Doping and Conductivity Limitations in Sb:SnO₂ Nanowires Grown by the Vapor Liquid Solid Mechanism

Matthew Zervos, Andreas Othonos, Eugenia Tanasă, and Eugeniu Vasile

ABSTRACT: Sb doped SnO₂ nanowires have been grown via the vapor liquid solid mechanism on fused SiO₂ at 800 °C and 1 mbar under a flow of Ar and O₂ by using an excess of metallic Sb in conjunction with Sn. We obtain highly crystalline Sb:SnO₂ nanowires with diameters of 100 nm, lengths up to 100 μm, and a tetragonal rutile crystal structure that contains Sb donor impurities as confirmed by Raman spectroscopy. The Sb:SnO₂ nanowires have a maximum carrier density of 8 × 10¹⁸ cm⁻³ and conductivity of 2500 S/m at 300 K determined from THz conductivity spectroscopy and the Hall effect, which are significantly higher than 3 × 10¹⁶ cm⁻³ and 11 S/m in undoped SnO₂ nanowires. The one-dimensional electron gas charge distribution has a maximum at the core but extends all the way up to the surface as shown via the self-consistent solution of the Poisson-Schrödinger equations in contrast to the case of undoped SnO₂ where the surface depletion leads to a confinement of the charge distribution to the core by taking into account the energetic position of the Fermi level with respect to the conduction band at the surface. We show that the Sb impurities are not incorporated into the SnO₂ lattice through the Au particles, while higher growth temperatures between 900 to 1000 °C and/or lower growth pressures between 10⁻² to 10⁻¹ mbar do not result into the incorporation of Sb impurities in the SnO₂ nanowires. This is attributed to the depletion of metallic Sb during the temperature ramp, before the onset of one-dimensional growth and/or the re-evaporation of Sb impurities arriving on the surface of the SnO₂ nanowires and implies a fundamental doping limitation that is challenging to overcome especially in view of the fact the one-dimensional growth was suppressed under a significant excess of Sb.

INTRODUCTION

SnO₂ nanowires (NWs) have been investigated extensively for the realization of novel energy conversion and storage devices as well as sensors, and in the past, we have grown SnO₂ NWs by the vapor liquid solid (VLS) mechanism at 800 °C and 10⁻¹ mbar on Si and fused SiO₂ (f-SiO₂). The SnO₂ NWs obtained under these conditions have a carrier density of the order of n ≈ 10¹⁶ cm⁻³ and mobility of μ = 70 cm²/(V s) as determined by THz conductivity spectroscopy (TCS). Consequently, they require doping in order to obtain higher carrier densities and conductivities and as a result improve the performance of devices. High conductivity SnO₂ NWs have been previously obtained via the incorporation of donor impurities such as Sb, Mo, and Fe, while more recently, Ma et al. showed theoretically that a strain controlled semiconductor to semimetal transition is possible via the incorporation of Pb in SnO₂. However, in most cases, Sb has been used in conjunction with Sn, and in the past, Sn:Sb NWs have been grown via the VLS mechanism by Wan et al. at 900 °C by using metallic Sn and Sb with a mass ratio of Sn/Sb that varied between Sn/Sb = 20 and 24 under a flow of Ar with a trace of O₂, but the flow was not explicitly stated. The Sb:SnO₂ NWs had metallic-like conductivities, i.e., ρ = 10⁻⁴ Ω cm and were used as gas sensors. Similarly, Li et al. obtained Sb:SnO₂ NWs at 800 °C via the VLS mechanism using Sn/Sb = 19 under a flow of N₂. The SnO₂ NWs had a resistivity of ρ = 12.7 Ω cm, while the Sb:SnO₂ NWs had a ρ = 10⁻³ Ω cm and were used as biosensors. Others like Rui-Jie et al. have grown lightly doped Sb:SnO₂ NWs at 900 °C using Sn/Sb = 1000 under Ar with a trace of oxygen and obtained ρ = 10⁻³ Ω cm with a mobility of μ = 54.43 cm²/(V s), in which case, the Sb:SnO₂ NWs were used as transistors. It is worthwhile pointing out that branched and hyperbranched Sb:SnO₂ NWs have also been obtained using similar growth conditions. In all of the above cases, the growth temperature varied between 800 and 950 °C, and the mass ratio of Sn/Sb between 20 and 1000, which gave Sb:SnO₂ NWs with ρ = 10⁻³–10⁻⁴ Ω cm; however, the growth pressure and flow of O₂ was not controlled or explicitly stated, although it has a direct effect on the partial pressures of Sn and Sb and as a result on the properties of the Sb:SnO₂ NWs.

