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Growth of ^{18}O isotopically enriched ZnO nanorods by two novel VPT methods

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ABSTRACT

We have developed two novel vapour phase transport methods to grow ZnO nanorod arrays isotopically enriched with ^{18}O. Firstly, a three-step process used to grow natural and Zn-enriched ZnO nanorods has been further modified, by replacing the atmospheric O_2 with enriched $^{18}O_2$, in order to grow ^{18}O-enriched ZnO nanorods using this vapour-solid method on chemical bath deposited buffer layers. In addition, ^{18}O-enriched ZnO nanorods were successfully grown using ^{18}O isotopically enriched ZnO source powders in a vapour-liquid-solid growth method. Scanning electron microscopy studies confirmed the success of both growth methods in terms of nanorod morphology, although in the case of the vapour-liquid-solid samples, the nanorods' *c*-axes were not vertically aligned due to the use of a non-epitaxial substrate. Raman and PL studies indicated clearly that O-enrichment was successful in both cases, although the results indicate that the enrichment is at a lower level in our samples compared to previous reports with the same nominal enrichment levels. The results of our studies also allow us to comment on both levels of enrichment achieved and on novel effects of the high temperature growth environment on the nanorod growth, as well as suggesting possible mechanisms for such effects. Very narrow photoluminescence line widths, far narrower than those reported previously in the literature for isotopically enriched bulk ZnO, are seen in both the vapour-solid and vapour-liquid-solid nanorod samples demonstrating their excellent optical quality and their potential for use in detailed optical studies of defects and impurities using low temperature photoluminescence.

1. Introduction

ZnO nanostructures have been synthesized in a wide variety of different morphologies. These include thin films [1], nanorods, nanowires [2–5], nanowalls [6], nanodisks [7], and a range of other "nano" morphologies [8,9]. The production of ZnO nanorods for use in optical and nano-optoelectronic applications and studies is of particular interest [10–12]. Growth of ZnO nanostructures using high temperature methods such as vapour phase transport (VPT) leads to very high quality material demonstrating excellent single crystallinity and optical properties because the small nanostructure footprint reduces the generation of extended defects associated with lattice mismatch with the substrate. Furthermore, nanostructure growth also potentially enables relatively simple control of isotopic concentrations since the amounts of source material as well as material being produced are relatively small. Isotopic enrichment is a very useful technique in the study of impurities in semiconductor materials such as ZnO, particularly using optical methods where shifts in spectral features can provide important information on the properties (including chemical constituents) of both intrinsic and defect-related optical features [13–18]. Reports using isotopically enriched bulk single crystal ZnO samples have included studies of bandgap energies, phonon frequencies and linewidths and heat capacity. However in all cases these samples had quite poor optical quality, e.g. reported photoluminescence (PL) line widths of ~5 meV and ~2–8 meV [19,20].

The use of isotopically enriched nanostructured material allows us to combine the two key advantages mentioned above (excellent optical quality and control of isotopic concentration) for the study of the optical properties of the semiconductor material. Recently, we reported for the first time the successful growth of Zn-isotopically enriched ZnO nanorods by a VPT process on chemical bath deposition (CBD)-grown buffer layers, which showed good isotopic enrichment and excellent optical properties [21]. In the present work, we report two relatively fast, easy, reliable and novel methods of growing O-isotopically enriched ZnO nanorods of very high crystalline quality, which display

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excellent optical quality as determined by low temperature PL studies. The samples produced here are suitable for detailed defect studies. We have grown ZnO nanorod samples enriched with ^{18}O and $^{16/18}O$, as well as natural ^{16}O samples using these two novel growth methods. Furthermore, our studies allow us to comment on both the levels of enrichment achieved and on some effects of the high temperature growth environment on the nanorod growth. Our data show that the source of ^{16}O contamination must come from sources of oxygen already chemically bound within the growth system and we discuss three potential mechanisms relevant to different samples; (i) diffusion/migration of ^{16}O from the unenriched buffer layer in the case of the vapour-solid (VS) samples, (ii) exchange of ^{18}O with ^{16}O in the polycrystalline quartz/alumina tubes/boats at high temperature and (iii) the ubiquitous presence of adsorbed water layers on all surfaces in the growth system which could lead to an exchange of ^{18}O with ^{16}O, acting as a source of ^{16}O contamination.

2. Materials and methods

2.1. Modified Vapour-Solid CTR-VPT method

This growth method is a three step process involving the deposition of an initial buffer layer of ZnO nanorods using drop coating and CBD, followed by the main growth of the nanorods using carbothermal reduction VPT (CTR-VPT). CBD, VPT and CTR-VPT are well established methods used to grow ZnO nanorods [2,5,22–24]. This specific growth method used here is described in the following references [2,3,25]. It was previously modified to produce Zn-enriched nanorods as reported recently [21] and is further modified here to produce ^{18}O-enriched nanorods.

The ZnO nanorods were grown on Si (100) substrates 0.5 mm thick and 1–4 cm^2 in area. The first stage of the growth process, seed layer preparation, was carried out as described in reference [21]. This process produces a thin layer (< 25 nm) [26] of crystallographically aligned ZnO crystallites on the surface, which act as nucleation sites for nanorod growth at later stages [2,27]. The second stage of growth was the deposition of a ZnO buffer layer using an NaOH-based CBD technique, again described in reference [21]. This process leaves a layer of *c*-axis aligned ZnO nanorods which acts as a buffer layer for subsequent growth of larger nanorods using VPT. Neither the seed nor the buffer layers are isotopically enriched; they have the natural O isotope abundances. Because the PL intensities seen from CBD layers is many orders of magnitude less than that from VPT nanostructures, our PL studies are clearly dominated by emission from the isotopically enriched CTR-VPT grown nanorods, similar to the results seen in our earlier work [21].

