) are the formation of rotational domains due to rotational-symmetry mismatch [25] and the potential oxidation of the GaN or the oxygen in-diffusion into the GaN. Most critical is the nucleation phase of the oxide layer during which the GaN surface is exposed to the oxygen plasma used for the PAMBE oxide growth. During this phase, sufficiently high growth temperatures may facilitate the exchange of nitrogen in the GaN surface by the oxygen, resulting in the formation of an interfacial Ga_2O_3 layer.

In this work, the PAMBE growth of epitaxial ATO and ITO contacts on GaN-based LEDs is demonstrated. Their epitaxial alignment, structural, and electrical properties were determined. The optical transmission of ATO films on the c-plane sapphire substrates were measured and compared to electron-beam evaporated, non-epitaxial, indium tin oxide (eb-ITO) films, which have been optimized and widely used as a transparent contact for conventional devices. Then, ATO films were grown by PAMBE on InGaN/GaN LED wafers as transparent p-contacts for the improvement of current spreading. Based on transmission-line-model (TLM) measurements, the ATO growth temperature was optimized to minimize the contact resistance between ATO and p-type GaN. For comparison, an eb-ITO film was grown on an LED wafer and the current–voltage (I–V) characteristics of the InGaN/GaN LEDs fabricated with the ATO contacts were compared to those with the eb-ITO contacts. Finally, we also grew an epitaxial PAMBE ITO film on an LED wafer using the optimized growth temperature that resulted in minimum contact resistance of the ATO contact, and determined the ITO film transport properties.

2. Experimental

The epitaxial ATO and ITO layers were grown in a Varian/Veeco 620 PAMBE system equipped with standard shuttered effusion cells to supply Sn (99.99999%), In (99.99999%), and Sb (99.999%), an RF plasma source (Veeco, Unibulb) run at 200 W to provide activated oxygen, and a nude ion gauge to measure the beam-equivalent pressure (BEP) at the substrate position. A pyrometer was used to measure the substrate temperature. Further details on the growth and transport properties of our single crystalline ATO and ITO are given in Refs. [18] and [3], respectively. For the ATO growth, the Sn and Sb temperatures were fixed at 1157 °C and 530 °C, respectively. The Sn and oxygen BEPs were 6.4×10^{-5} and 2.0×10^{-3} Pa (4.8×10^{-7} and 1.5×10^{-5} Torr), respectively. The ITO film was grown using In and Sn temperatures of 950 and 1000 °C, respectively, resulting in a Sn-concentration of 3.3×10^{21} cm^{-3} (measured by calibrated secondary ion mass spectrometry). The In, oxygen, and Sn BEPs were 8.9×10^{-5}, 1.6×10^{-3}, and 6.3×10^{-6} Pa (6.7×10^{-7}, 1.2×10^{-5}, and 4.7×10^{-8} Torr), respectively, corresponding to slightly oxygen-rich growth conditions. For comparison, non-epitaxial "eb-ITO" films with a thickness of 300 nm were deposited by electron-beam evaporation using ITO pellets with a weight composition of 90% In_2O_3 and 10% SnO_2. To improve the eb-ITO conductivity and transparency, an optimized annealing performed under a mixed N_2 and O_2 ambient for 10 min followed by an N_2 ambient for 3 min at 600 °C.

To study their optical absorption, a 510 nm-thick ATO film and a 300 nm-thick eb-ITO film for comparison were grown on the c-plane sapphire substrate. The ATO film was grown at a substrate temperature of 700 °C, consistent with the best growth conditions for single-crystalline Sb-doped SnO_2 on r-plane sapphire from the previous study that resulted in a resistivity of 6.7×10^{-4} Ω cm [18]. The optical absorption was examined by a Shimadzu UV 3600 UV–Vis-NIR Spectrometer.

The InGaN/GaN multi-quantum well LED wafer with an emission wavelength of 465 nm was grown on a c-plane sapphire substrate by metalorganic chemical vapor deposition. The LED structure comprised an unintentionally doped GaN layer, a Si-doped n-GaN layer with an electron concentration of 7×10^{18} cm^{-3}, an 8-period InGaN/GaN multi-quantum well structure, and a Mg-doped p-GaN top layer with a hole concentration of 1×10^{18} cm^{-3}. Before loading into the Varian/Veeco 620 PAMBE growth chamber, the quarter LED wafer pieces diced from 2 in. wafers were ultrasonically cleaned in acetone and isopropanol, and then etched in a diluted HCl solution to remove the native oxide on the surface.

The PAMBE growth of ATO and ITO was initiated after the quarter LED wafers were baked in the growth chamber in vacuum at 550 °C for 30 min. (To prevent surface oxidation of the GaN we omitted the usual surface treatment at 680 °C under oxygen plasma.) Three 300 nm-thick ATO layers were grown for 30 min at growth temperatures of 600, 650, and 700 °C, respectively, on separate quarter LED wafers to study their impact on the specific contact resistance between ATO and p-type GaN layer. One 160 nm-thick ITO layer was grown for 15 min at a substrate temperature of 600 °C on another quarter LED wafer. The ITO growth was initiated by opening the oxygen, In, and Sn shutters simultaneously to avoid detrimental oxidation of the GaN surface and terminated by simultaneously closing In, Sn and oxygen shutters and turning off the oxygen supply. After growth the ITO film was kept at growth temperature in vacuum for 90 s before cool down to minimize the ITO resistivity by removing compensating oxygen interstitials [3]. The surface morphology of the ATO and ITO films on the LED wafer was measured by a Veeco Dimension 3100 atomic force microscope (AFM) operated in tapping-mode. X-ray diffraction (XRD) measured by a PANalytical X'Pert PRO MRD using a Cu K_α source with a Ge(220) hybrid monochromator and a 1 mm-wide receiving slit in front of the detector was used to investigate their structural quality and epitaxial orientation.

After the ATO film was deposited on the LED wafers, the fabrication of the 290×490 μm^2 large top-emitting LEDs began with the formation of a mesa structure which was partially etched by inductively coupled plasma (ICP) until the n-type GaN was exposed. Finally, a Ti/Al/Ni/Au (10/200/10/500 nm) layer as p- and n-electrodes was then deposited by e-beam evaporator. The LEDs with eb-ITO contacts were also