Received: July 11, 2018
Revised: September 9, 2018
Published: September 10, 2018
In contrast to the above, Jean et al.\textsuperscript{14} has grown Sb:SnO\textsubscript{2} NWs at 1 mbar by using Sn/Sb = 10 at higher temperatures of 1000 °C under a flow of Ar with a trace amount of O\textsubscript{2} while Kumar et al.\textsuperscript{15} on the other hand obtained Sb:SnO\textsubscript{2} NWs at considerably lower temperatures and pressures, i.e., 450 °C and 10\textsuperscript{−4}−10\textsuperscript{−5} mbar, respectively, in which case, the oxygen partial pressure was 4 × 10\textsuperscript{−4} mbar. The current through the Sb:SnO\textsubscript{2} NWs increased by a factor of 5 upon excitation with ultraviolet (UV) light, suggesting that they may be used as UV photodetectors. Finally, it is also worthwhile pointing out that only Klamchuen et al.\textsuperscript{16} has grown Sb:SnO\textsubscript{2} NWs by using Sn and Sb\textsubscript{2}O\textsubscript{3} as opposed to metallic Sb. The Sb:SnO\textsubscript{2} NWs were grown via the VLS mechanism on (110) Al\textsubscript{2}O\textsubscript{3} by pulsed laser deposition between 550 to 750 °C at 10\textsuperscript{−2} mbar under Ar:O\textsubscript{2} with a ratio of 1000:1 and the resistivity of the Sb:SnO\textsubscript{2} NWs varied between 10\textsuperscript{−3} and 10\textsuperscript{−2} Ω cm.

The growth and properties of Sb:SnO\textsubscript{2} NWs is still a topic of active interest\textsuperscript{17,18} due to the fact that Sn and Sb are not expensive compared to In, which in turn is an important incentive for improving the conductivity and attaining even higher carrier densities in Sn:SnO\textsubscript{2} NWs that are comparable to those of Sn:In\textsubscript{2}O\textsubscript{3} NWs.\textsuperscript{19}

Consequently, here we have carried out a detailed investigation into the growth, doping, and electrical properties of Sb:SnO\textsubscript{2} NWs grown by the VLS mechanism on f-SiO\textsubscript{2} between 700 to 900 °C under a flow of Ar and O\textsubscript{2} by using metallic Sn in conjunction with an excess of Sb, i.e., 0 < Sn/Sb < 10, and by varying the growth pressure between 10\textsuperscript{−2} to 10\textsuperscript{−1} mbar in order to understand the doping and conductivity limitations related to the incorporation of the Sb donor impurities.

We obtain a high yield and uniform distribution of Sb:SnO\textsubscript{2} NWs over the 10 × 10 mm f-SiO\textsubscript{2} that have diameters of ∼100 nm, lengths up to 100 μm, and a tetragonal rutile crystal structure. We do not observe the formation of other oxides such as Sb\textsubscript{2}O\textsubscript{3}, S\textsubscript{2}O\textsubscript{3}, or SbO\textsubscript{2}, but we confirmed the existence of the Sb donor impurities in the SnO\textsubscript{2} NWs by Raman spectroscopy (RS) and energy dispersive X-ray analysis (EDX) analysis. We describe the growth and impurity incorporation mechanism in detail and show that the Sb:SnO\textsubscript{2} NWs have a maximum conductivity of 2500 S/m and carrier density of 8 × 10\textsuperscript{22} cm\textsuperscript{−3}. These are significantly larger than the conductivity and carrier density of undoped SnO\textsubscript{2} NWs, which were 11 S/m and 3 × 10\textsuperscript{18} cm\textsuperscript{−3}, respectively, obtained under the same growth conditions. Higher growth temperatures between 900 to 1000 °C and lower growth pressures between 10\textsuperscript{−2} to 10\textsuperscript{−1} mbar result into a significant reduction of the conductivity of the Sb:SnO\textsubscript{2} NWs, keeping all else equal, which is attributed to the depletion of the available Sb during the temperature ramp, before the onset of one-dimensional growth and the re-evaporation of Sb impurities from the surface of the Sb:SnO\textsubscript{2} NWs. In addition, we show that the one-dimensional electron gas charge distribution has a maximum at the core but extends all the way up to the surface as shown via the self-consistent solution of the Poisson-Schrödinger equations in the effective mass approximation in contrast to the case of undoped SnO\textsubscript{2} NWs, in which the surface depletion leads to the confinement of the charge distribution in the vicinity of the core.

