Growth of c-axis oriented ZnO nanowires from aqueous solution: The decisive role of a seed layer for controlling the wires' diameter

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Abstract

ZnO nanowires were grown from an aqueous solution at low temperature (95 °C) on Corning glass and silicon (100) substrates. It turns out that the deposition of a thin ZnO seed layer on the substrates prior to the chemical growth is crucial for obtaining c-axis oriented ZnO nanowires with controllable dimensions. The nanowires' diameter increases with the grain size of the ZnO seed layer. On the other hand, aqueous solution growth on bare substrates leads to the formation of flowerlike nanostructures, consisting of nanorods, with no preferred growth orientation. The dimensions and morphology of these complex nanostructures depend mainly on growth time. Furthermore, the complex ZnO nanostructures do not show high transmittance, while the nanowires are highly transparent in the visible part of the spectrum.

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1. Introduction

Zinc oxide (ZnO) is a well-studied transparent direct wide band-gap semiconductor ($E_g=3.37$ eV) with a large exciton binding energy ($\approx 60$ meV), which allows efficient excitonic emission at room temperature (RT) [1,2]. ZnO nanowires, in particular, have attracted a great attention in the last years due to their applications in sensors, cantilevers as well as in optoelectronic devices such as light-emitting diodes and excitonic solar cells [3,4]. Law et al. [5] have applied ZnO vertically oriented nanowires in dye-sensitized solar cells and reported a full Sun efficiency of 1.5%. Ravirajan et al. have fabricated hybrid polymer/ZnO photovoltaic devices with vertical oriented nanorods, resulting in a power conversion efficiency of 0.2%. It turns out that the morphology and dimensions of the ZnO nanorods strongly affect charge recombination and device performance [6].

Different chemical and physical methods have been applied in the last years for creating a large variety of ZnO nanostructures with shapes ranging from nanowires to nanobelts and even nanosprings [3]. For instance, high temperature vapor–liquid–solid (VLS) growth with the use of catalysts [7,8], pulsed laser deposition [9], electrochemical deposition in porous membranes [10], metal vapor transport using Zn sources [11], physical vapor transport using ZnO and graphite powders [12], chemical vapor deposition using zinc acetylacetone hydrate [13], thermal oxidation of ZnS [14], metalorganic chemical vapor deposition (MOCVD) using diethylzinc and O₂ or N₂O as precursors [15] and aqueous solution growth [16–18] have been reported amongst other techniques.

Aqueous solution approaches for the growth of ZnO nanostructures are considered advantageous, compared with other methods, mainly due to low growth temperature and good potential for large-scale production. Vayssieres et al. [16,17] have first demonstrated the growth of ZnO oriented micro- and
nанороды на проводящие стеклянные подложки и подложки Si при 95 °C. Андре́с-Вергес и др. [18] уже установили, что при выдержке образцов в реакционной среде в присутствии гидролиза нитрата цинка и цинка хлорида в присутствии гексаметилентетраминов в реакционной среде, pH и температуре. Тиан и др. [19] более поздним временем научили понижение температуры синтетического процесса для формирования сложных наноструктур, в которых цитрат ангины использовались для контроля кристаллического морфологического процесса. В последнее время, многие группы отмечали, что выращивание сложных ZnO наноструктур происходит при выдержке в течение нескольких часов. Это было утверждено, что ZnO покрытие на подложку необходимо для инициирования равномерного роста ориентированных наноструктур из реакционной среды. Наши результаты показывают, что сложные наноструктуры являются критически важными для управления морфологией и размерами выращенных ZnO наноструктур.

2. Экспериментальная часть

Наши исследования состояли из двух этапов. В первом этапе, ZnO тонкие пленки с толщиной 60 и 140 нм, которые были использованы в качестве подложек для выращивания сложных наноструктур, были приготовлены в растворе соли синтеза/спинов в отсутствие среды. Цинк ацетат гидрат был впервые растворен в растворе соли синтеза/спинов, затем приготовленный раствор был вставлен на Corning стекло и Si (100) подложки, которые затем сшились при температуре 95 °C на 60 мин. Отрезки были вновь вставлены в воздух на 60 мин. Толщина пленки измерялась с помощью профилометра (alpha-step 100, Tencor).

