Carbothermal reduction growth of ZnO nanostructures on sapphire – comparisons between graphite and activated charcoal powders

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Abstract

ZnO nanostructures were grown by the vapour phase transport (VPT) method on *a*-plane sapphire substrates via carbothermal reduction of ZnO powders with various carbon powders. Specifically, graphite powder and activated charcoal powder (of larger total surface area but similar mesh size) were used. ZnO nanostructures can be grown at lower temperatures (~800^{0}C) using activated charcoal than those required using graphite powder. Furthermore the morphologies of ZnO nanostructures obtained using activated charcoal were different to those obtained using graphite. At higher temperatures (~950^{0}C), where well-aligned nanorods were obtained using graphite powder, no nanostructures were found using activated charcoal. In contrast to previous results on Si substrates we find that the effects on ZnO nanostructure growth on *a*-sapphire cannot be explained solely in terms of increased Zn vapour pressure due to enhancement of the carbothermal reduction reaction rate by the high surface area activated charcoal.

1. Introduction

Carbothermal reduction (CTR) is the process by which a metal can be extracted from its corresponding metal oxide compound via reaction with carbon [1]. This process is used in the vapour phase transport (VPT) growth of zinc oxide (ZnO) nanostructures using Zn vapour produced by CTR of ZnO powders. The carbon source has immense influence in the growth process as it can change the required temperature for growth, which is a very important issue. This effect has been reported by Y.S Lim *et al.* [2] for ZnO nanostructure growth on Si substrates. Au-catalysed ZnO nanostructure growth on Si is generally complicated by two factors. Firstly, Zn alloys with both the substrate and the Au catalyst during growth [3]. Secondly, the lack of epitaxial match to Si means that the nanostructures grown are generally not aligned normal to the substrate and the growth direction is random [3, 4]. These difficulties are eliminated in growth on *a*-plane sapphire which in principle provides a more controlled morphology and less complicated growth mechanism and thus is a useful system in which to study and isolate various aspects of ZnO nanostructure growth, despite the limitations of the substrate in terms of cost and lack of electrical conductivity. We report data on the growth of ZnO nanostructures on *a*-sapphire using two different carbon sources; (a) graphite powder and (b) activated charcoal (AC) powder. These powders have similar mesh sizes but the AC has a total surface area 100 times that of the graphite powder. It is known [5] that ZnO nanostructures can be grown using graphite powder at temperatures above 900^{o}C on *a*-plane sapphire substrates. Our aim was to study the effects of AC as the carbon source for CTR on sapphire and to compare our data to the previous data on Si substrates, with the goal of establishing the range of effective growth temperatures for aligned nanostructure growth. We report here preliminary data on these topics which indicate that the AC has a substantial effect on ZnO nanostructure growth on sapphire as it can change the morphologies of

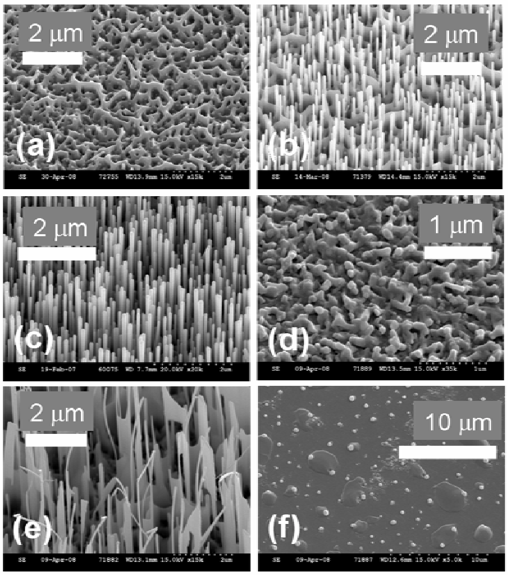

Fig. 1. FESEM images of ZnO nanostructures; grown using graphite at (a) 850 ^{o}C (b) 900 ^{o}C (c) 950 ^{o}C and grown using activated charcoal at (d) 750 ^{o}C (e) 850 ^{o}C (f) 950 ^{o}C.

nanostructures at particular growth conditions which is not apparent from previous work on Si. In addition, some future directions are proposed.