## METHODS

Sb:SnO\textsubscript{2} NWs were grown using a 1” hot wall, low pressure chemical vapor deposition (LPCVD) reactor capable of reaching 1100 °C that was fed via a micro flow leak valve positioned on the upstream side, just after the gas manifold consisting of four mass flow controllers. A chemically resistant rotary pump that can reach 10\textsuperscript{−3} mbar was connected downstream. For the growth of the Sb:SnO\textsubscript{2} NWs, metallic Sn and Sb (Aldrich, 2–14 Mesh, 99.9%) were mixed and weighed with an accuracy of ±1 mg. The mass of Sn and Sb was always 0.1 g. Square samples of ∼10 × 10 mm fused SiO\textsubscript{2} (f-SiO\textsubscript{2}) were cleaned sequentially in trichloroethylene, methanol, acetone, and isopropanol, rinsed with deionized water, and dried with nitrogen. Subsequently, a thin layer of ∼1 nm Au was deposited on the surface of the f-SiO\textsubscript{2} by sputtering. The elemental Sb and Sn as well as the f-SiO\textsubscript{2} were loaded in a quartz boat that was positioned at the center of the LPCVD reactor, after which it was pumped down to 10\textsuperscript{−4} mbar and purged with 500 standard cubic centimeters per minute (scm) of Ar for 10 min at 10\textsuperscript{−4} mbar. Subsequently, the temperature was ramped up to 800 °C at 30 °C/min using the same flow of Ar. Upon reaching 800 °C, a flow of 10 sccm O\textsubscript{2} was added to the flow of Ar in order to grow the Sb:SnO\textsubscript{2} NWs over 5 min at 10\textsuperscript{−1} mbar, followed by cool down without O\textsubscript{2}. Care was taken to maintain a clean high temperature zone for the growth of the Sb:SnO\textsubscript{2} NWs. These growth conditions are exactly the same as those used previously for the growth of undoped SnO\textsubscript{2} NWs.\textsuperscript{7}

Initially, the growth pressure and temperature were varied between (a) 700 to 900 °C and (b) 10\textsuperscript{−1} to 10\textsuperscript{−2} mbar in order to determine the optimum conditions for the growth of Sb:SnO\textsubscript{2} NWs using Sb and Sn with a mass ratio of Sn/Sb = 10, keeping all else equal. After establishing the optimum growth temperature and pressure, i.e., 800–900 °C and 1 mbar, we varied the mass ratio of Sn/Sb between 0.1 and 10, i.e., Sn/Sb = 9/1, 8/2, 7/3, 6/4, 5/5, 4/6, 3/7, 2/8, 1/9, 0.

The morphology, crystal structure, and composition of the Sb:SnO\textsubscript{2} NWs were determined by scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive X-ray analysis (EDX), and Raman spectroscopy (RS). High resolution transmission electron microscopy (HRTEM) was carried out using a TECNAI F30 G\textsuperscript{2} S-TWIN operated at 300 kV. The electrical properties of the Sb:SnO\textsubscript{2} NWs on f-SiO\textsubscript{2}, i.e., conductivity and carrier density, were measured by THz conductivity spectroscopy (TCS) and the Hall effect after a dry transfer of Sb:SnO\textsubscript{2} NWs on 10 × 10 mm f-SiO\textsubscript{2} and the formation of a planar network of Sb:SnO\textsubscript{2} NWs with In contacts at the four corners as described in detail elsewhere.\textsuperscript{2,18}

## RESULTS AND DISCUSSION

### Growth and Structural Properties of Sb:SnO\textsubscript{2} NWs.

In the past, we have shown that the reaction of Sn with O\textsubscript{2} at 800 °C and 10\textsuperscript{−2} mbar results into a high yield, uniform growth of SnO\textsubscript{2} NWs on 1 nm Au/Si(001) with diameters of ∼50 nm and lengths up to ∼100 μm. The SnO\textsubscript{2} NWs grow by the VLS mechanism, whereby Sn vapor enters the Au particles on the surface of Si (001) and forms liquid Au:Sn particles, since the Au:Sn alloy is liquid at 280 °C, even with a 20% Sn content. Upon saturation, solid SnO\textsubscript{2} forms beneath the liquid Au:Sn particles via the reaction with O\textsubscript{2} at the triple phase junction, leading to one-dimensional growth,\textsuperscript{20} A schematic representation of the VLS growth mechanism for SnO\textsubscript{2} NWs is shown in Figure 1a. The SnO\textsubscript{2} NWs obtained under these growth conditions have a tetragonal rutile crystal structure, and we have shown previously that they exhibit broad photo-luminescence with a maximum at ∼550 nm or 2.6 eV, which is smaller than the energy band gap of SnO\textsubscript{2}, i.e., 3.7 eV, due to
radiative recombination via surface states that are related to oxygen vacancies and which reside energetically in the energy band gap of SnO$_2$.\textsuperscript{21} More importantly, we have shown that the SnO$_2$ NWs grown under these conditions have a carrier density of the order of $10^{16}$ cm$^{-3}$ and mobility of 70 cm$^2$/V s from THz conductivity spectroscopy.\textsuperscript{2} Consequently, doping is required in order to increase their conductivity and enable their use in energy conversion and storage devices.

