
Study of defect behaviour in Ga₂O₃ nanowires and nano-ribbons under reducing gas annealing conditions: applications to sensing

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Abstract: The growth of monoclinic Ga₂O₃ nanowires, nano-ribbons and nano-sheets has been investigated. Results indicate that high quality single crystal nanowires can be grown at 900°C using an Au catalyst, while single crystal nano-ribbons and nano-sheets require no metal catalyst for growth. Since bulk Ga₂O₃ is a promising material for high temperature gas sensing, Ga₂O₃ nanowires and nano-ribbons may prove to enhance the sensing capability due to the high surface area. We have investigated the nature of defects in this material using Electron Spin Resonance, photoluminescence and scanning electron microscopy, in as grown material, as well as under annealing in a reducing gas (H₂) at various high temperatures. Results indicate the presence of an oxygen deficiency in the material, resulting in a conduction electron signal that becomes enhanced with annealing. The eventual loss of this signal is attributed to hydrogen etching of the nanowires, leading to a loss of material.

Keywords: Ga₂O₃ nanowires; nano-ribbons; VLS growth; electron spin resonance; photoluminescence; gas sensing.

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1 Introduction

One-dimensional structures, such as carbon nanotubes and semiconductor nanowires, are currently of great interest due to their unique physical properties and potential applications [1–3]. A number of applications have been investigated for such 1D structures, including nanoscale devices [4,5] and sensor applications [6]. Bulk monoclinic gallium oxide (β -Ga₂O₃) is a wide band gap semiconductor ($E_g = 4.9$ eV), which exhibits conduction and luminescence properties [7,8] with applications to opto-electronics and high temperature gas sensing [9–13]. Recently, several groups have reported the growth of β -Ga₂O₃ nanowires by various techniques [14–17] using the vapour liquid solid (VLS) mechanism, with either Au, Ni or oxygen as a catalyst. Since this material (in bulk or thin film) shows promise for gas sensing, it is important to examine the possible sensor-related properties of Ga₂O₃ nanowires, which have a very large surface to volume ratio and thus may result in higher sensitivity devices.

In this manuscript, we will present results on the growth of β -Ga₂O₃ nanowires and examine their optical and structural properties. We will also address a possible sensor-type application of such wires, that of high temperature reducing gas sensing.

2 Experimental

Elemental Ga of 99.995% purity was used as the starting material. The substrate material used included Si(100) and Si(111), and GaAs(100) substrates, which were first ultrasonically cleaned by placing each sample in acetone and then in methanol for a duration of five minutes. Following the cleaning procedure, the samples were dried using N₂ gas. After the cleaning process, the Si samples were covered with a 20 nm Au film, which was deposited in vacuum using an electron beam. The source material (Ga metal) was then placed at one end of a 4" alumina boat, with the substrate at the opposite end. The boat was then inserted into a quartz tube inside a tube furnace, which was evacuated to a base vacuum of 40 mTorr using a mechanical pump. The furnace was then heated to temperatures between 700°C and 1000°C. Several gas feed valves and flow controllers were connected to the other end of the tube, allowing a controlled flow of argon and oxygen gas to pass over the alumina boat. During the heat up cycle, the evacuated quartz tube was flushed several times with argon gas in order to reduce the initial oxygen content. Once at temperature, the growth was initiated by the flow of a 6 : 1 ratio of argon to oxygen, at 60 sscm and 10 sscm, respectively. The quartz tube pressure remained

