Synthesis of Tin Nitride Sn$_x$N$_y$ Nanowires by Chemical Vapour Deposition

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Abstract Tin nitride (Sn$_x$N$_y$) nanowires have been grown for the first time by chemical vapour deposition on n-type Si(111) and in particular by nitridation of Sn containing NH$_4$Cl at 450 °C under a steady flow of NH$_3$. The Sn$_x$N$_y$ nanowires have an average diameter of 200 nm and lengths ≥5 μm and were grown on Si(111) coated with a few nm’s of Au. Nitridation of Sn alone, under a flow of NH$_3$ is not effective and leads to the deposition of Sn droplets on the Au/Si(111) surface which impedes one-dimensional growth over a wide temperature range i.e. 300–800 °C. This was overcome by the addition of ammonium chloride (NH$_4$Cl) which undergoes sublimation at 338 °C thereby releasing NH$_3$ and HCl which act as dispersants thereby enhancing the vapour pressure of Sn and the one-dimensional growth of Sn$_x$N$_y$ nanowires. In addition to the action of dispersion, Sn reacts with HCl giving SnCl$_2$ which in turn reacts with NH$_3$ leading to the formation of Sn$_x$N$_y$ NWs. A first estimate of the band-gap of the Sn$_x$N$_y$ nanowires grown on Si(111) was obtained from optical reflection measurements and found to be ≈2.6 eV. Finally, intricate assemblies of nanowires were also obtained at lower growth temperatures.

Keywords Tin nitride · Nanowires · Synthesis · Chemical vapor deposition

Introduction

Nitrides and in particular, group III-Nitride (III-N) compound semiconductors such as GaN, InN and AlN have been investigated intensively over the past decade due to their applications in electronic and optoelectronic devices like field effect transistors, light emitting diodes and lasers [1–3]. III-N semiconductors are especially attractive because their band-gap can be tailored from 0.7 eV in InN [4] up to 6.2 eV in AlN [5] but also due to the strained induced charges that provide an extra degree of freedom which can be used to tailor the band-profile and consequently the properties of devices [6].

However, in contrast to III-N compound semiconductors there are few investigations on group IV-Nitride (IV-N) compounds such as Ge$_3$N$_4$ [7, 8] and even less on Sn$_3$N$_4$ [9–22].

Tin nitride Sn$_3$N$_4$ is a relatively unknown semiconductor and the first investigation of Sn$_3$N$_4$ was carried out by F. Fisher et al. [9] as early as 1908. It has an energy band-gap that was estimated to be ≈1.5 eV [11] and so far Sn$_3$N$_4$ thin films have been grown by a variety of methods [12–19], including, atmospheric pressure chemical vapour deposition (APCVD) using halides [12, 13], metal organic chemical vapour deposition (MOCVD) [14], sputtering [15–18] and ammonothermal synthesis [19, 20]. Thin films of Sn$_3$N$_4$ have also been proposed as materials for optical storage [21, 22] since it was demonstrated that it dissociates into β-Sn upon exposure to a focused beam of light but also as a material for batteries [23].

Not surprisingly there are very few investigations on Sn$_3$N$_4$ nanostructured materials and it appears that the only study carried out so far concerns the synthesis of Sn$_3$N$_4$ nanoparticles (NPs) on Au coated Si(001) via chemical vapour deposition (CVD) using SnCl$_4$ · 5H$_2$O as a solid...
precursor, by Nand et al. [24]. To date, there is no report on the synthesis of Sn₃N₃ nanowires (NWs) despite the fact that nanowires constitute a fundamental building block for the development of nanoscale devices such as the third generation solar cells which require low cost, nanostructured materials.

Therefore in order to complement our earlier investigations on the synthesis and properties of InN NWs and related oxides such as In₂O₃ and SnO₂ NWs [25–27], a preliminary investigation on the growth of Sn₃N₃ NWs was undertaken.

Here the synthesis of the first Sn₃N₃ NWs on Au/Si(111) is described and it is shown that Sn₃N₃ nanowires (NWs) can not be grown via the direct nitridation of Sn over a broad range of temperatures i.e. between 300–800 °C due to the formation of Sn droplets on the surface of the Si(111). While there is evidence of one dimensional (1D) growth occurring at 500 °C via the direct nitridation of Sn, the yield is extremely poor. One-dimensional growth was promoted and significantly enhanced via the incorporation of NH₄Cl in the Sn and its sublimation which acts as a dispersant thereby enhancing the vapour pressure of Sn. Sn₃N₃ NWs with an average diameter of 200 nm were obtained at 450 °C while intricate assemblies of NWs have also been obtained at lower temperatures.