Initially, we tried to grow Sb:SnO$_2$ NWs on f-SiO$_2$ by using metallic Sn and Sb with Sn/Sb = 10 at 800 °C and 10$^{-1}$ mbar. However, we did not observe any significant changes in the conductivity of the SnO$_2$ NWs. Similarly, we did not observe any improvement in the conductivity by changing the growth pressure from 10$^{-2}$ to 10$^{-3}$ mbar, keeping all else equal. In contrast, highly conductive Sb:SnO$_2$ NWs on f-SiO$_2$ were readily obtained at 800 °C and 1 mbar by using Sn/Sb = 10, suggesting the successful incorporation of the Sb donor impurities into the SnO$_2$ NWs. More specifically, the conductivity of the Sb:SnO$_2$ NWs on f-SiO$_2$ was very similar to that of undoped SnO$_2$ NWs at 2.5 × 10$^{-2}$ and 3.5 × 10$^{-1}$ mbar but changed dramatically above 5 × 10$^{-1}$ mbar. This effect has not been observed previously but was reproducible and constitutes a doping and conductivity limitation that needs to be understood in an effort to obtain higher carrier densities in Sb:SnO$_2$ NWs that are comparable to those in Sn:In$_2$O$_3$ NWs. We suggest that the incorporation of Sb impurities into the SnO$_2$ NWs is limited between 10$^{-1}$ and 10$^{-2}$ mbar mainly due to the complete transfer of Sb into the gas stream during the temperature ramp and before the onset of one-dimensional growth. This is a direct consequence of the fact that Sn has a low melting point of 232 °C and vapor pressure of 10$^{-5}$ mbar at 800 °C, while Sb has a higher melting point of 630 °C, it has a significantly higher vapor pressure of 10$^{-1}$ mbar at 800 °C. In other words, the metallic Sb and Sn will both melt under a flow of Ar during the temperature ramp, but the Sb will be transferred completely into the gas stream before the occurrence of one-dimensional growth, especially when the growth pressure falls between 10$^{-1}$ and 10$^{-2}$ mbar. The incorporation of Sb impurities into the SnO$_2$ NWs is not inhibited between 10$^{-2}$ to 10$^{-2}$ mbar due to the formation of Sb$_2$O$_3$, Sb$_3$O$_5$, or SbO$_2$ over the metallic Sn via its reaction with O$_2$ supplied during the growth step, since the partial pressure of O$_2$ is considerably smaller at 10$^{-2}$ to 10$^{-2}$ mbar than what it is at 1 mbar. It should be emphasized at this point that we did not obtain any SnO$_2$ NWs at all without supplying O$_2$ during the growth step. Hence, the residual O$_2$ under a flow of Ar after purging and during the temperature ramp was negligibly small to result into significant oxidation of the metallic Sn and Sb. This is also substantiated by the fact that we did not obtain a high density and uniform distribution of Sb:SnO$_2$ NWs over the 10 × 10 mm f-SiO$_2$ at 800 °C and 10 mbar precisely due to the oxidation of the metallic Sn and Sb via its reaction with O$_2$, which was visible at the end of the growth and which limited the supply of Sn to the Au particles on f-SiO$_2$.

In an attempt to optimize further the growth conditions, we changed the growth temperature, which is also critical for the successful incorporation of Sb impurities, from 700 to 750, 775, 800, and 900 °C using Sn/Sb = 10, in which case, we obtained a uniform distribution of Sb:SnO$_2$ NWs over the 10 × 10 mm f-SiO$_2$ only above 750 °C. Sn has an even lower vapor pressure than 10$^{-5}$ mbar at 700 °C, so one-dimensional growth of Sb:SnO$_2$ NWs was not promoted at 700 °C, simply due to the limited amount of Sn arriving at the Au catalyst particles on f-SiO$_2$. On the other hand, higher temperatures above 900 °C result into a significant transfer of the Sb impurities into the gas stream before the onset of one-dimensional growth, and as a result, the doping level is smaller. Having established the optimum growth temperature and pressure, i.e., 800 to 900 °C and 1 mbar, we prepared a systematic series of Sb:SnO$_2$ NWs on f-SiO$_2$ at 800 °C and 1 mbar with Sn/Sb = 9/1, 8/2, 7/3, 6/4, 5/5, 4/6, 3/7, 2/8, 1/9, and 0.