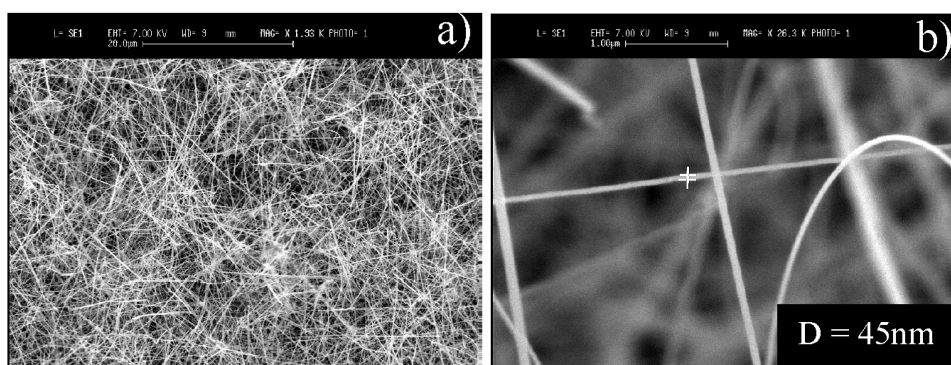
generally in the 6 Torr range while flowing the Ar/O₂ gas mixture. For the annealing studies, flowing Ar/hydrogen mixture was used. As-grown nano-ribbons and nanowires were examined for structure and composition using a Leica Cambridge Stereoscan 360FE scanning electron microscope (SEM) with EDX capabilities, a Hitachi High Resolution Transmission Electron Microscope (HRTEM), and Raman spectroscopy. Since bulk Ga₂O₃ has found application in high temperature sensing of reactive gasses such as hydrogen, the evolution of defects for as grown material and material annealed in a hydrogen atmosphere was also studied using electron spin resonance (EPR) and photoluminescence, using the 351 nm line of the Ar⁺ ion laser. This was done in order to determine the effects that high surface area nanostructures may have on the sensing capabilities of this system.

3 Results and analysis

3.1 Growth of Ga_2O_3 nanowires using Au catalyst

Although it was possible to grow nanowires using a GaAs substrate with a Ni catalyst [16], the wire morphology could not be fully optimised. However, the best results were obtained using Au as a catalyst on a Si substrate with a solid Ga source. A temperature range between 700°C and 1000°C (nanowire growth temperature) was investigated, with results showing no nanowire growth below 775°C or above 900°C. The optimal growth conditions were when the Si growth substrate (and thus the nanowires) was between 800°C and 900°C and the Ga evaporation temperature was roughly 100° below the nanowire growth temperature. An example of the wires grown under optimal conditions is shown in Figure 1(a) and (b). As can be seen, the wires are very straight, with no noticeable growth anomalies.

Figure 1 SEM images of monoclinic Ga_2O_3 nanowires grown at 900°C, using an Au catalyst and a Si substrate

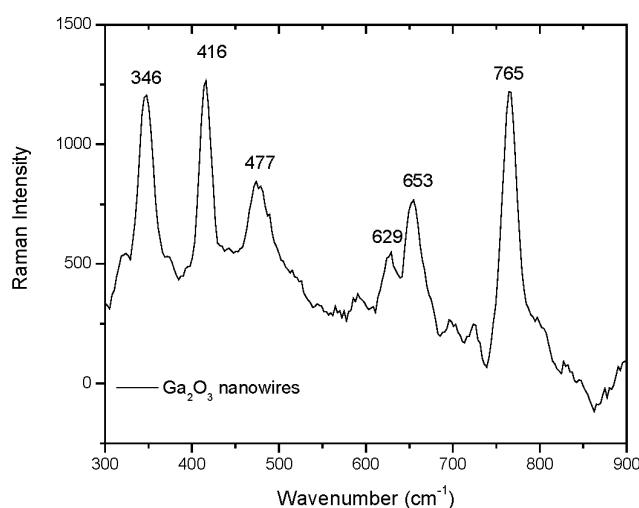


The nanowires grew with an average diameter of 40–50 nm and lengths as long as 50 μ m have been observed for longer growth times.

3.2 Characterisation of the nanowires

In order to fully establish the structural and chemical composition of these wires, Raman spectroscopy was used. The Raman spectrum for the nanowires in Figure 1 is shown in Figure 2. The Raman lines for bulk β -Ga₂O₃ are at 198, 346, 416, 476, 630, 653 and 766 cm⁻¹ and have been reported by Sulikowski et al. [18] and Zhang et al. [17]. The bands between 300–600 cm⁻¹ correspond to bending vibrations while those above 600 cm⁻¹ are due to Ga-O₄ tetrahedral stretching [18]. A comparison between the lines for bulk β -Ga₂O₃ and those of the nanowires shown in Figure 2 confirms that the nanowires consist of stoichiometric β -Ga₂O₃. Thus, the Raman analysis indicates that the wires consist of monoclinic Ga₂O₃, which is an optimal structure for high temperature sensing applications [19].