**Experimental Procedure**

The Sn₃N₃ NWs were grown using an APCVD reactor which consists of four mass flow controllers (MFC’s) and a horizontal quartz tube furnace, capable of reaching a maximum temperature of 1,100 °C. Initially, fine Sn powder (Aldrich, < 150 µm, 99.5%) was loaded into a quartz boat together with a square piece of Si(111) approximately 7 mm x 7 mm in size, which was coated with a few nm’s of Au. The Au layer was deposited via sputtering at a slow rate using an Ar plasma under a pressure <10⁻¹⁴ mBar. The Au/Si(111) sample was positioned ≈ 5 mm downstream from the Sn and subsequently the boat was loaded into the APCVD reactor and positioned directly above the thermocouple used to measure the heater temperature at the centre of the quartz tube. After loading the boat at room temperature (RT), Ar (99.999%) was introduced at a flow rate of 500 standard cubic centimetres per minute (sccm) for 5 min in order to purge the tube and eliminate O₂ and H₂O. Following this the temperature was ramped to the desired growth temperature in a NH₃ flow of 250 sccm at a rate of 30 °C/min. Upon reaching the growth temperature (T_G) the flow of NH₃ was maintained at 250 sccm for a further 60 min after which the tube was allowed to cool down over at least an hour, in a flow of 50 sccm NH₃. The sample was removed only when the temperature was lower than 100 °C.

In order to enhance the one dimensional growth of Sn₃N₃ NWs an equal amount of anhydrous NH₄Cl (VWR Int 99.9%) was added to the Sn and mixed thoroughly in the boat. Then the same gas flows and temperature-time profile described above was employed. A summary of the temperatures and conditions is given in Table 1. The morphology of the Sn₃N₃ NWs was examined with a TESCAN scanning electron microscope (SEM) while the crystal structure and the phase purity of the Sn₃N₃ NWs were investigated using a SHIMADZU, XRD-6000, X-ray diffractometer with a Cu Ka source while a scan of θ–2θ in the range between 10° and 80° was performed. Finally, optical spectroscopy was carried out using a standard spectrophotometer UV/V (Perkin–Elmer Lambda 950) in the reflection mode at near normal incidence to the surface of the sample.

### Table 1 Maximum diameter (Ø) of Sn droplets (DPs) and Sn₃N₃ NWs obtained from heating up Sn under NH₃ and from the reaction of Sn + NH₄Cl respectively, at different temperatures. In all cases a ramp rate of 30 °C/min was used to reach T_G under 250 sccm’s of NH₃ which was then maintained for a further 60 min at the growth temperature and after which the reactor was allowed to cool down to RT in a reduced flow of 50 sccm’s NH₃.

| T_G (°C) | Max Ø of Sn DPs (Sn:NH₃) | Max Ø Sn₃N₃ NWs (Sn + NH₄Cl:NH₃) |
|----------|----------------------------|----------------------------------|
| 300      | No DPs                     | No NWs                           |
| 400      | 200 nm                     | 200 nm                           |
| 450      | –                          | 200 nm                           |
| 500      | 500 nm                     | No NWs                           |
| 600      | 500 nm                     | No NWs                           |
| 700      | 2.0 µm                     | –                                |
| 800      | 5.0 µm                     | –                                |

**Results and Discussion**

As stated above the only investigation on the synthesis of nanostructured Sn₃N₃ is that of single phase, cubic tin nitride nanoparticles grown via atmospheric pressure-halide vapour phase epitaxy by Nand et al. [24]. In particular Nand et al. employed SnCl₄ · 5H₂O as a source of Sn and used 10 nm Au/Si(001) p-type substrates that were positioned at different distances from the SnCl₄ · 5H₂O, along the reactor. The SnCl₄ · 5H₂O was heated up to 500 °C under a flow of NH₃ and N₂ and the temperatures of the samples along the reactor were 400, 300 and 150 °C, respectively. However, Nand et al. [21] did not obtain any NWs. Before discussing the synthesis of the Sn₃N₃ NWs obtained here it is instructive to consider first the synthesis...
of SnO$_2$ NWs on 0.5 nm Au/Si(111) that were previously obtained by heating up Sn in an inert gas flow of 100 sccm Ar at 30 °C/min up to 800 °C and then maintaining the flow of Ar at this temperature for a further 90 min before cool down [27]. A typical SEM image of the SnO$_2$ NWs obtained in this way is shown in Fig. 1a from which it is clear that a large yield of SnO$_2$ NWs was obtained with an average diameter of 50 nm due to the reaction of Sn with residual O$_2$ in the APCVD reactor. Performing the reaction under a direct flow of O$_2$ leads to the formation of SnO$_2$ around the molten Sn which limits the vapour pressure significantly and hence the growth of NWs. As a consequence the molten Sn upstream always had a grey like, non reflective appearance at the end of the process, while no droplets were observed among the SnO$_2$ NWs. A similar process was also used recently for the growth of In$_2$O$_3$ NWs at 700 °C [26].