We obtained a uniform distribution of Sb:SnO$_2$ NWs for all Sn/Sb > 0.1 over the 10 × 10 mm f-SiO$_2$ with diameters of ~100 nm and lengths up to 100 μm as shown by the SEM images in Figure 2, from which one may clearly observe the Au–Sn nanoparticles on their ends, which suggests that they grow by the VLS mechanism. The Sb:SnO$_2$ NWs exhibited clear peaks in the XRD as shown in Figure 3, corresponding to the tetragonal rutile crystal structure of SnO$_2$. We did not observe any significant change in the position of the principal (110) and (101) peaks of SnO$_2$ with Sn/Sb, which suggests that the incorporation of Sb into the lattice of SnO$_2$ did not result into a change of the lattice constant as we have observed previously in Sn:In$_2$O$_3$ NWs.\textsuperscript{19} This is due to the fact that the Van der Walls radii of Sn and Sb are 2.25 and 2.06 Å, respectively, which in turn implies that the Sb atoms may be readily incorporated into the host lattice of SnO$_2$. In addition,
we do not observe the formation of any oxides related to Sb such as Sb$_2$O$_3$ and Sb$_2$O$_5$, which have melting points of 656 and 380 °C, respectively, or the occurrence of Sb$_2$O$_6$, i.e., SbO$_2$, which is known to break down into Sb and O$_2$ at 930 °C. In short, the Sb:SnO$_2$ NWs have the pure tetragonal rutile crystal structure of SnO$_2$. A typical TEM image of the Sb:SnO$_2$ NWs obtained with Sn/Sb = 2/8 is shown in Figure 4 along with HRTEM images depicting the (110) crystallographic planes of SnO$_2$. The Sb:SnO$_2$ NWs are highly crystalline overall, but one may observe the existence of an amorphous surface shell with a thickness of ~2 nm. We did not observe the existence of any other oxides such as SbO$_2$, Sb$_2$O$_5$ or Sb$_2$O$_3$ by HRTEM consistent with the XRD. The existence of the Sb donor impurities in the SnO$_2$ NWs was confirmed by Raman spectroscopy (RS) as shown in Figure 5 in agreement with the findings of Costa et al.,$^{17,18}$ who recently investigated the structural properties of Sb:SnO$_2$ NWs obtained via the VLS mechanism at 950 °C. The Sb:SnO$_2$ NWs were obtained by using Sb and Sn at 200 mbar under a flow of 100 sccm Ar and 5 sccm O$_2$, and they obtained a minimum resistivity of $\rho = 10^{-1}$ Ω cm and corresponding carrier density of $6 \times 10^{18}$ cm$^{-3}$ determined from the Hall effect. From the EDX shown as an
inset in Figure 5. We find that the Sb:SnO2 NWs contained Sb, but we were not able to detect the Sb by EDX for Sn/Sb > 2. Despite the fact that we observed the Sb impurities in the SnO2 NWs by EDX and RS, we did not find them in the Au particles as shown by the EDX in Figure 4, from which we confirmed the existence of Sn in Au.

It is important to mention at this point that one-dimensional growth was strongly suppressed for 0 < Sn/Sb < 0.1, i.e., under a significant excess of Sb. In addition, we did not obtain any SbO2 NWs at 800 °C and 1 mbar by using only Sb, and we did not detect any Sb in the Au particles on f-SiO2 after trying to grow SbO2 NWs. Evidently, it is not possible to use a significant excess of Sb together with Sn, i.e., Sn/Sb < 0.1, to obtain high carrier densities in SnO2 NWs. This constitutes another important limitation that has not been observed previously and is most likely attributed to the formation of a liquid Sb−Sn alloy during the temperature ramp, which will be transferred into the gas stream, leaving little or no Sn for the growth of SnO2 NWs during the growth step.

Before describing the electronic properties of the Sb:SnO2 NWs, it is necessary to consider in detail the impurity incorporation mechanisms in Sb:SnO2 NWs. There are two distinct mechanisms for the incorporation of Sb impurities into SnO2 NWs: (a) by the VLS mechanism through the liquid Au:Sn particles and/or (b) through the surface of the SnO2 NWs as shown in Figure 1b,c, respectively.