Figure 2 Raman spectrum, of the nanowires shown in Figure 1, corresponding to monoclinic Ga₂O₃

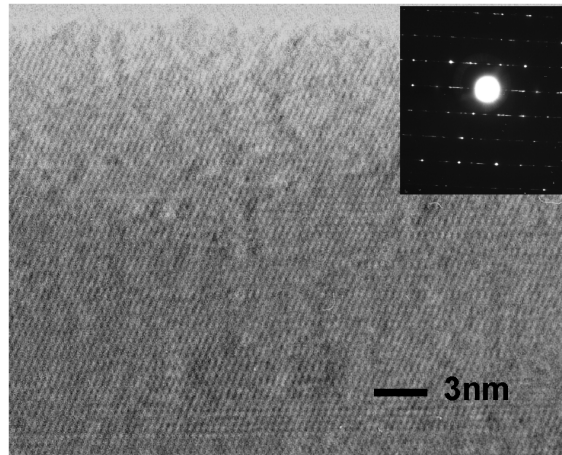


The crystallinity of these nanowires has also been examined, and a high resolution TEM image of a single wire, along with the diffraction image, is shown in Figure 3. The single crystal nature of the nanowires can be determined from both the lattice fringes as well as the diffraction image. Some stacking faults are also evident along the wire length, as is evident from Figure 3.

The monoclinic Ga₂O₃ nanowires also exhibit an intense blue luminescence, near 475 nm, as has been reported by other groups [16]. The emission in the blue region has been attributed to the presence of oxygen vacancies [20]. In fact, Binet and Gourier [21] have suggested that this blue PL is produced by the recombination of an electron on an oxygen donor vacancy with a hole on an acceptor (such as a Ga vacancy). Interestingly, this 475 nm emission has been reported only in nanowires that have been produced using Au as a catalyst [15]. The nanowires, which have been grown using a Ni catalyst, exhibit a PL which is more blue shifted toward the UV [16]. The importance of the metal catalyst has also been investigated. In fact, no nanowire growth was obtained without a metal catalyst under the conditions described above. Thus, the metal catalyst, which forms a liquid eutectic with the Ga vapour, is critical, suggesting the growth

process follows the well known vapour-liquid-solid (VLS) growth mechanism [22]. This is further supported by the fact the tip of the nanowires consists of this eutectic alloy drop, as would be expected in the VLS mechanism.

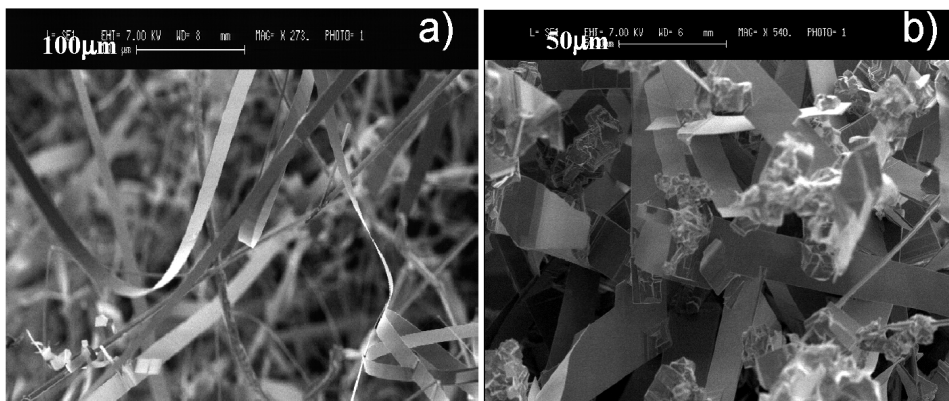
Figure 3 HRTEM and associated diffraction image of Ga_2O_3 nanowires grown at $900^\circ C$, showing lattice fringes