At first sight it would seem that the synthesis of Sn$_x$N$_y$ NWs by direct nitridation of Sn with NH$_3$ is feasible by changing from Ar to NH$_3$ since Sn, like In, has a low melting point [28] and InN NWs have been obtained by direct nitridation of Sn with NH$_3$ around the molten Sn which limits the vapour pressure significantly and hence the growth of NWs. As a consequence the molten Sn upstream always had a grey like, non reflective appearance at the end of the process, while no droplets were observed among the SnO$_2$ NWs. A similar process was also used recently for the growth of In$_2$O$_3$ NWs at 700 °C [26].

Apart from droplets, no nanostructures were obtained via the attempted nitridation of Sn with NH$_3$ in the temperature range 600 °C < $T_G$ < 800 °C. Turning on the flow of NH$_3$, after ramping up the temperature in an inert gas flow of Ar, did not lead to the growth of Sn$_x$N$_y$ NWs either but again resulted into the deposition of Sn droplets. However, there was some evidence of one-dimensional growth at $T_G = 500$ °C. Literally a few NWs with diameters $>500$ nm’s and lengths up to 3 μm appeared at a few locations on the Si(111) surface, hence the yield was extremely poor. Nevertheless, a further reduction of the growth temperature down to 300 °C did not lead to any
significant deposition on the Si, no NWs were obtained and moreover, the Sn upstream lost its metallic shine due to the build up of a black deposit on the molten Sn which limited the vapour transport. In addition, no differences were observed upon changing the flow rate of NH₃ during the growth while keeping everything else equal at all temperatures so the direct nitridation of Sn alone under a flow of NH₃ is not effective and leads to the deposition of Sn droplets on the Au/Si(111) surface which impedes one-dimensional growth over a wide temperature range i.e. 300–800 °C as shown below in Table 1.

The XRD spectrum of the Sn droplets deposited at 800 °C is shown in Fig. 3 and is characterized by an intense peak corresponding to the (2 0 0) orientation of Sn and less intense but well resolved peaks corresponding to the (1 0 1), (3 0 1), (4 0 0) and (3 2 1) orientations. In addition to the Sn droplets the Al holder peaks have also been identified but no peaks associated with SnₓNᵧ were found.

These findings are in direct contrast with the case of InN where NWs can be grown by direct nitridation of In with NH₃ via a self-catalytic mechanism. The optimum heater temperature for the growth of InN NWs was found to be 600 °C where its vapour pressure is equal to 10⁻⁶ Torr. Large In droplets comparable in size to those in Fig 1b started appearing only at temperatures ≥800 °C in contrast to the Sn droplets whose density was large and persisted even down to 600 °C where its vapour pressure is <10⁻¹¹ Torr. It appears therefore that the Sn droplets are born out from the melt upstream and are transferred to the Si(111) surface where they coalesce to form larger droplets.

The tendency for one-dimensional growth observed at \( T_G = 500 \) °C during the direct nitridation of Sn with NH₃ was promoted by the addition of NH₄Cl into the Sn at a ratio of 1:1 by weight. The reaction of NH₄Cl with Sn was carried out under a flow of NH₃ keeping the flow rate, ramp rate and temperature profile identical to those used in the case of ‘direct nitridation’ of Sn with NH₃. A typical SEM image of SnₓNᵧ NWs obtained by the reaction of Sn with NH₄Cl under NH₃ at 450 °C is shown in Fig 2a. The SnₓNᵧ NWs have an average diameter of 200 nm’s and lengths up to 5 μm while the reaction of Sn with NH₃ always lead to the deposition of a white powder downstream, near the cool end of the reactor, in contrast to the direct nitridation of Sn with NH₃ where no by products occurred.

The XRD spectrum of the SnₓNᵧ NWs grown at 450 °C is shown in Fig. 4 and is characterized by the (2 2 0), (3 1 1), (5 1 1) and (4 4 0) peaks, which can be indexed to the hexagonal structure of SnₓN₄ [18]. The intense peak of Sn(200) observed in Fig. 3 has disappeared and once more the Al peaks appearing in the XRD spectrum of Fig. 4 due to the sample holder have been identified. Furthermore there are no peaks associated with SnO₂ [27].