We begin by considering the incorporation of the Sb impurities into the SnO2 NWs via the VLS mechanism by noting that the properties of the Au−Sn−Sb ternary have been investigated only up to about 300 °C, so it is difficult to predict its properties at elevated temperatures. Nevertheless, the properties of the Au−Sn−Sb ternary alloy are essentially defined by those of its three binary constituents, i.e., Au−Sn, Sn−Sb, and Au−Sb. The Sb−Sn alloy is liquid at 800 °C for all compositions, while the Au−Sb alloy like Au−Sn is also liquid at 800 °C for a relatively low content of ~20% Sb. One would then expect to have a liquid Au particle containing both Sn and Sb, but we did not detect any Sb in the Au particles on f-SiO2 after trying to grow SbO2 NWs at 800 °C and 1 mbar by using only Sb. It is reasonable then to suggest that Sb impurities may be adsorbed on the surface of the Au particles but will rapidly re-evaporate due to the excessively high vapor pressure of Sb at 800 to 900 °C. This is consistent with Simon et al., who found that the Au catalyst particles used to grow ZnO NWs on f-SiO2 do not contain a substantial amount of Zn due to the high partial pressure of Zn over Au−Zn, which leads to a very low sticking coefficient of Zn that prevents alloying and implies the existence of solid Au particles at 900 °C. The ZnO NWs in this case grow via the diffusion of Zn to the interface between the Au particles and the underlying f-SiO2. From the above, one may surmise that the Sb impurities are not incorporated into the SnO2 NWs via the VLS mechanism through the Au catalyst particles. Consequently, we consider the second mechanism, which was proposed by Klamcu et al., who found that the dopant distribution within the Sb:SnO2 NWs is not uniform due to the incorporation of impurities via a vapor solid (VS) mechanism rather than VLS. More specifically, they found that the doping level in SnO2 NWs grown at 650 °C was twice that obtained at 750 °C attributed to a suppression of impurity re-evaporation. The doping level did not increase further upon reducing the growth temperature from 650 to 550 °C, which was attributed to a reduction of the diffusion length of impurity adatoms on the surface of the SnO2 NWs and the presence of a temperature activated energy barrier, which is necessary for the incorporation of the Sb impurities into the host lattice of SnO2. As described below, the carrier density and conductivity of the Sb:SnO2 NWs obtained at 800 °C was higher compared than those obtained at 900 °C, which confirms the trend of Klamcu et al. Nevertheless, it is useful to mention that shortly after the proposal of this mechanism, Klamchuen et al. observed Sb on the Au particles by elemental mapping and explained that the impurities are mainly located around the catalyst, although they found that the size of the Au particles varied with the content of Sb2O3 used in their targets, which has a different vapor pressure than metallic Sb.

It is reasonable then to suggest that the Sb:SnO2 NWs grow via the VLS mechanism through the incorporation of Sn into the Au particles, but the Sb impurities are incorporated into the host lattice mainly through the sides of the SnO2 NWs by thermal diffusion or via the triple phase junction as shown in Figure 1c. The Sb impurities will be adsorbed on the surface of the Au particles or on the sides of the SnO2 NWs, but their re-evaporation rate will be higher at lower pressures, e.g., 10−1 to 10−2 mbar and/or higher temperatures, e.g., 900 and 1000 °C, due to the overtly high vapor pressure of Sb itself. This implies a fundamental limitation that might be difficult to overcome just by maintaining an adequate supply of Sb. In other words, one might separate the metallic Sn from Sb and maintain the latter at lower temperature in order to prevent the depletion of Sb between 10−1 to 10−2 mbar and/or higher temperatures, e.g., 900 and 1000 °C, but in the end, this will not prevent the re-evaporation of the Sb impurities from the surface of the SnO2 NWs.

Carrier Density and Conductivity of Sb:SnO2 NWs. The conductivity of the Sb:SnO2 NWs obtained at 800 °C and 1 mbar using different Sn/Sb was measured by TCS at room temperature as described in detail elsewhere. One of the main advantages of TCS is that it permits one to find the electrical conductivity of an ensemble of free-standing Sb:SnO2 NWs without the need to fabricate a device consisting of single Sb:SnO2 NWs with low resistance contacts, which is especially difficult if the carrier density is low as in the case of the undoped SnO2 NWs. A typical trace of the time evolution of the electric field through the Sb:SnO2 NWs as well as through fused SiO2 and undoped SnO2 NWs is shown in Figure 6. The corresponding conductivity extracted after taking the fast
Fourier transform is shown as an inset in Figure 6, from which we find that the highest conductivity of the Sb:SnO2 NWs obtained at 800 °C with Sn/Sb = 1/4 is ~3000 S/m. This is significantly larger than the conductivity of undoped SnO2 NWs, which was 11 S/m, corresponding to $3 \times 10^{16}$ cm$^{-3}$. Note that conductivity of Sb:SnO2 NWs obtained at 900 °C was smaller than those obtained at 800 °C due to the limited supply and incorporation of Sb impurities into the SnO2 NWs at elevated temperatures.

The carrier density of the Sb:SnO2 NWs as determined by the Hall effect is shown as an inset in Figure 6, from which one may observe an increase in the carrier density for Sn/Sb $< 1$. The carrier mobility of the SnO2 NWs was $70 \text{cm}^2/(V \text{s})$, in contrast to $20 \text{cm}^2/(V \text{s})$ obtained in the case of the Sb:SnO2 NWs attributed to ionized impurity scattering. We obtain a maximum carrier density of $8 \times 10^{18}$ cm$^{-3}$, but it is important to keep in mind that the free carrier density is not necessarily equal to the doping level. In fact, the carrier density is strongly dependent on the energetic position of the Fermi level at the surface of the Sb:SnO2 NWs, which in turn is governed by its stoichiometry and density of mid-gap states related to crystal imperfections. In order then to gain a better understanding of the electronic properties of this transparent conducting oxide, we calculated the conduction band (CB) potential profile and one-dimensional electron gas (1DEG) distribution along the radial direction via the self-consistent solution of the Poisson-Schrödinger (SCPS) equations in the effective mass approximation as described in detail elsewhere. In such a calculation, one begins with the solution of Schrödinger’s equation, taking a trial potential subject to specific boundary conditions, which gives the sub-band energies and wave functions. These are subsequently normalized in order to obtain the 1DEG charge distribution using the one-dimensional (1D) density of states (DOS) in conjunction with Fermi Dirac statistics. Finally, Poisson’s equation is solved, taking into account the ionized donor impurity distribution but also the electron charge distribution, to get a correction potential that is added onto the initial trial potential. The process is repeated until convergence is reached, after which charge neutrality is evaluated for completeness.