3.3 Self-catalysed growth of Ga_2O_3 nanoribbons and nanosheets

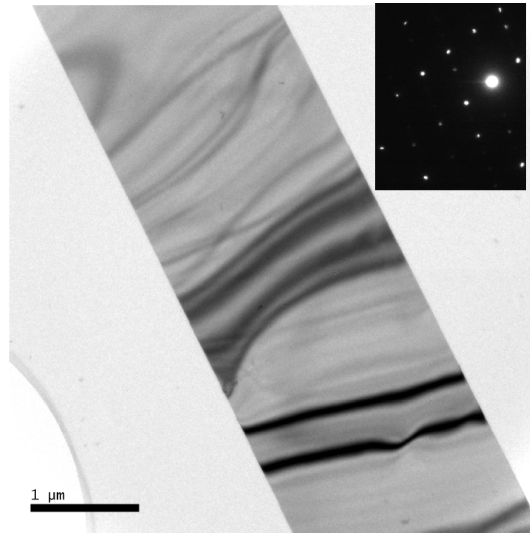
We also found that Ga metal itself can act as a catalyst directly, but in this case, only Ga_2O_3 nano-ribbons and nano-sheets can be formed. This growth process occurs directly on the Ga metal source material, when the temperature is between $850^\circ C$ and $900^\circ C$, with a 6 : 1 argon to oxygen gas ratio. An example of the nano-ribbons and nano-sheets, which can be formed in gram quantities, is shown in Figure 4(a) and (b). As can be seen, the nano-ribbons are generally on the order of $10\ \mu m$ or $15\ \mu m$ wide, only 10 s of nanometers thick, and longer than $300\ \mu m$, while the nano-sheets are generally $5\text{--}10\ \mu m$ on a side, and as thick as the nano-ribbons.

Figure 4 Ga_2O_3 nano-ribbons: (a) and nano-sheets and (b) formed at $900^\circ C$ directly on metal Ga surface



The nanoribbons are also single crystal, and some can be very thin, as shown in the HRTEM image and diffraction patterns in Figure 5. The stripes in the TEM image are bending contours, due to the very thin nature of the nano-ribbon.

Figure 5 TEM image of a thin Ga_2O_3 nanoribbon, along with the associated diffraction image



4 Sensor-related properties of Ga_2O_3 nanoribbons and nanowires

In general, nanowires or nano-ribbons are 2D structures with very small diameters, and thus they consist of a very high surface/volume ratio. This may prove beneficial when used in certain types of sensor applications, such as those which take advantage of surfaces and electrical properties, as well as others, which may take advantages of the nanowire geometry as well as the capability of nanowire manipulation.

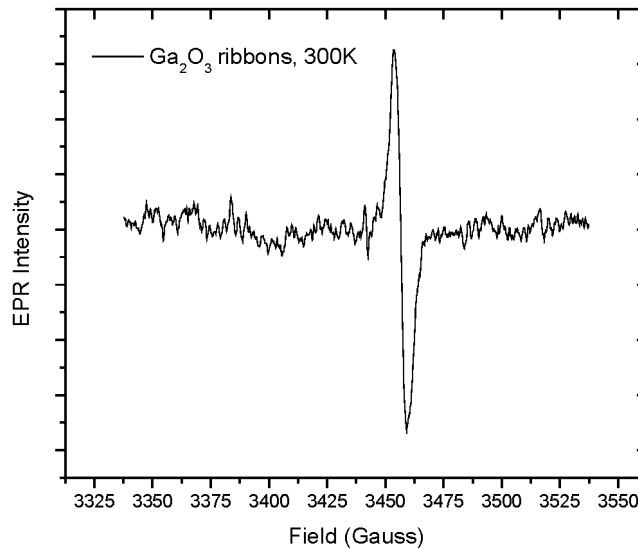
4.1 Defect-related properties of Ga_2O_3 nano-ribbons as a function H_2 anneals: application to high temperature gas sensing