Во втором этапе, ZnO наноструктуры были выращены на Corning стекле и Si (100) подложках на основе равновесной концентрации (0,01 М) водного раствора Zn(NO₃)₂ · 6H₂O и C₆H₁₂N₄ [16–18,28]. Решетка и подложки, предварительно покрытые ZnO покрытием, были приготовлены в Pyrex стеклянных бутылках с автоматически завинченными галогенными винтами и приготовлены в реакционной среде при 95 °C на 2 и 5 h в регулярном лабораторном oven. После завершения каждого этапа, образцы были тщательно промыты водой MilliQ для удаления остатков.

Fig. 1. XRD patterns of (a) ZnO samples grown by aqueous solution growth on bare Corning glass substrates for 2 h (red curve) and 5 h (light-blue dashed curve), (b) ZnO samples grown by aqueous solution growth for 2 h on Corning glass substrates with a 3-layered (60-nm-thick, green curve) and a 6-layered (140-nm-thick, magenta dashed curve) ZnO seed layer, (c) 3-layered (60-nm-thick, green curve) and 6-layered (140-nm-thick, magenta dashed curve) ZnO seed layers deposited via sol–gel on Corning glass substrates, and (d) ZnO samples grown by aqueous solution growth on silicon (100) substrates with a 6-layered (140-nm-thick) ZnO seed layer for 2 h (red curve) and 5 h (light-blue dashed curve). In the inset of (d) the XRD pattern of a 6-layered (140-nm-thick) ZnO seed layer deposited on Si (100) via sol–gel is presented. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
3. Results and discussion

Fig. 1 depicts X-ray diffraction patterns of the ZnO nanostructures deposited on Corning glass substrates by aqueous solution growth. The substrates used were either bare (Fig. 1a) or pre-coated with three or six ZnO thin layers deposited by the sol–gel/spin-coating technique (Fig. 1b and d). The thickness of the ZnO thin films is 60 and 140 nm for the three- and six-layered samples, respectively. It can be readily seen that, if no seed layer is applied onto the Corning glass substrates prior to the aqueous solution growth, all reflections corresponding to the hexagonal wurtzite P6(3)mc structure (JCPDS card file No. 36-1451) are present and there is no preferential growth orientation for neither 2 nor 5 h growth time (see Fig. 1a). On the other hand, when a ZnO seed layer, consisting of either three (60 nm) or six (140 nm) layers, is applied onto the Corning glass substrates prior to the aqueous solution growth, there is a clear preferential growth orientation of the ZnO nanostructured samples along the (002) crystallographic direction, i.e. perpendicular to the Corning glass substrates (2 h growth, Fig. 1b). This preferential growth orientation is directly related to the presence of the ZnO seed layers [21]. As it can be observed in Fig. 1c, both the three- and six-layered thin films exhibit the ZnO wurtzite hexagonal structure and grow preferentially along the (002) direction. Therefore, they indeed act as seed layers and assist the preferential growth of the chemically grown ZnO nanostructures along the c-axis, i.e. the (002) crystallographic direction. Moreover, it can be observed that the samples deposited by aqueous solution growth show much larger and sharper (002) reflections than the seed layers (Fig. 1b and c). The Full-Width at Half-Maximum (FWHM) value for the (002) peak varies between 0.205° and 0.245° for the ZnO seed layers, while it is 0.176° and 0.174° for the ZnO samples grown on a 140-nm-thick ZnO seed for 2 and 5 h, respectively. It is therefore concluded that the occurrence of a thin ZnO seed layer is crucial for the growth of well-crystalline, (002) oriented ZnO samples onto Corning glass substrates.