The SCPS calculations were carried out by taking into account the effective mass and dielectric constant of SnO$_2$, i.e., $m^\ast_e = 0.3^{27,28}$ and $\epsilon_s = 13.5^{25,30}$ respectively. In addition, we have taken into account the electron affinity of SnO$_2$, i.e., $\chi = 4.8$ eV, and the work function of stoichiometric SnO$_2$ is $\phi = 5.5$ eV according to Rachut et al. which is in agreement with Klein et al. Note that higher values of $\phi = 7.74$ eV have also been reported for SnO$_2$, but the work function of SnO$_2$ prepared under reducing growth conditions is smaller and varies between $\phi = 4.1 - 4.48$ eV, which implies that the Fermi level is energetically located in the conduction band taking into account that $\chi = 4.8$ eV. Consequently, the work function of stoichiometric SnO$_2$, i.e., $\phi = 5.5$ eV, lies in the middle of the range of values listed above, and the Fermi level in this case falls ~0.7 eV below the conduction band edge at the surface of SnO$_2$ in accordance with Kar et al. However, the work function and energetic position of the Fermi level with respect to the conduction band edge in a semiconductor is also dependent on the doping level. According to electronic structure calculations, the Sb impurities in SnO$_2$ form a band that has an energetic overlap with the conduction band and a nearly free electron structure, i.e., behaves like a metallic band so the Fermi level in the Sb:SnO$_2$ NWs is expected to reside above the CB. This is also consistent with Farahani et al., who showed that there is a surface electron accumulation layer in epitaxial SnO$_2$ layers grown by molecular beam epitaxy on r-Al$_2$O$_3$ due to the fact that the Fermi level is pinned ~0.3 eV above the CB edge at the surface. Similarly, Ke et al. have shown that the donor impurity level lies above the CB edge in ultrathin films of SnO$_2$ when the thickness is larger than 10 nm.

We have taken the Fermi level to reside ~0.3 eV above the CB edge at the surface of the Sb:SnO$_2$ NWs. The energy band diagram and charge distribution of a 40 nm diameter Sb:SnO$_2$ NW taking a uniform distribution of donors with $N_D = 5 \times 10^{18}$ cm$^{-3}$ throughout is shown in Figure 7. The CB edge potential profile is U-like across the diameter of the Sb:SnO$_2$ NW, and the electric field is zero, i.e., a flat band condition exists at the core of the Sb:SnO$_2$ NW by virtue of Gauss’s law. The potential is U-like due to the fact that the Fermi level is fixed, i.e., $E_F = E_C = 0.3$ eV on opposite sides of the surface of the Sb:SnO$_2$ NW, and we have taken a uniform distribution of positively ionized donor impurities. We find that nine sub-bands fall below the Fermi level and the ground level sub-band is situated at ~0.298 eV, which give a 1DEG charge

Figure 6. Time evolution of the THz electric field strength through the f-SiO$_2$, undoped SnO$_2$, and Sb:SnO$_2$ NWs; inset shows the conductivity (S/m) of the Sb:SnO$_2$ NWs versus f (GHz) obtained at 800 °C and 1 mbar using Sn/Sb = 6/4, 4/6, 2/8.

Figure 7. SCPS CB potential profile and 1DEG charge distribution versus distance along the radial direction of a Sb:SnO$_2$ NW with a diameter of 40 nm taking $E_C = E_F = 0.3$ eV at the surface and assuming a uniform distribution of ionized donor impurities $N_D = 5 \times 10^{18}$ cm$^{-3}$; inset shows the case of an undoped SnO$_2$ NW.
distribution that has a maximum at the core but extends all the way up to the surface, where it displays a smaller local maximum. Both potential and 1DEG charge distribution are overall symmetric. This is different to the potential profile and charge distribution in epitaxial Sb:SnO₂ layers, in which case, the energetic position of the Fermi level with respect to the CB edge is different at the surface and in the bulk, giving rise to a 2DEG that is strongly confined in a quasi-triangular potential well along one direction perpendicular to the surface. In essence, the boundary conditions governing the potential profile and charge distribution are different in the case of the 2DEG in a bulk layer of Sb:SnO₂ and 1DEG in Sb:SnO₂ NWs.