2. Experimental details

Nanostructured ZnO was grown using VPT via the VLS mechanism on *a*-plane (11-20) sapphire substrates [3, 5] with Au as a catalyst for the VLS mechanism. The gold was deposited by evaporation and the equivalent thickness was 5 nm. The growth was performed in a single zone furnace within a horizontal quartz tube (inner diameter = 4 cm). The source materials used were (i) ZnO powder (5N) and graphite powder (6N, 200 mesh) and (ii) ZnO powder and AC (untreated, 100-400 mesh range). In both cases the powders were well mixed and in the ratio 1:1 by mass). For the type (i) source growth was attempted at 850^{o}C, 900^{o}C and 950^{o}C. For the type (ii) source growth was attempted at temperatures from 750^{o}C-950^{o}C at 50^{o}C intervals. The substrate and source powders were placed in a quartz boat at the central part of the furnace [3, 5]. The Ar flow rate was 90 sccm during the growth. All other growth conditions were the same for both source powder types. Field Emission Scanning Electron Microscopy (FESEM - Hitachi S-4300) measurements were performed on all samples. X-Ray Diffraction (XRD - Bruker AXS D8 advance texture diffractometer) measurements were also performed. The total surface area of graphite and activated charcoal powders was measured using the Brunauer-Emmett-Teller (BET) method with a Quantochrome instrument. The temperature profile of the source powder as a function of time was measured using a 'K' type thermocouple placed directly above and close to the source powder for nominal furnace temperatures from 800^{o}C-950^{o}C for both type (i) and (ii) sources at 50^{o}C intervals.

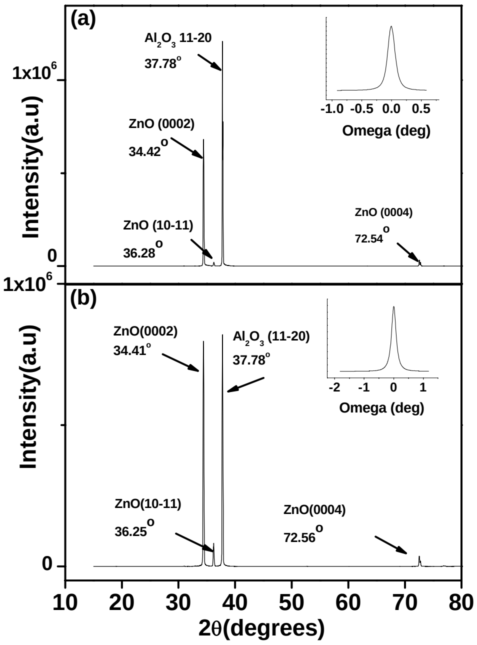

Fig. 2. XRD data for ZnO nanostructures samples as described in text; (a), (b) are θ-2θ data for two samples and insets are rocking curve data for corresponding ZnO (0002) peak.

3. Results and discussions

Fig. 1 (a)-(c) are FESEM images of the samples grown using type (i) source powder and show aligned ZnO nanorod/nanowall and nanorod structures in (b) and (c), which show typical evidence for the VLS mechanism with Au dots at nanorod tips [6]. For type (i) powder we do not observe any nanostructures below 900^{o}C on sapphire (fig. 1 (a)). For the type (ii) source (fig. 1 (d)-(f)) nanostructure growth starts from 800^{o}C and no growth is seen beyond 900^{o}C. At 750^{o}C ZnO nucleation starts and at 950^{o}C no ZnO growth is found with only scattered gold clusters observed. 850^{o}C is the only temperature where a regular arrangement of nanorod/nanowall structures can be observed. In fig. 1(e) we can see that the nanorods grown at 850^{o}C are not hexagonally facetted and have Au dots at the tip, which again indicates that the growth process follows the VLS mechanism. The evidence for VLS growth is less clear for the nanostructures grown at 800^{o}C and 900^{o}C which have a foam-like morphology (not shown).