It has been reported previously that polycrystalline thin films of Ga_2O_3 are quite effective as a base material for high temperature sensing of oxygen [23], reducing gases [23,24], as well as for hydrocarbons [25]. The important feature of this material is the high temperature stability and thermal stability (melting T is near 1900°C). As noted, this material is n-type due to the presence of oxygen vacancies, which makes it ideal for use in sensors that are based on the changes in the electrical properties, since the material does not have to be doped using traditional doping atoms. This is especially critical in nanowires, which are quite difficult to dope. In the case of oxygen sensing, Ga_2O_3 polycrystalline thin films have been used in the temperature range of $700\text{--}1000^\circ\text{C}$, taking advantage of bulk effects [26]. At lower temperatures ($<700^\circ\text{C}$), the Ga_2O_3 thin films have been studied for reducing gas sensing, mainly taking advantage of surface effects [27,28]. In fact, at 600°C , a significant resistance lowering effect has been noted for such sensors when subjected to a 1% H_2 gas in atmosphere [27]. In view of these results and

the fact that Ga_2O_3 nanowires and nano-ribbons consist mostly of surfaces, it is important to investigate the behaviour of the defect states associated with the oxygen vacancy (which leads to the electrical behaviour) at higher temperatures and as a function of H_2 gas and to examine the stability of these nanostructures.

In order to investigate this, Ga_2O_3 nano-ribbons and nanowires were produced as discussed above. Electron spin resonance and photoluminescence spectroscopies were used to track the effect of anneals in 5% H_2 and Ar gas mixture at higher temperatures, and SEM was used to track the changes in the structural properties of the nanowires with the heat treatments. Since gram quantities of the nano-ribbons could be obtained, they were ideal for the EPR measurements. The EPR results for a fresh sample (at room temperature) are shown in Figure 6. As can be seen, the resonance is quite sharp, with a g value of 1.961, which is similar that reported by Binet and Gourier [21] in the case of single crystal Ga_2O_3 . This resonance does not show a marked dependence on the measurement temperature [29], and thus one can conclude that it is due to de-localised conduction electrons, which most likely originate from the oxygen vacancy site. This is in agreement with the results of Binet and Gourier [21].

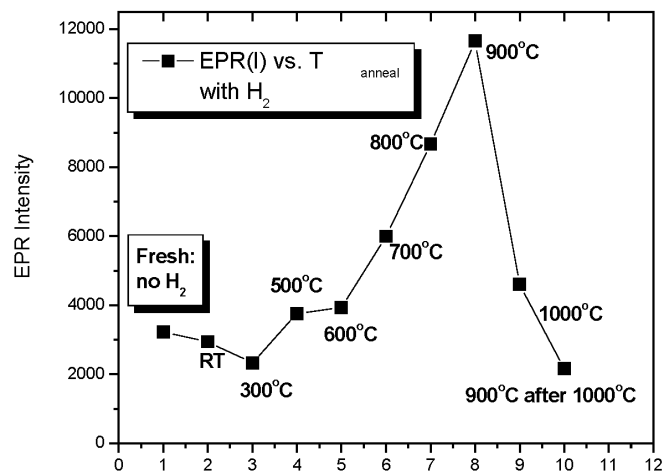
Figure 6 EPR spectrum of the nano-ribbons at 300 K



It is these de-localised electrons which result in the n-doping of the existing material, and thus, it is important to examine the behaviour of this resonance (and thus these conduction electrons) with higher temperature anneals in a reducing atmosphere, such as hydrogen, which is one of target gases in sensing using this material in bulk form. Since the gas sensors discussed above are generally based on the electrical properties of the Ga_2O_3 material, any changes of the de-localised electron signal can directly affect the sensitivity of such devices. Thus, experiments have been carried out in which the nano-ribbons have been subjected to various temperatures anneals in a H_2/Ar atmosphere, and the resonance at $g = 1.961$ has been measured after each treatment, in order to assess the changes in the oxygen defect signal. The results are shown in Figure 7.

As can be seen, although the signal intensity drops slightly in the first anneal at 300°C, further anneals at higher temperatures result in continuous increases in the conduction electron signal, and at 900°C, the conduction electron signal increased by a factor of 4. Further anneals at higher temperatures lead to a significant drop of the signal strength. This large increase of the signal at 900°C suggests that a gas sensor based on the conductivity in these nano-ribbons may indeed exhibit enhanced sensitivity in the high temperature regime. In order to further understand the changes in the EPR shown in Figure 7, photoluminescence spectroscopy (PL) combined with SEM have been employed.