It is also noted that the thickness of the seed layer strongly affects the crystallinity of the ZnO samples grown from aqueous solution. In particular, the crystallinity of the ZnO nanostructured samples improves with increasing thickness of the seed layer. In the case of 2 h growth, for example, the FWHM values of the (002) peak are 0.202° and 0.176° for the samples grown on 60- and 140-nm-thick seed layers, respectively. It is furthermore observed that increasing aqueous solution growth time on a seed layer of a specific thickness leads to slightly smaller FWHM values (0.176° and 0.174° for 2 and 5 h growth time respectively on Corning glass substrates pre-coated with a 140-nm-thick ZnO seed layer). It is thus concluded that the most significant

![Fig. 2. SEM images of ZnO nanostructures grown by aqueous solution growth on bare Corning glass substrates for (a) 2 h and (b) 5 h, and on bare silicon (100) substrates for (c) 2 h and (d) 5 h. In the inset of (b) the hexagonal cross section of the ZnO nanorods is clearly observed.](image-url)
The parameter, which affects the crystallinity of the ZnO samples deposited by aqueous solution growth, is the thickness of the seed layer and not the growth time.

The same behavior is qualitatively observed for the samples grown on silicon (100) substrates. In this case, one can also observe the peaks corresponding to the Si (100) and (200) crystallographic planes (see Fig. 1d and inset herein). The FWHM values for the (002) ZnO peak are 0.181° and 0.178° for the 2 and 5 h samples grown on a 140-nm-thick ZnO seed layer, respectively. It is therefore concluded that, irrespectively of the substrate used, Corning glass or silicon (100), the presence of a seed layer leads to the formation of ZnO samples with very good crystallinity and a preferential growth orientation along the c-axis, i.e., perpendicular to the substrate.

SEM micrographs of ZnO samples deposited by aqueous solution growth on bare silicon (100) substrates are depicted in Fig. 2c and d for 2 and 5 h, respectively. Flowerlike nanostructures, consisting of nanorods, occur for both periods. With increasing growth time the nanostructures become gradually larger. For 2 h growth the nanorods’ diameter is 300–400 nm and their length varies from 4 to 5 μm, while in the case of 5 h growth the nanorods display a typical diameter of ~600–700 nm and length of ~6–8 μm. It is concluded that the ZnO nanostructured samples deposited on bare Corning glass and silicon (100) substrates by aqueous solution growth do not consist of oriented nanorods, in accordance with the XRD results which show that all reflections of the ZnO wurtzite structure are present (see Fig. 1a).

Fig. 2a and b show SEM micrographs of ZnO samples deposited on bare Corning glass substrates for 2 and 5 h, respectively. As it can be readily observed, for 2 h growth, flowerlike microstructures occur, consisting of nanorods with a diameter ranging from 200 to 300 nm and length of ~2–3 μm. However, the size of the flowerlike nanostructures is not uniform, while a few of single rods (diameter ~350 nm, length ~2–3 μm) are also present. When the growth time increases to 5 h, the flowerlike architectures develop further and become dominant with substrate coverage of ~80%. They consist of uniform nanorods with a typical diameter of around 400–500 nm and length of several microns (~5–6 μm). All nanorods have hexagonal cross-section (see the inset of Fig. 2b), implying the occurrence of the wurtzite ZnO crystal structure as it was also demonstrated by XRD (see Fig. 1a).

Fig. 3a and b depict SEM micrographs of the ZnO samples deposited by aqueous solution growth for 2 h on Corning glass substrates pre-coated with 60- and 140-nm-thick seed layers, respectively. It can be readily seen that these samples exhibit a totally different morphology, i.e., nanowires’ arrays occur. These nanowires emerge perpendicular to the substrates applied, are quite dense and uniform, while they all display a hexagonal cross-section. These remarks are in agreement with the XRD results which clearly demonstrate that the ZnO samples deposited by
aqueous solution growth on pre-coated Corning glass substrates exhibit the wurtzite hexagonal crystal structure and show a preferential growth orientation along the (0 0 2) direction (see Fig. 1b and d). It is furthermore observed that the nanowires' diameter increases with the seed layer thickness. As the seed layer thickness increases from 60 to 140 nm, the wires' diameter rises from $\sim 80 \pm 10$ to $\sim 100 \pm 10$ nm. This increase in the wires' diameter is directly related to the grain size of the ZnO seed layer. The grain size as well as the roughness of the seed layers gradually increase with thickness, i.e., the number of the spin-coated layers (see Fig. 4a). As it can be seen from Fig. 4a, the grain size of the 60- and 140-nm-thick seed layers is $67 \pm 4$ and $92 \pm 5$ nm, respectively, i.e., quite close to the diameter values of the corresponding ZnO nanowires' arrays. It is therefore concluded that the occurrence of a ZnO seed layer is a prerequisite for obtaining well-oriented ZnO nanowires onto Corning glass substrates via aqueous solution growth, and that the seed layer's grain size strongly affects the ZnO nanowires' diameter, i.e., the wire diameter increases with the grain size of the seed layer. When the growth time increases from 2 to 5 h, the diameter of the nanowires remains almost constant (see Fig. 3b and c for 2 and 5 h growth on a 140-nm-thick seed layer, respectively). It thus seems that the growth time does not significantly influence the wires' diameter.