Fig. 1 (b) and (e) show similarities in ZnO morphology and in both cases growth follows the VLS mechanism. XRD data for both are shown in fig. 2 ((a) for type (i) powder at 900^{0}C and (b) for type (ii) powder at 850^{o}C), which have similar morphologies). Fig. 2(a) and (b) show the 2θ-ω scans of the two samples and the same peaks are seen for

ZnO ((0002), (0004), (10-11) at 34.4°, 72.5° and 36.2°, respectively) and for *a*-plane sapphire at 37.8°. The presence of the ZnO (10-11) peak appears to be associated with the wall-like structures in both samples and is very much weaker in XRD data from nanorod-only samples grown at 950°C using graphite (fig. 1(c) – XRD data not shown). The insets of Fig. 2(a) and (b) show the rocking curves for the ZnO (0002) peak of both samples. The FWHM of Fig. 2 (a) inset is ~0.18° and for the (b) inset is ~0.15°, indicating good crystalllinity and alignment of the fraction of the deposit with [0001] texture. The temporal temperature profile was measured at all growth temperatures for both sources (not shown) and is virtually identical at all temperatures which indicates that the source temperature doesn't vary due to the CTR reaction with different powders.

Growth of ZnO nanostructures at temperatures of ~ 800°C is consistent with previous reports for growth on Si with carbon black (another non-graphitic form of carbon [7]). This is attributed by these authors to the fact that AC can produce a sufficiently high partial pressure of Zn vapour for growth to proceed via carbothermal reduction at lower temperatures compared to graphite powder. Whether this effect is a thermodynamic or kinetic effect remains unclear. The Gibbs' free energy of non-graphitic carbon species such as AC varies over a range of values from ~2kJ/mol to 20kJ/mol (referenced to graphite) depending on preparation, and this will affect the Ellingham diagram and equilibrium constant of the reaction [1, 8]. In addition, the high surface area of AC compared to graphite powders may also increase the reaction rate, via the intermediate products of the CTR [9]. We have measured the surface area by the BET method and obtain a value of 1000 m^2/g for AC compared to 10 m^2/g for graphite, which is similar to the results in reference [2]. The particle size i.e the external area of the two carbon powders, is similar and in the range of 100-400 mesh. The surface area indicated by BET is the total surface area including internal micro-/nano-pores. These data indicate that the internal surfaces of the carbon (which differ in area much more than the external surfaces) may play a major role and hints that the reaction rate kinetics may be increased by vapour interactions in intermediate steps of the CTR [7, 9]. However, we find that the increase in yield of ZnO nanostructured deposit is not monotonic with increasing temperature and specifically that no ZnO deposit is obtained at a nominal furnace temperature of 950°C using AC, while well-aligned ZnO nanostructures are obtained using graphite at this temperature. Clearly additional factors influence the growth. It is possible that the high rate of evolution of Zn and CO vapours from CTR using AC at this temperature displaces oxygen from the local region of the furnace (our system uses the residual oxygen in the chamber) thus inhibiting growth.

Future work on this topic will concentrate on (a) use of various mesh graphite and AC powders at various temperatures and (b) direct control of oxygen partial pressure within the furnace for both source types and growth various temperatures. One difficulty in linking theory to experiment in this area (and also for comparison with other published work) is the fact that AC and other forms of non-graphitic carbon show wide variability in material properties depending on preparation method [7]. Clearly systematic experiments will require careful and consistent carbon material sourcing.

4. Conclusion

We conclude that the internal structure of AC leads to significant differences in CTR of ZnO powders, which in turn enables low temperature (800°C) growth of ZnO nanostructures using this source. However, at higher temperatures other factors become important and no growth is seen for temperatures of 950°C and above using AC. The origin of these effects and the balance between thermodynamic and kinetic effects is unclear and will form the basis of future studies.

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