Figure 7 EPR spectra for the Ga₂O₃ nano-ribbons subjected to H₂/Ar atmosphere anneal at temperatures shown



The photoluminescence from these monoclinic Ga₂O₃ nanowires is shown in Figure 8(a), taken at room temperature prior to any annealing steps. An SEM micrograph of these wires is shown in Figure 8(b). Note that there is a high density of nanowires, having an average diameter between 40 nm and 80 nm. The PL was obtained using the 351 nm line of an Ar⁺ laser. As can be seen, the PL line peaks near 475 nm, as has been reported by other groups [16] and a weaker line near 425 nm is also present. The emission in this blue region has been attributed to the presence of oxygen vacancies [20] and Binet and Gourier [21] have suggested that this blue PL is produced by recombination of an electron on an oxygen vacancy with a hole on an acceptor, such as a Ga vacancy. If this model is correct, one would expect that the emission band in the blue would be correlated with the presence of oxygen vacancy defects. Thus, it is interesting to examine the effect of the annealing steps reported above on the PL behaviour in this system. Due to the ease of handling and annealing, a high density of Ga₂O₃ nanowires, grown on a Si substrate, was employed for this phase of the study. An example of the PL intensity changes as a function of anneals in an H₂/Ar atmosphere for various temperatures is shown in Figure 9(a) and (b). As can be seen, the general behaviour of the PL intensity tracks the behaviour of the EPR signal. There is also a maximum of the intensity after a higher temperature anneal, after which the intensity drops to below detectability at the highest anneal temperature.

Figure 8 (a) Photoluminescence and (b) SEM micrograph of the Ga₂O₃ nanowires

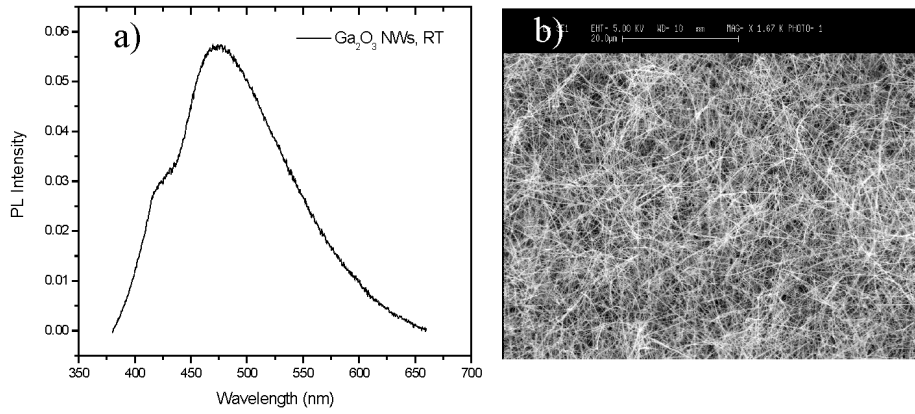
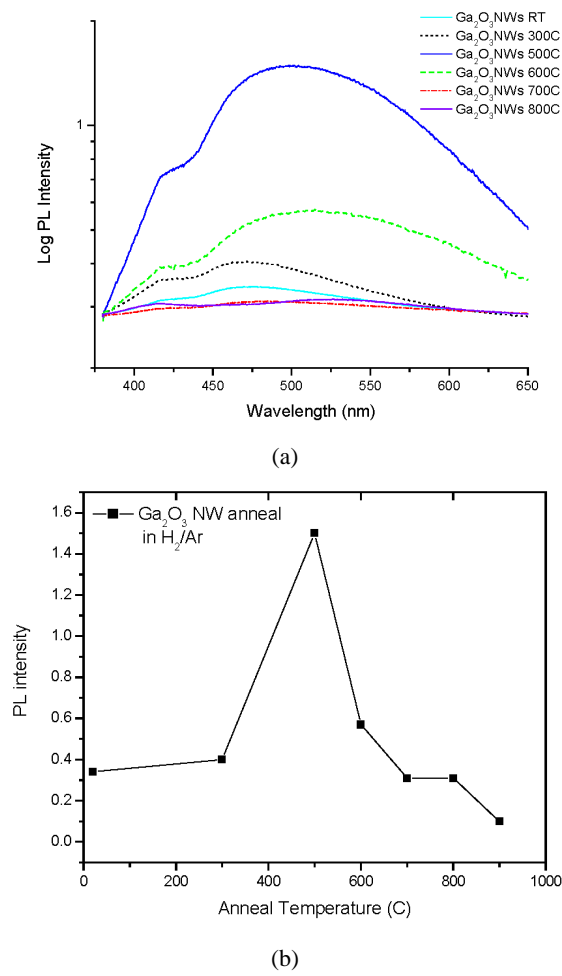