The promotion of one dimensional growth is attributed to the dissociation of NH₄Cl. Upon increasing the temperature NH₄Cl undergoes sublimation at 338 °C and

Fig. 2 a SnₓNᵧ NWs grown on Au/Si(111) at the optimum temperature of 450 °C using a Sn:NH₄Cl mixture under a flow of 250 sccm’s NH₃ b high magnification SEM image of SnₓNᵧ NWs
The decomposition of NH₄Cl enhances the sublimation weight loss of NH₄Cl is over 90% when heated expected to be reduced only by a few tens/C176. The sublimation process is endothermic and the temperature is of NH₄Cl increases by a factor of 10⁴ when changing the rates would be more suitable. In addition to acting as a dispersant, the sublimation of NH₄Cl yields HCl which reacts with Sn leading to the formation of SnCl₂ according to, 3SnCl₂ + 4NH₃ → Sn₃N₄ + 12HCl (4) leading to the growth of Sn₃N₄ NPs on 10 nmAu/Si(111) that were placed at various positions along the reactor but also similar to the growth of Sn₃N₄ thin films by APCVD using halides, by Gordon et al. and Takahashi et al. [12, 13].

A similar kind of reaction was also used to grow InN nanocrystals on Si(111) whereby the incorporation of NH₄Cl into the In lead to the complete elimination and transfer of the In into the gas stream where it formed primarily InCl which in turn reacted with the NH₃ leading to the formation of InN nanocrystals with diameters of 300 nm [30].

While the addition of NH₂Cl in Sn did not result into its complete transfer in the gas stream like with In, it provided nonetheless the necessary HCl for the formation of SnCl₂ which subsequently reacts with NH₃ on the Au/Si(111) leading to the one dimensional growth of Sn₃N₄. Interestingly the distance of the sample from the Sn:NH₄Cl mixture was found to be critical and for distances >10 mm the reaction led to the formation of closely packed NPs with sizes <100 nm on the Au/Si(111) most probably due to the lower vapour pressure of the SnCl₂.

Although the details of the growth mechanism are not understood thoroughly at present it is suggested that the Sn₃N₄ NWs grow self catalytically from Sn₃N₄ NPs although the role of the Au which appears to enhance the one dimensional growth still needs to be clarified [32, 33].

A first estimate of the band-gap of the Sn₃N₄ nanowires grown on Si(111) was obtained from optical reflection measurements using a UV–IR spectrometer at near normal incidence on both the NW sample and the Si(111) substrate for comparison, shown in Fig. 5. Clearly evident is the distinct difference in the reflection spectra from the substrate and the NWs. Also evident is the band edge of the Sn₃N₄ NWs which is estimated to be approximately 2.6 eV [31].

In addition to Sn₃N₄ NWs that were obtained at T_G = 450 °C there is also evidence for the formation of more complex nanostructures obtained for T_G < 450 °C as shown in Fig. 6a and b. However, their density was smaller compared to that in Fig. 2a due to the lower growth temperature which limits the amount of Sn transferred over to the Si(111). The radial growth of NWs from the droplet shown in Fig 6a is very similar to the case of InN [25] whereby nucleation centres form on the surface of droplets which then facilitate radial growth [32]. Moreover, the circular arrangement of NWs shown in Fig. 6b is due to the constant sublimation of NH₄Cl in NH₃.
the formation of droplets that accumulate near the periphery of well defined circles similar to the growth of In$_2$O$_3$ nano pyramids that self assemble in the form of wreaths due to the reaction of In with NH$_4$Cl in a flow of N$_2$ [30].

Conclusions

The first tin nitride, Sn$_x$N$_y$ nanowires have been grown by CVD on Au coated Si(111) via the reaction of Sn with NH$_4$Cl at 450 °C under a steady flow of NH$_3$. Attempting direct nitridation of Sn with NH$_3$ leads to the formation of Sn droplets due to the reducing action of the NH$_3$ which eliminates O$_2$ in the reactor and which in turn inhibits one-dimensional growth over a wide temperature range between 300–800 °C. The formation of large Sn droplets was suppressed by adding NH$_4$Cl which dissociates into NH$_3$ and HCl by sublimation at 338 °C and acts as a dispersant thereby enhancing the vapour pressure of Sn. Furthermore the Sn reacts with HCl and yields SnCl$_2$ which subsequently reacts with NH$_3$ leading to the formation of Sn$_x$N$_y$ nanowires which have diameters of 200 nm and lengths up to 5 μm. Finally nanowires protruding from droplets and intricate assemblies of NWs arranged in the shape of wreaths were also obtained at temperatures <450 °C. The synthesis of metal (M)-nitride i.e. M$_x$N$_y$ nanowires where the metal component is readily available and has a low cost, is expected to be important for third generation solar cells based on nanostructured semiconductor materials.

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