The potential profile and charge distribution of the Sb:SnO₂ NWs shown in Figure 7 was obtained by assuming a uniform distribution of positively ionized impurities throughout the Sb:SnO₂ NWs. However, Sb impurities are incorporated into the SnO₂ NWs via thermal diffusion through its surface, so we expect the density of the donor impurities to be larger at the surface. This is consistent with McGinley et al., who showed that the surface of SnO₂ particles is terminated by an oxygen-rich layer but when doped n-type with Sb, the impurities are located near the surface of the SnO₂ particles with an oxidation state of five. We find that the potential profile and charge distribution of the Sb:SnO₂ NWs do not change drastically by including the positively ionized donor impurities between \( r = 10 \) and \( 20 \) nm only. In other words, the potential and charge distribution are again symmetric and similar to those shown in Figure 7. However, in this case, the 1DEG has a maximum at the core where the density of donor impurities is considerably smaller than that at the surface so the incorporation of Sb impurities into the SnO₂ NWs via diffusion through their surface may not be a drawback in the end as far as the carrier mobility is concerned. In contrast, the 1DEG charge distribution is strongly confined to the core of a Sb:SnO₂ NW by taking the Fermi level to be energetically located \( \sim 0.7 \) eV below the CB and a uniform distribution of positively ionized donor impurities with \( N_D = 10^{19} \text{cm}^{-3} \) as shown by the inset in Figure 7. The charge distribution and potential profile of undoped SnO₂ NWs is very similar to that shown in the inset of Figure 7, but the carrier density is 2 orders of magnitude lower, while no sub-bands fall below the Fermi level. In other words, the SnO₂ NWs are strongly depleted and have a considerably smaller conductivity.

Despite the fact that high carrier densities and conductivity may be difficult to achieve in SnO₂ NWs by using metallic Sb or other sources such as Sb₂O₅, etc., during growth at elevated temperatures, it is useful to mention in closing that the doping limitations described above may be overcome by suitable post growth processing and barriers that will prevent the evaporation of Sb.

**CONCLUSIONS**

Sb:SnO₂ NWs have been grown via the VLS mechanism on f-SiO₂ at 800 °C and 1 mbar under a flow of 500 sccm Ar and 10 sccm O₂ by using metallic Sb and Sn. We obtain highly crystalline Sb:SnO₂ NWs with diameters of 100 nm and lengths up to 100 μm, which have a tetragonal rutile crystal structure and observed clear peaks related to the Sb donor impurities, as indicated by RS and EDX. The Sb:SnO₂ NWs have a maximum 1DEG density of \( 8 \times 10^{18} \text{cm}^{-2} \) and high conductivities of \( \sigma = 2500 \text{S/m} \) at 300 K as determined by TCS and the Hall effect; these values are significantly higher than \( 3 \times 10^{18} \text{cm}^{-2} \) and 11 S/m in undoped SnO₂ NWs. The 1DEG charge distribution and potential profile of the Sb:SnO₂ NWs was determined via the self-consistent solution of the Poisson-Schrödinger equations in the effective mass approximation by taking the Fermi level to be energetically located \( \sim 0.3 \) eV above the conduction band edge at the surface. This results into a 1DEG charge distribution that has a maximum at the core but extends all the way up to the surface. In contrast, the 1DEG charge distribution in the undoped SnO₂ NWs is completely confined to the core due to the surface depletion by virtue of the fact that the Fermi level is located \( \sim 0.7 \) eV below the conduction band edge at the surface.

Higher growth temperatures between 900 to 1000 °C and/or lower growth pressures between \( 10^{-2} \) to \( 10^{-3} \) mbar result into a reduction of the conductivity of the Sb:SnO₂ NWs, which is attributed to the depletion of the metallic Sb during the temperature ramp before the onset of one-dimensional growth and/or the re-evaporation of Sb impurities arriving on the surface of the Sb:SnO₂ NWs. In addition, one-dimensional growth is suppressed when \( 0 < \text{Sn}/\text{Sb} < 0.1 \). These constraints and doping limitations are strictly related to the overall large partial pressure of Sb and may be overcome to a certain extent by supplying ex situ and separately the Sb and Sn during the growth step, in which case, the impurity incorporation will only be limited by the temperature activated thermal diffusion through the surface of the SnO₂ NWs and the re-evaporation rate of the Sb impurities. Higher carrier densities and conductivities that are comparable to those of Sn:In₂O₃ NWs may be difficult and challenging to obtain using metallic Sb during growth, and alternative strategies using Sb as a donor impurity should be focused on doping by post growth processing of the SnO₂ NWs.

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: zervos@ucy.ac.cy.*

**ORCID**

Matthew Zervos: 0000-0002-6321-233X

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors at the Polytechnic University of Bucharest acknowledge EU-funding POSCCE-A2-O2.2.1-2013-1/Axa Prioritara 2, Project No. 638/12.03.2014, Code SMIS-CSNR 48652.

**REFERENCES**