Figure 9 (a) Photoluminescence behaviour as a function of anneal temperature and (b) plot of PL intensity as a function of temperature for the nanowires

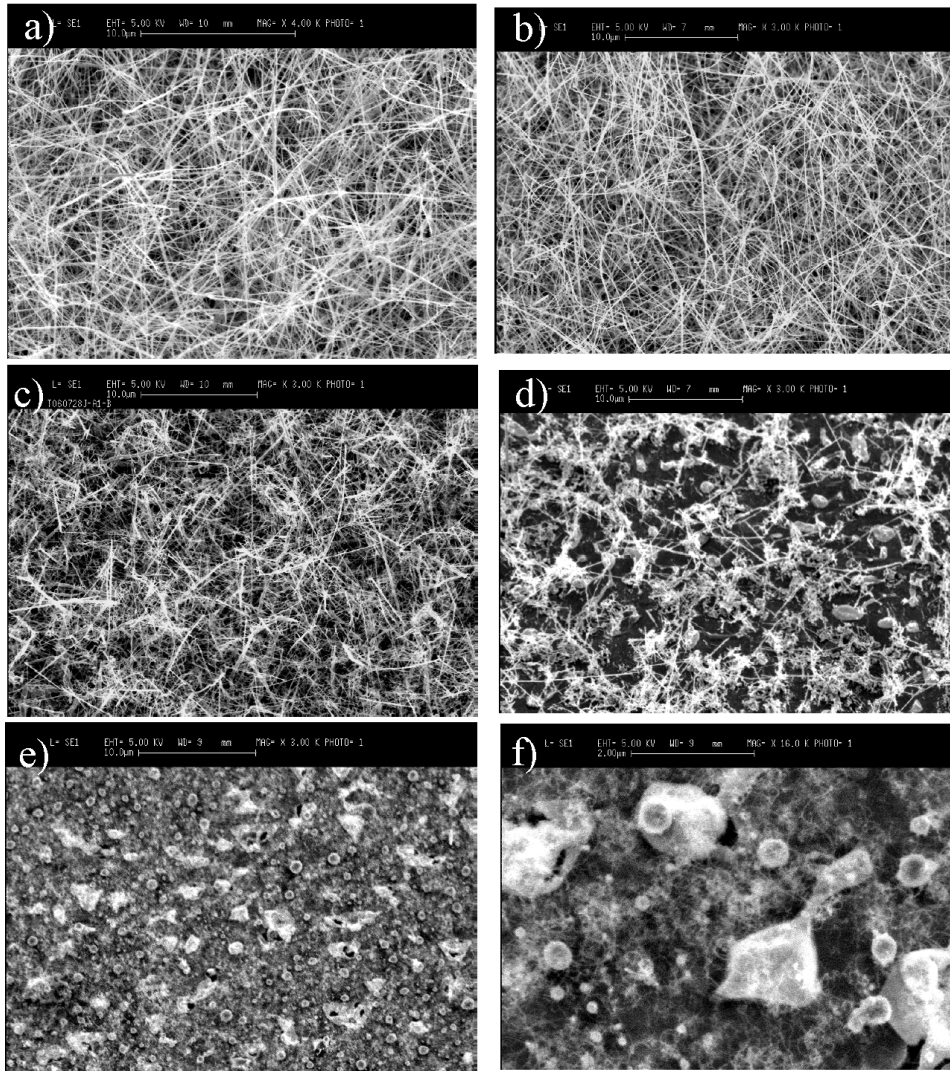


5 Discussion

In view of these results, let us first consider the significant increase in both the EPR intensity and the PL intensity upon anneals in an H_2/Ar atmosphere. First of all, it is clear that there is a direct correlation between the oxygen vacancy density, obtained from EPR, and the blue PL intensity, as discussed above. Let us now consider a possible explanation for the significant increase in the oxygen vacancy concentration with the initial annealing treatments. It should be kept in mind that all these materials were grown at $900^\circ C$, which would suggest that an equilibrium vacancy concentration produced at that temperature should not be changing at lower temperatures under the same annealing and cooling conditions, since one would already expect the highest vacancy concentrations to be produced at the high growth temperature. Thus, the increase in the vacancy concentration must be due to the presence of the H_2 gas, which is not present during growth. It is well known that these materials are used for H gas sensing [27,28] and thus one possible scenario as to how hydrogen reacts with the Ga_2O_3 material is as follows. Since these nano-materials consist of very high surface areas, which should exhibit significant strains on the bonds near the surface due to their small diameters, it is likely that hydrogen reacts with the strained surface bonds on the Ga_2O_3 , breaking Ga-O bonds, and reacting with the oxygen to form water. This water vapourises, due to the high temperatures involved, and is evacuated by the vacuum pump. This would lead to an oxygen deficit in the network structure, and thus an increase in the oxygen vacancy concentration, as seen from EPR and the PL. The question which now must be addressed is the apparent drop and almost total disappearance of the oxygen vacancy signal in both EPR and PL as a function of higher temperature. In order to investigate this, we have monitored the structural properties of the nanowires, along with the PL, for each annealing temperature, using SEM. The results for several temperatures are shown in Figure 10(a)–(f). The initial sample consists of a high density 3D network of nanowires, having diameters between 40 nm and 80 nm. Anneals at $300^\circ C$ and $500^\circ C$ do not affect these nanowires, nor the density, as shown in Figure 10(b). However, as the temperature increases to $700^\circ C$, one can see a change in the nanowire density, as evidenced in