Fig. 3d displays a SEM micrograph of ZnO nanowires grown for 5 h by aqueous solution growth on a silicon (1 0 0) substrate, which was pre-coated with a 140-nm-thick ZnO seed layer. The nanowires' diameter is around $55 \pm 5$ nm, much smaller than that obtained on Corning glass substrates, a behavior which is directly related to the grain size of the seed layer. As it can be seen in Fig. 4b, the grain size of the 140-nm-thick seed layer deposited via sol–gel on a silicon (1 0 0) substrate is $50 \pm 4$ nm, which is almost the half of that on Corning glass ($92 \pm 5$ nm). The larger grain size of the ZnO seed layer deposited on Corning glass is possibly related with better promotion of the nucleation due to the higher affinity of ZnO to Corning glass as compared to silicon (1 0 0) [30]. This higher affinity seems to also influence the growth rate, this being slightly larger in the case of Corning glass. It can be finally observed that although the nanowires are quite dense and uniform, they are not as well-aligned as the ones grown on Corning glass.
The morphology of the 140-nm-thick seed layer deposited on the Corning glass substrates by aqueous solution growth at 95°C substrates at low temperature (95°C). The substrates used were either bare or pre-coated with a thin ZnO seed layer deposited via the sol–gel/spin-coating method. It is concluded that the presence of a ZnO seed layer is crucial for the formation of well-aligned, c-axis oriented ZnO nanowires with good crystallinity. The diameter of the nanowires increases with the grain size of the ZnO seed layer and varies between 50 and 110 nm depending on the substrate used. On the other hand, if no seed layer is applied, flowerlike nanostructures occur, consisting of nanorods with a diameter ranging from 200 to 700 nm and length of ~2–8 μm, depending on growth time and substrate applied. In this case, all crystallographic planes exist and there is no preferred growth orientation. Finally, it is shown that the ZnO flowerlike nanostructures are not well transparent, while the ZnO nanowires’ arrays show very high transmittance in the visible part of the spectrum, reaching values comparable to those of the seed layers.

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4. Conclusions

ZnO nanostructures were grown from an aqueous solution on Corning glass and silicon (100) substrates at low temperature (95°C). The substrates used were either bare or pre-coated with a thin ZnO seed layer deposited via the sol–gel/spin-coating method. It is concluded that the presence of a ZnO seed layer is crucial for the formation of well-aligned, c-axis oriented ZnO nanowires with good crystallinity. The diameter of the nanowires increases with the grain size of the ZnO seed layer and varies between 50 and 110 nm depending on the substrate used. On the other hand, if no seed layer is applied, flowerlike nanostructures occur, consisting of nanorods with a diameter ranging from 200 to 700 nm and length of ~2–8 μm, depending on growth time and substrate applied. In this case, all crystallographic planes exist and there is no preferred growth orientation. Finally, it is shown that the ZnO flowerlike nanostructures are not well transparent, while the ZnO nanowires’ arrays show very high transmittance in the visible part of the spectrum, reaching values comparable to those of the seed layers.

References


Fig. 5. Optical transmittance spectra of (a) ZnO flowerlike nanostructures grown by aqueous solution growth at 95°C on bare Corning glass substrates for 2 h (red dashed curve) and 5 h (blue solid curve) and (b) ZnO nanowires’ arrays grown on a 140-nm-thick seed layer for 2 h (red dashed curve) and 5 h (blue solid curve); the green dotted curve displays the transmittance spectrum of the 140-nm-thick ZnO seed layer deposited via sol–gel. For comparison reasons, in both (a) and (b), one can see the transmittance spectrum of bare Corning glass substrate (black dotted curve). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)