The third stage in the growth of ZnO nanorods was CTR-VPT. ZnO powder (60 mg) and graphite powder (60 mg) were carefully mixed to produce a fine homogeneous powder mixture. This powder was then spread over a length of about 2 cm in an alumina boat. The Si wafer was suspended above the powder with the ZnO buffer layer facing downwards towards the powder. The alumina boat was then placed into a quartz tube (inner diameter 37 mm) in a single temperature zone horizontal tube. The exhaust end of the tube was then sealed using a valve. At the other end, a series of valves connect the tube to a vacuum pump, N and O gases and Ar gas via mass flow controllers (MFC). A small regulator was used to control the pressure of the $^{18}O_2$ (99%, Sigma Aldrich) lecture bottle. A digital pressure gauge was also present. The tube was slowly evacuated using the vacuum pump to a pressure of < 1 mbar. Following this, the tube was refilled to atmospheric pressure with artificial 'air' that contained ~21% $^{18}O_2$ and ~79% N_2. Replicating normal atmosphere by only changing the oxygen isotopic mass was important as the VPT growth reaction is known to be sensitive to changes in partial pressures [28]. This mixture was left for about 15 min to allow the gasses to mix and fill the entire tube evenly. The Ar flush at 90 sccm was then started, the exhaust valve opened, and after 5 min the temperature was raised to 925 °C for 1 h. The furnace was then allowed to cool for several hours. When the temperature reached about 350 °C, the Ar flow was stopped and the alumina boat removed. This resulted in the growth of ZnO nanorods aligned with their *c*-axes normal to the substrate, as they grow well aligned on the buffer layer [3].

This CTR-VPT growth process is based on the reduction of ZnO source material by the graphite to produce Zn vapour and carbon monoxide (CO). The Zn vapour is then re-oxidised in a VS process at the energetically favourable sites provided by the aligned CBD buffer layer using residual O_2 present in the tube following the Ar flush (rather than the O initially in the ZnO powder, which is captured by C to form CO). In order to grow ZnO nanorods enriched with ^{18}O isotopes, it was necessary to remove all the residual natural O_2 (i.e. $^{16}O_2$) from the tube, and then reintroduce $^{18}O_2$ gas as described above.

Three samples were produced using this method: natural $Zn^{16}O$ by evacuating the tube and re-filling with $^{16}O_2$ and N_2, isotopically enriched ZnO by re-filling with $^{18}O_2$ and N_2, and a mixed 50:50 $Zn^{16/18}O$ sample by using a mixture of both oxygen isotopes with N_2. These samples are labelled as the 'VS' samples.

This method had the disadvantage of requiring significant quantities of isotopically enriched $^{18}O_2$ gas, but was otherwise very successful in terms of achieving growths. In order to confirm that only the residual O_2, which can be evacuated and replaced with $^{18}O_2$, contributes to the O in the ZnO nanorods, growth of a nanorod sample was attempted by this method in a pure N_2 atmosphere only. Following this control growth, there was no evidence of VPT nanowire growth at all. Thus, it was confirmed that there is no significant contribution to the VPT growth from O_2 from the ZnO source material, or from older/residual deposited ZnO material on the tube walls from previous growths. This is consistent with previous work in our group that found that the growth process is quenched when the residual O_2 in the tube is sufficiently depleted by a longer Ar flow during the initial steps of the CTR-VPT process, e.g. after about 15–30 min Ar flow [29,30].

2.2. Vapour-Liquid-Solid VPT method

This method makes use of direct oxidation of Zn metal to effectively "trap" the ^{18}O to form a $Zn^{18}O$ powder, which could then be used in a vapour-liquid-solid (VLS) VPT growth method. In this case, it is the sublimation of ZnO source powder that provides both the Zn and O_2 vapours for subsequent growth. Consequently, in order to produce ^{18}O-enriched ZnO nanorods, it was necessary to produce enriched ZnO source powder. Zn powder (99.9%, Alfa Aesar) was oxidised by placing ~160 mg of such powder in an alumina boat in the furnace and evacuating the tube to < 1 mbar. The tube was then filled with ~200 mbar of either $^{16}O_2$ or $^{18}O_2$ and ~550 mbar of N_2 giving a total pressure of ~ 750 mbar, which was experimentally found to be a suitable gas composition to achieve the required oxidation in a reasonable time period at the temperatures used. This mixture was left to settle for about 15 min before the furnace was heated to 800 °C for one hour. About 60–90 mg of oxidised powder was recovered from the boat after each run due to some of the produced ZnO depositing on the tube edges. Separate boats and tubes were used for each isotope and smaller tubes of 18 mm internal diameter were used here to reduce the amount of $^{18}O_2$ gas needed as it was in limited supply.

^{18}O-enriched ZnO nanorods were then synthesized using a VLS method with an Au catalyst. The method used was based on previous work on VPT by direct oxidation [31,32]. The setup shows some similarities to that described previously, albeit also with some notable differences. This furnace contained two alumina tubes, one inside the other. Approximately 120 mg of ZnO powder acted as the source material and was spread over about 5–6 cm in an alumina boat and placed at the centre of the furnace. About 7–8 pieces of Si (100) substrate (~0.5 mm thick and ~1 cm^2 in area) had 10 nm of Au deposited on them by plasma sputter coating and were placed in