Figure 10(c). Even higher temperatures lead to a significant loss of nanowires due to evaporation (Figure 10(d)), and by $900^\circ C$, almost no nanowires remain and the PL is almost all gone, corresponding to loss of the nanowires (see Figure 10(e–f)). If these nanowires are annealed under similar conditions with Ar only, no such loss of material occurs. Thus, the reason for the nanowire loss at these temperatures is the small diameter of the wires, which are more easily etched and evaporated by the hydrogen gas. This is consistent with previous results [27] on the reduction of Ga_2O_3 polycrystalline thin films at high temperatures by high partial pressure of H_2 .

In view of these results, it is most likely that the decrease of the EPR and PL signal is not due to a decrease in the vacancy concentration, but due to loss of the nanowire material, most likely from the reaction with hydrogen. This loss of signal occurs at a higher temperature in the case of the EPR measurement, since nano-ribbons were used, which are larger structures and thus do not etch as fast as the nanowires.

Figure 10 SEM micrographs of the nanowires: (a) as grown; (b) after 500°C; (c) after 700°C; (d) 800°C and (e–f) after 900°C anneals



6 Conclusion

We have grown Ga_2O_3 nanowires and nanoribbons and we have studied their properties as a function of hydrogen annealing at various temperatures using EPR, PL and SEM. Our results indicate that these nano-materials exhibit enhanced conduction electron density and enhanced blue photoluminescence intensity at temperatures below 900°C, most likely due to the reaction of hydrogen with the high surface area material, creating an increased number of oxygen vacancies in the process. Our results also indicate that the EPR and PL results track quite well, confirming the suggestion that the blue PL originates from the recombination of an electron on an oxygen vacancy with a hole.

The marked drop of the vacancy concentration at high anneal temperatures has been correlated with the loss of nanowire material, suggesting that the role of hydrogen includes the removal of material from the surface, leading to a complete disappearance of nanowires at the highest temperatures. Due to the increased electron donor signals at higher temperatures, this material should exhibit enhanced electrical conduction in the presence of hydrogen, making it a potentially very sensitive sensor, due to the high surface area. However, the etching of the material at higher temperatures must also be taken into considerations when using this nano-material for high temperature sensing.

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